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Study of Catalytic Hydrogenation of 1, 4-Benzenediol over Ru/HY catalyst

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Abstract: Liquid-phase catalytic hydrogenation of 1, 4-benzenediol is an environmentally friendly routine for 1, 4-cyclohexanediol production. The key to increasing product yield is to develop catalysts with high catalytic performance. In this work, Ru/HY catalysts were prepared and applied to the hydrogenation of 1, 4-benzenediol to 1, 4-cyclohexanediol. The activity of catalyst was investigated by XRD, TEM. The change of the HY acid content was discussed by pyridine adsorption infrared. The optimal reaction conditions were investigated. 3.0% Ru/HY catalyst exhibited high activity with conversion of 1, 4-benzenediol and selectivity of 1, 4-cyclohexanediol up to 96.5% and 68.3%, respectively. Furthermore, based on the study of Ru/HY structure, a plausible reaction mechanism for the selective formation of 1, 4-benzenediol was proposed.

Key words: Ru/HY catalyst; catalytic hydrogenation; 1, 4-Benzenediol; 1, 4-Cyclohexanediol; mechanism

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The reduction of unsaturated compounds to obtain corresponding saturated compounds is an important step in preparation of fine chemicals and pharmaceuticals^[1]. At present, various catalysts are frequently used in this kind of hydrogenation reaction owing to easy product separation and high catalyst activity. Much research has been devoted to developing better catalysts, e. g. Pt^[2], Ru^[3], Pd^[4], Au^[5], Ni^[6], Co^[7] and Cu^[8] based catalysts. It has been found that Ru is the most active catalyst for the reduction. For example, hydrogenation of methyl oleate over Ru/TiO₂, Ru Sn/TiO₂ catalysts were studied^[9]. Many carriers, such as TiO₂^[9], SBA-15^[3], c-Al₂O₃^[4], activated carbon^[10, 11] have also been attempted.

1, 4-cyclohexanediol is important pharmaceutical intermediate and new materials monomer; a cancer drug, HMGCoA reductase, Gn II h/ III a antagonist, intermediate of succinylsulfathiazole, liquid-crystal materials etc. With 1, 4-benzenediol as crude material can generate 1, 4-cyclohexanediol, it was rarely reported in domestic and overseas. Hydrogenation of 1, 4-benzenediol studies had been previously reported, Ad-

kins and Billica et al^[12]. found cis-trans-1, 4-cyclohexanediol as products. Philippe and Rezan et al^[13]. have studied using 1, 4-benzenediol as raw material on Pd/C catalyst and they indicated yield of 1, 4-cyclohexanediol was 5%.

In the present work, author functionalized the HY molecular sieve by loading ruthenium particles, and applied this catalyst to the hydrogenation of 1, 4-benzenediol with high performance under mild conditions. The 3.0% Ru/HY catalyst prepared by precipitation method and reduced in a hydrogen flow exhibited superior activity.

1 Experimental

1.1 Catalyst Preparation

The load ruthenium catalysts were prepared by precipitation method. The support HY molecular sieve was calcined for 4 h before use at 773 K. RuCl₃ · 3H₂O (11.7 mmol/L) aqueous solution and HY was added in three-neck flask (500 mL). The suspension was heated up to 333 K and stirred for 1 h, then (NH₄)₂CO₃ (1.0 mol/L) solution was added drop-

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wise. After stirring for 22 h, the resulting slurry was filtered to obtain a grey cake and a colourless filtrate, confirming the complete precipitation of Ru as Ru carbonate. The samples were dried at 333 K and then milled and screened to a particle size in the range of 180 ~ 200 mesh. The reduction of the catalyst was carried out at 773 K at an H_2 flow rate of 60 mL min^{-1} for 3 h. The activated carbon was pretreated by hydrochloric acid (4 mol/L). Ru/C catalyst was prepared in the same manner as described above.

1.2 Activity measurement

Hydrogenation of 1, 4-benzenediol was carried out in a stirred stainless steel reactor of 500 mL. The reactor was filled with 5 g 1, 4-benzenediol, 250 mL ethanol and 0.5 g catalyst. The reactor was washed with nitrogen for three times before each reaction. Then the hydrogen was introduced into the reaction system to achieve a certain pressure (3.5 MPa), stirred vigorously by magnetic stirrer (800 r/min). The reaction temperature was controlled at around 425 K. The products and reactant sample were drawn at appropriate time intervals and the reactants and products were analyzed by GC (Bei Fen, GC 3420A) and GC-MS (Agilent 6890/5973N).

2 Results and Discussion

2.1 Characterization

The wide-angle XRD patterns of Ru/HY catalysts reduced by hydrogen in Fig. 1 did not show any characteristic diffraction peak of Ru particles, indicating that the Ru particles were well dispersed on the surface of HY molecular sieve, which might correspond to reported results in the literature^[14]. This agrees well with the TEM images of Ru catalysts and the average Ru particle size for Ru/HY catalysts is about 1.7 ~ 1.8 nm (Fig. 3).

2.2 Optimization of Reaction Conditions for 1, 4-benzenediol hydrogenation

2.2.1 Influence of time on reaction Fig. 4 shows the result for the reaction of 1, 4-benzenediol as a function of reaction time over Ru/HY catalyst at a reaction temperature of 423 K. It was observed that the conversion of 1, 4-benzenediol increased smoothly with

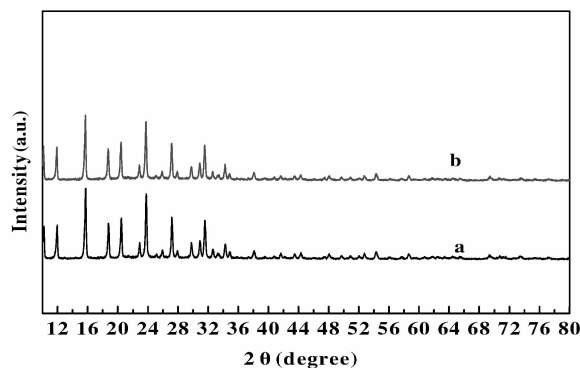


Fig. 1 XRD patterns of HY (a) and fresh Ru/HY catalyst (b)

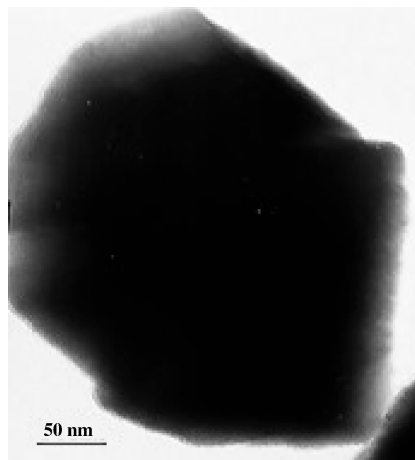


Fig. 2 TEM micrograph of the HY sample

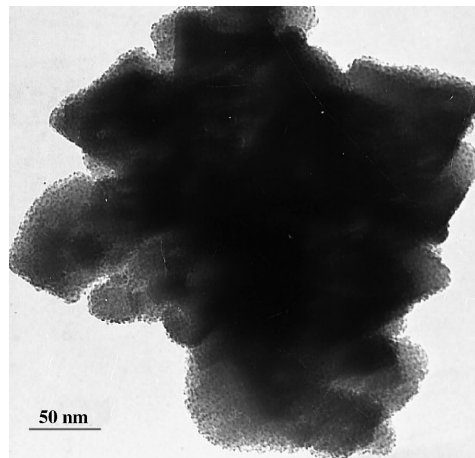


Fig. 3 TEM micrograph of the Ru/HY sample

the reaction time up to 5 h, gives 96% conversion of 1, 4-benzenediol, however, the selectivity of 1, 4-cyclohexanediol decreased with the reaction time, owing to further dehydration of 1, 4-cyclohexanediol and the generation of product of more cyclohexanol etc. The se-

lectivity of cyclohexanol increased, meanwhile the generation of the 4-hydroxycyclohexanone would continue to generate 1, 4-cyclohexanediol.

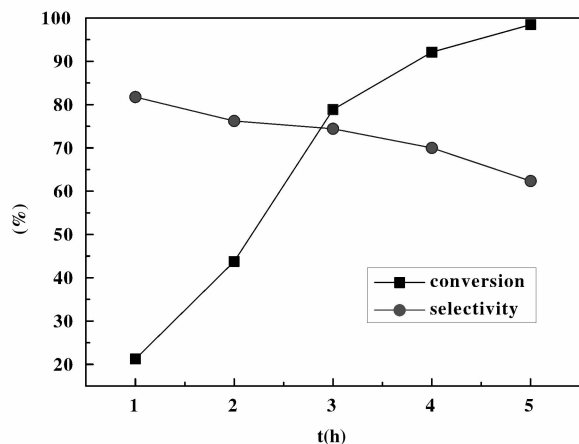


Fig. 4 Influence of time on reaction

Reaction conditions: Wcat 0.5 g; P 3.5 MPa; T 423 K; 1, 4-benzenediol 5.0 g; solvent ethanol 250 mL.

2.2.2 Influence of H_2 pressure on reaction The influence of H_2 pressure on the conversion of 1, 4-benzenediol and the selectivity of 1, 4-cyclohexanediol over Ru/HY catalysts is shown in Fig. 5. It indicated that the conversion of 1, 4-benzenediol increased smoothly with the H_2 pressure up to 4.0 MPa. According to Henry's law, when hydrogen pressure of the system was increased, the amount of hydrogen dissolved in reaction media also was increased, namely the concentration of hydrogen was increased and improved the reaction rate, eventually improved the reactants conversion. However, as the amount of H_2 pressure below 2.5 MPa, the selectivity of 1, 4-cyclohexanediol increased with increasing the amount of H_2 pressure, then reached a maximum value of 76% at 2.5 MPa. Further increase the amount of H_2 pressure, the selectivity decreased, owing to further dehydration of 1, 4-cyclohexanediol and the generation of product of more cyclohexanol.

2.2.3 Influence of temperature on reaction The effect of reaction temperature on the conversion of 1, 4-benzenediol and the selectivity of 1, 4-cyclohexanediol over Ru/HY has been also investigated and the results are shown in Fig. 6. The conversion of 1, 4-benzenediol increased with temperature increasing, but the se-

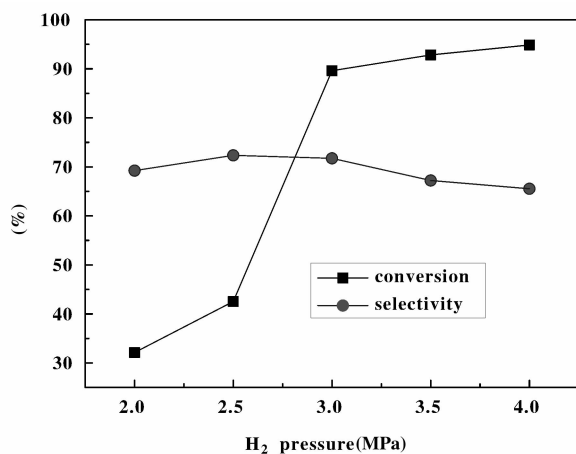


Fig. 5 Influence of H_2 pressure on reaction

Reaction conditions: Wcat 0.5 g; t 4 h; T 423 K; 1, 4-benzenediol 5.0 g; solvent ethanol 250 mL.

lectivity of 1, 4-cyclohexanediol decreased with temperature increasing, owing to further dehydration of 1, 4-cyclohexanediol and the generation of product of more cyclohexanol. So, it is concluded that the optimum reaction temperature is 423 K.

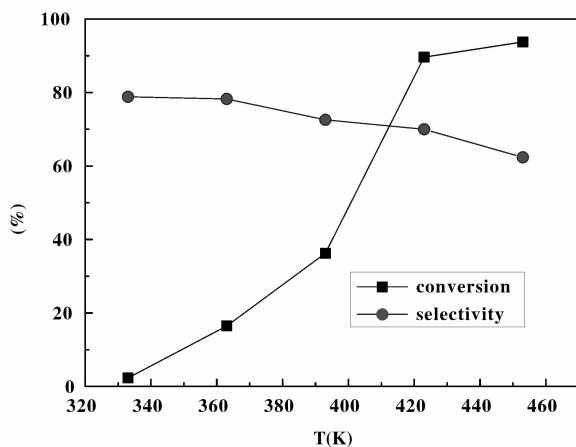


Fig. 6 Influence of temperature on reaction

Reaction conditions: Wcat 0.5 g; t 4 h; P 3.5 MPa; 1, 4-benzenediol 5.0 g; solvent ethanol 250 mL.

2.2.4 Influence of the amounts of catalyst on reaction

The effect of the amount of Ru/HY on the conversion of 1, 4-benzenediol and the selectivity of 1, 4-cyclohexanediol is shown in Fig. 7. It can be seen that the conversion of 1, 4-benzenediol increased from 37% to 88% with the increase of the amount of Ru/HY from 0.2 g to 0.4 g. Further increase the amount of Ru/HY

leads to a slight decrease in the conversion of 1, 4-benzenediol. This may be due to the fact that the excessive catalyst decreases the utilization of catalyst. As the amount of Ru/HY increased, the selectivity of 1, 4-cyclohexanediol changed slightly around 70%. Thus 0.5 g Ru/HY is a suitable amount in this reaction.

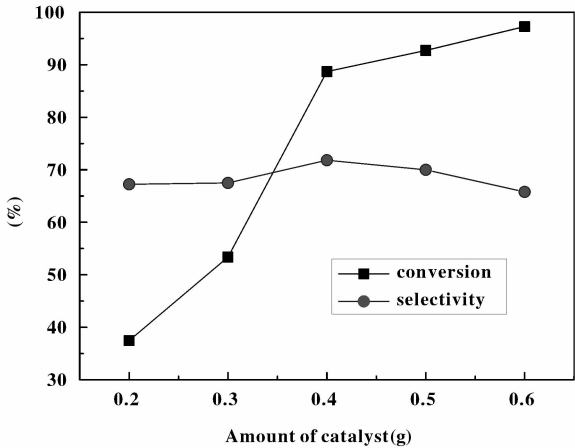
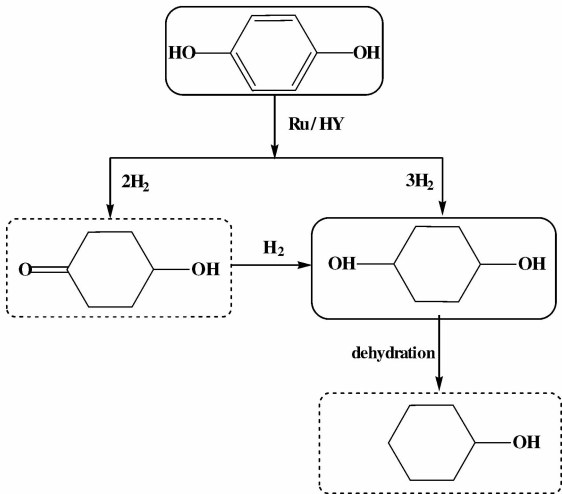


Fig. 7 Influence of the amounts of catalyst on reaction
Reaction conditions; T 423 K; t 4 h; P 3.5 MPa; 1, 4-benzenediol 5.0 g; solvent ethanol 250 mL.

2.3 Catalysis mechanism

The selective formation of 1, 4-benzenediol over Ru/HY catalysts is might be due to the plausible mechanism as shown in Scheme 1.



Scheme 1 Plausible reaction mechanism for the formation of 1, 4-Cyclohexanediol, cyclohexanol and 4-hydroxycyclohexanone

In order to investigate the difference of the unload ruthenium HY and load ruthenium HY, the Pyridine adsorption infrared is good way to investigate the change of the HY acid content.

In the Pyridine adsorption infrared, the 1 450 cm⁻¹ is corresponding to the L acid and 1 540 cm⁻¹ is corresponding to the B acid. From the Fig. 8, it shows the B acid makes a large proportion in the unload ruthenium HY, however, the L acid dominate a very big proportion in the load ruthenium HY. From the Fig. 8, it is also proved that the acid content^[15] of HY has a great change. From Table 1, we know that the unload ruthenium HY has very low activity in catalytic hydrogenation, so we may confirm that the L acid may have impetus function to the reaction.

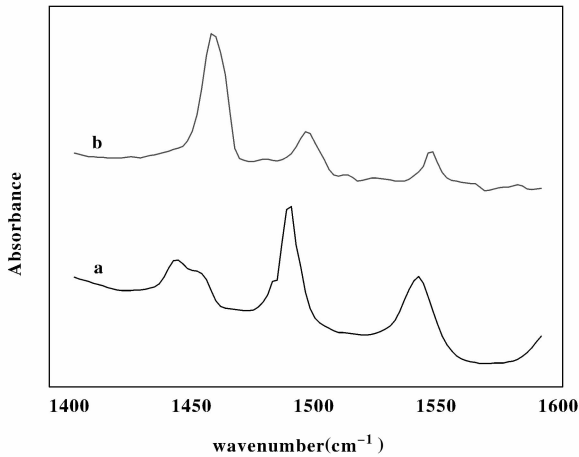


Fig. 8 Pyridine adsorption infrared of the HY;
a. the unload ruthenium HY, b. the load ruthenium HY

2.4 Reactivity of catalysts in 1, 4-benzenediol hydrogenation

The effect of different carriers catalysts on the reaction were investigated. Using 1, 4-benzenediol hydrogenation as reaction was researched as contrast experiments. In experiment, the activated carbon and HY molecular sieve as carriers were selected to prepare ruthenium-based catalysts. In Table 1, the results show that the activated carbon has low activity in catalytic hydrogenation. However, Ru/HY has the highest activity, the conversion of 1, 4-benzenediol and selectivity of 1, 4-Cyclohexanediol were 96.5% and 68.3% on ruthenium-based HY catalysts, respectively.

Table 1 Evaluation of different carrier catalysts

| Catalysts | Reaction time (h) | Conversion (%) | Selectivity (%) |
|------------------|----------------------|-------------------|--------------------------|
| unload HY | 4 | 0 | – |
| activated carbon | 4 | 0 | – |
| Ru/HY | 4 | 96.5 | 68.3 |
| Ru/C | 4 | 32.0 | 89.5(scCO ₂) |
| Ru/C | 4 | 18.9 | 66.2 |

Reaction conditions: 1, 4-benzenediol 5.0 g; solvent ethanol 250 mL; Wcat 0.5 g; t 4 h; T 423 K; P 3.5 MPa.

3 Conclusion

The HY-supported ruthenium catalysts exhibited maximum catalytic activity for the hydrogenation of 1, 4-benzenediol to 1, 4-cyclohexanediol. Reaction conditions had obvious influences on catalytic activity. The optimal loading, calcination temperature and reduction temperature of Ru/HY catalysts were 3.0% , 773 K and 423 K. Ru/HY catalyst exhibits high activity, with conversion of 1, 4-benzenediol and selectivity of 1, 4-cyclohexanediol up to 96.5% and 68.3% , respectively.

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Ru/HY 催化剂催化对苯二酚加氢研究

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摘 要: 对苯二酚液相加氢制备 1,4-环己二醇的途径环境友好, 关键是研究高催化活性的催化剂来提高产物产率. 我们以 Ru/HY 为催化剂用于对苯二酚加氢. 用 XRD, TEM 对催化剂进行了表征, 通过吡啶吸附红外对 HY 酸性的变化进行了讨论. 对其反应条件进行了优化. 结果表明 3.0% Ru/HY 的催化剂表现出高的活性, 对苯二酚的转化率和 1, 4-环己二醇的选择性分别为 96.5% 和 68.3%. 我们还基于对 Ru/HY 催化剂结构的研究探讨并提出相应的反应机理.

关键词: Ru/HY 催化剂; 催化加氢; 对苯二酚; 1, 4-环己二醇 ;机理