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Efficient hydrogenation of aromatic aldehydes to corresponding benzyl alcohols over Ni-B/MIL-101

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Ni-B amorphous alloys particles incorporated on MIL-101 was prepared by simple reduction impregnation method. N_2 sorption, X-ray diffraction, H_2-chemisorption, thermo gravimetric analysis, and transmission electron microscopy characterization results revealed that high dispersion amorphous Ni-B alloys particles were formed on MIL-101. And the as-synthesized catalyst exhibited excellent catalytic activities for liquid-phase hydrogenation of aromatic aldehydes to corresponding benzyl alcohol.

Introduction

The reduction of aromatic aldehydes to corresponding alcohol is one of the most important chemical processes in industry and in synthesisoriented research laboratories. Catalytic transfer hydrogenations using e.g. 2-propanol as hydrogen donor have been frequently used for this reduction reaction in recent years [1]. Homogeneous noble metal catalysts, such as Ru, Pd complexes [2-4] are general used catalysts for these kinds of reactions, but they often suffer from difficulties encountered in the recovery and reuse of expensive catalysts, and the necessity for co-catalysts (base and ligand). Metal-based heterogeneous catalysts were also considered because of their advantages in catalyst recovery and recycling. Supported nanoparticle (NP) catalysts, such as Ni [5] and Pt [6] have been reported to act as effective and reusable catalysts for these kinds of hydrogen transfer reactions. However, such heterogeneous processes need to be improved because usage of the catalysts has been very high, while the conversion of the reactant and the selectivity of the desired product have been very low.

The catalytic hydrogenation under H_2 atmosphere represents an alternative, which has now been promoted using noble metals[7-11]. For example, palladium is proved to be effective for the hydrogenation of aromatic aldehydes under mild conditions. And, adams catalyst (combined with $FeCl_3$) is also very active at room temperature and 1 bar hydrogen pressure for the reaction [12]. However, in view of the high cost of these noble metal catalysts, transition metals (Cu, Co and Ni) based are frequently employed for hydrogenation reaction [13-15]. Whereas, there are only a few reports concerned about the hydrogenation of aromatic aldehydes over transition metals catalysts, and which often suffered from poor benzyl alcohols yield [16-18].

Since 1980s, 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. In particular, Ni-B amorphous alloys have exhibited excellent catalytic activity and selectivity equivalent or superior to those of conventional catalysts in various hydrogenations [19-21]. However, the quite poor stability of the amorphous alloys has limited their applications in industry. Recently, several methods have been revealed to improve its stability. Among of them, incorporate the Ni-B on a support has drawn people's much attentions [22-24]. And thus, the properies of the support has brought an obvious influence on the catalytic performance of the catalysts [25].

Metal-organic frameworks (MOFs) are a new class of porous polymeric material. The distinctive features of MOFs such as higher surface areas, adjustable pore size and chemical tenability make them as an attractive catalyst support [26]. For example, MIL-101, a chromium-based MOF was reported have a high surface area (4500-5500 m^2/g), mesoporous nature and stability in water. And, in recent studies, some noble or low cost metals such as Ag, Pt, Pd, Cu has been incorporated with MIL-101 and displayed excellent performance in reactions [27-31]. These results encouraged us to develop an MOFs supported Ni-B catalyst for the hydrogenation of aromatic aldehydes under H_2 atmosphere. In view of the special propertis of MOFs, a low cost Ni-B/MOFs amorphous alloy catalyst may exhibited better performance than the Ni-B catalysts supported on general support, such as SiO_2, Al_2O_3. To the best of our knowledge, the incorporation of Ni-B amorphous on MOFs and employed for the hydrogenation of aromatic aldehydes has not been reported, yet.

In this contribution, as one of the most studied MIL-101 was chosen as support. And, Ni-B/MIL-101 amorphous alloys were developed by reduction impregnation method. The as-synthesized catalyst was studied by N_2 sorption, X-ray diffraction (XRD), H_2-chemisorption, thermo gravimetric analysis, as well as transmission electron microscopy. It was found that the obtained catalyst exhibited excellent catalytic activities for liquid-phase hydrogenation of aromatic aldehydes to benzyl alcohols.

Results and discussion

Catalysts characterization

N_2 sorption and dispersion of the catalysts

The surface area for the sample was calculated from N_2 isotherms using the Brunauer-Emmett-Teller (BET) model. As can be seen from Table 1, the surface area of the MIL-101was much bigger than that of SiO_2, and reached to 2678 (m^2/g), which is similar to those reported by others [32]. The Ni-B/MIL-101 shows a smaller specific surface area than MIL-101. This is mainly caused by the occupying of some cavities by amorphous alloy particles. Table 1 also shows that, even with a similar Ni loading, the Ni dispersion on Ni-B/MIL-101 is about 2 times of that of Ni-B/SiO_2, demonstrated that the bigger surface area faciliated the dispersion of the Ni-B, which is in accordance with the TEM results (Electronic Supplementary Information, Fig. S1).

Table 1 N_2 sorption and dispersion results for the samples.

Sample	surface area (m^2/g)	Pore volume(cm^3/g)	Ni loading (wt%)	Ni dispersion (%)
SiO_2	4	0.01	-	-
MIL-101	2678	1.26	-	-
Ni-B/SiO_2	6	0.04	7.6	6.3
Ni-B/MIL-101	640	0.38	7.2	12.8

XRD

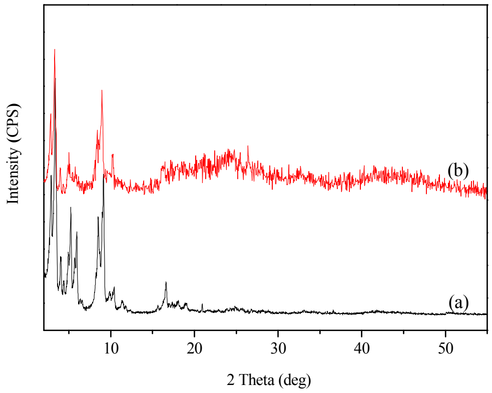


Fig.1 XRD patterns of (a) MIL-101and (b) Ni-B/MIL-101

The XRD pattern (Fig.1) of the synthesized MIL-101 was in agreement with that of reported by Férey et al [33], indicating the successful synthesis. The XRD pattern of Ni-B/MIL-101 is similar to pattern of MIL-101. And, the sharp and strong peaks at 2-4° reveal the presence of both micropores and mesopores, which confirmed that the crystalline structure of MIL-101 was preserved after nickel loading and reduction. Fig.1 also shows that some of the pores of MIL-101 on the catalyst might be blocked during the preparation due to the observation of the changes occurred in the width and relative intensity of XRD patterns, however this in in consistent with the N_2 sorption result. It should be noted that no typical patterns of nickel and a broad peak at $2\theta=45^\circ$ was observed, which was attributed to the typical amorphous structure of the Ni-B amorphous alloy, indicating that the Ni^{2+} was reduced completely and Ni-B amorphous alloy was formed over the MIL-101.

TG

Thermo stability properties of Ni-B/MIL-101 were investigated by a TG analyzer. As shown in Fig.2, two distinct weight loss steps are displayed on MIL-101 and Ni-B/MIL-101. The first weight loss occurring during the lower temperature range from room temperature to 275 °C is due to the desorption of physically adsorbed water on MIL-101, the second weight loss in the higher temperature range from 275 to 350 °C is definitely owing to the collapse of framework of MIL-101[33]. These results demonstrated that Ni-B/MIL-101 exhibited roubst stability under 325°C, and the loading of Ni-B had no significant influence on the stability of MIL-101. Fig.2 also shows that the weight of adsorbed water on MIL-101 is bigger than that of Ni-B/MIL-101, this may be due to the loss of surface area and pore volum of Ni-B/MIL-101 as compared with MIL-101 as shown in Table 1.

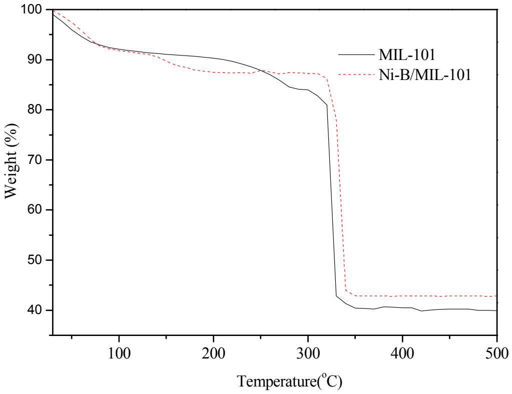


Fig.2 TG curves of MIL-101and Ni-B/MIL-101

Catalytic performance of Ni-B/MIL-101

The catalytic performance of Ni-B/MIL-101 was evaluated, and the obtained reaction mixture was confirmed by GC-MS. It was found that (Table 2) Ni-B/MIL-101 displayed a much better catalytic performance than Ni-B/SiO_2 for the hydrogenation of benzaldehyde, and the yield of benzyl alcohol reached to 88.7%. Clearly, the predominant activity of Ni-B/MIL-101 could be attributed to the highly dispersed Ni-B alloys in the framework of MIL-101. Pd/Al_2O_3, which was proved to be effective for the reduction of benzaldehyde in previous reports [34] was also prepared as reference. The characterizations of Pd/Al_2O_3 were presented in the Electronic

Table 2 The catalytic performance of the catalysts

Catalysts	Conversion /%	Yield /%	TON	TOF /h^{-1}
Pd/Al_2O_3	92.2	23.6	81.2	163.7
$Ni\text{-}B/SiO_2$	46.0	34.7	63.0	126.1
Ni-B/MIL-101	90.0	88.7	83.7	167.5

Reaction conditions: reaction temperature (80□), catalyst amount (1.3mmol, based on the metal species), Substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa), reaction time (2h).

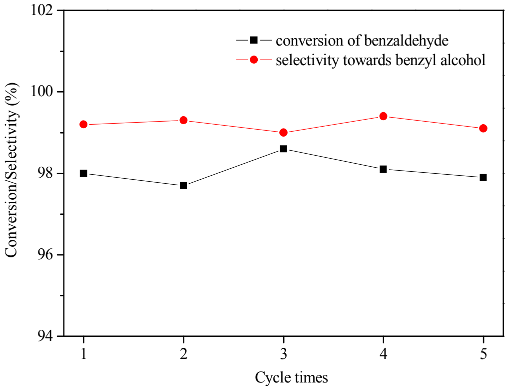
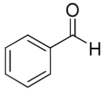
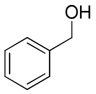
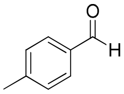
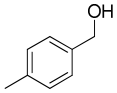
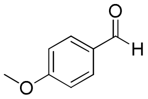
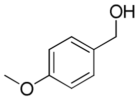
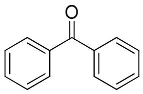
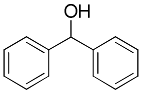
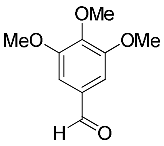
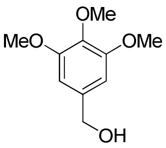
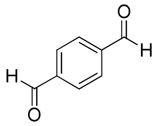
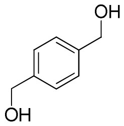
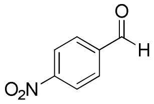
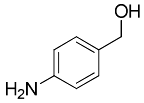
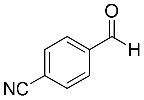
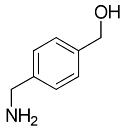


Fig.3 The catalytic performance of Ni-B/MIL-101 for 5 runs

Table 3 The reaction results of aromatic aldehydes

Entry	Substrate	Product	T(℃)	Conversion (%)	Yield (%)	TON	TOF (h^{-1})
1			100	98.0	97.4	92.0	183.9
2			100	98.3	97.5	92.0	184.1
3			100	98.5	96.6	89.8	179.6
4			120	93.8	97.0	85.9	171.8
5			110	99.6	97.6	91.8	183.5
6			130	86.6	96.3	78.7	157.5
7			100	98.8	96.6	90.1	180.2
8			100	98.4	96.6	89.8	179.6

Reaction conditions: catalyst amount (1.3mmol, based on the metal species), Substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa), reaction time (2h).

Supplementary Information. As can be found from Table 2, a better performance was also observed for Ni-B/MIL-101 than the previous reported Pd/Al_2O_3, since the poor selectivity towards benzyl alcohol of the Pd/Al_2O_3 catalyst (Electronic Supplementary Information, Table S2).

The catalytic performance of Ni-B/MIL-101 was evaluated, and the obtained reaction mixture was confirmed by GC-MS. It was found that (Table 2) Ni-B/MIL-101 displayed a much better catalytic performance than Ni-B/SiO_2 for the hydrogenation of benzaldehyde, and the yield of benzyl alcohol reached to 88.7%. Clearly, the predominant activity of Ni-B/MIL-101 could be attributed to the highly dispersed Ni-B alloys in the framework of MIL-101. Since palladium is proved to be effective for the hydrogenation of aromatic aldehydes. Pd/Al_2O_3 was prepared as reference. The characterizations of Pd/Al_2O_3 were presented in the Electronic Supplementary Information. As can be found from Table 2, a better performance was also observed for Ni-B/MIL-101 than the previous reported Pd/Al_2O_3, since the poor selectivity towards benzyl alcohol of the Pd/Al_2O_3 catalyst (Electronic Supplementary Information, Table S2).

The influence of reaction conditions were also evaluated, and the obtained results are present in the Electronic Supplementary Information (Table S3-S6). As can been found, the conversion of benzaldehyde and selectivity towards toluene reached to 100.0% and 99.3% at the optimum conditions (reaction temperature 80℃; catalyst amount 1.3mmol, based on the metal species; substrate 30mmol; methanol 100 mL; hydrogenation pressure 1.5Mpa; reaction time 2h). Since the collapse of framework of MIL-101 was found above 325°C (Fig.2). The Ni-B/MIL-101 was evaluted under a temperature range from 60 to 340℃(Electronic Supplementary Information, Table S2). It can be seen that the conversion of benzaldehyde remains at an almost constant value under 280□, and then descends obviously. However, an obvious deactivation was observed when the reaction temperature above 300 ℃, signifying quick catalyst deactivation took place. Based on the thermo stability properties of Ni-B/MIL-101, we propose this deactivation may be due to the collapse of the MIL-101 framework.

To further investigate the catalytic performance of Ni-B/MIL-101, the recyclability of the catalyst was tested in five consequent runs, and the results are shown in Fig.3. As can be observed, without obvious deactivation of the catalyst was detected within 5 runs, which implied that the catalyst has a well stability. To search for possible leaching effects, the hydrogenation activity of the separated reaction mixture was investigated. No further conversion was detected. We therefore assume that Ni leaching is rather low during the reaction under the optimum conditions. In addition, ICP-OES measurements of the catalyst for each run did not show a reduction of the Ni loading, confirming our assumption(Electronic Supplementary Information, Fig.S6).

To further study the activity of Ni-B/MIL-101, the generality of Ni-B/MIL-101 was investigated through a collection of aromatic aldehydes， the obtained results are summarized in Table 3. All the selected aromatic aldehydes could be transformed to benzyl alcohols with yield above 96.0%. It should be noted that the catalyst did not exhibited selectivity for -CN and -NO_2 groups on the aromatic compounds (entry 7, 8 in Table 3). However, the yield of the obtained benzyl alcohols were still more than 96.0%. Thus, the generality of the catalyst for the hydrogenation of aromatic aldehydes could be proved by the reaction results in Table 3.

Experimental

Materials and catalysts preparation

MIL-101 was synthesized and purified according to the method described by Kaske et al [32]. The briefly procedures are summarized as follows: $Cr(NO_3)_2$•$9H_2O$ (6.0g), terephthalic acid (3.76 g), hydrofluoric acid (0.75 ml) and 75 ml H_2O were mixed completely and heated in a programmable oven to 220 ℃ for 8 h. After cooling, the mixture was filtered to eliminate excess of terephthalic acid. The MIL-101 was first activated hydrothermally in ethanol at 100 ℃ for 4 h and then separated using a fine pore fritted glass filter. The solid was dried at 150 ℃, in air overnight to obtained fine powdered MIL-101.

Ni-B/MIL-101 amorphous alloy catalysts were prepared by a reductive impregnation method. 2.0g MIL-101 was impregnated with an aqueous solution of 1.20 g $NiCl_2$•$6H_2O$. Then, it was dried at 393 K for 2 h to exclude the residual water. The precursor was reduced by adding 1.0 M aqueous KBH_4 aqueous dropwise with gentle stirring in an ice-water bath. The obtained precipitate was washed by deoxygenated distilled water until the washings were pH≈7. The catalyst was further washed with absolute ethanol three times to replace residual water and then stored under absolute ethanol for future use. A Ni-B/SiO_2 catalyst as reference was prepared according to the same procedure as presented before. Pd/Al_2O_3 was also prepared as as reference according to previous studies [34].

Catalysts characterization

The BET (Brunauer-Emmett-Teller) specific surface areas, and total pore volumes were measured via nitrogen adsorption/desorption using a NOVA 2000e analyzer (Quantachrome, US). The loading of Ni on the catalysts were identified by inductively coupled plasma analysis (ICP) on a Varian 710-ES spectrometer. H_2-chemisorption was carried out on a TP-5000 instrument from Xianquan Ltd, The dispersion values of Ni and Pd based catalysts were calculated from H_2 chemisorptions using a dynamic pulse method[35-38]. Powder X-ray diffraction (XRD) was performed on a Rigaka D/max 2500 X-ray diffractometer, using Cu-Kα radiation and scanning 2θ from 2° to 55°, operated at 40 kV and 100 mA. Thermo gravimetric properties of MIL-101 and MIL-101 supported catalyst were measured with a STA 409PC thermo gravimetric (TG) analyzer. High-resolution transmission electron microscopy (HR-TEM) images were observed using a JEOL electron microscope (JEM-2010), powder samples were dispersed on a carbon-coated copper grid for analysis.

Catalytic test

The benzaldehyde hydrogenation was performed as follows: Benzaldehyde (30mmol), catalyst (1.0g), methanol (100 mL) were mixed in a 300 mL stainless steel autoclave equipped with a mechanical stirrer and electrical heating system. Being replaced with H_2 for three times at room temperature, the autoclave was pressurized with H_2 to 1.5 MPa, and heated to the temperature. Then the hydrogenation reaction was started by stirring the reaction mixture vigorously. The stirring rate was kept at 400 r/min and reaction allowed to proceed for 2 h. The components of the reaction mixture was confirmed by GC-MS (Polaris Q, Thermo Finngan, America, HP-1 capillary column, 30 m × 0.25 mm, 0.2 μm film thickness) equipped with an ion trap MS detector. The composition of the reaction mixture was monitored by GC with an OV-1701 capillary column (30m× 0.25 mm, 0.2 μm film thickness).

The hydrogenation of other aromatic aldehydes was carried out followed the same procedures as presented above.

Conclusions

In conclusion, we have successfully synthesized Ni-B amorphous alloys particles incorporated on MIL-101 based on simple reduction impregnation method. The nanocomposites exhibited excellent catalytic activities for liquid-phase hydrogenation of aromatic aldehydes to corresponding benzyl alcohol.

Acknowledgements

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Notes and references

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Graphical abstract

Ni-B amorphous alloys particles incorporated on MIL-101 was prepared by simple reduction impregnation method, and exhibited excellent catalytic activities for liquid-phase chemoselective hydrogenation of aromatic aldehydes to corresponding benzyl alcohol.