



A brief review of mesoporous silica materials for efficient CO₂ capture: synthesis, modifications, and integrated computational molecular modelling approaches

Chui Keat Lim¹ · Syamima Nasrin Mohamed Saleh² · Mohd Azmier Ahmad¹ · Sunarti Abd Rahman³ · Chew Thiam Leng⁴ · Bassim H. Hameed⁵ · Noorhidayah Ishak⁶ · Azam Taufik Mohd Din¹

Received: 4 August 2026 / Accepted: 2 September 2026

© The Author(s), under exclusive licence to the Institute of Chemistry, Slovak Academy of Sciences 2026

Abstract

Effective CO₂ capture technologies are crucial for achieving Sustainable Development Goal 13, addressing urgent climate change mitigation. The efficacy of these technologies hinges on the properties of adsorbent materials. Amine-functionalized mesoporous silica materials exhibit significant potential for CO₂ capture owing to their high adsorption capacity and selectivity. However, current synthesis and functionalization methods lack efficiency, and the underlying molecular mechanisms remain incompletely elucidated. This review accentuates existing knowledge on the synthesis, modification, and computational modelling of amine-functionalized mesoporous silica materials, emphasizing key mechanisms and factors influencing CO₂ capture performance. By integrating experimental findings with molecular dynamics and density functional theory modelling, this work elucidates the intricate interactions within these materials to optimize their synthesis and functionalization, providing a detailed guide on silica model construction and the correlation of atomic-level mechanisms with lab data. A central focus is placed on the pivotal role of computational modelling in deciphering CO₂ adsorption mechanisms on amine-functionalized mesoporous silica. Given the escalating impacts of global climate change, this study underscores the necessity for sustained research and technological advancements in CO₂ capture. Ultimately, this review aims to provide a robust foundation for future investigations and contribute to the global sustainability agenda.

✉ Syamima Nasrin Mohamed Saleh
mssnasrin@unimas.my

✉ Azam Taufik Mohd Din
chazam@usm.my

¹ School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

² Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

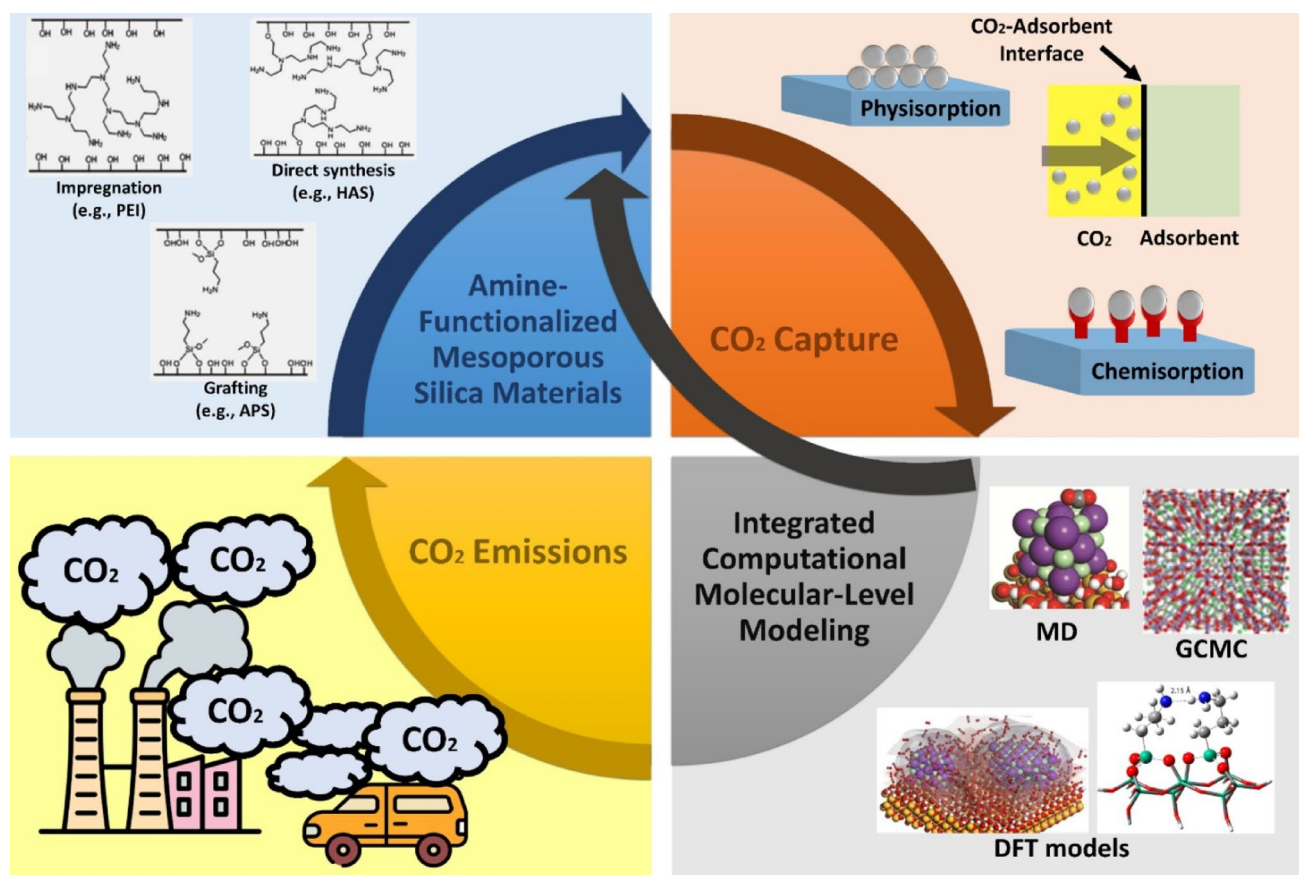
³ Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Persiaran Tun Khalil Yaakob, 26300 Gambang, Kuantan, Pahang, Malaysia

⁴ Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

⁵ Department of Chemical Engineering, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

⁶ Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Arau, Perlis, Malaysia

Graphical abstract



Keywords CO₂ adsorption · Density functional theory (DFT) · Mesoporous silica · Amine functionalization · Molecular modelling

Introduction

The rise in greenhouse gas emissions has always been a troubling environmental concern since the beginning of the industrial revolution, which has indirectly caused climate change and global warming. The increase in anthropogenic activities and energy consumption has resulted in a heavy reliance on fossil fuels to generate more energy to meet the demand, which remains the primary contributor to greenhouse gas emissions. Despite advancements in renewable energy technology to reduce human dependency on fossil fuels, emissions continue to increase, posing significant challenges in achieving global climate goals. Thus, significant efforts are being made to mitigate greenhouse gas emissions, with carbon dioxide (CO₂), the primary greenhouse gas, being a major target for reduction.

Carbon capture technologies, classified into pre-combustion, post-combustion, oxyfuel, and chemical looping processes, have been continuously developed and researched to

mitigate problems associated with CO₂ emissions (Raganati et al. 2021). Post-combustion carbon capture is more widely implemented compared to other methods due to its simplicity and adaptability. Adsorption using solid sorbents and absorption using amines are the current popular methods to be used. According to (Soo et al. 2024), adsorption referred to the process of CO₂ adhere onto a solid surface, whereas absorption involves the CO₂ dissolving into solvent, namely amines. Nevertheless, due to the disadvantages of amine absorption of being energy intensive, equipment corrosion by amines, and solvent degradation problems (Hosseinpour et al. 2023), adsorption using solid sorbents, as a greener alternative, has been proposed. Aside from requiring lower energy relative to amine absorption, the simplicity and flexibility of scaling up an adsorption process makes it more attractive to be used and retrofitted in the industry (Raganati et al. 2021).

Various solid sorbent materials are being researched, for instance, activated carbon, silica, polymer, and metal-organic-frameworks (MOFs) (Petrovic et al. 2021;

Dziejarski et al. 2023). However, since each material has its own inherent weakness, ongoing research studies are being conducted to increase their CO₂ adsorption capability. Mesoporous adsorbents such as ordered mesoporous silica have recently gained attention for application in CO₂ adsorption due to the high porosity and increased specific surface area caused by the presence of mesopores, which could facilitate the diffusion of CO₂ gases into the adsorbents (Macario et al. 2005; Chew et al. 2010). Moreover, the uniform and organized mesopore structure, as well as the abundance of silanol group on mesoporous silica could ease the functionalization of materials, which are critical for enhancing CO₂ capture performance (Hiyoshi et al. 2004b; Chew et al. 2010; Sardo et al. 2021).

Figure 1 presents a bibliometric analysis of the collaborative network among researchers of mesoporous materials, particularly in CO₂ capture applications, as shown by scholarly publications. The lines connecting the nodes showed co-authorship or citation relationships, with each node indicating one author. The size of each node corresponded to the frequency of publications or citations. The central node, “Navik 2024”, emphasized important scholars who have played a crucial role in connecting diverse research themes within the community and in disseminating knowledge. To-date, review papers have discussed previous works on mesoporous silica-based materials aimed at improving their

CO₂ capture performance. Hence, a summary of their contributions has been listed in Table 1.

In short, Table 1 shows that these reviews have primarily focused on the synthesis, functionalization, and CO₂ capture performance of mesoporous silica materials. Several recent review articles have also explored the synthesis and performance of amine-functionalized mesoporous silica for CO₂ capture as well (Chen et al. 2017; Fan and Jia 2022; Hack et al. 2022; Moon et al. 2023; Navik et al. 2024; Wang et al. 2024a). From their findings, it can be concluded that mesoporous silica materials possess promising features and structural characteristics that could greatly enhance their CO₂ adsorption capability. Nevertheless, knowledge on the adsorption mechanisms at the molecular level remains limited. Unlike previous reviews that predominantly focus on experimental synthesis and CO₂ uptake performances, this review offers an integrated analysis that combines experimental methods with atomistic-level computational approaches such as Density Functional Theory (DFT), Grand Canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulation. Specifically, particular emphasis is placed on model construction strategies and theoretical insights into adsorption mechanisms, detailing the transition from amorphous structures to highly functionalized, site-specific models, which are rarely addressed in prior literature. Thus, this paper aimed to bridge the gaps by provide

Fig. 1 Bibliometric analysis of scholarly collaboration on mesoporous silica materials in CO₂ capture application research

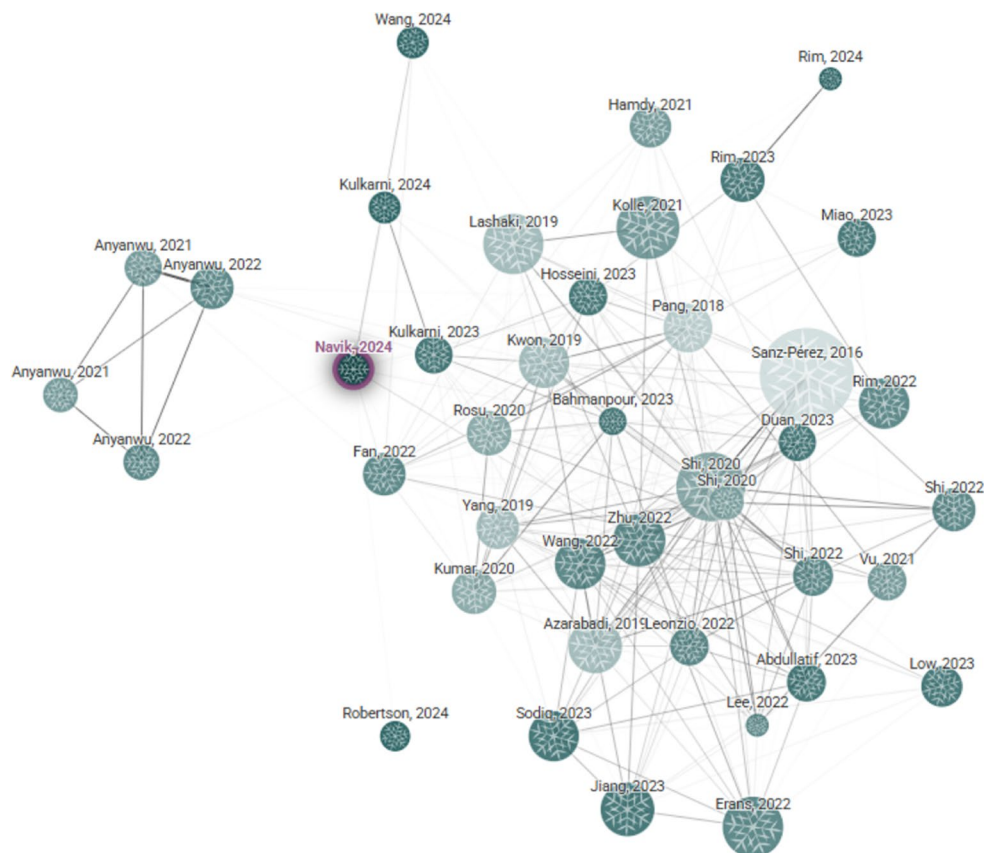


Table 1 Comparative analysis of previous review articles on amine-functionalized mesoporous silica materials for CO₂ capture

Title	DFT	MD	GCMC	Industrial perspective	Main contribution	References
Amine-silica composites for CO ₂ capture: A short review	×	×	×	Brief discussion	This paper concisely overviewed the development and characterization of amine-silica composite materials. Furthermore, CO ₂ capture performance under dry and humid conditions using amine-silica composite materials is thoroughly evaluated and discussed in this review.	Chen et al. (2017)
Functional mesoporous silica nanomaterials for catalysis and environmental applications	×	×	×	Brief discussion	This review provides a comprehensive overview of various types of mesoporous silica materials, focusing on their morphology, pore architecture and the effects of synthesis methods. Besides, it briefly highlights the application of mesoporous silica in CO ₂ capture.	Singh et al. (2020)
Fly ash, from recycling to potential raw material for mesoporous silica synthesis	×	×	×	Moderate discussion	This paper reviews the methods for synthesizing mesoporous silica materials from fly ash, with CO ₂ capture as one of the key environmental applications. Additionally, it also identifies the key challenges related to fly ash variability, synthesis efficiency, and their limitations for industrial scale applications.	Miricioiu and Niculescu (2020)
Progress in amine-functionalized silica for CO ₂ capture: Important roles of support and amine structure	×	×	×	Moderate discussion	This review systematically summarizes the roles of amine-functionalized silica materials in enhancing CO ₂ capture performance and maintaining their structural integrity. Moreover, this paper also provides valuable insights into the key deactivation mechanisms of amine-functionalized silica adsorbents.	Fan and Jia (2022)
Carbon capture using porous silica materials	×	×	×	Moderate discussion	This review provides a focused discussion on functionalized porous silica materials for CO ₂ capture, with a particular emphasis on amine-functionalized silica materials for and strategies for improved adsorption performance.	Amarawera et al. (2023)
Distribution and mobility of amines confined in porous silica supports assessed via neutron scattering, NMR, and MD simulations: Impacts on CO ₂ sorption kinetics and capacities	×	✓	×	Brief discussion	This paper offers a systematic review of the distribution, structure, and mobility of amines confined in mesoporous silica supports, providing valuable insights into design strategies for these materials, particularly for CO ₂ capture applications. The paper also mentioned the usage of molecular dynamics techniques, though mostly in understanding amine structure and distribution in mesoporous silica.	Moon et al. (2023)
The potential utility of dendritic fibrous nanosilica as an adsorbent and a catalyst in carbon capture, utilization, and storage	×	×	×	Moderate discussion	This paper provides comprehensive analyses of dendritic fibrous nanosilica (DFNS) for CO ₂ capture, utilization, and storage.	Lim et al. (2024)
The capture and catalytic conversion of CO ₂ by dendritic mesoporous silica-based nanoparticles	×	×	×	Moderate discussion	This review highlights the unique structural properties of dendritic mesoporous silica nanoparticles (DMSNs). Additionally, in this review, a detailed discussion on the use of amine-functionalized DMSNs and metal oxide doped DMSNs for CO ₂ capture is provided.	Wang et al. (2024b)
Atmospheric carbon dioxide capture by adsorption on amine-functionalized silica composites: A review	×	×	×	Moderate discussion	This paper offers a comprehensive review of amine-functionalized silica composite materials for direct CO ₂ capture, summarizing key synthesis techniques, adsorption mechanisms, and parameters influencing CO ₂ capture performance. Furthermore, this paper identifies current challenges associated with these adsorbent materials and proposes strategies for their improvement.	Navik et al. (2024)
Synthesis of mesoporous silica using the sol-gel approach: Adjusting architecture and composition for novel applications	×	×	×	Brief discussion	This review focuses on mesoporous silica materials synthesized via sol-gel technique. Additionally, this paper provides a comprehensive elaboration on the variations in mesoporous silica architectures prepared via this method under different conditions, offering valuable insights for the development of these materials for CO ₂ capture applications.	Han et al. (2024b)

Table 1 (continued)

Title	DFT	MD	GCMC	Industrial perspective	Main contribution	References
Recent advances in amine-functionalized silica adsorbents for CO ₂ capture	✓	×	×	Moderate discussion	The paper provides insights on latest development of amine-functionalized silica and highlighted the factors affect the CO ₂ adsorption performance of amine functionalized silica. It mentioned the CO ₂ adsorption mechanism of amine functionalized silica, though limited on molecular modelling simulation aspects.	Wang et al. (2024a)
Review on CO ₂ capture using amine-functionalized materials	×	×	×	Brief discussion	This work reviews the different type of amine-functionalized materials and their tolerance for moisture and impurities. Mechanistic studies using DFT coupled with nuclear magnetic resonance (NMR) method are only mentioned in brief.	Hack et al. (2022)
Molecular simulation techniques as applied to silica and carbon-based adsorbents for carbon capture	✓	✓	✓	Moderate discussion	Reviewed DFT, MD, and GCMC simulations of silica- and carbon-based adsorbents and compared modelling predictions with experimental CO ₂ adsorption behaviour.	Wadi et al. (2023)
Applications of molecular simulation for CO ₂ capture in solid adsorbents: A review	✓	✓	✓	Moderate discussion	Reviewed molecular simulation approaches for a broad range of solid adsorbents and correlated computational predictions with experimental adsorption performance.	Nguyen et al. (2025)
Recent progress on advanced solid adsorbents for CO ₂ capture: From mechanism to machine learning	✓	✓	×	Comprehensive discussion	Reviewed advanced solid adsorbents with emphasis on adsorption mechanisms, sustainability, economic considerations, and future development of carbon capture technologies.	Khosrowshahi et al. (2024)
A brief review of mesoporous silica materials for efficient CO ₂ capture: Synthesis, modifications, and integrated computational molecular modelling approaches	✓	✓	✓	Comprehensive discussion	Reviewed the synthesis, amine functionalization, adsorption mechanisms, and CO ₂ capture performance of mesoporous silica materials, while integrating experimental findings with DFT, MD, and GCMC approaches to provide molecular-level insights into adsorption behaviour, practical implementation challenges, and future research directions.	Present review

a deeper understanding by integrating computational modelling approaches to elucidate and describe focusing on how the combination of DFT, MD, and GCMC techniques can complement each other in the study of CO₂ adsorption mechanisms and the underlying processes. This integration of experimental and computational approaches could pave new ways for innovative solutions to mitigate greenhouse gas emissions effectively. Hence, the major contributions of this review would be as follows:

1. A brief and concise discussion on mesoporous silica materials and the limitations of pristine silica in CO₂ capture applications.
2. A summary of various functional group modifications to enhance CO₂ capture performance.
3. An in-depth discussion on molecular-level optimization of amine-functionalized mesoporous silica adsorbent materials using molecular dynamics approach.
4. Insight into CO₂ binding mechanisms via functional group-surface interactions using the DFT approach.

Recent review articles have also combined experimental observations with computational approaches to improve

the understanding of CO₂ adsorption on solid adsorbents. For example, Wadi et al. (2023) reviewed the application of DFT, MD, and GCMC simulations for silica- and carbon-based adsorbents, whereas Nguyen et al. (2025) discussed molecular simulation techniques across a broad range of solid adsorbents and compared simulation results with experimental observations. Khosrowshahi et al. (2024) further reviewed advanced solid adsorbents by incorporating adsorption mechanisms, sustainability considerations, and machine learning approaches. Although these reviews provide valuable insights, they mainly focus on computational methodologies or broad classes of adsorbents. In contrast, the present review specifically examines amine-functionalized mesoporous silica by integrating synthesis methods, surface functionalization strategies, experimental adsorption performance, and complementary DFT, MD, and GCMC studies to provide a unified perspective on material design and adsorption behaviour. Overall, this review has offered brief but critical insights on molecular dynamics and DFT modelling approaches to correlate the experimental findings with molecular-level behaviours of mesoporous silica materials for CO₂ capture.

Mesoporous silica as potential adsorbents for CO₂ capture

Synthesis of mesoporous silica

Ordered mesoporous silica is one of the commonly used mesoporous materials for separating CO₂ from other gases, owing to its high specific surface area and pore volume. The first ordered mesoporous silica ever reported was M41S in the 1990s (Beck et al. 1992). Since then, various ordered mesoporous silica materials have been synthesized, with the most common ones being MCM-41 and SBA-15. Owing to their high thermal stability and well-defined pore structures, these materials have been investigated for a wide range of applications, including catalysis, adsorption, drug delivery, and sensing. In CO₂ capture research, they are commonly used as model supports for investigating adsorption behaviour and developing surface functionalization strategies (Saleh et al. 2024a; b; Candela-Noguera et al. 2024). In recent years, ordered mesoporous silicas, such as MCM-41

and SBA-15, have been widely investigated as model adsorbents for CO₂ capture because of their high surface areas, large pore volumes, and tunable pore structures (Amaraweera et al. 2023). These materials provide well-defined platforms for studying adsorption mechanisms and evaluating surface functionalization strategies. However, their relatively complex synthesis and the use of organic structure-directing agents increase production costs, which currently limit their direct application in large-scale industrial CO₂ capture. Figure 2 illustrates the simplified schematic representation of the synthesis pathways for mesoporous silica materials via four different techniques.

As shown in Fig. 2a, mesoporous silica can be synthesized using the sol-gel method (Emrie 2024). This method involves the use of a sol (a colloidal suspension), as a precursor for the growth and formation of inorganic networks, and a gel (an intermediate) for forming crosslinked networks in a continuous liquid phase. The first stage in the sol-gel method is when the precursor, typically tetraethyl orthosilicate (TEOS), undergoes hydrolysis with a solvent. This is

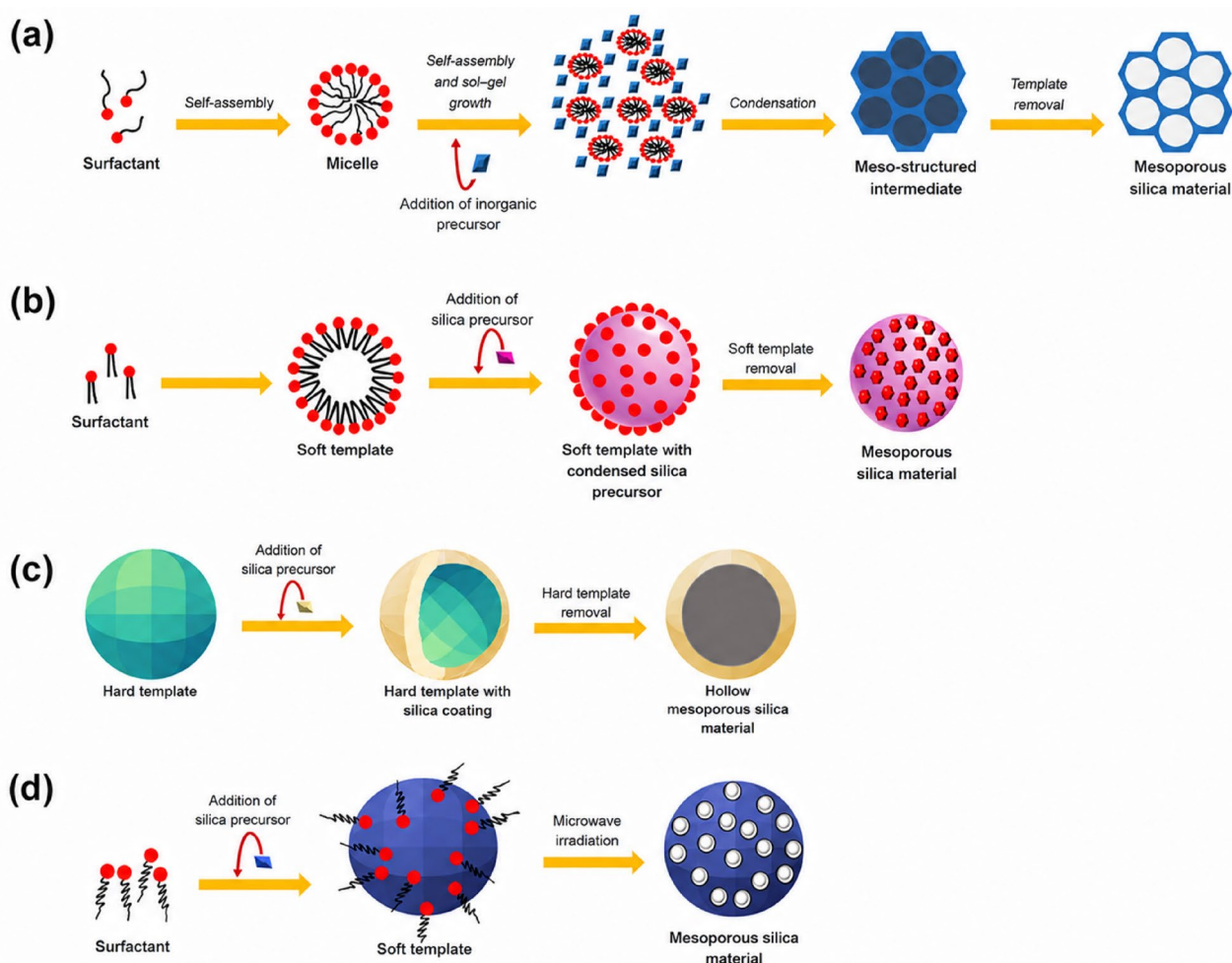


Fig. 2 Schematic representation of the synthesis pathways for mesoporous silica materials: **a** sol-gel method, **b** soft-template method, **c** hard-template method, and **d** microwave-assisted method

followed by condensation as the second stage, where siloxane bonds (Si–O–Si) are formed either from the reaction between two silanol groups, or from the reaction between the alkoxide and silanol groups. The resultant porous silica material can then be obtained through a template removal process via calcination. Both stages in the sol–gel method are dependent on the pH of the reaction condition. In an acidic condition, the rate of hydrolysis is high but fewer siloxane bonds and higher concentrations of silanol groups will be formed due to the slow nucleation during the condensation stage. On the other hand, in a basic condition, highly branched polymers will be formed due to the slow hydrolysis rate, followed by the fast nucleation during the condensation stage. Surfactants and copolymers can be added as surface directing agents. These surface directing agents can aggregate into a micellar structure, providing a scaffold for the precursor to condense around. The micellar structure determines the pore size and structure of the mesoporous silica, as well as the mesophase of the material. The surface directing agents that are commonly used to synthesize MCM-41 and SBA-15 are cetyltrimethylammonium bromide (CTAB) and Pluronic-123 (P123), respectively (Kumar et al. 2017; Emrie 2024).

Other synthesis methods for mesoporous silica include the template-assisted technique and the microwave-assisted technique (Kumar et al. 2017). Template-assisted techniques can be broadly classified into the soft template (Fig. 2b) and hard template (Fig. 2c) techniques. Based on the soft template technique, a surface directing agent is used as the template for the precursor to condense around, which relies on the surface directing agent to self-assemble into micellar structures or liquid crystals (Zhang et al. 2019b). Meanwhile, the hard template technique involves a porous solid that functions as a framework for the materials. The precursor will infiltrate the surfaces and pores of the hard template, which is then solidified. This is followed by a chemical or thermal removal of the template to obtain the mesoporous material. By using this technique, the resultant products would have the complementary structure or negative image of the hard template (Hoffmann et al. 2006; Kumar et al. 2017). In the microwave-assisted technique, microwave irradiation is used to promote faster chemical reactions and ensure uniform heating, as shown in Fig. 2(d). The precursor and surfactant are first prepared in a Teflon vessel and the mixture is then subjected to microwave irradiation. The formation of the desired mesoporous material is accelerated, as heat is directly provided to the mixture, leading to a shorter synthesis time (Kamarudin 2016; Kumar et al. 2017). Studies that have successfully synthesized mesoporous silica materials using different techniques are presented in Table 2.

Table 2 highlights the trade-offs between different synthesis methods, and the textural properties and scalability of these mesoporous silica materials. Different synthesis techniques can produce mesoporous silica materials with distinct structural and porous characteristics. Previous studies have shown that mesoporous silica prepared via the sol–gel technique exhibited inherent inhomogeneity compared to other methods (Chen et al. 2009; Han et al. 2024a). When comparing the soft and hard template-assisted syntheses, mesoporous silica samples synthesized via the hard template technique showed more defined structures compared to samples synthesized via the soft template technique. This could be because the soft template technique relies on self-assembly, which often lacks precise structural control. Overall, the structural precision and textural properties of mesoporous silica adsorbents for CO₂ capture applications are very dependent to the choice of synthesis technique used.

Physicochemical characteristics of mesoporous silica-based adsorbents

Generally, silica materials with hexagonal arrays of homogeneous pores arrangements, such as MCM-41 and SBA-15, are considered highly ordered mesoporous materials. Due to their distinct physicochemical and structural characteristics, they are the desired choice for CO₂ capture applications. Table 3 presents a summary of the reported physical properties and CO₂ uptakes by two types of mesoporous silica materials. The results tabulated in Table 3 demonstrate that the adsorption capacities that could be achieved with pure mesoporous silica materials, particularly with SBA-15 and MCM-41. This is because the porous structures of SBA-15 and MCM-41 are crucial in facilitating CO₂ capture.

Table 3 shows that the highest maximum CO₂ capture using mesoporous SBA-15, with surface areas between 626 and 788 m²/g, is achieved by Oliveira et al. (2023), with CO₂ uptake of 1.85 to 2.16 mmol/g. MCM-41 synthesized by the same research group achieved a CO₂ uptake of at least 1.27 mmol/g (Oliveira et al. 2023, 2025). It should be noted that the optimal surface area range shown in Table 3 is between 626 and 964 m²/g. The adsorption capacities of materials with a surface area above this range tend to be lower. A few of the adsorption capacities of the mesoporous silica materials listed in this table are relatively lower than the earlier mentioned CO₂ capture values, even when the surface area is within the specified range. This difference indicated that each synthesis technique and methodology could significantly influence the CO₂ affinity of the adsorbent materials.

Muchan et al. (2020) examined the performance of (3-Aminopropyl)triethoxysilane (APTES) grafted onto

Table 2 A list of previous studies on mesoporous silica adsorbents for CO₂ capture, as synthesized using different techniques

Mesoporous material	Technique	Structural morphology	Advantages	Disadvantages	References
MCM-41	Sol–gel	Hexagonal, uniform mesopores	<i>Synthesis</i> Simple and cost-effective process. Easy for functionalization. Wide range of synthesis parameters. <i>Textural</i> High surface area. Uniform mesopores.	<i>Synthesis</i> Time-consuming due to aging. Energy-intensive. <i>Textural</i> Inhomogeneity. Limited stability under extreme conditions. Risk of pore collapse. <i>Upscaling</i> Hard to maintain uniformity.	Kamardin and Alias (2013), Loganathan et al. (2015)
SBA-15, MCM-41	Soft template	Hexagonal, ordered mesopores	<i>Synthesis</i> Controlled synthesis of uniform mesopores. Easy for functionalization. <i>Textural</i> Tuneable pore size. <i>Upscaling</i> Suitable for large scale applications.	<i>Synthesis</i> Complex surfactant removal process. Long synthesis time. <i>Textural</i> Residual template affects textural uniformity. Limited precision towards pore size. <i>Upscaling</i> Reduced scalability due to surfactant removal. Higher costs for large scale applications.	Zhang et al. (2022), Dan et al. (2023), Luján Ferreira et al. (2024)
KIT-6	Hard template	Cubic, 3D interconnected pores	<i>Synthesis</i> Allows synthesis of highly ordered meso-structures. Stable synthesis at high temperatures. <i>Textural</i> Well-defined 3D interconnected pores. High thermal and mechanical stability. Reliable method for precision. <i>Upscaling</i> Suitable for large scale applications.	<i>Synthesis</i> Tedious template removal process. <i>Textural</i> Template removal may damage pore walls. Limited flexibility for pore size tuning. <i>Upscaling</i> Time and cost-intensive for large scale applications.	Wang et al. (2023)
SBA-15, MCM-41	Microvawe-assisted	Disordered, worm-like pores; Hexagonal, ordered mesopores	<i>Synthesis</i> Rapid synthesis. Short synthesis time. <i>Textural</i> Suitable for functionalized adsorbents. <i>Upscaling</i> Promising short time prototyping.	<i>Synthesis</i> Requires specialized microwave reactors. <i>Textural</i> Irregular morphology may occur. Limited pore size control. <i>Upscaling</i> Limited scalability for large scale applications. High cost of microwave reactors.	Oliveira et al. (2023, 2025)

various mesoporous silica materials, such as MCM-41, SBA-15, and KIT-6 for CO₂ capture. Figure 3 shows the characterization results of the synthesized materials. Figure 3a–d show that the synthesized mesoporous silica materials exhibited the typical morphologies of MCM-41 and SBA-15. Figure 3e shows the FTIR spectra of all studied materials, including the APTES-functionalized mesoporous silicas. All typical siloxane (Si–O–Si) and silanol (Si–OH) bands could be observed in all the synthesized materials. Figure 3(f) shows the XRD patterns for MCM-41, SBA-15, and KIT-6. The hexagonal close-packed structure of both MCM-41 and SBA-15 could be observed as peaks at 2θ of 2.6° (1 0 0) and 0.90° (1 0 0), respectively. Hence, these

findings indicated that the typical chemical bonds and structures of mesoporous silica materials were retained in these samples, even after their grafting with APTES.

In 2021, SBA-15 is synthesized by Ojeda-López et al. (2021) to study the isosteric enthalpy behaviour of CO₂ capture, and Fig. 4 shows their findings from their work. Figure 4a–d confirm the typical morphology of SBA-15 materials and prove the successful synthesis of this material. Figure 4e shows the Si NMR spectra for SBA-15 and SBA-15-APTES synthesized in their work. SBA-15 can be identified by the presence of silanol (Si–OH bonds) and siloxane (Si–O–Si bonds) groups, both of which are denoted as “Q” in the NMR spectroscopy. When SBA-15 is functionalized

Table 3 A summary of the reported physical properties and CO₂ uptakes of mesoporous MCM-41 and SBA-15

Mesoporous material	Surface area (m ² /g)	CO ₂ Uptake (mmol/g)	T (°C)	P (MPa)	CO ₂ (%)	Flow rate (cm ³ /min)	References
MCM-41	985	0.25	40	–	15	65	Thi Le et al. (2014)
SBA-15	665	0.64	25	0.1	100	–	Sánchez-Vicente et al. (2015)
SBA-15	793	0.91	10	0.1	100		Munguía-Cortés et al. (2018)
MCM-41	992	0.75	25	0.1	100	50	Rao et al. (2018)
MCM-41	1007	0.63	25	0.1	15	20	Muchan et al. (2020)
SBA-15	737	0.71	25	0.1	15	20	Muchan et al. (2020)
KIT-6	672	0.52	25	0.1	15	20	Muchan et al. (2020)
SBA-15	735	0.53	30	0.1	–	–	Ojeda-López et al. (2021)
SBA-15-MW60	788	2.16	0	0.1	100	–	Oliveira et al. (2023)
SBA-15-MW80	626	1.85	0	0.1	100	–	Oliveira et al. (2023)
MCM-41-MW60	999	1.44	0	0.1	100	–	Oliveira et al. (2023)
MCM-41-MW80	744	1.32	0	0.1	100	–	Oliveira et al. (2023)
MCM-41	770	0.4	25	0.1	–	–	Kuppireddy et al. (2024)
MCM-41_MW40-0.5	964	1.27	25	0.1	100	–	Oliveira et al. (2025)
MCM-41_MW80-2	1096	<1.27	25	0.1	100	–	Oliveira et al. (2025)

with amines, it contains “T” sites, which represent the R-Si bonds (R represents the organic residues) seen in APTES molecules. The presence of these groups indicated that APTES has been successfully grafted onto SBA-15 in this work. Figure 4(f) shows that both materials exhibit comparable XRD diffraction patterns, with three peaks associated with refraction planes at (1 0 0), (1 1 0), and (2 0 0). The peaks showed the hexagonal arrangement of cylindrical mesopores found in typical SBA-15 materials. The diffraction peaks of SBA-15-APTES have shifted to low Q (or low 2θ), implying that the unit cell (hexagonal) of the mesopore arrays became larger. Similar phenomenon is also observed in (Goscianska et al. 2017). As for the isosteric adsorption enthalpy, they estimated from Clausius-Clapyron equation and found that for SBA-15 based material, the values decrease as CO₂ coverage increases. They also reported that this change is primarily due to chemical composition, which in their study, the functionalization of amine group onto SBA-15.

Meanwhile, Fig. 5 shows the TEM micrographs of microwave-irradiated mesoporous MCM-41 and SBA-15 at temperatures of 60 and 80 °C (Oliveira et al. 2023). Figure 5a–d show that this approach could improve the regularity and structural integrity of silica channels, which are crucial for effective CO₂ capture. The most important bond shown in the FTIR spectra, as represented in Fig. 5e, to confirm modification with polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) is the N-H bond, referring to the amine functional groups, –NH₂. Along with FTIR spectra, the XPS spectra in Fig. 5f could also confirm silica surface modification. Amine-modified MCM-41 silicas show signals from C 1s, N 1s, Si 2p, and O 1s, with N and C signals increasing after PEI or TEPA impregnation, as shown

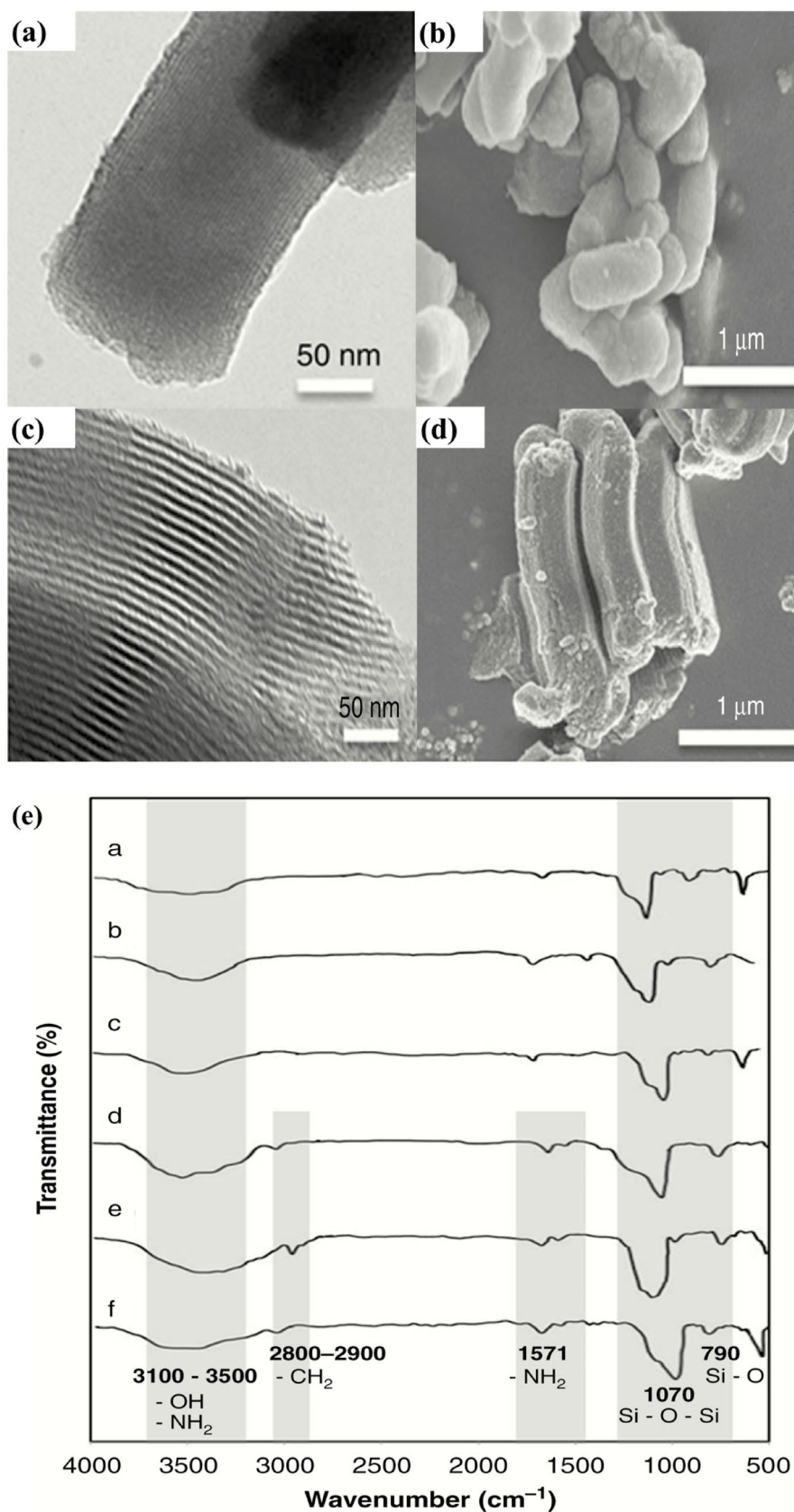
in the Si NMR spectra in Fig. 5g. These results showed that the structural integrity of the samples, created by the microwave-irradiation method employed in this work, has facilitated the access to amine-groups very well, which is crucial for enhanced CO₂ capture.

In general, the CO₂ capture results for the reported works in Table 3 are satisfactory, demonstrating the capability of pristine silica materials to adsorb CO₂, depending on the operating condition. In fact, the structure of mesoporous MCM-41 and SBA-15 consists of Si–OH groups on the surface and Si–O–Si groups within the framework. The Si–OH groups on the particle surface enhance the adsorbent–CO₂ molecules contact, while the high surface area, and thermal and mechanical stabilities of silica materials contribute to their performance in CO₂ capture applications.

Limitations of pristine mesoporous silica as adsorbent

A previous study reported that CO₂ adsorption on mesoporous silica is primarily governed by weak interactions between CO₂ molecules and surface silanol (Si–OH) groups, together with interactions with siloxane (Si–O–Si) linkages, as supported by adsorption isotherms and heat of adsorption measurements (Loganathan et al. 2015). Although ordered mesoporous silica can be used as adsorbents for CO₂ adsorption, the weak reactivity of its surface caused by the residual hydroxyl group, namely silanol group, could only allow it to form hydrogen bond with foreign gaseous molecules, making it less effective in CO₂ capture (Szczodrowski et al. 2009; Zelenák et al. 2017). Consequently, the CO₂ adsorption capability of pure mesoporous silica is largely depended on the availability of the silanol groups.

Fig. 3 Characterization results of the APTES-functionalized mesoporous silica materials: **a** TEM micrograph of MCM-41; **b** SEM micrograph of MCM-41; **c** TEM micrograph of SBA-15; **d** SEM micrograph of SBA-15; **e** FTIR spectra for MCM-41, SBA-15, functionalized MCM-41, and functionalized SBA-15; and **f** XRD patterns for MCM-41, SBA-15, and KIT-6 (Muchan et al. 2020)



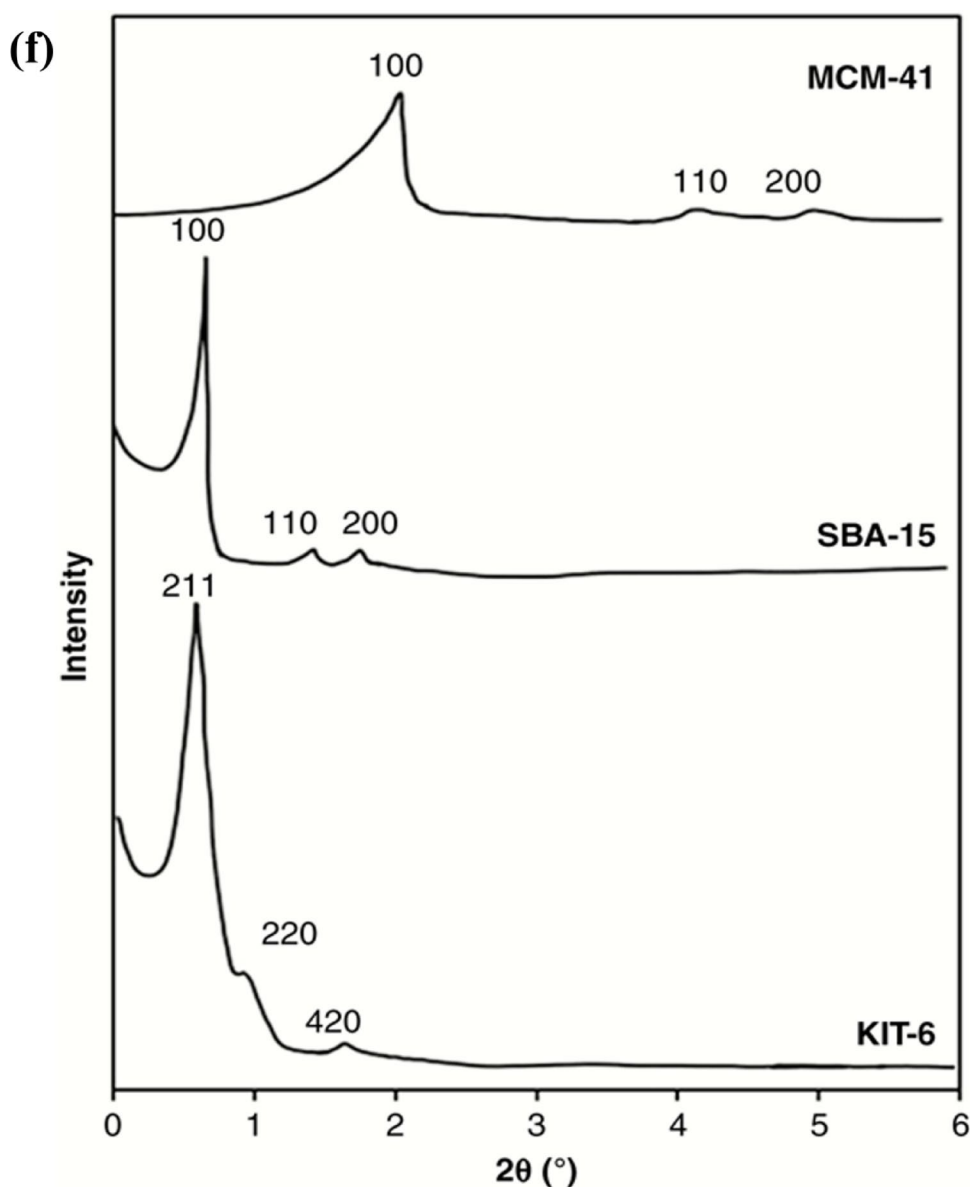


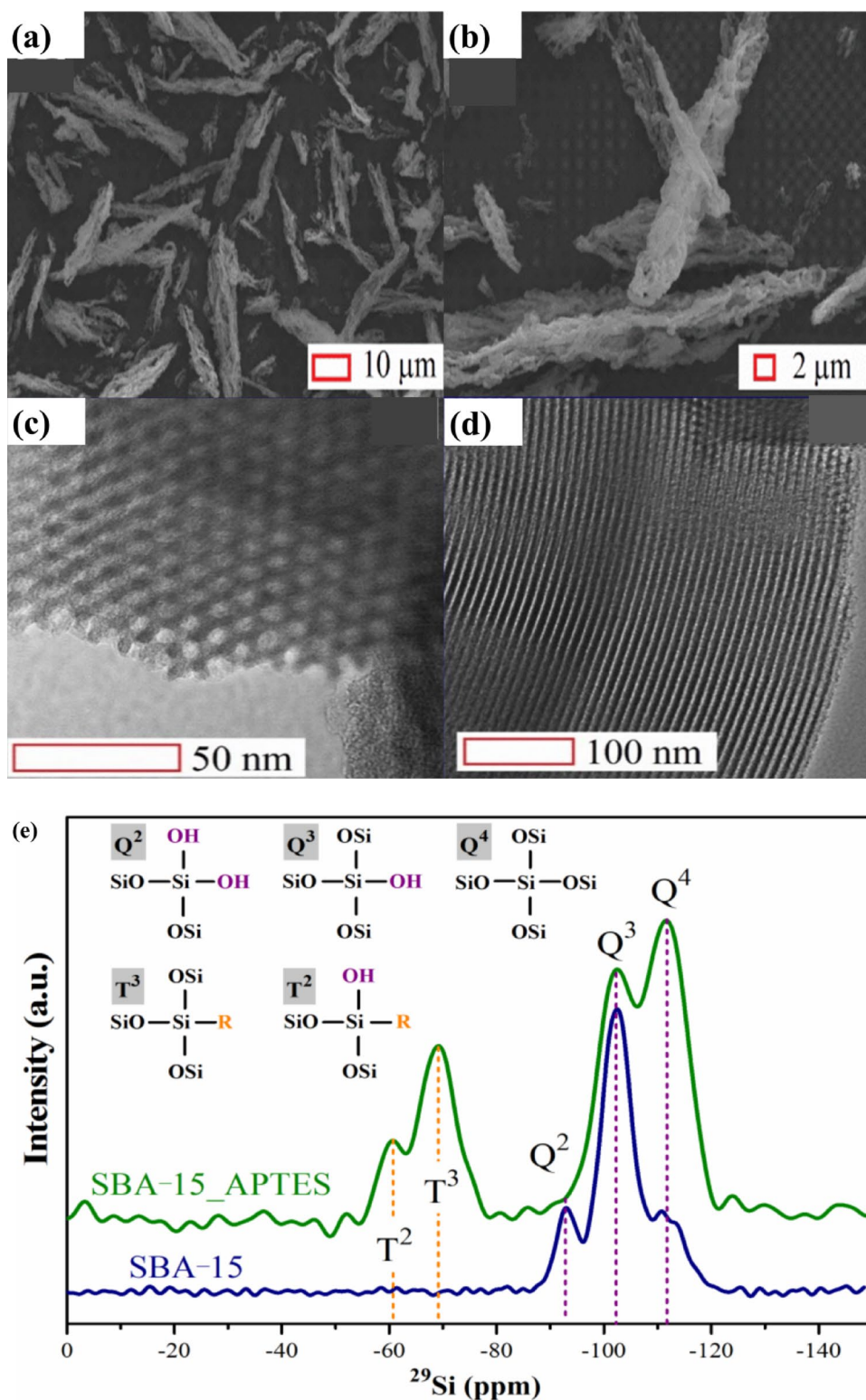
Fig. 3 (continued)

Therefore, functionalization is required to enhance the CO_2 adsorption capability of mesoporous silica. However, calcination is the typical template removal method, which involves the dehydroxylation of silica to condense the silanol groups (Benamor et al. 2012; Arias et al. 2025). This method could lead to a decrease of surface silanol groups, which are crucial for post-synthesis modification. Nonetheless, a high amount of silanol groups could detrimentally affect the hydrothermal stability of the mesoporous silica materials. Thus, efforts have been made to preserve as much silanol groups as possible during the template removal process (Ghaedi and Zhao 2022; Arias et al. 2025).

Thermal stability is crucial for practical application to avoid severe degradation at high temperatures. While

mesoporous silicas are often recognized for their robustness in dry environments, a clear distinction must be made between thermal stability and hydrothermal stability, as these materials respond differently to heat depending on the presence of moisture. Earlier in 2002, thermal stability of various mesoporous silica was investigated by Cassiers et al. (2002). They found out that the thermal stability of silica is related to wall thickness and silica precursor. For silica precursor, they noticed that the mesoporous silica synthesized using fumed silica exhibit superior thermal stability compared to those made using TEOS, with MCM-41 and MCM-48 suffering about 80% loss in BET surface area at 750°C for TEOS-made whereas for fumed silica-made MCM-41 and MCM-48, they still retain around 80% of initial surface

Fig. 4 SEM micrographs of SBA-15 at **a** 10 μm and **b** 2 μm ; TEM micrographs of SBA-15 at **c** 50 nm and **d** 100 nm; **e** Si NMR spectra for SBA-15 and SBA-15_APTES; and **f** XRD patterns for SBA-15 and SBA-15_APTES (Ojeda-López et al. 2021)



area at 850 °C. For material synthesized using TEOS, they also noticed that SBA-15 exhibited higher thermal stability compared to MCM-41 and HMS due to having thicker wall.

The thermal stability of SBA-15 is typical high, up to 500–600 °C as they are commonly obtained by calcination

around that particular temperature ranges and beyond that, it suffered loss of porosity, though it is able to maintain the mesoporous structure of material (Mitran et al. 2020). Da Silveira et al. (2014) reported that the ordered hexagonal 2D porous structure of SBA-15 still persisted at 900 °C, through

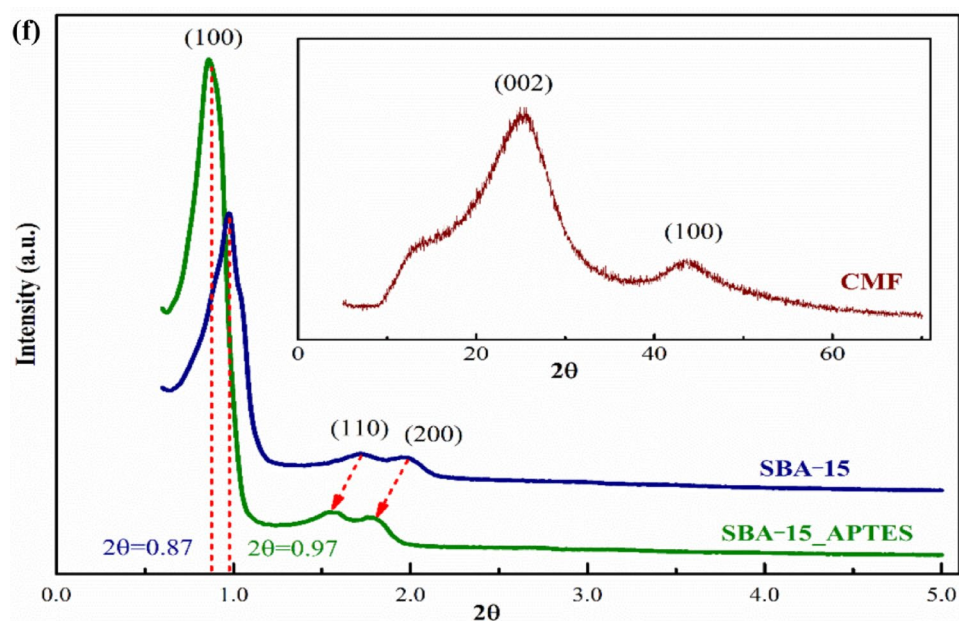
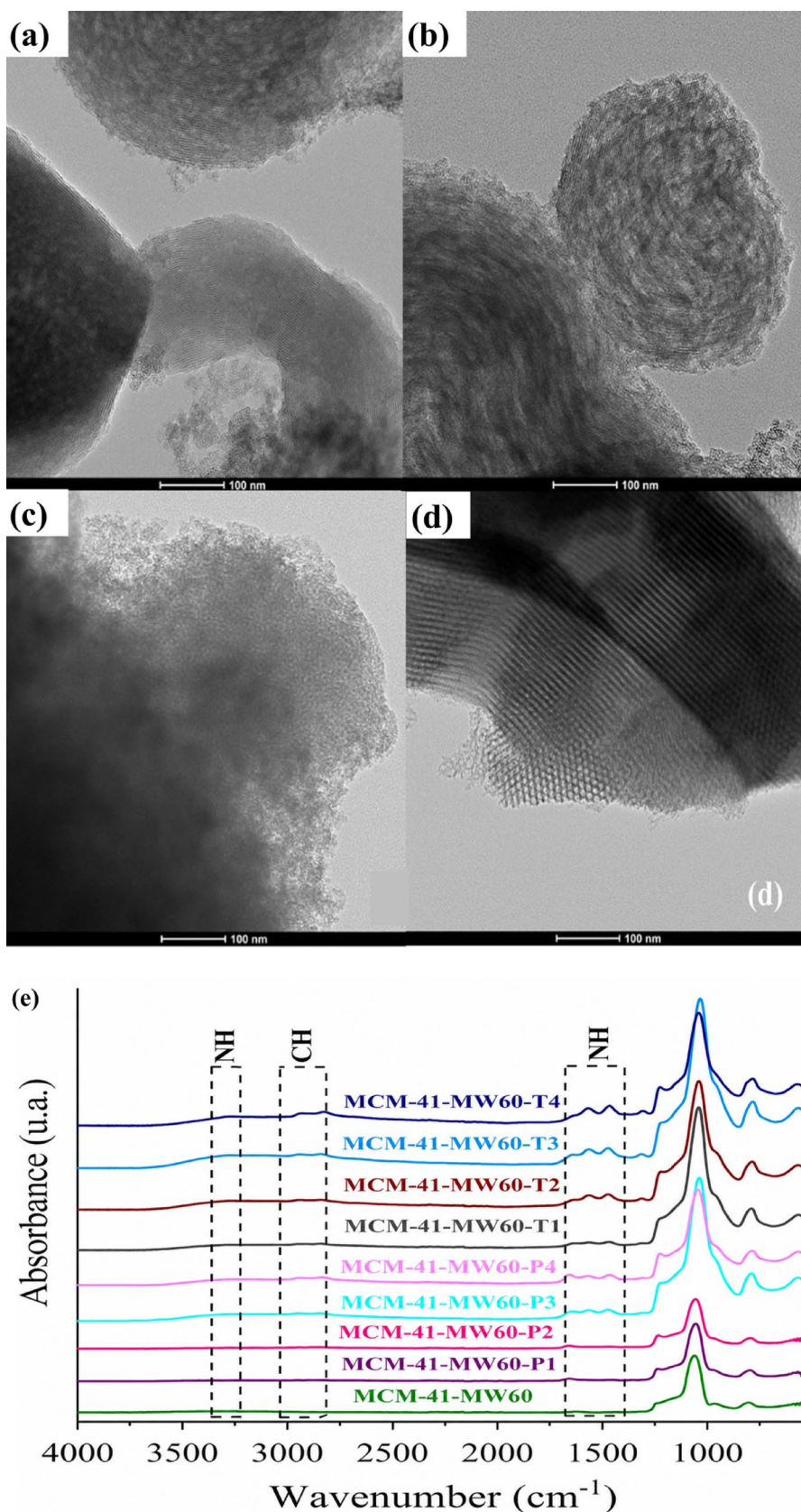


Fig. 4 (continued)

small-angle X-ray scattering pattern and BET characterization. Similarly, XRD study by Mitran et al. (2020) found out that at 900 °C, the (100) characteristics peak of SBA-15 still persists, though the other peaks (110) and (200) are already hardly visible at particular temperature. They also reported the significant degradation in specific surface area and pore volume at higher temperature (above 500 °C). In another study by Shah and Ramaswamy (2008), they reported that the (100) characteristics peak still exist even at 1473 K (1200 °C). It should be noted that these studies are conducted as in heat treatment in dry environment at high temperatures. According to Da Silveira et al. (2014), the loss of porosity could be explained through geometric contraction model, in which the cylindrical pores diameter of silica diminishes while the length remains constant, leading to gradual thickening of silica walls as the pores shrink inward. High temperatures can induce the condensation of surface silanol groups and contraction of silica lattice, which smoothed the interior mesopore surface, causing the framework walls to thicken and the pore radius to shrink inward—effectively a “geometric collapse” of the radius. The model is in agreement with their observation and the work by Mitran and colleagues, where the unit cell parameter and pore size of SBA-15 decreases while the wall thickness increases in increasing temperature. There are also attempts to improve the thermal stability of SBA-15 through the modification with tin, ceria, and zirconium (Shah and Ramaswamy 2008; Usami et al. 2012; Mitran et al. 2020). Nevertheless, these showed that pristine SBA-15 is able to withstand high temperatures for practical applications.

While thermal stability of silica commonly referred to ability of silica to maintain the framework structure in high temperatures process and dry environment, such as calcination and heat treatment, the hydrothermal stability of silica, on the other hand, specifically refers to thermal stability of silica in the presence of water or steam, and is generally much lower. Silica suffers from low hydrothermal stability due to the hydrolysis of Si–O–Si bonds in the presence of water (Chew et al. 2010). Since water may also be present in the post-combustion flue gas, as in a real-life situation, it could affect the CO₂ adsorption process of mesoporous silica. Water molecules being able to form hydrogen bonds with silanol groups could compete with CO₂ molecules during adsorption, further reducing available adsorption sites for CO₂. A study has revealed that SBA-15 and SBA-16 experienced structural degradation after exposure to boiling water for 10 days, as evidenced by decreasing BET surface areas (Guo et al. 2006). The structural disintegration of MCM-41 and MCM-48 was also reported in the presence of water at approximately 370 K, which was attributed to the hydrolysis of Si–O–Si bonds, as indicated by their XRD and magic angle spinning NMR results (Kim and Ryoo 1996). These findings have highlighted the challenges in maintaining the structural integrity of mesoporous silica materials in humid conditions. Galarneau et al. (2007) have also studied the stability of SBA-15 and MCM-41 synthesized at different temperatures in water. They reported that SBA-15 synthesized at 60 and 100 °C experienced structural changes (decreasing pore volume) during water treatment for 4 h at room temperature and reflux at 100 °C for 4 h. Meanwhile, SBA-15 synthesized at 130 °C only experienced a slight

Fig. 5 Characterization results of different synthesized silicas: TEM micrographs of **a** MCM-41-MW60, **b** MCM-41-MW80, **c** SBA-15-MW60, and **d** SBA-15-MW80; **e** FTIR spectra of MCM-41-MW60 and MCM-41-MW80 impregnated with PEI and TEPA; **f** XPS spectra of MCM-41-MW60, MCM-41-MW80, SBA-15-MW60, and SBA-15-MW80; and **g** Si NMR spectra of MCM-41-MW60, MCM-41-MW80, SBA-15-MW60, and SBA-15-MW80 (Oliveira et al. 2023)



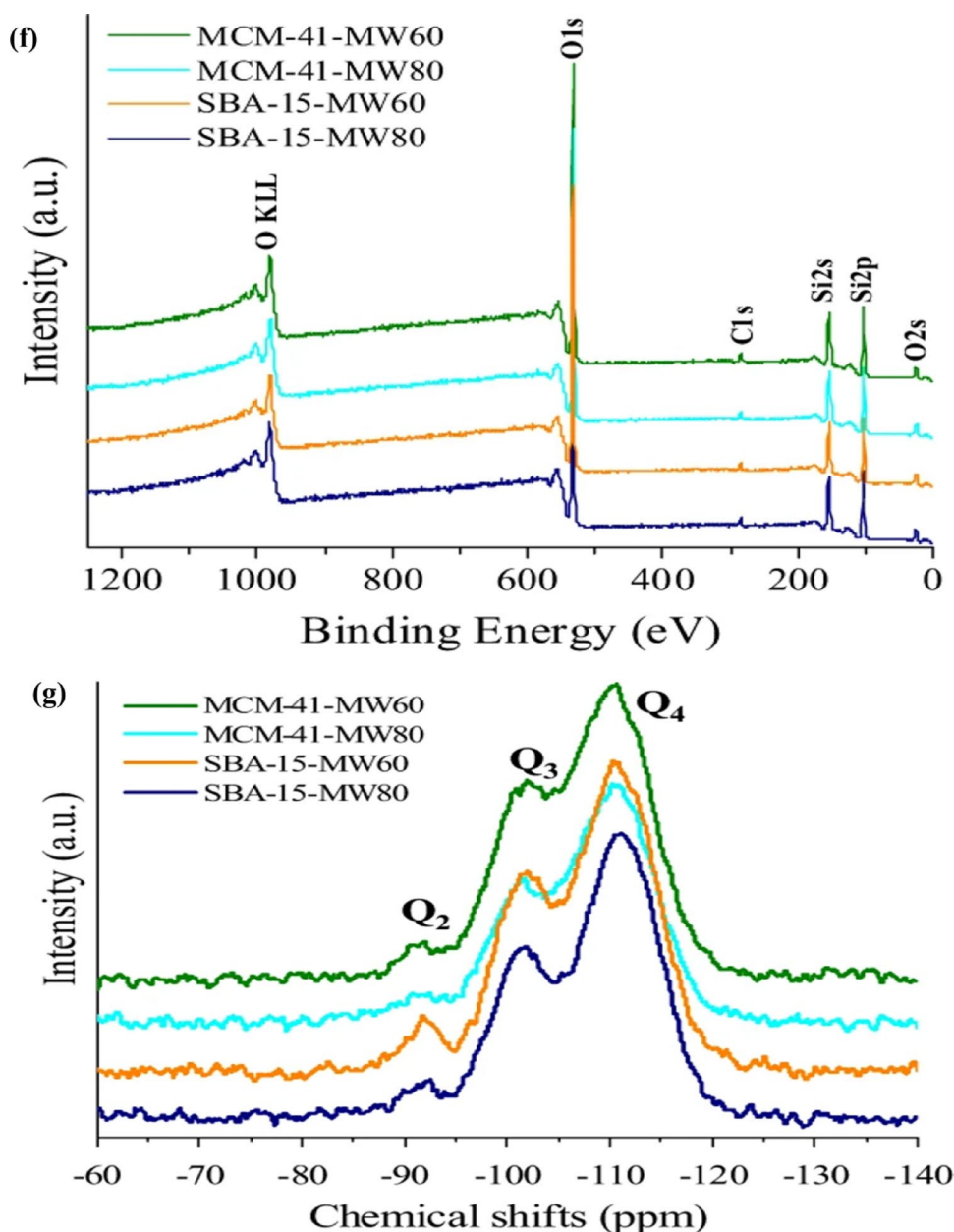


Fig. 5 (continued)

decrease in its specific surface area (Galarneau et al. 2007). Owing to its relatively thinner walls compared to SBA-15, MCM-41 also experienced significant structural changes (decreasing BET surface area, pore size, and pore volume), more so than SBA-15. This unpredictability in reactivity to hydrothermal temperatures could be a serious issue when using these materials in environments with large quantities of water vapour.

Because steam stripping could be used to desorb CO_2 from adsorbents, hydrothermal stability in steam is important. Zhang et al. (2005) studied the hydrothermal stability of SBA-15 in steam. They reported that the BET surface

area was decreased by approximately 62% after their sample underwent steam treatment at 600 °C for 24 h, as well as the destruction of mesostructured SBA-15 under steam treatment at 800 °C due to fast and severe recombination of Si–O–Si bonds. Then, they modified the synthesis procedure to obtain SBA-15 with different wall structures to understand the effect of wall structure on hydrothermal stability. The results showed that mesoporous silica with thicker walls and more micropores exhibited better hydrothermal stability (Zhang et al. 2005). These findings were similar to the findings obtained by (Cassiers et al. 2002). They found that SBA-16 and KIT-6 were able to withstand

mild hydrothermal steam treatment at 400 °C, with 15% to 20% decrease of mesoporous volume compared to MCM-41, with approximately 40% to 50% decrease. Interestingly, they also found that MCM-47 experienced lesser structural degradation than other hexagonal mesoporous silica samples, which could be attributed to different pore structures and curvatures (Cassiers et al. 2002). Consequently, several modifications have been performed to improve the hydrothermal stability of mesoporous silica in water and steam (Ryoo and Jun 1997; Kim et al. 1999; Yu et al. 2001; Park et al. 2001; Liu et al. 2003; Xia and Mokaya 2004; Zhang et al. 2005). The crucial findings of the previous studies implied that certain synthesis procedures could improve some of the structural flaws observed in mesoporous silicas.

Competitive adsorption with water is also an issue for mesoporous silica in CO₂ capture process. As mentioned earlier, moisture exists in industrial flue gas. Mesoporous silica contains surface silanol groups, thus they are also prone to adsorb water through the formation of hydrogen bond between water molecules and silanol groups. This creates direct competition because water adsorbs on the same specific adsorption site as CO₂, as reported in literature (Stevens et al. 2008). Because both molecules possess electromagnetic properties, with water having a permanent dipole moment and CO₂ a quadrupole moment, meaning any modification on surface chemistry simultaneously affect the affinity for both compounds. Recent study by Avellaneda et al. (2024) reported that SBA-15 have high affinity for water through the CO₂ and H₂O co-adsorption breakthrough experiment. At higher relative humidity levels (20–50% RH), when co-adsorbed with CO₂, water molecules occupy CO₂ sites and can create liquid films on the surface that block CO₂ diffusion, significantly reducing adsorption capacity. This is particularly detrimental towards practical application as it will severely compromises the CO₂ adsorption performance in practical applications. The water adsorption on mesoporous silica could be explained as 2-stages mechanism: at low relative pressure, the adsorption is driven by surface-water interactions whereas at high relative pressure, the process is driven by water-water interactions through hydrogen bonding within pore volume, leading to capillary condensation (Hertl and Hair 1969; Cauvel et al. 1997; Liu et al. 2017). While pristine silica performance suffers in these conditions, there are several studies that reported amine-modified silica seems to have improved CO₂ adsorption performance in presence of moisture, which will further discussed in the next section.

In short, while pristine mesoporous silicas have promising potentials for CO₂ capture due to their morphological structures, their application is severely constrained by several factors, such as competitive adsorption by water molecules and their hydrothermal instability. The synthesis of

mesoporous silica with optimized structural features, such as tuned porosity and increased wall thickness has emerged as a critical solution for improving CO₂ capture performance and the durability of the mesoporous silica materials. Moving forward, research into amine-functionalized mesoporous silica materials is seen as an effective solution to achieve this objective.

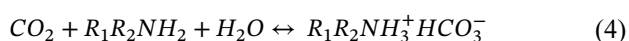
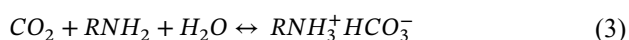
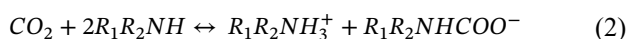
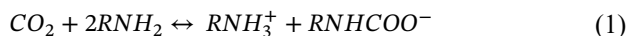
Techniques for amine-functionalization of silica for CO₂ adsorption

CO₂ is an acidic gas. Therefore, most surface functionalization methods are inclined towards increasing the basicity of the adsorbent surface. A study reported that the strength and quantity of acid sites could negatively affect CO₂ adsorption on adsorbents with acidic properties. They also postulated that specific surface areas would be more important relative to total acidic sites (Gouveia et al. 2020). They have also studied alkaline materials for CO₂ adsorption and reported the highest adsorption capacity of 159.1 mg/g, achieved by calcined Layered Double Hydroxides (LDH). Their finding showed that for alkaline samples, the number of basic sites were relatively more important. This could be because CO₂ capture was initiated not only by physisorption, but also by chemisorption, which occurred via chemical interaction with the basic sites on the LDH material.

Functionalization of ordered mesoporous silica with amine groups is the most common modification method, with several studies reporting improvements in CO₂ adsorption performances (Yan et al. 2022). Amine containing functional groups are basic in nature and aminosilanes, such as (3-Aminopropyl)triethoxysilane (APTES) and (3-Aminopropyl)trimethoxysilane (APTMS) are commonly used to functionalize ordered mesoporous silica. Aside from that, polyethylenimine (PEI), tertaethylenepentamine (TEPA), and tetraethylenetetramine (TETA) are also used for the functionalization of silica. It is important to distinguish between grafting and impregnation. Organosilanes such as APTES and APTMS react with surface silanol groups to form covalent Si–O–Si bonds, whereas polymeric amines such as PEI and TEPA are typically introduced by pore impregnation through physical interactions. Amine modification on silica generally resulted in chemisorption due to the formation of surface intermediate groups.

Compared to dry conditions, amine-functionalized mesoporous silica would perform comparably well in CO₂ adsorption in wet conditions, considering the competitive adsorption with water molecules. The presence of moisture might even enhance CO₂ adsorption performance using amine-functionalized silica (Li et al. 2016; Lee et al. 2017; Pacheco et al. 2022; Hack et al. 2022). Experimental data confirms this, with studies reporting the increase

in adsorption capacity (Zhao et al. 2010, 2013; Zhang et al. 2017; Avellaneda et al. 2024). As described in Hack and co-workers' work, the presence of water shifts the reaction mechanism to form bicarbonate instead of carbamate, allowing for more favourable CO₂ to amine ratio, especially for primary and secondary amines, which theoretically doubling CO₂ capture efficiency (Hack et al. 2022). The typical reaction mechanism pathways are shown in the following schemes for primary amine (Eqs. 1 and 3) and secondary amine (Eqs. 2 and 4) in both dry (Eqs. 1 and 2) and moist condition (Eqs. 3 and 4) (Pirzadeh et al. 2025).



Nevertheless, recent computational studies coupled with the use of nuclear magnetic resonance (NMR) revealed that not only carbamate and bicarbonate species formed during the adsorption process with amine-modified adsorbent, but there are also formation of multiple other compounds, which will be further discussed in DFT computational studies analysis section (Afonso et al. 2019; Sardo et al. 2021).

However, the possible trade-offs are the requirement of additional thermal energy for desorption and causing slower adsorption kinetics, as noted in Surkatti et al. (2025). Further increase in water content may also affect the adsorption capability of the amine-modified mesoporous silica. At higher humidity level, the water film will form on the surface of adsorbent, which creates additional mass transfer resistance, possibly slows down the reaction kinetics and limits the CO₂ accessibility to active sites (Avellaneda et al. 2024; Pirzadeh et al. 2025). Amine groups also capable to form hydrogen bond with water molecules. Coupled with the fact that surface modification will reduce the pore size and specific surface area, competitive adsorption between CO₂ and water might occurred if the humidity level exceeds beyond optimal level (Wu et al. 2021). As mentioned earlier, increasing the CO₂ adsorption capacity would also increase the tendency to adsorb water. Avellaneda et al. (2024) also studied the CO₂ capture performance on APTES grafted amine SBA-15 in humid condition. They noticed the improvement in adsorption capacity for about 35% for the grafted amine silica when RH % is 20%. They also observed that the grafted amine silica adsorbed more water compared to pristine silica. They highlighted that while the presence of water could promote CO₂ adsorption through the formation of bicarbonates, desorption on grafted materials could be

difficult as the process is partly irreversible as confirmed by their H₂O adsorption isotherm where the desorption branch does not join the adsorption branch. This could affect the application in industrial usage as higher amount of heat energy is required to desorb the water, which could increase the cost. Moreover, as modification on silica reduce the pore size and specific surface area, at higher RH%, grafted samples can reach total pore volume filling (100%), which may eventually limit the capacity for CO₂ by physically plugging the material.

Interestingly, loading amine like PEI also form protective layer to shield the underlying framework to certain extent. As mesoporous silica like MCM-41 has thinner wall and more susceptible to hydrothermal decay, it can lead to rapid structural collapse in such condition. In a study by Xu et al. (2005), they modified MCM-41 with PEI and reported that PEI modified MCM-41 exhibited better hydrothermal stability than pristine MCM-41 and stable over 10 CO₂ adsorption-desorption cycles under the humid conditions. This showed that polymer-like amine could provide protective effect that shielding the underlying framework from hydrothermal decay.

Common functionalization techniques, such as impregnation, grafting, and direct synthesis are presented in Table 4, with their respective CO₂ adsorption performance. Table 4 shows that adsorption capacities may vary, even when using the same functionalization agent, for example, APTES. This observation suggested the influence of other experimental factors, such as temperature and pressure. Different adsorbent materials were reported to have performed differently at different temperatures and pressures, illustrating how critical these variables would be for CO₂ capture. While mesoporous silica typically exhibits physisorption with CO₂, which is an exothermic process where adsorption capacity decreases with temperature, an initial increase temperature leads to an increase in observed CO₂ adsorption capacity. For instances, in Table 4, TEPA-impregnated materials and PEI-modified materials seems to exhibit better performance at higher temperatures. This could be attributed to improved mass-transfer kinetics, where higher temperature enhanced the mobility of bulky amine chains, facilitating the diffusion of CO₂ to previously inaccessible active sites within the mesopores (Kong et al. 2026). However, beyond certain optimal temperature, the thermodynamic effect dominates and adsorption capacity decreases as the CO₂-amine interaction become less stable and the desorption rate increases. Different amine-functionalization agents also have variable degrees of effectiveness due to differences in the final molecular structure of the adsorbent materials that could affect how they interact with CO₂. Bulkier amines, for example, may facilitate or restrict CO₂ adherent to the

Table 4 Various amine-functionalized mesoporous silica samples and their CO₂ adsorption performances

Material	Functionalization agent	Adsorption capacity (mmol/g)	T (°C)	P (MPa)	CO ₂ (%)	Flow rate (cm ³ /min)	References
<i>Impregnation method</i>							
SBA-15	APTES and lysine	4.53	25	0.2	2	65	Luján Ferreira et al. (2024)
SBA-15	APTES and lysine	3.11	25	0.16	2	65	Luján Ferreira et al. (2024)
SBA-15 (p)	TEPA	5.39	75	0.1	20	60	Zhang et al. (2018)
SBA-15	TEPA	3.48	75	0.1	10	100	Zhao et al. (2013)
SBA-15	TEPA	3.67 ^a	75	0.1	10	100	Zhao et al. (2013)
Si-MCM-41	50 wt% PEI	2.26	100	0.1	100	100	Ahmed et al. (2017)
Al-MCM-41	PEI	1.27	75	—	60	100	Li et al. (2024)
MCM-41	50 wt% PEPA and 5 wt% MPEG	2.39	50	—	15	30	Wang et al. (2019)
SBA-15	50% wt TEPA	3.7	45	0.1	15	100	Sanz-Pérez et al. (2013)
SBA-15	PEI 60wt%	2.68	95	—	15	30	Klinthong et al. (2016)
SBA-15	PEI 40wt%	1.40	40	0.1	44.4	90	Henao et al. (2020)
SBA-15	PEI	3.14	45	0.1	100	—	Olea et al. (2013)
SBA-15	TEPA	3.73	45	0.1	100	—	Olea et al. (2013)
SBA-15	PEI	3.89	45	0.1	15	—	Olea et al. (2013)
MCM-41	PEI 50wt%	3.53	25	0.1	100	50	Rao et al. (2018)
<i>Grafting method</i>							
SBA-15	APTES	1.60	25	—	P _{CO₂} = 0.015 MPa	—	Wang and Yang (2011)
SBA-15	N ¹ -(3-trimethoxysilylpropyl)diethylenetriamine	3.03	90	0.1	—	—	Anyanwu et al. (2021)
SBA-15 ^b	N ¹ -(3-Trimethoxysilylpropyl)diethylenetriamine	1.28	25	0.1	100	—	Anyanwu et al. (2022)
SBA-15 ^c	N ¹ -(3-Trimethoxysilylpropyl)diethylenetriamine	1.28	25	0.1	100	—	Anyanwu et al. (2022)
SBA-15 ^d	N ¹ -(3-Trimethoxysilylpropyl)diethylenetriamine	2.3	75	0.1	100	—	Anyanwu et al. (2022)
SBA-15 ^e	N ¹ -(3-Trimethoxysilylpropyl)diethylenetriamine	2.45	75	0.1	100	—	Anyanwu et al. (2022)
SBA-15	EDA	0.45	25	0.1	15	30 ^g	Zheng et al. (2005)
SBA-15	EDA	1.93	22	0.1	100	30 ^g	Zheng et al. (2005)
MCM-41	APTES (50wt%)	2.41	25	0.1	100	50	Rao et al. (2018)
SBA-15	3-[2-(2-Aminoethylamino)ethylamino]propyl trimethoxysilane	1.88	25	—	5	—	Jahandar Lashaki and Sayari (2018)
KIT-6	APTES	1.56	30	0.1	100	—	Kishor and Ghoshal (2015)
SBA-15	(3-trimethoxysilylpropyl)diethylenetriamine	1.28	35	—	15 ^f	30	Hiyoshi et al. (2004a)
<i>One-pot/direct synthesis method</i>							
Mesoporous silica powders	PEI (0.32 mol ratio)	3.34	95	—	15	30	Klinthong et al. (2016)
MCM-41	APTES	1.18	35	—	15	30	Klinthong et al. (2013)
MCM-41	APTES	1.74	25	—	100	30	Klinthong et al. (2013)
<i>Double functionalization</i>							

Table 4 (continued)

Material	Functionalization agent	Adsorption capacity (mmol/g)	T (°C)	P (MPa)	CO ₂ (%)	Flow rate (cm ³ /min)	References
MCM-41	APTES grafted (30wt%) and TEPA impregnation (40wt%)	3.50	70	0.1	15	40	Wang et al. (2015)
MCM-41	Aminopropyl grafted and TEPA impregnation (50wt%)	2.36	45	0.1	100	–	Sanz et al. (2015)

^aWet, relative humidity = 95%^bDry grafting at grafting temperature 85 °C and reaction time 3 h^cDry grafting at grafting temperature 30 °C and reaction time 3 h^dWet grafting at grafting temperature 85 °C and reaction time 3 h with 0.6mL H₂O/g SiO₂^eWet grafting at grafting temperature 30 °C and reaction time 3 h with 0.6mL H₂O/g SiO₂^fWith 12% H₂O^gFlow rate at standard temperature and pressure condition (T = 273 K and P = 0.1 MPa)

adsorbent depending on their location or position within the silica framework.

The specific surface area and porosity of the materials are also equally important for CO₂ adsorption, especially the porosity. A high total pore volume is essential for accommodating large quantities of amines while maintaining a uniform dispersion. Having larger specific surface area and pore size could theoretically accommodate more amine on mesoporous silica, which improve the CO₂ uptake. This is evidenced by the work of Kishor and Ghoshal (2017), which they reported that amine-modified mesoporous silica with larger pore volume such as SBA-15 and KIT-6 with interconnected pore network having improved sorption capacity. Their work also reported 3D interconnected pores network in KIT-6 facilitated the adsorption diffusion kinetics compared to MCM-41 and SBA-15, which leads to higher adsorption rate. Similar finding also reported in mesoporous silica MCM-48 which exhibited similar 3D interconnected pore structure in study by Hori et al. (2017). Interconnected networks allow CO₂ molecules to find “detours” around local amine blockages, ensuring high amine accessibility throughout the entire particle. While high surface area is the dominant factor for physisorption in pristine silica, if the pore size is too small, it will still affect the efficient loading of amine onto the surface. Insufficient volume leads to amine agglomeration on the external surface, which blocks the pore entrances, especially with bulkier amine at high loading, reducing their mobility and preventing CO₂ from reaching internal active sites. Nevertheless, they are not the only elements that could influence CO₂ capture performance. The chemical composition of the functionalized surface is also important, as evidenced by the variations in adsorption capacities seen across adsorbents with similar surface areas. The available surface silanol groups on mesoporous silica served as primary sites that anchor the impregnated or grafted amine. This is especially

important in grafted amine, as the silanol concentration on surface dictated how much amine could functionalized onto the mesoporous silica compared to the impregnated silica that typically can accommodate higher amine loading.

Impregnation

Functionalization of silica through impregnation can be achieved in two ways, namely the dry (Eskandari et al. 2019) and wet (Abdullah et al. 2020) methods, where the primary difference between both methods is in the way by which solvent is added to the surface of the porous silica support. The dry impregnation method involves adding a certain amount of solvent just enough to fill only the pores of the solid silica material. Meanwhile, the wet impregnation method involves immersing the solid silica material in a large volume of solvent and then the excess solvent is removed by drying. Chemical loading could be easily controlled by employing this method. Thus, impregnation involves chemically modifying the physiochemical properties of adsorbents.

As listed in Table 4, Ahmed et al. (2017) employed a simple impregnation process to synthesize PEI-functionalized Si-MCM-41. Their sample achieved a high CO₂ adsorption capacity of 47.93 mg/g at 25 °C, and 99.44 mg/g at 100 °C. However, for regeneration study, they noticed a gradual decrease in adsorption capacity over the 6 adsorption-desorption cycles. The authors suggested that it might be due to carbamide formation or strong interaction between CO₂ molecules and amino groups which resulted in incomplete desorption. Similarly, Klinthong et al. (2016), also utilised impregnation process to synthesis PEI-containing SBA-15 to compared with PEI-containing SBA-15 obtained through one-pot synthesis, which will discussed in the later section. Other studies have also investigated different impregnation methods using different amines and co-functionalization

procedures, which influenced CO₂ capture performance and stability (Zhang et al. 2018; Wang et al. 2019). Zhang et al. (2018) discovered that impregnating uncalcined SBA-15 (SBA-15(p)) with TEPA has improved its cyclic performance and reusability, resulting in greater stability and a CO₂ adsorption capacity of 5.0 mmol/g, even after 9 cycles (Zhang et al. 2018). Wang et al. (2019), on the other hand, added methoxypolyethylene glycol (MPEG) together with polyethylene polyamine (PEPA), onto mesoporous silica, which significantly increased the equilibrium adsorption capacities by improving amine dispersion and interaction with CO₂ (Wang et al. 2019). They reported the adsorption capacity only drop 5% after 10 adsorption-desorption cycles under dry and humid conditions, suggesting that the modified material is comparatively stable. Moreover, a co-dispersion technique was employed using APTES and L-lysine to co-functionalize SBA-15 using impregnation process in a study by Luján Ferreira et al. (2024). It was observed that a unique synergy existed between these two amine precursors, which increased CO₂ adsorption capacity from 3.39 mmol/g to 4.53 mmol/g at 2 bar, room temperature. These studies have emphasized the relevance of amine combinations over single-amine functionalization, thus, offering insight into the novel method of multi-amine functionalization techniques to enhance CO₂ capture performance. Possibly, the introduction of multiple amines groups increases the availability and amount of active binding sites that can have strong interaction with CO₂ molecules, which improve the CO₂ adsorption, up to certain limits. In conclusion, mixing multiple amine precursors or including co-dispersants like MPEG could considerably improve the functional properties of mesoporous adsorbent materials. The result could be a synergistic effect that could be crucial in specific industrial CO₂ capture applications. These findings demonstrated the role of co-dispersions in improving the performance of amine-functionalized adsorbents.

These studies have discovered that impregnation caused the physical attachment of amine functional groups to the surface or pores of the SBA-15 material. In all reported works, the amine group was bound to the surface of SBA-15 via physisorption, with no covalent bonding observed. Amine-impregnation may suffer loss or leaching issue during several adsorption and desorption cycles, reducing the overall performance of amine-functionalized SBA-15 materials via impregnation method. As a result, amine leaching could pose a stability issue for long-term cyclic operation. In a study by Zhao et al. (2013), they found out about 8.2 and 5.8 wt% of TEPA amine loss from fresh adsorbent after 10 cycles of adsorption-desorption under dry and humid conditions respectively. In another study by Ahmadian Hosseini and Jahandar Lashaki (2023), they reported that TEPA-impregnated silica with 40 wt% loading experienced

severe amine loss about 55% over 50 successive adsorption-desorption cycles and loss around 29% of initial CO₂ uptake, despite having high initial CO₂ uptake of 5.61 wt% at 25 °C in adsorption stage. On the other hand, they reported that bulkier PEI amine-impregnated silica with the same 40 wt% loading is relatively more stable compared to TEPA-impregnated silica over the same regeneration cycles, only suffered about 1.4% amine loss and 0.8% CO₂ uptake loss of its initial uptake of 5.20 wt%. Nevertheless, this shows that high initial uptake in impregnated silicas does not guarantee long-term industrial success and amine leaching is detrimental to practical CO₂ capture application in a long term.

The impregnation process involves a solvent being combined with amine-containing materials, followed by the addition of the mixture to silica. Then, the solvent is evaporated to obtain the amine-functionalized silica composite. The amines on the silica surface and inside the pores act as the adsorption sites. Thus, total pore volume of the silica material and amine density will be the deciding factors on the amount of amines that can be dispersed into the silica (Zhao et al. 2021; Dziejarski et al. 2023). The amine species tends to agglomerate if the accommodation capacity is exceeded. Furthermore, pore blockage might occur as well, which could limit the overall CO₂ adsorption performance of the amine-functionalized silica. Collectively, these studies suggest that combining different amine functionalities can improve amine distribution and adsorption performance, although the extent of the improvement depends on the type of amines used, the functionalization method, and the pore structure of the silica support.

Grafting

Compared to the impregnation method, grafting involves chemically and covalently bonding the functionalization agent onto the surface of adsorbents or solid supports. A thin layer of the functionalization agent will attach to the surface but does not block the pores. If the functionalization agent is silane (or aminosilane), Si–O–Si covalent bonds will be formed on the surface of the mesoporous silica. There are two types of post-synthesis grafting, namely dry grafting and wet grafting. As their names suggest, dry grafting is performed in the absence of water, while wet grafting involves attaching the functionalization agent in the presence of water. In a conventional dry grafting process, silica is first dried to remove moisture before calcination and then dispersed in a solvent (generally anhydrous toluene). The functionalization agent (aminosilane) is then added, followed by reflux, and the mixture is heated and dried. The amount of amine attached to the silica surface depends on the availability of the surface silanol groups.

However, some functionalization agents might not be able to fully attach onto the silica surface. Hence, as an alternative, in wet grafting, hydrated silica is used to provide water to facilitate the hydrolysis of unreacted alkoxy ligands with free aminosilane to improve surface coverage (Harlick and Sayari 2005; Chew et al. 2010).

Table 4 shows that Anyanwu et al. (2022), and Wang and Yang (2011) have both investigated novel techniques to optimize amine-grafting on SBA-15 material. Anyanwu et al. (2022) discovered that low-temperature grafting helped preserve the structural integrity of amine functionalities while increasing amine loading, which was critical to enhance CO₂ capture while avoiding thermal degradation (Anyanwu et al. 2022). Wang and Yang (2011), on the other hand, reported that CO₂ capture was significantly improved when silanol density was increased by the different template removal techniques (Wang and Yang 2011). This finding showed that the physical preparation of silica surface prior to grafting could have a major impact on the final adsorption capacities of the synthesized adsorbent materials.

Meanwhile, Kishor and Ghoshal (2015) emphasized the importance of water in the grafting environment (Kishor and Ghoshal 2015). They discovered that wet grafting was more efficient for amine dispersion and functionalization than dry grafting techniques. Their study has also emphasized the relevance of solvent selection in the grafting process, supporting the results obtained by Wang and Yang (2011), which showed that silanol-based pre-treatment approaches could increase the grafting performance, and thereby lead to enhanced CO₂ capture.

Another research group investigated the influence of pore volume and size on CO₂ capture performance, and they reported that higher pore volumes and larger pore sized amine-functionalized SBA-15 have improved amine accessibility and CO₂ adsorption kinetics (Lashaki and Sayari 2018). These physical characteristics of the silica material have been critical in improving the performance of amine-grafted silicas. Their findings were also consistent with the synthesis technique used by Wang and Yang (2011), which showed that silica structural properties have a major influence on the final adsorbent material. Compared to amine impregnated silica, amine grafted silica seems to exhibit better stability during cyclic operations since the amine is covalently bonded onto silica. Rao et al. (2018) have conducted a comparative study on grafting and impregnation. They observed that the CO₂ uptake of PEI-impregnated MCM-41 was 4.75 time greater than pristine MCM-41 at 50 wt% loading whereas the uptake of APTES-grafted MCM-41 was 3.2 times greater than MCM-41, at the same loading. The average observed adsorption rate by impregnated MCM-41 is also appeared to be higher than grafted MCM-41 (0.1141 mmol/s > 0.0062 mmol/g). Cyclic stability test

was conducted for 5 adsorption-desorption cycles, which they reported that the PEI-impregnated MCM-41 suffered about 14.22% loss in CO₂ uptake whereas for APTES-grafted MCM-41, it only decreases by 5.19%. Overall, their findings indicated that impregnation increased CO₂ adsorption capacities due to increased amine loading efficiency, about 89.10% for impregnation while 23.18% for grafting at the same 50 wt% loading, though it is also depended on type of amine, the mesoporous silica used and the functionalization condition. This means more amines can be physically loaded into silica pores through impregnation process. Furthermore, as mentioned earlier, grafting is limited by density of available surface silanol groups for chemical bonding. On the other hand, grafting improved cyclic stability of the adsorbent, albeit the CO₂ adsorption capacity is lower relatively. Moreover, grafted adsorbent can withstand much higher temperatures than impregnated ones, as reported by Quang et al. (2016). They found out that APTES-grafted silica experienced thermal degradation at 205 °C whereas PEI-impregnated silica started to degrade at 160 °C. They also reported that the APTES-grafted silica exhibited relatively constant CO₂ uptake as compared to PEI-impregnated one, where the uptake decreases significantly about 16.6%. Fayaz and Sayari (2017) also reported that steam exposure did not reduce amine loading on wet grafted silica, demonstrating the hydrothermal stability of grafted silica, although prolonged exposure still resulted in partial collapse of the framework. These findings showed that in cases where long-term stability is as critical as initial adsorption capacity, the choice between impregnation and grafting techniques should be based on the specific operating requirements.

Some researchers performed double functionalization, which may include a combination of impregnation and grafting techniques to synthesize amine-functionalized silica adsorbents. The obtained materials reportedly contained the characteristics of both grafted and impregnated samples, with excellent CO₂ adsorption capabilities. Similar to double impregnation as in Luján Ferreira and co-workers' work, this method also aims to improve the CO₂ adsorption performance by increasing the amine loading. Sanz et al. (2015) functionalized MCM-41 with aminopropyl, ethylenediamine, and diethylenetriamine organosilanes before functionalizing it with pentaethylenhexamine (PEHA), phenethylamine (PEA), and TEPA. Double functionalization has increased amine content, while preserving amine functionality in capturing CO₂. Adsorption capacity of up to 2.364 mmol/g was obtained in this work (Sanz et al. 2015). Meanwhile, Wang et al. (2015) developed amine-functionalized MCM-41 grafted with APTMS and impregnated with TEPA. MCM-41 (APTMS 30% + TEPA 40%) showed a greater maximum CO₂ adsorption capacity of 3.50 mmol/g

than the individual CO₂ adsorption capacity of MCM-41-TEPA50% and MCM-41-APTMS50% which were 2.25 and 1.74 mmol/g, respectively (Wang et al. 2015). It is important to note that grafting should be performed first to allow for fixation space for impregnated amine to bond onto it through hydrogen bond (Chen et al. 2017; Zhang et al. 2019a; Wang et al. 2024a). A study by Fujiki and colleagues also reported an increase in thermal stability through hydrophilicity and nucleophilicity of introduced functional group in double functionalized (grafted and impregnated) amine-silica, aside from improving adsorption capability (Fujiki et al. 2015).

Direct synthesis

Another functionalization method is through direct synthesis. This one-pot synthesis method integrates amine-containing polymer, monomer, surfactant, and silica precursor together for in-situ polymerisation, via hydrolysis, and co-condensation. The amine functional groups would be chemically and covalently bonded to the silica matrix, providing a strong framework for CO₂ capture. Aside from being a time-saving process, this one pot-synthesis allows the more uniform distribution of functional groups that would not block the pores (Zhao et al. 2021). Klinthong et al. (2016) reported a one-pot synthesis of PEI-modified SBA-15, with the direct addition of PEI into a water/methanol mixture and TEOS. They reported that this direct synthesis route only required 4% of the required time of the conventional two-step synthesis method. This method has not only reduced the consumption of chemical reagents by 50% but also notably decreased synthesis time and overall cost. The adsorption performance of an optimized sample with 32% PEI loading exhibited the highest adsorption capacity of 147 mg/g at 15% CO₂ in N₂ flow at 95 °C. This result was comparable and slightly higher than the adsorption capacity of PEI-impregnated SBA-15 of their work at 132 mg/g (Klinthong et al. 2016). The cyclic stability of one-pot synthesis adsorbent was also relatively stable over 10 adsorption-desorption cycles and comparable with PEI-impregnated silica. Thus, this demonstrates the benefits of direct synthesis method, which could achieve a high CO₂ capture performance, with process simplification and substantial resource savings.

In short, this investigation on various amine-functionalization techniques and functional groups for the modification of mesoporous silica has revealed substantial advancements in the design of adsorbent materials for improved CO₂ capture. These procedures, which ranged from impregnation, advanced grafting, and direct synthesis methods, have highlighted the adaptability of mesoporous silica. They have also underlined the important correlation between the properties of functional groups and CO₂

adsorption performance. Moving from the practical aspects of material functionalization to the theoretical frameworks for these modifications, it has become clear that a better understanding of molecular interactions is essential, which can be achieved through advanced molecular-level modelling, such as molecular dynamics (MD) and Density Functional Theory (DFT).

DFT methodology and models of mesoporous Silica

Theoretical methods and computational techniques in CO₂ adsorption

Although experimental methods could provide gas capture capabilities, for example adsorption capacity, detailed adsorbate-adsorbent interactions and adsorption mechanisms are crucial to predict the molecular behaviour of adsorbent materials for practical applications. Molecular modelling involves theoretical and computational approaches to represent molecular structures numerically and to simulate their behaviour using the principles of classical and quantum physics (Duru and Duru 2020). Over the years, molecular modelling using computational simulation has been gaining attention in the adsorption field. Continuous efforts are being made to improve the accuracy of these simulations. Examples of widely used computational techniques include molecular dynamics (MD), Grand Canonical Monte Carlo computation method (GCMC), and density functional theory (DFT)-based computation. Among them, the DFT is a quantum mechanical modelling method that can provide information regarding material properties and the interactions between molecules, which are useful for understanding the CO₂ adsorption mechanism onto adsorbents.

The DFT can be applied in the adsorption field to provide insight into adsorption mechanisms in terms of adsorption energy (Eq. 5):

$$E_{ad} = E_{system} - (E_{adsorbent} + E_{adsorbate}) \quad (5)$$

where E_{ad} refers to the adsorption energy of adsorbate on the adsorbent, $E_{adsorbent}$ refers to the energy of adsorbent, $E_{adsorbate}$ refers to the energy of the adsorbate, and E_{system} refers to the total system energy of adsorbate adsorbed over the adsorbent. Based on the convention of Eq. 5, a negative E_{ad} would indicate more stable adsorption and stronger interaction. This can help determine whether the interaction is physisorption or chemisorption or involving both. The DFT is also able to calculate the electron density redistribution upon CO₂ adsorption, providing insights into bonding characteristics and charge transfer. Adsorption configurations

and preferred binding sites can also be determined using the DFT. Further applications of DFT and related case studies will be explored in a later section.

Introduction to DFT

The DFT revolves around solving the time-independent Schrödinger equation (Eqs. 6 and 7) and electron density function, $n(r)$ (Eq. 8) is the basis set of the electronic system, which contain important information to be used for finding the solution to Schrodinger equation:

$$H\psi = E\psi \quad (6)$$

$$\left[\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + V(r_i) \right] \psi = E\psi \quad (7)$$

$$n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \quad (8)$$

where H is Hamiltonian operator, ψ is the eigenstate of Hamiltonian, N is the number of electrons, m is electron mass, $\hbar$ is Planck's constant, E is the ground-state energy of electrons, V is the potential energy, r_i is the probability of N electrons at particular sets of coordinates, and ψ_i^* is the conjugate complex of ψ . There are two fundamental theorems in the DFT, as proven by Kohn and Hohenberg (Hohenberg and Kohn 1964; Kohn and Sham 1965), which are: (i) the ground-state energy from the Schrodinger equation is a unique functional of the electron density and (ii) the electron density that minimises the energy of the overall functional is the true electron density corresponding to the full solution of Schrödinger solution (Sholl and Steckel 2009). The Hohenberg-Kohn theorem can be written in terms of single electron wave functions, as shown in Eq. 9.

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}] \quad (9)$$

The Kohn–Sham equation is similar to the Schrödinger equation of a fictitious system of non-interacting electrons that have the same density as a real system of interest. The introduction of the Kohn–Sham equation makes the DFT more practical (Kohn and Sham 1965; Burke and Wagner 2013; Morgante and Peverati 2020). The use of Kohn–Sham density functional theory allows the kinetic energy of an electron to be computed more accurately in terms of Kohn–Sham orbital, in a way analogous to Hartree-Fock method (Baseden and Tye 2014). The Kohn–Sham equation is expressed as shown in Eq. 10:

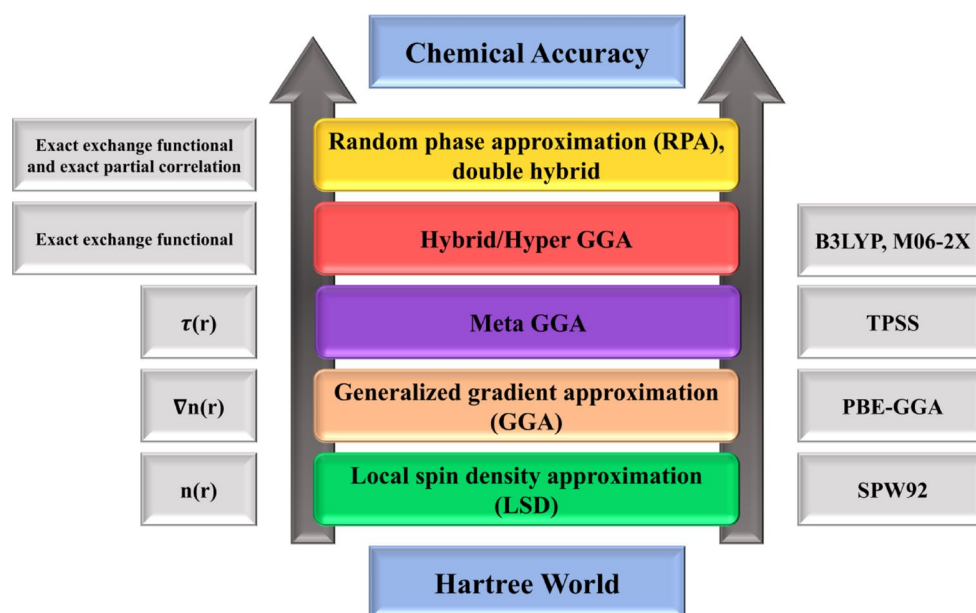
$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{\text{XC}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r) \quad (10)$$

where V_H is the Hartree potential that includes self-interaction contribution potential of electron and V_{XC} is the exchange-correlation contribution potential. To solve the Kohn–Sham equation, iterative calculation is required starting from an initial guess of electron density and most importantly, the exchange-correlation functional needs to be defined. However, the true electron density cannot be obtained and the exact form of energy functional is not known. It is extremely difficult to obtain ground-state energy, as it is a many-body problem. As a result, approximations need to be done for the exchange-correlation functional of the system of electrons. Several exchange-correlation functional approximations can be used. For instance, the local density approximation is the simplest approximation with the assumption of uniform electron gas, generalized gradient approximation, Perdew-Burke-Ernzerhof functional (PBE), and Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional.

In 2001, Perdew and his research group categorised the DFT exchange-correlation functional in the form of Jacob's ladder, where higher rungs required more addition physical information and lesser approximation by incorporating the parameters from lower rungs (Perdew and Schmidt 2001; Perdew et al. 2005). Figure 6 shows the illustrative representation of Jacob's ladder, which is a hierarchical structure where each rung represents a progressive enhancement in the approximation accuracy of exchange-correlation functions.

The Local Spin Density (LSD) approximation, which located at the lowest rung on the ladder, is the simplest level. It is ideal for simple homogeneous systems since it employs the local electron density, $n(r)$, to approximate the exchange correlation energy. The second level, known as the Generalised Gradient Approximation (GGA), combines the gradient of electron density, $\nabla n(r)$, with the local density. This approach increases precision in materials with variable electron densities and molecular systems. The incorporation of the kinetic energy density, $\tau(r)$, into the Meta GGA enhances the accuracy of approximation of correlation and electronic exchange effects in complex molecules. The next level combines Hartree-Fock theory's precise exchange and GGA. M06-2X and B3LYP are functionals that have been shown to improve precision in a variety of chemical processes. These methods incorporate a component of second-order perturbation theory at the top of the ladder, as well as non-local correlation effects. The Random Phase Approximation (RPA) is particularly beneficial and applicable for systems where long-term correlation effects are crucial (Perdew and Schmidt 2001; Perdew et al. 2005).

Fig. 6 Jacob's ladder in the DFT for the progression of exchange-correlation functional approximations (Perdew and Schmidt 2001; Perdew et al. 2005; Sholl and Steckel 2009; Wang 2014; Liao et al. 2022)



Although higher rungs include more parameters and more constraints to obtain more accurate results, this does not imply that the functional approximation at the lower rungs is entirely useless. They could provide relatively close results, which would also be easier to understand and better suited for certain applications, while higher rungs usually require more computational costs. Therefore, it is necessary to choose the functional based on the system and appropriately to balance the computational cost and accuracy. It is highly recommended to check out these reference materials to understand DFT in details: (Hehre et al. 1972; Becke 1993; Stephens et al. 1994; Perdew et al. 1996, 2005; Sholl and Steckel 2009; Mardirossian and Head-Gordon 2017).

Important parameters in DFT

As mentioned in the previous section, the correct selection of exchange-correlation functionals is important to ensure the accuracy of the computation based on available computational power. There are also some critical parameters that need to be defined for DFT computations, for example, k-point, pseudopotential, and cutoff energy. In the DFT, k-points refer to a grid of sampling points in the reciprocal space or the Brillouin zone of a periodic material. They are used to approximate integrals over Brillouin zone instead of using all the points in the Brillouin zone for computations. They are usually generated using a Monkhorst-Pack grid and the density of the k-point grid is determined by the system's symmetry and the desired accuracy (Monkhorst and Pack 1976). To obtain more accurate and well-converged results, a higher value of k-points should be used and should be balanced between computational cost and convergence.

Cutoff energy refers to the number of plane wave functions being used as basic functions to represent electronic wave functions. Using higher cutoff energy would result in more accurate results, but with higher computational cost and usage, whereas lower cutoff energy may lead to faster computations but inaccurate results. Typically, the cutoff energy depends on the pseudopotential used and a convergence test can be performed by increasing the cutoff energy incrementally until the total energy of the system converges to obtain reliable results. Although it is important to use large cutoff energy for accurate results, and to include plane waves that oscillate on short-length scales in real space, it is problematic due to the complex interactions of core electrons. As chemical bonding and other material properties are dominated by valence electrons, pseudopotential is used to simplify core electron interactions and reduce the computational burden of the system. Another important thing in the DFT is geometry optimization, which is the process of finding the most stable atomic arrangement (lowest-energy configuration) of a system by minimising the total energy of the system. This is done by iteratively adjusting the atomic positions and/or lattice parameters to ensure that the structures are in equilibrium and yield realistic structures for reliable computation.

Integration of the DFT approach with other simulation techniques

Molecular dynamics (MD)

The DFT can be used in conjunction with other simulation techniques to simulate and provide more insight regarding the adsorption process. Molecular dynamics (MD) is

a simulation technique for computing the equilibrium and transport properties of classical many-body systems (Frenkel and Smit 2002). It involves solving kinetic equations that govern the microscopic time evolution of many-body problems numerically (Tuckerman and Martyna 2000; Villena et al. 2024). While the DFT provides information about the electronic structures and interaction energy between adsorbate and adsorbent, MD simulation allows users to monitor exactly how the adsorption process happens in the evolution of time. This includes the location, orientation, and arrangement of the adsorbate in the adsorbent, which complement the DFT by providing dynamic and time-resolved insights into the adsorption process.

Defining the force field is usually a standard approach to provide input to model the interaction between particles in MD simulation after the initial configuration of the system is set up. The DFT can be used to provide the initial parameters for the MD simulation, typically force field parameters. Aside from using the DFT to perform geometry optimization and calculate the binding energies between CO₂ and amine functionalized MCM-41, it was also used to develop force field parameters for MD simulations (Chen et al. 2023). Moreover, the MD can also be used to simulate adsorption isotherms and isosteric heat of adsorption, which can be used to cross-check the DFT results of the adsorption energies.

Grand canonical Monte Carlo (GCMC)

The Grand Canonical Monte Carlo (GCMC) simulation technique can also be paired with DFT computation in an adsorption study. Typically, the GCMC method is typically used in the gas adsorption field. It is similar to the MD simulation techniques in that it uses classical mechanics and statistical mechanics, yet it is not time-dependent like the MD simulation, meaning the simulation process is conducted for a system in equilibrium (Yun et al. 2002; Yang et al. 2017). The GCMC involves random sampling, which depends on randomly generated new configurations sampled from a Boltzmann distribution based on the Metropolis method (Yang et al. 2017). A new configuration is created by adding a trial particle with uniform probability density, or deleting a trial particle randomly with probability-balancing insertion, or moving particles to new positions and orientations. Then, the insertion, deletion, or translation is accepted or rejected based on certain acceptance rules. The GCMC simulation allows the number of molecules in the adsorbed phase to fluctuate, while keeping the temperature, volume, and chemical potential constant in the grand canonical ensemble. This set up mimics the experimental conditions in equilibrium, whereby the chemical potential and temperature of gas inside and outside must be equal (Frenkel and

Smit 2002). The GCMC complements the DFT and MD, as they allow for the study of adsorption equilibrium in varying pressures (for example, the amount of adsorbate adsorbed in function of pressure and temperature) and pressure-dependent adsorption behaviour, which the DFT is unable to simulate, while the MD would take a longer time to simulate the equilibrium due to different gas properties in bulk and in the interface region. Detailed information regarding the GCMC and the MD can be found in the published works of Allen and Tildesley (2017), and Frenkel and Smit (2002) (Frenkel and Smit 2002; Allen and Tildesley 2017).

Integrated molecular modelling of mesoporous silica

Molecular modelling involves theoretical and computational approaches to numerically represent molecular structures and to simulate their behaviour using the principles of classical and quantum physics. Before any computations can be made, it is important to construct a molecular model structure for computation and for visualization. Previous studies have constructed molecular models of mesoporous silica using the GCMC method, as well as classical molecular mechanics and the MD simulation method. Initially, an amorphous silica model is used as the basis structure, followed by various adjustments and modifications by carving pores on the amorphous silica model. Surface roughness or defects are also added to simulate a realistic mesoporous silica model. To simulate the silanol groups on the silica surface, the terminal silica atoms on the surface of the silica and the remaining dangling bonds are terminated and saturated with H atoms.

Earlier attempts at the model construction of MCM-41 mesoporous silica have been compiled by Sonwane et al. (2005) (Sonwane et al. 2005). They have highlighted the importance of incorporating surface roughness to improve the accuracy of simulating a silica structure. They studied and compared the compiled models with their constructed model that incorporated surface roughness based on the modifications proposed by Feuston and Higgins (1994) (Feuston and Higgins 1994) using MD simulation. Overall, the simulated MCM-41 structure was able to reproduce the effective volume and surface area, as characterized by the inclusion of surface roughness and gave a reasonably close match to the representative experimental XRD and WAXS results (Sonwane et al. 2005). Most notably, their findings revealed physical deformations on the pore surface, which might have a significant influence on the structural integrity and adsorption capabilities of the specific materials. This modelling refinement has highlighted the need for precise structural characterization in improving the prediction accuracy of computational models for mesoporous silica.

Figure 7 depicts the different structural characteristics and molecular configurations of mesoporous silica materials across different conditions and models.

A comprehensive review of theoretical model structures and characterization of amorphous silica-based catalysts using the DFT computational method is summarized by Tielens et al. (2020) (Tielens et al. 2020). They mentioned that the earlier DFT-based silica models were proposed by Ugliengo et al. (2008) (Ugliengo et al. 2008) and their own earlier work (Tielens et al. 2008). Ugliengo et al. (2008) constructed a DFT-based realistic model of hydroxylated amorphous silica and MCM-41 mesoporous silica using periodic DFT calculations with the B3LYP hybrid exchange-correlation functional, which is commonly employed to accurately describe the electronic structure and adsorption interactions in silica-based systems. Their atomistic model was validated with experimental finding (XRD diffraction and IR spectra), achieving similar results. The same model was used several years later to conduct an in-depth theoretical study about the structural properties, morphology, and adsorption properties with N_2 , CO_2 , and H_2O gases (Ugliengo et al. 2008; Coasne

and Ugliengo 2012). Tielens et al. (2008) also utilised an ab initio MD method and periodic DFT calculations to construct a hydroxylated amorphous silica model. They achieve good agreement with the experimental silanol coverage measurements, as shown in Fig. 7(a) (Tielens et al. 2008). PBE functional and PAW pseudopotential were used. The PBE functional, which belongs to the generalized gradient approximation (GGA) family, was employed to describe the exchange-correlation energy of electrons, providing a good balance between computational efficiency and accuracy for modelling silica-based materials. In addition, the projector augmented-wave (PAW) pseudopotential was used to accurately represent the interaction between valence electrons and atomic cores while reducing the computational cost compared with all-electron calculations. They also performed ab initio-based NMR calculations on the constructed model for characterization and comparison with their experimental results. Even though B3LYP is at the higher rung of Jacob's ladder and appears to be better for computational accuracy, their silica model was able to reproduce the overall density and distribution of silanol groups, with silanol coverage of

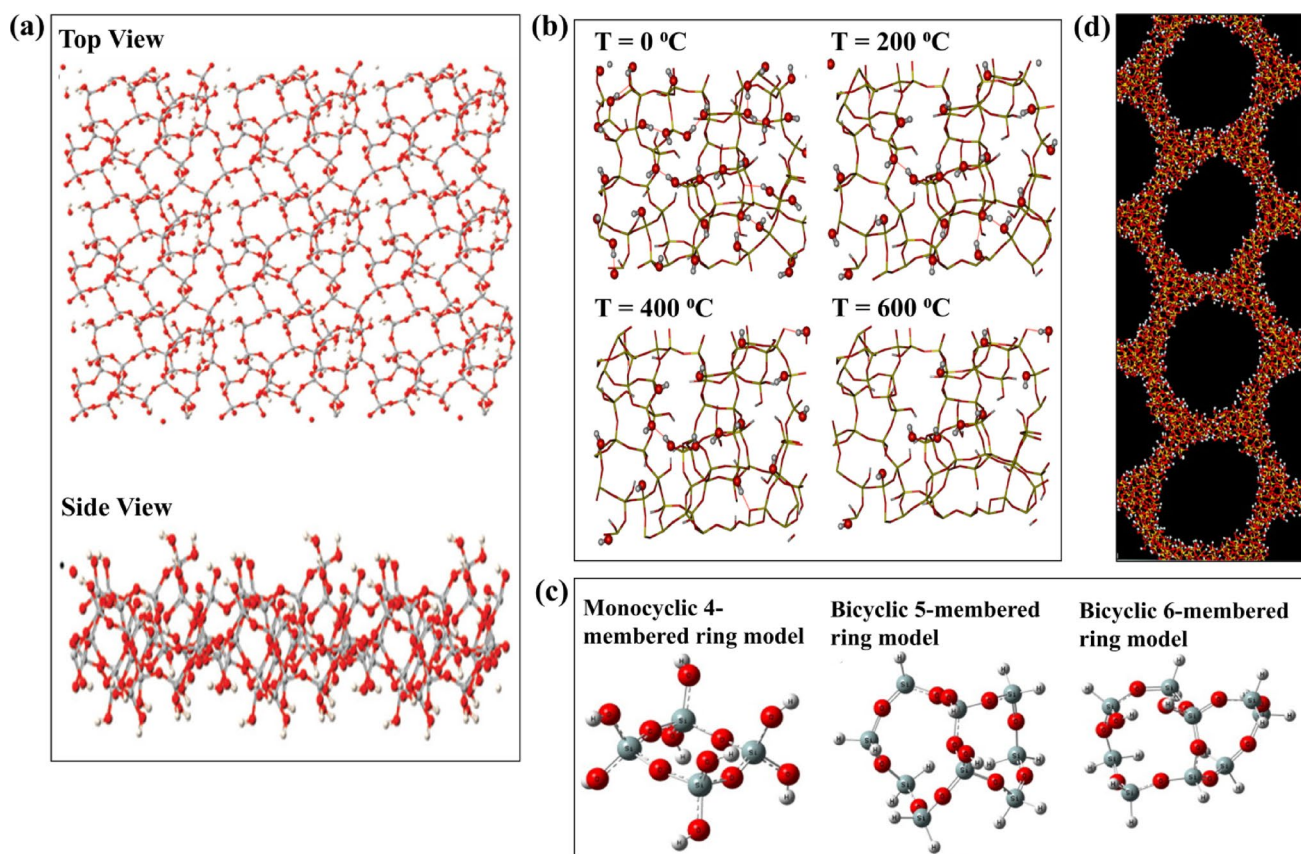


Fig. 7 Structural dynamics of various mesoporous silica materials: **a** top and side view of a typical silica model (Reprinted (adapted) with permission from ref. Copyright (2008). American Chemical Society.), **b** temperature-induced transformation of a typical silica model (Reprinted (adapted) with permission from ref. Copyright (2014).

American Chemical Society.), **c** molecular models of mesoporous SBA-15 ring cluster models (Reprinted from ref. (Wang et al. 2011), Copyright (2011), with permission from Elsevier.), and **d** optimized mimetic MCM-41 model (Reprinted (adapted) with permission from ref. Copyright (2008). American Chemical Society)

5.8 OH/nm², which were comparable with the experimental results (Tielens et al. 2008). In conclusion, their work has highlighted the balance between precision and computing requirements, which is especially important for simulating complicated materials such as MCM-41.

Dehydroxylation is a process where water molecules and siloxane bridges are formed by the condensation of silanol groups upon heating, which typically occur during the template removal step using high temperature calcination. This process can occur over a wide range of temperatures. Ewing et al. (2014) proposed models of amorphous silica using a combination of classical molecular modelling and density functional theory to simulate the thermodynamics-limited dehydroxylation process. The resultant theoretical silica model, which consisted of less than 300 atoms, was able to accurately describe and represent the physics and chemistry of real surfaces. This model was characterized by the macroscopic measurements of the temperature dependence of silanol number and type, as shown in Fig. 7(b) (Ewing et al. 2014). Their work has, for the first time, highlighted the use of hybrid modelling techniques in capturing both the kinetic and thermodynamic aspects of mesoporous silica materials across different temperature ranges. The integration of these computational methods provided further insight into the structural evolution related to specific synthesis conditions, which is a crucial representation of thermal-dependent material designs.

Surface relaxation of the silica models was performed using the CP2K computational package (VandeVondele et al. 2005), which is widely employed for periodic density functional theory (DFT) calculations of condensed-phase systems. The calculations used the Perdew-Burke-Ernzerhof (PBE) (Perdew et al. 1996) generalized gradient approximation (GGA) exchange-correlation functional together with the Goedecker-Teter-Hutter (GTH) pseudopotentials (Goedecker et al. 1996; Krack 2005) to describe the interactions between valence electrons and atomic cores. A triple-zeta valence polarized (TZVP) (VandeVondele and Hutter 2007) basis set was adopted to provide an appropriate balance between computational accuracy and efficiency, while a plane-wave cutoff energy of 350 Ry was applied to ensure numerical convergence of the electronic structure calculations. Different approaches were used to simulate the process of the silanol group being temperature dependent, where the condensation of silanol followed the lowest dehydroxylation energy pattern (thermodynamically favourable) (Ewing et al. 2014). As a result, the distribution of silanol groups on silica surface became a function of temperature. This could be applied in similar studies to accurately represent mesoporous silica models or other amorphous materials for a range of temperatures.

As mentioned in the previous section, the integration of the GCMC with the DFT offers powerful approaches for studying adsorption processes, as they combine equilibrium statistical insights with atomistic-level accuracy. Using the combination of GCMC and DFT, a theoretical study was conducted on the adsorption of CO₂, N₂, and flue gas. The results of this study, with a full atomistic model of MCM-41, are as shown in Fig. 7(d) (Zhuo et al. 2008). In their work, the atomic charges of the MCM-41 cluster models were calculated using the DFT with electrostatic potential fitting (ESP) (Singh and Kollman 1984; Merz 1992; Bayly et al. 1993; Bakalarski et al. 1996), while the Dreiding force field (Mayo et al. 1990) was used for dispersive interaction. The geometry optimization of the MCM-41 cluster models was performed using the Perdew-Wang functional (Perdew and Wang 1992). Meanwhile, the double numerical plus polarization basis set was used for the cluster models, along with semicore pseudopotential. Hydroxyl groups were introduced on the pore surface of the model randomly, with 7 to 8 OH/nm². Overall, their theoretical results were close to the experimental measurements, with pore radius of approximately 15 Å with Gaussian-like distributions and hexagonally arranged (Zhuo et al. 2008). Their GCMC simulated isotherm results and isosteric heat of CO₂ adsorption were also closely matched with the experimental results. Based on their simulation results, they reported that CO₂ preferentially adsorbed on the active sites on the pores of the mimetic MCM-41 due to stronger Coulombic interactions, whereas N₂ adsorbed homogeneously on the pore surface. This showed that the DFT could be used in conjunction with the GCMC to optimize the model and to provide atomistic information regarding the adsorption process. The same model was modified and used in their subsequent theoretical study on CO₂ adsorption using amine-grafted mesoporous material (Zhu et al. 2012).

The geometric accuracy of a silica model is also important in computational simulations to ensure the accuracy of calculations. To explore in-depth the molecular structure of SBA-15, the structural units and geometrical conformation of SBA-15 is studied using the DFT, as shown in Fig. 7c (Wang et al. 2011). The geometry optimization of SBA-15 cluster models, with monocyclic and bicyclic silica rings, was performed using B3LYP functional (Becke 1993) with 6–31(d) basis set (Hariharan and Pople 1973; Francel et al. 1982). Their results showed that monocyclic silica rings were not suitable as cluster model to represent SBA-15 mesoporous silica due to the great discrepancies between the computed structural parameters and the experimental results. The monocyclic rings have also changed into irregular conformations. On the other hand, they reported that the bicyclic silica cluster model could be a reasonable cluster model of SBA-15. Based on their results of geometry optimization

and releasing energy, the main possible structural elements for SBA-15 in the descending order were 6-membered ring > 5-membered ring > 7-membered ring > 8-membered ring > 4-membered ring. They have inferred that the 6-membered and 5-membered rings were the most suitable ones to represent the SBA-15 model. They have also compared the theoretical results with the experimental measurements of the IR spectra, with the Si-O bending and stretching bands of all cluster models closely matching the experimental measurements (Wang et al. 2011). Hence, the works by Zhu et al. (2012) and Wang et al. (2011) have proven the need for choosing suitable cluster models to ensure the relevancy of the obtained simulation results to the actual materials.

Meanwhile, Fig. 8 shows the detailed analyses of various mesoporous silica models under various conditions by previous studies. The functionalization of mesoporous silica involves modifying its surface chemistry to improve its adsorption performance. The common approach to model functionalized silica is by replacing the surface silanol groups with the desired functional groups. Once a base silica model is constructed, functional groups are then

introduced computationally at specific sites, which are selected to mimic experimental patterns, typically in the grafting method. For instance, as shown in Fig. 8(a), Zhu et al. (2012) employed MD simulations to simulate the structural dynamics of amine-grafted MCM-41 by randomly replacing the surface hydroxyl groups (Zhu et al. 2012). Their study was able to simulate a full atomistic model to show the molecular interactions within the pores of the MCM-41 using CO₂, N₂, and H₂O. According to the findings of their study, CO₂ preferentially adsorbed at specific active sites inside the pores, which showed that site-specific interactions and molecular organisation would be crucial for optimising CO₂ capture performance.

Another research group employed the DFT to study the geometric and electronic structures of SBA-15 models based on the experimental crystallographic structure of alpha quartz (Mafra et al. 2017). As shown in Fig. 8b, to simulate amine-functionalized mesoporous silica, they grafted amino-organosilanes directly on top of the cluster models, binding with three silanol groups, and Si and O atoms are fixed throughout the simulation. This figure

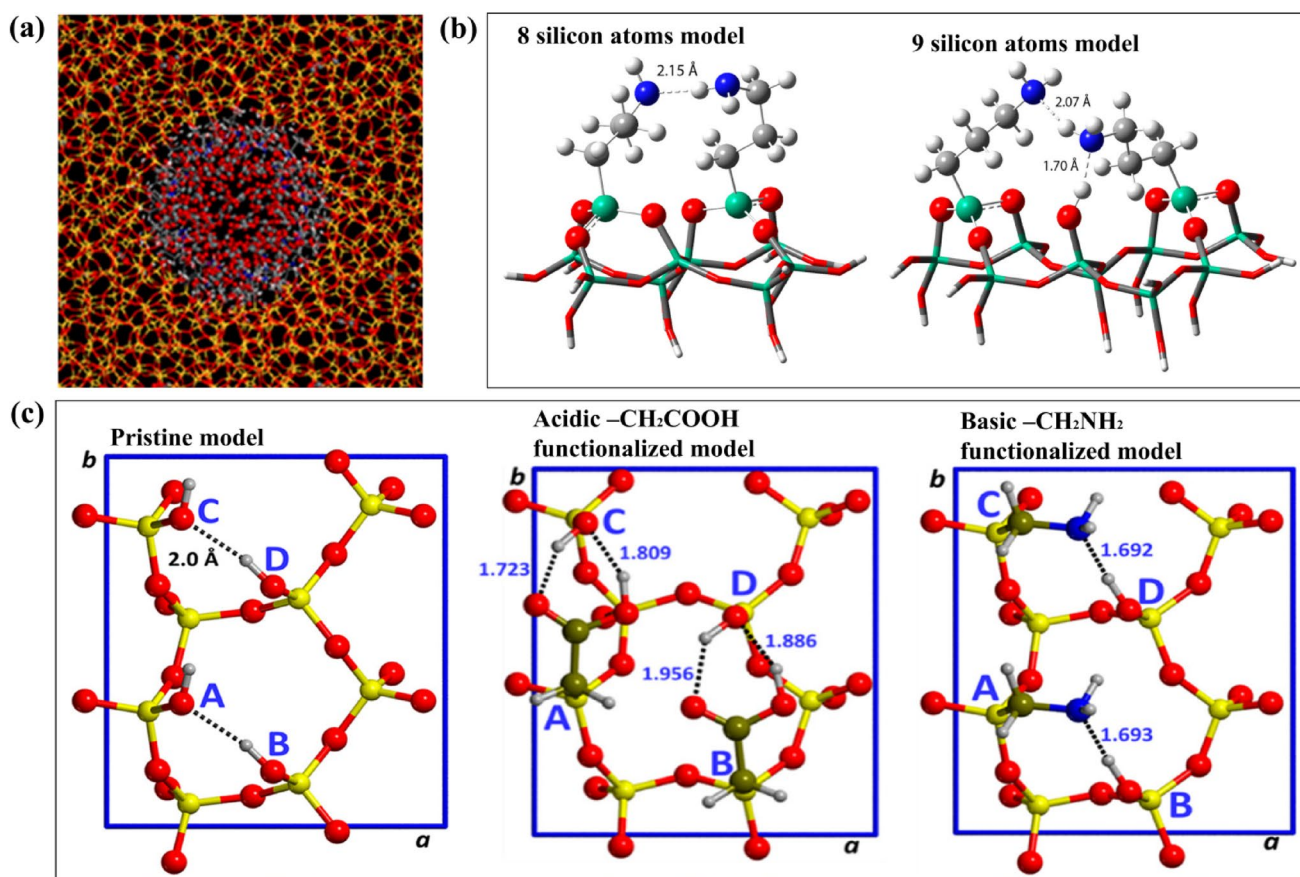


Fig. 8 The structural evolution of functionalized mesoporous silica models at various conditions: **a** a densely populated 24% amine-grafted MCM-41 model at 50 kPa (Reprinted from ref., Copyright (2012), with permission from Elsevier.); **b** a comparison of amine-functionalized SBA-15 models with colour coding, as follows; green:

Si, red: O, blue: N, grey: C, and white: H (Reprinted (adapted) with permission from ref. (Mafra et al. 2017). Copyright (2017). American Chemical Society.); and **c** pristine, acidic, and basic crystalline silica models (Reprinted (adapted) with permission from ref. Copyright (2015). American Chemical Society.)

shows the subtle differences in the spatial arrangement between the 8-silicon atoms model and the 9-silicon atoms model, which would influence their molecular behaviour later. Overall, molecular modelling of mesoporous silica has advanced from basic amorphous structures to highly functionalized and customised models that can be used to simulate adsorption scenarios. However, the model would need to be accurately constructed to be able to capture and simulate the realistic distribution of functional groups and their dynamic interactions under different conditions. This study has aimed to extend the understanding on how a molecular-level modelling such as the addition of different amounts of silicon atoms, could influence the structural architecture and chemical reactivity of SBA-15. Overall, this current work could be particularly valuable because it has focused on the accuracy of molecular structure, which is a necessity when developing materials for specific gas adsorption behaviours.

Similarly, Corno et al. (2015) modelled the acidic- and basic-functionalized crystalline silicas by substituting the surface silanol group with the desired acidic and basic functional groups in their study (Corno et al. 2015). As illustrated in Fig. 8c, a significant difference can be observed in bond lengths when the crystalline silica models undergo surface functionalization using acidic and basic groups. Thus, this work was able to visualise how molecular modifications could alter the structural dynamics, and the physical and chemical properties of silica materials, which would be essential for targeted CO₂ capture applications. To summarize, Zhu et al. (2012) employed MD simulations to visualise complete adsorption dynamics, Mafra et al. (2017) used DFT to improve the precision of their structural model, and Corno et al. (2015) studied the functional implications of when using acidic and basic functional groups. In conclusion, while each computational approach has its individual advantages, the integration of these approaches, as proven in the reported articles, has resulted in a more complete understanding of the properties of mesoporous silica materials. This comprehensive technique has improved the predictability of silica materials' performance in real-world applications such as CO₂ capture, while simultaneously enhancing simulation accuracy.

DFT analysis of CO₂ adsorption on mesoporous silica

Theoretical analysis of functional group and surface interactions

The functionalization of mesoporous silica surfaces would significantly alter their adsorption properties, making them suitable for targeted applications, for example, CO₂ capture.

From a theoretical standpoint, understanding the interaction between functional groups and the silica surface would provide critical insights into how these modifications could influence CO₂ adsorption performance. Adsorption of CO₂ molecules onto mesoporous silica typically occurs through physisorption, driven by the weak hydrogen bond of silanol groups. This initial physisorption usually acts as a baseline for more selective and stronger subsequent chemical interactions. After functionalization, the silica surface is prepared in such a way that could facilitate chemisorption by enabling specific chemical interactions. These chemical interactions are significant because they could influence the intensity and reversibility of CO₂ capture in specific materials.

Most of the previous studies have focused on amine-functionalized silica and its interaction with CO₂ molecules was often associated with chemisorption that forms stable products, aside from physisorption. Among the amine functional groups, ammonium carbamate would preferentially form in primary amine-bonded CO₂, whereas for the secondary amine and tertiary amine, carbamic acid and bicarbonate species would predominantly form in their respective case, as observed in several studies (Shimon et al. 2018; Sardo et al. 2021, 2024; Szego et al. 2021). These findings indicated that the composition of the amine group has a considerable influence on the type and stability of the CO₂ binding sites, thereby contributing to the overall CO₂ capture efficiency.

NMR spectroscopy is a widely used characterization tool in adsorption studies. It provides atomic-level insights regarding the dynamics and diffusion of CO₂, information on local structures, and the type of adsorption species that are formed during CO₂ adsorption (Bernin and Hedin 2018). It can distinguish different adsorption mechanisms by analysing the chemical, electronic, and magnetic environments of nuclei involved in CO₂ binding. A detailed examination of these environments could aid in understanding the microscopic interactions that control the CO₂ adsorption dynamics. Solid-state NMR (ssNMR) is typically applied for solid and semi-solid materials and is often combined with magic angle spinning (MAS) to improve its resolution and sensitivity (Reif et al. 2021). Computational techniques such as the DFT can be used in combination with ssNMR to complement each other. While the DFT provides information about electronic structure and adsorption energy, it can also be used to calculate tensor related to the NMR phenomena (Sardo et al. 2024). This combination offers a synergistic toolset for characterising and optimising mesoporous silica materials for CO₂ capture applications. Moreover, the DFT can be used to simulate the molecular structures of the material, which can validate and compared with the experimental ssNMR data to reveal the adsorption mechanism and the

underlying interaction of the intermediate species. Recently, a comprehensive review was conducted on the use of NMR methods and computational modelling strategies in CO₂ adsorption studies (Sardo et al. 2024). The authors have highlighted and summarized the advancements in exploring gas adsorption mechanisms and CO₂ speciation in silica adsorbents with the help of ssNMR and computational tools, such as the DFT, MD, and GCMC.

A critical survey of all reported chemisorbed CO₂ species formed in primary amine-modified mesoporous silica in both dry and humid conditions was performed by Afonso et al. (2019) (Afonso et al. 2019) using the NMR and DFT methods. Figure 9 depicts a variety of CO₂-amine adducts on different functionalized mesoporous silica surfaces, providing a visual illustration of the chemical interactions and spatial configurations that can occur between CO₂ molecules and various amine groups from various sources. These studies basically revisited the chemisorbed species reported and

hypothesized in literature. They filled the gaps by conducting new ssNMR experiments, assisted by DFT calculations, specifically using M06-2X functional (Zhao and Truhlar 2008), with 6-31(G) basis set (Hariharan and Pople 1973; Francel et al. 1982) for geometry optimization, calculation of NMR shielding tensors, which describe how the local electronic environment surrounding a nucleus influences its magnetic shielding in an external magnetic field and enables the prediction of NMR chemical shifts, and calculation of Gibbs energies of the formation of chemisorbed species. Each adduct is depicted in Fig. 9 in 2D and 3D to emphasizing the structural variations and the potential interactions or formation of chemical bonding. These 2D and 3D visual models were derived from DFT calculations and simulations to aid in understanding how various amine configurations could influence CO₂ adherent properties, which are critical for improving CO₂ capture technologies.

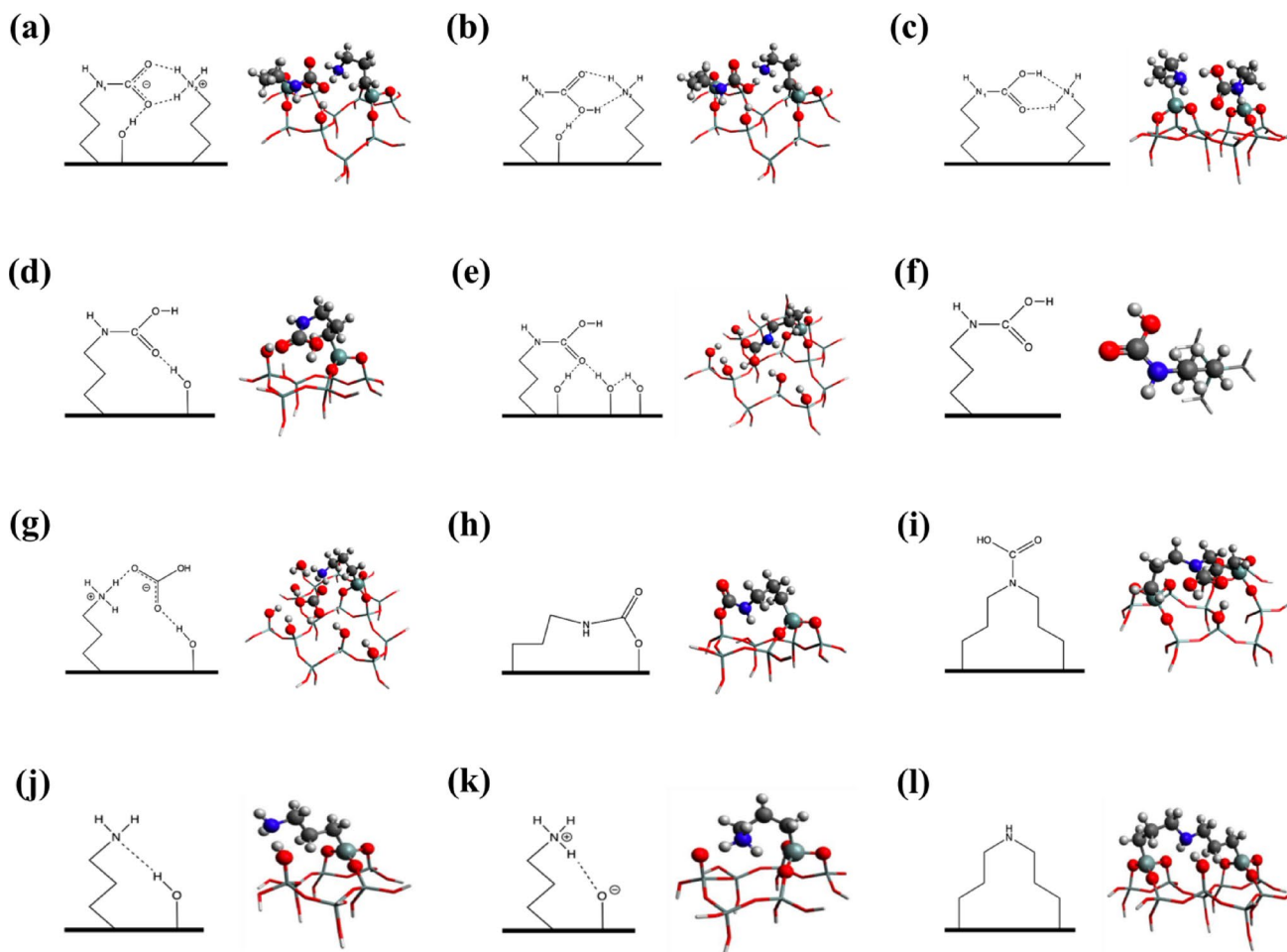


Fig. 9 2D and 3D structural diversity of chemisorbed CO₂ species on amine/ammonium adducts on functionalized mesoporous silica surfaces: **a** ammonium carbamate, **b** carbamic acid, 2 amine, 1 silanol, **c** carbamic acid, 2 amine, 0 silanol, **d** carbamic acid, 1 amine, 1 silanol, **e** carbamic acid, 1 amine, 5 silanol, **f** carbamic acid, 1 amine, 0 silanol,

g ammonium bicarbonate, **h** silyl propyl-carbamate, **i** dithere carbamic acid, **j** amine, **k** ammonium siloxide, and **l** dithere amine with colour coding as follows; white: H, dark grey: C, blue: N, red: O, and light grey: Si. (Reprinted (adapted) with permission from ref. (Afonso et al. 2019). Copyright (2019). American Chemical Society.).

The studied chemisorbed species included carbamic acid, alkylammonium carbamate, ammonium bicarbonate, silyl-propyl carbamate, and ditethered carbamic acid. Their simulated results confirmed that carbamic acid and carbamate moieties were the predominant CO_2 species, which were comparable with the experimental values. For dry CO_2 capture, the results seem to be followed the reaction product (carbamate species) of typical mechanism mentioned in the earlier section. They reported that these species were slightly more stable than bicarbonate, and significantly more stable than both silyl-propyl carbamate or detethered carbamic acid in a decreasing order of stability (Afonso et al. 2019). However, in humid conditions, they claimed that the existence of bicarbonate species is complicated to verify. Another computational study by the same group few years later reported that for primary amines, the CO_2 capture under humid condition favours the conversion of carbamic acid into carbamate ion pairs (Sardo et al. 2021). The water network facilitates proton transfer, increasing the abundance of carbamates. Nevertheless, they do explicitly report bicarbonate species as dominant when CO_2 adsorption was performed on tertiary amine-modified mesoporous silica under humid conditions. Similar findings have also reported in a computational study by Al Mohtar and Pinto (2022) on CO_2 capture by primary and secondary amine-modified silica. They reported that the presence of water reduces the Gibbs free energy of activation for carbamate formation up to 7 times compared to dry condition, which increase adsorption reaction rate by 5 to 8 orders of magnitude and that moisture favours the formation of ammonium carbamate over carbamic acid, which they confirmed through comparing DFT calculated vibrational analysis and NMR analysis with the experimental values. Compared to carbamate, they found that bicarbonate exhibited higher energy barriers and product energy, which is not as favourable comparatively.

Afonso et al. 2019 also reported the discrepancy in the formation of silyl-propyl carbamate. Although its presence has been proposed in earlier studies, their results suggested that this species was thermodynamically unfavourable. Similarly, in a theoretical DFT study conducted by Başaran et al. (2021) to elucidate the CO_2 capture mechanism of amine-functionalized silica, they found that carbamate and carbamic acid were the main adsorption products over APTMS and MAPS-modified mesoporous silica (Başaran et al. 2021). Their formation depended on the nearest neighbour interactions (amine-amine and amine-surface interactions), which was further proven by Afonso et al. (2019). They have also highlighted the importance of amine density in the formation of carbamate and carbamic acid, as well as CO_2 adsorption performance. In short, these papers suggested that the structural aggregation of amines and the

silica surface chemistry (silanol groups) play a much larger role in determining the reaction products than the simple presence or absence of water.

Such detailed molecular-level visualization could contribute to the theoretical investigation of interactions between functional groups and CO_2 , thus illustrating how molecular configurations could affect binding efficiencies and capacities. This type of analysis is critical for synthesising adsorbent materials with an optimized design with tailored functional groups for effective and selective CO_2 capture. This observation aligned with the data analysis by Yıldız et al. (2019). They reported that amine density has the most significant impact on chemisorption efficiency, which was a finding that resonated with the computational and experimental analyzes reported by Başaran et al. (2021). Based on their computation and simulation results, hydrogen bonding interactions with silanol functional groups and neighbouring amines exhibited significant effects on the stability of the adsorption products, which validated the mechanistic insights into how amine configurations could affect CO_2 adsorption kinetics and capture performance.

Interestingly, another research group studied the effect of various functional group modifications on CO_2 adsorption using mesoporous silica SBA-15. Experimental and theoretical analysis through DFT have been conducted, emphasising the nature of functional groups that could significantly dictate the adsorption mechanism as either physisorption or predominant chemisorption (Cueto-Díaz et al. 2023). The functionalization agents used in their study included hyperbranched polymeric amidoamine (PAMAM) moieties and a collection of sulphur and nitrogen-derived functional groups ($-\text{SH}$, $-\text{SO}_3\text{H}$, $-\text{guanidine}$, $-\text{NH}_2$, $-\text{NCO}$, $-\text{N}_3$). Geometry optimization of molecules and complexes was performed with B3LYP functional (Lee et al. 1988; Becke 1993; Stephens et al. 1994) and aug-cc-pVDZ basis set, including empirical dispersion method, D3 with Becke-Johnson damping parameters (Grimme et al. 2011). Boys-Bernardi full counterpoise method was also used to correct for basis set superposition error (BSSE). From their computational results, the binding energies of the complexes ranged from -4.3 to -22.0 kJ/mol, in which the strongest interaction was in the following order: $-\text{SO}_3\text{H} > -\text{NH}_2 > -\text{NCO} > -\text{Gdn} > -\text{N}_3 > -\text{SH}$. Their electron density analysis using the QTAIM theory has revealed several intermolecular interactions: hydrogen bonds in $-\text{SH}$, $-\text{SO}_3\text{H}$ and guanidine, tetrel bonds (a non-covalent interaction involving the electrophilic carbon atom of CO_2 and an electron donor) in $-\text{NH}_2$, $-\text{SO}_3\text{H}$ and guanidine, and the dipole-dipole interactions in N_3 and NCO , indicating that the adsorption process was predominantly governed by physisorption.

Nevertheless, based on the isosteric heat of adsorption results, it appeared that NH_2 and guanidine-functionalized

SBA-15 also exhibit chemisorption process, together with the existing physisorption. Their charge transfer analysis revealed that CO₂ molecules were preferentially attracted to negative atoms due to bearing a positive carbon centre. The Mulliken charges also showed that CO₂ would become slightly polar when adsorbed onto the functional group and a small amount of charge transfer to ligand occurred (Cueto-Díaz et al. 2023). Overall, they reported that the NH₂-functionalized SBA-15 has the highest adsorption capacity of 1.15 mmol/g at 50 °C and 1 bar based on their adsorption isotherm results. This adsorbent also exhibited the highest heat of adsorption and adsorption capacity, showing that NH₂ groups could be used for effective CO₂ capture. On the other hand, polymeric-based PAMAM-modified SBA-15 displayed poor adsorption performance, despite containing higher amounts of NH₂ groups, which could be due to pore blockage owing to high steric hindrance. Overall, their theoretical results and experimental results were comparable, except for SO₃H and NCO complexes. These complexes have strong theoretical interactions but low experimental adsorption performance that have been attributed to inefficient functionalization, interaction with water that reduced the amount of sulphur-containing ligands on the surface, and loss of porosity caused by sulphur-containing ligands from possible pore blockage (Cueto-Díaz et al. 2023).

A study on the synthesis of SO₃H-functionalized mesoporous silica reported that the SO₃H groups were only weakly coupled on the silica without any hydrogen bonds formed because of their bulkiness based on the NMR and DFT results (Tsai et al. 2011). They reported that these groups' weak attachment to the silica matrix could have compromised their functionalization effectiveness that contributed to structural integrity loss under harsh conditions. This could explain the loss of porosity in SO₃H-functionalized SBA-15 in the work by Cueto-Díaz et al. (2023). Overall, from the theoretical perspective, the DFT could play a pivotal role in elucidating the interaction mechanisms between functional groups and mesoporous silica surface, while complementing experimental ssNMR by validating the adsorption species and offering insights into their impact on CO₂ adsorption properties and performance.

Mechanistic insights into CO₂ capture on functionalized mesoporous silica

Understanding the mechanism of CO₂ binding on functionalized mesoporous silica is critical for adsorbent design and further modification for improvement. Adsorption can be classified into physisorption and chemisorption. Functionalization can strengthen the interaction between CO₂ molecules and silica surface by shifting the adsorption mechanism from predominantly physisorption to chemisorption or a

combination of both, influencing the efficiency and selectivity of CO₂ capture. Unravelling the adsorption mechanism requires a combination of experimental and computational approaches to bridge the gap between observed phenomena and molecular interactions. DFT calculation could help provide insights regarding the adsorption process by identifying the types of adsorptions, either physisorption or chemisorption, or potentially both, through adsorption energy. These calculations are often supported by experimental data to ensure that theoretical predictions meet practical outcomes. Typically, the energetic threshold that differentiates physisorption from chemisorption is considered to be approximately 0.5 eV per adsorbed molecule (Chaturvedi and Sharma 2022).

Tehrani et al. (2023) performed an experimental study and a DFT study on CO₂ adsorption using polydopamine (PDA)-modified MCM-41 (Hossein Tehrani et al. 2023). Polydopamine contains catechol and amine group, which could be used for functionalising mesoporous silica for CO₂ adsorption. Figure 10a displays the un-interacted optimized individual structures of PDA-modified MCM-41. Meanwhile, Fig. 10b depicts the interaction of the mesoporous material with CO₂ molecules based on the DFT technique, which is critical for understanding the material's potential in CO₂ capture applications.

Their experimental results showed that the highest CO₂ adsorption capacity achieved was 5.12 mmol/g at 25 °C and 1 bar with 10% PDA, with good cyclic stability over 10 adsorption-desorption cycles and only loss about 0.83% of initial CO₂ uptake. Next, the DFT study was performed using the exchange-correlation of PBE density functional (Perdew et al. 1996), with all-electron double numerical polarised basis set. To account for the van der Waals interaction, they utilised DFT-2 scheme (Grimme 2006) to include the effects. They found that the PDA moiety was strongly attached to Si atoms in MCM-41 from the short binding distance of 2.2 Å. Their DFT computations revealed that the adsorption energy was −13.48 kcal/mol (56.4 kJ/mol or 0.585 eV), indicating CO₂ to be energetically favoured and strongly adsorbed, which aligned with their experimental results (Hossein Tehrani et al. 2023). Moreover, the charge transfer results showed 0.25 electrons being transferred from PDA moiety to MCM-41, inferring that PDA on the surface of MCM-41 might have acted as an electron acceptor when it interacted with CO₂. When CO₂ molecules were adsorbed onto the PDA-functionalized MCM-41, approximately 0.24 electrons were transferred from CO₂ to PDA moiety. They were mostly localised on the carbon atoms of the central phenyl ring of the PDA, which proved that CO₂ could adsorb strongly on PDA-functionalized MCM-41, thus enhancing CO₂ capture performance. The computation results were in good agreement with the experimental

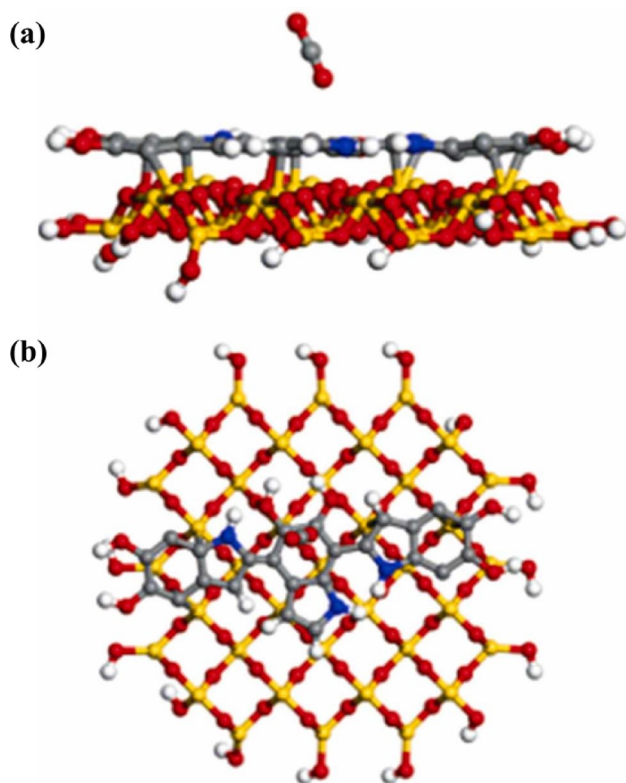


Fig. 10 Optimized structural models: **a** PDA-modified MCM-41 and CO₂ molecule; and **b** the interaction between PDA-modified MCM-41 with CO₂ molecules. (Reprinted from ref. (Hossein Tehrani et al. 2023), Copyright (2023), with permission from Elsevier.)

results of adsorption capacity. This study has shown that the presence of multiple functional groups within a single functionalization agent like PDA could significantly enhance CO₂ adsorption performance due to the synergistic effects between different binding sites. In short, this study has highlighted the role of functional groups in increasing the number of adsorption sites and enhancing interactions with CO₂ molecules, as important factors in the design of a targeted adsorption process.

Similarly, periodic DFT slab calculations were conducted to study the behaviour of different functionalized mesoporous phenylene-silicas (Ph-PMO) on CO₂ adsorption (Lourenço et al. 2016). Included in the calculations were the exchange-correlation functional of PBE-GGA (Perdew et al. 1996), with non-spin polarisation that included van der Waals interaction correction (Grimme 2006; Fajin et al. 2012; Ramalho et al. 2013). PAW pseudopotential and cut-off energy of 415 eV were used. In terms of the amine-functionalized phenylene-silicas (Ph-PMO, NH₂-Ph-PMO, APTMS-grafted Ph-PMO, and NH₂-Ph-PMO), their adsorption results revealed that the amount of adsorbed CO₂ and in Henry's constant for CO₂ adsorption in increasing order are as follows: Ph-PMO < NH₂-Ph-PMO < APTMS-grafted

NH₂-Ph-PMO < APTMS-grafted Ph-PMO. They reported that the type of amines used could affect the adsorption performance more than the nitrogen content in the materials, suggesting that the interaction between CO₂ and alkyl amine was stronger than aromatic amines. Their DFT computation results were also comparable with their experimental results, where the calculated CO₂ interaction energy was the highest for APTMS-grafted Ph-PMO (−29.0 kJ/mol), the lowest for Ph-PMO (−19.8 kJ/mol), with APTMS-grafted Ph-PMO and NH₂-Ph-PMO exhibiting close values of −25.9 and −26.2 kJ/mol, respectively. Moreover, based on the optimized models' configurations, they reported that CO₂ would preferentially adsorb with the silanol group in Ph-PMO. In the case of NH₂-Ph-PMO, CO₂ interacted with both silanol and amino groups. On the other hand, for APTMS-grafted materials, CO₂ interacted with the acidic hydrogen of alkyl chains in APTMS. For APTMS-grafted NH₂-Ph-PMO, CO₂ also adsorbed on silanol groups, whereas for APTMS grafted Ph-PMO, the CO₂ interaction occurred with the amino groups instead. They inferred that the main cause for the improved adsorption performance might be due to CO₂ being adsorbed on more than one adsorption site. They have also performed DFT calculations for CO₂ adsorption on different functional groups (−NO₂, isopropylamine, −CH₂NH, and −SO₃H) on Ph-PMO silica as a guideline for the synthesis of new potential adsorbents. They found that the sample with −CH₂NH₂ functional group exhibited the strongest interaction energy with CO₂ molecules of approximately −31.1 kJ/mol, which was higher than the energy exhibited by APTMS-functionalized Ph-PMO silica and could be a potential CO₂ adsorbent candidate (Lourenço et al. 2016). Notably, these findings could infer that alkyl amines exhibited stronger CO₂ interactions than aromatic amines. This was likely due to the less delocalised electron environment in alkyl amines, which could facilitate stronger dipole interactions with CO₂. Hence, their study has confirmed the importance of chemical structure in the design of functional groups, thereby further validating that the DFT could provide theoretical foundation to guide and develop more efficient adsorbents.

Using a combination of DFT, MD, and GCMC simulations, Kwon et al. (2017) studied and evaluated CO₂ adsorption on alkali metal chloride (LiCl, NaCl, and KCl)-modified SBA-15 adsorbents. The DFT was used to develop force field parameters for subsequent MD and GCMC simulations (Kwon et al. 2017). PBE functional (Perdew et al. 1996) was used for calculating functional options with double numerical basis sets with polarization (Delley 1990, 2000). B3LYP functional 6-31G** basis set (Becke 1993) was used for the charge and geometric computation of individual gas molecule to ensure that each gas molecule was in neutral charge. The interatomic interaction computation, DFT-D3

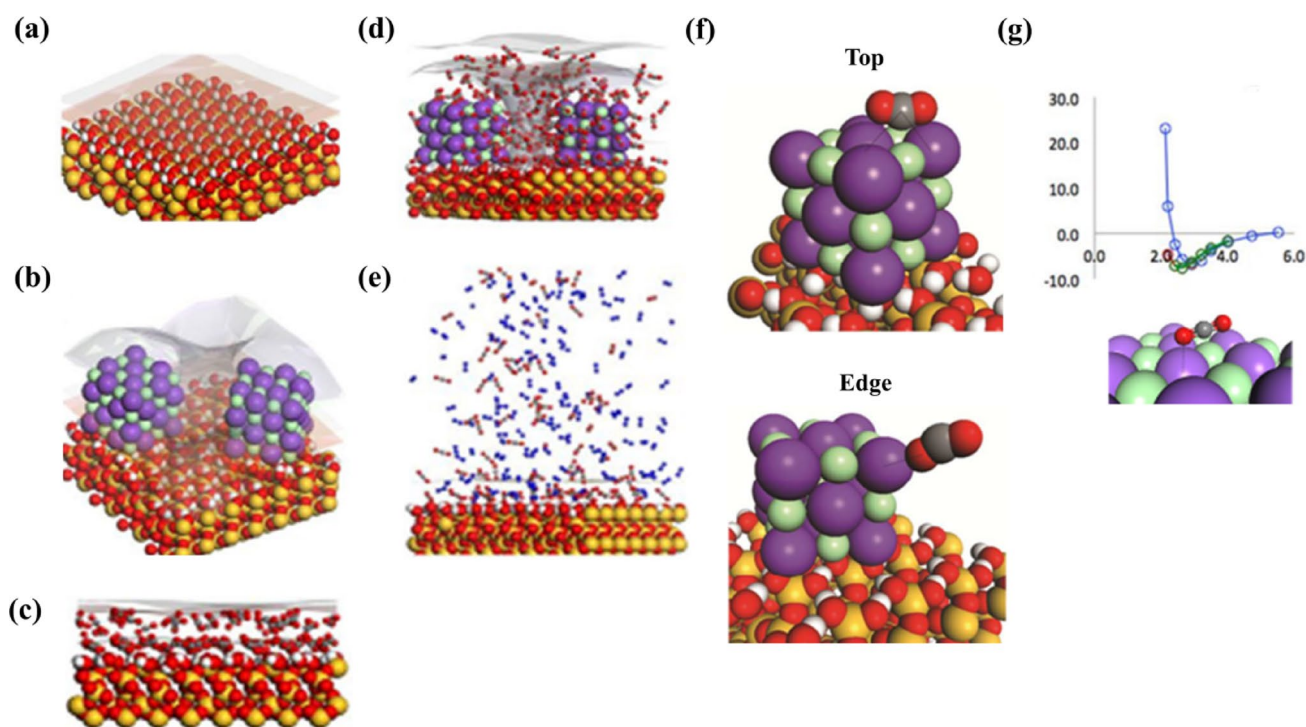


Fig. 11 MD simulation of electrostatic field profiles of adsorbents at 273 K on different adsorbents: **a** SBA-15 and **b** KCl/SBA-15; MD simulations after adsorption of pure CO₂: **c** SBA-15 and **d** KCl/SBA-15; **e** MD simulations over SBA-15 under 40 mol% CO₂ with 60 mol% N₂; **f** geometry optimization of CO₂ adsorption at the top and

edge of KCl/SBA-15 cluster models; and **f** binding energy profiles of CO₂ gas molecules on the KCl/SBA-15 surface. Colour coding as follows: white: H, grey: C, blue: N, purple: K, red: O, yellow: Si, and green: Cl. (Reprinted (adapted) with permission from ref. (Kwon et al. 2017). Copyright (2017). American Chemical Society.)

(Burns et al. 2011; Ehrlich et al. 2011) with Beck-Johnson damping function (Grimme et al. 2011) was utilised to correct any dispersion corrections. The force field parameters were developed based on the interaction energy between CO₂ and the adsorbents by projecting them into the van der Waals interaction and electrostatic interaction. Their MD and GCMC simulation results, using the DFT developed force field, were in good agreement with their experimental data compared to universal force field and Dreiding.

Figure 11 collectively illustrates the findings on structural and energetic aspects of CO₂ adsorption on mesoporous SBA-15 modified by KCl, as studied through MD and DFT techniques by Kwon et al. (2017). Their computational results revealed that the adsorption on alkali metal chloride-modified SBA-15 was not strong to form carbonates complex, as the adsorption energies were lower than 0.3 eV. Based on the geometry optimization process, they reported that the strongest adsorption sites for CO₂ molecules were located at the top and edge sites of the KCl cluster. Thus, they postulated that the enhanced electrostatic field formed at regions between neighbouring KCl particles on the SBA-15 surface might be the cause for the stronger interaction with CO₂ molecules compared to pristine SBA-15 (Kwon et al. 2017). They also found that CO₂ molecules have higher affinity to KCl/SBA-15, which could be attributed to the

low Madelung potential energy (the electrostatic potential shift of an ion in crystal lattice or ionic solid) compared to other materials. This means that more charges were transferred, leading to more electron delocalization distribution of surface oxygen and resulting in an efficient overlap with orbitals of CO₂ molecules. These results indicated that the KCl-modified SBA-15 could be a potential adsorbent, which demonstrated the useful combination of computational tools to provide insight regarding the adsorption process (Burghaus 2013). However, the findings that alkali metal chloride alterations did not significantly enhance CO₂ adsorption as predicted by the computation modelling approach and the interaction potential models may require more refinement to improve their predictive accuracy and reduce the discrepancy range between simulated and experimental values.

Similarly, Zhu et al. (2012) utilised DFT-based force field in their GCMC simulation of their theoretical study and molecular simulation on CO₂ adsorption using amine-grafted mesoporous silica MCM-41 (Zhu et al. 2012). The MCM-41 model was based on their previous work (Zhuo et al. 2008) and the adsorbate-adsorbent interactions have been described by combinations of Lennard-Jones potential and Columbic potential. The Lennard-Jones potential accounts for short-range van der Waals interactions, including

attractive dispersion forces and repulsive forces between atoms. In contrast, the Coulombic potential describes the electrostatic interactions arising from the partial charges of atoms and molecules. Together, these two potentials provide a comprehensive description of the non-bonded interactions involved in CO₂ adsorption on amine-functionalized mesoporous silica. PBE functional with double numerical plus polarization basis set was used for the DFT calculation. In their work, they have reported a method that could be used for describing the chemical interaction between CO₂ and amine group in the adsorption process with enhanced physical interaction. They first obtained the interaction energy between the amine group and CO₂ molecules from the DFT computation, which was -0.00756 Ha. Then, the interaction energy was enlarged in the GCMC to simulate and control the adsorption process, since a general force field was not able to simulate the strong interaction (Zhu et al. 2012). Based on their CO₂/N₂ adsorption simulation, they reported that the CO₂ adsorption capacity and CO₂/N₂ selectivity began to increase when the grafted amine groups were increased, which accurately reflected the experimental observation. As for the adsorption sites, CO₂ molecules were adsorbed around active amino groups, while N₂ molecules were adsorbed at the pore surface of MCM-41. Overall, this study has made substantial contributions towards understanding how amine density could influence adsorption capacity and selectivity, which were crucial elements in optimizing CO₂ adsorbent designs. However, the limitation faced by this study was its narrowed focus on a specific type of functionalized mesoporous silica, thus potentially overlooking a broader applicability for other types of mesoporous materials or functional groups.

Mafra et al. (2018) employed DFT calculations, coupled with ssNMR method in their study on possible applications of different types of amine-functionalized mesoporous silica SBA-15 in natural gas or biogas purification process (Mafra et al. 2018). The exchange-correlation functional used was a hybrid M06-2X functional, as proposed by Zhao and Truhlar (2008, 2006) (Zhao and Truhlar 2006, 2008) based on meta GGA and standard 6-31(d) basis set (Hariharan and Pople 1973; Francel et al. 1982). Based on their experimental results, they reported that tertiary amine did not beneficially affect CO₂ adsorption. Instead, the functionalization using primary and secondary amine presented better CO₂ adsorption performance, and at very low-pressure ranges, the primary and secondary amines did not react completely with CO₂. Interestingly, they found that physisorbed CO₂ molecules interacted with the formed chemisorbed species at pressure higher than 40 kPa., which could possibly explain the observed high selectivity beyond amine saturation region, and might be due to the interaction between amine species with very polar carbamic acid at the pore surfaces

with the quadrupolar CO₂ molecules. They have also estimated the reaction Gibbs energy of CO₂ with amine using DFT computation, which aligned with the experimental results (Henry's constant, selectivity), where stronger interaction with CO₂ molecules displayed more negative Gibbs energy and giving high selectivity (Mafra et al. 2018).

In an earlier work using the same approach, they focused on the chemisorbed CO₂ product species on amine-functionalized mesoporous silica and confirmed their likely existence. A total of three species were identified and they found that these species were involved in the hydrogen bond, with either the silanol groups or the alkylamines on the silica surface, as validated by DFT calculations (Mafra et al. 2017). Thus, this work has disputed a long-held traditional understanding about CO₂ capture mechanisms by highlighting the complex interaction of amine type, steric hindrance, and substrate effects. In conclusion, these critical analyzes have not only added to the existing understanding of this topic but also pave the way for the design of novel adsorbents that could optimally and effectively perform in real-world CO₂ adsorption applications. Future researchers could use these findings to improve amine functionalization techniques and mesoporous silica materials' properties by combining data from all computational molecular-level techniques towards increasing CO₂ capture performance.

Future perspective and challenges

To simulate the adsorption process accurately, precise models are required for the molecular modelling. However, it might be difficult to completely capture all the realistic behaviours in modelling, since it requires significant computational power and time. The large size of mesoporous frameworks and the need for periodic boundary conditions could make accurate modelling a time-consuming endeavour. Such complexity increases further when simulating functionalized surfaces or hybrid systems. Moreover, the selection of appropriate exchange-correlation function is also critical to ensure accurate and precise computations. No universal functional could perfectly capture all types of interactions, thus necessitating approximations and corrections to 100% match the real-case scenario. As mentioned in the previous section, the consideration of appropriate k-points and cutoff energy is crucial to ensure the accuracy of the results, with higher values of k-point and cutoff energy providing more reliable results or outcomes. However, higher computational cost and longer computational time would be required, especially for larger and more complex systems.

A prevalent systematic error called delocalization error might occur in the DFT method. Delocalization error is

caused by an unphysical interaction of electrons resulting from approximation, which arises due to incomplete cancellation of self-interaction energy and may cause Kohn–Sham orbitals that are highly localised to be improperly destabilized with approximate exchange–correlation functionals and unpaired electrons tend to delocalize spatially to minimize self-interaction (Sholl and Steckel 2009). This kind of system also poses a challenge to DFT computation, as mentioned in a study by Cohen et al. (2012) (Cohen et al. 2012). Fortunately, efforts to understand and correct these errors are on-going, with significant contributions from many researchers who have developed methodologies to mitigate these negative effects (Cohen et al. 2012; Hait and Head-Gordon 2018; San-Fabián Maroto and Sancho-García 2019; Yang et al. 2020).

Beyond the computational challenges discussed above, the development of new amine-functionalized mesoporous silica adsorbents is also constrained by practical considerations related to the choice of functional groups and coupling agents. Although numerous amine-containing compounds have been reported, only a limited number, particularly APTES, APTMS, PEI, and TEPA, are repeatedly employed in the literature. Their widespread use is not solely due to favourable CO₂ adsorption performance, but also because these materials are commercially available, relatively well established, and can be readily incorporated onto mesoporous silica using grafting or impregnation methods.

In contrast, many alternative functional groups remain underexplored. One important reason is the limited availability of suitable silane coupling agents. Some functional groups do not have commercially available silane derivatives, whereas others require multi-step organic synthesis before surface functionalization can be carried out. These additional synthetic steps increase preparation costs, reduce reproducibility, and may limit their adoption for large-scale research. Furthermore, bulky or multifunctional coupling agents may experience steric hindrance during grafting, resulting in lower grafting densities, partial pore blockage, or reduced accessibility of adsorption sites.

Economic considerations should also be taken into account when designing new functionalized adsorbents. Future studies should evaluate not only adsorption capacity but also the commercial availability of coupling agents, synthesis complexity, long-term stability, regeneration performance, and overall production cost. The development of low-cost coupling agents, simplified functionalization strategies, and sustainable silica precursors may improve the feasibility of large-scale preparation and facilitate the future implementation of amine-functionalized mesoporous silica adsorbents for CO₂ capture.

The exploration of additional functional group modifications, particularly bio-based functionalization agents,

remains an important research direction. However, future developments should also consider the commercial availability of suitable coupling agents, synthesis complexity, production cost, and long-term stability to ensure that newly developed adsorbents are both technically effective and practically feasible for CO₂ capture applications. There are also potential improvements in simplified functionalization techniques for mesoporous silica materials, such as the development of one-pot synthesis techniques or the adaptation of conditions that may better suit the real-world or industrial applications. Although CO₂, N₂ and water are the common major components in post-combustion flue gas, there are also impurities present in certain cases (Cheng et al. 2022). For instance, SO₂, O₂ and H₂S. Future adsorption study could be conducted to include the impurities as more realistic approach to practical and to investigate the effect of them on overall CO₂ uptake on mesoporous silica, through the use of molecular modelling together with experimental method. Finally, a comprehensive lifecycle assessment of the materials and processes should be integrated with computational molecular models to ensure that their environmental impact is minimized across the entire lifecycle of the adsorbents, from synthesis to disposal. To summarize, while recent advances in amine-functionalized mesoporous silica materials have shown promise in CO₂ capture, additional research and development are required to overcome current constraints and to realize their potential in long-term commercial applications.

Conclusion

In conclusion, the purpose of this review was to critically evaluate the use of molecular dynamics and DFT modelling methodologies to correlate experimental findings with the molecular-level behaviour of mesoporous silica materials, specifically amine-functionalized mesoporous silica materials in CO₂ capture applications. While previous reviews have extensively summarized synthesis and adsorption capacities, this work fills a critical gap by providing a systematic evaluation of silica model construction strategies-ranging from ring clusters to realistic amorphous structures with surface defects. This focus provides a necessary theoretical foundation for researchers to simulate realistic adsorption scenarios and correlate theoretical binding energies with experimental thermodynamic data. This current study has discovered that computational tools, techniques, or procedures used in modelling approaches, such as DFT and MD, are critical in comprehending computational molecular modelling. These findings have indicated that advances in integrated DFT and other computational approaches such as MD may influence future CO₂ capture

policies and practices. While this study has presented useful information, it is vital to acknowledge its limitations, for example, the particular emphasis it has placed on amine-functionalized mesoporous silica materials. Overall, this study could contribute to the understanding of integrated computational molecular modelling methodologies, while underlining the need for more research. Future research should focus on different functional group-modified mesoporous silica materials, as this field is relatively unexplored. Longitudinal research, as well as mixed- or hybrid-method strategies, may yield more reliable results for complex CO₂ adsorption technology. Future research should also include a diverse variety of demographic groups to better understand CO₂ adsorption in different conditions. Interdisciplinary collaborations may provide useful insights into CO₂ capture applications, which would enable innovative solutions. Researchers should also look at how new discoveries might be applied in practice, particularly in direct industrial effluent capture to improve the feasibility and efficacy of CO₂ capture equipment.

Acknowledgements This work was supported by the Ministry of Higher Education of Malaysia through Fundamental Research Grant Scheme (FRGS/1/2023/TK05/USM/02/4).

Author contributions Conceptualization: Chui Keat Lim, Syamima Nasrin Mohamed Saleh, Azam Taufik Mohd Din; Writing—original draft preparation: Chui Keat Lim; Writing—review and editing: Syamima Nasrin Mohamed Saleh, Sunarti Abd Rahman, Chew Thiam Leng, Noorhidayah Ishak; Visualization: Chui Keat Lim, Syamima Nasrin Mohamed Saleh; Supervision: Azam Taufik Mohd Din, Bassim H. Hameed; Resources: Azam Taufik Mohd Din, Mohd Azmier Ahmad, Bassim H. Hameed.

Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no conflict of interest.

References

- Abdullah N, Ainirazali N, Chong CC et al (2020) Influence of impregnation assisted methods of Ni/SBA-15 for production of hydrogen via dry reforming of methane. *Int J Hydrog Energy* 45:18426–18439. <https://doi.org/10.1016/j.ijhydene.2019.09.089>
- Afonso R, Sardo M, Mafra L, Gomes JRB (2019) Unravelling the structure of chemisorbed CO₂ species in mesoporous aminosilicas: a critical survey. *Environ Sci Technol* 53:2758–2767. <https://doi.org/10.1021/acs.est.8b05978>
- Ahmadian Hosseini A, Jahandar Lashaki M (2023) A comprehensive evaluation of amine-impregnated silica materials for direct air capture of carbon dioxide. *Sep Purif Technol* 325:124580. <https://doi.org/10.1016/j.seppur.2023.124580>
- Ahmed S, Ramli A, Yusup S (2017) Development of polyethylenimine-functionalized mesoporous Si-MCM-41 for CO₂ adsorption. *Fuel*

- Process Technol* 167:622–630. <https://doi.org/10.1016/j.fuproc.2017.07.036>
- Al Mohtar A, Pinto ML (2022) Water effect on CO₂ adsorption kinetics in amine-functionalized silicas assessed using the density functional theory. *J Phys Chem C* 126:5159–5166. <https://doi.org/10.1021/acs.jpcc.1c10716>
- Allen MP, Tildesley DJ (2017) Computer simulation of liquids, 2nd edn. Oxford University Press, Oxford
- Amaraweera SM, Gunathilake CA, Gunawardene OHP et al (2023) Carbon capture using porous silica materials. *Nanomaterials* 13:2050. <https://doi.org/10.3390/nano13142050>
- Anyanwu J-T, Wang Y, Yang RT (2021) SBA-15 functionalized with amines in the presence of water: applications to CO₂ capture and natural gas desulfurization. *Ind Eng Chem Res* 60:6277–6286. <https://doi.org/10.1021/acs.iecr.1c00415>
- Anyanwu J-T, Wang Y, Yang RT (2022) Tunable amine loading of amine grafted mesoporous silica grafted at room temperature: applications for CO₂ capture. *Chem Eng Sci* 254:117626. <https://doi.org/10.1016/j.ces.2022.117626>
- Arias AN, Páez Jerez AL, Tesio ÁY et al (2025) Optimization of surface silanol groups in mesoporous SBA-15 and KIT-6 materials: effects on APTES functionalization and CO₂ adsorption. *Microporous Mesoporous Mater* 382:113394. <https://doi.org/10.1016/j.micromeso.2024.113394>
- Avellaneda GL, Denoyel R, Beurroies I (2024) CO₂/H₂O adsorption and co-adsorption on functionalized and modified mesoporous silicas. *Microporous Mesoporous Mater* 363:112801. <https://doi.org/10.1016/j.micromeso.2023.112801>
- Bakalarski G, Grochowski P, Kwiatkowski JS et al (1996) Molecular and electrostatic properties of the N-methylated nucleic acid bases by density functional theory. *Chem Phys* 204:301–311. [https://doi.org/10.1016/0301-0104\(95\)00413-0](https://doi.org/10.1016/0301-0104(95)00413-0)
- Başaran K, Topçubaşı BU, Davran-Candan T (2021) Theoretical investigation of CO₂ adsorption mechanism over amine-functionalized mesoporous silica. *J CO₂ Utilization* 47:101492. <https://doi.org/10.1016/j.jcou.2021.101492>
- Baseden KA, Tye JW (2014) Introduction to density functional theory: calculations by hand on the helium atom. *J Chem Educ* 91:2116–2123. <https://doi.org/10.1021/ed5004788>
- Bayly CI, Cieplak P, Cornell W, Kollman PA (1993) A well-behaved electrostatic potential based method using charge restraints for deriving atomic charges: the RESP model. *J Phys Chem* 97:10269–10280. <https://doi.org/10.1021/j100142a004>
- Beck JS, Vartuli JC, Roth WJ et al (1992) A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J Am Chem Soc* 114:10834–10843. <https://doi.org/10.1021/ja00053a020>
- Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652. <https://doi.org/10.1063/1.464913>
- Benamor T, Michelin L, Lebeau B, Marichal C (2012) Flash induction calcination: A powerful tool for total template removal and fine tuning of the hydrophobic/hydrophilic balance in SBA-15 type silica mesoporous materials. *Microporous Mesoporous Mater* 147:334–342. <https://doi.org/10.1016/j.micromeso.2011.07.004>
- Bernin D, Hedin N (2018) Perspectives on NMR studies of CO₂ adsorption. *Curr Opin Colloid Interface Sci* 33:53–62. <https://doi.org/10.1016/j.cocis.2018.02.003>
- Burghaus U (2013) Surface science studies of carbon dioxide chemistry. In: *New and future developments in catalysis*. Elsevier, pp 27–47
- Burke K, Wagner LO (2013) DFT in a nutshell. *Int J Quantum Chem* 113:96–101. <https://doi.org/10.1002/qua.24259>
- Burns LA, Mayagoitia ÁV-, Sumpter BG, Sherrill CD (2011) Density-functional approaches to noncovalent interactions: a comparison of dispersion corrections (DFT-D), exchange-hole dipole

- moment (XDM) theory, and specialized functionals. *J Chem Phys* 134:084107. <https://doi.org/10.1063/1.3545971>
- Candela-Noguera V, Alfonso M, Amorós P et al (2024) In-depth study of factors affecting the formation of MCM-41-type mesoporous silica nanoparticles. *Microporous Mesoporous Mater* 363:112840. <https://doi.org/10.1016/j.micromeso.2023.112840>
- Cassiers K, Linssen T, Mathieu M et al (2002) A detailed study of thermal, hydrothermal, and mechanical stabilities of a wide range of surfactant assembled mesoporous silicas. *Chem Mater* 14:2317–2324. <https://doi.org/10.1021/cm0112892>
- Cauvel A, Brunel D, Di Renzo F et al (1997) Hydrophobic and hydrophilic behavior of micelle-templated mesoporous silica. *Langmuir* 13:2773–2778. <https://doi.org/10.1021/la962059i>
- Chaturvedi KR, Sharma T (2022) Carbonated nanofluids for EOR and improved carbon storage. In: *Nanotechnology for CO₂ utilization in oilfield applications*. Elsevier, pp 71–84
- Chen D, Li L, Tang F, Qi S (2009) Facile and scalable synthesis of tailored silica nanorattle structures. *Adv Mater* 21:3804–3807. <https://doi.org/10.1002/adma.200900599>
- Chen C, Zhang S, Row KH, Ahn W-S (2017) Amine-silica composites for CO₂ capture: a short review. *J Energy Chem* 26:868–880. <https://doi.org/10.1016/j.jechem.2017.07.001>
- Chen J, Moon HJ, Kim KI et al (2023) Distribution and transport of CO₂ in hyperbranched poly(ethylenimine)-loaded MCM-41: a molecular dynamics simulation approach. *ACS Appl Mater Interfaces* 15:43678–43690. <https://doi.org/10.1021/acsami.3c07040>
- Cheng Z, Li S, Liu Y et al (2022) Post-combustion CO₂ capture and separation in flue gas based on hydrate technology: a review. *Renew Sustain Energy Rev* 154:111806. <https://doi.org/10.1016/j.rser.2021.111806>
- Chew T-L, Ahmad AL, Bhatia S (2010) Ordered mesoporous silica (OMS) as an adsorbent and membrane for separation of carbon dioxide (CO₂). *Adv Colloid Interface Sci* 153:43–57. <https://doi.org/10.1016/j.cis.2009.12.001>
- Coasne B, Ugliengo P (2012) Atomistic model of micelle-templated mesoporous silicas: structural, morphological, and adsorption properties. *Langmuir* 28:11131–11141. <https://doi.org/10.1021/la3022529>
- Cohen AJ, Mori-Sánchez P, Yang W (2012) Challenges for density functional theory. *Chem Rev* 112:289–320. <https://doi.org/10.1021/cr200107z>
- Corno M, Delle Piane M, Monti S et al (2015) Computational study of acidic and basic functionalized crystalline silica surfaces as a model for biomaterial interfaces. *Langmuir* 31:6321–6331. <https://doi.org/10.1021/acs.langmuir.5b01828>
- Cueto-Díaz EJ, Castro Muñoz A, Suárez García F et al (2023) Effect of surface organo-silanization on SBA-15 mesoporous silicas in CO₂ adsorption processes: design, synthesis, and computational studies. *Ind Eng Chem Res* 62:11001–11015. <https://doi.org/10.1021/acs.iecr.3c00475>
- Da Silva T, Awano CM, Donatti DA et al (2014) About the thermal stability and pore elimination in the ordered hexagonal mesoporous silica SBA-15. *Microporous Mesoporous Mater* 190:227–233. <https://doi.org/10.1016/j.micromeso.2014.02.023>
- Dan H, Lei H, Luo J et al (2023) Efficient adsorption of CO₂ by amino-functionalized short pore SBA-15: influence of pore length on adsorption capacity and amino efficiency. *J Environ Chem Eng* 11:111379. <https://doi.org/10.1016/j.jece.2023.111379>
- Delley B (1990) An all-electron numerical method for solving the local density functional for polyatomic molecules. *J Chem Phys* 92:508–517. <https://doi.org/10.1063/1.458452>
- Delley B (2000) From molecules to solids with the DMol3 approach. *J Chem Phys* 113:7756–7764. <https://doi.org/10.1063/1.1316015>
- Duru IA, Duru CE (2020) Molecular modeling and density functional theory calculation of the coordination behavior of 4,5-dichloroimidazole with Cu(II) ion. *Sci Afr* 9:e00533. <https://doi.org/10.1016/j.sciaf.2020.e00533>
- Dziejarski B, Serafin J, Andersson K, Krzyżyńska R (2023) CO₂ capture materials: a review of current trends and future challenges. *Mater Today Sustain* 24:100483. <https://doi.org/10.1016/j.mtsust.2023.100483>
- Ehrlich S, Moellmann J, Reckien W et al (2011) System-dependent dispersion coefficients for the DFT-D3 treatment of adsorption processes on ionic surfaces. *ChemPhysChem* 12:3414–3420. <https://doi.org/10.1002/cphc.201100521>
- Emrie DB (2024) Sol-gel synthesis of nanostructured mesoporous silica powder and thin films. *J Nanomaterials* 2024:1–16. <https://doi.org/10.1155/2024/6109770>
- Eskandari S, Dong A, De Castro LT et al (2019) Pushing the limits of electrostatic adsorption: charge enhanced dry impregnation of SBA-15. *Catal Today* 338:60–71. <https://doi.org/10.1016/j.catto.2019.06.082>
- Ewing CS, Bhavsar S, Veser G et al (2014) Accurate amorphous silica surface models from first-principles thermodynamics of surface dehydroxylation. *Langmuir* 30:5133–5141. <https://doi.org/10.1021/la500422p>
- Fajín JLC, Cordeiro DS, Gomes MN, Illas JRB F (2012) On the need for spin polarization in heterogeneously catalyzed reactions on nonmagnetic metallic surfaces. *J Chem Theory Comput* 8:1737–1743. <https://doi.org/10.1021/ct3001415>
- Fan Y, Jia X (2022) Progress in amine-functionalized silica for CO₂ capture: important roles of support and amine structure. *Energy Fuels* 36:1252–1270. <https://doi.org/10.1021/acs.energyfuels.1c03788>
- Fayaz M, Sayari A (2017) Long-term effect of steam exposure on CO₂ capture performance of amine-grafted silica. *ACS Appl Mater Interfaces* 9:43747–43754. <https://doi.org/10.1021/acsami.7b15463>
- Feuston BP, Higgins JB (1994) Model structures for MCM-41 materials: a molecular dynamics simulation. *J Phys Chem* 98:4459–4462. <https://doi.org/10.1021/j100067a037>
- Franci MM, Pietro WJ, Hehre WJ et al (1982) Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J Chem Phys* 77:3654–3665. <https://doi.org/10.1063/1.444267>
- Frenkel D, Smit B (2002) *Understanding molecular simulation: from algorithms to applications*, 2nd edn. Academic, San Diego
- Fujiki J, Yamada H, Yogo K (2015) Enhanced adsorption of carbon dioxide on surface-modified mesoporous silica-supported tetraethylenepentamine: Role of surface chemical structure. *Microporous Mesoporous Mater* 215:76–83. <https://doi.org/10.1016/j.micromeso.2015.05.037>
- Galarneau A, Nader M, Guenneau F et al (2007) Understanding the stability in water of mesoporous SBA-15 and MCM-41. *J Phys Chem C* 111:8268–8277. <https://doi.org/10.1021/jp068526e>
- Ghaedi H, Zhao M (2022) Review on template removal techniques for synthesis of mesoporous silica materials. *Energy Fuels* 36:2424–2446. <https://doi.org/10.1021/acs.energyfuels.1c04435>
- Goedecker S, Teter M, Hutter J (1996) Separable dual-space gaussian pseudopotentials. *Phys Rev B* 54:1703–1710. <https://doi.org/10.1103/PhysRevB.54.1703>
- Goscianska J, Olejnik A, Nowak I (2017) APTES-functionalized mesoporous silica as a vehicle for antipyrine – adsorption and release studies. *Colloids Surf A* 533:187–196. <https://doi.org/10.1016/j.colsurfa.2017.07.043>
- Gouveia LGT, Agustini CB, Perez-Lopez OW, Gutterres M (2020) CO₂ adsorption using solids with different surface and acid-base properties. *J Environ Chem Eng* 8:103823. <https://doi.org/10.1016/j.jece.2020.103823>
- Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comput Chem* 27:1787–1799. <https://doi.org/10.1002/jcc.20495>

- Grimme S, Ehrlich S, Goerigk L (2011) Effect of the damping function in dispersion corrected density functional theory. *J Comput Chem* 32:1456–1465. <https://doi.org/10.1002/jcc.21759>
- Guo W, Li X, Zhao XS (2006) Understanding the hydrothermal stability of large-pore periodic mesoporous organosilicas and pure silicas. *Microporous Mesoporous Mater* 93:285–293. <https://doi.org/10.1016/j.micromeso.2006.03.009>
- Hack J, Maeda N, Meier DM (2022) Review on CO₂ capture using amine-functionalized materials. *ACS Omega* 7:39520–39530. <https://doi.org/10.1021/acsomega.2c03385>
- Hait D, Head-Gordon M (2018) Delocalization errors in density functional theory are essentially quadratic in fractional occupation number. *J Phys Chem Lett* 9:6280–6288. <https://doi.org/10.1021/acs.jpclett.8b02417>
- Han Y, Zhang L, Yang W (2024a) Synthesis of mesoporous silica using the sol–gel approach: adjusting architecture and composition for novel applications. *Nanomaterials* 14:903. <https://doi.org/10.3390/nano14110903>
- Han Y, Zhang L, Yang W (2024b) Synthesis of mesoporous silica using the sol–gel approach: adjusting architecture and composition for novel applications. *Nanomaterials* 14:903. <https://doi.org/10.3390/nano14110903>
- Hariharan PC, Pople JA (1973) The influence of polarization functions on molecular orbital hydrogenation energies. *Theoret Chim Acta* 28:213–222. <https://doi.org/10.1007/BF00533485>
- Harlick PJE, Sayari A (2005) Amine grafted, pore-expanded MCM-41 for acid gas removal: effect of grafting temperature, water, and amine type on performance. *Stud Surf Sci Catal* 158:987–994. [https://doi.org/10.1016/S0167-2991\(05\)80439-2](https://doi.org/10.1016/S0167-2991(05)80439-2)
- Hehre WJ, Ditchfield R, Pople JA (1972) Self-consistent molecular orbital methods. XII. Further extensions of Gaussian—type basis sets for use in molecular orbital studies of organic molecules. *J Chem Phys* 56:2257–2261. <https://doi.org/10.1063/1.1677527>
- Henao W, Jaramillo LY, López D et al (2020) Insights into the CO₂ capture over amine-functionalized mesoporous silica adsorbents derived from rice husk ash. *J Environ Chem Eng* 8:104362. <https://doi.org/10.1016/j.jece.2020.104362>
- Hertl W, Hair ML (1969) Adsorption of water on silica. *Nature* 223:1150–1151. <https://doi.org/10.1038/2231150a0>
- Hiyoshi N, Yogo K, Yashima T (2004a) Adsorption of carbon dioxide on modified mesoporous materials in the presence of water vapor. *Stud Surf Sci Catal* 154:2995–3002. [https://doi.org/10.1016/S0167-2991\(04\)80583-4](https://doi.org/10.1016/S0167-2991(04)80583-4)
- Hiyoshi N, Yogo K, Yashima T (2004b) Reversible adsorption of carbon dioxide on amine-modified SBA-15 from flue gas containing water vapor. *Stud Surf Sci Catal* 153:417–422. [https://doi.org/10.1016/S0167-2991\(04\)80289-1](https://doi.org/10.1016/S0167-2991(04)80289-1)
- Hoffmann F, Cornelius M, Morell J, Fröba M (2006) Silica-based mesoporous organic–inorganic hybrid materials. *Angew Chem Int Ed* 45:3216–3251. <https://doi.org/10.1002/anie.200503075>
- Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. *Phys Rev* 136:B864–B871. <https://doi.org/10.1103/PhysRev.136.B864>
- Hori K, Higuchi T, Aoki Y et al (2017) Effect of pore size, aminosilane density and aminosilane molecular length on CO₂ adsorption performance in aminosilane modified mesoporous silica. *Microporous Mesoporous Mater* 246:158–165. <https://doi.org/10.1016/j.micromeso.2017.03.020>
- Hossein Tehrani NHM, Ardjmand M, Bazmi M et al (2023) Polydopamine-modified mesoporous silica materials as a novel adsorbent for superior CO₂ adsorption: experimental and DFT study. *J Environ Chem Eng* 11:110451. <https://doi.org/10.1016/j.jece.2023.110451>
- Hosseinpour M, Shojaei MJ, Salimi M, Amidpour M (2023) Machine learning in absorption-based post-combustion carbon capture systems: a state-of-the-art review. *Fuel* 353:129265. <https://doi.org/10.1016/j.fuel.2023.129265>
- Kamarudin KSN, Alias N (2013) Adsorption performance of MCM-41 impregnated with amine for CO₂ removal. *Fuel Process Technol* 106:332–337. <https://doi.org/10.1016/j.fuproc.2012.08.017>
- Kamarudin NHN (2016) Microwave-assisted synthesis of mesoporous silica nanoparticles as a drug delivery vehicle. *MJAS* 20:1382–1389. <https://doi.org/10.17576/mjas-2016-2006-17>
- Khosrowshahi MS, Aghajari AA, Rahimi M, Maleki F, Ghiyabi E, Rezanezhad A, Bakhshi A, Salari E, Shayesteh H, Mohammadi H (2024) Recent progress on advanced solid adsorbents for CO₂ capture: from mechanism to machine learning. *Mater Today Sustain* 27:100900. <https://doi.org/10.1016/j.mtsust.2024.100900>
- Kim JM, Ryoo R (1996) Disintegration of mesoporous structures of MCM-41 and MCM-48 in water. *Bull Korean Chem Soc* 17:66–68. <https://doi.org/10.5012/BKCS.1996.17.1.66>
- Kim JM, Jun S, Ryoo R (1999) Improvement of hydrothermal stability of mesoporous silica using salts: reinvestigation for time-dependent effects. *J Phys Chem B* 103:6200–6205. <https://doi.org/10.1021/jp990394k>
- Kishor R, Ghoshal AK (2015) APTES grafted ordered mesoporous silica KIT-6 for CO₂ adsorption. *Chem Eng J* 262:882–890. <https://doi.org/10.1016/j.cej.2014.10.039>
- Kishor R, Ghoshal AK (2017) Amine-modified mesoporous silica for CO₂ adsorption: the role of structural parameters. *Ind Eng Chem Res* 56:6078–6087. <https://doi.org/10.1021/acs.iecr.7b00890>
- Klinthong W, Chao K-J, Tan C-S (2013) CO₂ capture by as-synthesized amine-functionalized MCM-41 prepared through direct synthesis under basic condition. *Ind Eng Chem Res* 52:9834–9842. <https://doi.org/10.1021/ie400865n>
- Klinthong W, Huang C-H, Tan C-S (2016) One-pot synthesis and pelletizing of polyethylenimine-containing mesoporous silica powders for CO₂ capture. *Ind Eng Chem Res* 55:6481–6491. <https://doi.org/10.1021/acs.iecr.6b00644>
- Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. *Phys Rev* 140:A1133–A1138. <https://doi.org/10.1103/PhysRev.140.A1133>
- Kong S, Jin L, Yu H et al (2026) BZA-based ternary mixed amine absorbent for carbon dioxide capture: performance and mechanism analysis. *Sep Purif Technol* 389:136785. <https://doi.org/10.1016/j.seppur.2026.136785>
- Krack M (2005) Pseudopotentials for H to Kr optimized for gradient-corrected exchange–correlation functionals. *Theor Chem Acc* 114:145–152. <https://doi.org/10.1007/s00214-005-0655-y>
- Kumar S, Malik MM, Purohit R (2017) Synthesis methods of mesoporous silica materials. *Mater Today: Proc* 4:350–357. <https://doi.org/10.1016/j.matpr.2017.01.032>
- Kuppredy S, Varghese AM, Araj HA et al (2024) A combined experimental and simulations assessment of CO₂ capture and CO₂/H₂ separation performance of aminosilane-grafted MCM-41 and pore-expanded MCM-41. *Microporous Mesoporous Mater* 377:113220. <https://doi.org/10.1016/j.micromeso.2024.113220>
- Kwon S, Kwon HJ, Choi JI et al (2017) Enhanced selectivity for CO₂ adsorption on mesoporous silica with alkali metal halide due to electrostatic field: a molecular simulation approach. *ACS Appl Mater Interfaces* 9:31683–31690. <https://doi.org/10.1021/acsami.7b04508>
- Lashaki JM, Sayari A (2018) CO₂ capture using triamine-grafted SBA-15: the impact of the support pore structure. *Chem Eng J* 334:1260–1269. <https://doi.org/10.1016/j.cej.2017.10.103>
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789. <https://doi.org/10.1103/PhysRevB.37.785>
- Lee JJ, Chen C-H, Shimon D et al (2017) Effect of humidity on the CO₂ adsorption of tertiary amine grafted SBA-15. *J Phys Chem C* 121:23480–23487. <https://doi.org/10.1021/acs.jpcc.7b07930>

- Li K, Kress JD, Mebane DS (2016) The mechanism of CO₂ adsorption under dry and humid conditions in mesoporous silica-supported amine sorbents. *J Phys Chem C* 120:23683–23691. <https://doi.org/10.1021/acs.jpcc.6b08808>
- Li X, Peng K, Zhao X et al (2024) Amine-functionalized mesoporous silica derived from natural phyllosilicate for efficient CO₂ adsorption. *Appl Clay Sci* 256:107433. <https://doi.org/10.1016/j.clay.2024.107433>
- Liao X, Lu R, Xia L et al (2022) Density functional theory for electrocatalysis. *Energy Environ Mater* 5:157–185. <https://doi.org/10.1002/eem2.12204>
- Lim SY, Younis SA, Kim K-H, Lee J (2024) The potential utility of dendritic fibrous nanosilica as an adsorbent and a catalyst in carbon capture, utilization, and storage. *Chem Soc Rev* 53:9976–10011. <https://doi.org/10.1039/D4CS00564C>
- Liu L, Tan S (Johnathan), Horikawa T et al (2017) Water adsorption on carbon-a review. *Adv Colloid Interface Sci* 250:64–78. <https://doi.org/10.1016/j.cis.2017.10.002>
- Liu Y-H, Lin H-P, Mou C-Y et al (2003) Chemical coating of the aluminum oxides onto mesoporous silicas by a one-pot grafting method. *Stud Surf Sci Catal* 146:311–314. [https://doi.org/10.1016/S0167-2991\(03\)80387-7](https://doi.org/10.1016/S0167-2991(03)80387-7)
- Loganathan S, Tikmani M, Ghoshal AK (2015) Pore-expanded MCM-41 for CO₂ adsorption: experimental and isotherm modeling studies. *Chem Eng J* 280:9–17. <https://doi.org/10.1016/j.cej.2015.05.103>
- Lourenço MAO, Siquet C, Sardo M et al (2016) Interaction of CO₂ and CH₄ with functionalized periodic mesoporous phenylene-silica: periodic DFT calculations and gas adsorption measurements. *J Phys Chem C* 120:3863–3875. <https://doi.org/10.1021/acs.jpcc.5b11844>
- Luján Ferreira M, Pedernera M, Esperanza Adrover M (2024) Enhanced CO₂ capture by functionalization of SBA-15 with APTES and L-lysine. *Chem Eng J* 498:155431. <https://doi.org/10.1016/j.cej.2024.155431>
- Macario A, Katovic A, Giordano G et al (2005) Synthesis of mesoporous materials for carbon dioxide sequestration. *Microporous Mesoporous Mater* 81:139–147. <https://doi.org/10.1016/j.micromeso.2005.02.002>
- Mafra L, Čendak T, Schneider S et al (2017) Structure of chemisorbed CO₂ species in amine-functionalized mesoporous silicas studied by solid-state NMR and computer modeling. *J Am Chem Soc* 139:389–408. <https://doi.org/10.1021/jacs.6b11081>
- Mafra L, Čendak T, Schneider S et al (2018) Amine functionalized porous silica for CO₂/CH₄ separation by adsorption: which amine and why. *Chem Eng J* 336:612–621. <https://doi.org/10.1016/j.cej.2017.12.061>
- Mardirossian N, Head-Gordon M (2017) Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Mol Phys* 115:2315–2372. <https://doi.org/10.1080/00268976.2017.1333644>
- Mayo SL, Olafson BD, Goddard WA (1990) DREIDING: a generic force field for molecular simulations. *J Phys Chem* 94:8897–8909. <https://doi.org/10.1021/j100389a010>
- Merz KM (1992) Analysis of a large data base of electrostatic potential derived atomic charges. *J Comput Chem* 13:749–767. <https://doi.org/10.1002/jcc.540130609>
- Miricioiu MG, Niculescu V-C (2020) Fly ash, from recycling to potential raw material for mesoporous silica synthesis. *Nanomaterials* 10:474. <https://doi.org/10.3390/nano10030474>
- Mitran R-A, Culita DC, Atkinson I (2020) Thermal stability enhancement of mesoporous SBA-15 silica through nanoconfinement of ceria nanoparticles. *Microporous Mesoporous Mater* 306:110484. <https://doi.org/10.1016/j.micromeso.2020.110484>
- Monkhorst HJ, Pack JD (1976) Special points for Brillouin-zone integrations. *Phys Rev B* 13:5188–5192. <https://doi.org/10.1103/PhysRevB.13.5188>
- Moon HJ, Carrillo JMY, Jones CW (2023) Distribution and mobility of amines confined in porous silica supports assessed via neutron scattering, NMR, and MD simulations: impacts on CO₂ sorption kinetics and capacities. *Acc Chem Res* 56:2620–2630. <https://doi.org/10.1021/acs.accounts.3c00363>
- Morgante P, Peverati R (2020) The devil in the details: a tutorial review on some undervalued aspects of density functional theory calculations. *Int J Quant Chem* 120:e26332. <https://doi.org/10.1002/qua.26332>
- Muchan P, Saiwan C, Nithitanakul M (2020) Investigation of adsorption/desorption performance by aminopropyltriethoxysilane grafted onto different mesoporous silica for post-combustion CO₂ capture. *Clean Energy* 4:120–131. <https://doi.org/10.1093/ce/zhaa003>
- Munguía-Cortés L, Pérez-Hermosillo I, Ojeda-López R et al (2018) APTES-functionalization of SBA-15 using ethanol or toluene: textural characterization and sorption performance of carbon dioxide. *J Mex Chem Soc*. <https://doi.org/10.29356/jmcs.v6i14.457>
- Navik R, Wang E, Ding X et al (2024) Atmospheric carbon dioxide capture by adsorption on amine-functionalized silica composites: a review. *Environ Chem Lett* 22:1791–1830. <https://doi.org/10.1007/s10311-024-01737-z>
- Nguyen W, Vo APN, Bhat NS et al (2025) Applications of molecular simulation for CO₂ capture in solid adsorbents: a review. *J Mol Liq* 434:128046. <https://doi.org/10.1016/j.molliq.2025.128046>
- Ojeda-López R, Domínguez-Ortiz A, Felipe C et al (2021) Isothermic enthalpy behavior of CO₂ adsorption on micro-mesoporous materials: carbon microfibers (CMFs), SBA-15, and amine-functionalized SBA-15. *J Compos Sci* 5:102. <https://doi.org/10.3390/jcs5040102>
- Olea A, Sanz-Pérez ES, Arencibia A et al (2013) Amino-functionalized pore-expanded SBA-15 for CO₂ adsorption. *Adsorption* 19:589–600. <https://doi.org/10.1007/s10450-013-9482-y>
- Oliveira MR, Cecilia JA, De Conto JF et al (2023) Rapid synthesis of MCM-41 and SBA-15 by microwave irradiation: promising adsorbents for CO₂ adsorption. *J Sol-gel Sci Technol* 105:370–387. <https://doi.org/10.1007/s10971-022-06016-3>
- Oliveira MR, Barboza YT, Santos KS et al (2025) High-pressure CO₂ adsorption on MCM-41: efficiency of microwave-assisted synthesis. *Sep Purif Technol* 360:130871. <https://doi.org/10.1016/j.seppur.2024.130871>
- Pacheco M, Bordonhos M, Sardo M et al (2022) Moisture effect on the separation of CO₂/CH₄ mixtures with amine-functionalised porous silicas. *Chem Eng J* 443:136271. <https://doi.org/10.1016/j.cej.2022.136271>
- Park D-H, Nishiyama N, Egashira Y, Ueyama K (2001) Enhancement of Hydrothermal stability and hydrophobicity of a silica MCM-48 membrane by silylation. *Ind Eng Chem Res* 40:6105–6110. <https://doi.org/10.1021/ie0103761>
- Perdew JP, Schmidt K (2001) Jacob's ladder of density functional approximations for the exchange-correlation energy. In: *AIP Conference Proceedings*. AIP, Antwerp (Belgium), pp 1–20
- Perdew JP, Wang Y (1992) Accurate and simple analytic representation of the electron-gas correlation energy. *Phys Rev B* 45:13244–13249. <https://doi.org/10.1103/PhysRevB.45.13244>
- Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. *Phys Rev Lett* 77:3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>
- Perdew JP, Ruzsinszky A, Tao J et al (2005) Prescription for the design and selection of density functional approximations: more constraint satisfaction with fewer fits. *J Chem Phys* 123:062201. <https://doi.org/10.1063/1.1904565>

- Petrovic B, Gorbounov M, Masoudi Soltani S (2021) Influence of surface modification on selective CO₂ adsorption: a technical review on mechanisms and methods. *Microporous Mesoporous Mater* 312:110751. <https://doi.org/10.1016/j.micromeso.2020.110751>
- Pirzadeh K, Daneshmand-Jahromi S, Chou N et al (2025) Adsorption of CO₂ from impurity-rich flue gas on mesoporous silica foam: a performance-preserving approach. *J Environ Chem Eng* 13:120463. <https://doi.org/10.1016/j.jece.2025.120463>
- Quang DV, Hatton TA, Abu-Zahra MRM (2016) Thermally stable amine-grafted adsorbent prepared by impregnating 3-aminopropyltriethoxysilane on mesoporous silica for CO₂ capture. *Ind Eng Chem Res* 55:7842–7852. <https://doi.org/10.1021/acs.iecr.5b04096>
- Raganati F, Miccio F, Ammendola P (2021) Adsorption of carbon dioxide for post-combustion capture: a review. *Energy Fuels* 35:12845–12868. <https://doi.org/10.1021/acs.energyfuels.1c01618>
- Ramvalho JPP, Gomes JRB, Illas F (2013) Accounting for van der Waals interactions between adsorbates and surfaces in density functional theory based calculations: selected examples. *RSC Adv* 3:13085. <https://doi.org/10.1039/c3ra40713f>
- Rao N, Wang M, Shang Z et al (2018) CO₂ adsorption by amine-functionalized MCM-41: a comparison between impregnation and grafting modification methods. *Energy Fuels* 32:670–677. <https://doi.org/10.1021/acs.energyfuels.7b02906>
- Reif B, Ashbrook SE, Emsley L, Hong M (2021) Solid-state NMR spectroscopy. *Nat Rev Methods Primers*. <https://doi.org/10.1038/s43586-020-00002-1>. 1:2
- Ryoo R, Jun S (1997) Improvement of hydrothermal stability of MCM-41 using salt effects during the crystallization process. *J Phys Chem B* 101:317–320. <https://doi.org/10.1021/jp962500d>
- Saleh SNM, Ahmad MY, Ul-Hamid A, Abdullah AZ (2024a) Elucidation of synergism in Ce-Zr/SBA-15 mesoporous catalysts and the effects on the activity in selective glycerol to lactic acid reaction. *Powder Technol* 444:120048. <https://doi.org/10.1016/j.powtec.2024.120048>
- Saleh SNM, Rohman FS, Ul-Hamid A, Abdullah AZ (2024b) Roles of Ce1–xZrxO2/SBA-15 in selective catalytic glycerol conversion to lactic acid process: process behaviors and kinetic analyses. *Waste Biomass Valor*. <https://doi.org/10.1007/s12649-024-02651-9>
- San-Fabián Maroto E, Sancho-García J-C (2019) Emerging DFT methods and their importance for challenging molecular systems with orbital degeneracy. *Computation* 7:62. <https://doi.org/10.3390/computation7040062>
- Sánchez-Vicente Y, Stevens LA, Pando C et al (2015) A new sustainable route in supercritical CO₂ to functionalize silica SBA-15 with 3-aminopropyltrimethoxysilane as material for carbon capture. *Chem Eng J* 264:886–898. <https://doi.org/10.1016/j.cej.2014.12.002>
- Sanz R, Calleja G, Arencibia A, Sanz-Pérez ES (2015) CO₂ capture with pore-expanded MCM-41 silica modified with amino groups by double functionalization. *Microporous Mesoporous Mater* 209:165–171. <https://doi.org/10.1016/j.micromeso.2014.10.045>
- Sanz-Pérez ES, Olivares-Marín M, Arencibia A et al (2013) CO₂ adsorption performance of amino-functionalized SBA-15 under post-combustion conditions. *Int J Greenhouse Gas Control* 17:366–375. <https://doi.org/10.1016/j.ijggc.2013.05.011>
- Sardo M, Afonso R, Jużków J et al (2021) Unravelling moisture-induced CO₂ chemisorption mechanisms in amine-modified sorbents at the molecular scale. *J Mater Chem A* 9:5542–5555. <https://doi.org/10.1039/D0TA09808F>
- Sardo M, Morais T, Soares M et al (2024) Unravelling the structure of CO₂ in silica adsorbents: an NMR and computational perspective. *Chem Commun* 60:4015–4035. <https://doi.org/10.1039/D3CC05942A>
- Shah P, Ramaswamy V (2008) Thermal stability of mesoporous SBA-15 and Sn-SBA-15 molecular sieves: an in situ HTXRD study. *Microporous Mesoporous Mater* 114:270–280. <https://doi.org/10.1016/j.micromeso.2008.01.013>
- Shimon D, Chen C-H, Lee JJ et al (2018) ¹⁵N solid state NMR spectroscopic study of surface amine groups for carbon capture: 3-aminopropylsilyl grafted to SBA-15 Mesoporous Silica. *Environ Sci Technol* 52:1488–1495. <https://doi.org/10.1021/acs.est.7b04555>
- Sholl D, Steckel JA (2009) Density functional theory: a practical introduction. Wiley, Hoboken, NJ
- Singh UC, Kollman PA (1984) An approach to computing electrostatic charges for molecules. *J Comput Chem* 5:129–145. <https://doi.org/10.1002/jcc.540050204>
- Singh B, Na J, Konarova M et al (2020) Functional mesoporous silica nanomaterials for catalysis and environmental applications. *Bull Chem Soc Jpn* 93:1459–1496. <https://doi.org/10.1246/bcsj.20200136>
- Sonwane CG, Jones CW, Ludovice PJ (2005) A model for the structure of MCM-41 incorporating surface roughness. *J Phys Chem B* 109:23395–23404. <https://doi.org/10.1021/jp051713c>
- Soo XYD, Lee JJC, Wu W-Y et al (2024) Advancements in CO₂ capture by absorption and adsorption: a comprehensive review. *J CO₂ Utilization* 81:102727. <https://doi.org/10.1016/j.jcou.2024.102727>
- Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J Phys Chem* 98:11623–11627. <https://doi.org/10.1021/j100096a001>
- Stevens RW, Siriwardane RV, Logan J (2008) In situ Fourier transform infrared (FTIR) investigation of CO₂ adsorption onto zeolite materials. *Energy Fuels* 22:3070–3079. <https://doi.org/10.1021/e800209a>
- Surkatti R, Abdullatif YM, Muhammad R et al (2025) Comparative analysis of amine-functionalized silica for direct air capture (DAC): Material characterization, performance, and thermodynamic efficiency. *Sep Purif Technol* 354:128641. <https://doi.org/10.1016/j.seppur.2024.128641>
- Szczodrowski K, Prélôt B, Lantenois S et al (2009) Effect of heteroatom doping on surface acidity and hydrophilicity of Al, Ti, Zr-doped mesoporous SBA-15. *Microporous Mesoporous Mater* 124:84–93. <https://doi.org/10.1016/j.micromeso.2009.04.035>
- Szego AE, Jaworski A, Hedin N (2021) Chemisorption of CO₂ on diaminated silica as bicarbonates and different types of carbamate ammonium ion pairs. *Mater Adv* 2:448–454. <https://doi.org/10.1039/D0MA00658K>
- Thi Le MU, Lee S-Y, Park S-J (2014) Preparation and characterization of PEI-loaded MCM-41 for CO₂ capture. *Int J Hydrog Energy* 39:12340–12346. <https://doi.org/10.1016/j.ijhydene.2014.04.112>
- Tielens F, Gervais C, Lambert JF et al (2008) Ab initio study of the hydroxylated surface of amorphous silica: a representative model. *Chem Mater* 20:3336–3344. <https://doi.org/10.1021/cm8001173>
- Tielens F, Gierada M, Handzlik J, Calatayud M (2020) Characterization of amorphous silica based catalysts using DFT computational methods. *Catal Today* 354:3–18. <https://doi.org/10.1016/j.cattod.2019.03.062>
- Tsai H-HG, Chiu P-J, Jheng G-L et al (2011) Synthesis and solid-state NMR characterization of cubic mesoporous silica SBA-1 functionalized with sulfonic acid groups. *J Colloid Interface Sci* 359:86–94. <https://doi.org/10.1016/j.jcis.2011.03.072>
- Tuckerman ME, Martyna GJ (2000) Understanding modern molecular dynamics: techniques and applications. *J Phys Chem B* 104:159–178. <https://doi.org/10.1021/jp992433y>
- Ugliengo P, Sodupe M, Musso F et al (2008) Realistic models of hydroxylated amorphous silica surfaces and MCM-41 mesoporous material simulated by large-scale periodic B3LYP calculations. *Adv Mater* 20:4579–4583. <https://doi.org/10.1002/adma.200801489>

- Usami Y, Hongo T, Yamazaki A (2012) Thermal stability and behavior of platelet-shaped SBA-15 containing Zr. *J Porous Mater* 19:897–902. <https://doi.org/10.1007/s10934-011-9547-9>
- VandeVondele J, Hutter J (2007) Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J Chem Phys* 127:114105. <https://doi.org/10.1063/1.2770708>
- VandeVondele J, Krack M, Mohamed F et al (2005) Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput Phys Commun* 167:103–128. <https://doi.org/10.1016/j.cpc.2004.12.014>
- Villena MA, Kaya O, Schwingenschlögl U et al (2024) Density functional theory and molecular dynamics simulations for resistive switching research. *Mater Sci Engineering: R: Rep* 160:100825. <https://doi.org/10.1016/j.mser.2024.100825>
- Wadi B, Golmakani A, N.Borhani T et al (2023) Molecular simulation techniques as applied to silica and carbon-based adsorbents for carbon capture. *Energies* 16:5013. <https://doi.org/10.3390/en16135013>
- Wang L-W (2014) Divide-and-conquer quantum mechanical material simulations with exascale supercomputers. *Natl Sci Rev* 1:604–617. <https://doi.org/10.1093/nsr/nwu060>
- Wang L, Yang RT (2011) Increasing selective CO₂ adsorption on amine-grafted SBA-15 by increasing silanol density. *J Phys Chem C* 115:21264–21272. <https://doi.org/10.1021/jp206976d>
- Wang Z, Wang D, Zhao Z et al (2011) A DFT study of the structural units in SBA-15 mesoporous molecular sieve. *Comput Theor Chem* 963:403–411. <https://doi.org/10.1016/j.comptc.2010.11.004>
- Wang X, Chen L, Guo Q (2015) Development of hybrid amine-functionalized MCM-41 sorbents for CO₂ capture. *Chem Eng J* 260:573–581. <https://doi.org/10.1016/j.cej.2014.08.107>
- Wang X, Zeng W, Zhang H et al (2019) The dynamic CO₂ adsorption of polyethylene polyamine-loaded MCM-41 before and after methoxypolyethylene glycol codispersion. *RSC Adv* 9:27050–27059. <https://doi.org/10.1039/C9RA05404A>
- Wang S, Jiao Y, Li Z et al (2023) Modulating the acidity and accessibility of HZSM-5@Al-KIT-6 catalysts for the tandem catalytic upgrading of lignin pyrolysis vapors. *Appl Catal A* 656:119129. <https://doi.org/10.1016/j.apcata.2023.119129>
- Wang J, Feng X, Wen S et al (2024a) Recent advances in amine-functionalized silica adsorbents for CO₂ capture. *Renew Sustain Energy Rev* 203:114724. <https://doi.org/10.1016/j.rser.2024.114724>
- Wang Y, Huang L, Li S et al (2024b) The capture and catalytic conversion of CO₂ by dendritic mesoporous silica-based nanoparticles. *Energy Environ Mater* 7:e12593. <https://doi.org/10.1002/eeem2.12593>
- Wu J, Zhu X, Yang F et al (2021) Easily-synthesized and low-cost amine-functionalized silica sol-coated structured adsorbents for CO₂ capture. *Chem Eng J* 425:131409. <https://doi.org/10.1016/j.cej.2021.131409>
- Xia Y, Mokaya R (2004) Enhanced hydrothermal stability of Al-grafted MCM-48 prepared via various aluminations routes. *Microporous Mesoporous Mater* 74:179–188. <https://doi.org/10.1016/j.micromeso.2004.06.017>
- Xu X, Song C, Miller BG, Scaroni AW (2005) Influence of moisture on CO₂ separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41. *Ind Eng Chem Res* 44:8113–8119. <https://doi.org/10.1021/ie050382n>
- Yan H, Zhang G, Xu Y et al (2022) High CO₂ adsorption on amine-functionalized improved macro-/mesoporous multimodal pore silica. *Fuel* 315:123195. <https://doi.org/10.1016/j.fuel.2022.123195>
- Yang X, Rees RJ, Conway W et al (2017) Computational modeling and simulation of CO₂ capture by aqueous amines. *Chem Rev* 117:9524–9593. <https://doi.org/10.1021/acs.chemrev.6b00662>
- Yang X, Zheng X, Yang W (2020) Density functional prediction of quasiparticle, excitation, and resonance energies of molecules with a global scaling correction approach. *Front Chem* 8:588808. <https://doi.org/10.3389/fchem.2020.588808>
- Yıldız MG, Davran-Candan T, Günay ME, Yıldırım R (2019) CO₂ capture over amine-functionalized MCM-41 and SBA-15: exploratory analysis and decision tree classification of past data. *J CO₂ Utilization* 31:27–42. <https://doi.org/10.1016/j.jcou.2019.02.010>
- Yu J, Shi J-L, Chen H-R et al (2001) Effect of inorganic salt addition during synthesis on pore structure and hydrothermal stability of mesoporous silica. *Microporous Mesoporous Mater* 46:153–162. [https://doi.org/10.1016/S1387-1811\(01\)00269-4](https://doi.org/10.1016/S1387-1811(01)00269-4)
- Yun J-H, He Y, Otero M et al (2002) Adsorption equilibrium of polar/non-polar mixtures on MCM-41: experiments and Monte Carlo simulation. *Stud Surf Sci Catal* 144:685–692. [https://doi.org/10.1016/S0167-2991\(02\)80197-5](https://doi.org/10.1016/S0167-2991(02)80197-5)
- Zelenák V, Magura J, Zelenáková A, Smolková R (2017) Carbon dioxide and methane adsorption over metal modified mesoporous SBA-15 silica. *Pure Appl Chem* 89:493–500. <https://doi.org/10.1515/pac-2016-1121>
- Zhang F, Yan Y, Yang H et al (2005) Understanding effect of wall structure on the hydrothermal stability of mesostructured silica SBA-15. *J Phys Chem B* 109:8723–8732. <https://doi.org/10.1021/jp044632>
- Zhang H, Goepfert A, Olah GA, Prakash GKS (2017) Remarkable effect of moisture on the CO₂ adsorption of nano-silica supported linear and branched polyethylenimine. *J CO₂ Utilization* 19:91–99. <https://doi.org/10.1016/j.jcou.2017.03.008>
- Zhang G, Zhao P, Hao L, Xu Y (2018) Amine-modified SBA-15(P): a promising adsorbent for CO₂ capture. *J CO₂ Utilization* 24:22–33. <https://doi.org/10.1016/j.jcou.2017.12.006>
- Zhang G, Zhao P, Hao L et al (2019a) A novel amine double functionalized adsorbent for carbon dioxide capture using original mesoporous silica molecular sieves as support. *Sep Purif Technol* 209:516–527. <https://doi.org/10.1016/j.seppur.2018.07.074>
- Zhang L, Jin L, Liu B, He J (2019b) Templated growth of crystalline mesoporous materials: from soft/hard templates to colloidal templates. *Front Chem* 7:22. <https://doi.org/10.3389/fchem.2019.00022>
- Zhang L, Qi L, Han Y et al (2022) Amino-functionalized pore-expanded MCM-41 for CO₂ adsorption: effect of alkyl chain length of the template. *Ind Eng Chem Res* 61:9331–9341. <https://doi.org/10.1021/acs.iecr.2c01337>
- Zhao Y, Truhlar DG (2006) Comparative DFT study of van der Waals complexes: rare-gas dimers, alkaline-earth dimers, zinc dimer, and zinc-rare-gas dimers. *J Phys Chem A* 110:5121–5129. <https://doi.org/10.1021/jp060231d>
- Zhao Y, Truhlar DG (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor Chem Acc* 120:215–241. <https://doi.org/10.1007/s00214-007-0310-x>
- Zhao G, Aziz B, Hedin N (2010) Carbon dioxide adsorption on mesoporous silica surfaces containing amine-like motifs. *Appl Energy* 87:2907–2913. <https://doi.org/10.1016/j.apenergy.2009.06.008>
- Zhao A, Samanta A, Sarkar P, Gupta R (2013) Carbon dioxide adsorption on amine-impregnated mesoporous SBA-15 sorbents: experimental and kinetics study. *Ind Eng Chem Res* 52:6480–6491. <https://doi.org/10.1021/ie3030533>
- Zhao P, Zhang G, Yan H, Zhao Y (2021) The latest development on amine functionalized solid adsorbents for post-combustion CO₂ capture: analysis review. *Chin J Chem Eng* 35:17–43. <https://doi.org/10.1016/j.cjche.2020.11.028>

- Zheng F, Tran DN, Busche BJ et al (2005) Ethylenediamine-modified SBA-15 as regenerable CO₂ sorbent. *Ind Eng Chem Res* 44:3099–3105. <https://doi.org/10.1021/ie049488t>
- Zhu Y, Zhou J, Hu J, Liu H (2012) The effect of grafted amine group on the adsorption of CO₂ in MCM-41: a molecular simulation. *Catal Today* 194:53–59. <https://doi.org/10.1016/j.cattod.2012.02.022>
- Zhuo S, Huang Y, Hu J et al (2008) Computer simulation for adsorption of CO₂, N₂ and flue gas in a mimetic MCM-41. *J Phys Chem C* 112:11295–11300. <https://doi.org/10.1021/jp803428n>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.