

Effects of Yttrium Doping on the Performance of Ru-Based Catalysts for Hydrogenation of Fatty Acid Methyl Ester

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Abstract

The highly dispersed supported ruthenium-yttrium (Ru-Y) bimetallic catalysts were prepared by impregnation method and their catalytic performance for hydrogenation of ester was fully investigated. The catalyst was characterized by X-ray diffraction and field emission scanning electron microscopy. The results show that the average particle diameter of the bimetallic crystallites was less than 10 nm. The effects of the reaction temperature, the hydrogen pressure, the amount of catalyst and the proportion of yttrium in catalyst on the hydrogenation of ester were studied. The experimental results show that the introduction of yttrium not only changed the chemical and textural properties of ruthenium-based catalyst but also controlled the formation of Ru-Y alloy. The Ru-Y catalyst (Ru-2%Y/TiO₂) exhibited high catalytic activity and good selectivity towards the higher alcohols. Under optimal reaction conditions of 240°C and 5 MPa hydrogen pressure, the conversion of palm oil esters was above 93.4% while the selectivity towards alcohol was above 99.0%.

Keywords

Yttrium-Doped, Ruthenium-Based Catalyst, Fatty Acid Methyl Ester, Hydrogenation

1. Introduction

Fatty alcohols (FALCs) and their derivatives are widely used as surfactants, lubricants, solvents, synthetic detergents, antifoaming agents, perfumes, cosmetics and pharmaceuticals, and as additives in many industrial products [1]. Naturally, derived FALCs approximately accounts for 65% of the world's steadily growing fatty alcohol

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demand. They are special products obtained from natural fats and oils by the hydrogenation of fatty acids or fatty acid methyl esters (FAME) [2]. The best method of converting an acid to the corresponding alcohol is through the esters because esters are less corrosive and can be reduced to alcohols with considerably higher yields, and esters can be obtained from acids in nearly quantitative yields.

Since the last century, the natural-fatty-alcohol-based surfactants have gained growing significance in the detergent market due to their excellent washing properties and superior biodegradability. Therefore, the hydrogenation of FAME to the corresponding FALCs is of great industrial importance. And the concern of catalyst research is raised because catalyst is the key technology for the effective production of FALCs and the successful utilization of natural FAME. Many efforts have been made to develop high active catalysts [3] [4]. Most of these studies concentrated on the characterization of the catalyst or mechanism of the reaction but as lower catalytic activity or selectivity towards FALCs.

During the last decade, the development of biodiesel has been emphasized. Biodiesel is defined as a fatty acid methyl ester obtained by the trans-esterification route of renewable biological sources with methanol. It can offer abundant feedstock for the hydrogenation to obtain FALCs. Therefore, the research subject is to focus on improving the selectivity and yield of FALCs to the highest possible. It is reported that depositing the amorphous alloys on support [3] [5] [6] and adding promoters such as Au and Ag to the amorphous [7] are useful ways to improve their thermal stability and catalytic activity. In this study, the ruthenium-yttrium (Ru-Y) bimetallic catalysts were prepared through impregnation method and their performances of the hydrogenation of methyl palmitate to fatty alcohol were investigated. The effects of reaction conditions such as the reaction temperature, the hydrogen pressure, the proportion of yttrium, the amount of catalyst and the solvent on the hydrogenation of methyl palmitate were studied. The conversion of methyl palmitate could reach high at mild reaction conditions.

2. Experiment

2.1. Chemicals

RuCl₃ (Sinopharm Chemical Reagent Co., Ltd., >99.6%), Y(NO₃)₃ (Sinopharm Chemical Reagent Co., Ltd., >99.9%), Methyl palmitate (Aladdin Reagent Co. Ltd., >99.9%), TiO₂ (100 - 160 mero), hydrogen (99.99%) and the other reagents were used as received.

2.2. Preparation of Catalyst

All the catalysts were prepared by the impregnation method in aqueous suspensions. The metallic precursors (such as ruthenium chloride and yttrium nitrate) were dissolved in deionized water. Then, the titania was impregnated with above solution for overnight. And water was employed by evaporation at 333 K for 5 h. Next, the samples were dried at 393 K for 12 h. The solids were subjected to calcination treatment for 4 h at 673 K under air flow and reduced by hydrogen for 3 h at 453 K.

In order to eliminate the surface acidity of the catalyst, the catalyst was treated with barium nitrate and washed with deionized water until the absence of barium cations. The solids were dried for 6 h under vacuum. For the bimetallic catalysts, with monovalent concentration of 5 wt% in Ru and 2.5 wt% in Y was employed, designated as 5% Ru - 2.5% Y/TiO₂.

2.3. Characterization of the Supported Catalyst

The powder XRD patterns were recorded at room temperature on a Philips X'Pert Pro MPD X-ray diffraction with Cu-K_α radiation at 50 kV and 35 mA. The 2θ angles were scanned from 15° to 75° at a rate of 0.1(°)/s. High-resolution TEM (HRTEM) images were obtained on a Philips TECNAIF-30 FEG instrument at an accelerating voltage of 300 V. The sample was dispersed with dry ethanol.

2.4. Investigation on the Catalytic Activity

The reaction was performed in a 60 mL stainless autoclave with a glass linear and magnetic stirrer. A typical procedure for hydrogenation of methyl palmitate (**Scheme 1**) is as follows: the appropriate amounts of palm oil esters, catalyst and cyclohexane were directly introduced into the autoclave, followed by a purge with hydrogen several times. Hydrogen was introduced until the desired hydrogen pressure was reached. The reaction was car-

ried out under the designed conditions for a desired time. After the reaction, the autoclave was quickly cooled in a water bath and vented. The liquid products were separated from the reaction mixture by decantation and analyzed by GC 4002A (SUPELLOWAX™10 0.25 mm × 0.25 μm × 30 m), incorporating an FID detector. The solid residue obtained was reused in the next reaction.

3. Results and Discussion

3.1. Characterization of the Supported Catalyst

In order to further identify the crystalline phase of Ru in the catalyst, power X-ray diffraction patterns of the six solids with different metal loadings were obtained, as shown in **Figure 1**. The XRD pattern of titania exhibit the typical reflections of titania at 18°. The XRD patterns of Ru/TiO₂ exhibit the typical reflections at 29°, 55° and 64°. As the yttrium dopes on the Ru-based catalyst, the typical reflection of yttrium at 38° and 48° were found. Meanwhile, the characteristic peak of ruthenium (29°) shifts slightly from 29° to 25° while the other peaks are still observed. As the yttrium loadings increase from 1wt% to 2.5 wt%, the ruthenium peaks are remarkably weakened and the other low-angle reflection peaks almost disappear. Further increasing the yttrium loadings, the characteristic peaks of ruthenium and yttrium are still observed again. This indicates that Ru and Y species are highly dispersed in the support, which is possible due to the not calcinated catalyst. This is probably caused by yttrium entering into the interspaces of titania and forming the Ru-Y alloy at the surface of the catalyst, which is in agreement with other reports [2]. According to the above analysis, it is assumed that the size distribution of the highly dispersed Ru and Y crystallites is small when w(Y) was 2.5 wt%. The deduction is also confirmed by the TEM images shown in **Figure 2**.

3.2. Catalytic activity of Ru-Y/TiO₂

3.2.1. Effect of Y Doping Amounts on the Catalytic Activity

To evaluate the catalytic activity of Ru-Y/TiO₂, the hydrogenation of methyl palmitate was chosen as a probing reaction. In all the runs, the selectivity for 1-hexadecanol in the products was more than 99%, only trace amounts of by-products palmitic acid were detected by GC-MS.

In order to investigate the effect of the amount of Y in catalyst on the hydrogenation, several kinds of catalysts with different amount of Y were used in the hydrogenation of methyl palmitate. It is clear from **Table 1** that the amount of Y shows a significant influence on the catalytic activity for hydrogenation of methyl palmitate. It is evident that conversion rates increase with Y doping amounts and selectivity is all above 99.9%. When



Scheme 1. Hydrogenation of methyl palmitate.

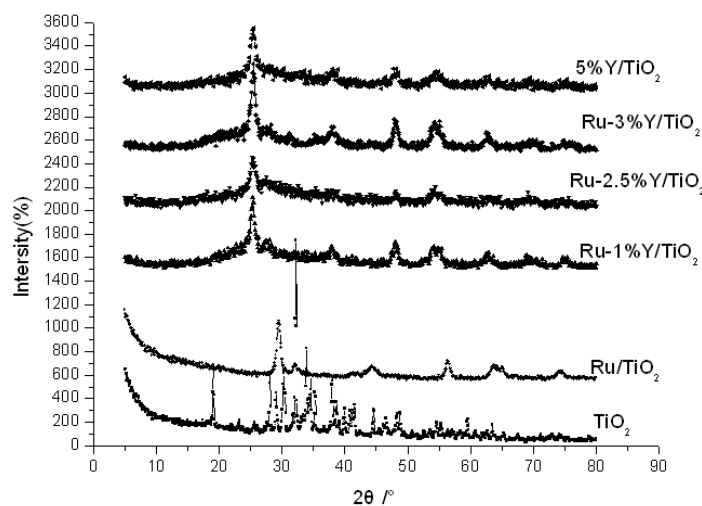


Figure 1. The XRD patterns of the catalysts.

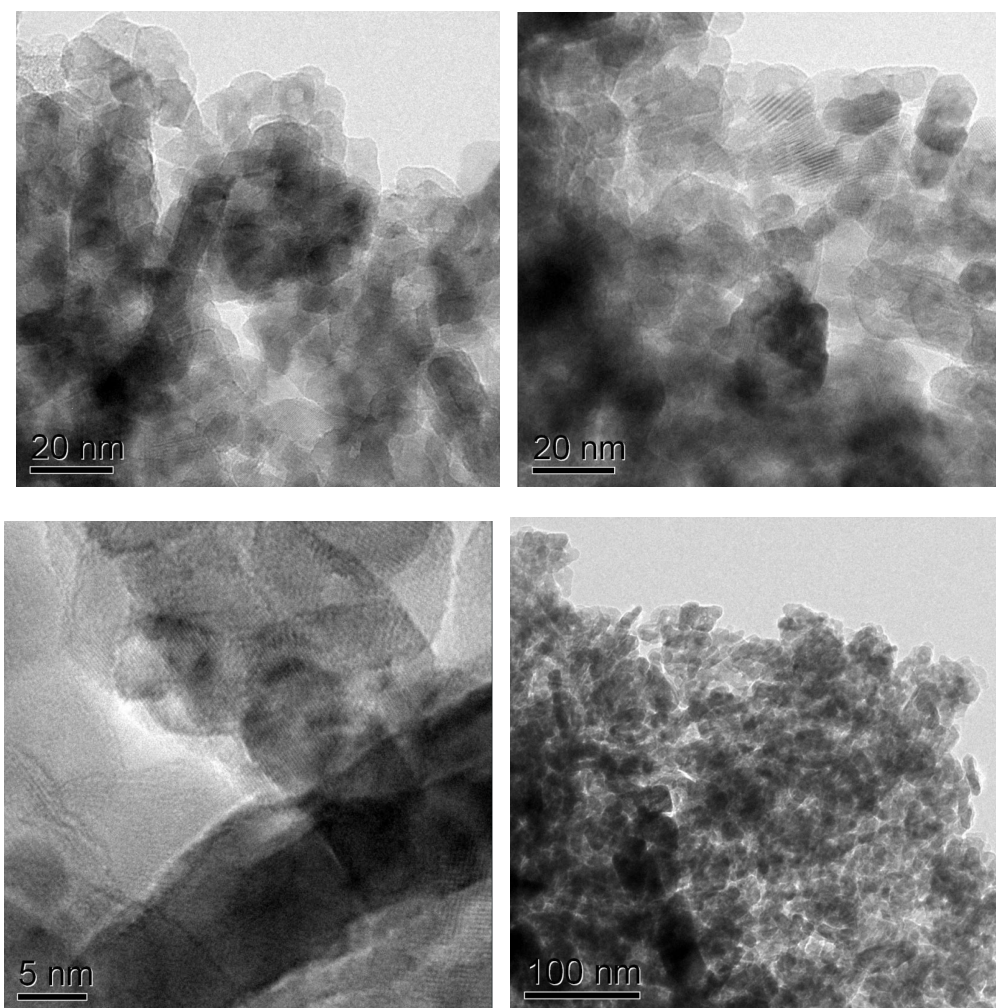


Figure 2. The TEM pictures of Ru-Y/TiO₂ catalysts.

Table 1. Effect of the amount of yttrium on the catalytic activity.

The amount of yttrium %	0	0.5	1	1.5	2	5*
Conversion (%)	10.4	29.3	72.5	75.8	93.4	0

Reaction conditions: catalyst 30 mg, methyl palmitate 1.85 mmol, cyclohexane 1 mL, 220°C, 5 MPa, 10 h. *The supported catalyst was Y/TiO₂.

Y doping amount is 0.5%, the conversion rate is just 29.3%. However, when Y doping amount is 2%, the conversion rate reached up to 93.4%. The doping of rare earth metals is one of the efficient methods to improve the activity of supported metal catalysts. This is probably due to the 4f electrons in Y electronic structure. Its outermost electronic structure is $4f^{1+n}5d^{0-1}6s^2$. Most of the earth metals have no 5d electron, so they could easily lose two 6s electrons, one d electron or f electron to form trivalent cations whose outermost electron configuration is $4f^n5s^26p^2$. From the electronic structure, the 5d orbital is empty, which provides a good electron transferring orbital and could be used as an electron transferring station with catalytic action. With the increasing of Y doping amounts, Y scrambles for electrons to reduce the composite of electron hole pair on TiO₂ surface so that more O²⁻ or O²⁻-OH are generated on the catalyst surface which has higher catalytic activity. Meanwhile, the specific electronic structure and larger radius of earth metals lead to lattice expansion on Ru/TiO₂ surface, which is beneficial to the generation of catalytic active center, increasing of catalytic active center numbers and improving of adsorption capacity of catalysts to hydrogen so as to increase conversion rates.

3.2.2. Effect of Temperature on the Catalytic Activity

The effect of temperature on the catalytic activity is shown in **Table 2**. It is clear from **Table 2** that the temperature also shows a significant influence on the catalytic activity for the hydrogenation of ester. The results indicate that the activity increases when the temperature rises from 180 °C to 240 °C. The tendency is similar to that of the hydrogenation of ester catalysed by Ru-based catalyst.

3.2.3. Effect of Hydrogen on the Catalytic Activity

Under the same conditions, the effect of the hydrogen pressure on the hydrogenation reaction of methyl palmitate was studied by altering the hydrogen pressure. When using 1.85 mmol methyl palmitate, 30 mg catalyst and 1 mL cyclohexane at 220 °C for 10 h, the results are listed in **Table 3**. It indicates that the activity increases when the pressure rises from 3 MPa to 7 MPa. Higher pressure could increase the concentration of hydrogen in the solution and thereby accelerates the hydrogenation.

3.2.4. Recycling of the Catalyst

To investigate the stability of catalyst, the reaction mixture was separated from the catalyst by decantation after the reaction and analyzed by GC. The catalyst was directly reused for the next run. The results of hydrogenation are shown in **Table 4**. No dramatic fall in the catalytic activity is observed at any point of time during the seven experiments, which further confirms the fact that the active metals are immobilized at the surface of titania. It is noteworthy that the catalytic activity of Ru-Y/TiO₂ increases to some extent in the recycling experiments, which further indicates that there is an induction time to form the catalytical active species. In the successive recycling runs, no induction time is needed for the high catalytic activity.

4. Conclusion

The supported ruthenium-yttrium bimetallic catalysts were prepared by impregnation and their catalytic performances for hydrogenation of ester were evaluated. The XRD and TEM results reveal that the active metals are highly dispersed and the alloy is formed by Ru with Y. The catalytic results indicate that the catalytic activity of Ru-Y/TiO₂ depends on the loading of yttrium. The ruthenium-yttrium catalyst (Ru-2%Y/TiO₂) exhibits high catalytic activity and good selectivity towards the higher alcohols compared with Ru/TiO₂ and Y/TiO₂. Furthermore, the catalyst can be easily separated from the organic products and reused for seven times without significant decrease of activity and selectivity.

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Table 2. Effect of temperature on the catalytic activity.

Temp. (°C)	180	200	220	230	240	250
Conversion (%)	3.9	7.5	23.2	29.3	50.3	65.7

Reaction conditions: catalyst 25 mg, methyl palmitate 1.85 mmol, cyclohexane 1 mL, 5 MPa, 10 h.

Table 3. Effect of hydrogen on the catalytic activity.

P_{H_2} (MPa)	3	4	5	6	7
Conversion (%)	38.0	56.2	72.5	74.8	78.2

Reaction conditions: catalyst 25 mg, methyl palmitate 1.85 mmol, cyclohexane 1 mL, 220 °C, 10 h

Table 4. Recycling experiment of the catalyst.

Cycle	1	2	3	4	5	6	7
Conversion (%)	43.1	44.5	47.4	49.3	56.9	52.1	50.6

Reaction conditions: catalyst 25 mg, methyl palmitate 1.85 mmol, cyclohexane 1 mL, 5 MPa, 6 h, 240 °C.

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References

- [1] Weissermel, K. and Arpe, H.-J. (1994) *Industrielle Organische Chemie*. 4th Edition, VCH Verlagsgesellschaft mbH, Deerfield Beach.
- [2] Echeverri, D.A., Marín, J., Restrepo, G. and Riso, L. (2009) Characterization and Carbonylic Hydrogenation of Methyl Oleate over Ru-Sn/Al₂O₃: Effects of Metal Precursor and Chlorine Removal. *Applied Catalysis A: General*, **366**, 342-347. <http://dx.doi.org/10.1016/j.apcata.2009.07.029>
- [3] Yuan, P., Liu, Z.Y., Sun, H.J. and Liu, S.C. (2010) Influence of Calcination Temperature on the Performance of Cu-Al-Ba Catalyst for Hydrogenation of Esters to Alcohols. *Acta Physico-Chimica Sinica*, **26**, 2235-2241. <http://dx.doi.org/10.3866/PKU.WHXB20100642>
- [4] Figueiredo, F.C.A., Jordão, E. and Carvalho, W. (2008) Adipic Ester Hydrogenation Catalyzed by Platinum Supported in Alumina, Titania and Pillared Clays. *Applied Catalysis A: General*, **351**, 259-266. <http://dx.doi.org/10.1016/j.apcata.2008.09.027>
- [5] He, L., Li, X., Lin, W., Cheng, H., Yu, Y., Fujita, S., Arai, M. and Zhao, F. (2014) The Selective Hydrogenation of Ethyl Stearate to Stearyl Alcohol over Cu/Fe Bimetallic Catalysts. *Journal of Molecular Catalysis A: Chemical*, **392**, 143-149. <http://dx.doi.org/10.1016/j.molcata.2014.05.009>
- [6] Vigier, K., Pouilloux, Y. and Barrault, J. (2012) High Efficiency CoSn/ZnO Catalysts for the Hydrogenation of Methyl Oleate. *Catalysis Today*, **195**, 71-75. <http://dx.doi.org/10.1016/j.cattod.2012.04.027>
- [7] Zheng, J., Lin, H., Wang, Y., Zheng, X., Duan, X. and Yuan, Y. (2013) Efficient Low-Temperature Selective Hydrogenation of Esters on Bimetallic Au-Ag/SBA-15 Catalyst. *Journal of Catalysis*, **297**, 110-118. <http://dx.doi.org/10.1016/j.jcat.2012.09.023>

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