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Article

Ru nanoparticles supported on hydrophilic mesoporous carbon catalyzed low-temperature hydrodeoxygenation of microalgae oil to alkanes at aqueous-phase

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ABSTRACT

The processing of an energy carrier such as microalgae oil into valuable fuels and chemicals is quite promising. Aqueous-phase processing is suitable for this purpose because the separation of intrinsic water from the algae cell is difficult. In this study, we synthesized ruthenium (Ru) nanoparticles supported on highly hydrophilic mesoporous carbon to catalyze the quantitative hydrodeoxygenation (HDO) of microalgae oil to alkanes in a one-pot process at a low temperature (140 °C) in the aqueous phase. The mesoporous carbon was obtained by single-step calcination of starch and zinc chloride in nitrogen. The as-obtained carbon showed high surface areas and pore volumes, allowing high dispersion of Ru nanoparticles. The surface of the carbon material was rich in hydroxyl groups, as evidenced by X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy, and thermogravimetric analysis (TGA) measurements. As a result, the carbon material contacted preferably with the water phase versus the organic phase, improving the accessibility of substrates. On the other hand, the contact angle test results speculated the superior hydrophilic nature of mesoporous Ru/C (ZnCl₂, starch) than commercial Ru/C. Both kinetics modeling and *in situ* IR monitoring in water revealed the superior performance of the hydrophilic mesoporous and hydrophilic Ru/C compared to a commercial Ru/C for the tandem hydrogenation of stearic acid and decarbonylation of stearyl alcohol. The herein designed hydrothermal carbon material was highly active, environmentally benign, sustainable, and recyclable material, and could be potentially used for other hydrogenation reactions in the aqueous phase.

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1. Introduction

Bio-oil from liquefaction of biomass such as algae oil, triglycerides, fatty acids, lignin, and carbohydrates holds great potential to partially replace traditional non-renewable fossil fuels [1–10]. When the bio-oil was directly used in diesel en-

gines, for example, algae-derived bio-oil cause engine issues such as carbon deposits, injector coking, and further oil ring sticking due to the high viscosity and high oxygen contents of these compounds [11,12]. Thereby, such bio-oil cannot be used directly as a fuel without a previous reduction on metal catalysts [13]. Due to the hydrophilic and polar nature of the multi-

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ple oxygen-containing functional groups of triglycerides and derivatives, it is quite difficult to directly separate bio-oil from the water. Thus, aqueous-phase reactions represent promising routes for the conversion of lipid into valuable hydrocarbon bio-fuels.

The selective hydrodeoxygenation (HDO) of lipid was performed using sulfur- and non-sulfur-containing metal catalysts due to their relatively high stability in non-polar phases [1,14]. Ni- and Co- based catalysts are used for the HDO of fatty acids and lipids into alkanes at ca. 260–380 °C in hydrogen (H₂) [15–19]. Fatty acids were converted at 65% conversion into long-chain hydrocarbons at 300 °C over non-sulfided Pd/Al-SBA-15 in dodecane at 25 bar of H₂ [20]. PdNi/HZSM-5 catalyzed the deoxygenation of stearic acid into alkanes via a tandem process at 280 °C in limonene under a N₂ atmosphere [21]. In a recent study [22], PtIr/ γ -Al₂O₃ catalyzed the deoxygenation of lipid in ethyl-cyclohexane at high temperatures (400 °C) in the absence of H₂. However, these deoxygenation reactions have been conducted under drastic temperatures (above 300 °C) using polluted solvents.

Porous carbons are attractive materials because of their high surface area, tunable pore structures, and facile functionalization [23,24]. Carbon and N-C supported metal (Ru, Pd, Pt) catalysts have also been applied for HDO of triglycerides and fatty acids into useful chemicals [25–29]. Among them, mesoporous-supported Pd/C achieved 15% conversion of stearic acid into alkanes at a high temperature of 360 °C in a 5 vol% argon-H₂ atmosphere [27]. Similarly, Pd/C was used for the catalytic deoxygenation of stearic acid in dodecane at 300 °C, achieving 98% selectivity of alkanes [28]. Compared to reactions carried out in dodecane, non-solvent reaction systems showed slower decarboxylation rates on fatty acids over Pt/C at 350 °C [29]. Since water is ubiquitous in biomass and a green solvent, allowing easy bi-phasic separation of insoluble alkanes. Thus, it is important to develop an efficient stable catalyst able to operate at low temperatures in the aqueous phase. In this sense, carbon materials have particular characteristics that make them stable in polar solvents (e.g., water).

Hydrophilic carbon materials are more relevant for aqueous-phase reactions due to their water compatibility. In this context, we focused herein on the synthesis of highly hydrophilic mesoporous carbon-supported ruthenium (Ru) nanoparticles. This catalyst showed superior performance in the catalytic HDO of a microalgae oil into alkanes (100% yield) at low temperatures (140 °C) in water. More importantly, the surface of the synthesized carbon material was rich in –OH groups. These groups increased the hydrophilicity of the carbon material as revealed by the contact angle experiments, which facilitated the good dispersion in water and better contact with the substrates. Kinetics modelling and *in situ* IR monitoring of the stearic acid HDO in water further revealed superior performance of Ru/C (ZnCl₂, starch) in the tandem hydrogenation of stearic acid and decarbonylation of stearyl alcohol reactions.

2. Experimental

2.1. Chemicals

All chemicals obtained from commercial suppliers were used as received: glucose (99%, Sigma-Aldrich), starch (Weifang fengzheng flour Co.), saw dust (Shenzhen kanuo pet Co.), alpha cellulose (Aladdin Industrial Co), melamine (99%, Sinopharm), activated carbon (Sigma-Aldrich), RuCl₃·3H₂O (99.9%, Amethyst), PdCl₂ (J&K, >59.5 wt%), PtCl₄ (J&K, ≥58 wt%), ZnCl₂ (98%, Sinopharm), Cu(CH₃COO)₂·H₂O (98%, Sinopharm), Co(NO₃)₂·6H₂O (99%, Aladdin Industrial Co), Ni(NO₃)₂·6H₂O (≥98%, Sinopharm), SiO₂ (Shanghai maikun), microalgae oil was received by Verfahrenstechnik Schwedt GmbH, stearic acid (Sinopharm), HCl (>36%, Sinopharm), sulphuric acid (98%, Shanghai Richjoint), diethyl ether anhydrous (Sinopharm, AR), HUSY (SiO₂:Al₂O₃ = 5, The Catalyst Plant of Nankai University), Nitrogen, hydrogen gases and air (99.999 vol. %) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

2.1.1. Synthesis of mesoporous carbon support from starch

In a typical procedure, the mesoporous carbon support was prepared using starch and zinc chloride. The weight ratio of starch to zinc chloride was kept as (1:2). The mixture of these substances were ground in agate mortar to about 1 hour to mix well and transferred to the ceramic boat for calcinations. The calcination was carried out in N₂ flow at 3.3 °C min^{−1} at 800 °C and kept for 1 h. The calcinations furnace was naturally cooled to the room temperature and the sample was crushed into powder form in agate mortar. The sample was treated with 3M HCl to remove the zinc chloride thoroughly. The sample was filtered and washed several times using DI water as far as Cl[−] ion could not be detected in supernatant. Finally, the mesoporous carbon was dried in an oven at 60 °C and kept for 20 h.

2.1.2. Synthesis of Ru/C (ZnCl₂ starch) via wet impregnation method

The nanoparticles such as Ru were introduced into the mesoporous carbon support via wet impregnation method. Nanoparticles were loaded in Ru (5 wt%) by wet impregnation method. After impregnation the sample was dried well in oven. Finally, the sample was reduced under H₂ flow at 350 °C for 4 h (flowing rate = 100 mL min^{−1}, heating rate: 2 °C min^{−1}) and named as Ru/C (ZnCl₂ starch).

2.1.3. Synthesis of Ru/N-doped carbon support from starch

The nitrogen doped carbon support was synthesized using starch, melamine and zinc chloride with the weight ratio of (1:1:3). The mixture of these substances were ground in agate mortar to an hour to mix well and transferred to ceramic boat for calcinations. The calcination was performed in nitrogen flow at 3.3 °C min^{−1} at 800 °C for 1 h. The calcinations furnace was naturally cooled to ambient temperature and the sample was crushed into powder form in agate mortar. The sample was treated with 3M HCl to remove the zinc chloride thoroughly. The sample was filtered and washed several times using DI water as far as Cl[−] ion was not detected in supernatant. Finally, the product N-C was dried in an oven at 60 °C and kept for 20 h. The Ru nanoparticles (5 wt%) were loaded into the N-C support via wet impregnation method. After impregnation

the samples were dried well in oven. Finally, the samples were reduced under hydrogen flow at 350 °C for 4 h (flowing rate = 100 mL min⁻¹, heating rate: 2 °C min⁻¹).

2.1.4. Synthesis of Ru/N-doped carbon support from glucose

In a typical procedure the nitrogen doped carbon support was synthesized using melamine, glucose and zinc chloride. The weight ratio of glucose to melamine was taken as (1:1). The weight ratio of glucose and zinc chloride was kept as (1:3). The mixture of these three substances were ground in agate mortar to one hour to mix well and transferred to ceramic boat for calcinations. The calcination was carried out in nitrogen flow at 3.3 °C min⁻¹ at 800 °C for 1 h. The calcinations furnace was naturally cooled to ambient temperature and the sample was crushed into powder form in agate mortar. The sample was treated with 3M HCl to remove the zinc chloride. The sample was filtered and washed several times using DI water as far as no Cl⁻ ion was detected in supernatant. Finally, the product N-C was dried in an oven at 60 °C for 20 h. Ru nanoparticles (5% wt) were introduced into the N-C support via wet impregnation method. After impregnation the samples were dried well in oven. Finally, the samples were reduced under hydrogen flow at 350 °C for 4 h (flowing rate = 100 mL min⁻¹, heating rate: 2 °C min⁻¹).

2.1.5. Synthesis of Ru/C from saw dust and alpha cellulose

The crushed saw dust/alpha cellulose was washed well using DI water and dried in an oven. Firstly, 4 g of dried saw dust/alpha cellulose was taken and treated with concentrated sulphuric acid at 60 °C for two hours until the yellow colour turned into black. Then, the black saw dust/alpha cellulose was thoroughly washed with ultra pure water and dried well. Finally, the product was passed through the wet impregnation method using Ru (5 wt% loading) and then reduced the catalyst. The reduction was performed using hydrogen flow at 350 °C for 4 h (flowing rate = 100 mL min⁻¹, heating rate: 2 °C min⁻¹).

2.1.6. Synthesis of the Ru catalysts supported on activated carbon, SiO₂ and HUSY

The nanoparticles Ru were introduced into other different supports including activated carbon, SiO₂ and other metal zeolite such as HUSY via wet impregnation method and then reduced. The samples were reduced using hydrogen flow at 350 °C for 4 h (flowing rate = 100 mL min⁻¹, heating rate: 2 °C min⁻¹).

2.2. Catalytic characterization

Powder X-ray diffraction (XRD) patterns were used to investigate the structure and crystal size by Rigaku Ultima IV X-ray diffractometer utilizing Cu-K α radiation (λ = 1.5405 Å) operated at 35 kV and 25 mA. N₂ adsorption measurements were carried out at 77 K on a BEL-MAX gas/vapor adsorption instrument. The surface areas were measured by the Brunauer-Emmett-Teller (BET) method. The IR spectra of adsorbed butanoic acid (IR-butanoic acid) were recorded with a Nicolet

NEXUS 670 FTIR spectrometer equipped with an in-situ IR cell. Scanning electron microscopy images (SEM) were taken by the Hitachi S-4800 microscope. To illuminate crystal morphology and size, transmission electron microscopy (TEM) images were obtained by the FEI Tecnai G2 F30 microscope working at 300 kV. The calcined samples were characterized using temperature-programmed reduction by a TP-5080 adsorption instrument (equipped with a TCD detector). The gas product was a mixed gas of 5% H₂/He, and the heating rate was 5 °C min⁻¹. The Raman spectra were collected on a Raman spectrometer of (JY, HR 800) applying a 514-nm laser. X-ray photoelectron spectroscopy (XPS) were performed with Al K α ($h\nu$ = 1486.6 eV) radiation on a Thermo Scientific K-Alpha spectrometer. Charging effects were corrected by using the C 1s peak owing to adventitious carbon with EB fixed at 284.6 eV.

2.3. Catalytic tests

In a typical hydrodeoxygenation process, 0.1 g catalyst (Ru/C (ZnCl₂ starch), 0.2 g stearic acid (or 0.2 g oils) and 80 ml DI water were placed into micro reactor. The autoclave was purged with N₂ three times to remove the residual air and then introduced reaction gas (5 MPa H₂) at ambient temperature. The reaction was performed in the micro reactor at 140 °C and kept for 6 h with the stirring speed of 500 rpm. The autoclave was cooled to ambient temperature naturally. After the reaction, diethyl ether was added to the aqueous solvent to extract the products and substrate, and then analyzed by GC-FID and the products were identified by GC-MS.

2.4. Test of the algae oil components

Microalgae oil (5.0 g), methanol (100 mL), and CaO (0.8 g) were added into a micro reactor. The reactor was then flushed with nitrogen at ambient temperature for three times. After removal of N₂, it was heated up to 80 °C. The reaction was carried out for 2 h at a stirring speed of 600 rpm. After cooling down to room temperature, the liquid products were analyzed by GC coupled with GC-MS.

3. Result and discussion

3.1. Characterization of the physical and chemical properties of the Ru/mesoporous carbon catalyst

A catalyst with a Ru loading of 5 wt% on a mesoporous carbon support was prepared by a wet impregnation method (Ru/C). The mesoporous carbon support was synthesized using starch (i.e., highly organized mixture of two carbohydrate polymers namely, amylose and amylopectin) as a carbon source and zinc chloride (ZnCl₂) as an activating Lewis acid and dehydrating agent (Figure S1). The physico-chemical properties of the Ru/mesoporous carbon (ZnCl₂ starch) were subsequently compared to those of a Ru/commercial activated carbon (AC). The powder X-ray diffraction (XRD) pattern of the Ru/AC catalyst (Figure 1a) revealed diffraction peaks at 38.4°, 43.5°, 69°, and 77° corresponding to the planes of a hexagonal

Fig. 1. (a) XRD patterns, (b) Raman spectra, FTIR spectra of adsorbed CO on the surface of (c) Ru/C (ZnCl₂ starch), (d) Ru/AC catalysts at room temperature in CO at 50 mL min⁻¹ flow rate, (e) N₂ adsorption and desorption isotherms (inset shows the pore size distribution), (f) SEM, (g) TEM, and (h) elemental mapping of C, Ru and O for Ru/C (ZnCl₂ starch).

close-packed (hcp)-structure of Ru (100), (101), (110), and (112), respectively. In contrast, Ru/C (ZnCl₂ starch) showed no Ru characteristic peaks, suggesting a good dispersion of Ru nanoparticles and low particle size. The diffraction peaks at 44° and ca. 23° can be ascribed to the (100) planes of graphene and the (002) planes of a pseudo-graphitic phase, respectively [30]. The Raman spectroscopy results are shown in Fig. 1b. The D band (1345 cm⁻¹) and the G band (1590 cm⁻¹) corresponded to disordered and graphitic carbon, respectively. The intensity ratio of the D and G peaks (*I_D/I_G*) provided information about structural defects [31]. The *I_D/I_G* ratio of Ru/C (ZnCl₂ starch) was lower (0.85) than that of Ru/AC (0.90), suggesting the ex-

istence of a lower number of structural defects and more graphitic carbons in Ru/C (ZnCl₂ starch).

To provide additional evidence of the surface composition, the Fourier transformed infrared spectroscopy (FTIR) spectra of the catalysts were obtained after adsorption of carbon monoxide (CO) (Figures 1c and 1d). The infrared (IR) spectrum was deconvoluted into three peaks namely, a low intensity peak at 2134 cm⁻¹, a very intense peak at 2078 cm⁻¹, and an unsymmetrical broad peak at 2016 cm⁻¹ which corresponded to Ru^{δ+}-(CO)_x, Ru^{δ+}-(CO)₂, and Ru⁰-CO adsorption bands, respectively [32,33]. The spectra were recorded for 120, 300, 600, and 1800 s. Ru/C (ZnCl₂ starch) displayed three peaks after

1800 s at 2134, 2078, and 2016 cm^{-1} , and the peak at 2078 cm^{-1} was significantly broader and more intense than that of the Ru/AC catalyst, demonstrating the existence of different Ru nanoparticles.

Nitrogen sorption was performed to examine the surface area and porosity of the catalysts. The isotherms (Figure 1e) and textural properties of the respective catalysts are shown in Table S1. The specific surface area of the Ru/C (ZnCl_2 starch) catalyst calculated by the Brunauer-Emmet-Teller (BET) method was $S_{\text{BET}} = 1550 \text{ m}^2 \text{ g}^{-1}$, whereas the pore volume and pore size were measured to be $0.5812 \text{ cm}^3 \text{ g}^{-1}$ and 5.15 nm, respectively. Ru/AC showed a specific surface area, pore volume, and pore size of S_{BET} of $830 \text{ m}^2 \text{ g}^{-1}$, $0.2484 \text{ cm}^3 \text{ g}^{-1}$, and 3.68 nm, respectively. Thus, the Ru/C (ZnCl_2 starch) catalyst possessed a higher surface area, pore volume, and pore size compared to the Ru/AC catalyst. The pore size distribution revealed the existence of mesoporosity in the Ru/C (ZnCl_2 starch) catalyst. Thereby, the high surface area, large pore volume, and high pore size (mesoporosity) of Ru/C was beneficial for the adsorption of fatty acids [34].

Scanning electron microscopy (SEM) images of the catalysts revealed different morphologies (Figure 1f). Ru/C (ZnCl_2 starch) had a porous morphology. In contrast, large carbon particles were observed in the SEM images of the Ru/AC cata-

lyst (see Figure S5). The dispersion and size of the Ru particles were investigated by transmission electron microscopy (TEM, Figures 1h and S6). The images revealed that the nanoparticles of Ru on the carbon (ZnCl_2 starch) were well distributed (Figure 1g) and showed a relatively low size ($3.6 \pm 0.1 \text{ nm}$) compared to those of Ru/AC ($4.3 \pm 0.4 \text{ nm}$, Fig. S6). TEM mapping revealed a good distribution of C, Ru, and O on the surface of the Ru/C (ZnCl_2 starch) catalyst (Figures 1h and S7).

3.2. Characterization of the surface hydroxyl groups of Ru/C

The FTIR spectra for the catalysts (Figure 2a) revealed three main peaks for hydroxyl ($-\text{OH}$) stretching, $\text{C}=\text{C}$, and $-\text{OH}$ out-of-plane bending at 3400, 1530, and 1092 cm^{-1} , respectively. Both catalysts displayed peaks at 3400 and 1530 cm^{-1} corresponding to $-\text{OH}$ stretching and $\text{C}=\text{C}$ bonds, respectively. Interestingly, the Ru/C (ZnCl_2 starch) catalyst showed an intense and broad peak at 1092 cm^{-1} , confirming the existence of hydroxyl group (i.e., OH out of plane bands). But this peak was not found in Ru/AC.

Thermogravimetric analysis (TGA) of the catalysts revealed three peaks at temperatures lower than 100 $^{\circ}\text{C}$, within 120–579 $^{\circ}\text{C}$, and at 580 $^{\circ}\text{C}$ corresponding to the dehydration (removal of moist), removal of oxygenated groups, and de-

Fig. 2. (a) *In situ* FTIR spectra, (b) TGA curves, XPS spectra of (c) Ru/C (ZnCl_2 starch), (d) Ru/AC, (e) comparison of C-O peaks and (f) dispersion of Ru/C (ZnCl_2 starch) and Ru/AC catalysts in aqueous and ether phases. The bottom layer corresponds to the hydrophilic water and the upper was hydrophobic ether layer (extractor) after the hydrogenation-decarbonylation of fatty acid.

composition of support, respectively (Figure 2b). Ru/C (ZnCl₂ starch) showed four times weight loss (13%) than Ru/AC (3%), in line with FTIR measurements indicating a higher amount of –OH groups on Ru/C (ZnCl₂ starch).

The X-ray photoelectron spectroscopy (XPS) spectra of Ru/C (ZnCl₂ starch) and Ru/AC showed a peak at 284.6 eV (Figures 2c and 2d) corresponding to the graphitic carbon [35]. The peak at 286.5 eV can be attributed to an *sp*² carbon bonded to a heteroatom, which suggested the presence of C–OH groups on the catalysts [36]. Importantly, the peaks of these C–OH bonds showed different intensities for the two catalysts, as shown at Figure 2e. It was noted that, the peak of Ru/C (ZnCl₂ starch) at 286.5 eV was more intense than that of Ru/AC, suggesting the presence of a higher number of C–OH bonds compared to Ru/AC, in line with the above mentioned TGA and FTIR results. It should be noted that the Ru/C (ZnCl₂ starch) catalyst was well dispersed in the aqueous phase, whereas Ru/AC was preferably found in the non-aqueous phase (ether phase) after reaction (Figure 2f). These data showed that Ru/C was highly hydrophilic as a result of its hydroxyl contents on the surface, and thus can be easily dispersed in water. Thereby, contact between the catalyst and the substrate was facilitated on Ru/C (ZnCl₂ starch) in the water, leading to good performance towards the hydrodeoxygenation of stearic acid.

Contact angle tests are quite important to address the wetting properties of different supports with the polar and non-polar solvents [37,38]. Based on contact angle tests with water on Ru/C (ZnCl₂ starch) (21.32°) and Ru/AC (23.78°) (see Figure 3), it can be speculated that Ru/C (ZnCl₂ starch) is more hydrophilic than Ru/AC by comparing the different interaction angles with water. The higher hydrophilic property on Ru/C (ZnCl₂ starch) may be derived from the abundant surface –OH groups as discussed in the former part (Figure 2). In comparison, the contact angle tests with non-polar solvents of cyclohexane and diethyl ether consistently demonstrated Ru/C (ZnCl₂ starch) showed smaller contact angles compared to Ru/AC (Figure 3), probably due to the more abundant graphitic

structures in the carbon material as indicated by the peak at 1590 cm^{–1} of Raman spectra in Figure 1b.

3.3. Screening of supported Ru catalysts for the hydrodeoxygenation of fatty acids in water

To evaluate the activity of the different materials, several catalysts with similar Ru loadings (5 wt%) were synthesized (Figures S1–S4) on a range of supports derived from starch, glucose, AC, alpha cellulose, and sawdust as well as silicon dioxide (SiO₂) and HUSY. The catalytic results are shown in Table 1. Among the catalysts evaluated, Ru/C (ZnCl₂ starch) displayed the best performance (100% conversion of stearic acid: 88% yield to heptadecane and 12% to octadecane). Interestingly, Ru/C (starch) showed a 78% yield to heptadecane and an 8% yield to octadecane under identical conditions. Thus, the activation of carbon with ZnCl₂ played an important role in enhancing the yield of heptadecane. ZnCl₂ can be preferably used as activating agents to produce pores in carbon materials [39,45] due to their facile removal after calcinations via acid etching process over AlCl₃ and FeCl₃ [46,47]. Likewise, AlCl₃ and FeCl₃ can be intercalated between graphitic layers of carbon materials, increasing the interlaminar spacing and producing strong acid catalysts [47] which might affect the activity of the catalysts. The catalysts supported on AC and glucose showed good conversions to high stearic alcohol (52% and 44%) and low heptadecane (43% and 6%) yields, respectively. In contrast, catalysts supported on saw dust and alpha cellulose showed the lowest conversion (26% and 47%) and stearic alcohol (3% and 7%) and heptadecane (1% and 3%) yields, respectively. Starch and glucose nitrogen-doped carbon (N-C) supports also showed good conversion and high stearic alcohol yields (70% and 75%), although low yields to heptadecane (9.6% and 5%) were achieved, respectively. The nitrogen functionalities on the support may favour strong adsorption of stearic acid yielding stearic alcohol [39]. The catalysts supported on HUSY and SiO₂ showed good conversions and produced lower heptadecane (73% and 58%) and stearic alcohol (1% and 34%) yields, respectively, compared to Ru/C (ZnCl₂

Fig. 3. Contact angle tests with (a) water, (b) cyclohexane, and (c) diethyl ether on Ru/C (ZnCl₂ starch) and Ru/AC samples.

Table 1

Catalytic performance of different Ru-based catalysts for the stearic acid hydrodeoxygenation reactions.

Entry	Catalyst	Conv. (%)	Yield (%)			
			<i>n</i> -C ₁₇ H ₃₆	C ₁₈ H ₃₇ O	<i>n</i> -C ₁₈ H ₃₈	Ester
1	Ru/N-C (starch)	100	10	70	2	18
2	Ru/C calcined (starch) ^a	100	78	6	8	8
3	Ru/C (ZnCl ₂ starch)	100	88	—	12	—
4	Ru/N-C (glucose)	100	5	75	10	10
5	Ru/activated carbon (AC)	100	43	52	2	3
6	Ru/C (glucose)	92	6	44	4	38
7	Ru/C (alpha cellulose)	43	3	7	—	33
8	Ru/C (saw dust)	26	1	3	—	22
9	Ru/Silica	100	58	34	8	—
10	Ru/HUSY	100	73	1	8	18

Reaction conditions: 0.1 g catalyst (5wt% Ru), 0.2 g stearic acid in 80 mL water at 160 °C and 5.0 MPa H₂ for 6 h. ^a The calcined carbon support derived from starch without using ZnCl₂.

Fig. 4. Stearic acid conversion at different temperatures: (a) 100 °C, (b) 120 °C, (c) 140 °C, and (d) 160 °C. Reaction conditions: Ru/C (ZnCl₂ starch) catalyst (0.1 g), stearic acid (0.2 g), 5.0 MPa (H₂), and water (80 mL) with stirring at 500 rpm.

starch). Under optimized conditions (140 °C, 5.0 MPa H₂), Ru/C (ZnCl₂ starch) achieved the heptadecane and octadecane yields of 88% and 12%, respectively, with 100% conversion of stearic acid.

The results depicted in the Table S2 showed that Ru was found to be more effective [40] for cascade hydrogenation-decarbonylation reactions compared to Pd, Pt, Co, Ni and Cu nanoparticles. The optimum temperature for the hydrogenation-decarbonylation of stearic acid was found to be 160 °C (Figure S8a) over Ru/C (ZnCl₂ starch). As the temperature increased, the stearic alcohol yield decreased in favour of alkane produced via decarbonylation of stearic alcohol. At temperatures up to 120 °C, the stearic alcohol remained as the dominant product (45%), and above this temperature (140 °C and 160 °C), alkanes remained the dominant product (72% and 100%, respectively). It may indicate that, low temperatures favored the hydrogenation of stearic acid while high temperatures facilitated the decarbonylation of stearic alcohol [41–44].

By studying the effects of hydrogen on hydrogenation and decarbonylation reactions at the optimized temperature (160 °C), we found the optimum hydrogen pressure over Ru/C (ZnCl₂ starch) to be 5.0 MPa (Figure S8b). The alkane yield over Ru/C (ZnCl₂ starch) increased with time to reach 100% (88% heptadecane, 12% octadecane yield; 6 h, Figure 4d). On the other hand, the alkane and stearic alcohol yields increased with time over the Ru/AC catalyst up to 6 h, resulting in 100% conversion (43% heptadecane, 52% stearic alcohol, 2% heptadecane, and 3% ester, Figure S9). The kinetic data at different temperatures (120–160 °C) up to the optimized time of 6 h

over Ru/C (ZnCl₂ starch) are shown in Figure 4.

3.4. Aqueous-phase stearic acid hydrogenation and decarbonylation: a kinetic study

Based on the observations and analyses of the main products obtained by HDO of stearic acid over Ru/C (ZnCl₂ starch) at different temperatures (Figure 4), we proposed herein a reaction network (see Scheme S1). The major route contained two main steps, namely, hydrogenation of stearic acid to stearyl alcohol and decarbonylation/hydrogenation of stearyl alcohol to heptadecane. In addition, stearic alcohol can be also transformed to the corresponding ester (minor product at low temperatures). Meanwhile, stearic alcohol can be dehydrated to octadecene (not detected due to fast sequential hydrogenation steps) and then converted into octadecane which is also a minor route. The reaction network further demonstrated that hydrogenation is the primary and fastest step, forming stearic alcohol (k_1); afterwards, stearic alcohol is decarbonylated to the target product heptadecane (k_2) with a relatively low rate.

The concentration of hydrogen before and after was assumed to be unchanged (zero order). Guided by the information from the reaction network (Scheme S1), the major reaction route and the reaction equations are shown in Figures 5a and 5b. The fitting curves for the individual steps of stearic acid hydrogenation and decarbonylation (measured by MATLAB software) are plotted in Figures S10 and S11, whereas the individual fitted values are compiled in Table 2.

The fitted data for stearic acid hydrogenation and decar-

Table 2

Calculation results of rate constants for the individual steps of k_1 (stearic acid hydrogenation) and k_2 (stearic alcohol decarbonylation) reactions over Ru/C (ZnCl₂ starch) and Ru/AC catalysts.

Catalyst	T (°C)	k_1 (min ⁻¹)	k_2 (min ⁻¹)
Ru/C (ZnCl ₂ starch)	100	0.0023	0.0015
Ru/C (ZnCl ₂ starch)	120	0.0037	0.0031
Ru/C (ZnCl ₂ starch)	140	0.0054	0.0061
Ru/C (ZnCl ₂ starch)	160	0.0124	0.0074
Ru/AC	160	0.0082	0.0027

bonylation revealed that the primary steps of hydrogenation were faster (0.0023, 0.0037, 0.0054, and 0.0124 g⁻¹ min⁻¹) than the decarbonylation steps (0.0015, 0.0031, 0.0061, and 0.0074 g⁻¹ min⁻¹) at 100, 120, 140, and 160 °C, respectively. Within the 100–160 °C reaction temperature range, the hydrogenation rate of -COOH (k_1) and decarbonylation of -CH₂OH (k_2) increased with temperature. When the temperature increased from 100 to 160 °C, k_1 rapidly increased (5.4-fold) from 0.0023 to 0.0124 g⁻¹ min⁻¹, while k_2 gradually increased (4.9-fold) from 0.0015 to 0.0074 g⁻¹ min⁻¹, further proving a high temperature dependence. The rate constants k_1 and k_2 obtained for Ru/AC were relatively lower than those shown by Ru/C (ZnCl₂ starch) at 160 °C, confirming that the hydrogenation of stearic acid and the decarbonylation of stearic alcohol were carried out at relatively lower rates over Ru/AC catalyst (Figures S9 and S11). The activation energy (E_a) values calculated for the hy-

Fig. 5. Reaction steps (a) and individual reaction equations (b) for stearic acid hydrogenation-decarbonylation to alkanes in water.

Fig. 6. Arrhenius plots for the hydrogenation of stearic acid and decarbonylation of stearyl alcohol over Ru/C (ZnCl₂ starch) at temperatures of 100, 120, 140, and 160 °C.

drogenation of stearic acid and the decarbonylation of stearic alcohols were 30.0 and 37.1 kJ mol⁻¹ over Ru/C (ZnCl₂ starch), respectively (Figure 6). The main liquid and gaseous products detected by gas chromatography coupled with mass spectroscopy (GC-MS) after aqueous phase transformation of stearic acid are depicted in Figures S12 and S13, respectively. Likewise, GC revealed the presence of CH₄ and no CO, which confirmed that CO reacted with H₂ to form methane via methanation in the gas phase (Figure S13).

3.5. *In situ* IR measurements of C₄ acid hydrodeoxygenation in water

In a subsequent step, we conducted *in situ* FTIR to investigate the adsorption and hydrodeoxygenation of butyric acid (as a representative of stearic acid) on the two Ru/C catalysts. The experimental data (Figure 7a) revealed a peak at 1720 cm⁻¹

Fig. 7. *In situ* FTIR for (a) butyric acid adsorption in He at room temperature. *In situ* FTIR for hydrogenation-decarbonylation over (b) Ru/C (ZnCl₂ starch) and (c) Ru/AC (activated carbon) catalysts in H₂ at 160 °C (1–6 h) with a flow rate of 50 mL min⁻¹.

Fig. 8. (a) Fatty acid composition of the microalgae oil used herein and nomenclature represents the number of carbon atoms and the number of C=C double bonds. For instance, the alkyl chain of the present fatty acid contains 14 carbon atoms and no double bond. (b) Distribution of alkane contents from microalgae oil as detected by GC-MS. (c) Product distribution for transformation of microalgae oil over Ru/C (ZnCl₂ starch) catalyst at 140 °C. (d) Recycling tests of hydrogenation and decarbonylation of stearic acid over Ru/C (ZnCl₂ starch) catalyst (treated by sequential hydrogen reduction).

produced by the carbonyl group of pure butyric acid. Ru/C (ZnCl₂ starch) displayed an adsorption peak at 1720 cm⁻¹ for butyric acid. In contrast, the Ru/AC catalyst did not display such peak at 1720 cm⁻¹, because of its weak adsorption of butyric acid (see Table S1).

In situ FTIR measurement may reveal the mechanism for the transformation of fatty acids (butanoic acid) into alkanes (propane) in H₂ at 160 °C over Ru/C (ZnCl₂ starch). The experimental data are presented in Figure 7b. It was observed that no hydrogenation took place after 1 h. But after 2 h, the peak at 1720 cm⁻¹ disappeared and peaks appeared at ca. 2800 and 3300 cm⁻¹ corresponding to alkyl (–R) and alcohol (–OH) groups, respectively, which confirmed the hydrogenation of fatty acids to fatty alcohols [39]. Interestingly, peak at 3430–3500 cm⁻¹ corresponding to the –OH of alcohol disappeared after 4 h, revealing the complete decarbonylation (–CO) of fatty alcohol to alkanes (final product) via cascade hydrogenation-decarbonylation reactions.

In contrast, due to the weak adsorption peaks for the carbonyl group of Ru/AC, *in situ* FTIR could not observe the hydrogenation and decarbonylation processes (see Figure 7c).

3.6. The hydrodeoxygenation HDO of microalgae oil over Ru/C in water

The scope of the aqueous-phase hydrogenation-decarbonylation reaction was further extended to the feedstock of microalgae oil. The microalgae oil was completely transformed into alkanes (99.6% total alkanes and 92.8% heptadecane) at a relatively low temperature of 140 °C. After the reaction, the colour of the microalgae oil changed completely. The chemical composition of the algae oil (see Figure 8a) and the chemical composition of the alkane products determined by GC-MS are shown in Figures 8b and S14. Likewise, the distribution of products obtained during the transformation of microalgae oil over Ru/C (ZnCl₂ starch) at 140 °C are shown in Figure 8c as a function of time. C₁₄–C₂₄ fatty acids and fatty alcohols were the main intermediates, and C₁₃–C₂₃ alkanes were the final target products.

The stability of the Ru/C (ZnCl₂ starch) catalyst was investigated by recycling the catalysts after several stearic acid hydrogenation and decarbonylation experiments. After the reaction, the catalyst was separated and reduced again before using fresh reactants. The catalyst was found to disperse well in water (Figure 2f), and was reactive even after eight consecutive runs, revealing high stability (Figure 8d). After eight cycles, the used Ru/C (ZnCl₂ starch) catalyst was characterized by XRD (Figure S15) and TEM (Figure S16), and slight changes were observed. The recycling tests and characterization measure-

Fig. 9. Mechanism for the transformation of microalgae oil into alkanes.

ments revealed that the catalyst used was sustainable, recyclable, and environmentally benign.

The mechanism for transformation of microalgae oil into alkanes can be explained in base of hydrogenation, hydrogenolysis, and decarbonylation steps (see Figure 9). First, the microalgae oil undergoes hydrogenation to yield hydrogenated triglyceride, which undergoes further hydrogenolysis to fatty acids. Ru nanoparticles further hydrogenate the fatty acids into fatty alcohols through an intermediate aldehyde in the presence of high-pressurized H_2 [32,39]. The high hydrophilicity of the Ru/C ($ZnCl_2$ starch) catalyst favoured its good dispersion in water, facilitating the fast hydrogenation and decarbonylation steps occurred at the low temperatures in the aqueous phase.

4. Conclusions

While the preparation of water-tolerant and hydrothermally stable catalysts is quite important for aqueous-phase reactions, many supports are easily damaged by steaming. Carbon materials are quite stable and have high surface areas. However, they are highly hydrophobic but less hydrophilic, making it difficult to contact the reactants in water. Here, we synthesized highly hydrophilic mesoporous carbon-supported Ru nanoparticles to catalyze quantitative HDO of microalgae oil to alkanes

in water at a low temperature of 140 °C.

The mesoporous carbon produced by calcination of starch and $ZnCl_2$ in N_2 showed high surface areas and pore volume, which allowed high dispersion of Ru nanoparticles. The surface of the carbon material was rich in $-OH$ groups, as evidenced by XPS, IR, and TGA measurements. These hydroxyl groups increased the hydrophilicity of the carbon material, which was well dispersed in water and facilitated contact with the substrates. Likewise, contact angle test results speculated the superior hydrophilic nature of mesoporous Ru/C ($ZnCl_2$, starch) than commercial Ru/C. In addition, Ru/C showed high durability after consecutive runs. The results of this study provide a facile and universal method for preparing efficient hydrogenation catalysts operating at high temperatures in the aqueous phase.

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Graphical Abstract

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Ru nanoparticles supported on hydrophilic mesoporous carbon catalyzed low-temperature hydrodeoxygenation of microalgae oil to alkanes at aqueous-phase

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This work focuses on the synthesis of Ru nanoparticles supported on mesoporous carbon rich in $-OH$ groups, which makes it to be more hydrophilic. This catalyst delivered the tandem hydrogenation and decarbonylation reactions, producing 100% yield of diesel-range alkanes at a low temperature of 140 °C in aqueous phase.

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亲水性介孔碳负载Ru纳米粒子催化海藻油低温水相加氢脱氧制烷烃

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摘要: 将海藻油等能源载体加工成有价值的燃料和化学品具有广阔的应用前景。由于从藻类细胞中分离固有水非常困难, 因此以水相为溶剂适合含水海藻油的转化。而制备耐水且水热稳定的催化剂非常重要, 因为许多载体容易被蒸汽破坏。其中, 碳材料相当稳定, 具有高的比表面积。然而, 它们具有高度的憎水性, 亲水性较差, 因此很难与水中的反应物接触。

本文中, 我们合成了以高度亲水性介孔碳为载体的钌/碳催化剂, 用于催化海藻油在低温(140 °C)下一锅法于水相中定量加氢脱氧成烷烃。首先以淀粉和氯化锌为原料, 在氮气中一步煅烧制备了介孔炭。其中, 淀粉用作碳源, 氯化锌则作为活化的路易斯酸和脱水剂。所得碳具有高的比表面积和孔体积, 使得Ru纳米粒子具有较高的分散性。XPS表征表明, Ru/AC在286.5 eV处有一个与杂原子结合的 sp^2 碳峰, 表明催化剂上存在C–OH基团。值得注意的是, Ru/C–ZnCl₂催化剂在286.5 eV时的峰值比Ru/AC催化剂的峰值更强, 显示Ru/C–ZnCl₂表面有更多的C–OH键。FTIR光谱研究表明, 两种催化剂分别在3400和1530 cm⁻¹处出现对应于O–H拉伸和C=C键的振动峰。有趣的是, Ru/C–ZnCl₂催化剂在1092 cm⁻¹处显示出强且宽的峰证实了羟基的存在。但在Ru/AC催化剂中没有观察到该峰。催化剂的热重分析显示, 在低于100 °C、120–579 °C和580 °C的温度下分别出现三个峰, 分别对应于脱水(表面水分)、去除含氧基团和载体分解。Ru/C–ZnCl₂催化剂的失重率(13%)是Ru/AC(3%)的4倍, 与FTIR测试结果一致, 表明Ru/C–ZnCl₂催化剂上的羟基含量较高。XPS、IR和TGA结果表明, 碳材料表面富含羟基。另一方面, 对Ru/C–ZnCl₂和Ru/AC催化剂进行了与水的接触角实验, 通过比较Ru/C–ZnCl₂和Ru/AC与水的不同作用角, 进一步证实了Ru/C–ZnCl₂比Ru/AC具有更好的亲水性。我们认为, 碳材料相对于有机相优先地与水相接触, 提高了基底的可接近性。同样, 亲水性碳材料由于其水相容性而更适合于水相反应。

催化剂对硬脂酸的反应结果显示, Ru/AC催化剂转化率为100%, 硬脂醇收率52%, 正庚烷收率43%, 酯收率3%。而Ru/C–ZnCl₂催化剂的硬脂酸转化率为100%, 正庚烷产率为88%, 正十八烷产率为12%。原位FTIR研究了模型化合物丁酸在两种钌/碳催化剂上的吸附和加氢脱氧作用。实验结果表明, 丁酸在Ru/C–ZnCl₂催化剂上显现了1720 m⁻¹处丁酸的羰基振动峰, 这是由于其多孔性和对丁酸的吸附。相比之下, Ru/AC催化剂在1720 cm⁻¹处未见出峰显示对丁酸的弱吸附。总之, 在硬

脂酸的串联加氢和脱羰反应中, 亲水性介孔和亲水性Ru/C-ZnCl₂催化剂的动力学模拟和在水中的原位红外监测均显示出比商用Ru/AC催化剂优越的性能. 本文设计的水热碳材料是一种高活性、环境友好、可持续、可循环利用的材料, 在水热条件下的加氢反应中表现出很好的应用潜力.

关键词: 海藻油; 硬脂酸; 十七烷; 亲水性碳材料; 加氢脱氧; Ru/C催化剂

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