

Study of The Pd-B/ γ -Al₂O₃ Amorphous Alloy Catalyst

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Abstract: The Pd-B/ γ -Al₂O₃ amorphous alloy catalyst and Pd/ γ -Al₂O₃ crystalline metal catalyst were prepared by KBH₄ reduction and routine impregnation, respectively. Pd-B/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ catalysts were characterized by XRD and SEM. It was found that the catalytic activity of the Pd-B/ γ -Al₂O₃ amorphous alloy catalyst was higher than that of the Pd/ γ -Al₂O₃ crystalline metal catalyst in the anthraquinone hydrogenation.

Keywords: Routine impregnate, KBH₄ reduction, anthraquinone hydrogenation.

Schlesinger *et al.*¹ found that the black pellets were catalytically active when they electrolysed water with a mixture of cobalt (nickel) salt and KBH₄ solution as catalyst. In the 1960', Brown² found that the pellets mentioned above had catalytic activity similar to Raney Ni in hydrogenation reactions. Morop *et al.*³ proved that these black pellets were Ni-B amorphous alloy.

Since Smith⁴ reported the catalytic character of amorphous alloy for the first time, people have been interested in studying the amorphous catalyst⁵⁻⁷. Much attention was paid to study Ni (Co, Fe)-B (P) amorphous alloy. In this paper, a new Pd-based catalyst, the Pd-B/ γ -Al₂O₃ amorphous alloy catalyst, was prepared by the impregnation and chemical reduction by KBH₄. Its amorphous character was determined by XRD and SEM. During the anthraquinone hydrogenation, the hydrogenation efficiency over Pd-B/ γ -Al₂O₃ amorphous alloy catalyst reduced by KBH₄ is much higher than the corresponding Pd/ γ -Al₂O₃ crystalline metal catalyst reduced by hydrogen.

Experimental

The Pd-B/ γ -Al₂O₃ amorphous alloy catalyst was prepared by the following procedures: γ -Al₂O₃ pellets (20-30meshs) were impregnated with PdCl₂ aqueous solution and dried at room temperature for 24 h. The Pd²⁺ on the support was then reduced by adding 1mol/L KBH₄ solution dropwise. The reaction lasted about 0.5 h until no significant

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bubbles were observed in the solution. The resulting Pd-B/ γ -Al₂O₃ sample was washed thoroughly with distilled water first and then with alcohol subsequently.

For comparison, a Pd/ γ -Al₂O₃ crystalline metal catalyst was prepared in the same procedure as the reference 8.

Results and Discussion

The catalytic activity of the as-prepared Pd-B/ γ -Al₂O₃ amorphous alloy catalyst was measured using the hydrogenation of anthraquinone as a probe and by comparing to that of the corresponding Pd/ γ -Al₂O₃ crystalline metal catalyst. The hydrogenation of anthraquinone was carried out as follows. In a glass reactor, about 0.88 g catalyst was mixed with 10 mL anthraquinone work solution and 20 mL/min hydrogen stream was introduced at 333 K for 2 h. After hydrogenation, the reaction mixture was cooled to room temperature. The anthrahydroquinone solution was filtered. Then it was oxidized with oxygen to reform the original anthraquinone with concomitant formation of hydrogen peroxide. The hydrogen peroxide was then extracted by distilled water and titrated by KMnO₄ solution in acetic medium. The result of catalytic activity of the samples was shown in **Table 1**.

Table 1 The result of activity of catalysts

	Pd-B/ γ -Al ₂ O ₃	Pd/ γ -Al ₂ O ₃
Hydrogenation efficiency (g/L)	11.01	8.79

From **Table 1**, we learnt that the Pd-B/ γ -Al₂O₃ amorphous alloy catalyst was much more effectively than the Pd/ γ -Al₂O₃ crystalline metal catalyst in hydrogenation of anthraquinone, the activity rose up to 25%.

The XRD pattern of the fresh Pd-B/ γ -Al₂O₃ sample revealed that, except three peaks around $2\theta = 37.6, 45.8, 66.7^\circ$ which resulted from γ -Al₂O₃ support, only one broad peak around $2\theta = 40^\circ$ was observed, indicating a typical amorphous character of the sample, but the XRD pattern of Pd/ γ -Al₂O₃ sample showed a sharp peak around $2\theta = 40^\circ$, indicating a typical crystalline character of the sample.

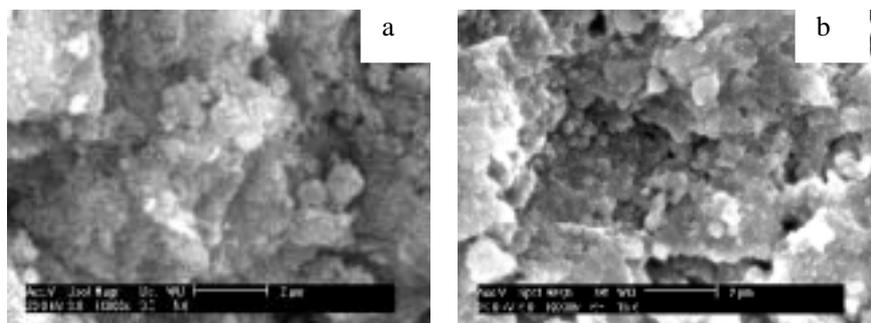
Figure 1 SEM morphologies of samplesa. Pd-B/ γ -Al₂O₃ b. Pd/ γ -Al₂O₃

Figure 1 shows the difference in the SEM morphologies of the Pd-B/ γ -Al₂O₃ amorphous alloy sample and Pd/ γ -Al₂O₃ crystalline metal sample. For the Pd-B/ γ -Al₂O₃ sample, the support was covered by a layer of the cotton like clusters of Pd-B amorphous alloy, in form thousands of small particles, whereas there was block like appearance on the surface of γ -Al₂O₃ because Pd/ γ -Al₂O₃ crystalline metal catalyst was prepared by calcining at 873 K. Being calcining at high temperature, made the active content of catalyst being sintered.

We believe that the Pd-B/ γ -Al₂O₃ amorphous alloy catalyst has the catalytic property which closely related to high dispersion of Pd on the surface of γ -Al₂O₃. In addition, amorphous alloy with short-range ordering and long-range dis-ordering structure which may provide the benefit to adsorb the reactant on the surface of catalyst. On the other hand, the well-distributed active sites are high legend-deficiency, well cooperated each other⁹. All of above reasons made to raise the catalytic activity of Pd.

Conclusion

The catalytic activity of the Pd-B/ γ -Al₂O₃ amorphous alloy catalyst reduced by KBH₄ was higher than that of Pd/ γ -Al₂O₃ crystalline metal catalyst calcined at 873 K, reduced by H₂. The high activity of the Pd-B/ γ -Al₂O₃ amorphous alloy catalyst is closely related to high dispersion of active content on the surface of the support.

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