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Hydrogelator as growth-controlling agent for enhancing the catalytic activity of NiB amorphous alloy catalyst

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Abstract
A series of NiB-x (x denotes as the molar ratio of hydrogelator:Ni) amorphous alloys were prepared using a hydrogelator, 2,4-(3,4-dichlorobenzylidene)-D-sorbitol (DCBS), as the controlling agent and were tested in the selective hydrogenation of benzophenone to benzhydrol. The effect of different amounts of DCBS addition on the activity of the NiB amorphous alloys was investigated. The addition of small amounts of DCBS during NiB preparation could markedly improve its activity. The conversion of benzophenone was 96.6% and the yield of benzhydrol can reach 82.0% under the optimal reaction conditions over the NiB-0.015 catalyst. The high activity of NiB catalysts is attributed to the regulation effect of three-dimensional networks formed by DCBS, which could inhibit the agglomeration of NiB particles during preparation and make them more dispersed, resulting in larger surface areas and more active Ni sites. The Brunauer–Emmett–Teller method, transmission electron microscopy, H_2-chemisorption and temperature-programmed desorption of hydrogen measurements indicated these results.

Keywords Amorphous alloy · Hydrogelator · Controlling agent · Hydrogenation · Benzophenone

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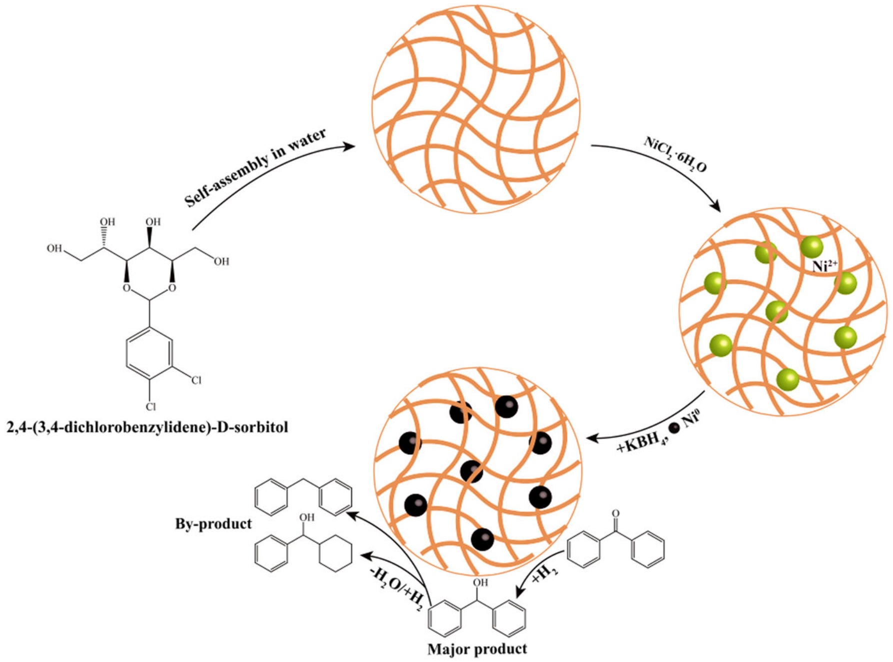
Introduction

Benzhydrol and its derivatives are important chemical intermediates which have attracted much attention of chemical and pharmaceutical researchers [1]. For example, benzhydrol is an important precursor for many bioactive compounds, such as drugs for pollenosis, allergic conjunctivitis and hives. Considering that traditional chemical reduction or synthesis routes are not environmentally friendly, catalytic hydrogenation of benzophenone to produce benzhydrol over metal catalysts has attracted much interest due to the green nature process and the ready availability of suitable starting materials. Presently, noble metal catalysts, such as palladium [2, 3], platinum [4, 5], silver [6–8] and rhodium [9], have been used extensively for benzophenone hydrogenation and catalytic hydrogenation of other unsaturated organic compounds, but the high prices have limited their application for large-scale production. In addition, Raney Ni is another common catalyst used in this conversion, but its pyrophoric nature has limited its further application [10]. Therefore, it is necessary to find efficient non-noble metal catalysts for the selective hydrogenation of benzophenone.

Amorphous alloy catalysts have also attracted much attention especially in the hydrogenation of unsaturated compounds containing C=C and C=O groups, due to their unique isotropic nature and high concentration of coordinative unsaturated sites [11–13]. Unfortunately, the small nanoparticles prepared by the chemical reduction method are unstable and tend to aggregate into large particles, resulting in catalysts with broad size distributions and lower catalytic activity. In order to overcome this drawback, various techniques such as ultrasound, metal modifiers and polymers have been used to improve the NiB preparation and then enhance the performance of the catalysts. For instance, Li and co-workers [14] have developed a simple approach for synthesizing a hollow structured Ni–Co–B amorphous alloy catalyst for 2-ethyl-2-hexenaldehyde hydrogenation, and these hollow sphere catalysts have exhibited higher activities than a Ni–Co–B solid catalyst. Furthermore, the use of the three-dimensional networks formed by gelator as a growth controller has been demonstrated to be a potentially useful method to prepare metal nanoparticles with a more dispersed morphology [15]. For example, Begum et al. [16] have synthesized poly(*N*-isopropylacrylamide-co-acrylic acid) [p(NiPAco-AAc)] microgel to dispersed Ag nanoparticles by free radical precipitation polymerization in aqueous medium. Liu and co-workers [17] have synthesized Se and Ag nanoparticles in agarose hydrogel and have found that the morphology of the nanoparticles could be controlled by adjusting the concentration of the gelator and metals salts. Moreover, Farooqi and co-workers have prepared functionalized polymer microgels to study their pH sensitivity, thermal stability and catalysis mechanism in relevant catalytic reactions [18–21]. Naseem and co-workers have described in detail the stability of Pt NPs within responsive microgel networks [5]. However, the use of a low molecular weight gelator in amorphous alloy preparations to enhance their catalytic performance has rarely been reported.

In a conclusion of our previous works on NiB preparation [22–24], a hydrogelator, 2,4-(3,4-dichlorobenzylidene)-D-sorbitol (DCBS; Scheme 1), was



Scheme 1 Schematic representation for the synthesis of a NiB amorphous alloy catalyst and the hydrogenation of benzophenone

selected as a new additive in the preparation of NiB amorphous alloys to achieve the activity improvement of NiB catalysts. DCBS can be dissolved in water and self-assembled into three-dimensional networks. Then, NiB nanoparticles were fabricated inside the networks by the chemical reduction of nickel ions using KBH_4 as the reduction agent. It was found that NiB exhibited good activity in benzophenone hydrogenation with a small amount of DCBS addition during the preparation. The relationship between the catalytic performance and the hydrogelator addition of the catalysts has been investigated and clarified based on the reaction and characterization results.

Experimental

Catalyst preparation

All chemicals were analytical or technical grades purchased from Baoding Huaxin Reagent and Apparatus and used without further purification. Raney Ni was obtained from Aladdin. NiB amorphous alloys were prepared by the process of chemical reduction using KBH_4 as the reducing agent. A typical procedure for the preparation of NiB amorphous alloys is as follows [22–25]: 1.18 g $NiCl_2·6H_2O$ was dissolved in 10 mL distilled water, then, 25 mL KBH_4 $_{(aq)}$ (25 mmol,) containing NaOH (0.20 M) was added dropwise to the above solution with vigorous stirring in an ice bath. The obtained black precipitate was washed with distilled water until neutral. Then, the catalyst was further washed with absolute ethanol three times to replace residual water and stored in absolute ethanol for use. Upon the addition of DCBS during preparation, a certain amount of additive was dissolved in distilled water to form a transparent solution. The solution was used as a solvent for $NiCl_2 \cdot 6H_2O$ and KBH_4 instead of distilled water, and the preparation procedure was the same as described above. The obtained catalysts were denoted as NiB-*x* (*x* is the molar ratio of hydrogelator:Ni).

Catalyst activity test

Catalyst activity testing was carried out in a 100-mL stainless steel autoclave equipped with electric heating and a mechanical stirrer system. The catalyst (0.05 g), benzophenone (2 g) and ethanol (50 mL) were successively added into the autoclave and the reactor was filled with H_2 three times followed by evacuation, pressurized with H_2 to 2.5 MPa and heated to 373 K. Hydrogenation was then started by stirring the reaction mixture (400 r/min) when the temperature reached 373 K and was kept for 60 min. The reaction mixtures were analyzed by gas chromatography on a 30-m HP-5 capillary column. The product structures were confirmed by using GC–MS on a thermo Trace1300-ISQ instrument.

Catalyst characterization

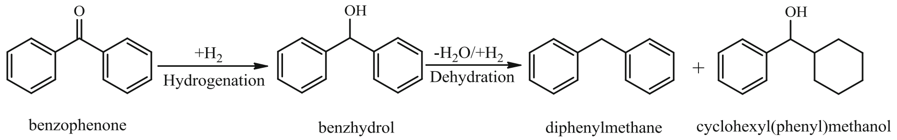
The nickel contents of the catalysts were analyzed by inductively coupled plasma spectrometry (ICP) on an Agilent 7500a spectrometer. The Brunauer–Emmett–Teller (BET) surface area was measured using a Micromeritics Tristar II 3020 surface area and pore analyzer. X-ray diffraction (XRD) patterns were acquired on a Bruker D8 diffractometer using CuKα radiation. Transmission electron microscopy (TEM) images of the catalysts were obtained on a FEI Tecnai G2 F20 S-TWIN microscope. H_2-chemisorption and temperature-programmed desorption of hydrogen (H_2-TPD) were performed using a Micromeritics Autochem II 2920 instrument to measure the active nickel of the catalysts. FT-IR spectra of catalysts were taken on a Bruker VERTEX 70 Fourier-transform spectrophotometer.

Results and discussion

Catalyst selection

Firstly, a series of NiB amorphous alloys were prepared by adding different amounts of DCBS and were tested in the selective hydrogenation of benzophenone to investigate the effect of DCBS addition. As shown in Table 1, for the NiB catalyst, the conversion of benzophenone was 73.9% and the selectivity for benzhydrol was 89.0%. It is apparent that the NiB showed lower activity in this transformation compared to Raney Ni, which is a frequently-used commercial catalyst in hydrogenation. In particular, with the addition of a small quantity of DCBS during

Table 1 Catalytic performance of NiB catalysts in benzophenone hydrogenation



Sample	Molar ratio (gelator:Ni)	Conversion (%)	Selectivity (%)				Yield of benzhydrol (%)
			Benzhydrol	Diphenylmethane	Cyclohexyl(phenyl)methanol	Others	
NiB		73.9	89.0	5.8	4.8	0.4	65.8
NiB-0.005	0.005:1	77.4	87.9	5.9	5.9	0.3	68.0
NiB-0.010	0.010:1	94.5	85.2	8.2	6.0	0.6	80.5
NiB-0.015	0.015:1	96.6	84.9	7.9	6.5	0.7	82.0
NiB-0.020	0.020:1	96.8	80.9	11.1	7.2	0.8	78.3
Raney Ni		88.4	84.9	10.8	2.2	2.1	75.1

Reaction conditions: benzophenone 2.0 g, catalyst 0.05 g, ethanol 50 ml, reaction temperature 373 K, initial P (H_2) 2.5 MPa, reaction time 60 min, stirring rate 400 r/min preparation, the catalytic performance of the NiB catalysts obviously improved. For instance, when the amount of DCBS increased from 0.005:1 to 0.015:1 (molar ratio, gelator:Ni), the conversion of benzophenone increased from 77.4 to 96.6%. We assumed that the aggregates formed by DCBS induced good dispersion of active Ni species, hence accounting for the good activity of the NiB catalysts. Meanwhile, the selectivity of benzhydrol was decreased slightly from 87.9 to 84.9%. On the other hand, when NiB-0.02 used as catalyst, the conversion of benzophenone was not obviously increased, but the selectivity of benzhydrol decreased from 84.9 to 80.9%. The experimental results demonstrated that the three-dimensional networks were efficient enough to avoid the agglomeration of NiB when the molar ratio of gelator:Ni is 0.015, while more addition of DCBS may cause a decrease of benzhydrol selectivity. We ascribed the decrease of benzhydrol selectivity as attributed to the adsorbed residue DCBS molecules on the surface of catalyst. The FT-IR spectra of the NiB-*x* catalysts showed a broad peak centered at 3445 cm^{-1} corresponding to the asymmetric stretching vibration of –OH groups [26], which had not been detected in the traditionally prepared NiB sample, indicating a small amount of residual DCBS molecules on the surface of the catalysts (Fig. S1). In addition, the peak became larger with an increasing amount of DCBS during preparation, indicating that more DCBS molecules were adsorbed on the surface of the catalysts as more DCBS was added to the preparation system. Then, the –OH group in the DCBS molecules may accelerate the adsorption of benzhydrol through the hydrogen bond, which will induce dehydration or further hydroganation of the aromatic ring of the obtained benzhydrol to diphenylmethane or cyclohexyl(phenyl)methanol. GC–MS results demonstrated that the main by-products were diphenylmethane and cyclohexyl(phenyl)methanol, which is in good agreement with our assumption (Fig. S2). The same result can also be obtained from the experimental data of selectivity in Table 1. When the amount of DCBS increased from 0.005:1 to 0.020:1, the selectivity of diphenylmethane increased from 5.9 to 11.1%, and the selectivity of cyclohexyl(phenyl)methanol also increased, from 4.8 to 7.2%, and meanwhile the selectivity of benzhydrol decreased from 87.9 to 80.9%. The increase of by-product selectivity was almost equal to the decrease of benzhydrol selectivity, which is also consistent with the assumption. Finally, NiB-0.015 is proven to have the best performance in benzophenone hydrogenation among the DCBS self-assembly-assisted NiB catalysts.

Optimization of reaction conditions

The effect of the temperature on the hydrogenation of benzophenone over NiB-0.015 is illustrated in Fig. 1. The conversion of benzophenone was only 4.8%, with the selectivity as high as 100% at a lower reaction temperature (313 K). However, the activity was improved rapidly with the increase of temperature with a slight loss of the selectivity. The conversion of benzophenone can reach up to 96.6% with the selectivity of benzhydrol at 84.9% and the temperature was 373 K. In addition, the selectivity to benzhydrol obviously decreased (dropped to 9.3%) when the temperature further increased to 393 K. The conversion of benzophenone increased with the increasing reaction temperature, but the selectivity decreased. The reason

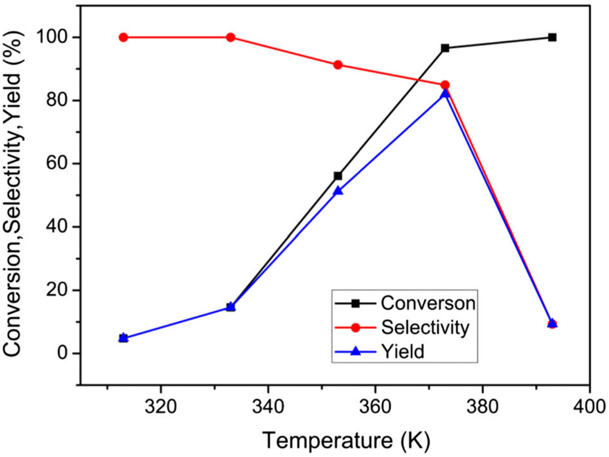


Fig. 1 Effect of temperature on the hydrogenation of benzophenone to benzhydrol (reaction conditions: benzophenone 2.0 g, catalysts 0.05 g, ethanol 50 ml, initial *P* (H_2) 2.5 MPa, reaction time 60 min, stirring rate 400 r/min)

for the decrease of selectivity may be that the high temperature promotes dehydration or further hydrogenation of the benzhydrol. However, the curve about the yield of benzhydrol showed a trend of decreasing after increasing, and the maximum value was found at 373 K. During this temperature, the yield of benzhydrol could reach 82.0%. Thus, 373 K is chosen as the proper reaction temperature.

The influence of reaction time on the benzophenone hydrogenation is shown in Fig. 2. It was found that the conversion of benzophenone increased considerably,

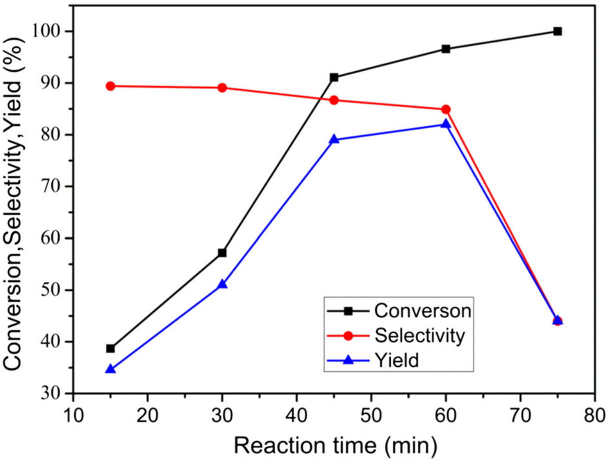


Fig. 2 Effect of reaction time on hydrogenation of benzophenone to benzhydrol (reaction conditions: benzophenone 2.0 g, catalysts 0.05 g, ethanol 50 ml, reaction temperature 373 K, initial *P* (H_2) 2.5 MPa, stirring rate 400 r/min)

from 38.7 to 96.6%, when the reaction time increased from 15 to 60 min, and then increased slightly to 100% with a further increase of the reaction time to 75 min. Furthermore, the selectivity of benzhydrol decreased to 44.0% after 75 min. Prolonging the reaction time promoted the adsorption of substrates on the surface of the catalyst then increased the conversion of benzophenone. On the other hand, a longer reaction time also accelerated the adsorption of benzhydrol, which resulted in the gradual decrease of benzhydrol selectivity. Similar to the discussion of temperature above, the yield of benzhydrol showed a similar trend of decreasing after increasing and reached the maximum value at 60 min. Thus, in the view of yield tendency and transformation efficiency, 60 min has been chosen as the proper reaction time.

Catalyst characterization

XRD patterns of NiB and NiB-0.015 are shown in Fig. 3. Both of the catalysts presented one broad peak at around $2\theta = 45°$, which belongs to the characteristic diffraction peak of metal boride, but no diffraction peaks corresponding to the crystalline of Ni_2B were detected in either sample [27, 28]. The XRD results confirmed the typical amorphous structure of the prepared catalysts [29, 30], indicating that the addition of DCBS had not changed the amorphous structure of the NiB catalysts [31]. Meanwhile, no peaks related to Ni crystal were observed in the catalysts [32], further indicating the amorphous nature of the Ni.

The nickel content, BET surface area and H_2-chemisorption values of NiB, and NiB-0.015 were measured and the results are listed in Table 2. It was found that the NiB-0.015 has a larger surface area compared to NiB. With respect to H_2-chemisorption, NiB-0.015 also shows a higher value (0.022 cm^2/g) than the traditional NiB catalyst (0.009 cm^2/g), which indicated that the surface of the

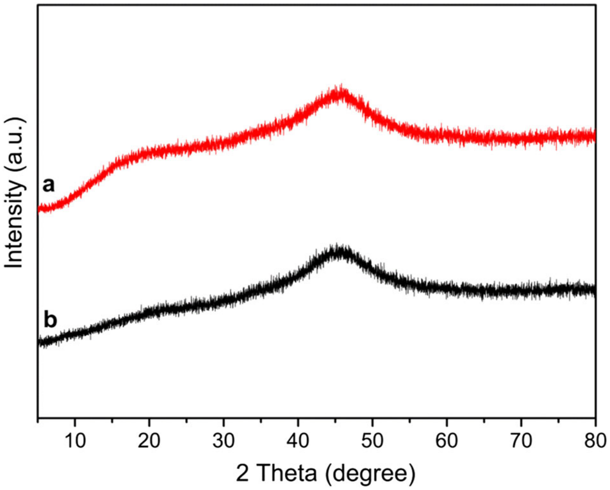


Fig. 3 XRD patterns of the amorphous alloy catalysts: **a** NiB and **b** NiB-0.015

Table 2 Physicochemical properties of the amorphous alloy catalysts

Sample	Nickel content (wt%)	Substrate:metal	Surface area (m^2/g)	H_2-chemisorption (cm^2/g)
NiB	85.6[a]	15:1	13.9	0.009
NiB-0.015	85.5[a]	15:1	21.3	0.022

[a] Based on ICP results

catalyst became larger with the addition of DCBS during preparation. Furthermore, both catalysts have the similar nickel content (85.6% for NiB and 85.5% for NiB-0.015, based on the ICP result). The above results illustrated that, with the addition of DCBS during preparation, the obtained NiB-0.015 catalyst should have more active sites compared to the NiB catalyst with similar nickel contents and larger surface area.

The surface morphology of the NiB and NiB-0.015 catalysts were recorded using TEM. As shown in Fig. 4, the particles of both catalysts presented an approximately spherical morphology, which is consistent with the previously reported Ni-based amorphous alloy catalysts [31]. It should be noted that a cotton-like structure was obtained from the NiB sample, which resulted from obvious agglomeration of the catalyst particles. The agglomeration may lead to coverage of some active centers and thus decreases the hydrogenation activity. Fortunately, this agglomeration could be inhibited with the addition of DCBS. The particles of NiB-0.015 become well dispersed and the particle size distribution decreased to around 10 nm. It is worth noting that, in aqueous medium, DCBS can self-assemble into three-dimensional networks with the fibers of a few hundred nanometers [26]. The hydrogelator, DCBS, significantly influenced the morphology and particle size of the NiB amorphous catalysts, subsequently affecting their surface areas. This is mainly because the hydrogelator self-assembled in water and formed a three-dimensional network structure, which could effectively inhibit the agglomeration of NiB nanoparticles [26]. This feature may be of benefit to the exposure of more active sites and the rapid transportation of hydrogenation-relevant substrates, which explains the higher hydrogenation activity and H_2-chemisorption value for this

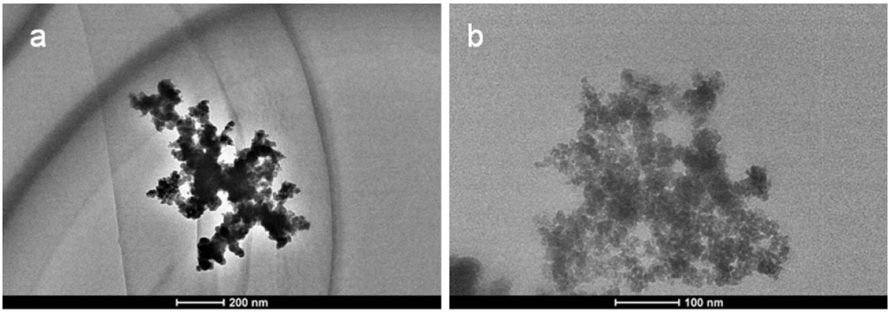


Fig. 4 TEM images of **a** NiB and **b** NiB-0.015

catalyst. In addition, no evidence for the existence of fibers formed by DCBS was obtained on the surface of NiB-0.015 from the corresponding TEM image. Therefore, we propose that most of the DCBS may be removed by washing during the preparation which avoids the agglomeration of the particles mainly in the reduction process.

H_2-TPD curves of NiB and NiB-0.015 samples are shown in Fig. 5. NiB exhibits three main peaks at around 347 K, 411 K, and 510 K and a shoulder peak at 551 K, indicating the presence of four types of absorbing sites on the surface of NiB catalysts. The NiB-0.015 also exhibited three main desorption peaks centered at 348 K, 421 K and 498 K, while the shoulder peak centered at 551 K in the NiB sample could not be detected in the NiB-0.015 sample. Furthermore, the two lower-temperature desorption peaks in NiB-0.015 become smaller and have the tendency to shift to a higher temperature, with the higher temperature desorption peak also decreasing to a lower temperature. It can be concluded that the active sites in NiB-0.015 have a trend to become uniform with the regulating effect of DCBS during the preparation [33].

Kinetics of catalytic reduction of benzophenone

In order to investigate the mechanism of benzophenone hydrogenation over NiB catalysts, we have studied the effect of different benzophenone to catalyst molar ratios and hydrogen pressure on the reaction. As shown in Table S1, when the catalyst dosage increased under the hydrogen pressure of 2.5 MPa (other reaction conditions unchanged), the conversion of benzophenone increased from 9.4 to 96.6%, indicating that, with more catalyst added to the reaction system, more active sites are provided for adsorption of benzophenone thus accelerating the hydrogenation reaction. According to the Langmuir–Hinshelwood mechanism,

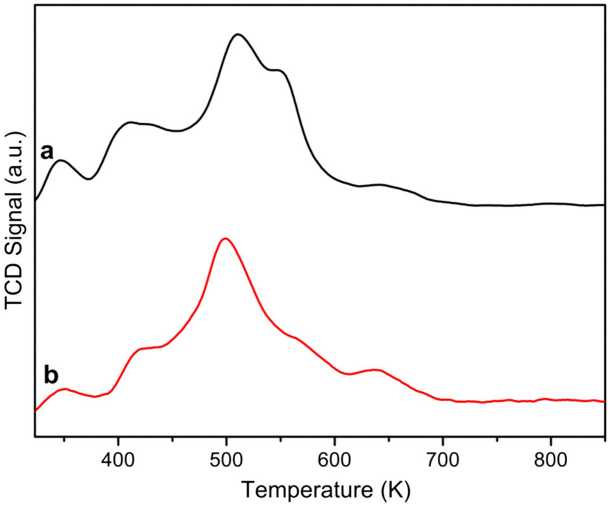


Fig. 5 H_2-TPD profiles of **a** NiB and **b** NiB-0.015

benzophenone and H_2 should both adsorb on the surface of the nanoparticles. When the concentration of benzophenone is high, more substrates were absorbed on the surface of the catalysts, which inhibited the absorption of H_2, resulting in lowering the reaction rate. In addition, we also raised the hydrogen pressure from 2.5 to 5.0 MPa under the same benzophenone to catalyst ratio (30:1), and the conversion of benzophenone increased from 51.3 to 70.9%. These results indicated that higher concentrations of H_2 facilitate its adsorption on the active site, thus facilitating the benzophenone hydrogenation. Therefore, we conclude that the catalytic hydrogenation of benzophenone obeys the Langmuir–Hinshelwood mechanism [34, 35].

Conclusion

In conclusion, a novel chemical reduction preparation method was developed for NiB catalysts by using a hydrogelator as the growth controlling agent. The catalysts prepared with DCBS showed relatively good activity for benzophenone hydrogenation, much better than traditional NiB and Raney Ni catalysts. Under the optimized reaction conditions, the conversion of benzophenone and the selectivity to benzhydrol were 96.6% and 84.9%, respectively. Based on the results of catalyst characterizations, it was found that the addition of a hydrogelator during preparation could make the NiB exhibit larger surface areas, more active centers and smaller particles, thus enhancing the activity of the corresponding catalysts.

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