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Ni–La–B amorphous alloys supported on SiO₂ and γ -Al₂O₃ for selective hydrogenation of benzophenone

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ABSTRACT

The liquid phase selective hydrogenation of benzophenone was studied over Ni–La–B amorphous alloys supported on SiO₂ and γ -Al₂O₃, respectively, and the effect of the carriers was subject to detailed examination. Based on characterization data, SiO₂ was suggested to have a planar structure and γ -Al₂O₃ a porous structure, which markedly influenced the activity and stability of the supported catalysts. Use of ultrasound during catalyst preparation was found to make the particle sizes of the samples smaller, leading to the active particles being more dispersed on the carrier and leading to an increase in the conversion of benzophenone. Using ultrasound protocols, a Ni–La–B amorphous alloy supported on SiO₂ (Ni–La–B/SiO₂-u) initially showed better activity and selectivity than a Ni–La–B amorphous alloy supported on γ -Al₂O₃-u. The main reason for the deactivation of Ni–La–B/SiO₂-u was ascribed to the adsorption of reactants and products onto the catalyst surface and their coverage of the active Ni sites.

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1. Introduction

Benzhydrol is an important industrial precursor for many bioactive products, such as treatments for hives, pollenosis, serum disease, allergic conjunctivitis, and acute circumscribed edema [1]. Considering that traditional chemical reduction methods are not usually environmentally friendly [2], selective hydrogenation of benzophenone to benzhydrol over metal catalysts is the preferred protocol. Noble metals including palladium, platinum, and rhodium have been studied extensively for this reaction, but their application is limited due to high catalyst cost or low selectivity to benzhydrol [3–5]. Raney Ni has been commonly used in this conversion, but its pyrophoric nature and the consequent serious safety hazards have limited its further application [6].

On the other hand, Ni–B amorphous alloys have attracted much attention due to their interesting intrinsic properties such as short-range order, long-range disorder, and high dispersion, as well as their potential applications, especially for catalytic hydrogenation [7–15]. For instance, Chen et al. have studied the effects of W, Mo,

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Ru on a Ni–B amorphous alloy catalyst for p-chloronitrobenzene hydrogenation, and these doped catalysts exhibited higher activities than the undoped one and Raney Ni [15]. Whereas, poor stability has limited further application of these unsupported amorphous alloy catalysts in industry, such supported Ni–B amorphous alloy catalysts have attracted increasing attention in hydrogenation reactions due to their better stability [16–19]. For example, Xie et al. have reported that a Ni–Co–B amorphous alloy supported on carbon nanofibers exhibited similar activity to Raney Ni and good stability over five consecutive runs [19].

Recently, we have developed an ultrasound-assisted chemical reduction method to synthesize a Ni-La-B amorphous alloy catalyst for selective hydrogenation of benzophenone to benzhydrol. The Ni-La-B nanoparticles thus obtained showed high activity and selectivity owing to the synergistic effect between La addition and ultrasound [11], but also exhibited poor stability for recycling. Consequently, to achieve an active and stable Ni-B amorphous alloy catalyst for the selective hydrogenation of benzophenone, a series of carriers were examined to obtain supported Ni-La-B amorphous alloy catalysts. SiO₂ and γ -Al₂O₃ were selected for detailed investigation because they had different and typical structures and both showed good performances. Thus, special attention has been concentrated on Ni-La-B amorphous alloys supported on SiO₂ and γ -Al₂O₃ in an attempt to correlate their catalytic performances with their structures based on a range of characterizations.

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2. Experimental

2.1. Catalyst preparation

Unless otherwise stated, all chemicals were purchased from Baoding Huaxin Reagent and Apparatus Co., Ltd. and were used as received without further purification. The supported Ni-La-B amorphous alloy catalysts were prepared by a reductive impregnation method. The carrier M (M: SiO₂ or γ -Al₂O₃, 5.0 g) was first calcined at 673 K for 4 h, and impregnated with an aqueous solution of 2.98 g NiCl₂·6H₂O and 0.14 g La(NO)₃·6H₂O (molar ratio La:Ni = 1:40). It was then dried at 393 K for 2 h to exclude residual water. The precursor was reduced by adding 1.0 M aqueous KBH₄ aqueous dropwise with gentle stirring in an ice-water bath. The molar ratio of B/Ni was adjusted to 4:1 to ensure that all the nickel cations on the carrier were reduced. After the reduction was complete, the black precipitate was first washed with oxygen-free deionized water several times until neutral, followed by washing with absolute ethanol three times to remove the residual water and water-soluble impurities. Finally, the obtained catalyst was denoted as Ni-La-B/M and the final material was kept under absolute ethanol for future use. When ultrasound was applied during the preparation process, the catalyst so obtained was denoted as Ni-La-B/M-u.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8-ADVANCE X-ray diffractometer with Cu K α radiation. Bulk compositions were identified by inductively coupled plasma analysis (ICP) on a Varian 710-ES spectrometer. BET surface area, pore size and pore volume were measured using a Micromeritics Tristar II 3020 surface area and pore analyzer. Scanning electron microscopy (SEM) was performed on a JEOL JSM-7500 electron microscope. X-ray photoelectron spectroscope using Mg K α X-ray source for excitation. H₂-chemisorption, temperature programmed desorption of H₂ (H₂-TPD) and temperature programmed desorption of NH₃ (NH₃-TPD) were carried out on a TP-5000 instrument from Xianquan Ltd.

2.3. Catalytic tests

Liquid phase benzophenone hydrogenation was conducted as follows: methanol (200 mL), benzophenone (6.0 g), and catalyst (2.0 g) were mixed in a 500 mL stainless steel autoclave equipped with a mechanical stirrer and electrical heating system. The reactor was filled with H_2 three times and evacuated to exclude air. It was then filled with hydrogen to a pressure of 2.5 MPa, followed by slow heating (4 K/min) to the reaction temperature. On reaching 403 K, hydrogenation was started by stirring the reaction mixture vigorously. The stirring rate was kept at 400 r/min and reaction allowed to proceed for 60 min. Reaction mixtures were analyzed by gas chromatography using a 30 m SE-54 capillary column. The used catalysts were separated by leaching or centrifugation, washed with absolute ethanol, and then kept in absolute ethanol for recycling.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the four supported Ni–La–B amorphous alloy samples. After subtracting the background spectrum of SiO₂ and γ -Al₂O₃, the patterns were almost the same. A broad peak at 2θ = 45° was observed, which was attributed to the



Fig. 1. XRD patterns of the supported amorphous alloy catalysts. (a) Ni–La–B/SiO₂; (b) Ni–La–B/SiO₂-u; (c) Ni–La–B/γ-Al₂O₃; (d) Ni–La–B/γ-Al₂O₃-u.

typical amorphous structure of the Ni–B amorphous alloy, indicating that the use of carriers and ultrasound had not changed the amorphous structure of the Ni–La–B catalysts [17,20].

3.2. Structure properties

The results of composition, Ni loading, BET surface area, pore size, pore volume and Ni dispersion of the catalysts, together with the structural properties of the carriers, are summarized in Table 1. As can be seen, the catalysts have similar Ni loadings and all lower than that of the pure Ni-La-B catalyst in our previous study [11]. Particularly, SiO₂ and the catalysts supported on SiO₂ showed very small surface area and pore volume, indicating that SiO₂, Ni-La-B/SiO₂ and Ni-La-B/SiO₂-u may have planar structures, with almost no pores in them. Table 1 also shows that the surface area and pore volume of the catalysts supported on γ -Al₂O₃ decreased slightly compared with γ -Al₂O₃ itself, which can be due to the occupation of some pores of this carrier by small amorphous alloy particles. Furthermore, the surface area and pore volume of Ni–La–B/ γ -Al₂O₃-u increased by 6.8% and 3.6%, respectively, compared with Ni–La– B/γ -Al₂O₃. Noticeably, all the ultrasoundassisted Ni-La-B samples showed lower pore size but higher Ni dispersion than the conventionally prepared ones. Thus, the uses of ultrasound are proved to inhibit the agglomeration of Ni-La-B particles supported on both carriers, making the active Ni species more dispersed on them.

3.3. Scanning electron micrography

Fig. 2 shows SEM images of the supported amorphous alloy catalysts. Each sample displayed cotton-like morphology, consistent with other reported Ni-based amorphous alloy catalysts [21]. It was also observed that the particle sizes of the samples became smaller when ultrasound was used, indicating that the Ni–La–B amorphous alloy particles in Ni–La–B/SiO₂-u and Ni–La–B/ γ -Al₂O₃-u were homogeneously dispersed on the surface.

3.4. X-ray photoelectron spectroscopy

Chemical composition of the catalyst surface was determined by XPS. These results, together with the corresponding characteristics of binding energy values of Ni $2p_{3/2}$, B 1s and La $3d_{5/2}$, are listed in Table 2.

As can be seen, both Ni^0 and Ni^{2+} were detected at about 852 and 856 eV, respectively, by applying the curve fitting

Table 1

Structural properties of the carriers and supported amorphous alloy catalysts.

Sample	Composition (atomic ratio)	Ni loading (wt %)	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Ni dispersion ^a (%)
SiO ₂	-	-	4	9.9	0.01	-
Ni-La-B/SiO ₂	Ni1La0.028B0.992/SiO2	7.5	6	28.8	0.04	7.3
Ni-La-B/SiO ₂ -u	Ni1La0.028B0.869/SiO2	8.1	8	12.4	0.03	8.4
γ -Al ₂ O ₃	-	-	201	8.3	0.42	-
Ni-La-B/y-Al ₂ O ₃	Ni1La _{0.027} B _{1.107} /γ-Al ₂ O ₃	7.2	161	6.9	0.28	7.5
Ni-La-B/y-Al ₂ O ₃ -u	$Ni_1La_{0.028}B_{1.162}/\gamma - Al_2O_3$	6.8	172	6.7	0.29	8.8

^a Calculated from the H₂-chemisorption [24].



Fig. 2. SEM images of the supported amorphous alloy catalysts. (a) Ni-La-B/SiO₂; (b) Ni-La-B/SiO₂-u; (c) Ni-La-B/γ-Al₂O₃; (d) Ni-La-B/γ-Al₂O₃-u.

procedure [22]. It is known that hydrogen molecules are adsorbed and activated on the Ni⁰ sites before the hydrogenation process. Therefore, the amount of Ni⁰ on the surface of the nickel-based catalyst is crucial for its activity in catalytic hydrogenation. Furthermore, Ni–La–B/SiO₂-u had a higher surface Ni⁰ content than Ni–La–B/SiO₂, indicating that more active centers were distributed on the surface of this ultrasound-produced catalyst. On the other hand, for the Ni–La–B/ γ -Al₂O₃-u sample, both Ni⁰ and Ni²⁺ content were lower than those of Ni–La–B/ γ -Al₂O₃, probably due to the porous structure of γ -Al₂O₃ and the use of ultrasound. Ultrasound should make the active component more dispersed and cause some small Ni particles to migrate into the pores of γ -Al₂O₃, although not detectable by XPS. Considering that boron oxide formation is believed to be inevitable in Ni–B amorphous alloy catalysts produced by aqueous KBH₄ reduction [23], there were also two characteristic peaks in B 1s spectra. The peaks of B 1s centered at around 187 and 191 eV can be assigned to pure B and oxidized B, respectively [22]. The La 3d peaks of the samples were found to be at about 835 eV, indicating that lanthanum existed as La₂O₃ [12,13] in the catalysts and was not reduced by KBH₄ [11]. Furthermore,

Table 2

XPS results on the surface characters of the supported amorphous alloy catalysts.

Catalyst	Binding er	Binding energy (eV)				Surface a	Surface atomic ratio (%) ^a				
	Ni 2p _{3/2}		B 1s		La 3d _{5/2}	Ni		В		La	
	Ni ⁰	Ni ²⁺	B ⁰	B ³⁺	La ³⁺	Ni ⁰	Ni ²⁺	B ⁰	B ³⁺	La ³⁺	
Ni-La-B/SiO ₂	852.6	855.7	187.7	191.7	835.5	19.6	30.4	7.3	30.9	11.8	
Ni-La-B/SiO ₂ -u	852.6	855.7	187.1	191.7	835.5	24.9	22.8	17.3	23.6	11.4	
Ni-La-B/y-Al ₂ O ₃	852.5	856.0	187.9	191.8	835.5	15.9	28.0	12.5	42.4	1.2	
Ni-La-B/y-Al ₂ O ₃ -u	852.4	856.0	187.7	191.6	835.5	13.9	24.7	8.4	51.2	1.8	

^a Relative amount.

only a little La could be detectable on the surface of Ni–La–B/ γ -Al₂O₃ and Ni–La–B/ γ -Al₂O₃-u, probably due to the porous structure of γ -Al₂O₃. Most of basic La₂O₃ are believed to migrate into the pores of acidic γ -Al₂O₃, thus not detectable by XPS. The nearly same amounts of La in the body of the catalysts based on the ICP results (Table 1) proved this assumption.

3.5. Temperature programmed desorption

NH₃-TPD profiles of ultrasound-assisted Ni-La-B catalysts are presented in Fig. 3A. For Ni–La–B/ γ -Al₂O₃-u, the peaks centered at 430-620 K are assigned to the weakly acidic sites and the peak centered approximately at 700 K is assigned to the moderately-strong acidic sites; whereas, Ni-La-B/SiO₂-u only showed one weak NH₃ desorption peak at around 670 K. It is apparent that Ni-La-B/SiO₂u showed smaller acidic amounts than Ni–La–B/ γ -Al₂O₃-u, which can be due to the stronger acidity of γ -Al₂O₃ compared with SiO₂. It has been reported that acidic sites can accelerate the formation of dehydration by-products [3]. Thus, Ni–La– B/γ -Al₂O₃-u should result in lower selectivity resulting from its stronger and larger amounts of acidic sites. Fig. 3B shows the H₂-TPD profiles of ultrasound-assisted Ni-La-B catalysts. It is obvious that the extents of hydrogen desorption of Ni–La–B/ γ -Al₂O₃-u are much larger than those of Ni–La–B/SiO₂-u, indicating that the porous structure of γ -Al₂O₃ might favor the dispersion of Ni–La–B particles in its pores, resulting in the formation of more active Ni centers in it [14].

3.6. Reaction results

A series of Ni–La–B amorphous alloy catalysts supported on SiO₂ or γ -Al₂O₃ was prepared and tested in the hydrogenation of benzophenone under the optimized reaction conditions, and the results are listed in Table 3.

As can be seen, Ni–La–B/SiO₂-u showed a good conversion (91.5%) and selectivity (92.5%) to benzhydrol, only a little lower than those of the unsupported one [11] and obviously higher than those of Ni–La–B/ γ -Al₂O₃-u. Considering the different structure of Ni–La–B/SiO₂-u and Ni–La–B/ γ -Al₂O₃-u, the hydrogenation of benzophenone is suggested to occur on the outer surface of the catalysts. The active Ni centers in Ni–La–B/SiO₂-u are proposed to be dispersed on the surface due to the planar structure of SiO₂; whereas the active Ni centers in Ni–La–B/ γ -Al₂O₃-u are mostly dispersed in the internal channels originally due to

Table 3

Catalytic performance of the supported Ni-La-B catalysts.

Catalyst	Conversion of benzophenone (%)	Selectivity to benzhydrol (%)	Selectivity to diphenylmathane (%)	Selectivity to others (%)
Ni-La-B/SiO ₂	75.6	92.1	4.5	3.4
Ni-La-B/γ-Al ₂ O ₃	69.1	91.9	5.7	2.4
Ni-La-B/SiO ₂ -u	91.5	92.5	3.7	3.8
Ni-La-B/y-Al ₂ O ₃ -u	83.4	85.3	9.6	5.1

Reaction conditions: 2.0 g catalyst, 6.0 g benzophenone, 200 mL methanol, temperature 403 K, initial hydrogen pressure 2.5 MPa, and reaction time 60 min. Others: dicyclohexylmethanol, dicyclohexylketone, cyclohexylphenylmethanol, and cyclohexylmethylbenzene.

Table 4

XPS results on the surface compositions of the fresh and used catalysts.

Catalyst	Binding energy of Ni 2p _{3/2} (eV)		Surface atomic ratio (%)							
	Ni ⁰	Ni ²⁺	С	0	Ni	В	La	Si	Al	
Ni-La-B/SiO ₂ -u ^a	852.6	855.7	47.6	31.7	2.1	1.8	0.5	16.3	-	
Ni-La-B/SiO ₂ -u ^b	852.6	855.7	61.5	25.4	1.5	<0.1	0.3	11.2	-	
Ni-La-B/y-Al ₂ O ₃ -u ^a	852.4	856.0	35.1	41.8	2.2	3.4	0.1	-	17.4	
Ni-La-B/ γ -Al ₂ O ₃ -u ^b	852.5	855.8	47.1	36.0	2.3	<0.1	<0.1	-	14.7	

^a Signifies fresh catalyst.





(B) H₂-TPD; (a) Ni-La-B/SiO₂-u and (b) Ni-La-B/ γ -Al₂O₃-u.



Scheme 1. Major processes of benzophenone hydrogenation.

the porous structure of γ -Al₂O₃. This is believed to be the main reason that the fresh Ni-La-B/SiO₂-u showed higher activity than the fresh Ni–La–B/ γ -Al₂O₃-u, although the former had obviously lower total hydrogen adsorption sites. Furthermore, GC-MS analysis showed that the main by-product was diphenylmethane, which is the product of dehydration of benzhydrol or direct hydrogenolysis of benzophenone [3,4] (Scheme 1). The stronger and larger amounts of acidic sites in Ni–La–B/ γ -Al₂O₃-u, based on the NH₃-TPD results, which will accelerate dehydration of benzhydrol, are believed to be the main reason for the lower selectivity of this catalyst. On the other hand, the conversions of benzophenone were found to increase about 15% after the use of ultrasound to prepare the catalysts. Thus, the effect of ultrasound is proposed to favor the dispersion of Ni-La-B alloy particles on the catalysts surface and pores due to its acoustic cavitations, making them smaller and more active.

3.7. Stability test

Stability tests of Ni-La-B/SiO₂-u and Ni-La-B/_γ-Al₂O₃-u were carried out and the results are shown in Fig. 4. As can be seen, Ni-La-B/SiO₂-u showed poor stability (Fig. 4a). A marked deactivation occurred with the conversion of benzophenone dropping from 91.5% to 44.2% in only the second run using the recycled Ni-La-B/SiO₂-u, implying that the catalyst deactivated quickly. However, the selectivity to benzhydrol remained above 92.0% during the whole test. On the other hand, Ni-La-B/ γ -Al₂O₃-u showed different performances in the stability test, as shown in Fig. 4b. The conversion of benzophenone remained at a high level and even exhibited a little increase after each cycle, and the selectivity to benzhydrol first stabilized at about 80.0% and then decreased to 68.8% after four cycles and finally reached 62.5% for the sixth cycle. Therefore, Ni–La–B/ γ -Al₂O₃-u was proved to have better stability in comparison with Ni-La-B/SiO₂-u in this reaction.

In order to find the reason for the above results, the used Ni–La–B samples were characterized by XPS and compared with the fresh ones. As can be seen from Table 4, the chemical states of Ni $2p_{3/2}$



Fig. 4. Stability of Ni–La–B/SiO₂-u (a) and Ni–La–B/ γ -Al₂O₃-u (b). (Reaction conditions: 2.0 g catalyst, 6.0 g benzophenone, 200 mL methanol, temperature 403 K, initial hydrogen pressure 2.5 MPa, and reaction time 60 min.)



Fig. 5. Proposed deactivation mechanism of Ni–La–B/SiO₂-u (a) and Ni–La–B/ γ -Al₂O₃-u (b).

kept stable after the usage, whereas the carbon content increased for both the used samples. Thus, the adsorption of reactants and products on the catalysts surfaces and their coverage on the active Ni sites, as also proven by SEM images, TG and Ni dispersion results of the used catalysts, are believed to be main reasons for the deactivation of the catalysts.

Furthermore, the loss of active Ni species may be another possible reason, especially for Ni–La–B/SiO₂-u (Fig. 5a). In particular, the amount of Ni on the surface of the used Ni–La–B/ γ -Al₂O₃-u increased slightly even if the amount of C had increased. This can be attributed to the structural properties and recycle process of Ni–La–B/ γ -Al₂O₃-u. The long time infusion and stirring at a high speed should partly destroy the porous structure of Ni–La–B/ γ -Al₂O₃-u, breaking up the larger particles and causing the active Ni species dispersed in the channel to migrate onto the surface of the catalyst (Fig. 5b).

An interesting observation during the recycling of Ni–La–B/ γ -Al₂O₃-u supports this assumption. Simple filtration could not separate the used Ni–La–B/ γ -Al₂O₃-u from reaction mixtures entirely even after two cycles, with many tiny particles suspended in the solution, although centrifugation worked effectively. Moreover, the damage to the structure of Ni–La–B/ γ -Al₂O₃-u should also result in exposure of more acidic Al₂O₃ species on the catalyst surface, resulting in the increase of the dehydrated by-products and the decrease of the selectivity to benzhydrol. The NH₃-TPD results of the fresh and used Ni–La–B/ γ -Al₂O₃-u samples also supported this conclusion.

4. Conclusions

In conclusion, Ni–La–B amorphous alloy supported on SiO₂ and γ -Al₂O₃ showed relatively good activity for benzophenone hydrogenation. It was found that ultrasound could make the particles more dispersed on the carriers, providing more active centers and enhancing the activity of both supported catalysts. Ni–La–B/SiO₂-u was proved to have the best initial activity due to its planar structure and more dispersed active Ni species on its surface, but showed poor stability in this sequence. The main reason for the deactivation of Ni–La–B/SiO₂-u was ascribed to the adsorption of reactants and products onto the catalyst surface, covering the active Ni sites. On the contrary, Ni–La–B/ γ -Al₂O₃-u exhibited lower original activity, but stable activity with slightly decreasing selectivity, due to its porous structure and exposure of more acidic Al₂O₃ species during the recycle process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. molcata.2012.07.018.

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