Note

Efficient conversion of D-glucose into D-sorbitol over MCM-41 supported Ru catalyst prepared by a formaldehyde reduction process

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ABSTRACT

Ru/MCM-41 catalyst prepared by an impregnation–formaldehyde reduction method showed higher catalytic activity and sorbitol selectivity than other catalysts in the hydrogenation of glucose. SEM and XRD indicated the partial surface properties of Ru/MCM-41. Moreover, Ru dispersion and Ru surface area of Ru/MCM-41 were determined by pulse chemisorption, and the result further proved that Ru/MCM-41 had higher catalytic activity. A catalyst recycling experiment demonstrated that Ru/MCM-41 was a better catalyst and it could be reused three or four times. A speculated mechanism was proposed to illustrate the detailed process of D-glucose hydrogenation to produce sorbitol.

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1. Introduction

D-Sorbitol formed by the reduction of the free aldehyde group of D-glucose has been widely used in the food industry, as well as drugs, cosmetics, toothpaste and so on. Moreover, D-sorbitol is an important intermediate for the production of L-ascorbic acid.[1] The source of raw materials for preparation of D-sorbitol is very abundant in the pulp and paper industry. In addition, D-sorbitol can be further degraded into lower polyols that are downstream products in the petrochemical industry,[2] which could increase the added value of D-sorbitol (see Scheme 1).

The catalytic hydrogenation of D-glucose into D-sorbitol has been well studied in the literature. Experimental results showed that D-glucose is converted to D-sorbitol according to the Langmuir–Hinshelwood rate law where the reaction between adsorbed D-glucose and dissociated hydrogen was rate determining.[3] The most commonly used catalyst for this process is Raney nickel,[4–6] which usually is activated with lye. Moreover, Raney nickel could be formed with different addition agents such as Cr, Fe, and Mo.[7] However, Ni catalysts show deactivation after recycling several times during the hydrogenation of D-glucose. Like other hexitols, sorbitol also forms chelate complexes with nickel (or Fe, Cu) easily in aqueous solution; these complexes are stable under alkaline conditions, which results in nickel being left in the sorbitol solution.[6,8,9] Most important is that the nickel must be completely removed from the sorbitol solution when it is used in the food industry, or as medicine or cosmetics, which results in high

additional costs. Therefore, researchers begin to look for new catalysts that could prevent metal and support leaching in the acidic and chelating reaction medium. Furthermore, these new catalysts should be resistant to metal sintering and poisoning.

In recent years, low ruthenium loading catalysts have been found to replace nickel-based catalysts, which show much less or no deactivation.[5,10,11] Although ruthenium is much more expensive than nickel, it may be of interest for industrial uses as it is more active than nickel, and this catalyst shows no leaching. Hoffer et al. studied selective hydrogenation of D-glucose by carbon supported Ru catalysts when compared with that of Raney-type Ni.[12] The authors found that the Ru/C catalysts displayed higher activities, and that Ru did not leach into the reaction solution. The activity of the catalyst was proportional to the Ru surface area and independent of the preparation method. The Cr/Fe promoted Raney-type Ni catalyst exhibited the highest activity, but significant Fe was detected in the reaction mixture. The catalytic activity of Ru/ supported catalysts partially depended on the organic promoters, precursors (ruthenium acetate[13] and ruthenium trichloride[14]) and supports (activated carbon,[10,12] Al$_2$O$_3$[15] and SiO$_2$[16]). Relevant research showed that the addition of organic promoters not only increased the adsorption amount of ruthenium, but also increased the adsorption strength of ruthenium on the support, and improved the surface properties of the Ru/C catalysts. Finally, the catalytic hydrogenation activity was enhanced.

Conventional impregnation and the incipient wetness techniques are the methods reported most frequently for the preparation of supported ruthenium catalysts. In this paper, MCM-41 molecular sieves are selected as the carrier, and the catalyst, Ru/ MCM-41, has been prepared by an impregnation–formaldehyde

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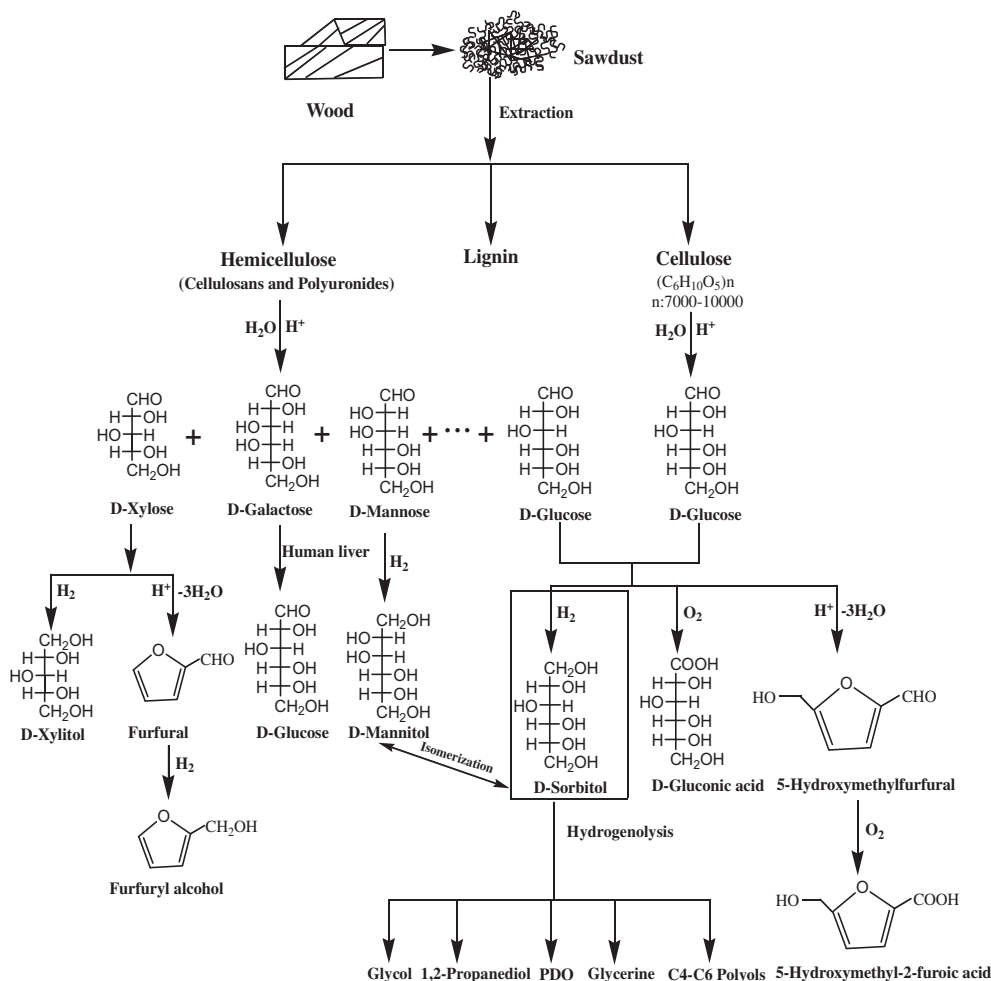
Scheme 1. Reaction network of the preparation and conversion of D-sorbitol.

reduction method, which is very simple and practical in comparison with the hydrogen reduction process, which is conducted at high temperatures and pressures. In contrast, the Ru/MCM-41 catalyst can be produced in large quantities by using a formaldehyde reduction method and it exhibits higher catalytic activity after being recycled several times. Regeneration involved only simple drying, without other complicated processing. Part of the unreduced catalyst could also be reduced when they are used in H_2 atmosphere conditions. In the present work, the Ru/MCM-41 catalyst has been applied in the hydrogenation of D-glucose to D-sorbitol, and its activity and selectivity are compared with those of other catalysts such as Ru/C. Pulse chemisorption, X-ray diffraction (XRD) and SEM are used to characterize the texture and surface properties of catalyst.

Fig. 1 shows the XRD patterns of MCM-41 and Ru/MCM-41. The MCM-41 carrier was composed of silica and alumina with the Si/Al ratio of 27. As shown in line (b), only a dispersion peak appeared at about 43° in Ru/MCM-41 prepared by formaldehyde reduction process without high temperature processing. The reason for this has to do with Ru loading, if the Ru loading is less than 5 wt %, Ru could hardly be observed as it was covered by the support as determined by XRD. Because the actual content of Ru in Ru/MCM-41 was 3.80 wt %, only a small peak appeared at about 43° in Ru/MCM-41. In related articles, if the catalyst was treated with high temperatures, the original dispersion peak disappears gradually and a series of crystalline phase peaks appeared.[16] When comparing line (a) with line (b), Ru/MCM-41 just had an obvious crystal-
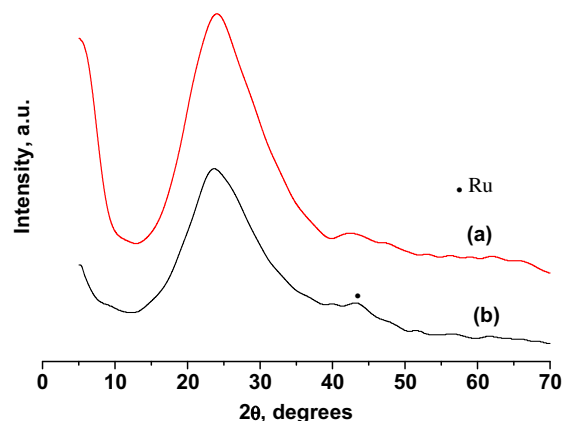

Figure 1. Powder XRD patterns of the carrier and catalyst: (a) MCM-41 and (b) Ru/MCM-41.

lite diffraction peak, and a distinct peak from the oxidation state of Ru did not appear.

Fig. 2 gives a scanning electron micrograph at high magnification showing the texture of Ru/MCM-41(fresh and used several times) and Ru/C(fresh). As can be seen from the picture (a–d), there was only little active Ru lost after being used once. Active Ru was stably loaded in the support MCM-41, which did not show significant leaching after being recycled several times. When Ru/MCM-41
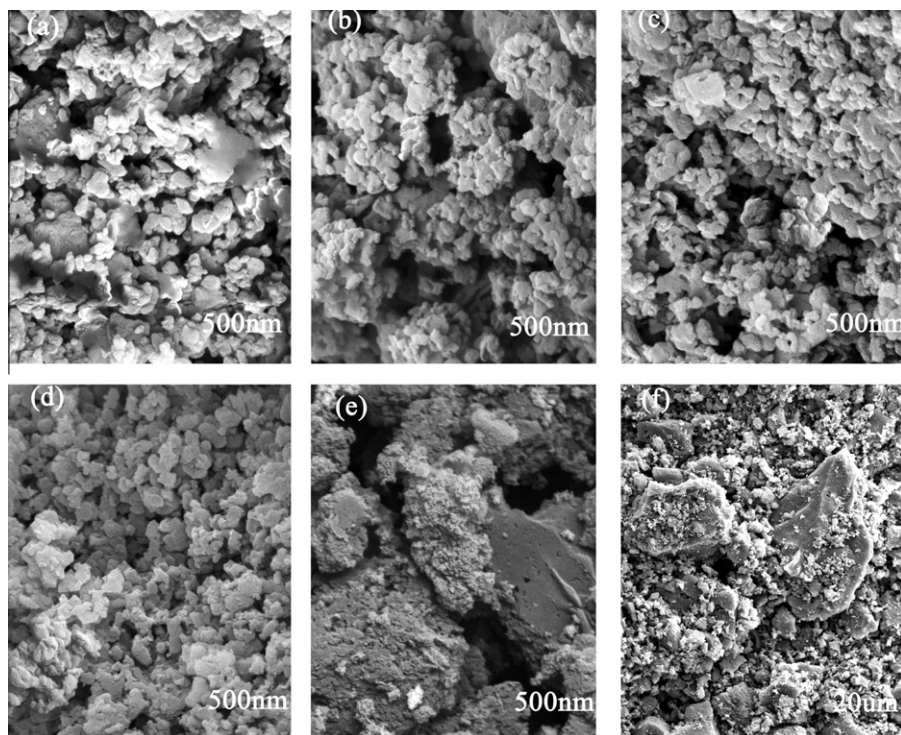
Figure 2. Scanning electron micrographs of catalysts: (a) Ru/MCM-41(fresh), (b) Ru/MCM-41(used once), (c) Ru/MCM-41(used twice), (d) Ru/MCM-41(used four times), and (e and f) Ru/C(fresh).

catalyst was used four times, there was remarkable agglomeration. Comparing Fig. 2(a) with Fig. 2(e or f), the results showed that Ru was uniformly distributed in support MCM-41 compared to activated carbon. From the above analysis, the basic characteristic of catalyst Ru/MCM-41 was stable and better than those of other catalysts.

Table 1 gives the main characteristics of the Ru/MCM-41 and Ru/C catalysts. The Ru/MCM-41(fresh) catalyst showed the highest metal dispersion, metallic surface area (m^2/g sample) and metallic surface area (m^2/g metal) when compared with those of other catalysts. The metal dispersion, metallic surface area (m^2/g sample) and metallic surface area (m^2/g metal) of Ru/MCM-41 catalyst decreased obviously after used being twice or four times. This was partly because a small amount of active Ru leached from the catalyst and some particles agglomerated when recycling times increased. Comparison of characteristic data of Ru/MCM-41(fresh) with Ru/C(fresh) and Ru/MCM-41 (fresh) showed much higher catalytic activity. The above experimental results were in agreement with the outcome shown in Fig. 5, and the activity of the catalyst was proportional to the dispersion of Ru and its surface area (m^2/g sample and m^2/g metal).

Different influencing factors were investigated in the conversion of D-glucose into D-sorbitol catalyzed by Ru/MCM-41. The effects of reaction time on the hydrogenation of D-glucose are shown in Fig. 3. The glucose conversion increased quickly when the reaction time was prolonged; at 3 h glucose was completely
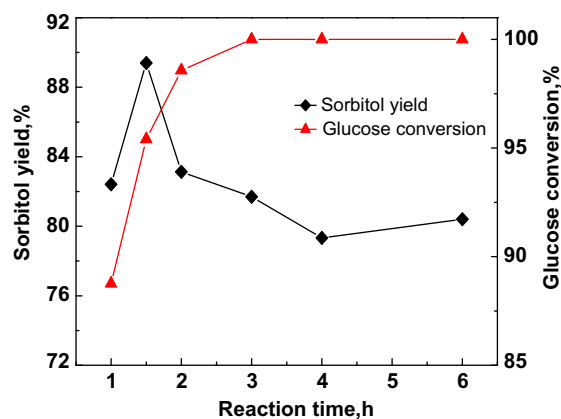

Figure 3. Effect of reaction time on the hydrogenation of D-glucose; 2.5 g D-glucose, 0.25 g Ru/MCM-41, 25 mL aqueous solution, 120 °C, 3 MPa H_2.

converted. At the early period of the hydrogenation, glucose was translated into sorbitol and the sorbitol yield reached the highest level at 1.5 h. The sorbitol yield declined as the reaction progressed. Perhaps the generated sorbitol is isomerized into mannitol during this process. In the meantime, a little sorbitol was degraded into lower alcohols such as ethylene glycol, glycerin, propanediol and other C4–C6 polyols. Hence, the optimum reaction time was 1.5 h.

Table 1
Characteristics of the applied catalysts

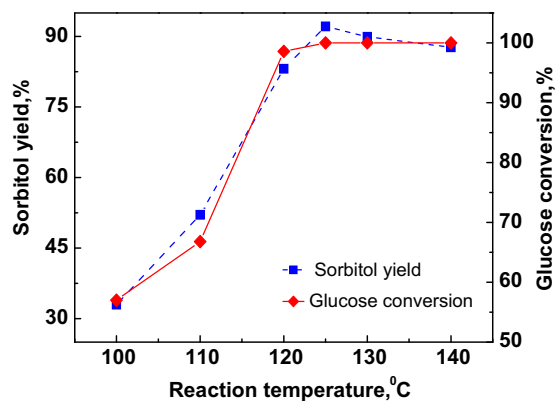| Catalyst	Metal dispersion (%)	Metallic surface area (m^2/g sample)	Metallic surface area (m^2/g metal)
Ru/MCM-41(fresh)	1.2587	0.2299	4.5980
Ru/MCM-41(used twice)	0.2438	0.0445	0.8908
Ru/MCM-41(used four times)	0.2135	0.0390	0.7801
Ru/C(fresh)	0.7592	0.1387	2.7735

Figure 4. Effect of reaction temperature on the hydrogenation of D-glucose; 2.5 g D-glucose, 0.25 g Ru/MCM-41, 25 mL aqueous solution, 2 h, 3 MPa H_2.

Figure 6. Effect of recycling times of catalyst on the hydrogenation of D-glucose; 2.0 g D-glucose, 0.2 g Ru/MCM-41, 20 mL aqueous solution, 120 °C, 2 h, 3 MPa H_2.

Fig. 4 illustrates the influence of reaction temperature on sorbitol yield and glucose conversion. At the initial stages, sorbitol yield increased steeply with a rise of temperature. When the temperature was higher, glucose underwent several degradation pathways, which produced some other products, leading to a decrease in sorbitol yield. The principal reaction was accomplished as the temperature reached 120 °C; the sorbitol yield was as high as 92.13% at 125 °C.

The relationship between catalyst usage and sorbitol yield or glucose conversion are indicated in Fig. 5. When there was no catalyst added, little sorbitol was produced during the reaction. The sorbitol yield increased with an increase in the amount of catalyst, when further increasing catalyst amount, the yield did not change significantly, and glucose had already been converted completely. In this experiment, the amount of reactant glucose was constant, when excessive dosage of catalyst was employed, no high conversion rate could be found in this experiment. Hence the sorbitol yield was relatively stable when the dosage of catalyst was 20 wt %.

The Ru/MCM-41 catalysts were recycled after each experiment by filtering the final solution and washing with de-ionized water. Catalysts were only dried at 50 °C in vacuum oven without other complex processing. As shown in Fig. 6, the catalytic activity of Ru/MCM-41 decreased slightly after being reused once; the sorbitol yield decreased from 83.13% to 68.21%. The main reason was that some reaction products could be bonded and accumulated on the surface of catalyst, which led to a decline in catalyst activity. Therefore, after recycling the catalyst three or four times, the
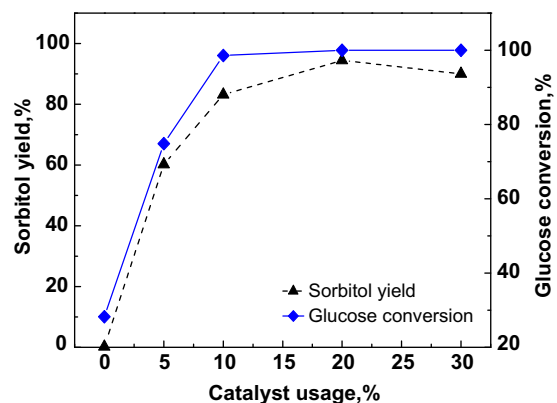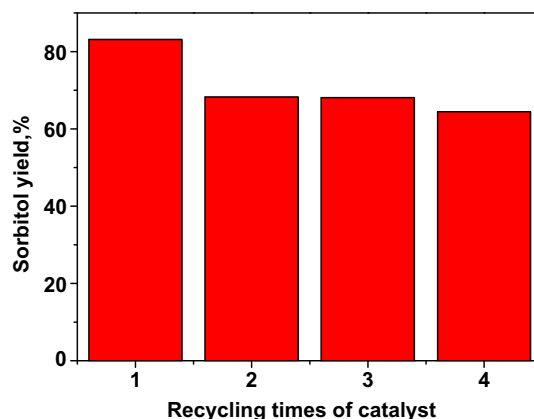
sorbitol yield was not found to reduce significantly. This result showed that Ru could be well loaded in MCM-41 support, and it could maintain higher catalytic activity and led to the conclusion that the Ru/MCM-41 catalyst had better activity and stabilization than that of other catalysts.

Comparing the catalytic activity of Ru/MCM-41 with other catalysts (Fig. 7) Ru/MCM-41 exhibited the highest catalytic activity under the same reaction condition; alumel showed the lowest catalytic activity. The catalytic activity of these catalysts ranged in descending order: Ru/MCM-41 > Ru/C > Pd/C > Nickel powder > alumel. The sorbitol yield and glucose conversion catalyzed by Ru/MCM-41 were the highest, and the product selectivity also was the highest. Ru/C revealed relatively high catalytic performance, the sorbitol selectivity was up to 59.7%. While catalyst Pd/C and Nickel powder showed lower sorbitol selectivity, this may be due to the weaker catalytic ability of Pd and Ni by comparison with Ru. As determined from the above analysis, the Ru/MCM-41 was a good catalyst in glucose hydrogenation.

Glucose hydrogenation over Ru/MCM-41 catalyst is a gas–liquid–solid three-phase catalytic reaction. As shown in Scheme 2, the mechanism of reducing glucose with H_2 on the catalyst surface is proposed to proceed as follows: First, H_2 was spread from air to the liquid membrane. Then H_2 dissolved in the gas–solution interface and it spread from the liquid membrane to glucose in the liquid phase. It is supposed that H_2 did not react with the carbonyl group of glucose, but instead was adsorbed by the active centers of

Figure 5. Effect of catalyst usage on the hydrogenation of D-glucose; 2.5 g D-glucose, 25 mL aqueous solution, 120 °C, 2 h, 3 MPa H_2.
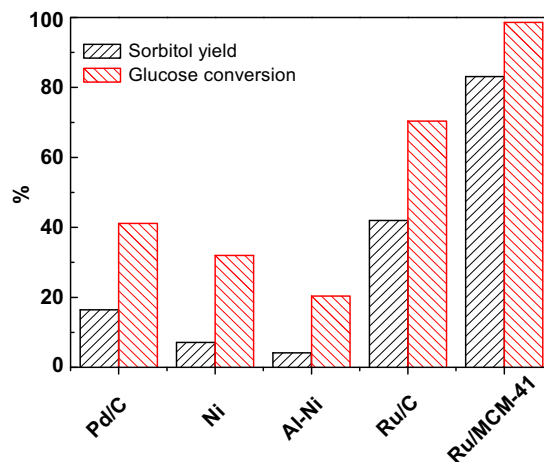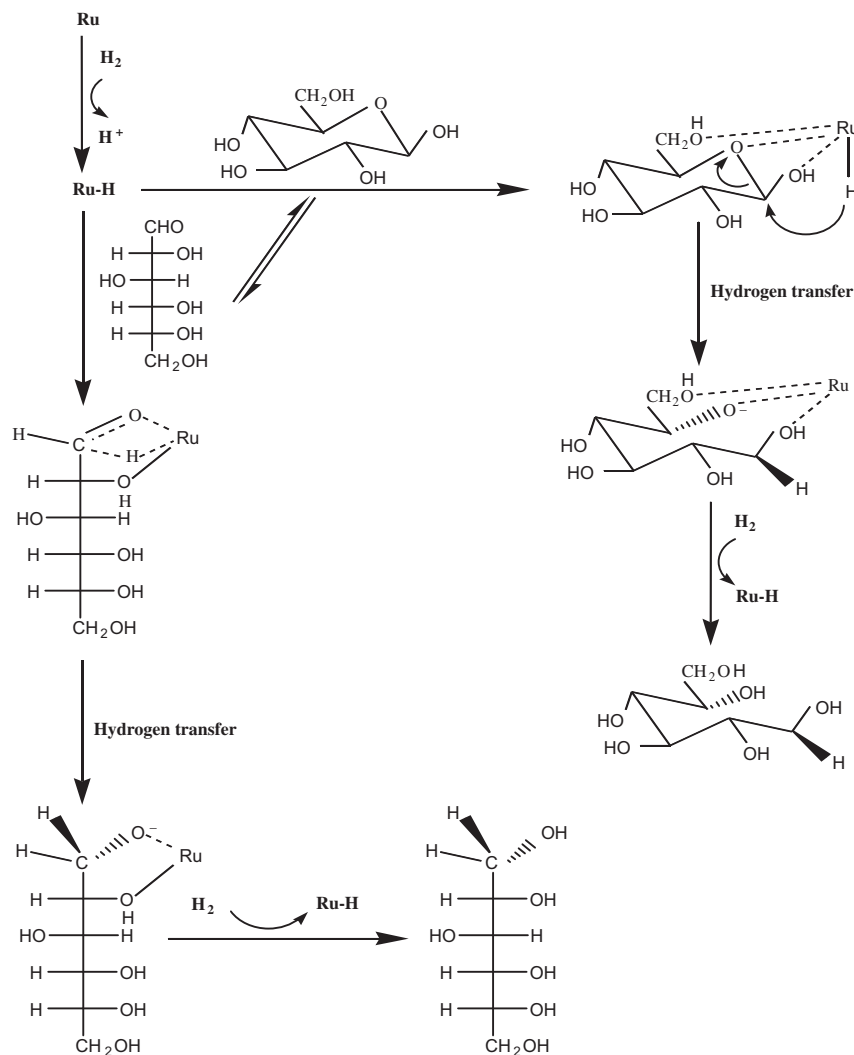

Figure 7. Effect of different catalysts on the hydrogenation of D-glucose; 2.5 g D-glucose, catalyst usage: 10%, 25 mL aqueous solution, 120 °C, 2 h, 3 MPa H_2.

Scheme 2.

the catalyst, producing activated H on the catalyst. Finally, glucose reacts with the activated H on the surface of catalyst, which is an irreversible reaction, and then the product desorbs from the catalyst and diffuses into the liquid phase. Therefore, glucose hydrogenation proceeds through H_2 dissolution, H_2 diffusion, H_2 adsorption on the active centers of the catalyst, to produce activated H. Finally, the carbonyl group in glucose reacted with the activated H on the surface of catalyst to produce D-sorbitol.

In conclusion, the Ru/MCM-41 catalyst prepared by an impregnation–formaldehyde reduction method showed higher catalytic activity in glucose hydrogenation, and exhibited greater product selectivity than other catalysts such as Ru/C, alumel, Ni powder, and Pd/C. Experimental results showed that the highest sorbitol yield, 94.43%, could be obtained at 120 °C when the amount of catalyst was 20% (based on glucose) and the reaction time was 2 h; the glucose conversion was as high as 100%. SEM revealed that Ru is well dispersed on the surface of MCM-41, the only dispersion peak appeared at about 43° in Ru/MCM-41 from XRD spectrum. Moreover, the results of Ru dispersion and Ru surface area (m^2/g sample and m^2/g metal) of Ru/MCM-41 further proved that Ru/MCM-41 had a higher catalytic activity than that of other catalysts. A catalyst recycling experiment demonstrated that Ru/MCM-41 sustained high catalytic activity after reusing several times. A proposed mechanism for D-glucose hydrogenation over Ru/MCM-41 catalyst to sorbitol involved a gas–liquid–solid three-phase catalytic reaction, in which the carbonyl group in glucose reacted with activated H as the main step.

2. Experimental

2.1. Materials

Ru/C (5 wt %), alumel (Ni content: 47%) and 5 wt % Pd/C were purchased from Aladdin Reagent Limited Company. A.P. reagents, including nickel powder and $RuCl_3$ were purchased from Tianjin Kermel Chemical Reagents Limited Company. Ru/MCM-41 (5 wt %) catalyst was prepared by an impregnation–formaldehyde reduction method. MCM-41 molecular sieve (alumina content: 3%) was employed as support material to prepare the homemade Ru/MCM-41 catalyst. $RuCl_3$ was selected as the precursor of Ru. First, $RuCl_3$ was dissolved with 5 wt % HCl, then MCM-41 was added. After being immersed for a while, the pH value of the solution was adjusted to 5–7 by 10 wt % NaOH, which was conducive to formaldehyde reduction. After completion of reduction, the obtained product was filtered, washed with demineralized water until chloride was washed out as detected by $AgNO_3$. The product was then dried overnight in a vacuum oven at 50 °C. During the whole process, the color of the sample changed from rufous to dark green, then it was light gray after reduction.

2.2. Catalyst characterization

Powder X-ray powder diffraction (XRD) was performed in a Bruker D8 Advance diffractometer using CuKα radiation. The operating voltage and current were 40 kV, 40 mA, respectively. The step length was 0.02° with scanning rate of 2° min^{-1}. The distribution of Ru particles in catalyst Ru/MCM-41 and Ru/C were determined with a scanning electron microscope (SEM) Nova Nano SEM 430 operating at 10 kV.

The properties of active Ru on support MCM-41 were determined by means of pulse chemisorption using Micromeritics Auto chem II 2920. The pretreatment of samples included the following steps: (1) heating up to 120 °C at the rate of 10 °C/min, waiting for 5 min; (2) then heating up to 220 °C with the same temperature rate speed, staying 5 min; (3) heating up to 220 °C at the same heating rate, leaving for an additional 5 min; (4) changing gas flow with 10% H$_2$ and Ar, gas velocity of 20 cm^2/min; (5) reducing the temperature to 50 °C at the rate of 20 °C/min. After these processes, then the experiment began. The obtained results are collected in Table 1.

2.3. Catalytic reaction

The conversion of glucose to sorbitol was performed with high pressure reactor (PARR 5500), Ru/MCM-41 catalyst and 10 wt % glucose was added to the reactor, and then the reaction was carried out at several temperatures under 3 MPa H$_2$ with a stirring rate of 500 rpm for a certain time. After the reaction, the solid catalyst was separated by filtration, and was regenerated by vacuum drying for the next use. The liquid products were analyzed by IC (Dionex ICS-3000) with CarboPac™ PA1 column. The eluents were NaOH and CH$_3$COONa with a flow rate of 0.25 mL/min. The sample loop had a volume of 50 μL. The column temperature was 30 °C.

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