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Influence of pretreatment on the catalytic performance of Ru/SBA-15 catalysts for glycerol hydrogenolysis

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ABSTRACT

Ru/SBA-15 catalysts were prepared by impregnation and were pretreated under different conditions, and were characterized by N₂ adsorption-desorption, X-ray diffraction, CO chemisorption, transmission electron microscopy, and the reaction of glycerol hydrogenolysis. The catalyst calcined in air had larger Ru particles, while the direct reduction of the catalysts with H₂ without air pre-calcination made the Ru particles dispersed well. As the H₂ reduction temperature increased, the Ru dispersion decreased. The turnover frequency (TOF) of the catalysts increased as the Ru dispersion decreased, indicating that Ru/SBA-15 catalyzed glycerol hydrogenolysis is a structure sensitive reaction.

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1. Introduction

Biodiesel has received much attention because it is environmentally friendly, renewable, and cheap. The increased global need for biodiesel is due to the large consumption of energy and shortage of fossil fuels [1]. Meanwhile, the increased production of biodiesel leads to the over-production of glycerol. The limited usage but large supply of glycerol is a problem [2]. Conversion of glycerol into more valuable downstream products can be performed by glycerol oxidation [3], glycerol dehydration [4], glycerol hydrogenolysis [5], and other ways. From glycerol hydrogenolysis, 1,3-propanediol (1,3-PD) and 1,2-propanediol (1,2-PD) are the main products. 1,3-PD is a high value chemical which is used to produce polyester (poly-

trimethylene terephthalate) [6]. 1,2-PD is widely used to produce antifreeze, polyester fibers and cosmetics [7]. It is now produced by the oxidation of propylene, which is in short supply, and so much attention has been paid to glycerol hydrogenolysis.

Glycerol hydrogenolysis has been much studied and many catalyst systems have been reported. As non-noble metal catalysts, Cu and Ni are often used [8–12]. With these non-noble metal catalysts, 70%–100% glycerol conversion and 40%–99% selectivity to 1,2-PD were obtained, but almost no 1,3-PD was obtained in glycerol hydrogenolysis. It was only in the case of Cu-H₄SiW₁₂O₄₀/SiO₂ [13] that 1,3-PD was obtained with a selectivity of 32.1%. As noble metal catalysts, Ru, Pt, Rh, Ir, and Pd are chosen for glycerol hydrogenolysis [14–18]. Huang et al.

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[19] reported that for a series of CuO/SiO₂ catalysts with different particle size, too large (14.7 nm) or too small (4.7 nm) Cu particle size gave lower activity. The Cu catalyst with 12.3 nm particle size gave the highest turnover frequency (TOF). They suggested that glycerol hydrogenolysis was a structure sensitive reaction. Wang et al. [15] used different loadings of Ru supported on CNTs to give different particle size of Ru. They found that the particle size of Ru of 5 nm gave the highest TOF.

Compared to the other supports of Ru catalysts reported in the references [20–23], SBA-15 has a high surface area and an ordered mesoporous structure, which would favor the high dispersion of Ru. Meanwhile, SBA-15 has few acid or basic sites, and would not affect the reaction. In this study, the influence of pretreatment conditions on the properties and catalytic performance of Ru/SBA-15 for glycerol hydrogenolysis was investigated. Due to the pretreatment conditions, Ru/SBA-15 catalysts with Ru different dispersions were obtained. The effect of Ru particle size on the activity of Ru/SBA-15 in glycerol hydrogenolysis is discussed.

2. Experimental

2.1. Materials and catalyst preparation

P123 (EO₂₀PO₇₀EO₂₀, $M_r = 5800$) was purchased from Aldrich. RuCl₃·4H₂O was bought from Shenyang Nonferrous Metal Research Institute. The other materials were all from Beijing Chemical Reagent Company. SBA-15 was prepared according to the literature method [24–26] and was calcined at 500 °C for 6 h. Ru/SBA-15 was prepared by impregnation [27–29]. RuCl₃·4H₂O was dissolved in water and a specific amount of SBA-15 support was added. After impregnation for 10 h at room temperature, the water was removed by evaporation. The solid was dried at 110 °C for 10 h. The precursor obtained was treated under different conditions. The dried precursor of 5%Ru/SBA-15 was directly reduced with pure H₂ at 300, 400, and 500 °C for 2 h, and the catalysts obtained were denoted as 5Ru/SBA-15(H₂-300), 5Ru/SBA-15(H₂-400) and 5Ru/SBA-15(H₂-500), respectively. The precursor of 5%Ru/SBA-15 was treated first with N₂ at 400 °C and then reduced with H₂ at 500 °C, and the catalyst was denoted as 5Ru/SBA-15(N₂-400/H₂-500). The precursor of 5%Ru/SBA-15 was treated first with N₂ at 700 °C and then reduced with H₂ at 700 °C, and the catalyst was denoted as 5Ru/SBA-15(N₂-700/H₂-700). Similarly, the precursor of 5%Ru/SBA-15 was calcined first in air at 300 °C and then reduced with H₂ at different temperatures, and the catalyst was denoted as 5Ru/SBA-15(Air-300/H₂- T) (T = temperature, °C).

2.2. Hydrogenolysis of glycerol

The hydrogenolysis of glycerol was carried out in a 100 mL stainless steel autoclave with magnetic stirrer. 40 wt% glycerol aqueous solution was prepared with pure glycerol from Alfa Aesar (99.95%) and deionized water. 10 mL of this solution and 0.15 g Ru/SBA-15 catalyst were used in the reaction. The standard reaction conditions were H₂ pressure 8 MPa at 160 °C

for 8 h.

After reaction, the autoclave was cooled down to 5 °C in ice, and the gas phase products were analyzed by a gas chromatograph (Beijing Weisifu-GC 6890) equipped with a TDX-01 ($\Phi 4$ mm $\times$ 2 m) column and a thermal conductivity detector. The external standard method was used for quantification. The liquid phase products were analyzed with a gas chromatograph (Lunan-SP 6890) equipped with a PEG-20M ($\Phi 0.22$ mm $\times$ 30 m) column and a flame ionization detector. The internal standard method was used for quantification.

The conversion of glycerol and the selectivity to products were calculated with the formulae below.

Conversion of glycerol = Sum of C mol of all products / C mol of glycerol before reaction $\times$ 100%

Selectivity = C mol of the product / Sum of C mol $\times$ 100%

The mass balance for the reaction was calculated from the moles of carbon in the glycerol before reaction and the moles of total carbon in all the products and unreacted glycerol after reaction. All mass balances were 95% $\pm$ 5%. The TOF was defined as the mole of converted glycerol per Ru atom on the surface per hour.

2.3. Catalyst characterization

N₂ adsorption-desorption was used to characterize the physical properties of Ru/SBA-15 and SBA-15 on a Micromeritics ASAP 2010C analyzer with the BET and BJH methods. All samples were treated at 300 °C in N₂ for 1.5 h and degassed at 300 °C for 4 h. N₂ adsorption-desorption experiment was carried out at -196 °C. The Ru dispersion in the 5%Ru/SBA-15 catalysts was measured with the CO pulse adsorption method on a Quantachrome CHEM-300 equipment. First, the catalyst was reduced in pure H₂ at a specific temperature, then it was cooled down in pure He to 30 °C. After that, CO was pulsed and the Ru dispersion was calculated. The phase structure of Ru/SBA-15 was determined by X-Ray diffraction (XRD). The characterization was carried out on a Rigaku D/max-RB diffractometer (powered at 40 kV and 200 mA) with Cu K α radiation ($\lambda = 0.154$ nm). High resolution transmission electron microscopy (HR-TEM) of Ru/SBA-15 was performed on a JEM-2010 JEOL equipment with an energy dispersive spectrometer (EDS).

3. Results and discussion

3.1. Properties of 5Ru/SBA-15 treated under different conditions

The N₂ adsorption-desorption isotherms of 5Ru/SBA-15 samples treated under different conditions are shown in Fig. 1. All the 5Ru/SBA-15 catalysts had the Type IV isotherm, similar to the SBA-15 support. This means that after loading Ru and treating under different conditions, the pore structure of 5Ru/SBA-15 had no obvious change. The pore diameter distributions of the samples are shown in Fig. 2. All samples had a similar pore distribution. Textural parameters including specific surface areas (A_{BET}), average pore diameter, and pore

Fig. 1. N₂ adsorption-desorption isotherms of 5Ru/SBA-15 with different treatment conditions. (1) 5Ru/SBA-15(H₂-300); (2) 5Ru/SBA-15(H₂-400); (3) 5Ru/SBA-15(H₂-500); (4) 5Ru/SBA-15(N₂-400/H₂-500); (5) 5Ru/SBA-15(N₂-700/H₂-700); (6) 5Ru/SBA-15(Air-300/H₂-230); (7) 5Ru/SBA-15(Air-300/H₂-300); (8) 5Ru/SBA-15(Air-300/H₂-400); (9) 5Ru/SBA-15(Air-300/H₂-500); (10) SBA-15.

volume are listed in Table 1. SBA-15 showed the largest surface area (856 m²/g). After impregnation, all 5Ru/SBA-15 samples showed smaller surface areas (650–700 m²/g) than SBA-15, indicating that loading Ru and pretreatment at different conditions had some influence on the surface area. The same trend was also seen for the average pore diameter and pore volume, with SBA-15 having the largest average pore diameter (5.2 nm) and pore volume (0.7 cm³/g).

The Ru dispersion on 5Ru/SBA-15 pretreated under different conditions are also presented in Table 1. All 5Ru/SBA-15 prepared by direct reduction with H₂ without prior calcination

Fig. 2. Pore diameter distribution of 5Ru/SBA-15 with different treatment conditions. (1) 5Ru/SBA-15(H₂-300); (2) 5Ru/SBA-15(H₂-400); (3) 5Ru/SBA-15(H₂-500); (4) 5Ru/SBA-15(N₂-400/H₂-500); (5) 5Ru/SBA-15(N₂-700/H₂-700); (6) 5Ru/SBA-15(Air-300/H₂-230); (7) 5Ru/SBA-15(Air-300/H₂-300); (8) 5Ru/SBA-15(Air-300/H₂-400); (9) 5Ru/SBA-15(Air-300/H₂-500); (10) SBA-15.

Table 1

Textural properties of 5Ru/SBA-15 with different treatment conditions.

Sample	A_{BET} (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)	Ru dis- persion (%)
SBA-15	856	5.2	0.7	—
5Ru/SBA-15(Air-300/H ₂ -230)	698	5.0	0.6	4.1
5Ru/SBA-15(Air-300/H ₂ -300)	673	4.9	0.6	2.2
5Ru/SBA-15(Air-300/H ₂ -400)	662	4.9	0.6	1.6
5Ru/SBA-15(Air-300/H ₂ -500)	670	4.8	0.6	0.6
5Ru/SBA-15(H ₂ -300)	654	5.1	0.7	37.2
5Ru/SBA-15(H ₂ -400)	695	5.1	0.6	35.3
5Ru/SBA-15(H ₂ -500)	650	4.9	0.6	32.9
5Ru/SBA-15(N ₂ -400/H ₂ -500)	648	4.9	0.5	28.9
5Ru/SBA-15(N ₂ -700/H ₂ -700)	554	4.8	0.6	16.1

had higher Ru dispersions (16.1%–37.2%). Among them, 5Ru/SBA-15(H₂-300) had the highest Ru dispersion of 37.2%. When the precursor was calcined in air and then reduced in H₂, (5Ru/SBA-15(Air-300/H₂-7)) the Ru dispersion decreased sharply. As the reduction temperature was increased from 230 to 500 °C, the Ru dispersion decreased from 4.1% to 0.6%.

In the small angle XRD patterns of 5Ru/SBA-15 shown in Fig. 3, all samples had a small peak at $2\theta = 1^\circ$, indicating that the preparation and treatment process, including calcination and reduction, did not destroy the hexagonal structure of SBA-15. In the wide angle XRD patterns of 5Ru/SBA-15 (Fig. 4), all samples showed the diffraction peaks of metallic Ru, but with different intensity. The peaks at $2\theta = 38.2^\circ$, 42.3° , and 44.1° corresponded to Ru(100), Ru(002), and Ru(101), respectively. These were consistent with the Ru⁰ phase in the reference [30]. For 5Ru/SBA-15(H₂-300), 5Ru/SBA-15(H₂-400), 5Ru/SBA-15(H₂-500), 5Ru/SBA-15(N₂-400/H₂-500), 5Ru/SBA-15(N₂-700/H₂-700), and 5Ru/SBA-15(Air-300/H₂-230), only the diffraction peaks of Ru(101) were found. For the samples with the treatment of calcination and reduction, the XRD peaks of Ru(100) and Ru(002) became clear when the reduction

Fig. 3. Small angle XRD patterns of fresh 5Ru/SBA-15 with different treatment conditions. (1) 5Ru/SBA-15(H₂-300); (2) 5Ru/SBA-15(H₂-400); (3) 5Ru/SBA-15(H₂-500); (4) 5Ru/SBA-15(N₂-400/H₂-500); (5) 5Ru/SBA-15(N₂-700/H₂-700); (6) 5Ru/SBA-15(Air-300/H₂-230); (7) 5Ru/SBA-15(Air-300/H₂-300); (8) 5Ru/SBA-15(Air-300/H₂-400); (9) 5Ru/SBA-15(Air-300/H₂-500).

Fig. 4. Wide angle XRD patterns of fresh 5Ru/SBA-15 with different treatment conditions. (1) 5Ru/SBA-15(H₂-300); (2) 5Ru/SBA-15(H₂-400); (3) 5Ru/SBA-15(H₂-500); (4) 5Ru/SBA-15(N₂-400/H₂-500); (5) 5Ru/SBA-15(N₂-700/H₂-700); (6) 5Ru/SBA-15(Air-300/H₂-230); (7) 5Ru/SBA-15(Air-300/H₂-300); (8) 5Ru/SBA-15(Air-300/H₂-400); (9) 5Ru/SBA-15(Air-300/H₂-500).

temperature was increased from 230 to 500 °C. These changes were in agreement with the Ru dispersion. The result showed that uncalcined and reduced 5Ru/SBA-15 had smaller Ru particles. After calcination at 300 °C in air, Ru particle size increased with the reduction temperature.

The TEM images of 5Ru/SBA-15(H₂-400) and 5Ru/SBA-15(Air-300/H₂-500) are shown in Fig. 5. Figure 5(a) showed that Ru had a size distribution between 1.9 and 5.4 nm, and the average Ru particle size was 3.3 nm, indicating that the Ru particles were homogeneous on the surface of SBA-15. Compared to 5Ru/SBA-15(H₂-400), the Ru particle size on 5Ru/SBA-15(Air-300/H₂-500) had a wider distribution (from 3.3 to 9.2 nm) with the average Ru particle size was 6.4 nm. At the same time,

it was clearly shown that the Ru particles of 5Ru/SBA-15(H₂-400) were spherical, but those of 5Ru/SBA-15(Air-300/H₂-500) were rod-like and were agglomerated along the channels. Meanwhile, after calcination, some larger particles were also formed. Since the particles of 5Ru/SBA-15(Air-300/H₂-500) were rods in shape, it has sharper XRD diffraction peaks.

With different treatment conditions, Ru/SBA-15 catalysts with different particle size were obtained. In the references [31–33], the Ru particle size was also changed by reduction and calcination at different temperatures. For the uncalcined precursor, which meant the absence of oxygen, the Ru species formed small clusters. When the precursors were calcined in air, the presence of oxygen affected the Ru particle size and formed Ru nanoparticles. High temperature calcination may also change the OH group of the support and further change the Ru particle size [33].

3.2. Effect of catalyst pretreatment conditions on the catalytic performance of 5Ru/SBA-15 in glycerol hydrogenolysis

The glycerol hydrogenolysis reaction results of 5Ru/SBA-15 with different treatment conditions are shown in Table 2. For 5Ru/SBA-15 samples with direct H₂ reduction, as the reduction temperature was increased from 300 to 500 °C, the Ru dispersion decreased, and the conversion of glycerol and the selectivity to CH₄ increased from 18.5% and 17.0% to 29.3% and 28.7%, respectively. At the same time, the selectivity to 1,2-PD decreased from 28.6% to 22.1%. 5Ru/SBA-15(N₂-400/H₂-500) and 5Ru/SBA-15(N₂-700/H₂-700) gave the similar results to 5Ru/SBA-15(H₂-500). After the Ru/SBA-15 was calcined at 300 °C and then reduced at 230 °C causing the Ru dispersion to sharply decrease from 16.1% to 4.1% (compared with 5Ru/SBA-15(N₂-700/H₂-700)), the conversion of glycerol decreased from 30.0% to 15.9%. As the reduction temperature was increased from 230 to 500 °C, the conversion of glycerol de-

Fig. 5. TEM images of fresh 5Ru/SBA-15(H₂-400) (a) and 5Ru/SBA-15(Air-300/H₂-500) (b).

Table 2

Catalytic performance of 5Ru/SBA-15 with different treatment conditions in glycerol hydrogenolysis.

Sample	Conversion (%)	Selectivity (%)							
		CH ₄	MeOH	EtOH	EG	1-PO	2-PO	1,2-PD	1,3-PD
5Ru/SBA-15(Air-300/H ₂ -230)	15.9	21.2	1.0	4.7	21.0	27.4	0.7	21.4	2.8
5Ru/SBA-15(Air-300/H ₂ -300)	12.4	19.4	1.3	3.3	20.5	21.8	0.6	29.0	4.1
5Ru/SBA-15(Air-300/H ₂ -400)	9.1	18.4	0.7	2.8	21.1	29.3	0.5	23.8	3.3
5Ru/SBA-15(Air-300/H ₂ -500)	6.4	19.3	1.3	3.0	23.8	24.8	0.7	23.1	3.9
5Ru/SBA-15(H ₂ -300)	18.5	17.0	1.2	6.1	21.6	22.2	0.9	28.6	2.3
5Ru/SBA-15(H ₂ -400)	18.6	22.6	0.8	4.6	20.5	22.9	0.7	25.2	2.6
5Ru/SBA-15(H ₂ -500)	29.3	28.7	1.3	5.5	19.3	20.5	0.8	22.1	1.8
5Ru/SBA-15(N ₂ -400/H ₂ -500)	30.0	25.9	1.2	5.8	16.7	27.9	0.6	20.1	1.9
5Ru/SBA-15(N ₂ -700/H ₂ -700)	28.9	28.8	0.8	4.6	17.7	23.9	0.5	21.7	1.9

Reaction conditions: 40 wt% glycerol 10 mL, Ru/SBA-15 0.15 g, H₂ pressure 8 MPa, 160 °C, 8 h, 700 r/min.

creased from 15.9% to 6.4% and the selectivity to 1,2-PD reached its maximum of 29.0% at 300 °C. On the other hand, for the calcined samples, the selectivity to CH₄ was slightly lower than that of directly reduced 5Ru/SBA-15. Although the Ru dispersions of 5Ru/SBA-15 were different, the distributions of the liquid products were similar.

By varying the reaction conditions and maintaining the conversion of glycerol at a similar level, the specific activity (TOF) of 5Ru/SBA-15 for glycerol hydrogenolysis was calculated. The results are also shown in Table 3. The results clearly showed that when the conversion of glycerol was similar, the selectivity to 1,2-PD and 1,3-PD on 5Ru/SBA-15(H₂-400) was the highest (47.9% and 5.0%, respectively). As the reduction temperature increased, the selectivity to 1,2-PD and 1,3-PD decreased somewhat. It can also be seen that as the Ru particle size increased (the Ru dispersion decreased), its TOF increased. The results obtained in the present study and in the references [19,34–37] suggested that glycerol hydrogenolysis over Ru/SBA-15 is a structure sensitive reaction. In the case of Ru/SBA-15 with a higher Ru dispersion, the small particles would have a strong adsorption of intermediates and decrease the ability to dissociate H₂ [36,37], and this effect would result in the decreased TOFs. Meanwhile, the relatively high selectivity to 1,2-PD and 1,3-PD on 5Ru/SBA-15(H₂-400) may be due to the strong adsorption of the intermediates, which would decrease the further hydrogenolysis of 1,2-PD and 1,3-PD. Similar results were found in the case of Cu/SiO₂ [19].

For the samples before and after reaction, the differences in the XRD diffraction peaks of Ru species were not significant (Fig. 6), except for the 5Ru/SBA-15(Air-300/H₂-400) catalyst. The reason may be that the catalysts were in a hydrothermal

environment during the reaction, and this may change the Ru particle size, which would make the diffraction peaks not obvious for the different Ru catalysts.

3.3. Effect of Ru loadings on the performance of Ru/SBA-15 in glycerol hydrogenolysis

The effect of Ru loadings on the performance of Ru/SBA-15

Fig. 6. Wide angle XRD patterns of spent 5Ru/SBA-15 with different treatment conditions. (1) 5Ru/SBA-15(H₂-300); (2) 5Ru/SBA-15(H₂-400); (3) 5Ru/SBA-15(H₂-500); (4) 5Ru/SBA-15(N₂-400/H₂-500); (5) 5Ru/SBA-15(N₂-700/H₂-700); (6) 5Ru/SBA-15(Air-300/H₂-230); (7) 5Ru/SBA-15(Air-300/H₂-300); (8) 5Ru/SBA-15(Air-300/H₂-400); (9) 5Ru/SBA-15(Air-300/H₂-500).

Table 3

Influence of reaction time on the catalytic performance of 5Ru/SBA-15 with different treatment in glycerol hydrogenolysis.

Sample	Conversion (%)	Selectivity (%)								TOF (h ⁻¹)
		CH ₄	MeOH	EtOH	EG	1-PO	2-PO	1,2-PD	1,3-PD	
5Ru/SBA-15(Air-300/H ₂ -230)-8h	15.9	21.2	1.0	4.7	21.0	27.4	0.7	21.4	2.8	284.1
5Ru/SBA-15(Air-300/H ₂ -300)-8h	12.4	19.4	1.3	3.3	20.5	21.8	0.6	29.0	4.1	418.6
5Ru/SBA-15(Air-300/H ₂ -400)-12h	15.9	20.2	0.5	2.9	18.8	22.5	0.5	30.9	3.7	482.2
5Ru/SBA-15(Air-300/H ₂ -500)-16h	14.2	22.5	0.6	4.5	15.8	27.8	0.9	25.4	2.5	852.6
5Ru/SBA-15(H ₂ -300)-5h	12.3	24.7	1.0	3.9	23.1	21.1	0.5	23.3	2.4	38.7
5Ru/SBA-15(H ₂ -400)-5h	11.3	14.1	0.4	1.9	20.5	9.9	0.3	47.9	5.0	37.5
5Ru/SBA-15(H ₂ -500)-3h	11.4	14.9	0.6	3.2	18.2	18.3	0.6	39.3	4.8	67.6
5Ru/SBA-15(N ₂ -400/H ₂ -500)-3h	16.8	19.0	0.6	3.9	17.7	21.0	0.7	33.1	3.9	113.5
5Ru/SBA-15(N ₂ -700/H ₂ -700)-3h	11.8	26.8	0.8	4.1	19.1	25.8	0.6	20.1	2.7	143.5

Reaction conditions: 40 wt% glycerol 10 mL, Ru/SBA-15 0.15 g, H₂ pressure 8 MPa, 160 °C, 700 r/min.

Table 4

Influence of Ru loadings on the catalytic performance of Ru/SBA-15 in glycerol hydrogenolysis.

Sample	Conversion (%)	Selectivity (%)							
		CH ₄	MeOH	EtOH	EG	1-PO	2-PO	1,2-PD	1,3-PD
1Ru/SBA-15(H ₂ -500)	4.0	10.7	0.5	1.9	15.0	19.8	0.9	44.0	7.2
3Ru/SBA-15(H ₂ -500)	10.8	17.1	0.6	3.1	18.8	19.4	0.7	35.7	4.5
5Ru/SBA-15(H ₂ -500)	29.3	28.7	1.3	5.5	19.3	20.5	0.8	22.1	1.8
8Ru/SBA-15(H ₂ -500)	35.4	30.3	1.1	5.1	15.5	18.8	0.8	26.9	1.4
10Ru/SBA-15(H ₂ -500)	42.9	40.3	1.2	5.1	12.7	13.8	0.9	25.1	0.8

Reaction conditions: 40 wt% glycerol 10 mL, Ru/SBA-15 0.15 g, H₂ pressure 8 MPa, 160 °C, 8 h, 700 r/min. **Fig. 7.** Wide angle XRD patterns of fresh Ru/SBA-15 with different Ru loadings. (1) 1Ru/SBA-15(H₂-500); (2) 3Ru/SBA-15(H₂-500); (3) 5Ru/SBA-15(H₂-500); (4) 8Ru/SBA-15(H₂-500); (5) 10Ru/SBA-15(H₂-500).

in glycerol hydrogenolysis is shown in Table 4. As Ru loading increased from 1% to 10%, the conversion of glycerol increased from 4.0% to 42.9%. At the same time, the selectivity to CH₄ also increased from 10.7% to 40.3%. For 1Ru/SBA-15 (H₂-500), the selectivity to 1,2-PD and 1,3-PD was the highest (44.0% and 7.2%, respectively). The XRD patterns of the Ru/SBA-15 samples with different Ru loadings are shown in Fig 7. The samples had the diffraction peak of metallic Ru (44.1°)[26]. The Ru loading in the range of 1%–10% did not affect the Ru particle size much.

4. Conclusions

Under different treatment conditions, the Ru dispersion on Ru/SBA-15 catalysts was changed, which influenced the catalytic performance in glycerol hydrogenolysis. Ru/SBA-15 cata-

lysts calcined in air followed by H₂ reduction had large Ru particle size, and gave lower activity. The direct reduction of the uncalcined Ru/SBA-15 precursor with H₂ gave higher Ru dispersion, and thus glycerol conversion increased over the Ru catalysts. As Ru dispersion decreased, the TOF increased at similar glycerol conversion. The results showed that glycerol hydrogenolysis over Ru/SBA-15 is a structure sensitive reaction.

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Graphical Abstract

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Influence of treatment on the catalytic performance of Ru/SBA-15 catalysts for glycerol hydrogenolysis

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Different treatment conditions gave Ru/SBA-15 catalysts with different Ru particle size, and they showed that glycerol hydrogenolysis over Ru/SBA-15 is a structure sensitive reaction.

Small Ru particle, Low TOF

SiO₂
Large Ru particle, High TOF
SiO₂

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预处理方法对Ru/SBA-15催化丙三醇氢解反应性能的影响

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摘要: 使用浸渍法结合不同预处理方法制备了一系列的Ru/SBA-15催化剂, 并将其应用于丙三醇氢解反应中. 使用N₂吸附-脱附、X射线衍射、CO化学吸附以及透射电子显微镜等方法对所制备Ru/SBA-15进行了表征. 结果表明, 催化剂前驱体经过空气焙烧后再经H₂还原的Ru/SBA-15催化剂上Ru的分散度较低, 而直接使用H₂处理较高. 同时, 随着H₂还原温度提高, Ru分散度逐渐降低. 保持反应活性接近时, 随着Ru分散度的降低, TOF增加. 表明Ru/SBA-15催化剂上丙三醇氢解是结构敏感反应.

关键词: 钌; 负载型催化剂; 丙三醇; 氢解反应; 预处理; 结构敏感反应

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