

Efficient Hydrogenation of Methyl Propionate over Boehmite-supported Ru–Pt Catalyst

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The bimetallic catalyst Ru–Pt/AIOOH exhibited good catalytic performance in water for the hydrogenation of methyl propionate to 1-propanol. The selectivity to 1-propanol of 97.8% was obtained with a conversion of 89.1% at 453 K, 5 MPa for 6 h. The incorporation of Pt for the improvement of the catalytic activity was attributed to promoting the reduction of Ru³⁺ to Ru⁰.

Alcohols are important raw materials in pharmaceutical and chemical industries. However, most alcohols have been produced by conventional reduction with stoichiometric amounts of metal–hydrides like LiAlH₄,¹ which is neither environmentally compatible nor economical. So the direct hydrogenation of carboxylic esters to the corresponding alcohols is of great importance in industrial processes. Copper-based catalysts have been widely applied for the hydrogenation of fatty esters,² but they usually require high hydrogen pressure (200–300 atm) and high temperature (200–300 °C) to achieve reasonable productivity. Therefore, many attempts have been made to develop some efficient catalysts for the hydrogenation of esters to alcohols under mild conditions. Heterogeneous bimetallic catalysts prepared from a group VIII metal and a second metal like Sn, Re, Ge, or W have been extensively explored.^{3–9} It has been found that Ru–Sn catalysts are the most effective for the hydrogenation of fatty esters to fatty alcohols³ as well as for the hydrogenation of dimethyl adipate to diol.^{5,6} Recently, the promoting role of Sn to Ru catalyst for the hydrogenation of ethyl lactate to 1,2-propanediol has also been reported by Fan et al.^{7,8} In addition, the catalytic performance of Ru–Sn/C can be further improved by adding Pt for the hydrogenation of 1,4-cyclohexanedicarboxylic acid to 1,4-cyclohexanedimethanol.⁹ In most of the reported investigations, traditional carriers such as TiO₂, γ -Al₂O₃, SiO₂, ZrO₂, and active carbon are often used. Additionally, all hydrogenations of esters are carried out in organic solvents. Boehmite (AIOOH) is widely used as a catalyst support,¹⁰ but there are no reports on boehmite-supported catalysts for the hydrogenation of esters. In the present work, we use methyl propionate as a model compound and Ru–Pt supported on AIOOH as a catalyst to investigate this system's hydrogenation property for esters. It exhibits good catalytic performance in environmentally benign water.

The monometallic and bimetallic catalysts (6.3 wt %) were prepared by impregnation and coimpregnation, respectively. Typically, γ -Al₂O₃ was added to an ethanol solution of RuCl₃ and/or H₂PtCl₆ with an appropriate concentration. The slurry was stirred overnight at room temperature. Next, the solvent was slowly removed under vacuum. The resulting solid was dried overnight at 120 °C and calcined in air at 400 °C for 4 h. Thereafter, the sample was reduced in water with hydrogen pressure of 3 MPa at 180 °C for 2 h, then filtered, and dried in vacu-

um for 10 h. Weighed amounts of catalyst, methyl propionate, and solvent were added to a 60-mL stainless autoclave equipped with a magnetic stirrer and an electric temperature controller. It was purged with H₂ three times, pressurized with H₂ to 5 MPa, and then heated to 180 °C with a stirring rate of 1000 rpm for 6 h. Samples were analyzed by GC-6890 (Agilent) with a FID detector and quartz capillary column (SE-30, 30 m \times 0.25 mm, 0.25 μ m film), and products were identified by comparison with standard samples and GC-MS.

X-ray diffraction (XRD) study was performed on a Rigaku D/max-rA instrument with a Cu K α radiation and in scan range of 10–70°. The X-ray photoelectron spectra (XPS) were recorded with a Kratos XSAM800 spectrometer (Mg K α radiation, operating at 15 mA and 12 kV). TPR experiments were performed on a laboratory-made apparatus. Samples were heated from 50 to 600 °C at a linear rate of 10 °C min⁻¹ under a flow of 5 vol % H₂/N₂.

The XRD pattern of Ru–Pt/AIOOH (Pt/Ru = 1/9) exhibited characteristic diffraction peaks assigned to boehmite (γ -AIOOH, JCPDS Card No. 21-1307),¹⁶ which suggested that γ -Al₂O₃ had been transformed into AIOOH. The peaks at 280.1 (Ru 3d_{5/2}) and 72.5 eV (Pt 4f_{7/2}) in XPS spectra¹⁶ of Ru–Pt/AIOOH (Pt/Ru = 1/9) indicated that Ru and Pt existed in Ru⁰ and electron deficient Ptⁿ⁺ (0 < n < 2), respectively.^{9,11} The TPR profiles of Ru–Pt/AIOOH showed that Pt supported on boehmite was not reduced to zero valence. When the Pt/Ru molar ratio was lower than 1/4, the reduction temperature of ruthenium decreased with increasing Pt loading and the reduction temperature was shifted from 215 °C for the monometallic Ru catalyst¹¹ to 155 °C for Ru–Pt (Pt/Ru = 1/4).¹⁶ When the Pt/Ru molar ratio was beyond 1/4, the reduction of ruthenium required a higher temperature and the reduction peak became weaker. This suggests that an excessive addition of Pt is unfavorable for the reduction of ruthenium.

The effect of support on the hydrogenation of methyl propionate is shown in Table 1. Among the tested catalysts, AIOOH-supported Ru–Pt exhibited the highest conversion of methyl propionate (89.1%) and selectivity to 1-propanol (97.8%) under the same conditions. Ru–Pt/NaY showed the lowest activity and selectivity. The selectivity over Ru–Pt/ γ -Al₂O₃ was similar to that over Ru–Pt/AIOOH, but the activity was obviously low in spite of the fact that γ -Al₂O₃ could be slowly transformed into AIOOH under the hydrogenation conditions. Ru–Pt/ZrO₂ and Ru–Pt/SiO₂ only gave moderate conversion. The difference of catalytic performance on different supports can be related to the intrinsic properties of the support. Many researchers have revealed that AIOOH is composed of Al–O double layers that are interconnected by hydrogen bonds between the hydroxy groups.¹² We speculate that the cooperation between the hydroxy groups on the surface of Ru–Pt/AIOOH and water as sol-

Table 1. Effect of support on the hydrogenation of methyl propionate^a

| Catalyst | Conv./% | Sel./% | | |
|---|---------|-------------------|-----------------|-------------------|
| | | 1-PO ^b | PA ^c | TREF ^d |
| Ru–Pt/AlOOH | 89.1 | 97.8 | 1.0 | 1.2 |
| Ru–Pt/ γ -Al ₂ O ₃ | 62.6 | 98.1 | 1.8 | 0.1 |
| Ru–Pt/ZrO ₂ | 60.3 | 95.1 | 3.9 | 1.0 |
| Ru–Pt/SiO ₂ | 70.9 | 41.7 | 57.4 | 0.9 |
| Ru–Pt/NaY | 42.1 | 34.7 | 64.6 | 0.6 |

^aConditions: 453 K, 5.0 MPa, 6 h, 0.2 mL of methyl propionate, 0.041 mmol catalyst, 3 mL of H₂O. ^b1-Propanol.

^cPropionic acid. ^dTransesterification.

Table 2. Effect of Pt content on the hydrogenation of methyl propionate over AlOOH-supported catalyst^a

| Entry | Pt/Ru (molar ratio) | Conv. /% | Sel./% | | |
|-------|------------------------|-------------|-------------------|-----------------|-------------------|
| | | | 1-PO ^b | PA ^c | TREF ^d |
| 1 | 0:1 | 69.9 | 89.8 | 9.1 | 1.1 |
| 2 | 1:19 | 87.8 | 96.8 | 1.6 | 1.6 |
| 3 | 1:9 | 89.1 | 97.8 | 1.0 | 1.2 |
| 4 | 1:6 | 90.2 | 94.5 | 3.8 | 1.7 |
| 5 | 1:4 | 95.0 | 91.7 | 7.1 | 1.2 |
| 6 | 1:2 | 92.5 | 73.8 | 23.7 | 2.5 |
| 7 | 1:1 | 94.8 | 58.0 | 40.2 | 1.8 |
| 8 | 4:1 | 93.7 | 33.2 | 65.8 | 1.0 |
| 9 | 1:0 | 93.4 | 15.1 | 84.0 | 0.9 |

^aConditions: 453 K, 5.0 MPa, 6 h, 0.2 mL of methyl propionate, 0.041 mmol catalyst, 3 mL of H₂O. ^b1-Propanol.

^cPropionic acid. ^dTransesterification.

vent probably promote the hydrogenation. Further mechanistic study of the role of water and hydroxy groups on the surface of the catalyst will be presented in a forthcoming paper.

Table 2 shows the effect of Pt content on the hydrogenation of methyl propionate to 1-propanol over Ru–Pt/AlOOH. It can be seen that the addition of Pt to the Ru catalyst remarkably improved the catalytic activity and selectivity. Compared with Ru/AlOOH, Ru–Pt/AlOOH with a small amount of Pt (Pt/Ru = 1/19, Entry 2) increased the conversion of methyl propionate from 69.9 to 87.8% and the selectivity to 1-propanol from 89.8 to 96.8%. The hydrogenation rate is obviously higher than that in the hydrogenation of propionic acid over magnesia-supported poly- γ -aminopropyl–siloxane–Ru complex at 240 °C and 5 MPa H₂ for 18 h.¹³ When the molar ratio of Pt to Ru was 1/4, the catalyst showed the lowest reduction temperature in TPR and gave the highest activity and yield to 1-propanol. It suggests that the proper amount of Pt, which promotes the reduction of Ru species, is crucial to improve the catalytic activity and selectivity in this system. Hara et al. found the optimal amount of Pt added to Ru–Sn/C catalyst to facilitate the reduction of ruthenium and then improved catalytic activity for the hydrogenation of 1,4-cyclohexanedicarboxylic acid.⁹ Our experimental results are in good agreement with the previous study. But an excessive addition of Pt led to a negative effect. After the molar ratio of Pt/Ru was beyond 1/4, the selectivity to 1-propanol decreased. Especially, when the Pt/Ru molar ratio was up to 4/1 (Entry 8), the catalytic activity and selectivity

of Ru–Pt/AlOOH were very close to that of monometallic Pt/AlOOH (Entry 9). It has been reported that platinum has lower enthalpy of sublimation than ruthenium and that it is preferentially enriched on the surface of the supported bimetallic clusters.^{14,15} XPS spectra of Pt in Ru–Pt/AlOOH demonstrated that Pt was difficult to reduce to zero valence. After the molar ratio of Pt/Ru was beyond 1/4, most metal active sites could be occupied by electron-deficient Ptⁿ⁺ to result in the low hydrogenation activity and selectivity. The result clearly showed that the hydrogenation of propionic acid and methyl propionate was difficult over Ptⁿ⁺-rich surface. We suggest that the electron-rich oxygen in the carboxylic group was easily adsorbed on the electron-deficient Ptⁿ⁺, so that it would promote the hydrolysis of ester in water to give propionic acid. To get some insights into this, the reactions of methyl propionate over the Ru–Pt/AlOOH and AlOOH were investigated in water without hydrogen at 180 °C for 6 h. It was found that the hydrolysis conversion rates of methyl propionate over Ru–Pt/AlOOH catalysts with the Pt/Ru molar ratio of 1/9 and 1/2 were 22.8 and 79.5%, respectively. However, only 2% of methyl propionate hydrolyzed over AlOOH under the same conditions. This indicated that the hydrolysis of methyl propionate was caused by Pt rather than by carrier AlOOH.

In conclusion, the bimetallic catalyst Ru–Pt/AlOOH exhibited good catalytic performance in water for the hydrogenation of methyl propionate to 1-propanol. The incorporation of Pt promoted the reduction of Ru³⁺ to Ru⁰.

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