A Multifunctional WO_3–ZrO_2-supported Platinum Catalyst for Remarkably Efficient Hydrogenolysis of Esters to Alkanes

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ABSTRACT: The hydrogenolysis of esters to alkanes is a key protocol for the synthesis of high-quality hydrocarbon fuels from renewable plant oils or fats. However, performing this process under mild energy-efficient conditions is challenging. Herein, we report a robust tungsten and zirconium oxide-supported platinum catalyst (Pt/WO_3–ZrO_2) for the hydrogenolysis of esters to alkanes at low temperatures (as low as 70 °C) and under ambient pressure (1 atm) of H_2. For example, tristearin undergoes complete conversion at 130 °C with more than 95% selectivity for the corresponding alkanes without carbon loss. In addition, the heterogeneous nature of the catalyst system reported herein permits multiple reuse of the catalyst without any significant loss of its high activity and selectivity. Mechanistic studies suggest that multifunctional nature (acid and redox properties) of the WO_3–ZrO_2 support plays an important role in the high activity of the catalyst.

INTRODUCTION

Generating energy from renewable sources instead of fossil resources is pivotal for realizing a sustainable and carbon-neutral society.[1] Moreover, using renewable sources contributes to the diversification of energy sources, which is essential for energy supply stabilization, especially considering recent geopolitical tensions. In this context, the hydrogenolysis of plant oils or fats to diesel-range hydrocarbons has received considerable attention in recent decades.[2] Compared with the industrially used base-catalyzed transesterification for synthesizing biodiesel in the form of fatty acid methyl esters, hydrogenolysis has the advantages of (i) yielding high-quality hydrocarbon fuels, which are currently produced from crude oil and (ii) not requiring the removal of free carboxylic acids, which are otherwise detrimental to the transesterification process owing to foam formation (Figure 1a).[3] Plant oil-derived hydrocarbon fuels are superior to those produced from crude oil because desulfurization is not necessary.[4]

Because plant oils or fats are primarily composed of triglycerides, which are esters derived from fatty acids and glycerol, the hydrogenolysis of esters to hydrocarbons is a key protocol for conversion to fuels.[5, 6] Generally, ester hydrogenolysis proceeds via two different pathways: decarboxylation/decarbonylation to produce hydrocarbons with one carbon less than that of the starting material, and hydrodeoxygenation without carbon loss (Figure 1b).[5, 6] Thus far, various heterogeneous catalysts have been developed for the hydrogenolysis of esters to hydrocarbons.[5, 6] Notably, most of these catalysts (e.g. supported metal sulfides or late transition metal catalysts) require harsh conditions (typically >250 °C), mainly yielding decarboxylation/decarbonylation products.[6] High temperatures generally result in the formation of coke or hydrocracking products, and the resultant carbon loss is problematic.[6] Compared with decarboxylation/decarbonylation catalysts, fewer catalysts (e.g. metal carbides[7] or supported metal catalysts[8]) have been developed for obtaining hydrodeoxygenation products with relatively high selectivities. However, high conversion and selectivity yet necessitate high reaction temperatures (>250 °C) or pressures (>1 MPa). Therefore, the catalytic processes for the hydrogenolysis of esters developed thus far are generally energy-intensive and predominantly exhibit carbon loss. Accordingly, generating energy from renewable plant oils or fats with minimum energy input using reusable heterogeneous catalysts and abundant molecular hydrogen is crucial yet challenging, and there is lack of a catalyst system that can promote the hydrogenolysis of esters to alkanes under low temperature and ambient pressure of H_2.[5–8]

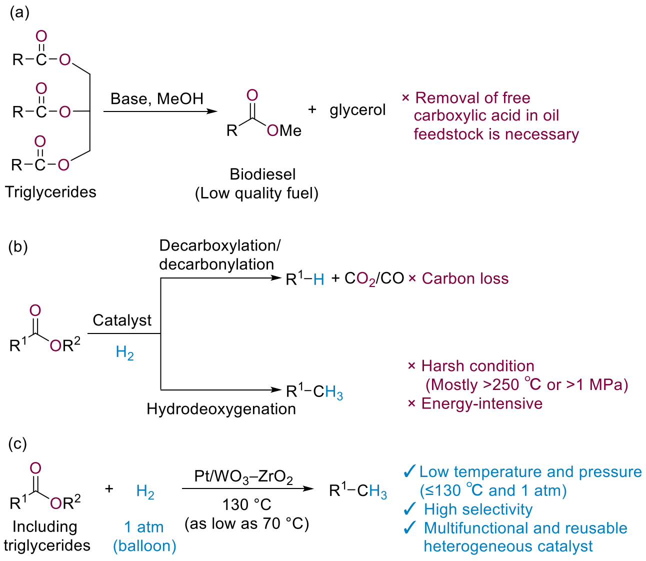


Figure 1. Overview of this work. (a) Base-catalysed transesterification. (b) Hydrogenolysis of esters (previous work). (c) This work: Pt/WO_3–ZrO_2-catalysed mild hydrogenolysis of esters to hydrocarbons.

Herein, we successfully developed mild and selective hydrogenolysis of oils to fuels using a multifunctional and robust supported Pt catalyst (Figure 1c). Our catalyst development was focused on the following two critical points: (i) efficient activation of the C–O bond in the ester, and (ii) supplying sufficient active hydrogen species even under low hydrogen pressure. We envisioned that WO_3 nanoclusters can efficiently activate the C–O bond because tungsten oxide supported on certain metal oxides like ZrO_2 become super acidic.[9] More importantly, WO_3 nanoclusters can function as a "hydrogen reservoir" to store hydrogen as protons and electrons owing to their redox property,[10] which would enable the low-pressure hydrogenolysis. In this study, we observe that tungsten oxide nanoclusters densely supported on zirconium oxide (WO_3–ZrO_2) are highly efficient support materials for hydrogenolysis of esters. The multifunctional nature (i.e. acid and redox properties) of the WO_3–ZrO_2 support can facilitate hydrogenolysis at temperatures as low as 70 °C and under ambient pressure (1 atm) of H_2. Benefiting from the mild conditions, hydrodeoxygenated products without decarboxylation/decarbonylation are obtained in excellent yields.

RESULTS AND DISCUSSION

Optimization of the catalysts. The WO_3–ZrO_2 support was prepared by impregnating ammonium metatungstate on ZrO_2, followed by calcination at 800 °C in air; the content of WO_3 was 19.6 wt%. Pt(0.25)/WO_3–ZrO_2 (the supported metal catalyst is designated as Pt(*x*)/support, where *x* is the wt% of Pt in the catalyst) was prepared by the incipient wetness impregnation method using Pt(acac)$_2$ (acac = acetylacetonate) as the precursor. Without any pre-treatment, the catalyst was directly used for the hydrogenolysis of methyl decanoate (**1a**), a model triglyceride compound, in dodecane at 130 °C under 1 atm of H_2 gas. The reaction proceeded efficiently to produce decane (**2a**) as the sole product (96% yield) without forming decarboxylated side products (Figure 2, entry 1). When the amount of Pt loaded onto Pt/WO_3–ZrO_2 was increased to 0.5 or 1 wt%, both the conversion and yield decreased (Figure 2, entries 1–3). Using Pt(1)/WO_3 as the catalyst, hydrogenolysis of **1a** produced **2a** in 16% yield, and Pt(1)/ZrO_2 resulted in only a trace amount of **2a** (Figure 2, entries 4 and 5). When the catalyst support was WO_3 dispersed on other metal oxides such as Al_2O_3 or CeO_2, the conversion and yield were considerably lower than those when WO_3–ZrO_2 was used as the support (Figure 2, entries 6 and 7). Overall, WO_3 dispersed on ZrO_2 as the support was the key for the mild hydrogenolysis of **1a** to **2a**. A control experiment using WO_3–ZrO_2 without the supported Pt species as the catalyst resulted in the formation of decanoic acid (**3a**) as the sole product, possibly via the surface acid-catalyzed hydrolysis of **1a** (Figure 2, entry 8). Therefore, supported Pt species are essential for activating H_2 to promote the hydrogenolysis of **1a**. Other metals like Pd, Ru, Ir, and Rh are less effective than Pt (Table S1).

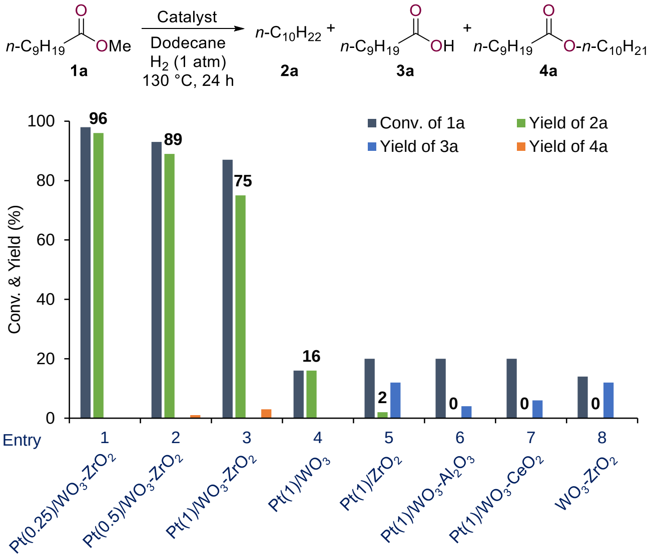


Figure 2. Hydrogenolysis of methyl decanoate (1a) to decane (2a) using various catalysts. Reaction conditions: **1a** (0.50 mmol), catalyst (Pt: 1.5 mol%), dodecane (2.0 mL), 130 °C, H_2 (1 atm), 24 h. Conversion and yields were determined by GC analysis. Pt(*x*)/support, where *x* is the wt% of Pt in the catalyst.

Characterization of Pt(0.25)/WO_3–ZrO_2. The powder X-ray diffraction (XRD) pattern of the fresh Pt(0.25)/WO_3–ZrO_2 catalyst indicates that the catalyst support is composed of monoclinic WO_3 and tetragonal and monoclinic ZrO_2 (Figure 3a). In addition, the Pt species are highly dispersed on the WO_3–ZrO_2 support because no peaks derived from Pt metal are observed (Figure 3a). Analyzing the catalyst using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) reveals the formation of finely dispersed WO_3 nanoclusters with an estimated size of approximately 2 nm on ZrO_2 (Figure 3b). Additionally, energy-dispersive X-ray spectroscopy (EDS) of Pt(0.25)/WO_3–ZrO_2 reveals that WO_3 nanoclusters are formed on ZrO_2 and that Pt species are finely dispersed on the support (Figure 3c–h). Furthermore, because no aggregated Pt nanoparticles are observed in either STEM or EDS analyses, the Pt species are also highly dispersed on the support. X-ray photoelectron spectroscopy (XPS) analysis of the freshly prepared catalyst demonstrates that the tungsten species contains both W^{6+} (37.8 and 35.7 eV) and W^{5+} (36.4 and 34.0 eV), and the W^{6+}-to-W^{5+} ratio is estimated to be 9:1 from the curve fitting of the spectrum (Figure 3i). After hydrogenolysis of **1a** for 12 h, the XPS spectrum of Pt(0.25)/WO_3–ZrO_2 reveals that the W^{6+}-to-W^{5+} ratio is reduced to 4:1, indicating that W^{6+} is reduced to W^{5+} during the reaction (Figure 3j).

Reuse and proof of the heterogeneous nature of the catalyst.

The reusability of the catalyst was investigated. The catalyst was easily retrieved from the reaction mixture by simple filtration with >95% recovery. The recovered catalyst was washed with acetone, ethanol, and hexane, calcined at 300 °C in air for 3 h, and subsequently used for the hydrogenolysis of **1a**. Following these regeneration procedures, the recovered catalyst could be reused at least five times without a significant decrease in the catalytic activity (Figure 4a).

The heterogeneous nature of the catalyst was verified as follows. For hydrogenolysis of **1a** under the same conditions shown in entry 1 of Figure 2, the catalyst was removed by subjecting the reaction mixture to hot filtration when the conversion of **1a** reached approximately 50%. Subsequently, the hydrogenolysis of the filtrate was performed under the same conditions. In this case, the conversion of **1a** remained unchanged, and thus, the reaction

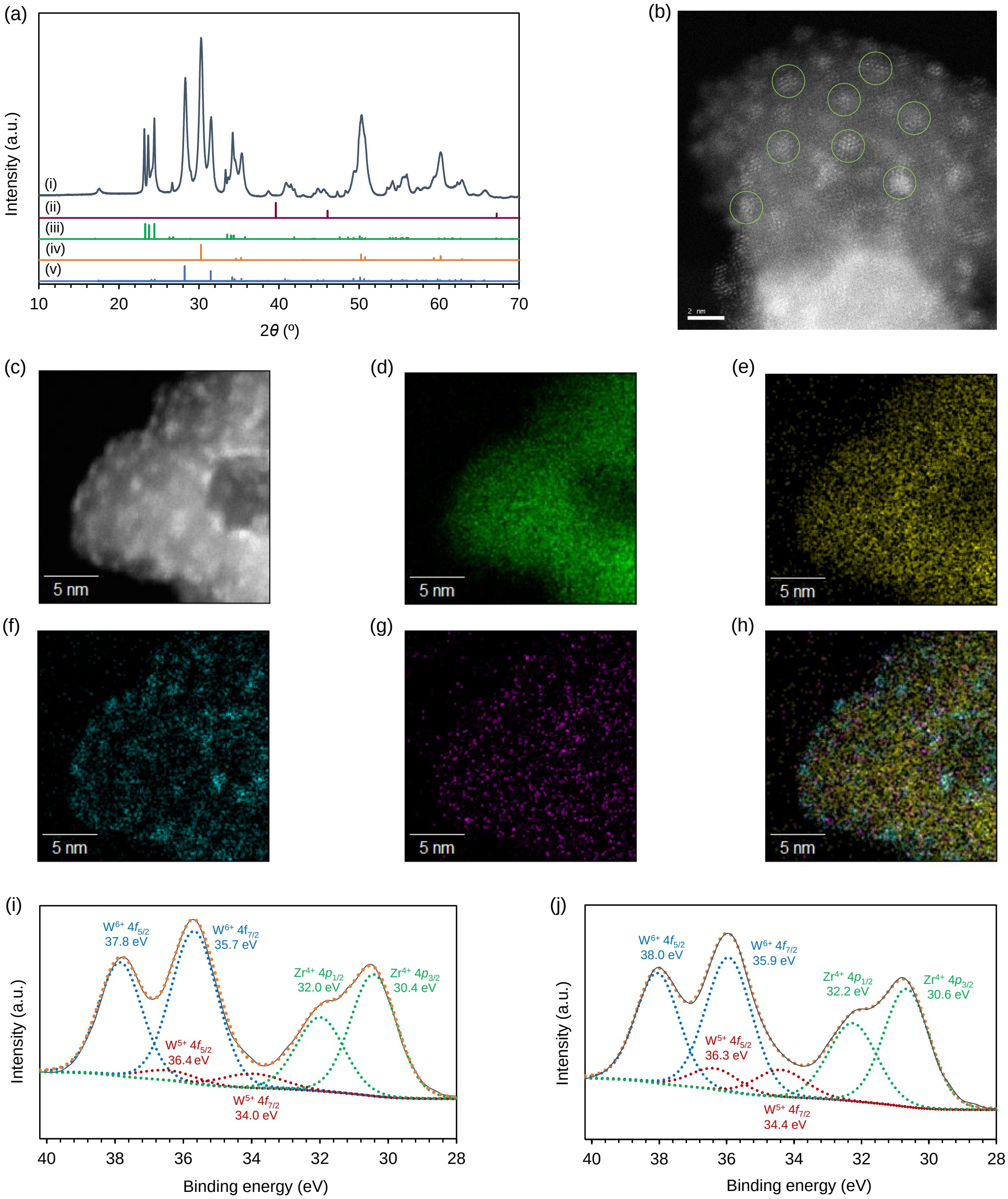


Figure 3. Characterization of the catalysts. (a) (i) XRD pattern of Pt(0.25)/WO_3–ZrO_2, and the powder diffraction file (PDF) of (ii) platinum metal (#1011109), (iii) monoclinic WO_3 (#1010618), (iv) tetragonal ZrO_2 (#2300612), and (v) monoclinic ZrO_2 (#1522143). (b) STEM image of Pt(0.25)/WO_3–ZrO_2. Green circles indicate WO_3 nanoclusters. (c) HAADF-STEM image of Pt(0.25)/WO_3–ZrO_2. (d) EDS elemental map of oxygen. (e) EDS elemental map of zirconium. (f) EDS elemental map of tungsten. (g) EDS elemental map of platinum. (h) Overlap of EDS elemental map of zirconium, tungsten, and platinum. (i) XPS spectrum of the fresh Pt(0.25)/WO_3–ZrO_2; the black line indicates the original spectrum; the blue, red, and green broken lines indicate the deconvoluted signals and the yellow broken line the sum of the deconvoluted signals. (j) XPS spectrum of Pt(0.25)/WO_3–ZrO_2 after the hydrogenolysis of **1a** for 12 h; indication of the lines is the same as (i).

was terminated (Figure 4b). In addition, when the filtrate was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), Pt species were not detected (below the detection limit, Pt <0.003%). Comprehensively considering this experimental evidence, Pt(0.25)/WO_3–ZrO_2 acts as a heterogeneous catalyst, and hydrogenolysis proceeds on the catalyst surface.[11]

Substrate scope. As shown in Table 1, Pt(0.25)/WO_3–ZrO_2 can be applied to the hydrogenolysis of various esters under ambient H_2 pressure. In general, the hydrogenolysis of linear aliphatic esters proceeds efficiently with excellent yields of the corresponding alkanes, irrespective of their chain lengths (Table 1, entries 1, 3, and 4). Particularly, hydrogenolysis of **1a** proceeds even at 70 °C, with an

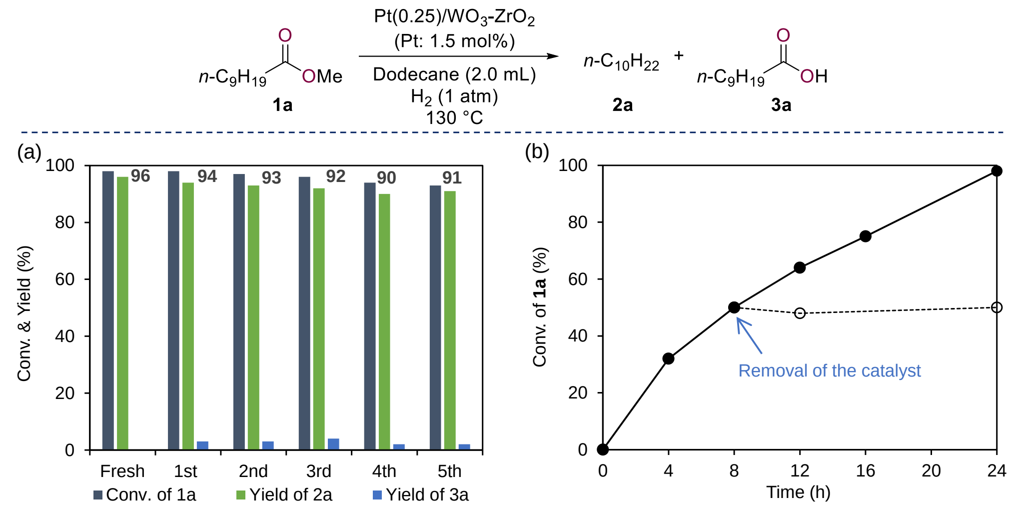
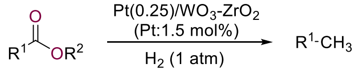
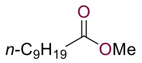
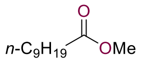
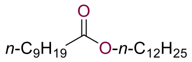
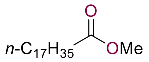
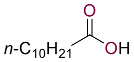
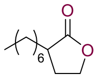
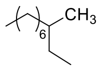
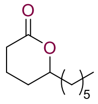
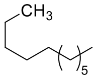
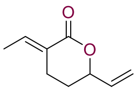
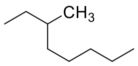
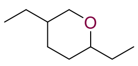
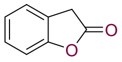
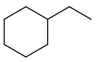
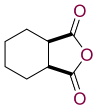
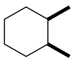
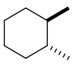


Figure 4. Reuse experiment and leaching test of the catalyst. (a) Catalyst reuse experiment for the hydrogenolysis of **1a**. Reaction time was 24 h. (b) The effect of removing the catalyst for the hydrogenolysis of **1a**. The filled and open circles indicate the conversion of **1a** without or after removal of the catalyst, respectively. Conversion and yields were determined by GC analysis.

Table 1. Substrate scope[a]



Entry	Substrate	Product	T (°C), t (h)	Yield (%)
1		n-C_9H_{19}−CH_3	130, 24	96
2[b]		n-C_9H_{19}−CH_3	70, 72	95
3[c]		n-C_9H_{19}−CH_3 n-$C_{12}H_{26}$	130, 24	>99 >99
4[d]		n-$C_{17}H_{35}$−CH_3	130, 24	95
5		n-$C_{10}H_{21}$−CH_3	130, 16	98
6			130, 24	>99
7			100, 24	>99
8[e,f]		 	90, 48	29 38
9[f]			80, 48	61
10[g]		 	110, 24	29 18

[a]Reaction conditions: substrate (0.50 mmol), Pt(0.25)/WO_3–ZrO_2 (Pt: 1.5 mol%), dodecane (2.0 mL), H_2 (1 atm). Conversion and yields were determined by GC analysis. [b]Pt(0.5)/WO_3–ZrO_2 (Pt: 3.0 mol%). [c]Undecane (2 mL) as the solvent. [d]Heptadecane was also formed in 3% yield. [e]Decane (2 mL) as the solvent. [f]Pt(1)/WO_3–ZrO_2 (Pt: 2.0 mol%). [g]Hexahydroisobenzofuran-1(3*H*)-one (4%) and octahydroisobenzofuran (6%) were also detected.

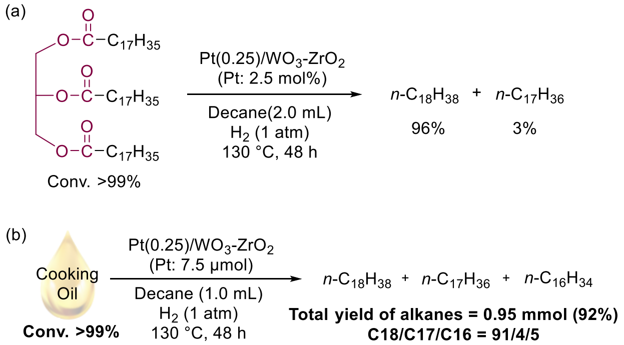
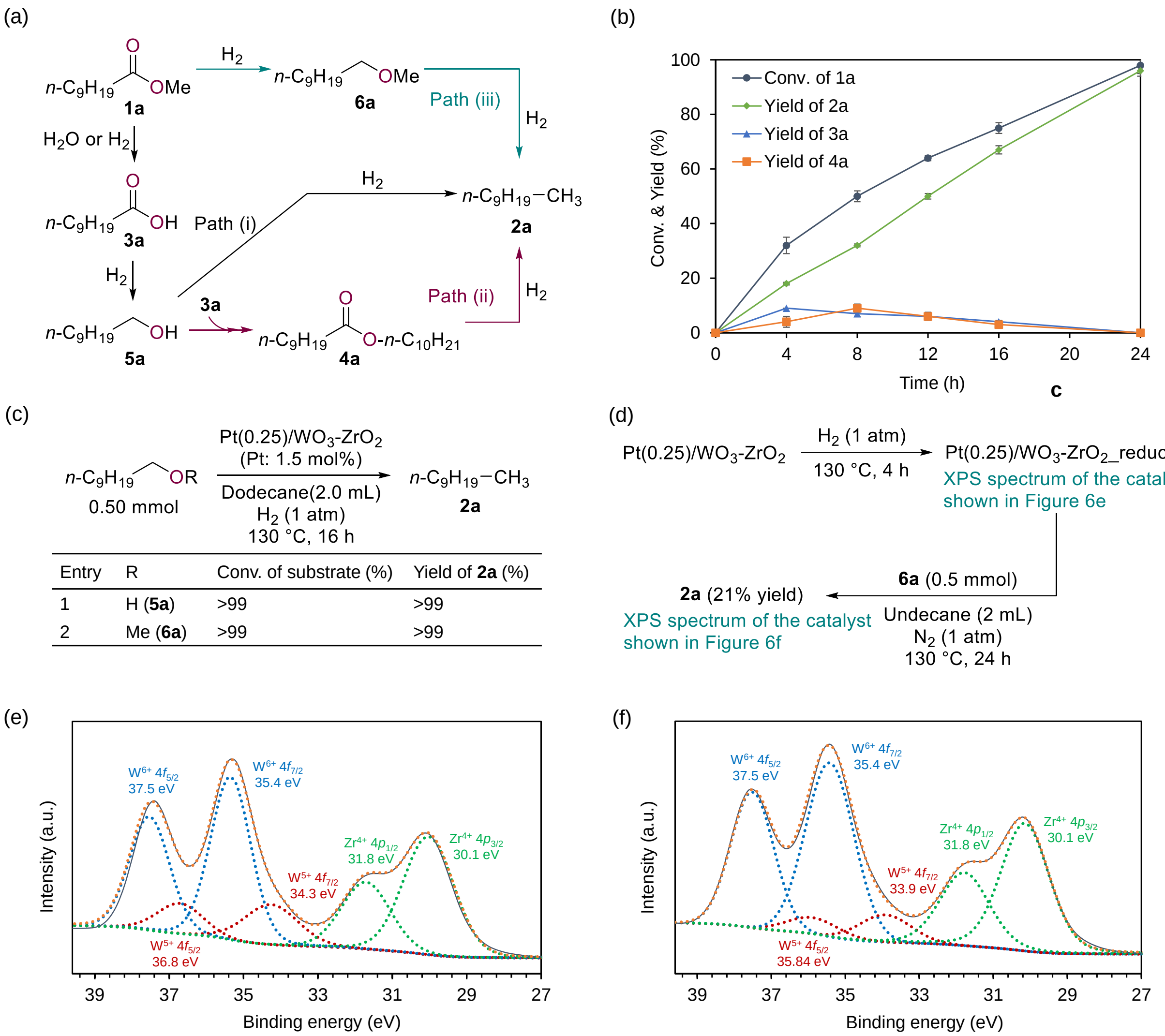


Figure 5. Hydrogenolysis of oils. (a) Tristearin. Reaction conditions: substrate (0.3 mmol), Pt(0.25)/WO_3–ZrO_2 (Pt: 7.5 μmol, 2.5 mol% with respect to the substrate), decane (2.0 mL), 130 °C, H_2 (1 atm), 48 h. (b) Cooking oil. The amount of C18 and C16 carboxylic acid esters in the oil is 3.3 and 0.16 mmol·g^{-1}, respectively. Reaction conditions: cooking oil (300 mg), Pt(0.25)/WO_3–ZrO_2 (Pt: 7.5 μmol), decane (1.0 mL), 130 °C, H_2 (1 atm), 48 h. Conversion and yields were determined by GC analysis.

excellent yield of **1a** (Table 1, entry 2). Additionally, the catalyst can be applied to the hydrogenolysis of carboxylic acids like decanoic acid, producing the corresponding alkane in 98% yield (Table 1, entry 5). Developing a catalyst that can promote hydrogenolysis of both esters and carboxylic acids is important because low-quality oil feedstocks, such as waste oils, typically contain acid impurities.[3] Traditional base-catalyzed transesterification requires extensive separation procedures to remove fatty acids from oil feedstocks owing to foam formation, because fatty acid salts are surfactants.[3] Therefore, the high activity of Pt(0.25)/WO_3–ZrO_2 for the hydrogenolysis of both aliphatic esters and acids indicates that the present catalyst system is more advantageous than the transesterification method for the conversion of plant oils or fats to fuels, because it involves simple procedures and produces high-quality hydrocarbon fuels. In addition to linear aliphatic esters, cyclic esters react efficiently to yield the corresponding ring-opened products (Table 1, entries 6–8). The



Entry	R	Conv. of substrate (%)	Yield of **2a** (%)
1	H (**5a**)	>99	>99
2	Me (**6a**)	>99	>99

Figure 6. Mechanistic studies. (a) Plausible reaction pathways. (b) Reaction profile for the hydrogenolysis of **1a**. Reaction conditions: **1a** (0.50 mmol), Pt(0.25)/WO_3–ZrO_2 (Pt: 1.5 mol%), dodecane (2.0 mL), 130 °C, H_2 (1 atm). (c) Hydrogenolysis of alcohol and ether. (d) Hydrogenolysis of **6a** using Pt(0.25)/WO_3–ZrO_2 pre-treated with H_2. (e) XPS spectrum of Pt(0.25)/WO_3–ZrO_2 pre-treated with 1 atm of H_2; the black line indicates the original spectrum; the blue, red, and green broken lines indicate the deconvoluted signals and the yellow broken line the sum of the deconvoluted signals. (f) XPS spectrum of Pt(0.25)/WO_3–ZrO_2 after hydrogenolysis of **6a**; indication of the lines is the same as (e). Conversion and yields were determined by GC analysis.

double bonds in 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP) do not withstand the reaction conditions, and saturated hydrocarbons are obtained (Table 1, entry 8). In addition, the corresponding ether is obtained as the side product in the hydrogenolysis of EVP, indicating that the hydrogenolysis possibly proceeds via an ether intermediate (Table 1, entry 8). For the hydrogenolysis of the aromatic ester, viz. 2-coumaranone, the aromatic ring is hydrogenated, and ethylcyclohexane is obtained in 61% yield (Table 1, entry 9). In addition to esters and carboxylic acids, a cyclic acid anhydride, viz. cis-1,2-cyclohexanedicarboxylic anhydride, reacts to produce cis- and trans-1,2-dimethylcyclohexane in 29% and 18% yields, respectively (Table 1, entry 10).

Subsequently, we performed hydrogenolysis of oils to hydrocarbons to demonstrate the potential application of the Pt(0.25)/WO_3–ZrO_2 catalyst for energy-efficient fuel production. Hydrogenolysis of tristearin results in an excellent yield of octadecane with the concomitant formation of a trace amount of the decarbonylated product heptadecane (Figure 5a). When cooking oil (canola oil; oil composition in Table S2) is directly subjected to the hydrogenolysis system, the total yield of hydrocarbons approaches 92%, while the original chain length is largely maintained (Figure 5b).

Mechanistic Studies. As summarized in Figure 6a, several reaction pathways coexist in the Pt(0.25)/WO_3–ZrO_2-catalyzed hydrogenolysis of esters: (i) the reduction of **1a** to 1-decanol (**5a**) via the carboxylic acid intermediate **3a**, followed by the hydrogenolysis of **5a**, yields **2a** as the final product; (ii) the alcohol intermediate **5a** reacts with **3a** to produce decyl decanoate (**4a**) by surface acid-promoted dehydrative esterification, and hydrogenolysis of **4a** results in **2a**; and (iii) the hydrodeoxygenation of **1a** to decyl methyl ether (**6a**) is followed by hydrogenolysis to **2a**.[12] The existence of pathways (i) and (ii) is validated by the following experimental results. The reaction profile for the hydrogenolysis of **1a** indicates that carboxylic acid **3a** is formed as a reaction intermediate by either hydrolysis or hydrogenolysis[13] (Figure 6b). Additionally, the profile shows that ester **4a**, which is formed as the reaction intermediate in the present catalyst system, supports the generation of alcohol intermediate **5a** during the reaction (Figure 6b). Through a separate experiment, we confirm that Pt(0.25)/WO_3–ZrO_2 shows excellent catalytic activity for the hydrogenolysis of alcohol **5a**, and a quantitative yield of **2a** is obtained (Figure 6c, entry 1). Pathway (iii) is substantiated by the following experimental evidence. The presence of ether intermediate **6a** is in accordance with our experimental observation of an ether side product in the hydrogenolysis of 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (Table 1, entry 8). In addition, hydrogenolysis of methyl ether **6a** proceeds efficiently using Pt(0.25)/WO_3–ZrO_2 as the catalyst, thus providing a quantitative yield of **2a** (Figure 6c, entry 2).

As mentioned previously, WO_3 nanoclusters highly dispersed on ZrO_2 are crucial for the high efficiency of the Pt(0.25)/WO_3–ZrO_2-catalyzed hydrogenolysis in this study.[14] In addition to the superacidity[9] of WO_3–ZrO_2 to activate C=O bonds in esters, H_2 can be stored in WO_3 nanoclusters as protons and electrons with the reduction of W^{6+} to W^{5+},[10] which contributes to the low-pressure hydrogenolysis in our catalyst system. When fresh Pt(0.25)/WO_3–ZrO_2 is treated with 1 atm of H_2 at 130 °C for 4 h, the W^{6+} species are reduced to W^{5+}, as revealed by XPS analysis of the catalyst. The W^{6+}-to-W^{5+} ratio decreases from 9:1 (fresh catalyst) to 3:1 (after reduction by H_2) (Figure 6e). When the reduced catalyst is subjected to hydrogenolysis of methyl ether **6a** under N_2 atmosphere, **2a** is obtained in 21% yield, and the W^{6+}-to-W^{5+} ratio increases to 7:1 (Figure 6f; details in the Supporting Information). These results strongly suggest that hydrogen activated by the supported Pt species spills over onto the WO_3 nanoclusters.[10] Consequently, the W^{6+} species are reduced to W^{5+}, and hydrogen stored in the WO_3 nanoclusters reduces the substrate with the concomitant reoxidation of W^{5+} to W^{6+}.

CONCLUSION

In summary, we successfully developed a highly efficient catalyst system for the hydrogenolysis of esters to alkanes using the Pt/WO_3–ZrO_2 catalyst at temperatures as low as 70 °C and under ambient pressure of H_2. Benefiting from mild conditions, hydrogenolysis proceeded with high selectivity to produce the corresponding alkanes with negligible amounts of decarboxylated/decarbonylated side products. Pt/WO_3–ZrO_2 served as a heterogeneous catalyst and could be reused five times, while retaining its high activity and selectivity. Mechanistic studies suggested that reaction pathways involving ether, carboxylic acid, or alcohol intermediates could coexist for hydrogenolysis. In addition to the efficient activation of C–O bonds by surface acid sites on the WO_3–ZrO_2 support, hydrogen stored in the WO_3 nanoclusters facilitated low-pressure hydrogenolysis. Because Pt/WO_3–ZrO_2 can also catalyze the mild hydrogenolysis of triglycerides and carboxylic acids to alkanes, our catalyst system is expected to be broadly applicable to the energy-efficient and economical conversion of plant oils and fats to fuels.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, Tables S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org."

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The authors declare no competing financial interest.

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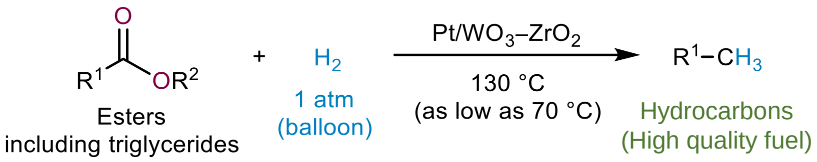

- ✓ Low temperature and pressure (≤130 °C and 1 atm)
- ✓ High selectivity without carbon loss
- ✓ Multifunctional and reusable heterogeneous catalyst