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# A Novel Ultrafine Ru-B Amorphous Alloy Catalyst for Glucose Hydrogenation to Sorbitol

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**Abstract:** An ultrafine Ru-B amorphous alloy catalyst was prepared by chemical reduction with $KBH_4$ in aqueous solution, which exhibited perfect selectivity to sorbitol (~100%) and very high activity during the liquid phase glucose hydrogenation, much higher than the corresponding crystallized Ru-B, the pure Ru powder, and Raney Ni catalysts. The correlation of the catalytic activity to both the structural and surface electronic characteristics was discussed briefly.

**Keywords:** Ru-B amorphous catalyst, hydrogenation, glucose, sorbitol.

Glucose hydrogenation to sorbitol is of great industrial importance since sorbitol is widely used as the additive in foods, drugs, cosmetics, and as an intermediate in the vitamin C synthesis. Besides small amount of sorbitol can be obtained naturally from red seaweed and some fruits, commercial large scale production of sorbitol has always relied on the hydrogenation of glucose, in which Raney Ni catalyst is frequently used[1-3]. In order to enhance the catalytic efficiency and overcome the environmental pollution, great attempts have been made to develop better catalysts instead of Raney Ni, such as supported noble metal catalysts[4-6]. Recently, amorphous alloy catalysts have caused much attention owing to their excellent activity and selectivity in various hydrogenating reactions[7-9]. Most of studies are focused on the Ni- and Co-based amorphous alloy catalysts. However, very little attention has been paid to Ru-based amorphous alloy catalysts. In this paper, we reported a novel ultrafine Ru-B amorphous alloy catalyst which exhibited very high activity during the glucose hydrogenation.

## Experimental

The Ru-B amorphous alloy was prepared by reducing $RuCl_3$ with excess $KBH_4$ ($BH_4^-/Ru^{3+}$ molar ratio = 5:1) in aqueous solution at room temperature. 2.0 mol/L $KBH_4$ solution containing 0.2 mol/L NaOH was added dropwise into $RuCl_3$ solution under magnetic stirring. The reaction was lasted for about 1.5 h to ensure the complete reduction of $Ru^{3+}$ in the solution. Then, the resulting Ru-B black solid was washed

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thoroughly with $H_2O$ until pH = 7 and finally, kept in water until the time of use. The corresponding crystallized Ru-B sample was obtained by treating the fresh Ru-B sample at 873 K for 2 h in the $H_2$ flow. For comparison, the Ru powder catalyst was also prepared by chemical reduction of $RuCl_3$ with $NH_2NH_2$ in NaOH solution at 373 K. Raney Ni was commercially available and used without additional activation.

The composition of catalysts was determined by ICP. Its surface morphology and particle size were both evaluated by transmission electron micrograph (TEM). Its structure was investigated by both X-ray diffraction (XRD) and selective area electronic diffraction (SAED). The surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS) with $Si_{2P}$ = 103.3 eV as a reference. Since the peak of metallic Ru in $Ru3d_{3/2}$ level just covered that of $C_{1S}$, only the peak in $Ru3d_{5/2}$ level was employed.

Liquid phase hydrogenation was carried out at 353 K and 4.0 MPa $H_2$ pressure in a stainless autoclave containing 50 mL 50% glucose in aqueous solution and 0.3 g Ru-based catalysts or 1.0 g Raney Ni. Each reaction was lasted 2 h, during which, the stirring rate was kept at 1800 rpm to exclude the diffusion effect. The initial activity of the hydrogenation was obtained by measuring the drop of the $H_2$ pressure with the reaction time which was then converted into the hydrogen uptake rate by using the ideal gas equation. The activity was expressed in both the specific activity ($R^m$, mmol/h·g) and the areal activity ($R^S$, mmol/h·$m^2$), respectively. $R^S$ could display the difference in the nature of the active sites since the dispersion effect has been excluded. In concept, the active surface area should be employed, as detected by either hydrogen or CO chemisorption. For the unsupported catalysts like the present ultrafine Ru-B amorphous alloy catalyst, the BET surface area may roughly be used instead of the active surface area. The products were analyzed by a gas chromatograph equipped with a 25 m OV 101 capillary column and a FID, which demonstrated that, under the present conditions, the sorbitol was the only product regardless of the catalysts, showing that the selectivity to sorbitol is perfect (100%). The glucose conversion was determined by a common chemical titration with Fehlings agent.

## Results and Discussion

The ICP analysis gave the composition of the fresh Ru-B sample of $Ru_{88.9}B_{11.1}$. The SAED picture of the fresh Ru-B sample displayed various diffractional circles, indicating that it was present in a typical amorphous structure, which was further confirmed by XRD patterns. For the fresh Ru-B sample, only one broad peak around $2\theta = 44^o$ indicative of the amorphous structure[10] was observed. When the sample was treated at elevated temperatures from 673 K to 873 K, the original broad peak disappeared gradually and various diffractional peaks appeared. Both the strength and the number of the diffractional peaks increased with the increase of the treating temperature and reached maximum at 873 K. These results demonstrated that the Ru-B amorphous alloy began to crystallize at 673 K and reached completion at 873 K. Owing to the deep decomposition of the Ru-B alloy, only the metallic Ru was identified on the XRD pattern of the crystallized Ru-B sample.

As shown in **Figure 1**, all the Ru species in the Ru-B amorphous alloy were present in the metallic state corresponding to the binding energy (BE) of 279.4 eV. However, the B species were present in forms of the B alloying with Ru, $NaBO_2$ and $B_2O_3$ corresponding to the BE of 188.3 eV, 191.5 eV and 193.0 eV, respectively[11]. In comparison with the standard BE values of the pure B and Ru, 1.1 eV positive shift and 0.6 eV negative shift in the BE of the alloying B and metallic Ru were observed, showing that partial electrons transferred from B to Ru in the Ru-B amorphous alloy. The relatively less shift in the BE of metallic Ru may be attributed to the much bigger size of the Ru atoms than that of the B atoms.

**Figure 1** XPS spectra of the Ru-B amorphous alloy catalyst

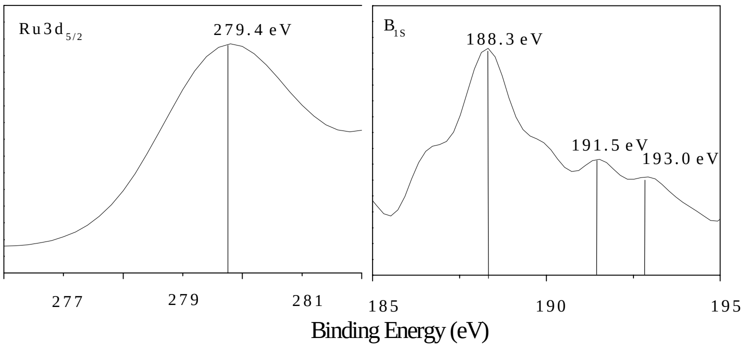


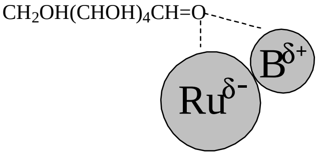
**Table 1** Some properties of the asprepared catalysts[a]

| Sample | $S_{BET}$ ($m^2$/g catal.) | Conversion (%) | $R^m$ (mmol/h·g Ru) | $R^S$ (mmol/h·$m^2$) |
|---|---|---|---|---|
| Fresh Ru-B | 12.71 | 95.1 | 504.2 | 39.7 |
| Cryst. Ru-B[b] | 5.70 | 23.1 | 57.9 | 10.2 |
| Ru powder | 8.06 | 22.2 | 57.0 | 7.1 |
| Raney Ni | 106 | 16.7 | 10.6 | 0.1 |

[a]Reaction conditions: 0.3 g Ru-based catalysts or 1.0 g Raney Ni, 50 mL glucose aqueous solution (50% w/w), T = 353 K, $PH_2$ = 4.0 MPa, reaction time = 2.0 h. [b]The crystallized Ru-B sample obtained by treating the fresh Ru-B sample at 873 K in $N_2$ flow for 2 h.

As shown in **Table 1**, the Ru-B amorphous catalyst exhibited excellent activity during the glucose hydrogenation. The specific activity ($R^m$) of the Ru-B amorphous catalyst was nearly 9 times higher than either the crystalline Ru-B or the pure Ru powder catalysts, and 50 times higher than Raney Ni catalyst. In accordance, the glucose conversion over the Ru-B amorphous catalyst was also much higher than that over any other three catalysts. Over the Ru-B amorphous catalyst, the glucose conversion reached 100% within 2.5 h. However, over other catalysts, much longer reaction time (> 5 h) was needed to get 100% glucose conversion. Furthermore, the Ru-B amorphous catalyst could be used repetitively during the glucose hydrogenation for more than 13 times without significant deactivation, showing its excellent durability under the present conditions. These results demonstrated that the as-prepared Ru-B amorphous catalyst may be used instead of Raney Ni in the glucose hydrogenation to produce sorbitol owing to its higher activity and longer lifetime which could compensate its higher cost.

The higher activity of the Ru-B amorphous catalyst than that of either the crystallized Ru-B or the pure Ru powder catalyst may partially be attributed to its higher dispersion, as shown in **Table 1**. The main reason may be the modification of the nature of Ru active sites by the alloying B since **Table 1** demonstrated that the $R^S$ of the Ru-B amorphous catalyst was also much higher than that of any other Ru-based catalysts. On one hand, it could be attributed to the unique amorphous structure which has been proved to be favorable for the hydrogenation[7]. On the other hand, it could be attributed to the electronic interaction between B and Ru in the Ru-B amorphous alloy, making Ru electron-enriched while B electron-deficient, as confirmed by aforementioned XPS spectra. Thus, the C=O group in the glucose molecule may be adsorbed on the Ru-B alloy *via* a side-bonding model, as shown in the following diagram[12].



The higher electron density on the metallic Ru may repel the lone pair electrons on the oxygen atom in C=O group[13]. Thus, less molecules may be adsorbed by the active sites of Ru which may favor the competitive adsorption of hydrogen and, in turn, enhance the activity. Our kinetic studies revealed that the glucose hydrogenation was zero-order with respect to glucose, while it was first-order with respect to hydrogen. Furthermore, the side-bond between O and B was also favorable for the hydrogenation, since the electron-deficient B may attract partial electrons from the C=O bond, making it activated. Detailed studies are being underway.

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