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Short communication

Heterogeneous esterification of fatty acids with methanol catalyzed by Lewis acidic organozirconium complexes with Keggin-type mono-aluminum-substituted polyoxotungstates

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ABSTRACT

Two Lewis acidic organozirconium complexes with α-Keggin-type mono-aluminum-substituted polyoxotungstates, $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}PW_{11}Al(OH)O_{39}ZrCp_2]_2$ (Cp = η^5-$C_5H_5^-$) (**TBA-P-Al-Zr**) and $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}SiW_{11}Al(OH)_2O_{38}ZrCp_2]_2{\cdot}2H_2O$ (**TBA-Si-Al-Zr**), were used as heterogeneous catalysts for the esterification of various fatty acids with methanol. For the esterification of linoleic acid at 80 ± 2 °C, **TBA-P-Al-Zr** exhibited 83% conversion after 6 h, approximately six times higher than that of **TBA-Si-Al-Zr**. **TBA-P-Al-Zr** also exhibited 69–90% conversion for the esterification of oleic acid, palmitic acid, myristic acid, and lauric acid with methanol at 80 ± 2 °C.

1. Introduction

Biodiesel consists of a mixture of alkyl (methyl or ethyl) esters of long chain free fatty acids and is industrially produced by the transesterification of oil or fats (triglycerides) with methanol or ethanol using a stoichiometric amount of a corrosive homogeneous base catalyst (e.g., KOH, NaOH, or methoxides) [1]. However, this process is strongly affected by the presence of free fatty acids (FFAs) because of possible saponification side reactions. Therefore, various types of acid catalysts, especially solid acid catalysts, have been developed for the esterification of FFAs with methanol or ethanol. These include sulfated zirconia [2,3], sulfonated carbon [4,5], Nafion-based composites [6], sulfonated and incompletely carbonized sugar, starch, or cellulose [7,8], zirconium-containing metal organic frameworks [9], layered zinc laurate and zinc stearate [10], and pyrene-based porous organic polymers [11].

Polyoxometalates (POMs) are also of interest in the fields of catalysis, surface science, and materials science because their chemical properties such as redox potentials, acidities, and solubilities in various media can be finely tuned by choosing appropriate constituent elements and countercations [12]. Among various types of POMs, free acidic POMs—known as heteropolyacids (HPAs)—are well-known acid catalysts because of their strong Brønsted acidity [13]. Supported HPAs (e.g., $H_3PW_{12}O_{40}$ and/or $H_3PMo_{12}O_{40}$ supported on zirconia, activated carbon fibers, zeolites, and silica) exhibit excellent catalytic activities or biodiesel production in heterogeneous systems [14]. Paralleling the efforts to develop HPA-based acid catalysts, Lewis acidic POMs have also been developed. Examples are $Na_{10}K_{22}[Zr_{24}O_{22}(OH)_{10}(H_2O)_2(W_2O_{10}H)_2(GeW_9O_{34})_4(GeW_8O_{31})_2]{\cdot}85\text{-}H_2O$ [15], $(n\text{-}Bu_4N)_6[\{W_5O_{18}Zr(\mu\text{-}OH)\}_2]{\cdot}2H_2O$, $(Et_2NH_2)_{10}[Zr(PW_{11}O_{39})_2]{\cdot}7H_2O$, $K_{15}H[Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2]{\cdot}25H_2O$, $Na_{14}[Zr_4(P_2W_{16}O_{59})_2(\mu_3\text{-}O)_2(OH)_2(H_2O)_4]{\cdot}10H_2O$ [16,17], $(n\text{-}Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}\{Al(OH_2)\}_2(\mu\text{-}OH)_2]{\cdot}4H_2O$ [18,19], $Rb_2Na_2[Al^{III}_4(H_2O)_{10}(\beta\text{-}As^{III}W_9O_{33}H)_2]{\cdot}20H_2O$, $(NH_4)_2Na_2[Al^{III}_4(H_2O)_{10}(\beta\text{-}Sb^{III}W_9O_{33}H)_2]{\cdot}20H_2O$ [20], $Na_8[\{Zr_4(H_2O)_4(\mu\text{-}OH)_2(\mu_3\text{-}O)_2\}(\alpha\text{-}1,4\text{-}PW_{10}O_{37})_2]{\cdot}17H_2O$ [21], and $Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Zr(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]{\cdot}26H_2O$ [22]. Although these Lewis acidic POMs are efficient catalysts for various organic syntheses, few examples of POM-based heterogeneous catalysts for biodiesel production have been reported; for example, $(C_{16}TA)H_4TiPW_{11}O_{40}$ ($C_{16}TA$ = cetyltrimethyl ammonium) has both Brønsted and Lewis acid sites and catalyzes the esterification of palmitic acid with methanol at 65 °C with 94.7% conversion after 6 h [23].

Recently, we synthesized the two organozirconium complexes with α-Keggin-type mono-aluminum-substituted polyoxotungstates, $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}PW_{11}Al(OH)O_{39}ZrCp_2]_2$ (Cp = η^5-$C_5H_5^-$) (**TBA-P-Al-Zr**) [24] and $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}SiW_{11}Al(OH)_2O_{38}ZrCp_2]_2{\cdot}2H_2O$ (**TBA-Si-Al-Zr**) [25]. We also demonstrated the catalytic activities of these compounds for the Meerwein-Ponndorf-Verley reduction of ketones with 2-propanol in both homogeneous and heterogeneous systems [25]. In this paper, we report the catalytic performances of **TBA-P-Al-Zr** and

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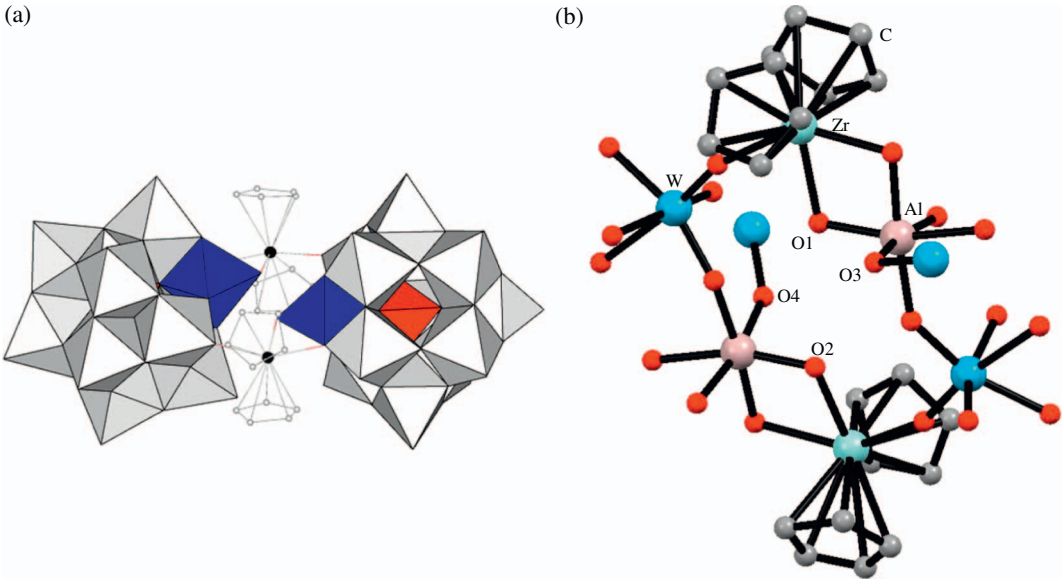

Fig. 1. (a) Polyhedral representation of the polyoxoanions **P-Al-Zr** and **Si-Al-Zr**. WO_6 and AlO_6 units are represented by the white and blue octahedra, respectively. The internal PO_4 or SiO_4 units are represented by the red tetrahedra. The black balls are zirconium atoms. Both **P-Al-Zr** and **Si-Al-Zr** are dimeric compounds, in which the two $\{SiW_{11}AlO_{40}\}$ units are bridged by two "bent sandwich" Cp_2Zr^{2+} fragments and (b) the partial structure around the zirconium and aluminum sites. The two and four protons in **P-Al-Zr** and **Si-Al-Zr** were located at (O1 and O2) and at (O1 – O4), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

TBA-Si-Al-Zr for the esterification of various FFAs with methanol in a heterogeneous system. The molecular structures of **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** are shown in Fig. 1(a).

2. Experimental

2.1. Materials

TBA-P-Al-Zr [24], **TBA-Si-Al-Zr** [25], $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]$ (**TBA-P-Al**) [26], $[(n\text{-}C_4H_9)_4N]_4K_{0.5}H_{0.5}[\alpha\text{-}SiW_{11}\{Al(OH_2)\}O_{39}]\cdot H_2O$ (**TBA-Si-Al**) [25], $Cp_2Zr(OTf)_2\cdot THF$ (OTf = $CF_3SO_3^-$) [24], $(n\text{-}Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}\{Al(OH_2)\}_2(\mu\text{-}OH)_2]\cdot 4H_2O$ [18], $Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Zr(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]\cdot 26H_2O$ [22], and $K_{15}H[Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 25H_2O$ [27] were synthesized as described in the literature. $H_3PW_{12}O_{40}\cdot 23H_2O$ (abbreviated as **HPW**) and ZrO_2 (99%, 5 μm) were obtained from Nippon Inorganic Colour & Chemical Co., Ltd. (Japan) and Aldrich, respectively. The number of water molecules in **HPW** was determined by TG/DTA analysis. **HPW** supported on ZrO_2 (abbreviated as **HPW**/ZrO_2) was prepared according to the literature [28]. The loading of **HPW** on ZrO_2 was 20 wt%. Linoleic acid (> 88%), oleic acid (> 99%), and palmitic acid (> 95%) were obtained from Wako Pure Chemical Industries, Ltd. Myristic acid (> 99%) and lauric acid (> 98%) were obtained from Tokyo Chemical Industry Co., Ltd. All reagents and solvents were obtained and used as received from commercial sources.

2.2. Instrumentation/analytical procedures

Infrared spectra were recorded on a Perkin Elmer Spectrum100 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analysis (DTA) data were obtained using a Rigaku Thermo Plus 2 series TG/DTA TG 8120. TG/DTA measurements were performed in air with a temperature increase of 4 °C min^{-1} between 20 and 500 °C. Solution ^1H (600.17 MHz), ^{13}C (150.92 MHz), and ^{31}P (242.95 MHz) NMR spectra were recorded in 5-mm-outer diameter tubes on a JEOL ECA-600 NMR spectrometer. The ^1H and ^{13}C NMR spectra were measured in acetonitrile-d_3 with reference to tetramethylsilane (TMS). Chemical shifts are reported as positive for resonances downfield of TMS (δ 0). The ^{31}P NMR spectra were measured in acetonitrile-d_3 with reference to an external standard (substitution method) consisting of 85% H_3PO_4 in a sealed capillary. Chemical shifts for the ^{31}P NMR spectra are reported as negative on the δ scale for resonances upfield of H_3PO_4 (δ 0). Potentiometric titration was carried out with 0.010 mol/L tetra-*n*-butylammonium hydroxide as a titrant under an Ar atmosphere [29]. **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** (0.010 mmol) were dissolved in acetonitrile (20 mL) at 25 °C, and the solution was stirred for approximately 5 min. The titration data were obtained with a pH meter (Mettler Toledo). Data points were obtained in millivolts. The tetra-*n*-butylammonium hydroxide solution (0.010 mol/L) was syringed into the suspension in 0.10-equivalent intervals. The Brønsted acidities of **TBA-P-Al-Zr**, **TBA-Si-Al-Zr**, and **HPW** in acetonitrile were evaluated using Hammett indicators (dicinnamalacetone; pK_a value of the protonated indicator is −3.0). The concentrations of the indicator and H^+ were adjusted to 3.5×10^{-5} and 4.9×10^{-3} M, respectively [30]. Specific surface areas and pore sizes were obtained through adsorption-desorption experiments in the BELSORP-max (MicrotracBEL Co., Ltd. Japan). Before analysis, the samples were degassed for 0.5 h under vacuum at 80 °C. The measurements were performed at −196 °C, and the specific surface area was calculated from the adsorption isotherm using the Brunauer-Emmett-Teller (BET) method.

2.3. Esterification of FFAs with methanol

A sample catalyst was placed in a 60 mL Schlenk tube in air. FFAs (linoleic acid, oleic acid, palmitic acid, myristic acid and lauric acid) and methanol (49.3 mmol) were added using a micropipette. The reaction mixture was heated in an oil bath at 60 ± 2 and 80 ± 2 °C. The reaction solution was analyzed by liquid chromatography (Shim-pack VP-ODS column, 4.6 mm × 150 mm). Values of the products were assigned by comparing the obtained results with the analysis results obtained from analyzing authentic samples under the same conditions. The conversion (%) and turnover number (TON) was calculated as $\{[\text{mol of substrate}]_0 - [\text{mol of substrate}]_t\}/[\text{mol of substrate}]_0 \times 100$ and $[\text{mol of corresponding product}]_t/[\text{mol of catalyst}]$, respectively.

3. Results and discussion

We examined the catalytic activities of **TBA-P-Al-Zr** and **TBA-Si-Al-**