



Robust ruthenium catalysts for the selective conversion of stearic acid to diesel-range alkanes



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ABSTRACT

Triglycerides represent a type of sustainable energy source and robust catalysts for triglycerides refining to biofuels are very challenging. Herein, we report supported ruthenium catalysts, optimized from group VIII metal catalysts, for the selective conversion of triglycerides to diesel-range alkanes under mild conditions. The catalyst supports and ruthenium loadings show significant impacts on the performance of ruthenium catalysts, and Ru/TiO₂ with ruthenium weight loading of 1.68% is optimized for the reaction. Typically, the platform compound stearic acid could be directly converted, or via 1-octadecanol as an intermediate product, to *n*-heptadecane and *n*-octadecane in *n*-heptane solvent using the optimized Ru/TiO₂ catalyst at 473 K and under 3 MPa H₂. On the basis of catalytic and spectroscopic characterization results, large ruthenium metal particles are established as the preferred active sites for stearic acid conversion. The complete reaction network of stearic acid deoxygenation on flat Ru (0001) is investigated by theoretical calculations. It is revealed that different pathways run simultaneously during the reaction and the adsorbed acyl species C₁₇H₃₅CO* are the key reaction intermediates for the catalytic deoxygenation on Ru (0001). The removal of adsorbed CO by hydrogenation is the rate-controlling step contributing to the highest energy barrier within the reaction network.

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1. Introduction

Nowadays, the diminishing fossil fuel reserves and the environmental problems caused by the excessive use of fossil fuels have triggered growing interest in alternative sustainable energy sources. Biomass, e.g. polysaccharides, lignin and triglycerides, is a very promising candidate with apparent advantages of abundance, low-cost and eco-friendliness [1–3]. Typically, triglycerides from natural oils or fats show great potential as a biomass energy source due to their extremely structural resemblance to diesel-type hydrocarbons [4–6]. Triglycerides can be selectively converted to applicable biofuels through refining processes with the reduction of their high oxygen content and related acidity.

Different strategies have been explored for the refining of triglycerides. Catalytic or enzymatic transesterification of triglycerides with methanol or ethanol, has been used commercially to product fatty acid alkyl esters, which can be viewed as the first-generation biodiesel [4,7–9]. Such alkyl esters, however, suffer from key disadvantages of high residual oxygen contents and high viscosities that limit their applications to some extent. Thermal cracking, also known as pyrolysis, of triglycerides represents an alternative strategy to derive biofuels [10,11]. While the loss of carbon and the decreasing energy content in products are inevitable, and the formation of aromatics and coke will further hinder the application of biofuels obtained. To overcome the drawbacks of transesterification and thermal cracking, the selective catalytic deoxygenation is developed. During the catalytic deoxygenation process, decarboxylation, decarbonylation and hydrodeoxygenation run simultaneously to efficiently remove the oxygen from the triglycerides and diesel-range alkanes are obtained as the final products. Under conventional hydrotreating conditions, standard hydrodesulfurization catalysts, e.g. sulphided nickel and molybdenum, are highly active in the conversion of triglycerides to

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straight chain alkanes [12,13]. However, the sulfur leaching from sulphides could not only lead to the deactivation of catalysts but also result in the contamination of the alkane products. Supported noble metals have also been extensively investigated for the catalytic deoxygenation of triglycerides or their model compounds and palladium/carbon represent a very promising catalyst in semi-batch reactor test if its deactivation is not considered [14–16]. Recently, bifunctional catalysts based on nickel metal and acidic supports have been developed for the quantitative conversion of triglycerides to diesel-range diesels via cascade reactions, which show great potential for the production of green biofuels at large scale [17–19]. According to the existing studies on the catalytic deoxygenation of triglycerides, it is very clear that catalyst is the key issue for the whole refining process. Among all the catalysts investigated, 4%Pt–4%Re/TiO₂ was reported to exhibit remarkable catalytic activity in the conversion of fatty acid at very low temperature [20]. New catalysts are being explored [21,22], however, adequate catalysts working under mild conditions are still challenging. Typically, the catalytic deoxygenation of triglycerides or their model compounds is performed at ~573 K [23], making this process energy-consuming and expensive for operation. Moreover, the high temperature will complicate the reaction network and keep us from the understanding of individual steps in the deoxygenation reaction.

In the present study, robust ruthenium catalysts are developed for the catalytic deoxygenation of triglycerides to diesel-range alkanes and the reaction temperature is successfully lowered by ~100 K to below 473 K. The active ruthenium sites are identified and the detailed deoxygenation reaction network is established via the combination of experimental observations and theoretical calculations.

2. Experimental

2.1. Preparation of supported metal catalysts

Common materials, i.e. SiO₂ (Sinopec, surface area: 206 m²/g), ZrO₂ (Alfa, surface area: 69 m²/g), TiO₂ (Degussa P25, surface area: 51 m²/g), CeO₂ (Acros, surface area: 51 m²/g) and active carbon (Alfa, surface area: 249 m²/g), were used as catalyst supports. Diffusible metal salts (H₂PtCl₆·xH₂O, PdCl₂, RuCl₃·xH₂O, RhCl₃·xH₂O and H₂IrCl₆·6H₂O, all from Acros) were dissolved in distilled water to derive aqueous solutions with metal concentration of 1.0 mg/mL and then used as precursors for supported metals. The catalysts were prepared by impregnating the supports with aqueous solution of metal salts in a rotary evaporator at constant temperature. In a typical preparation process of Ru/TiO₂, 18 mL RuCl₃ aqueous solution was added to 1 g TiO₂ support. The impregnated sample was well mixed and then evaporated in a rotary evaporator at constant temperature of 353 K. The as-prepared sample was carefully washed by distilled water, dried at 353 K overnight, calcined in flowing dry air at 523 K for 1 h and then reduced in 5%H₂/He at 523 K for 1 h (Ru/C sample was reduced at 673 K) prior to being used as catalyst.

2.2. Characterization techniques

The exact metal loadings in supported catalysts were analyzed on an IRIS Advantage inductively coupled plasma atomic emission spectrometer (ICP-AES).

The specific surface areas of samples were determined through N₂ adsorption/desorption isotherms at 77 K collected on a Quantachrome iQ-MP gas adsorption analyzer.

The X-ray diffraction (XRD) patterns of TiO₂ samples were recorded on a Bruker D8 ADVANCE powder diffractometer using

Cu-K α radiation ($\lambda = 0.1542$ nm) at a scanning rate of 4°/min in the region of $2\theta = 10$ –80°.

Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G² F20 electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

X-ray photoelectron spectra (XPS) of samples were recorded on a Kratos Axis Ultra DLD spectrometer with a monochromated Al-K α X-ray source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector. All spectra were recorded by using an aperture slot of 300 × 700 μ m. Accurate binding energies (± 0.1 eV) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV.

The dispersion of metal on support was determined by CO pulse adsorption on a chemisorption analyzer (Chemisorb 2720, Micromeritics). In a typical experiment, ca. 100 mg sample in the quartz reactor was first reduced in 5%H₂/He at 523 K for 1 h and purged with He at 523 K for 1 h to remove H₂ adsorbed on the surface of samples. After cooling down to room temperature in flowing He, pulses of 5%CO/He were injected to the reactor one pulse per minute until no further changes in signal intensity of outlet CO. The dispersion of metal was calculated assuming the equimolar adsorption of CO on metal.

The temperature-programmed reduction by hydrogen (H₂-TPR) experiments was carried out on a chemisorption analyzer (Quantachrome ChemBET 3000) with 5%H₂/Ar at a heating rate of 10 K/min from 300 to 1000 K. Prior to reduction, the sample (100 mg) was calcined in dry air at 523 K for 1 h.

FTIR spectra of CO adsorption on selected Ru/TiO₂ sample were collected on a Bruker Tensor 27 spectrometer with the resolution of 4 cm⁻¹. A self-supporting sample pellet was placed in the reaction chamber and the background spectrum was taken at 383 K in flowing He. After the He stream was switched to a gas mixture containing 1% CO in He, time-dependent FTIR spectra of CO adsorption Ru/TiO₂ were recorded at 383 K.

2.3. Catalytic evaluation and product analysis

The hydrodeoxygenation of stearic acid (Adamas, 99%) and its corresponding esters, i.e. methyl stearate (Adamas, 99%) and glycerol tristearate (Sigma, 99%), was performed in a high-pressure stainless autoclave (Xinyuan Chemical Machinery, Series CJK, 300 mL) at a stirring rate of 750 rpm. In a typical experiment, 0.2 g catalyst (micrometer-scale aggregates consisting of nano-scale particles; Fig. S1), 1 g stearic acid and 100 mL *n*-heptane solvent were well mixed in the autoclave and purged with pure N₂ at room temperature. The autoclave was heated to desired temperature (413–473 K) at a rate of 20 K/min and H₂ was then introduced at 3 MPa (total pressure, vapor pressure of *n*-heptane solvent at 413–473 K was 0.4–0.6 MPa) to initiate the reaction.

After reaction, the organic layer and aqueous layer were separated and the liquid organic products were analyzed by gas chromatography (Shimadzu GC-2010) and gas chromatography–mass spectrometry (Shimadzu GCMS-QP2010 SE), both with a RXI-5MS column (30 m, 0.25 mm i.d., stationary phase thickness 0.25 μ m). *n*-Eicosane was used as an internal standard for quantification and carbon balance of >90% was obtained for all reactions. The following temperature program was employed: isothermal heating at 323 K for 5 min, heating to 573 K with a rate of 10 K/min, and isothermal heating at 573 K for 10 min. After reaction, the gas products were qualitatively analyzed with a mass spectrometer (Pfeiffer Omnistar GSD 320).

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