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Mesoporous siliceous foam-supported CoB catalysts for hydrogen production via NaBH₄ hydrolysis

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Abstract:

In this work, mesoporous siliceous foam (MCF) was synthesized, and MCF supported CoB catalysts (CoB/MCF) for H₂ production via NaBH₄ hydrolysis were prepared with impregnation-reduction. Meanwhile, the influence of MCF dosage on the structural change and catalytic performance was studied, and optimal reaction conditions of H₂ production were further explored. According to XRD analysis, the amorphous structure still maintains with the addition of MCF. The results of SEM and BET show that the MCF has a modulation effect on the morphology, and an appropriate amount of MCF makes the catalyst possess flocculent structure with numerous pores and larger specific surface area, which enables abundant active sites to be exposed. XPS analysis further indicated that the Co sites were electron-enriched. These can be responsible for excellent activity and lower activation energy of the CoB catalyst with 50 mg MCF. According to the research findings of reaction conditions, the catalyst has high H₂ generation rate of 3.9 L·min⁻¹·g_{cat}⁻¹ under the optimal conditions (0.10 g sample, 30 °C, NaBH₄ and NaOH both at 5 wt.%).

Keywords: CoB-based catalysts; Mesoporous siliceous foam (MCF); High activity; H₂ generation rate; NaBH₄ hydrolysis

1. Introduction

Recently, the growing shortage of fossil energy and environmental pollution have become urgent global challenges [1, 2]. Hydrogen has been recognized as a highly appealing energy source due to its renewability, remarkable energy density and environmental friendliness [3, 4]. Nevertheless, the large-scale application is hindered significantly by the safe storage and transportation challenges [5, 6]. Chemical hydrides, especially NaBH_4 , are viewed as attractive hydrogen storage materials owing to high hydrogen storage density and rapid release of high-purity hydrogen at room temperature [7-9]. However, the efficient and controllable hydrogen production via NaBH_4 hydrolysis is restricted by favorable catalysts [10, 11]. Considering high activity, low cost and good reusability, non-noble metal CoB based catalysts have not only attracted special interest but also been widely studied [12-14].

Generally, CoB catalysts supported on appropriate carriers have been proven to remarkably avoid agglomeration, effectively improve dispersion and enhance catalytic performance [15, 16]. Commonly used supports mainly include metal oxides, various carbon materials and nickel foam, etc. [17-20], which usually provides large specific surface areas and enhances the dispersion of active species. Recently, mesoporous siliceous foam (MCF) has served as an appealing support in catalytic fields owing to its high surface area, large pores, adjustable pore structure and good thermal stability [21-23]. As reported, MCF has been adopted as a support for the Co catalyst in F-T synthesis and the catalyst exhibits superior activity and high selectivity. The outstanding performance is attributed to the fact that MCF possesses more open

porous structure which suppresses growth of Co particles and enhances cobalt dispersion [21]. In the field of CO₂ hydrogenation to methanol synthesis, MCF supported CuZn catalyst achieves excellent methanol formation yield at a low energy consumption, because the unique mesoporous structure and large pore size of MCF can promote the diffusion of active species [24]. In addition, MCF supported Pt with a considerably less content has been demonstrated to be a high-performance catalyst for selective hydrogenation, since the large mesopores of MCF facilitate the intraparticle diffusion of the reactants [25]. Based on the open porous structure and large pore size, MCF is expected to be employed as a support to obtain fine particles, high dispersion and beneficial diffusion.

In this work, MCF has been selected as the support and CoB/MCF catalysts were fabricated via the impregnation-reduction method for H₂ production from NaBH₄ hydrolysis. Through varying the dosage of MCF, the change rules of catalyst structure and activity have been carefully investigated and discussed. Meanwhile, the effects of reaction conditions (the amount of catalyst, temperature, concentrations of NaOH and NaBH₄) on catalytic activity have been also studied.

2. Experimental

2.1 Preparation of MCF and CoB based catalysts

The MCF support was prepared by the microemulsion template method. Specifically, 4.0 g PEO-PPO-PEO triblock copolymer (P123) was dissolved in HCl solution (75 mL, 1.6 M), and the mixture was warmed to 40 °C in a water bath while being vigorously stirred. Subsequently, 4.0 g tetramethylbenzidine (TMB), 10 mL of

tetraethyl orthosilicate (TEOS) and 46 mg NH_4F were added sequentially. After the thorough mixing, the solution was hydrothermally treated at 100 °C for 24 h, cooled naturally to room temperature. The resulting solid was collected by centrifugation and washing, and dried at 100 °C for 12 h. The final MCF support was obtained by calcination at 500 °C for 8 h.

MCF supported CoB catalysts were prepared by the impregnation-reduction method. Based on the cobalt salt dosage determined in our previous works [26], 1.6149 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 mL deionized water, followed by the addition of pre-determined MCF. After 1 h of ultrasonic treatment, 30 mL of a solution with both NaBH_4 and NaOH at 5 wt.% was added slowly with stirring. Upon completion of the reduction reaction, the black solid was collected by centrifugation and thoroughly washed with deionized water and ethyl alcohol. Subsequently, the resulting solid was dried under vacuum at 60 °C for 12 h. The addition of MCF was 0, 25, 50 and 75 mg and corresponding samples were labeled as CoB/MCF-0, CoB/MCF-25, CoB/MCF-50, and CoB/MCF-75, respectively. The schematic diagram of CoB/MCF catalysts preparation is shown in Fig. 1.

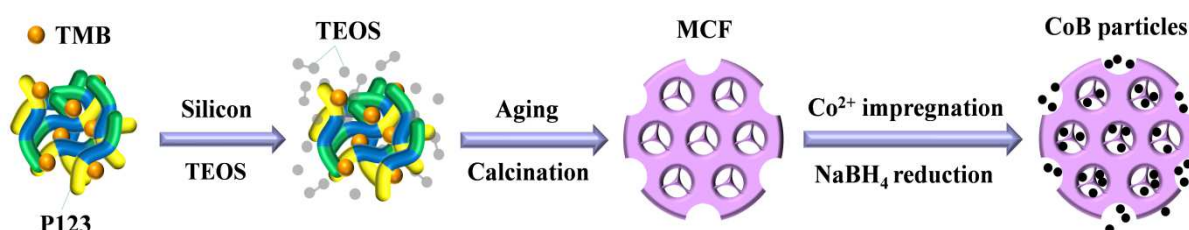


Fig. 1 - Schematic diagram of CoB/MCF catalysts preparation.

2.2 Catalyst characterization

The crystal structure and phase composition of catalysts was characterized by

X-ray powder diffraction (XRD, Germany Bruker D8 DISCOVER A25 X-ray diffractometer), with patterns recorded in the 2θ range of 20° - 80° at a scan speed of $4^\circ/\text{min}$. The surface morphology of the samples was analyzed via a Zeiss Sigma 300 scanning electron microscope (SEM) operating at 30 kV. Textural properties were derived from N_2 adsorption/desorption isotherms (TriStar II Plus Micromeritics, -196°C) using the BET and BJH methods. The surface composition and elemental states were measured using an Escalab 250Xi spectrometer with $\text{Al K}\alpha$ radiation for X-ray photoelectron spectroscopy (XPS) analysis.

2.3 Catalytic performance evaluation

The catalytic activity for NaBH_4 hydrolysis was determined by the water displacement method. 10 mL of 5 wt.% NaBH_4 and 5 wt.% NaOH alkaline solution was added to a round-bottom flask, which was placed in a water bath at 30°C . Subsequently, the catalyst (0.10 g) was added to the above solution and hydrogen gas volume was recorded at regular time intervals. The H_2 generation rate was calculated according to the actual amount of catalyst.

3 Results and discussion

3.1 Structural characterization of CoB/MCF catalysts

3.1.1 XRD phase analysis

The crystal structure and phase composition of the catalysts were analyzed by XRD, the XRD patterns of CoB and CoB/MCF catalysts were shown in Fig. 2. All experimental samples exhibit only a broad and weak diffraction peak around $2\theta=45.0^\circ$, which is characteristic of the typical amorphous CoB alloy [26]. This means that the

addition of MCF has no impact on the amorphous structure. The amorphous CoB phase with rich unsaturated surface coordination sites is believed to be active phase for hydrolysis reaction [18, 27]. Generally, a low-intensity peak of MCF can be observe around $2\theta=23.0^\circ$ [23, 28], and another characteristic peak is identified at $0.5\text{-}1.0^\circ$ by small-angle XRD [21]. However, no characteristic diffraction peak assigned to MCF is detected under current testing conditions, probably due to its low content or high dispersion [29, 30].

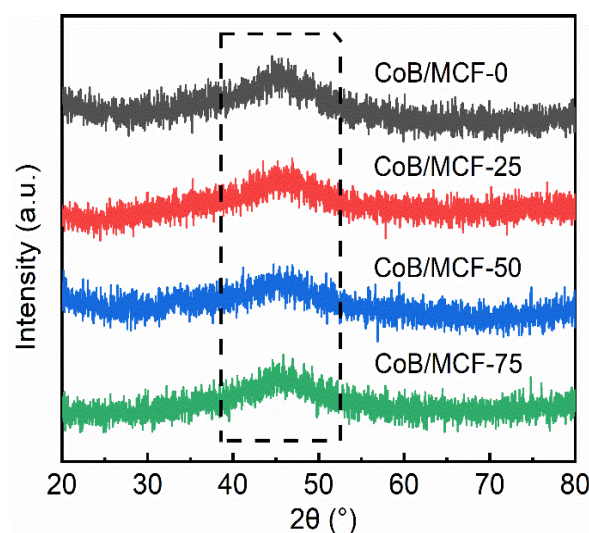


Fig. 2 - XRD patterns of catalysts.

3.1.2 SEM morphology observation

According to Fig. 3(a) and (b), MCF exists as uniform spheres with an average diameter of $\sim 6.4\ \mu\text{m}$ while pure CoB particles without MCF present severe agglomeration. It can be inferred that the formation of CoB particles tends to undergo homogeneous nucleation, resulting in agglomeration and particulate morphology. The poor dispersion of CoB particles can hinder the exposure of active component and decrease the catalytic activity. With the addition of 25 mg MCF, the dispersion is slightly improved and a little flocculent structure (circled in the figure) is observed in

Fig. 3(c). This phenomenon can be attributed to the fact that a small amount of MCF can provide a few heterogeneous nucleation sites, induce in-situ growth of CoB on the surface and reduce appropriately agglomeration, which is beneficial to the formation of flocculent structure. When the amount of MCF is increased to 50 mg, the surface morphology of CoB/MCF-50 changes dramatically (Fig. 3(d and e)). With the increase of MCF dosage, the abundant Si-OH groups on the surface can anchor more Co^{2+} , inducing the heterogeneous nucleation of CoB on the surface, thereby inhibiting effectively agglomeration. Eventually, the catalyst exhibits a puffy flocculent structure with abundant pores, which favors a larger specific surface area and greater exposure of the active component, thereby facilitating the catalytic reaction. When the MCF dosage is increased to 75 mg, the flocculent structure disappears and particle agglomeration exists for the CoB/MCF-75 sample, as shown in Fig. 3(f). With the presence of excess MCF, the limited Co source is dispersed over numerous MCF particles. The insufficient Co loading fails to form interconnected flocculent networks, and discrete CoB particles are generated instead. In summary, morphological transformation of the catalysts indicates that the MCF has a modulation effect on the nucleation and growth of CoB.

From the above SEM observations, it can be inferred that the MCF can act as heterogeneous nucleation sites to induce the in-situ growth of CoB and suppress the agglomeration. Meanwhile, it can be considered that an appropriate amount of MCF enables the catalyst to form a puffy flocculent structure with numerous pores. This structure can be helpful to the exposure of more active sites and improvement of

catalytic performance [13]. In this work, the CoB/MCF-50 catalyst is predicted to display relatively high catalytic activity.

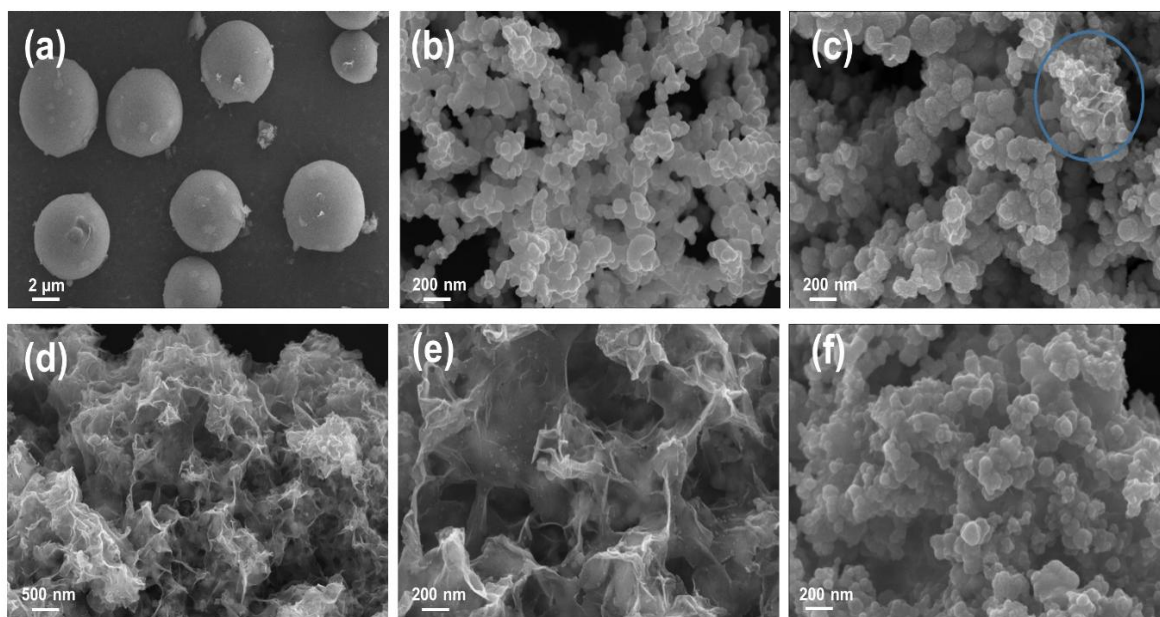


Fig. 3 - SEM micrographs of (a) MCF, (b) CoB/MCF-0, (c) CoB/MCF-25, (d, e) CoB/MCF-50 and (f) CoB/MCF-75.

3.1.3 BET characterization

The textural properties of representative samples CoB/MCF-0 and CoB/MCF-50 have been evaluated via low-temperature nitrogen adsorption (BET) and the results are shown in Fig. 4. Both samples exhibit hysteresis loops in adsorption-desorption curves from Fig. 4(a). Based on the IUPAC classification, both samples display IV-type isotherms, suggesting the existence of mesoporous structures [31]. According to previous reports, mesoporous channels can facilitate reactant diffusion and catalyst-reactant contact, consequently promoting the catalytic reactions [19]. Fig. 4(b) reveals a rather broad pore size distribution in the 10-40 nm range for both samples.

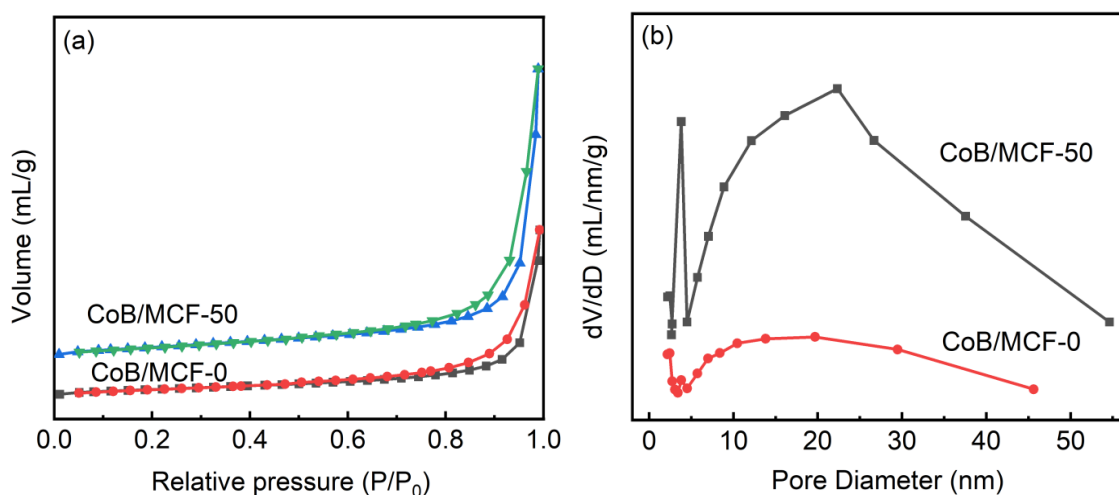


Fig. 4 - Nitrogen adsorption/desorption isotherms of typical catalysts (a) and pore-size distribution plots (b).

Table 1 - BET textural properties of catalysts.

Catalyst	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
CoB/MCF-0	14.9	0.04	22.3
CoB/MCF-50	23.8	0.16	25.7

The textural properties of catalysts are summarized in Table 1. Compared with pure CoB catalyst, CoB/MCF-50 shows a significantly higher specific surface area of 23.8 m²·g⁻¹ (representing an ~60% increase), as well as rises in pore volume and average pore diameter. The improvement in surface area contributes to higher catalytic activity by offering more accessible active sites for participating in NaBH₄ hydrolysis [11]. According to BET analysis, it is expected that the CoB/MCF-50 sample has high activity towards NaBH₄ hydrolysis.

3.1.4 XPS analysis of surface species

XPS measurements are employed to analyze the surface composition, elemental states and electronic interactions between cobalt and boron atoms. Fig. 5 exhibits the XPS spectra of the CoB/MCF-50 catalyst in the Co 2p and B 1s energy levels.

According to the Co 2p spectrum presented in Fig. 5(a), the XPS peaks at 781.1 eV and 782.6 eV correspond to the metallic Co (Co^0) and oxidized state Co (Co^{2+}), respectively [15, 32]. The metal cobalt is obtained mainly through reduction reactions, and part Co^0 species are oxidized to form Co^{2+} in the atmosphere during the catalyst preparation and storage process [33]. In addition, the content of Co^0 in total Co is calculated to be 49.1% on the basis of the XPS peak areas, indicating that the CoB/MCF-50 catalyst possesses more Co^0 species. For CoB-based catalysts, Co^0 are generally believed to be active species for NaBH_4 hydrolysis [34, 35].

From Fig. 5(b), it can be observed that two peaks at 188.3 eV and 192.1 eV are ascribed to alloyed B and oxidized B, respectively [26, 36]. Compared with the binding energy of pure B (187.1 eV), the alloyed B in the CoB/MCF-50 catalyst exhibits a positive shift of 1.2 eV. This shift indicates an electron-transfer process from B to the empty d-orbitals of Co, resulting in electron-deficient B atoms and electron-enriched Co atoms [37, 38]. Electron-enriched Co^0 are recognized as the active catalytic species for NaBH_4 hydrolysis [16], and the incorporation of 50 mg MCF significantly raises the electron density of these Co^0 sites, thereby accelerating the hydrolysis reaction [39].

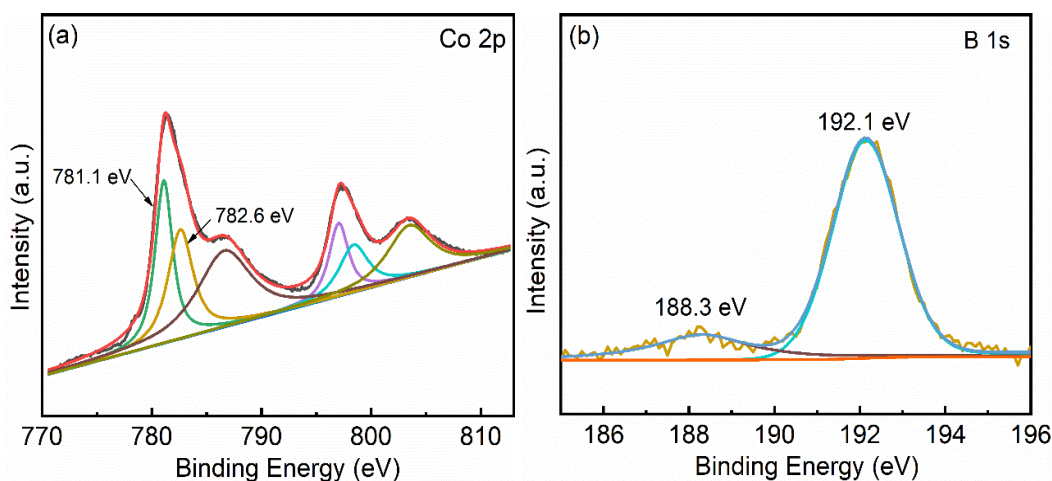


Fig. 5 - XPS results of CoB/MCF-50 showing the Co 2p region (a) and the B 1s region (b).

3.2 Catalytic activity

In this work, the catalytic activity has been evaluated by measuring the hydrogen production rate from NaBH_4 hydrolysis at 30 °C. Fig. 6 displays the curves of hydrogen volume as a function of reaction time and the histogram of hydrogen generation rate versus MCF addition amount. It can be observed that the hydrolysis reaction of NaBH_4 initiates instantly, showing no induction period from Fig. 6 (a). Moreover, the reaction times of MCF-supported CoB catalysts are remarkably shorter compared with that of the pure CoB sample, suggesting that the existence of MCF accelerates hydrolysis reaction. Specifically, the reaction duration gradually declines as the MCF dosage rises from 25 mg to 50 mg while excessive MCF (75 mg) prolongs the hydrolysis duration. As shown in Fig. 6 (b), the H_2 generation rate was determined to be $1.53 \text{ L} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ for the CoB catalyst without MCF. With the incorporation of MCF, the H_2 generation rates of CoB/MCF-25, CoB/MCF-50, and CoB/MCF-75 catalysts increased to 2.88, 3.92 and $2.20 \text{ L} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$, respectively. Obviously, adding MCF notably enhances the catalytic activity. Especially, when 50 mg of MCF is added, the CoB/MCF-50 catalyst obtains the maximum hydrogen generation rate among all the experimental samples.

According to SEM and BET analysis, an appropriate amount of MCF acts as heterogeneous nucleation sites to make CoB form a fluffy flocculent structure with numerous pores, which significantly increases the specific surface area. This facilitates the adsorption of reactants on active sites and enhances the catalytic activity.

Meanwhile, in combination with XPS results, electron-enriched Co^0 sites of CoB/MCF-50 catalyst can promote NaBH_4 hydrolysis. These account for the catalyst's high activity. Table 2 summarizes the activity of CoB/MCF-50 together with the recently reported catalysts for NaBH_4 hydrolysis. Evidently, the hydrogen generation rates of $\text{Co}_1\text{B}/\text{GNS}$ [16], $\text{Co-Ce-B}/\text{Chi-C}$ [40] and $\text{Co-B}/\text{MWCNT}$ [41] catalysts are 7.94 , 4.76 and $5.10 \text{ L} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$, respectively. Except for these three catalysts, CoB/MCF-50 is more active than other non-precious metal catalysts, indicating an excellent catalyst for NaBH_4 hydrolysis.

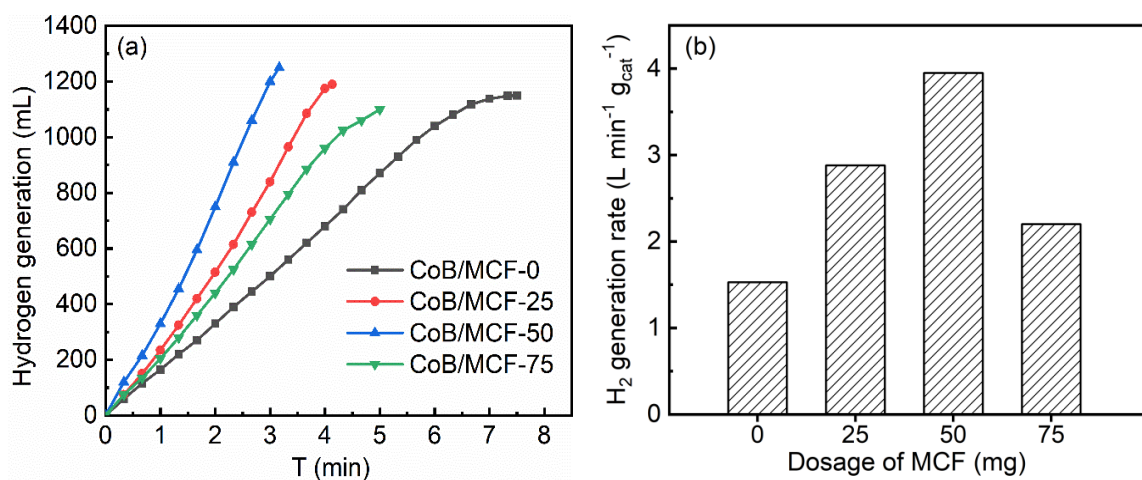


Fig. 6 - Hydrogen volume as a function of reaction time (a) and hydrogen generation rate versus MCF addition amount (b) (10 ml alkali solution includes 5 wt.% NaBH_4 and 5 wt.% NaOH , 0.10 g catalyst, 30°C).

Table 2 - Catalytic performance comparison between CoB/MCF-50 and related catalysts.

Catalyst	NaBH ₄ concentration (wt.%)	NaOH concentration (wt.%)	T (°C)	HGR (L·min ⁻¹ ·g _{cat} ⁻¹)	E _a (kJ·mol ⁻¹)	Ref.
BC/Co-B	1.5%	5%	30	3.89	56.37	[42]
CoB/CN	1.5%	5%	25	0.47	47.70	[43]
CoB/PANI	1%	5%	40	2.37	37.75	[44]
CoB/ZIF-8	1.67%	5%	35	0.51	57.72	[45]
Co ₁ B/GNS	1.5%	5%	30	7.94	38.80	[16]
CH ₃ COOH-kaolin-CoB	5%	1%	30	1.53	49.41	[46]
CoB/TiO _{2-x}	0.4%	0.4%	25	3.07	57.03	[35]
CoB/Ni-foam	5%	5%	25	1.64	44.47	[47]
Co-B/MWCNT	20%	3%	30	5.10	40.40	[41]
carbon-supported Co-B	0.76%	8%	30	3.90	57.80	[48]
Co-Cu-B/bcm	1%	2.5%	30	1.76	37.67	[12]
Co-Ce-B/Chi-C	1.5%	5%	30	4.76	33.10	[40]
Co-Zn-B/GP	3%	5%	30	2.18	35.92	[49]
CoB/MCF-50	5%	5%	30	3.92	38.10	This Work

3.3 Effects of reaction conditions on the catalytic activity

In this work, the CoB/MCF-50 catalyst with optimum activity was selected, and the effects of reaction conditions (catalyst dosage, reaction temperature, NaOH concentration and NaBH₄ concentration) on catalytic activity for NaBH₄ hydrolysis were further investigated.

3.3.1 Catalyst dosage

Fig. 7 presents the influence of catalyst dosage on hydrogen release from NaBH₄ solution. From Fig. 7(a), the reaction time decreases with increasing catalyst dosage, suggesting that hydrogen generation rates are improving. As shown in Fig. 7(b), when the catalyst dosage is adjusted from 0.05 to 0.20 g, the H₂ generation rate notably rises from 0.9 to 5.9 L·min⁻¹·g_{cat}⁻¹, be consistent with the results reported in

Ref. [6, 50]. On the basis of comprehensive consideration, 0.10 g catalyst is used here.

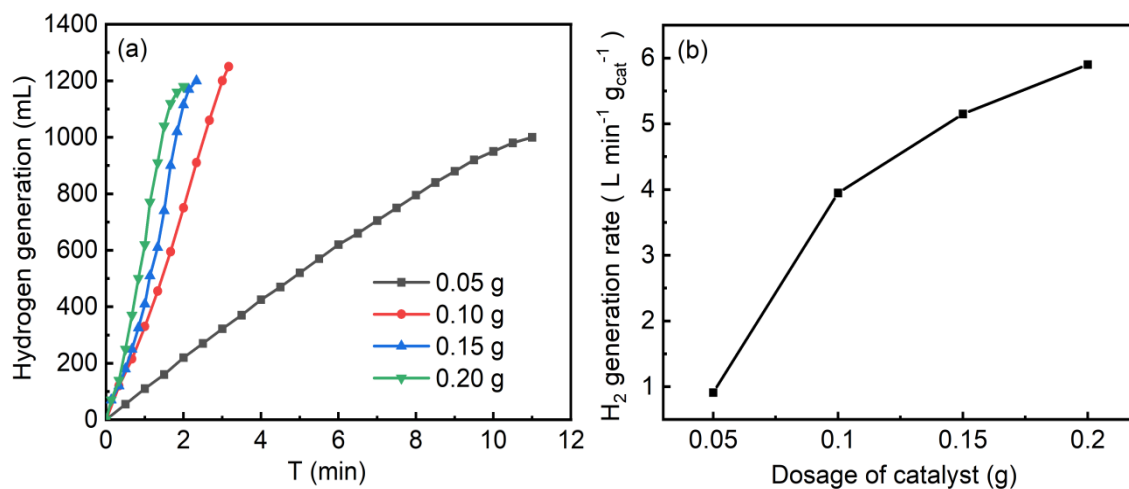


Fig. 7 - Hydrogen volume as a function of reaction time (a) and effect of catalyst dosage on hydrogen release rate in NaBH₄ solution (b)

3.3.2 Reaction temperature

To explore the influence of reaction temperature on the catalytic activity and determine the reaction activation energy of the CoB/MCF-50 catalyst, NaBH₄ hydrolysis reaction is conducted at various temperatures. As shown in Fig. 8(a), hydrogen generation exhibits a nearly linear increase with reaction time, indicating that the reaction shows pseudo-zero behavior. According to the slopes of each fitted linear part, the H₂ generation rates (r) and rate constants (k) at various reaction temperatures are calculated and listed in Table 3. Fig. 8(b) shows the Arrhenius relationship for the CoB/MCF-50 catalyst, plotting ln(k) against 1/T (reciprocal absolute temperature). The activation energy (E_a) is determined using the Arrhenius equation presented below:

$$\ln k = (-E_a/RT) + \ln A$$

The parameters A and R denote the pre-exponential factor and gas constant, respectively. The value of activation energy (E_a) is calculated as 38.1 kJ·mol⁻¹ from

its fitted slope. Table 2 summarizes the E_a values for NaBH_4 hydrolysis over various cobalt-based catalysts reported in the literature.

Compared with most of the supported CoB catalysts, the CoB/MCF-50 catalyst exhibits a lower activation energy, and its value is slightly above that of CoB/PANI [44]. Additionally, the E_a value of the CoB/MCF-50 catalyst is higher than those of metal-modified catalysts, such as Co-Cu-B/bcm [12], Co-Ce-B/Chi-C [40] and Co-Zn-B/GP [49].

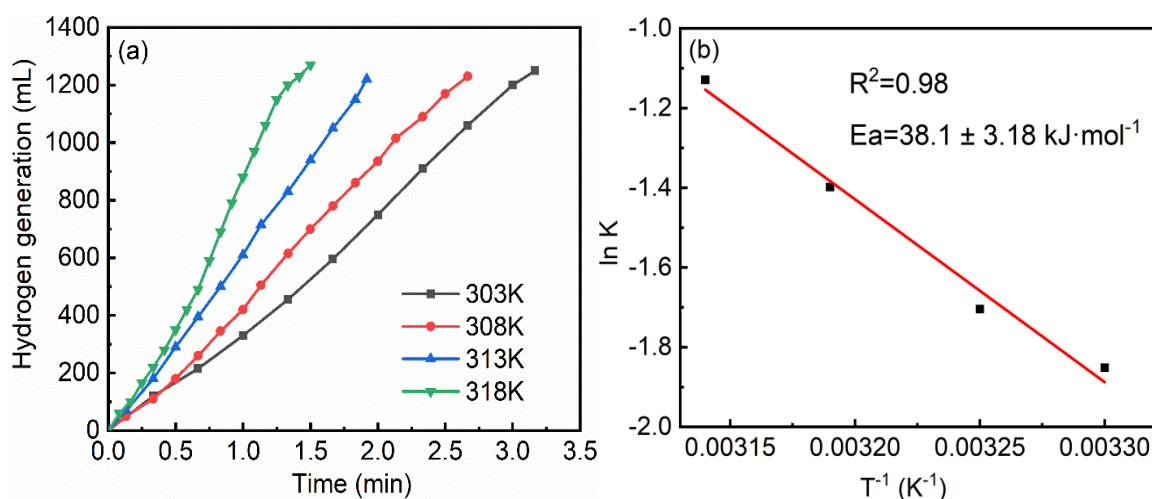


Fig. 8 - Hydrogen volume as a function of reaction time at various temperatures (a) and the Arrhenius plot of $\ln k$ vs. $1/T$ (b)

Table 3 - H_2 generation rates and rate constants for NaBH_4 hydrolysis catalyzed by the CoB/MCF-50 catalyst at various reaction temperatures

T (K)	$r \text{ (L}\cdot\text{min}^{-1}\cdot\text{g}_{\text{cat}}^{-1}\text{)}$	$k \text{ (mol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}\text{)}$	$1/T \text{ (K}^{-1}\text{)}$	$\ln k$
303	3.9157	0.1570	0.00330	-1.8515
308	4.6124	0.1819	0.00325	-1.7042
313	6.3651	0.2470	0.00319	-1.3982
318	8.4667	0.3234	0.00314	-1.1289

3.3.3 NaOH concentration

Fig. 9 depicts the effect of NaOH concentration on the catalytic hydrolysis reaction. Obviously, reaction times decrease as the NaOH concentration increases

from 1 to 5 wt.%. When the NaOH concentration is 5 wt.%, the H_2 generation rate reaches the maximum of $3.92 \text{ L} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. However, with a further rise in NaOH concentration up to 10 wt.%, the rate notably decreases. As reported, appropriate OH^- can participate in the catalytic reaction and enhance hydrogen generation rates [51]. Excess OH^- tends to promote the formation of the by-product NaBO_2 , which occupies active sites and blocks BH_4^- from reaching them [52, 53]. In this work, 5 wt.% is the optimal NaOH concentration.

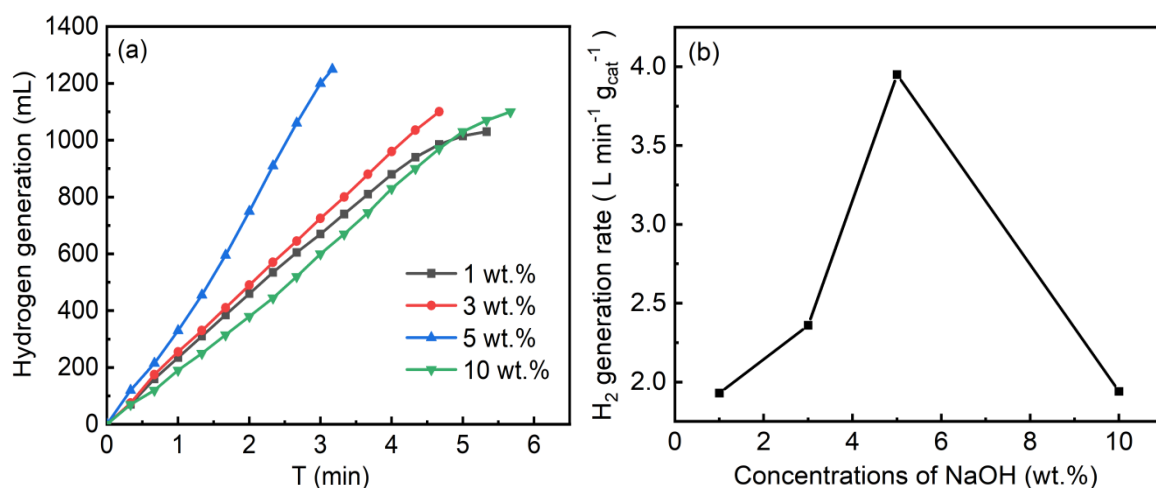


Fig. 9 - Effect of NaOH concentration on activity (a) and hydrogen generation rate (b) of CoB/MCF-50 catalyst (10 mL solution containing 5 wt.% NaBH_4 , 0.10 g catalyst, 30 °C)

3.3.4 NaBH_4 concentration

Fig. 10 clearly presents that NaBH_4 concentration significantly affects hydrogen generation rates. Especially, a maximum H_2 generation rate of $3.92 \text{ L} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ is achieved under the NaBH_4 concentration of 5 wt.%. According to the Ref. [54, 55], a proper NaBH_4 concentration can ensure full utilization of the catalyst surface active sites, while excess NaBH_4 leads to the generation of more NaBO_2 which covers the active site, prevents the contact between BH_4^- and active sites and impedes the mass transfer.

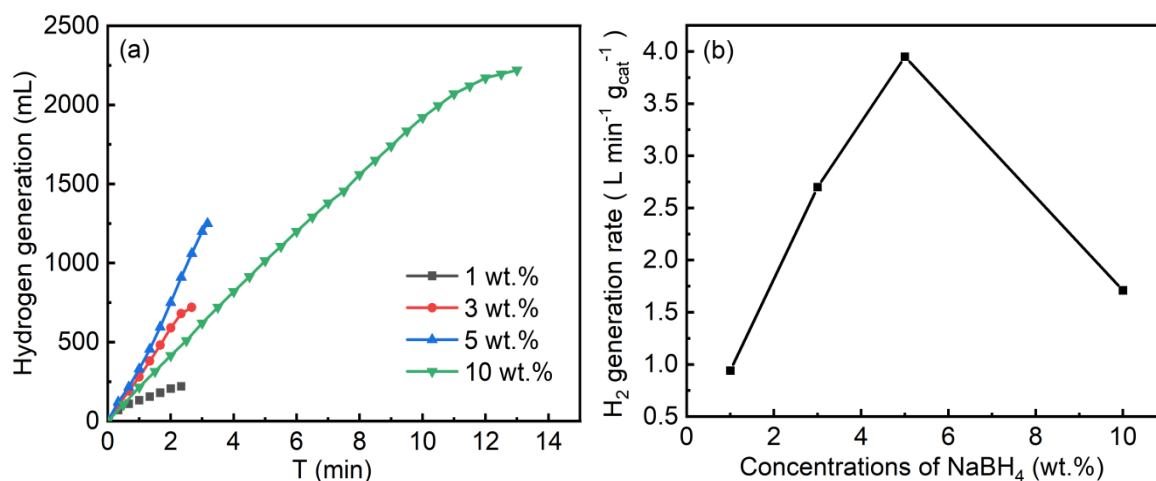


Fig. 10 - Effect of NaBH₄ concentration on activity (a) and hydrogen generation rate (b) of CoB/MCF-50 catalyst (10 mL solution containing 5 wt.% NaOH, 0.10 g catalyst, 30 °C)

4 Conclusion

Homemade MCF supported CoB catalysts were synthesized via a simple impregnation-reduction method. Through regulating MCF amounts, the variation patterns of structure characteristics and catalytic performance have been investigated in detail. It is found that the MCF has a modulation effect on the nucleation and growth of CoB and results in the transition from granular CoB (without MCF) to flocculent porous morphology. Moreover, adding 50 mg of MCF in the CoB catalyst leads to the flocculent structure with abundant pores, large specific surface area and electron-rich Co sites, which can account for high activity. Meanwhile, the optimal reaction conditions for NaBH₄ hydrolysis have been explored. The catalyst obtains high H₂ generation rate of 3.9 L·min⁻¹·g_{cat}⁻¹ under the optimal conditions (0.10 g sample, 30 °C, NaBH₄ and NaOH both at 5 wt.%), and possesses low activation energy of 38.1 kJ·mol⁻¹. The simple preparation method, high activity and low cost make CoB/MCF-50 a promising catalyst for hydrogen generation from NaBH₄ hydrolysis.

CRedit authorship contribution statement

Rongzhi Ren: Data curation, Writing-original draft. **Limin Shi:** Methodology, Writing-review & editing. **Chenying Lu:** Investigation, Data curation. **Xibo Xu:** Investigation, Validation. **Yujing Wang:** Resources, Formal analysis, Supervision.

Declaration of Competing Interest

The authors declare no competing financial interest.

Funding Declaration

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