Ru-Re/SiO₂ 催化剂上丙三醇氢解制丙二醇: 催化剂的酸性质与 Re 组分的作用

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摘要: 考察了 Ru-Re/SiO₂ 双组分催化剂的酸性质, 并探讨了 Re 组分在丙三醇氢解制丙二醇反应中对提高该催化剂性能所起的作用. 本文采用氨气程序升温脱附法和吸附吡啶原位红外光谱法表征了双组分 Ru-Re/SiO₂ 和单组分 Ru/SiO₂、Re/SiO₂ 催化剂的酸性质, 并比较了催化剂在丙三醇氢解反应中的催化性能. 结果显示, Ru-Re/SiO₂、Ru/SiO₂ 和 Re/SiO₂ 催化剂表面均有酸性位, 但 Ru-Re/SiO₂ 和 Re/SiO₂ 催化剂的酸量明显高于 Ru/SiO₂ 催化剂. 本文对不同 Re 含量的 Ru-Re/SiO₂ 催化剂的催化性能也进行了考察. Ru-Re/SiO₂ 催化剂的活性随催化剂表面的酸量增加而增大, 且催化剂表面的酸量与催化剂上铼氧化物的含量直接相关. 讨论了铼氧化物在 Ru-Re/SiO₂ 催化剂催化的丙三醇氢解反应过程中所起的作用.

关键词: 钌; 铼; 氧化铼; 丙三醇氢解; 丙二醇; 酸性质

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Glycerol Hydrogenolysis to Propanediols over Ru-Re/SiO₂: Acidity of Catalyst and Role of Re

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Abstract: The acidic property of Ru-Re/SiO₂ catalysts and the role of Re were investigated. The acidic properties of Ru-Re/SiO₂, Ru/SiO₂, and Re/SiO₂ were characterized by temperature programmed desorption of ammonia and in situ IR spectra of pyridine adsorption. Their catalytic performances in glycerol hydrogenolysis were compared. Ru-Re/SiO₂, Ru/SiO₂, and Re/SiO₂ possessed acid sites, but the site amounts of Ru-Re/SiO₂ and Re/SiO₂ were much higher than that of Ru/SiO₂. The activities of Ru-Re/SiO₂ with different Re contents were evaluated. The activity of Ru-Re/SiO₂ increased with the acid amount, which correlated with the amount of Re oxide on the catalyst. The role of Re oxide in Ru-Re/SiO₂ catalyzed glycerol hydrogenolysis was discussed.

Key words: catalyst acidity; ruthenium-rhenium catalyst; rhenium oxide; glycerol hydrogenolysis; propanediols

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The catalytic conversion of biodiesel-derived glycerol to high value chemicals has been widely studied in recent

years [1–6]. Glycerol can be converted to propanediols (1,2-propanediol and 1,3-propanediol) by catalytic hydro-

genolysis using heterogeneous catalysts such as Cu-based [3,4], Raney-nickel [4,5], Ru-based [6,7], and other noble metal (Rh, Pt, Au, etc.) catalysts [8–10]. Ru is an effective catalyst [6,7,11–13], but glycerol conversion and selectivities to propanediols over Ru catalysts are still not sufficient, and additives for Ru catalysts have been investigated [6,11–13].

The addition of Re gave significant promotion of the activity of Ru-based catalysts and their selectivities to propanediols, which has been reported in our previous works [11–13]. However, how did Re affect the activity of Ru-Re catalysts, and the role of Re are still not clear. It has been reported that the intra-molecular dehydration of glycerol to intermediates is one of the steps in glycerol hydrogenolysis to propanediols [6]. The acid sites on the catalyst are involved in the dehydration reaction. It has been reported that Re oxide possesses acid sites [14]. Therefore, it is interesting to investigate the acid property of Ru-Re catalysts and the relationship between acid property and activity. In this work, we examined the acidic property of Ru-Re/SiO₂ catalysts, and investigated the role of Re in promoting catalytic performance.

1 Experimental

1.1 Preparation of catalysts

Supported catalysts of 4.5%Ru-4.5%Re/SiO₂, 4.8%Ru/SiO₂, and 4.8%Re/SiO₂ were prepared by impregnation. The detailed procedures were described in previous papers [11–13]. Samples of Ru-Re/SiO₂ with different Re contents (4.7%Ru-0.9%Re and 4.6%Ru-3.1%Re) were also prepared. The loadings (wt%) of Ru and Re on the catalysts were nominal amounts based on the amounts of RuCl₃·4H₂O and HReO₄ used.

The prepared catalysts (calcined at 350 °C in air for 4 h), which were called fresh catalysts, were directly used in the hydrogenolysis of glycerol. The catalysts would undergo reduction under the reaction conditions during the hydrogenolysis. For comparison, a pre-reduced 4.5%Ru-4.5%Re/SiO₂ catalyst (with H₂/N₂ = 3/5, 80 ml/min at 450 °C for 4 h), which was denoted as pre-reduced 4.5%Ru-4.5%Re/SiO₂, was also used. The spent 4.5%Ru-4.5%Re/SiO₂ sample (denoted as spent 4.5%Ru-4.5%Re/SiO₂), which was recovered after the reaction, was recycled for hydrogenolysis, and then it was recovered again. This re-recovered catalyst was re-calcined at 350 °C in air for 4 h for regeneration. This regenerated catalyst was denoted as regenerated 4.5%Ru-4.5%Re/SiO₂.

Commercial reagents of ReO₃ (99.9%, powder) and Re⁰ metal powder (99.99%, 325 mesh) used as additives in Ru/SiO₂ catalyzed hydrogenolysis were purchased from

Alfa Aesar Company.

1.2 Characterization of catalysts

The acidic property of the catalysts was measured by NH₃ temperature-programmed desorption (NH₃-TPD) and in situ IR spectra of pyridine adsorption (pyridine-IR). The NH₃-TPD characterization was carried out on a flow TPR/TPD apparatus (CHEMBET 3000, Quantachrome). Desorbed NH₃ was measured by a quadrupole mass spectrometer (DM-200m, Ametek) using M/Z ratio 16 (NH₂) as the monitoring signal. In a typical experiment, the catalyst sample (about 0.1 g) was first treated at 400 °C for 2 h and cooled to 100 °C in high purity He gas flow (99.999%, 25 ml/min). Then the sample was saturated with the mixture gas of He and NH₃ (4.97% NH₃) at 100 °C and a flow rate of 25 ml/min for 1 h. This was subsequently purged with He flow at the same temperature to remove physical adsorbed NH₃ until there was no further change in the baseline of the QMS signal. Then, the sample was heated in He flow (25 ml/min) from 100 °C to 850 °C at 15 °C/min heating rate, and the mass signal was recorded. The amount of desorbed NH₃ from the samples was calculated by integrating the NH₃-TPD peak areas, which were calibrated by the mass signals of standard NH₃/He gases.

Pyridine-IR was used to characterize the acid type of the catalysts. The IR spectra were recorded with a FT-IR 750 spectrometer (NICOLET MAGNA). In a typical experiment, a sample was pressed into a self-supporting wafer (~20 mg) and placed into an in situ IR cell. The sample was heated in vacuum (1×10^{-3} Pa) at 450 °C for 2 h, and then cooled down to 90 °C. The treated sample was saturated with the probe molecule pyridine at 90 °C. Subsequently physisorbed pyridine was removed by heating under vacuum at 200 °C for 20 min. Then, the IR spectrum of adsorbed pyridine on the sample was recorded. The absorption band at 1450 cm⁻¹ was attributed to adsorbed pyridine on Lewis acid sites (PyL), while the absorption band at 1545 cm⁻¹ was due to adsorbed pyridine on Brönsted acid sites (PyH).

1.3 Hydrogenolysis of glycerol

The hydrogenolysis of glycerol was carried out in a 100 ml stainless steel autoclave. The detailed procedure and calculation of conversion of glycerol and product selectivities were described in previous papers [11–13]. The standard reaction conditions were 160 °C, 8 MPa H₂ pressure and 8 h reaction time using 10 ml 40 wt% glycerol aqueous solution and 0.15 g supported catalyst. After the reaction, the liquid and the solid catalyst in the mixture were separated by centrifugation and filtration. The products in the

Fig. 1. NH_3 -TPD profiles of the catalysts. (1) 4.5%Ru-4.5%Re/ SiO_2 ; (2) 4.8%Re/ SiO_2 ; (3) 4.8%Ru/ SiO_2 ; (4) pre-reduced 4.5%Ru-4.5%Re/ SiO_2 .

liquid phase were quantitatively analyzed with a gas chromatography (Lunan-SP 6890, PEG2 M, 30 m $\times$ 0.25 mm; FID detector).

2 Results and discussion

NH_3 -TPD characterization of fresh 4.5%Ru-4.5%Re/ SiO_2 , 4.8%Ru/ SiO_2 , and 4.8%Re/ SiO_2 catalysts were performed, and the results are shown in Fig. 1. For all three samples, NH_3 desorption peaks in the 100–300 $^\circ\text{C}$ range were observed, indicating the existence of weak acid sites. In addition, for 4.5%Ru-4.5%Re/ SiO_2 and 4.8%Re/ SiO_2 samples, small NH_3 desorption peaks in the 350–600 $^\circ\text{C}$ range were also detected, suggesting that there were small amounts of medium strength acid sites on the surfaces. In the NH_3 -TPD characterization, the integral areas of the NH_3 -TPD peaks corrected by the calibration with standard NH_3/He gases corresponded to the NH_3 amounts desorbed from the catalysts. The total area of the NH_3 -TPD peaks of 4.5%Ru-4.5%Re/ SiO_2 was obviously larger than that of 4.8%Ru/ SiO_2 . The quantitative analysis indicate that the total acid amount of the former was 67.4 $\mu\text{mol/g}$ and that of the latter was 10.9 $\mu\text{mol/g}$. The 4.8%Re/ SiO_2 sample also showed large NH_3 desorption peaks (total acid amount = 38.4 $\mu\text{mol/g}$). This observation is in agreement with the literature that Re oxide has acid sites [14]. On comparing the NH_3 -TPD characterization results of 4.5%Ru-4.5%Re/ SiO_2 , 4.8%Ru/ SiO_2 , and 4.8%Re/ SiO_2 , it is clear that the addition of Re to Ru/ SiO_2 increased the acid amount of Ru-Re/ SiO_2 .

The characterization results of pyridine-IR of 4.5%Ru-4.5%Re/ SiO_2 , 4.8%Ru/ SiO_2 , and 4.8%Re/ SiO_2 are shown in

Fig. 2. Spectra of pyridine-IR of 4.8%Re/ SiO_2 (1), 4.8%Ru/ SiO_2 (2), and 4.5%Ru-4.5%Re/ SiO_2 (3). LPY = coordinated pyridine (Lewis acid site).

Fig. 2. The peak at 1450 cm^{-1} , which was assigned to pyridine adsorbed species on Lewis acid sites, was observed with all three samples. However, there was no peak at 1540 cm^{-1} , which would indicate adsorbed pyridine on proton acid sites. These results indicate that the type of acid sites on the surface of 4.5%Ru-4.5%Re/ SiO_2 , 4.8%Ru/ SiO_2 , and 4.8%Re/ SiO_2 was Lewis acidic.

On the other hand, as reported in our previous papers, the addition of Re gave a significant promoting effect on the activity of Ru catalysts and their selectivities to propanediols in the hydrogenolysis of glycerol [11–13]. 4.5%Ru-4.5%Re/ SiO_2 showed much higher activity (51.7% glycerol conversion) than 4.8%Ru/ SiO_2 (16.8% glycerol conversion) [13]. This was consistent with the characterization results of the acid amounts on 4.5%Ru-4.5%Re/ SiO_2 and 4.8%Ru/ SiO_2 described above. That is, 4.5%Ru-4.5%Re/ SiO_2 had a larger acid amount than 4.8%Ru/ SiO_2 , and it showed higher hydrogenolysis activity. However, when fresh 4.5%Ru-4.5%Re/ SiO_2 was pre-reduced at 450 $^\circ\text{C}$ with H_2 , its activity decreased (23.8% glycerol conversion) [13]. This activity decrease corresponded to a decline of its acid amount. As shown in Fig. 1, the NH_3 -TPD profile of pre-reduced 4.5%Ru-4.5%Re/ SiO_2 revealed small NH_3 desorption peaks. The acid amount of pre-reduced 4.5%Ru-4.5%Re/ SiO_2 (11.5 $\mu\text{mol/g}$) was much smaller than that of fresh 4.5%Ru-4.5%Re/ SiO_2 (67.4 $\mu\text{mol/g}$). NH_3 -TPR results of Ru-Re/ SiO_2 and Re/ SiO_2 showed that Re oxide on the catalysts was reduced by H_2 into the Re^0 state at 350–450 $^\circ\text{C}$. Since Re oxide possesses acid sites [14], the decreases of acid amount and activity of pre-reduced 4.5%Ru-4.5%Re/ SiO_2 were probably due to the reduction of Re oxide on 4.5%Ru-4.5%Re/ SiO_2 to the Re^0 state.

From these results, it can be suggested that the state of the Re component (metal state or oxidized state) on 4.5%Ru-4.5%Re/ SiO_2 catalyst is an important factor that

Table 1 Effect of different Re additives on Ru/SiO₂

Catalyst	X/%	Yield (%)		
		PDO	PO	Others
Ru/SiO ₂ +ReO ₃	33.9	20.7	6.9	6.3
Ru/SiO ₂ +Re ⁰	19.8	9.6	6.1	6.5
Ru/SiO ₂	16.8	7.6	4.9	4.3

Reaction conditions: 160 °C, 8 MPa H₂, 8 h, 0.15 g Ru/SiO₂, Re/Ru molar ratio = 1/1, 10 ml glycerol aqueous solution (40 wt%).

X—glycerol conversion; PDO—1,2-propanediol + 1,3-propanediol; PO—1-propanol + 2-propanol; other—ethylene glycol + ethanol + methanol.

influences the activity of the catalyst. In order to further check the different influence of metal state Re and oxidized Re on the activity of 4.8%Ru/SiO₂ catalyst, Re⁰ metal powder and ReO₃ powder were used as the additives of the 4.8%Ru/SiO₂ catalyst. As shown in Table 1, the addition of ReO₃ additive gave a remarkable promoting effect on the conversion of glycerol and the yield of propanediols, while the Re⁰ metal additive showed no obvious promoting effect on the activity of 4.8%Ru/SiO₂. Therefore, the significant promoting effect of the Re component on the activity of 4.5%Ru-4.5%Re/SiO₂ was not from the Re⁰ metal state, but from the Re oxide state.

As described in the experimental part, the fresh catalysts used in the reaction would be reduced in situ. XPS characterization of spent 4.5%Ru-4.5%Re/SiO₂ revealed that the Ru component was in the metal state, while the Re component was mostly in the oxidized state, but also partly in the Re⁰ state [12,13]. For further checking the activity of the spent 4.5%Ru-4.5%Re/SiO₂ catalyst, the recycle of the spent 4.5%Ru-4.5%Re/SiO₂ (recovered after the first run reaction) was performed. Furthermore, after the second run reaction, the recycled 4.5%Ru-4.5%Re/SiO₂ was recovered again and regenerated (350 °C in air for 4 h), and this regenerated 4.5%Ru-4.5%Re/SiO₂ catalyst was also evaluated again in the hydrogenolysis. As shown in Table 2, the results revealed that the activity of the spent 4.5%Ru-4.5%Re/SiO₂ was lower than that of the fresh 4.5%Ru-4.5%Re/SiO₂, which suggested that the activity decrease of spent 4.5%Ru-4.5%Re/SiO₂ may be due to the some reduction to Re⁰ metal on the spent catalyst. For regenerated 4.5%Ru-4.5%Re/SiO₂ on which the Re component could be com-

Table 2 Comparison of fresh, spent, and regenerated 4.5%Ru-4.5%Re/SiO₂ catalysts

Catalyst	X/%	Yield (%)		
		PDO	PO	Others
Fresh 4.5%Ru-4.5%Re/SiO ₂	51.7	25.3	18.5	7.9
Spent 4.5%Ru-4.5%Re/SiO ₂	40.9	26.8	10.5	3.5
Regenerated 4.5%Ru-4.5%Re/SiO ₂	51.1	28.7	15.4	7.1

Reaction conditions are the same as in Table 1.

pletely oxidized to Re oxide state by the calcination treatment at 350 °C in air, the activity of the catalyst was recovered. These results indicated that Re in the oxidized state played an important role on the activity of Ru-Re/SiO₂ in glycerol hydrogenolysis. On the other hand, it can be seen from Table 2 that the yields of PDO over spent 4.5%Ru-4.5%Re/SiO₂ and regenerated 4.5%Ru-4.5%Re/SiO₂ were higher than that over fresh 4.5%Ru-4.5%Re/SiO₂. That is, the selectivities to PDO over spent 4.5%Ru-4.5%Re/SiO₂ and regenerated Ru-Re/SiO₂ were higher than that over fresh Ru-Re/SiO₂. This suggested that there may be some interaction between Ru and Re metal after the reaction. In a previous work from our group, we found that the pre-reduction of Ru-Re/SiO₂ with H₂ flow at high temperatures increased the selectivities to 1,2-propanediol and 1,3-propanediol, although the activity of the catalyst decreased [13]. Both the acidic properties and the interaction between Ru and Re metal influence the catalytic performance of Ru-Re bi-component catalysts, with the surface acid sites affecting the activity.

As discussed above, the addition of a Re component in the oxide state increased the acid amount of Ru-Re/SiO₂, and consequently promoted the catalytic activity. Therefore, the acid amount on the catalyst should have a relationship with the content of the Re component in Ru-Re/SiO₂. In the present study, a series of Ru-Re/SiO₂ samples with different Re contents were employed in glycerol hydrogenolysis. The reaction results are listed in Table 3. The activities of Ru-Re/SiO₂ with different Re contents increased with the increase of the Re/Ru molar ratio. However, Re alone without Ru showed very low activity. NH₃-TPD characterization of the Ru-Re/SiO₂ samples with different Re contents were also performed. The total acid amounts of 4.8%Ru/SiO₂, 4.7%Ru-0.9%Re/SiO₂, 4.6%Ru-3.1%Re/SiO₂, and 4.5%Ru-

Table 3 Influence of Re/Ru ratios on activity of Ru-Re/SiO₂ catalysts

Catalyst	Re/Ru molar ratio	X/%	Yield (%)		
			PDO	PO	Others
4.8%Ru/SiO ₂	Re = 0	16.8	7.6	4.9	4.3
4.7%Ru-0.9%Re/SiO ₂	Re/Ru = 0.10/1	36.6	16.1	14.5	6.0
4.6%Ru-3.1%Re/SiO ₂	Re/Ru = 0.37/1	45.8	22.9	16.7	6.2
4.5%Ru-4.5%Re/SiO ₂	Re/Ru = 0.54/1	51.7	25.3	18.5	7.9
4.8%Re/SiO ₂	Ru = 0	1.7	0.9	0.5	0.3

Reaction conditions are the same as in Table 1.

Fig. 3. Relationship of acid amount and activity of Ru-Re/SiO₂. (1) Glycerol conversion; (2) PDO yield.

4.5%Re/SiO₂ were 10.9, 16.7, 35.5, and 67.4 μmol/g, respectively. Glycerol conversion and yields of propanediols are plotted versus the total acid amount of Ru-Re/SiO₂ with different Re contents in Fig. 3. The conversion of glycerol and the yields of propanediols increased with the total acid amount, and the total acid amount correlated with the Re content on the catalyst. The relationship between the acid amount on Ru-Re/SiO₂ and the activity of the catalyst further confirmed the important role of acid sites and Re oxide in Ru-Re/SiO₂ in the hydrogenolysis of glycerol.

From the results above, the promoting effect of the addition of Re oxide on catalytic performance of Ru-Re/SiO₂ was due to the increase of acid amount of the catalyst. It was proposed in the literature [6] that glycerol hydrogenolysis to propanediols is a two-step reaction (the dehydration of glycerol and the hydrogenation of intermediates). In general, acid sites on the catalysts are involved in the dehydration step [15]. From the results above, it can be considered that the addition of Re oxide into the Ru/SiO₂ catalyst provide effective acidic sites on the surface of Ru-Re/SiO₂, which promoted the step of glycerol dehydration. Using the proposed reaction mechanism in the literature [4,6], we propose the mechanism on Ru-Re/SiO₂ catalyst of glycerol hydrogenolysis to propanediols shown in Scheme 1. Re oxide, which provided acidic sites on Ru-Re/SiO₂, was involved in the first step (intra-molecular dehydration of glycerol) of the catalytic hydrogenolysis of glycerol, while Ru⁰ metal sites was involved in the second step (hydrogenation of the intermediates). With the combination of Re oxide and Ru⁰ metal on the surface of Ru-Re/SiO₂, acidic sites (dehydration center) and metal sites (hydrogenation center) act in synergy in glycerol hydrogenolysis. Therefore, the bi-component Ru-Re/SiO₂ catalyst showed much higher activity than the Ru mono-component catalyst.

Scheme 1. Mechanism on Ru-Re/SiO₂ catalyst of glycerol hydrogenolysis.

3 Conclusions

Bi-component Ru-Re/SiO₂ and mono-component Ru/SiO₂ have acid sites, but the acid amount on Ru-Re/SiO₂ was much larger than on Ru/SiO₂. The increase in the acid amount on Ru-Re/SiO₂ was due to Re oxide on the catalyst. High temperature pre-reduction of Ru-Re/SiO₂ decreased the acid amount, and consequently resulted in a very low activity. There was a relationship between the acid amount and activity of Ru-Re/SiO₂ with different Re oxide contents. The synergy of Re oxide (acid sites) and Ru⁰ metal sites on Ru-Re/SiO₂ led to its high activity.

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