Liquid Phase Hydrogenation of Phenol to Cyclohexenone Over A Pd–La–B Amorphous Catalyst

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A La-doped Pd–B amorphous catalyst (Pd–La–B) was prepared by chemical reduction of mixed $PdCl_2$ and $LaCl_3$ with KBH_4. The La-dopant played a key role in stabilizing the amorphous structure since only the crystalline Pd–B was obtained without the La-dopant. During liquid phase phenol hydrogenation, the as-prepared Pd–La–B exhibited higher activity and better selectivity to cyclohexanone than the undoped Pd–B.

Cyclohexanone is widely used in industry (>400 million ton/year) for producing caprolactam, a monomer used in the synthesis of Nylon-6. Traditionally, cyclohexanone is produced via complete hydrogenation of phenol to cyclohexanol, followed by the dehydrogenation of cyclohexanol. Obviously, the selective hydrogenation of phenol to cyclohexanone is superior in saving energy, simplifying reaction steps and reducing waste disposal. However, this is a challenging task since the cyclohexanone is an active intermediate which could be further hydrogenated to cyclohexanol. Though very few catalysts have been reported to be suitable for the title reaction, among them, the Pd-Based catalysts are most frequently used. In order to achieve as high as possible selectivity to cyclohexanone, great attempts have been made to develop powerful catalysts, such as the modification of Pd-Based catalysts by metal or nonmetal additives, the change of the support etc.[1–3] Some catalysts exhibit pretty good activity and selectivity during gas phase phenol hydrogenation. However, our preliminary studies revealed that these catalysts were not suitable for the liquid phase phenol hydrogenation due to the low activity and selectivity and even the rapid deactivation. As well known, the amorphous alloy catalysts usually exhibit higher activity and better selectivity as well as stronger resistance against poisoning during various hydrogenation reactions.[4] Although a great number of metal boride amorphous alloys have been prepared through chemical reduction with BH_4^-, the Pd–B amorphous alloy has never been obtained due to its extremely poor thermal stability. In this paper, we reported a novel La-doped Pd–B amorphous alloy (Pd–La–B) which was more active and selective to cyclohexanone during liquid phase phenol hydrogenation. The stabilizing effect of the La-dopant on the amorphous structure and its promoting effect on the catalytic performance were discussed briefly.

The Pd–La–B sample was prepared by reducing mixed $PdCl_2$ and $LaCl_3$ with excess KBH_4 in aqueous solution at room temperature. Briefly, 2.0 M KBH_4 solution containing 0.2 M NaOH was added dropwise into 10 mL solution containing mixed $PdCl_2$ and $LaCl_3$ under magnetic stirring. The reaction was lasted for about 1.5 h to ensure the complete reduction of metallic ions in the solution. Then, the resulting Pd–La–B black solid was washed thoroughly with H_2O, then with ethanol (EtOH), and finally, kept in EtOH until the time of use. The content of the La-dopant in the Pd–La–B sample, expressed in the La/(Pd + La + B) molar ratio (χ_{La}), was adjusted by changing the amount of $LaCl_3$ in the solution. The undoped Pd–B sample ($\chi_{La} = 0$) was also prepared in the similar way but using the solution containing $PdCl_2$ alone.

The selected area electron diffraction (SAED) picture of the fresh Pd–La–B sample displayed diffractional cycles indicative of the amorphous structure which was further confirmed by the XRD pattern since only one broad peak around $2\theta = 45^\circ$ was observed. After being treated at 873 K for 2 h in N_2 flow, a series of diffractional peaks appeared on the XRD pattern, indicating the crystallization of the Pd–La–B amorphous alloy. The undoped Pd–B alloy displayed a similar XRD pattern to that of the Pd–La–B after being treated at 873 K, implying that the Pd–B alloy was originally present in the crystalline structure. The DSC analysis revealed that the Pd–La–B amorphous alloy began to crystallize at 573 K corresponding to an exothermic peak. However, no exothermic peak was observed from the DSC curve of the undoped Pd–B sample, which again confirmed that only the crystalline Pd–B alloy was obtained without the La-dopant. Thus, one could conclude that the La-dopant played a key role in stabilizing the Pd–B amorphous alloy structure.

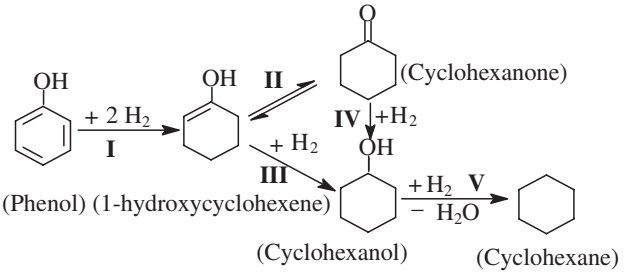
According to ICP analysis, the compositions of the Pd–La–B ($\chi_{La} = 1\%$) and the undoped Pd–B were determined as $Pd_{92}B_8$ and $Pd_{96}B_4$, respectively, indicating the B-enrichment induced by the La-dopant. Meanwhile, the BET surface area of the Pd–La–B catalyst was determined as 27 m^2/g, much higher than that of the undoped Pd–B catalyst (18 m^2/g). The TEM morphologies demonstrated that the La-dopant resulted in a remarkable increase in the dispersion degree of the as-prepared catalyst, corresponding to much smaller particle size and more homogenous distribution in the Pd–La–B catalyst than those in the undoped Pd–B catalyst, which could account for the higher surface area of the Pd–La–B catalyst. The XPS spectra of the undoped Pd–B sample revealed that almost all the Pd species were present in the metallic state corresponding to the binding energies (BE) of 335 eV in $Pd_{3d_{5/2}}$ level. However, the B species were present in the states of both the B alloying with Pd and the oxidized B, corresponding to BE of 188.0 and 191.7 eV in B_{1S} level. The BE value of the alloying B shifted positively by 0.9 eV in comparison with the standard BE value of the pure B (187.1 eV), showing that the alloying B donated partial electrons to the metallic Pd which could be understood by considering the assumption that the bonding electrons of the B occupied the vacant d-orbitals of metallic Pd.[5] The failure in observing the BE shift of the metallic Pd could be mainly attributed to the relatively bigger size of the Pd atom and the lower B content in the Pd–B alloy. Concerning the Pd–La–B sample at $\chi_{La} = 1\%$, two peaks around BE of 835.1 and 838.0 eV were observed in $La_{3d_{5/2}}$ level, corresponding to LaH_2 and La_2O_3, respectively. As no metallic La was present, it could be concluded that only the Pd–B amorphous alloy was formed during the chemical reduction of mixed Pd^{2+} and La^{3+} by KBH_4. The presence of the La_2O_3 could act as a support for the Pd–B alloy particles, resulting in higher BET surface area. Comparing the XPS spectra between the Pd–La–B and undoped Pd–B, it was found that, in the presence of the La-dopant, the BE values of both the metallic Pd and the alloying B shifted negatively by 0.3 and 0.5 eV, respectively. While, the BE of the La(III) in the La_2O_3 shifted positively by 0.4 eV in compar-

ison with the standard value. These results clearly confirmed the existence of the interaction between the Pd–B amorphous alloy and the La_2O_3, in which the La_2O_3 donated partial electrons.

The above results could be also accounted for the stabilizing effect of the La-dopant on the Pd–B amorphous alloy structure. On one hand, it could be attributed to the La-induced B-enrichment in the Pd–B alloy since, according to our previous studies on the Ni–B amorphous alloy, the increase in the B content might enhance the stability of the Pd–B amorphous alloy.[6] On the other hand, it could be attributed to the presence of the La_2O_3, which might serve as a support for the Pd–B alloy. The interaction between the Pd–B alloy particles and the La_2O_3, and the high dispersion of the Pd–B alloy particles on the La_2O_3 could retard the crystallization of the Pd–B amorphous alloy since the gathering and migration of the Pd–B alloy particles were effectively inhibited.[7]

Liquid phase hydrogenation of phenol was performed at 393 K and 1.0 MPa in a stainless steel autoclave in which 0.30 g catalyst, 5.0 g phenol and 30 mL EtOH were mixed. The reaction mixture was stirred vigorously at 1200 rpm to eliminate the diffusion effects. In each run of the experiments, the reaction mixture was sampled every 1 h. The products were analyzed by a gas chromatograph (GC 9800) equipped with a FID. The conditions for the analysis were as follows: 50 m AT FFAP capillary column, injector temperature 493 K, oven temperature 373 K, detector temperature 523 K, and 30 mL/min N_2 as the carrier gas. The reproducibility of the results was checked by repeating the runs at least three times on the same batch of catalyst and for another three times for a different batches of catalyst and was found to be within acceptable limits ($\pm$5% for the same batch of the catalyst and $\pm$10% for the different batches of the catalyst).

Figure 1 shows the reaction profiles of the phenol hydrogenation over the Pd–La–B at $\chi_{La} = 1\%$ and the undoped Pd–B catalysts, respectively. Besides the cyclohexanone as the main product, both cyclohexanol and cyclohexane were identified in the reaction mixture, indicating that the phenol hydrogenation under the present conditions might progress through the following scheme:[8]



No significant 1-hydroxycyclohexene was detected throughout the reaction progress, showing that it was a very active intermediate which might be easily converted into either the cyclohexanone via isomerization or the cyclohexanol via further hydrogenation. The cyclohexane was produced by cyclohexanol hydrogenolysis. Obviously, the Pd–La–B catalyst exhibited much better selectivity to cyclohexanone than the undoped Pd–B. The maximum cyclohexanone yield over the Pd–La–B catalyst could reach 79% while only less than 38% cyclohexanone yield could be obtained over the undoped Pd–B catalyst. The poor selectivity to cyclohexanone on the unpoded Pd–B catalyst was mainly attributed to the formation of cyclohexane, a product resulted from the deep hydrogenation of cyxlohexanol. The promoting effect of the La-dopant on the selectivity to cyclohexanone could be mainly attributed to the electron donation of La_2O_3 to the metallic Pd. Since the cyclohexanone was adsorbed on the catalyst surface adsorbed mainly through an "end-on" O–Pd coordination,[9] the high electron density on the Pd active center may repel the lone electron pair on the oxygen. This may facilitate the desorption of the cyclohexanone from the catalyst surface and in turn, may inhibit its deep hydrogenation. However, at higher concentration of the La modifier, the selectivity of cyclohexanone decreased since the basic La_2O_3 was unfavorable for the acid catalyzed isomerization of 1-hydroxycyclohexene to cyclohexanone.[10]

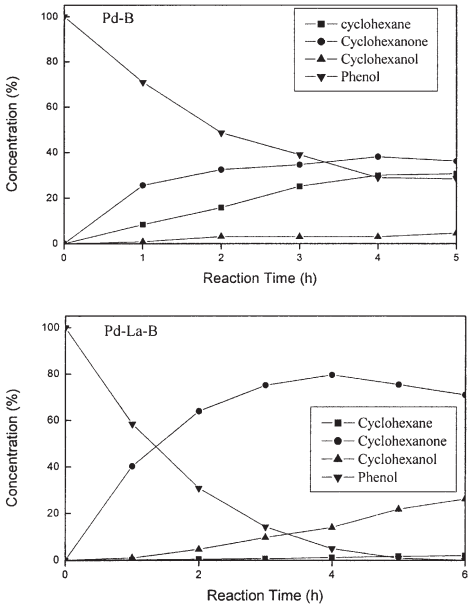


Figure 1. Reaction profiles of the phenol hydrogenation over the Pd–B and Pd–La–B ($\chi_{La} = 1\%$) catalysts. Reaction conditions are described in the text.

From the change of the phenol conversion with the reaction time, one could also see that the Pd–La–B catalyst was more active than the undoped Pd–B. Meanwhile, the initial hydrogen uptake rate per gram Pd (R_m = mmol/h·g Pd) and the initial hydrogen uptake rate per m^2 of the active surface area determined by hydrogen chemisorption (R_S = mmol/h·m^2 Pd) also confirmed the above conclusion. Furthermore, the activity of the undoped Pd–B catalyst decreased rapidly with the increase of cyclohexanone content. Only 71% phenol conversion could be obtained. The high surface area and the amorphous alloy structure of the Pd–La–B catalyst could be accounted for the promoting effect of the La-dopant on the activity. Meanwhile, as discussed above, the electron-donation of the La_2O_3 to the Pd active center could facilitate the cyclohexanone desorption from the catalyst surface and thus retard the deactivation of the Pd–La–B catalyst. Detailed studies are being underway.

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