COMMUNICATION

Highly selective and efficient catalytic conversion of ethyl stearate into liquid hydrocarbons over a Ru/TiO$_2$ catalyst under mild conditions†

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An efficient Ru/TiO$_2$ catalyst was successfully designed and synthesized for the deoxygenation of long chain fatty acid esters under mild conditions (200 °C, 3.0 MPa). This work provides an energy-economic route to upgrade the oils with high oxygen content into green biofuels.

The biomass-derived resources have attracted increasing interest as potential energy and chemical carriers in recent years, which can replace or partially replace the fossil feedstock for the sustainable production of transportation fuels and chemicals.[1] Among various biomass resources, such as carbohydrates, fats and oils, cellulose, starch *etc.*, vegetable oils are one kind of promising resources, which are mainly composed of triglycerides with high oxygen content, high viscosity, low volatility as well as instability, so it is difficult to use them as fuel directly.[2] Several approaches for upgrading triglycerides have been investigated including transesterification, fast pyrolysis, hydrotreatment, hydrocracking, hydrodeoxygenation, *etc.*[3] The transesterification is the most common method due to its relatively simple and easy operation, but its product as the transportation fuel suffers from engine problems because of the incomplete removal of oxygen.[4] Pyrolysis and hydrocracking are nonselective processes and it is usually difficult to control the products distribution and especially easy to produce coke, because of that most approaches are mainly performed under harsh conditions (350–600 °C, 10–20 MPa).[5] Hydrodeoxygenation has been paid more and more attention as one of the most promising ways for catalytic upgradation of biomass because the obtained products have similar properties to hydrocarbon fuels, which are often obtained from petroleum chemistry, and some progress in the hydrodeoxygenation reaction over the noble metal catalysts has been achieved.[6]

The catalytic deoxygenation of stearic acid, ethyl stearate and triglyceride was achieved over a Pd/C catalyst, however under harsh conditions: 300–360 °C, 1.0–2.7 MPa.[7] To overcome the harsh conditions, more active and efficient catalysts should be developed. Recently Pd/BaSO$_4$ was testified to be a potent catalyst for transforming aliphatic esters to high energy alkanes at lower temperature (270 °C) in supercritical hexane,[8] and a new approach for converting fatty acids to hydrocarbons was achieved in near or supercritical water over 5% Pt/C and 5% Pd/C catalysts.[9] Moreover, hydrogenation of carboxylic acids to alcohols and alkanes under relatively mild conditions of 60–130 °C and 0.5–2.0 MPa was performed successfully using Pt/TiO$_2$ and Pt–Re/TiO$_2$ catalysts.[10] In addition, deoxygenation of vegetable oils to biofuels has been recently investigated by using the conventional hydro-desulfurization catalyst NiMo/Al$_2$O$_3$, and the conversion of triglycerides was obtained in the range of 30–100% in a fixed-bed reactor at 260–280 °C, 3.5 MPa.[11]

Although some favorable results have been obtained, it is still a challenge to develop an efficient catalytic deoxygenation process for converting the oils to hydrocarbons from the standpoints of safety and energy-saving. In this work, we have firstly demonstrated that the Ru/TiO$_2$ catalyst is effective for the hydrodeoxygenation of fatty acid esters to hydrocarbons under very mild conditions (200–240 °C, 3.0 MPa), and fascinating results (nearly complete conversion and selectivity) have been obtained. In addition, the reaction rate of deoxygenation of fatty acid esters could be accelerated significantly by the addition of γ-Al$_2$O$_3$, and which should be ascribed to the synergistic effect of Ru/TiO$_2$ and γ-Al$_2$O$_3$.

Ethyl stearate was selected as a model compound in this work, the results of the hydrogenation of ethyl stearate over the Ru/TiO$_2$ catalyst are shown in Table 1. It is clear that the reaction rate increased with temperature and the selectivity to hydrocarbons increased with a decrease in stearyl alcohol upon extending the reaction time. Therefore, a possible reaction pathway has been proposed for the hydrogenation of ethyl stearate as shown in Scheme 1, the ethyl stearate was hydrogenated to stearyl alcohol and deoxygenated to octadecane and heptadecane in parallel, and then stearyl alcohol was deoxygenated to heptadecane and octadecane. The most fascinating result is that the hydrocarbons heptadecane and octadecane are produced with a selectivity over 99.9% and a conversion of 99.3% at the low temperature of 200 °C, which is the best one compared to all the results reported in the literature up to now. These results are very attractive in the upgradation of oils because of both the mild

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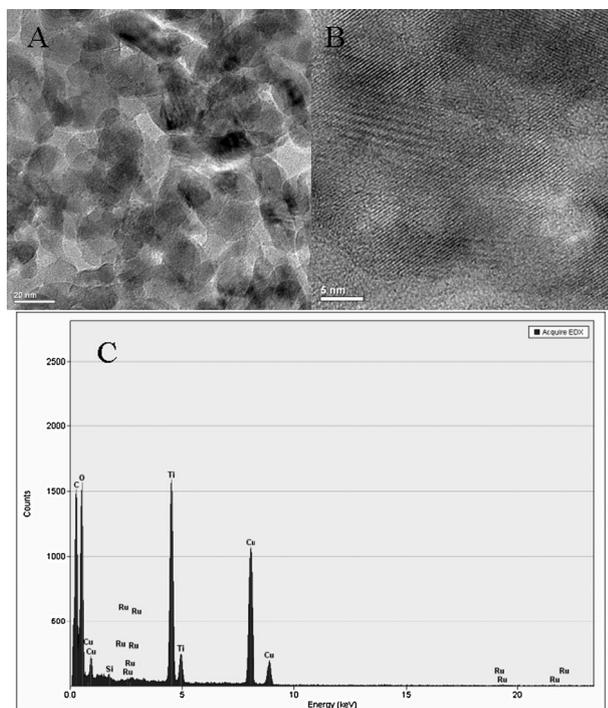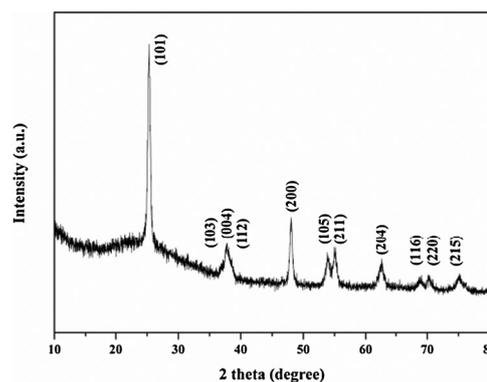
Table 1 Results for the hydrogenation of ethyl stearate with Ru/TiO_2[a]

Entry	T/°C	t/h	Conv. (%)	Select. (%)		
				Heptadecane	Octadecane	Stearyl alcohol
1	200	4	6.8	14.7	4.4	80.9
2	200	17	99.3	91.0	8.9	0.1
3	220	4	17.4	47.1	4.6	48.3
4	230	1	13.1	38.0	5.8	46.3
5	230	4	37.4	61.0	5.8	33.2
6	230	6	83.2	82.1	6.2	11.8
7	230	10	89.3	80.0	6.0	14.0
8	230	17	95.3	89.1	5.2	5.7
9	240	4	68.8	70.5	5.2	24.3

[a] Reaction conditions: ethyl stearate 1.0 mmol, Ru/TiO_2 3.0×10^{-6} mol based on Ru, hexane 5.0 ml, H_2 3.0 MPa.
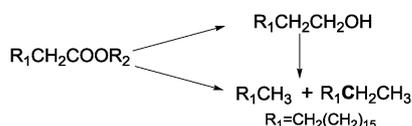
Scheme 1 Proposed reaction pathway of ethyl stearate.

reaction temperature and high reaction rate and selectivity. Usually, the catalytic deoxygenation of fatty acids or their derivatives is studied at a temperature range of 300–360 °C using Pd based catalysts. Surprisingly, the Ru/TiO_2 catalyst showed a very high activity and selectivity at such a low temperature of 200 °C. The high-resolution TEM and EDX spectra of a fresh Ru/TiO_2 catalyst shown in Fig. 1 indicated ruthenium species with a size of approximately 2.6 nm dispersed on the surface of the anatase TiO_2 support. In addition, the EDX spectrum showed emission of Ru, indicating that Ru nanoparticles existed on the surface of catalyst, even though

Fig. 1 (A) TEM image; (B) HRTEM image; (C) EDX spectrum of Ru/TiO_2 (1.0 wt%).

Fig. 2 XRD pattern of fresh Ru/TiO_2 catalyst.

Table 2 Results for the hydrogenation of ethyl stearate with the addition of γ-Al_2O_3[a]

Entry	t/h	Conv. (%)	Select. (%)		
			Heptadecane	Octadecane	Stearyl alcohol
1	1	52.9	75.2	7.3	17.5
2	4	98.6	91.0	8.1	1.0
3[b]	4	30.9	50.5	6.8	42.1
4[c]	4	3.0	—	—	—

[a] Reaction conditions: ethyl stearate 1.0 mmol, Ru/TiO_2 3.0×10^{-6} mol based on Ru, γ-Al_2O_3 100 mg, hexane 5.0 ml, 230 °C, H_2 3.0 MPa. [b] Reaction temperature: 200 °C. [c] Only 100 mg γ-Al_2O_3 was used, without Ru/TiO_2.

Ru was not detected by the XRD (Fig. 2) due to quite low loading of Ru.

Furthermore, the hydrogenation of ethyl stearate was accelerated significantly by the addition of γ-Al_2O_3 as shown in Table 2. The conversion increased up to 52.9% from 13.1% at 230 °C, 1 h (entry 1 in Table 2 and entry 4 in Table 1) and increased to 30.9% from 6.8% at 200 °C, 4 h (entry 3 in Table 2 and entry 1 in Table 1). However, pure γ-Al_2O_3 did not show activity for ethyl stearate hydrogenation to hydrocarbons when the Ru/TiO_2 catalyst was not used (Table 2, entry 4), indicating that the combination of γ-Al_2O_3 and Ru/TiO_2 should play a very important role in promoting the activity in the present reaction. Moreover, the deoxygenation of stearyl alcohol was also investigated in order to discuss the role of γ-Al_2O_3 and the reaction pathway. When only pure γ-Al_2O_3 was used, less than 3.0% conversion was observed, while 72.4% conversion was obtained with the use of Ru/TiO_2 (Table 3, entries 1 and 2). Surprisingly, the conversion enhanced significantly when γ-Al_2O_3 and Ru/TiO_2 were used together, it increased up to nearly 100% and the selectivity for hydrocarbons heptadecane and octadecane reached 100% (Table 3, entry 3). The results revealed that the addition of γ-Al_2O_3 could improve the conversion of stearyl alcohol, the intermediate in hydrogenation of ethyl stearate, to the desired hydrocarbon products, and heptadecane was produced as the dominant product with one carbon less than the fatty acid of the corresponding ester, which was in agreement with the literature.[8] It was speculated that the enhancement of activity in the presence of additional γ-Al_2O_3 may be ascribed to the following factors: one is that the surface acidic and basic properties of γ-Al_2O_3 may influence the present bond cracking

Table 3 Influence of γ-Al_2O_3 on the hydrogenation of stearyl alcohol[a]

Entry	Ru/TiO$_2$ (10^{-6} mol Ru)	Al$_2$O$_3$ (mg)	Conv. (%)	Select. (%)		
				Heptadecane	Octadecane	Hydrocarbons
1	—	100	<1.0	—	—	—
2	3	—	72.4	88.1	11.9	100.0
3	3	100	99.2	91.0	9.0	100.0

[a] Reaction conditions: stearyl alcohol 1.0 mmol, hexane 5.0 ml, 230 °C, H$_2$ 3.0 MPa, 1 h.

reaction, similar to the literature that γ-Al_2O_3 as an acid catalyst could promote the catalytic cracking of hydrocarbons in petroleum processing.[13] The other factor is the synergistic effect of Ru/TiO$_2$ and γ-Al_2O_3, that is the interaction between γ-Al_2O_3 and Ru nanoparticles of Ru/TiO$_2$ may improve the reaction rate. To examine this point we prepared the supported Ru catalysts with Al_2O_3 and SiO_2 and their activity was compared with that of Ru/TiO$_2$ as well as with those of the bare Al_2O_3, SiO_2 and TiO$_2$ supports (ESI†, Table S1). The Ru/Al$_2$O$_3$ catalyst and all the bare supports showed very low activity, conversion <5%, indicating that the combination of Al_2O_3 and Ru nanoparticles was not effective, and the speculation of the interaction between Al_2O_3 and Ru/TiO$_2$ could be ignored in the present reaction system. On the other hand, hydrogen spillover was considered, hydrogen dissociated firstly on the surface of Ru/TiO$_2$ and then spilled to the surface of γ-Al_2O_3, the deoxygenation of stearyl alcohol could be occurring partially on the surface of γ-Al_2O_3. In our previous work, the TPD results demonstrated that hydrogen spilled to the surface of TiO$_2$ or Au/TiO$_2$ from the Pd/TiO$_2$ with strong ability of hydrogen dissociation, and the reaction rate was enhanced largely when Pd/TiO$_2$ physically mixed with TiO$_2$ or Au/TiO$_2$ was used in the hydrogenation of citral.[14] A similar phenomenon has also been discussed by several research groups in recent years.[15] In this work the step of deoxygenation of stearyl alcohol was accelerated in the presence of γ-Al_2O_3, through the additional reaction occurring on the surface of γ-Al_2O_3 with spillover hydrogen. The adsorption behaviour of the ethyl stearate and stearyl alcohol over the γ-Al_2O_3 was explored with an initial molar ratio of the alcohol to ester of 0.8, after the adsorption under the identical conditions of reaction for 24 h, the GC analysis of the solution showed that the mole ratio decreased to 0.3 (error bar <0.05 for three experiments), which clearly indicated that the stearyl alcohol was preferably adsorbed on the γ-Al_2O_3, therefore stearyl alcohol hydrogenation was accelerated with the additional added γ-Al_2O_3. We also checked the influence of the amount of Al$_2$O$_3$ (Fig. S1, ESI†), when the amount of alumina added is lower than 30 mg, the conversion and selectivity were improved largely, however when the amount of alumina is >30 mg (30–100 mg), both the conversion and selectivtiy did not change so much (~95%).The conversion of the intermediate compound stearyl alcohol to hydrocarbons was mainly promoted, finally the whole reaction rate increased (Scheme 1).

For all the supported catalysts checked (Table S1, ESI†), interestingly, Ru/TiO$_2$ presented much higher activity compared to the Ru/Al$_2$O$_3$ and Ru/SiO$_2$ catalysts, suggesting that the support TiO$_2$ should be responsible for the obtained high activity, especially the combination of the Ru particles and

TiO$_2$ should play a vital role in the efficient catalytic performance. Most recently, Corma *et al.* found that ruthenium nanoparticles supported on titania were over three times more active than a conventional Ru/C catalyst for the hydrogenation of lactic acid. They demonstrated that the superior catalytic activity was due to a combined action of small ruthenium nanoparticles and the titania support and that the high activity observed with the Ru/TiO$_2$ catalyst may arise from the synergism of ruthenium crystallites of small size in activating the H$_2$ and the role of the TiO$_2$ support in adsorption and activation of the acid, probably in the periphery of the metal crystallites.[12] This should be suitable to the present result, that the carboxylic group may adsorb on the surface of TiO$_2$ and be activated, then react with the periphery hydrogen dissociated by Ru nanoparticles, resulting in it being a more efficient catalytic support compared to the Al_2O_3 and SiO_2. Furthermore, the stability of the Ru/TiO$_2$ catalyst under the reaction conditions was also checked, however, the activity presented a slight decrease due to the leaching of Ru species during the recycling. Further investigation on the improvement of the catalyst stability and the reaction mechanism is being carried out by our group.

In summary, the hydrogenation of a fatty acid ester to hydrocarbons was performed over the Ru/TiO$_2$ catalyst successfully under the mild conditions of 200–240 °C, 3.0 MPa, the temperature was much lower than that reported (300–360 °C) in the literature. Moreover, nearly 100% selectivity to hydrocarbons heptadecane and octadecane was obtained at the complete conversion of the fatty acid ester. Therefore, the present work provides an energy-economic route to upgrade the high oxygen content of oils into green biofuels as well as gives useful information for the deoxygenation of biomass to transport fuels under mild conditions. Moreover, the addition of γ-Al_2O_3 could enhance the reaction rate of the deoxygenation of stearyl alcohol largely *via* an acceptor of the spillover hydrogen, and thus extra hydrogenation occurs on the surface of γ-Al_2O_3. As a result, we have presented an efficient catalytic system for the deoxygenation of long chain fatty acid esters.

Acknowledgements

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