



Fabrication of NiO–Cu₃Mo₂O₉ Catalyst for Efficient Hydrogen Gas Production via Ammonia Borane Methanolysis

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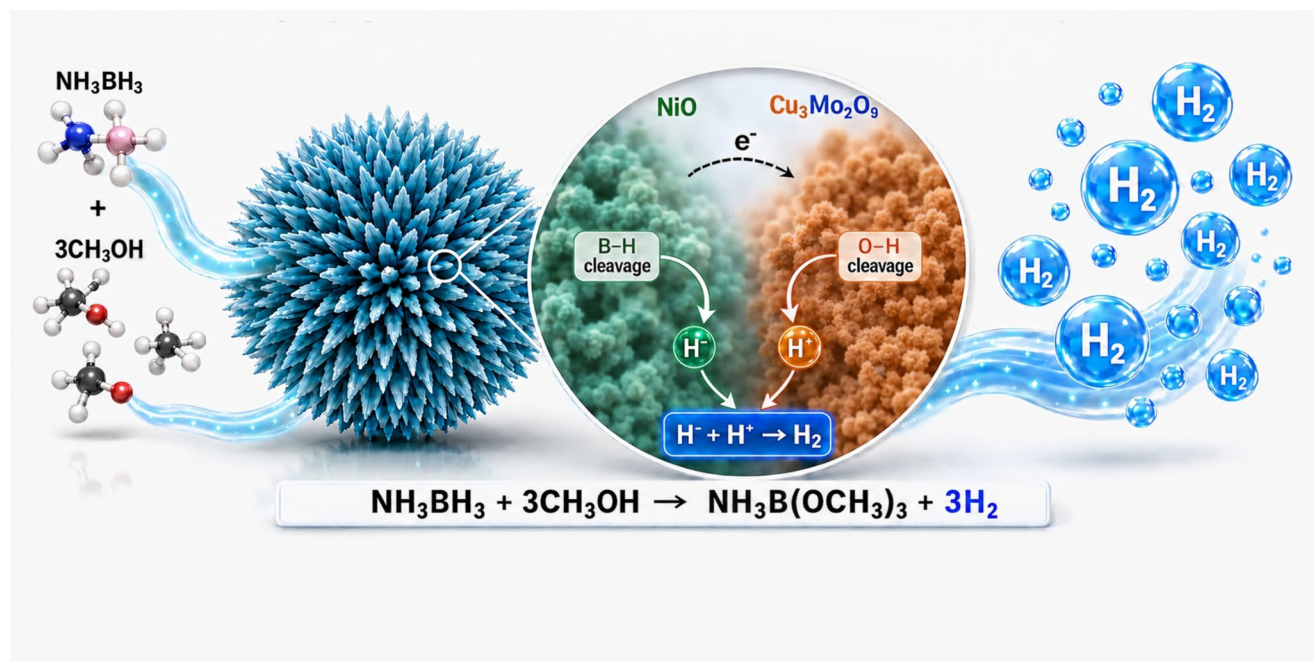
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Abstract

Hydrogen production *via* ammonia borane (AB) methanolysis is a promising strategy for H₂ supply. However, it requires high-performance catalysts that are low-cost and highly stable to efficiently catalyze the hydrogen generation reaction. Herein, we report a novel NiO–Cu₃Mo₂O₉ hierarchical nanocatalyst synthesized *via* a one-pot hydrothermal–calcination method for catalyzing hydrogen production through AB methanolysis. Systematic characterizations, including XRD, SEM, TEM, XPS, and BET analyses, were conducted to confirm the successful synthesis of NiO–Cu₃Mo₂O₉. The catalyst exhibited a low activation energy ($E_a = 18.9 \text{ kJ} \cdot \text{mol}^{-1}$), excellent stability (H₂ production rate = 170 mL H₂ · min^{−1}; retaining >90% of its initial activity after 6th cycle), and a high turnover frequency (TOF) of 49.8 min^{−1}. Furthermore, the NiO–Cu₃Mo₂O₉ catalyst demonstrated a synergistic effect, achieving a hydrogen generation rate (HGR) of 1,200 mL H₂ · g^{−1} · min^{−1}, compared with the Cu₃Mo₂O₉ catalyst (HGR = 360 mL H₂ · g^{−1} · min^{−1}). In addition, kinetic studies of AB methanolysis revealed that the reaction was temperature-dependent, with an optimum temperature of 30 °C (303 K). The catalytic reaction rate showed a positive correlation with both the AB dosage and the catalyst loading.

Graphical Abstract

Hydrogen evolution through methanolysis of ammonia borane (AB) catalyzed by NiO–Cu₃Mo₂O₉ catalyst



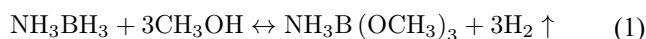
Keywords Hydrogen production · Ammonia borane · Methanolysis · NiO–Cu₃Mo₂O₉ catalyst

Abbreviations

AB	Ammonia borane
Ea	Activation energy
BET	Brunauer–Emmett–Teller
DFT	Density functional theory
EDS	Energy dispersive X-ray spectroscopy
FT-IR	Fourier transform infrared spectroscopy
HGR	Hydrogen generation rate
ICP-AES	Inductively coupled plasma - atomic emission spectrometry
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TOF	Turnover frequency
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

1 Introduction

Hydrogen (H_2) is considered an ideal energy carrier for future energy systems owing to its high energy density and environmentally benign combustion product, water. However, most conventional hydrogen production technologies, such as water electrolysis, steam methane reforming, and coal gasification, are either energy-intensive or heavily dependent on electricity generated from fossil fuels, resulting in significant carbon dioxide emissions. To address this challenge, alternative hydrogen sources have been extensively investigated. Among them, ammonia borane (AB, NH_2BH_2) has attracted considerable attention as a promising chemical hydrogen storage material due to its high hydrogen content (19.6 wt%), low molecular weight, excellent water solubility, high stability under ambient conditions, and low toxicity [1]. The methanolysis of AB for hydrogen generation (Eq. 1) is regarded as a mild, safe, and controllable hydrogen production approach. However, the reaction proceeds very slowly in the absence of an effective catalyst because of its unfavorable kinetics [2]. Therefore, the development of highly efficient, cost-effective, and durable catalysts is crucial for the practical implementation of AB-based hydrogen production technologies.



Among the AB methanolysis catalysts, transition metal oxides are the most promising candidate due to their abundant reserves, low cost, tunable electronic energy structures, and excellent CH_3OH/AB activation ability [1–3]. Among the metal oxides, copper-molybdenum (Cu–Mo) oxides have the potential activity in promoting B–H cleavage, while Mo boosts CH_3OH activation to generate reactive oxygen radical ($\bullet O$) [4]. However, hierarchical $Cu_3Mo_2O_9$

suffers from insufficient active sites, low electron transfer efficiency, and poor cyclic stability [5]. These flaws have limited the catalyst used in the high-performance application, hence the heterostructure-based modification of $Cu_3Mo_2O_9$ is necessary [6].

The introduction of a second metal component to construct a bimetallic or multi-metallic oxide catalyst is an effective strategy to optimize catalytic performance by regulating the electronic structure and enhancing the synergistic effect between components [7]. Nickel (Ni) is a typical transition metal with variable valence oxidation states (Ni^{2+}/Ni^{3+}). Previous studies have confirmed that Ni can form strong electronic interactions with Cu or Mo elements to improve catalytic activity [8–10]. For example, Li et al. [11] synthesized Z-scheme Vo–NiO–CuO heterostructures for visible-light-assisted AB methanolysis, where the strong interfacial electronic interaction between Ni and Cu facilitated efficient charge separation, optimized the adsorption energy of AB molecules on the catalyst surface, and formed dual active sites, achieving a high turnover frequency (TOF) of 35.3 min^{-1} . In addition, the heterostructure interface also plays some roles in improving catalytic activities by inducing charge redistribution, optimizing the electron transfer capacity, adjust the electron density of active sites, and strengthen the adsorption and activation of reactants [12, 13]. Wang et al. [13] synthesized $CuCo_2O_4$ –NiO heterostructures for AB methanolysis, where the interfacial interactions boosted the catalytic activity by 1.42-fold compared to pure $CuCo_2O_4$, reaching a remarkable hydrogen generation rate i.e. $870 \text{ mL } H_2 \cdot g^{-1} \text{ cat} \cdot \text{min}^{-1}$.

Recent studies have demonstrated that the rational regulation of catalyst architecture and interfacial electronic structures is crucial for efficient hydrogen production from liquid-phase chemical hydrides. Yao et al. [14] summarized the applications of metal oxide framework (MOF)-based catalysts, composites, and derivatives in hydrogen release from liquid-phase chemical hydrides [14]. More recently, Ni nanoparticles supported on a P-doped $Mo@Mo_2C$ heterostructure exhibited excellent activity toward ammonia borane methanolysis owing to the synergistic electronic modulation induced by P doping and the Mo/ Mo_2C hetero-interface [15].

Despite hydrolysis and methanolysis involve different solvent-activation processes, these studies demonstrated that heterointerface construction and electronic-structure regulation are effective strategies for developing efficient non-noble-metal catalysts. Although AB methanolysis has been widely recognized as a promising strategy for hydrogen production, its practical application remains limited by the high cost and scarcity of metal oxide-based catalysts. In this study, we report a low-cost NiO– $Cu_3Mo_2O_9$ catalyst synthesized *via* a facile hydrothermal–calcination method.

The prepared catalyst exhibited excellent catalytic performance toward AB methanolysis, demonstrating its potential as an economical alternative to noble-metal catalysts. This work provides a feasible approach for the development of Cu–Mo-based catalysts for hydrogen generation from AB and further enhances the understanding of the structure–activity relationship and catalytic mechanisms of hetero-structure catalysts.

2 Experimental Section

2.1 Materials

All the reagents and solvents were used directly without further purification. Ethanol absolute ($\geq 99.7\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Copper nitrate trihydrate [Cu(NO₃)₂·3H₂O] (Purity=99%), Nickel(II) hydroxide [Ni(OH)₂, Purity=61%], Ammonium molybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O] (Purity=99%) and ammonia borane [AB, NH₃BH₃] (Purity=97%) were obtained from the Shanghai Macklin Biochemical Co., Ltd.

2.2 Synthesis of NiO–Cu₃Mo₂O₉

The NiO–Cu₃Mo₂O₉ catalyst was prepared *via* a facile hydrothermal-calcination method and annealing method. In detail, (NH₄)₆Mo₇O₂₄·4H₂O (0.05 g, 0.04 mmol), Cu(NO₃)₂·3H₂O (0.05 g, 0.267 mmol) and Ni(OH)₂ (0.05 g, 0.54 mmol) were dissolved in 80 mL of deionized water and subsequently sonicated for 20 min to obtain a uniform solution. Subsequently, the resulting solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed tightly and maintained at 110 °C for 6 h at a constant temperature (110 °C). After the hydrothermal reaction, the autoclave was cooled to room temperature, and the resulting precipitate was harvested by high-speed centrifugation, and then thoroughly washed with deionized water and absolute ethanol for three times each to remove residual impurities. The washed precipitates were dried in a vacuum drying oven at 60 °C for 12 h to remove residual solvents. Thereafter, the obtained solid was ground into powder form using an agate mortar then transferred to an alumina crucible. Finally, the powder was calcined in a muffle furnace at 400 °C for 6 h with a heating rate of 5 °C min^{−1} under ambient air atmosphere. The resulting solid product was denoted as NiO–Cu₃Mo₂O₉ catalysts and stored in a desiccator for subsequent characterization and catalytic tests. The blanks, namely NiO and Cu₃Mo₂O₉ were also prepared, characterized and used for AB methanolysis for the comparison purpose. Single-phase Cu₃Mo₂O₉ and NiO were synthesized individually. Specifically, Cu₃Mo₂O₉ was

prepared using (NH₄)₆Mo₇O₂₄·4H₂O and Cu(NO₃)₂·3H₂O as the precursors by following the method as reported by Liao et al. [6] On another hand, pure NiO was prepared via the thermal decomposition of Ni(OH)₂ precursor, as described in detail by Liang et al. [16].

2.3 Characterizations

The surface morphology of the samples was investigated by scanning electron microscopy (SEM) using a Hitachi SU-8010 scanning electron microscope (Hitachi Ltd., Tokyo, Japan). Transmission electron microscopy (TEM) measurements were conducted using a Talos F200X high-resolution field-emission transmission electron microscope. Powder X-ray diffraction (XRD) analysis was performed over a 2θ range of 5–80° at a scanning rate of 10° min^{−1} using a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda=1.5406$ Å, 40 kV, and 40 mA). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was employed to determine the Cu/Ni/Mo molar ratios of the catalysts using a Spectro Arcos FHS12 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB QXi XPS system (Thermo Fisher Scientific, USA). All binding energies were calibrated using the C 1s peak of adventitious carbon at 284.8 eV as the reference. The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface areas of the obtained carbon materials, while the pore size distribution was calculated using density functional theory (DFT) based on a slit-pore NLDFT equilibrium model with a Quantachrome Autosorb-1 volumetric analyzer (Autosorb-iQ, USA). Fourier transform infrared (FT-IR) spectra were recorded using a Bruker TENSOR 27 spectrometer to monitor changes in the functional groups of the catalysts at different reaction times during the catalytic process.

2.4 Hydrogen Evolution Tests

The respective catalytic activities of NiO, Cu₃Mo₂O₉ and NiO–Cu₃Mo₂O₉ catalysts towards AB methanolysis were measured by using the water displacement method [17] as shown in Fig. 1. A thermostatic magnetic stirrer water bath was used to maintain the reaction temperature at 25 °C. The catalyst (100 mg) was added into Erlenmeyer flask, mixed with 10 mL of absolute methanol and sonicated for 15 min. On the other hand, in another Erlenmeyer flask, the AB methanolic solution was prepared by adding AB (0.1 g, 3 mmol) as well as NaOH (0.8 g, 0.02 mmol) into a 10 mL absolute methanol. Then, the prepared 10 mL AB solution was added using syringe into the Erlenmeyer flask, which contained catalyst. H₂ gas was released as the catalyst was in contact with the AB solution. The amount of H₂ gas released

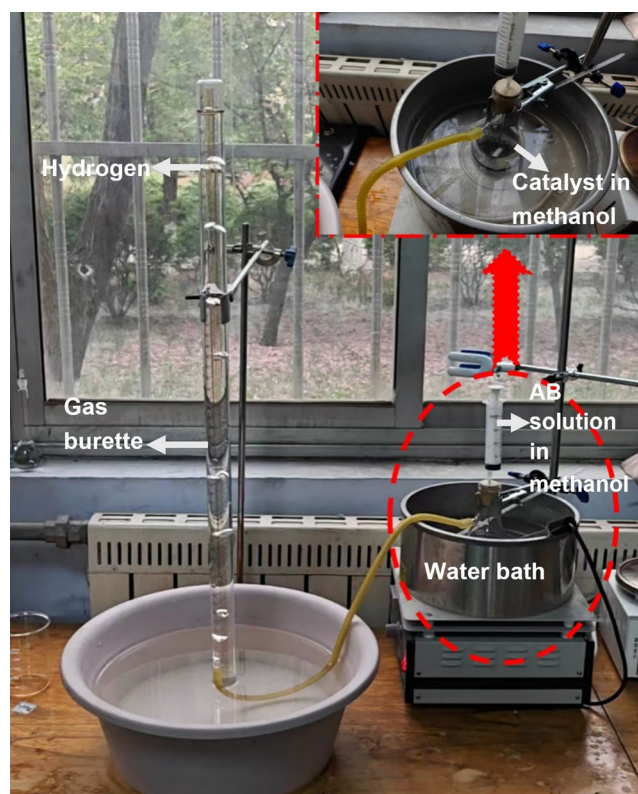


Fig. 1 The experimental setup of hydrogen gas measurement *via* water displacement. This figure shows the experimental setup of the catalyzed AB methanolysis reaction and the measurement of hydrogen gas production

was measured by water displacement in the gas burette as shown in Fig. 1.

The reusability tests were performed on the NiO–Cu₃Mo₂O₉ catalyst. After the first cycle of catalytic reaction, the catalyst was collected, cleaned with deionized water (5 mL x 3 times), and dried under open air. Then, the cleaned catalyst was reused for hydrogen gas production by following the same procedures as described above. The reusability test was stopped when the amount of hydrogen produced was reduced to 90% compared to the 1st cycle.

Meanwhile, the hydrogen generation rate (HGR, mL H₂·g⁻¹·min⁻¹) of catalysts in AB methanolysis was calculated from the slope of the kinetic curve in the linear range (Eq. 2):

$$\text{HGR} = V(\text{H}_2) / \text{mcat} \times t \quad (2)$$

where $V(\text{H}_2)$ (mL) = the hydrogen volume; mcat (g) = mass of metal (Cu and Ni and Mo), and t (min) = the time of methanolysis reaction.

The turnover frequency (TOF, min⁻¹) values of catalysts in AB methanolysis can be calculated through Eq. 3:

$$\text{TOF} = n(\text{H}_2) / n(\text{Cu} + \text{Ni}) t \quad (3)$$

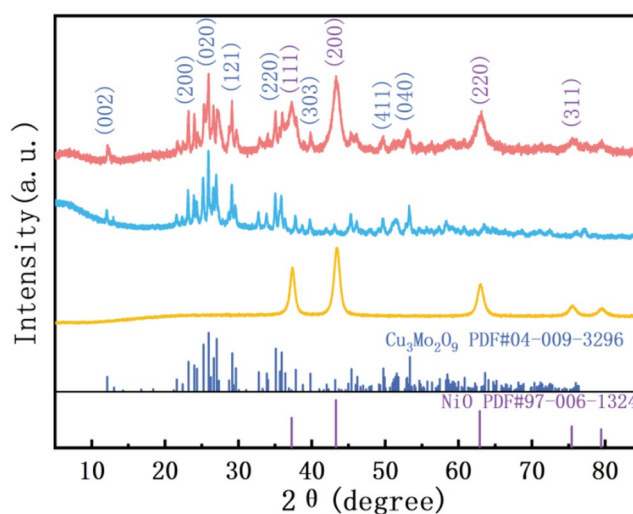


Fig. 2 The XRD spectral of NiO–Cu₃Mo₂O₉ (red), NiO (yellow and purple) and Cu₃Mo₂O₉ (light and navy blue). This figure shows the XRD spectral of the materials studied in this project

where $n\text{H}_2$ = the moles of hydrogen produced; $n(\text{Cu} + \text{Ni})$ = the total moles of Cu and Ni in catalysts applied to AB methanolysis; and t (min) = the reaction time.

3 Results and Discussion

3.1 Characterizations

As shown in Fig. 2, the diffraction peaks of Cu₃Mo₂O₉ can be well indexed to the standard JCPDS card No. 04-009-3296, with characteristic peaks located at 2θ values of 12.1°, 23.1°, 25.9°, 29.1°, 35.0°, and 39.7°, corresponding to the (002), (200), (020), (121), (220), and (303) crystal planes of the Cu₃Mo₂O₉ phase, respectively [18]. The XRD pattern of NiO exhibits sharp diffraction peaks at 37.2°, 43.3°, 62.9°, 75.4°, and 79.4°, which can be assigned to the (111), (200), (220), (311), and (222) crystal planes of cubic NiO (JCPDS card No. 97-006-1324), respectively [19]. For the NiO–Cu₃Mo₂O₉ composite, the diffraction pattern contains the characteristic peaks of both orthorhombic Cu₃Mo₂O₉ and cubic NiO, with no detectable impurity peaks. This finding indicates that the NiO–Cu₃Mo₂O₉ composite is a biphasic material in which NiO and Cu₃Mo₂O₉ coexist stably. Furthermore, the XRD results confirm that the introduction of NiO does not induce any phase transformation in Cu₃Mo₂O₉, and that the crystal structures of both components are well preserved in the composite.

The morphology and nanostructures of NiO–Cu₃Mo₂O₉ were further characterized by SEM, TEM, and elemental mapping (Fig. 3). As shown in Fig. 3a, the NiO–Cu₃Mo₂O₉ composite exhibits a hierarchical microspheres morphology assembled from nanosheet subunits, forming a porous and

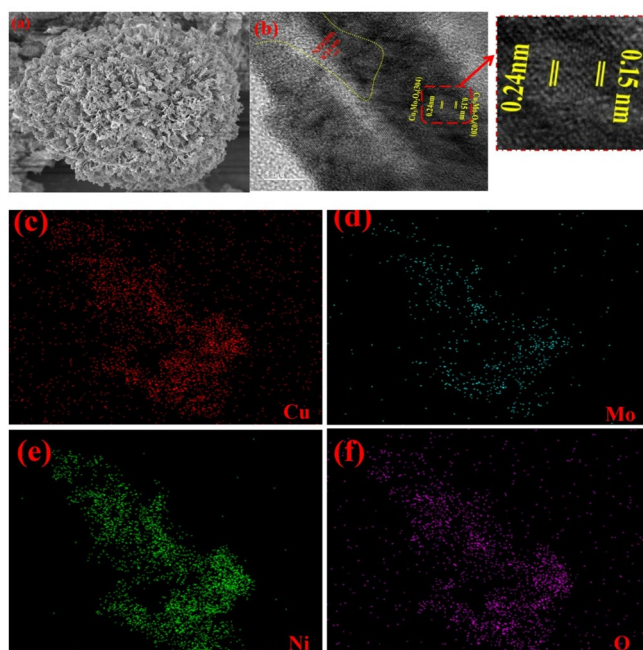


Fig. 3 **a** SEM images for NiO–Cu₃Mo₂O₉; **b** TEM images for NiO–Cu₃Mo₂O₉; and **c–f** the elemental mapping images (EDS) of **c** Cu; **d** Mo; **e** Ni; and **f** O. This figure shows the images of SEM, TEM and EDS for the catalyst namely NiO–Cu₃Mo₂O₉

interconnected structure. The TEM image (Fig. 3b) clearly reveals well-resolved lattice fringes with interplanar spacings of 0.24 nm, 0.15 nm, and 0.24 nm, corresponding to the (304) and (020) planes of Cu₃Mo₂O₉ and the (200) plane of cubic NiO, respectively [6, 20]. These distinct lattice spacings confirm the coexistence of both crystalline phases and the formation of heterointerfaces within the composite. Elemental mapping images (Fig. 3c–f) demonstrate that

Cu, Mo, Ni, and O are uniformly distributed throughout the entire microsphere without obvious elemental aggregation, indicating the homogeneous dispersion of the NiO and Cu₃Mo₂O₉ phases within the composite. This homogeneous elemental distribution is beneficial for the exposure of active sites and facilitates the transfer of charge carriers across the phase boundaries, thereby enhancing the catalytic performance of the material.

The textural properties of NiO–Cu₃Mo₂O₉, Cu₃Mo₂O₉ and NiO were investigated by N₂ adsorption-desorption measurements. As shown in Fig. 4a, all samples exhibit a type IV isotherm with an H₃-type hysteresis loop [21], which is characteristic of mesoporous materials with slit-like pores. Among them, Cu₃Mo₂O₉ exhibits the highest specific surface area (153.9 m² g^{−1}), followed by NiO–Cu₃Mo₂O₉ (129.3 m² g^{−1}), whereas NiO possesses the lowest surface area (33.3 m² g^{−1}). The pore size distribution curves (Fig. 4b) further confirm the mesoporous nature of all samples, with most pores concentrated in the range of 2–30 nm. The NiO–Cu₃Mo₂O₉ composite inherits the mesoporous structure of both components, which facilitates the diffusion of reactants and products and provides abundant active sites for catalytic reactions.

XPS analysis was performed on the NiO–Cu₃Mo₂O₉ composite to probe its chemical states and interfacial electronic interactions. In the Ni 2p spectrum (Fig. 5a), the Ni²⁺ (2p_{1/2} at 871.6 eV, 2p_{3/2} at 854.1 eV) and Ni³⁺ (2p_{1/2} at 873.6 eV, 2p_{3/2} at 856.1 eV) peaks in the composite are nearly identical to those in pure NiO (Ni²⁺: 871.6 eV, 854.2 eV; Ni³⁺: 873.3 eV, 856.0 eV) [2, 22]. The satellite peaks confirm the octahedral coordination of Ni²⁺ in the NiO phase, indicating that the chemical state of Ni remains

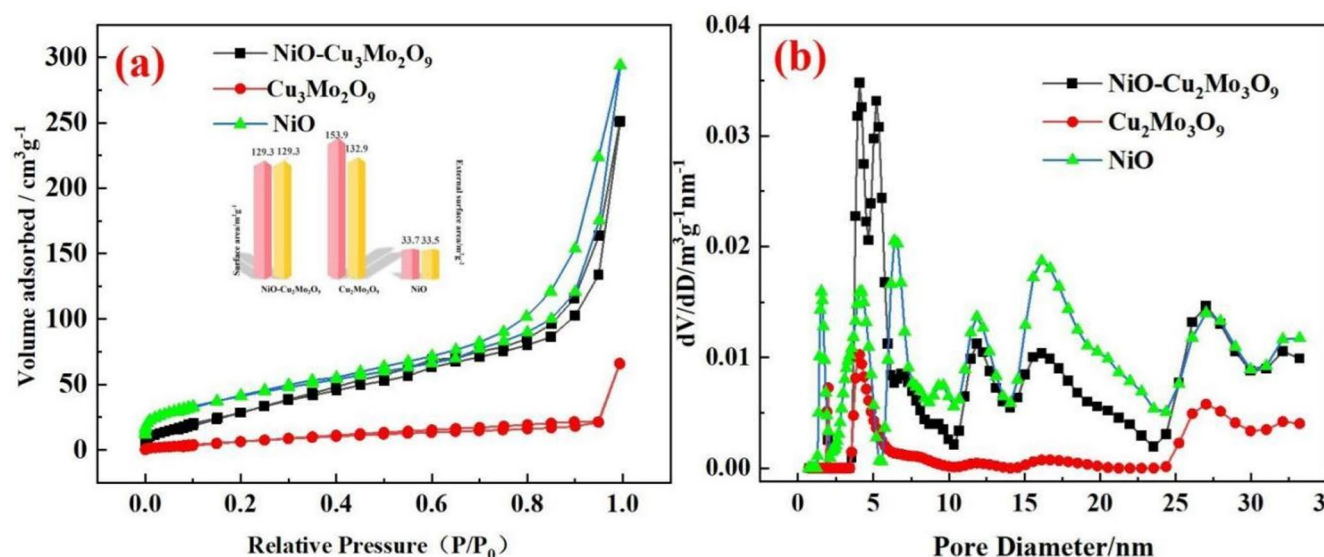


Fig. 4 **a** N₂ adsorption-desorption isotherms and internal/external surface area profiles of the NiO–Cu₃Mo₂O₉ (in the small window); and **b** the pore size distribution curves. This figure shows the results from BET analysis of the catalyst

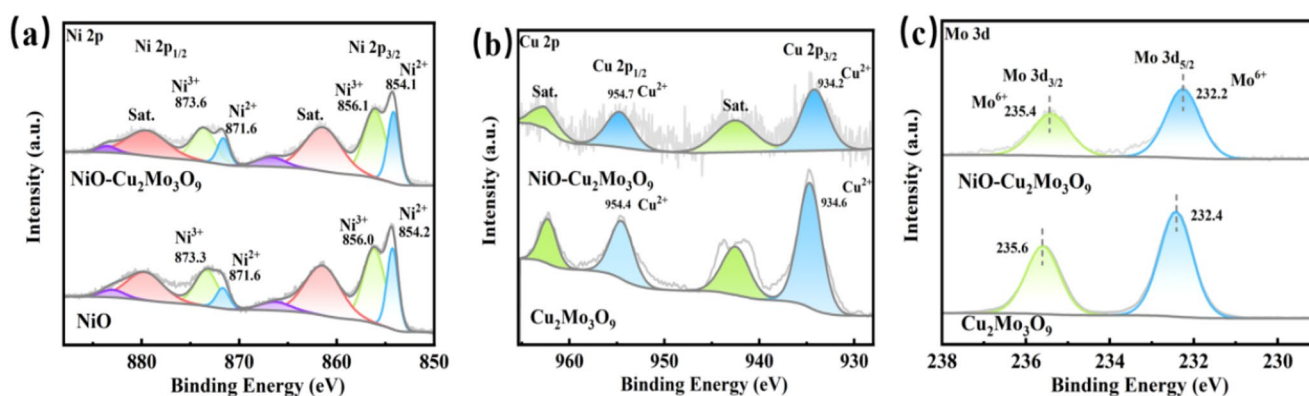


Fig. 5 XPS spectra for **a** Ni 2p of NiO–Cu₃Mo₂O₉ and NiO; **b** XPS spectra for Cu 2p of NiO–Cu₃Mo₂O₉ and Cu₃Mo₂O₉; **c** XPS spectra for Mo 3d of NiO–Cu₃Mo₂O₉ and Cu₃Mo₂O₉. The figure shows the results from XPS analysis to NiO, Cu₃Mo₂O₉ and the catalyst, NiO–Cu₃Mo₂O₉

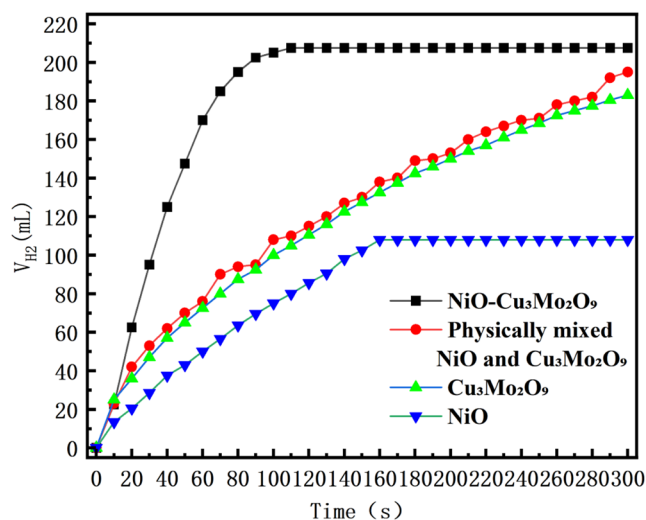


Fig. 6 Time-dependent H₂ production (mL) from ammonia borane solutions in the presence of NiO–Cu₃Mo₂O₉ (black line), NiO (navy blue line) and Cu₃Mo₂O₉ (green line) and physical mixture of NiO and Cu₃Mo₂O₉ (red line). This figure compares the hydrogen production from AB solution by using different catalyst used in this design

stable after composite formation [23]. In the Cu 2p spectrum (Fig. 5b), the Cu²⁺ 2p_{3/2} and 2p_{1/2} peaks in NiO–Cu₃Mo₂O₉ are located at 934.2 eV and 954.7 eV, respectively, which are shifted to lower binding energy by 0.4 eV (2p_{3/2}) and 0.3 eV (2p_{1/2}) relative to pure Cu₃Mo₂O₉ (934.6 eV, 954.4 eV). This shift suggests an increase in electron density around Cu atoms, arising from strong electronic interactions at the NiO–Cu₃Mo₂O₉ interface. In the Mo 3d spectrum (Fig. 5c), the Mo 3d_{5/2} and 3d_{3/2} peaks in NiO–Cu₃Mo₂O₉ appear at 232.2 eV and 235.4 eV, respectively, showing a slight shift of 0.2 eV toward lower binding energy compared to pure Cu₃Mo₂O₉ (232.4 eV, 235.6 eV) [6]. This shift reflects a subtle change in the chemical environment of Mo, further corroborating the interfacial electronic interactions between NiO and Cu₃Mo₂O₉. Overall, the XPS results confirm that the predominant chemical states of Ni (Ni²⁺/Ni³⁺), Cu (Cu²⁺),

and Mo (Mo⁶⁺) are preserved in the NiO–Cu₃Mo₂O₉ composite. The slight shifts in the binding energies of the Cu 2p and Mo 3d peaks provide direct evidence of strong interfacial electronic interactions between NiO and Cu₃Mo₂O₉, which modulate the electronic structure of the active sites and contribute to the enhanced catalytic performance of the composite [7, 24, 25].

3.2 H₂ Production Through AB Methanolysis

The hydrogen generation performance of NiO–Cu₃Mo₂O₉, Cu₃Mo₂O₉, and NiO toward AB methanolysis was systematically evaluated at 298.15 K, as shown in Fig. 6. The NiO–Cu₃Mo₂O₉ nanocomposite exhibited the highest catalytic activity, releasing approximately 200 mL of H₂ within only 100 s, corresponding to a hydrogen generation rate (HGR) of 1,200 mL H₂·g^{−1}·min^{−1}. In contrast, pristine Cu₃Mo₂O₉ showed a much slower reaction rate, requiring 300 s to generate approximately 180 mL of H₂ (HGR ≈ 360 mL H₂·g^{−1}·min^{−1}). In comparison, NiO exhibited negligible catalytic activity, producing less than 30 mL of H₂ even after 300 s with the HGR value of ~60 mL H₂·g^{−1}·min^{−1}. This significant enhancement in the catalytic activity of NiO–Cu₃Mo₂O₉ can be attributed to the strong interfacial synergistic effect between NiO and Cu₃Mo₂O₉. As evidenced by the XPS results, electron migration from NiO to Cu₃Mo₂O₉ modulates the surface valence states of Cu, Ni, and Mo, thereby optimizing the adsorption and activation of AB molecules at the active sites.

Indeed, the catalytic hydrogen production of the physical mixture of NiO and Cu₃Mo₂O₉ was also investigated at 298.15 K (as presented in the red line in Fig. 6). Among all the tested samples, the NiO–Cu₃Mo₂O₉ heterostructure catalyst exhibited the highest catalytic activity, producing approximately 208 mL of H₂ within 100 s (HGR = 1,248 mL H₂·g^{−1}·min^{−1}). In comparison, the physical mixture of NiO and Cu₃Mo₂O₉ required nearly 300 s to release only

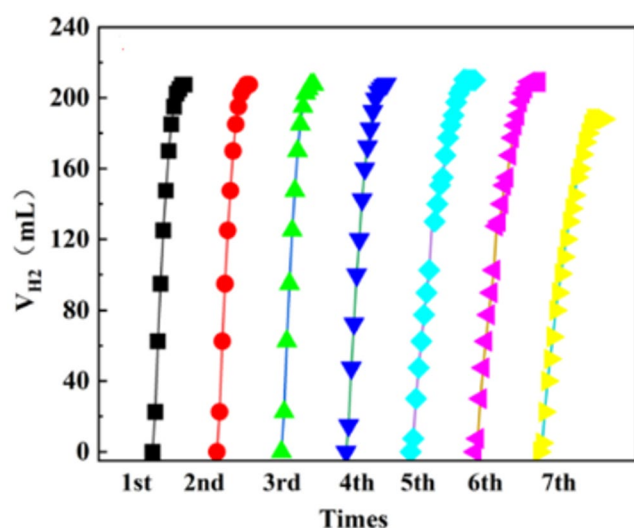


Fig. 7 The reusability test for AB methanolysis over NiO–Cu₃Mo₂O₉. The plot shows the reusability of the catalyst

195 mL of H₂. Indeed, the hydrogen production rate of the physical mixture of NiO and Cu₃Mo₂O₉ was similar to the one of Cu₃Mo₂O₉ alone. This also indicates that the hydrogen production of Cu₃Mo₂O₉ alone played more important role in the NiO–Cu₃Mo₂O₉ heterostructure catalyst. Indeed, the presence of NiO in the catalyst could lower the activation energy, E_a , of the catalyst and enhance the catalytic efficiency in hydrogen production. Further discussion on the E_a can be found under the kinetic session.

In fact, the hydrothermal-calcination approach produced a stable NiO–Cu₃Mo₂O₉ catalyst that promoted interfacial charge redistribution and synergistic B–H bond activation of the reactants, as evidenced by the XPS results. Consequently, the superior catalytic activity of the hydrothermal-calcination-derived NiO–Cu₃Mo₂O₉ catalyst was significantly higher than that of the physically mixed catalysts of NiO and Cu₃Mo₂O₉.

The cycling stability of NiO–Cu₃Mo₂O₉ was further evaluated over seven consecutive catalytic cycles, as shown in Fig. 7. The composite maintained stable performance from the 1st to the 6th cycle, consistently generating approximately 200 mL of H₂ within 100 s ($\text{HGR} = 1,200 \text{ mL H}_2 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$). However, the hydrogen production decreased to around 180 mL of H₂ within 100 s ($\text{HGR} = 1,080 \text{ mL H}_2 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) during the 7th cycle, indicating a slight deterioration in catalytic performance. This stability can be primarily attributed to the robust heterostructure of NiO–Cu₃Mo₂O₉, in which strong interfacial interactions help prevent the aggregation and loss of active metal sites during repeated cycling. These results collectively demonstrate that NiO–Cu₃Mo₂O₉ is a highly active and stable catalyst for AB dehydrogenation, making it a promising candidate for practical hydrogen storage applications. Furthermore, the cycling stability of

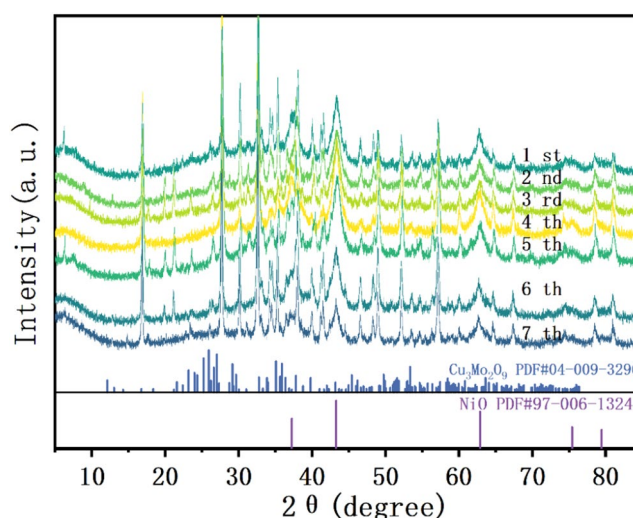


Fig. 8 XRD spectral of 1st to 7th reuse cycle of NiO–Cu₃Mo₂O₉ catalyst. The XRD spectral of each reused cycle is shown in the plot

NiO–Cu₃Mo₂O₉ is comparable to that of other reported catalysts, such as HCSS–Co₃O₄@CuO–NiO and Cu₃Mo₂O₉/NiMoO₄ (3:2) [3, 7].

Figure 8 shows the XRD spectral of the NiO–Cu₃Mo₂O₉ catalyst after reused up to seven cycles. Comparison of the XRD pattern obtained after the 7th reuse cycle with the 1st cycle reveals the weakened signals intensity in NiO component after 7th reuse cycle. The most obvious signal is the one at 0.63 nm corresponding to the (220) plane, where this signal at the 7th reuse cycle was significantly lower in intensity compared to the one in 1st cycle. The weakened signal of NiO indicates that the amount of NiO could be reduced after 7th reuse cycle and led to a decline in the catalyst's ability to generate H₂, thereby affecting its hydrogen production performance.

Figure 9a reveals the dosage effect of NiO–Cu₃Mo₂O₉ catalyst ranging from 10 to 150 mg to the hydrogen generation of AB methanolysis. As clearly depicted in the time-dependent H₂ volume curves, a progressive increase in both the hydrogen production rate and the final cumulative H₂ yield were observed with the increase of catalyst loading. This phenomenon can be attributed to the fact that the higher catalyst dosage, the more exposed active sites are. This has effectively accelerated the cleavage of B–H bonds in AB molecules and promote the methanolysis reaction.

To quantify the kinetic behavior, Fig. 9b presents the logarithmic plot of reaction rate versus catalyst concentration. The excellent linear fitting ($R^2 = 0.968$) yields the equation $\ln(\text{rate}) = 0.67 \ln[\text{cat.}] + 1.94$, in which the reaction order was determined to be 0.67. This result not only confirmed the positive correlation between the catalyst loading and the reaction rate but also provided a quantitative kinetic

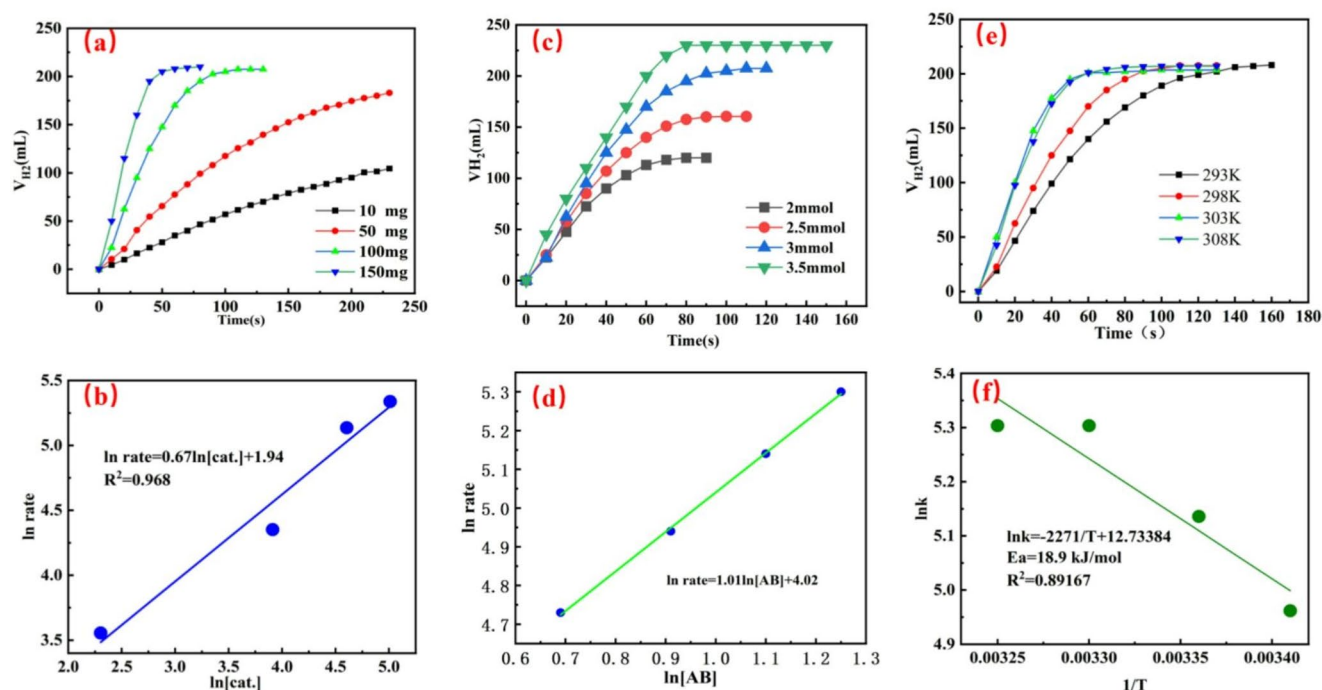


Fig. 9 Kinetics investigation: **a** the influence of the amount of NiO–Cu₃Mo₂O₉ on the hydrogen generation rate; **b** plot of ln(hydrogen generation rate), k , vs. $\ln[\text{cat}]$; **c** the influence of different dosages of AB on the hydrogen generation rate; **d** plot of ln(hydrogen generation rate) vs. $\ln[\text{AB}]$; **e** the influence of the reaction temperature on the hydrogen generation rate and; **f** plot of ln(hydrogen generation rate) vs. (recipro-

cal of reaction temperature, $1/T$). The figure shows the study of hydrogen production under different conditions namely AB concentration, catalysts amount and the temperature. In addition, the kinetic linear regressions of the highest amount hydrogen gas production under different conditions are also shown in the plots below of each condition

basis for the optimization of catalyst dosage in the practical application.

Then, the effects of different AB dosages (2.0–3.5 mmol) on the catalytic activity of NiO–Cu₃Mo₂O₉ were investigated (Fig. 9c). To quantitatively elucidate the relationship between AB concentration and hydrogen evolution rate, the kinetic order of the reaction with respect to AB concentration was determined by linear fitting of $\ln(\text{rate})$ vs. $\ln[\text{AB}]$ (Fig. 9d). The fitting yielded a slope of 1.01, indicating an approximately first-order kinetic behavior for the AB concentration dependence [1]. This near-unity order aligns closely with the ideal first-order kinetics (where rate is strictly proportional to substrate concentration), suggesting that the reaction rate is predominantly governed by the availability of AB molecules in the liquid phase under these conditions. Notably, this first-order behavior is consistent with reports on non-noble metal catalysts for AB methanolysis (e.g., hollow core@shell Co₃O₄@CuO–NiO catalyst), reflecting a common mechanistic pathway where the adsorption and activation of AB molecules on the catalyst surface are the rate-limiting steps [1, 26]. For the NiO–Cu₃Mo₂O₉ catalyst, the slope value of 1.01 has revealed the excellent accessibility of active sites to AB molecules, resulting in a critical factor for achieving high catalytic activity.

The catalytic performance of NiO–Cu₃Mo₂O₉ at different reaction temperatures (293–308 K) was also evaluated (Fig. 9e). As the reaction temperature increases, the hydrogen production rate and cumulative H₂ volume both rise significantly, which aligns with the Arrhenius principle: higher temperatures enhance molecular thermal motion and collision frequency, thus accelerating the reaction kinetics. Figure 9f displays the Arrhenius plot of AB methanolysis over the NiO–Cu₃Mo₂O₉ catalyst, with the regression equation of $\ln[k] = -2271/T + 12.73384$ and an R^2 value of 0.89167. The corresponding activation energy (E_a) is calculated to be 18.9 kJ/mol, which is relatively low compared to many reported AB methanolysis catalysts [3, 7, 24–27]. This low E_a value implies that the reaction can proceed efficiently under mild conditions, which is favorable for practical hydrogen generation application.

To evaluate the catalytic performance of our NiO–Cu₃Mo₂O₉ catalyst in AB methanolysis, the turnover frequency (TOF) as shown in Eq. 3 and activation energy (E_a) of different catalysts from other studies are compared in Table 1. The NiO–Cu₃Mo₂O₉ catalyst exhibited comparable catalytic activity, with a TOF value of 49.8 min^{−1} at 298 K compared to the other catalysts, such as Mo_{0.1}–Ni_{0.8}Cu_{0.2}O (TOF = 59 min^{−1}) [25], Co@Ni–MOF–NCA/NF (TOF = 20.54 min^{−1}) [26] and G–Cu/Ni–NiOx

Table 1 Comparison of TOF of some representative noble-metal-free catalysts

Catalysts	TOF (min ⁻¹)	E _a (kJ/mol)	Temperature (K)	Ref.
NiO–Cu ₃ Mo ₂ O ₉	49.8	18.9	298	This work
HCSS–Co ₃ O ₄ @CuO–NiO	67.1	43	298	[3]
Cu ₃ Mo ₂ O ₉ /NiMoO ₄ (3:2)	62.1	29.6	298	[7]
Cu _{0.8} Ni _{0.2} WO ₄ Nanoparticles	59.0	38.9	298	[24]
Mo _{0.1} –Ni _{0.8} Cu _{0.2} O nanowires	46.9	20.6	298	[25]
Co@Ni–MOFNCA/NF	20.54	39.72	298	[26]
G–Cu/Ni–NiO _x	17.72	ND	298	[27]

ND no data reported

(TOF = 17.72 min⁻¹) [27]. It is worth mentioning that the E_a value for NiO–Cu₃Mo₂O₉ is relatively lower (18.9 kJ/mol) than the other catalysts as listed in Table 1. Generally, low E_a value of a reaction always leads to a faster reaction rate. However, it is also well known that in AB methanolysis, the E_a and TOF of many catalysts are not directly correlated because the E_a for the overall reaction can be regarded as the algebraic sum of the activation energies for all the reactions. The activation energy of the rate-determining step (RDS) is the most important, the lower this value, the faster the reaction is. In this work, the low E_a of NiO–Cu₃Mo₂O₉ indicates that the activation energy of its rate-determining step is extremely low, which is fundamentally important for the AB methanolysis catalytic activity.

3.3 Mechanism of AB methanolysis

Understanding the reaction mechanism is essential for developing high-performance catalysts toward ammonia

borane (AB) methanolysis. Real-time FT-IR spectroscopy was employed to track the evolution of key chemical bonds during AB methanolysis catalyzed by NiO–Cu₃Mo₂O₉ (Fig. 10a and b). As depicted in Fig. 10a, characteristic bands at $\nu = \sim 3200\text{--}3400\text{ cm}^{-1}$ which is attributed to O–H or N–H vibration band and the IR frequency at 1600 cm^{-1} for O–H remained throughout the reaction. These IR frequencies are indeed attributed from the amine and hydroxyl groups in AB structure [27]. In contrast, the B–H stretching bands at $\nu = \sim 2100\text{ cm}^{-1}$ and $\sim 1178/1076\text{ cm}^{-1}$ diminished with reaction time, while a new B–O band emerges at $\sim 1320\text{ cm}^{-1}$, confirming the progressive cleavage of B–H bond and the formation of boron-based intermediates such as NH₃B(OCH₃)₃ [1].

Based on the XPS and real-time FT-IR results, together with previously reported mechanistic insights [28–32], a schematic reaction mechanism and bifunctional interfacial pathway are proposed for AB methanolysis over the heterostructured NiO–Cu₃Mo₂O₉ catalyst (Fig. 11). In the initial step, the NiO–Cu₃Mo₂O₉ catalyst promotes the adsorption and activation of both the AB and methanol molecules on its surface. Electron transfer occurs across the metal-oxide heterointerface, where charge redistribution among the Ni, Cu, and Mo species generates electron-deficient Ni sites and electron-enriched Cu sites [6]. The XPS binding-energy shifts provide clear evidence of interfacial electron transfer from NiO to Cu₃Mo₂O₉, leading to the formation of electron-deficient Ni δ^+ sites and electron-rich Cu δ^- sites at the heterointerface [6]. As illustrated in the enlarged mechanistic view in Fig. 11, the electron-deficient Ni δ^+ sites preferentially interact with the oxygen atom of the hydroxyl group in methanol, thereby enhancing O–H bond polarization and facilitating its cleavage.

Meanwhile, the electron-enriched Cu δ^- site facilitates electron back-donation to the σ^* orbital of the B–H bond

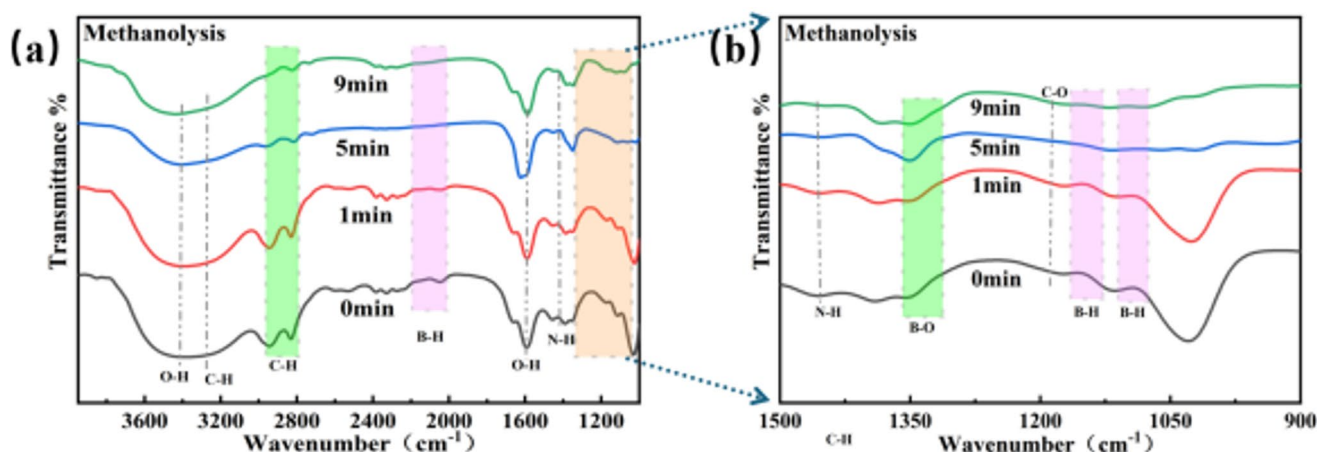


Fig. 10 (a) Real-time FT-IR spectra of AB methanolysis catalyzed by NiO–Cu₃Mo₂O₉ at different minutes, (b) Zoom-in FTIR Spectral within the region 1,500 cm⁻¹ to 900 cm⁻¹. The figure illustrates the real-

time IR spectral at different minutes of the AB methanolysis reaction. Based on the changes in the IR bands at different minutes, the changes of the bond in AB and methanol molecules can be predicted

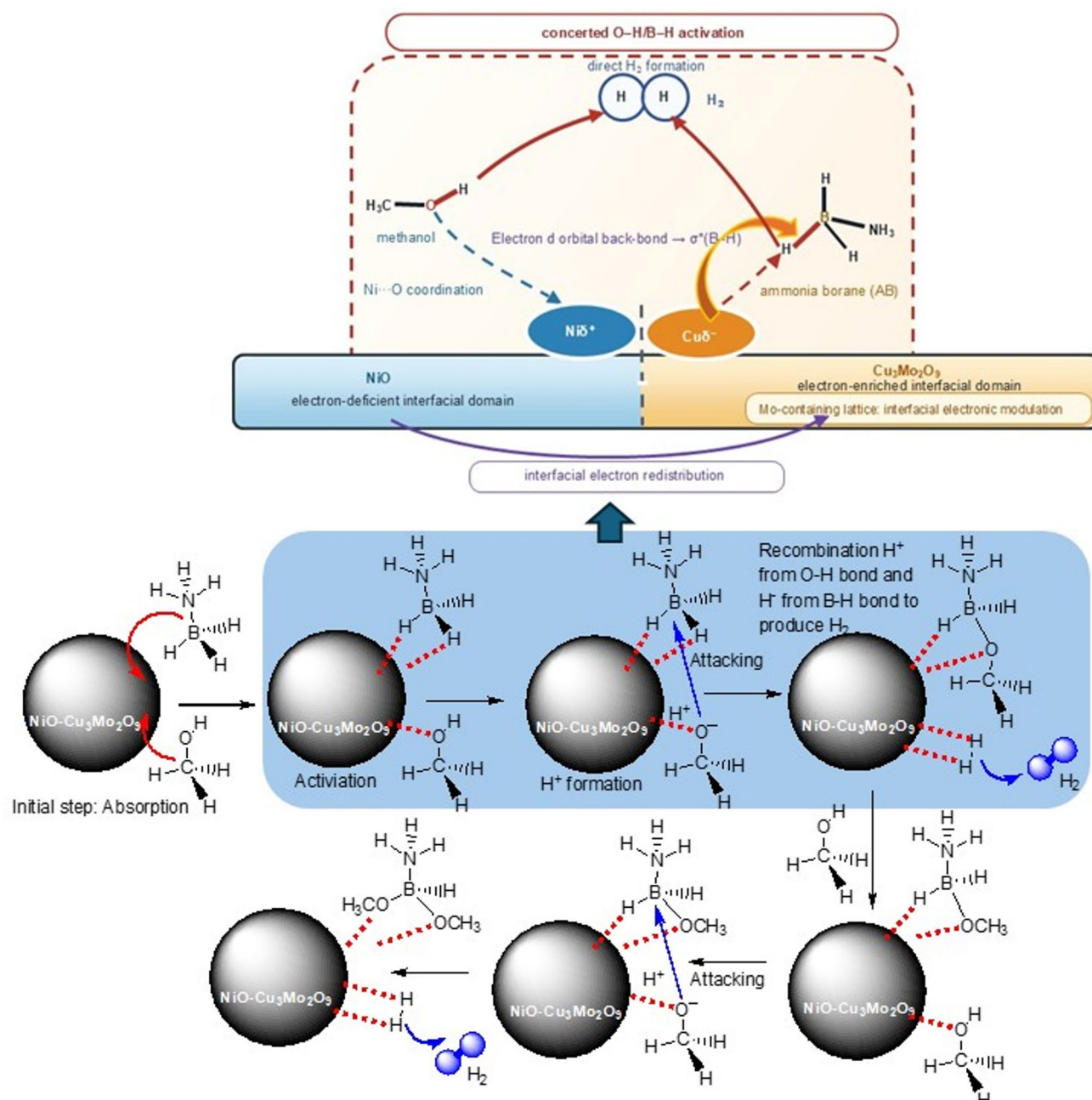


Fig. 11 Proposed catalytic mechanism of AB methanolysis by $\text{NiO-Cu}_3\text{Mo}_2\text{O}_9$ catalyst. Based on the IR spectral as shown in Fig. 10, the proposed mechanism of hydrogen gas formation from AB methanolysis is illustrated in Fig. 11

enhancing B-H activation. The heterolytic combination of H^- (from B-H) and H^+ (from O-H) at neighboring active site results in a H_2 molecule. The resulting boron-containing intermediates subsequently undergo methoxy substitution which can be observed the B-O band formation at approximately $1,320\text{ cm}^{-1}$ in the real-time FT-IR spectra. Finally, the boron-based compound is released from the catalyst surface as the by-product [28–32].

4 Conclusion

A hierarchically structured $\text{NiO-Cu}_3\text{Mo}_2\text{O}_9$ catalyst was successfully synthesized from NiO and $\text{Cu}_3\text{Mo}_2\text{O}_9$ through facile hydrothermal-calcination and annealing methods. The catalyst was proven to perform the catalytic activity toward AB methanolysis with the turnover frequency (TOF) value of 49.8 min^{-1} . The comparable TOF value was due to the low activation energy ($E_a = 18.9\text{ kJ}\cdot\text{mol}^{-1}$) which is assisted by the catalyst during for the reaction. The $\text{NiO-Cu}_3\text{Mo}_2\text{O}_9$

catalyst showed synergetic effect with a hydrogen generation rate (HGR) of 1,200 mL H₂·g⁻¹·min⁻¹ compared to the Cu₃Mo₂O₉ where the HGR=360 mL H₂·g⁻¹·min⁻¹. The superior catalytic behavior is primarily ascribed to the strong electronic synergy between NiO and Cu₃Mo₂O₉, which modulates the local electronic environment and enhances intrinsic site reactivity. In addition, kinetic studies on the catalytic performance of AB methanolysis also showed that the reaction was temperature dependent with the optimum temperature of 30 °C (303 K). The reaction was positive correlation between the reaction rate and the AB dosage as well as the catalyst loading.

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Author Contributions Wei Gong performed the experiment in catalyst synthesis, characterizations and H₂ measurements, and manuscript write-up. Xintao Li, Xianzheng Quan and Xingwei Liu performed the characterization of the catalyst, data collection and analysis. Qingfeng An helped in kinetic studies and data collection. Hao Li performed real-time FTIR spectroscopy analysis and producing the data in Sect. 3.3 and Fig. 10. Meng Guan Tay supervised the project and edited the manuscript.

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

Declarations

Competing Interests The authors declare no competing interests.

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