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

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

Chika Nozaki Kato[a,b,*], Tsukasa Ogasawara[a], Akari Kondo[a], and Daichi Kato[a]

[a] *Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan*

[b] *Green Chemistry Research Division, Research Institute of Green Science and Technology, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan*

---

[*] Corresponding author.

E-mail address: kato.chika@shizuoka.ac.jp (C. N. Kato).

1

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 = $\eta^5\text{-}C_5H_5^-$) (**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.

Keywords

Organozirconium complex, polyoxometalate, esterification, fatty acids, heterogeneous catalysis

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 for biodiesel production in heterogeneous systems [14]. Paralleling the efforts to develop HPA-based acid catalysts, Lewis acidic POMs have also been developed. Examples are $Na_{10}K_{22}[Zr_{24}O_{22}(OH)_{10}(H_2O)_2(W_2O_{10}H)_2(GeW_9O_{34})_4(GeW_8O_{31})_2]\cdot 85H_2O$ [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], $Na_8[\{Zr_4(H_2O)_4(\mu\text{-OH})_2(\mu_3\text{-O})_2\}(\alpha\text{-1,4-PW}_{10}O_{37})_2]\cdot 17H_2O$ [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 = $\eta^5\text{-}C_5H_5^-$) (**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 **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).

(Insert Fig. 1 here)

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 20wt%. 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 ^{1}H (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 ^{1}H 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

5

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-Zr** during the esterification of linoleic acid with methanol at 80 ± 2 °C. The molar ratio of linoleic acid to methanol was 1:176. Time courses are shown in Fig. 2. The catalytic activities are summarized in Table 1. Methyl linoleate was the main product, with >99% selectivity. Only a slight amount of methyl linoleate was observed in the absence of the catalyst. For

TBA-P-Al-Zr, the conversion after 6 h was 83%, reaching 99% after 12 h. At 60 ± 2 °C, the reaction rates decreased; however, the conversion after 6 h and 48 h reached to 8.8 and 95%, respectively, as shown in Fig. S1. In contrast, **TBA-Si-Al-Zr** showed a slower initial rate and lower conversion (15% after 6 h) than those of **TBA-P-Al-Zr** even at 80 ± 2 °C. The catalytic activities of **TBA-P-Al-Zr** were approximately six times higher than those of **TBA-Si-Al-Zr**, suggesting that the internal atoms in the Keggin units significantly affected the catalytic activities. After stirring the reaction solutions at 80 ± 2 °C for 6 h, **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** were immediately removed off by filtration through a membrane filter (JG 0.2 μm). The ^{1}H NMR spectra in acetonitrile-d_3 of the filtrates did not observe signals due to Cp ligands, Cp_2Zr^{2+} fragments, and tetra-n-butylammonium ions. For **TBA-P-Al-Zr**, ^{31}P NMR spectrum in acetonitrile-d_3 of the filtrate also showed no signal. These results indicated that **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** were found to be insoluble in the mixture of linoleic acid and methanol, and they did not leach into the reaction solution. During the esterification reactions, water was formed as a by-product; however, the Cp ligands were not released from the zirconium atoms, and Cp_2Zr^{2+} fragments were maintained on the surface of $[\alpha\text{-PW}_{11}\{\text{Al(OH}_2)\}\text{O}_{39}]^{4-}$ (**P-Al**) and $[\alpha\text{-SiW}_{11}\{\text{Al(OH}_2)\}\text{O}_{39}]^{5-}$ (**Si-Al**). This was also confirmed by the following experiments: **TBA-P-Al-Zr** or **TBA-Si-Al-Zr** (19.1 μmol) was stirred at 80 ± 2 °C for 6 h in methanol (2 mL) containing water (0.28 mmol), followed by filtration through a membrane filter (JG 0.2 μm) immediately. The ^{1}H NMR measurements in acetonitrile-d_3 of the filtrates did not detect the signals of Cp ligands and Cp_2Zr^{2+} fragments. Furthermore, to confirm whether **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** acted as heterogeneous catalysts, we also carried out the experiments as follows: **TBA-P-Al-Zr** or **TBA-Si-Al-Zr** (19.1 μmol) was stirred at 80 ± 2 °C for 6 h in methanol (2 mL), followed by filtration through a membrane filter (JG 0.2 μm) immediately. Then, linoleic acid (0.28 mmol) was added to the filtrates, and stirred the solutions at 80 ± 2 °C. After 6 h, the conversions were

0.4% and 0%, respectively.

Next, the solids collected by filtration were washed with methanol, water, and ethanol. The ^{31}P NMR spectrum in acetonitrile-d_3 of the solid of **TBA-P-Al-Zr** showed three signals at −11.89, −12.25, and −12.34 ppm with 0.4 : 1 : 1 intensities. The two signals at −12.25 and −12.34 ppm were assigned to the original **TBA-P-Al-Zr** (δ = −12.25 and −12.33). A new signal at −11.89 ppm would be due to the species generated by the interaction of **TBA-P-Al-Zr** with methanol; this was consistent with the result that ^{1}H NMR spectrum in acetonitrile-d_3 of the solid showed a signal of the methyl group of methanol at 3.28 ppm. The signals of Cp ligands were also observed at 6.86, 6.67, and 6.57 ppm, in which the two signals at 6.67 ppm and 6.57 ppm were assigned to the original **TBA-P-Al-Zr** (δ = 6.67 and 6.57). A new signal at 6.86 ppm would also be generated by the interaction of **TBA-P-Al-Zr** with methanol. In contrast, the solid of **TBA-Si-Al-Zr** showed four ^{1}H NMR signals of Cp ligands at 6.69, 6.64, 6.62, and 6.59 ppm, which were the same as those of the original **TBA-Si-Al-Zr** (δ = 6.69, 6.63, 6.62, and 6.59). Thus, the molecular structures of these compounds were maintained after the esterification reaction although the methanol interacted with **TBA-P-Al-Zr** was not completely removed off even after washing with water and ethanol. When a solid sample of **TBA-P-Al-Zr** was used as a catalyst in the second run for the esterification of linoleic acid with methanol at 60 ± 2 °C, the conversion after 48 h was approximately 97%, demonstrating that **TBA-P-Al-Zr** is recyclable. As control experiments, **TBA-P-Al** and **TBA-Si-Al**, which were used as molecular supports for the syntheses of **TBA-P-Al-Zr** and **TBA-Si-Al-Zr**, showed no reaction at 80 ± 2 °C for 6 h. Cp$_2$Zr(OTf)$_2$·THF and Cp$_2$ZrCl$_2$, which were also used as starting materials for the syntheses of **TBA-P-Al-Zr** and **TBA-Si-Al-Zr**, were soluble in the reaction solution at 80 ± 2 °C, and exhibited >98% conversion in a homogeneous system. These results indicate that the grafting reactions of Cp$_2$Zr^{2+} fragments onto the surfaces of **TBA-P-Al** and **TBA-Si-Al** were critical to generating

the active centers. $H_3PW_{12}O_{40} \cdot 23H_2O$ (abbreviated as **HPW**) was soluble in the solution at 80 ± 2 °C, and exhibited >99% conversions after 6 h in a homogeneous system. **HPW** supported on ZrO_2 (abbreviated as **HPW**/ZrO_2) also showed >99% conversions after 6 h; however, **HPW** was leached into the solution, as observed by ^{31}P NMR spectroscopy in acetonitrile-d_3 (Fig. S2). This result suggests that **HPW** leached into the solution and **HPW** grafted onto the surface of the ZrO_2 acted as homogeneous and heterogeneous catalysts, respectively. In contrast, ZrO_2 acted as a heterogeneous catalyst; however, the conversion after 6 h was 15%, which was lower than that of **TBA-P-Al-Zr**. Some Lewis acidic POMs (n-Bu$_4$N)$_3$H[γ-SiW$_{10}$O$_{36}${Al(OH$_2$)}$_2$(μ-OH)$_2$]·4H$_2$O (27.6 μmol) [18], K$_{15}$H[Zr(α$_2$-P$_2$W$_{17}$O$_{61}$)$_2$]·25H$_2$O (10.6 μmol) [16,17,27], Na$_8$[{Zr$_4$(μ-OH)$_2$(μ$_3$-O)$_2$(H$_2$O)$_4$}(α-1,4-PW$_{10}$O$_{37}$)$_2$]·17H$_2$O (8.5 μmol) [21], and Cs$_8$[(γ-SiW$_{10}$O$_{36}$)$_2${Zr(H$_2$O)}$_4$(μ$_4$-O)(μ-OH)$_6$]·26H$_2$O (10.0 μmol) [22] showed no reaction under the reported reaction conditions.

    TBA-P-Al-Zr was also observed to catalyze the esterification of oleic acid (the conversion after 6 h was 90%), palmitic acid (86%), myristic acid (75%), lauric acid (69%), and benzoic acid (the conversion after 69 h was 54%) to the corresponding ester products with selectivities of >99% at 80 ± 2 °C in a heterogeneous system, as shown in Table 2. Even in the presence of acetonitrile (where the system was homogeneous), the conversion after 96 h was 83% for the esterification of benzoic acid with methanol at 80 ± 2 °C, which was also higher than that of **TBA-Si-Al-Zr** (the conversion after 96 h was 22%). **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** were non-porous compounds, and both BET surface area was approximately 1.0 m^2/g. Thus, the texture of the catalyst is not the origin of the differences in catalytic activity. Although it is difficult to draw a simple comparison, the catalytic activities of **TBA-P-Al-Zr** were by no means inferior to some current solid catalysts, e.g., sulfated zirconia (the conversions after 8 h were 74.7 − 98% for the esterification of lauric, myristic, palmitic, stearic, oleic, and sebacic

acids with methanol at 60 °C) [2], sulfonated carbon (70% after 10 h for esterification of oleic acid with ethanol at 80 °C) [4], Nafion-based composites (ca. 80% after 40 h for esterification of palmitic acid in sunflower oil with methanol at 60°C) [6], and zirconium-containing metal organic frameworks (99% after 2 h for lauric acid esterification with methanol or ethanol at 60 °C) [9]. In particular, pyrene-based porous organic polymers exhibit high catalytic activities (88 − 94% of conversion after 10 h in the esterification of various FFAs even at room temperature) [11].

As determined by X-ray crystallography [24,25], **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** have the two and four protons located at (O1 and O2) and (O1, O2, O3, and O4) (see Fig. 1(b)), respectively. To determine whether the protons act as Brønsted acid sites, we measured the Brønsted acidity by using dicinnamalacetone (pK_a value of the protonated indicator is −3.0) as a Hammett indicator [30]. When a solution containing dissolved **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** in acetonitrile (the concentration of protons was 4.9 $\times 10^{-3}$ M) was added to an acetonitrile solution of dicinnamalacetone (3.5×10^{-5} M) at approximately 25 °C, an acidic color (red) was not observed. As a control experiment, we used a Brønsted acid catalyst, **HPW**, which yielded an acidic red color under the same reaction conditions. Here, the two and four protons in **TBA-P-Al-Zr** and **TBA-Si-Al-Zr**, respectively, can be deprotonated by the addition of OH⁻, as shown in Fig. S3 and as previously reported [25]. The deprotonated solids were obtained by the addition of two and four equiv. of tetra-*n*-butylammonium hydroxide aqueous solution to acetonitrile solutions containing dissolved as-prepared **TBA-P-Al-Zr** and **TBA-Si-Al-Zr**, respectively, followed by precipitation from diethyl ether in air. These solids showed no deactivation of their catalytic activities for the esterification of benzoic acid with methanol in acetonitrile at 80 ± 2 °C (conversions after 96 h were 82% and 20%, respectively). These results indicate that the protons in **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** did not act as Brønsted acid sites, and the Lewis acidic centers are responsible

for the catalysis of the carboxylic acid esterification reaction with methanol under the reported reaction conditions.

(Insert Tables 1 and 2, and Fig. 2 here)

To investigate the Lewis acid character, we observed the interactions of Lewis acidic sites in **TBA-P-Al-Zr** with benzoic acid using ^{31}P NMR spectroscopy. When 1, 2, 4, or 5 equiv. of benzoic acid were added to a solution containing dissolved **TBA-P-Al-Zr**, followed by stirring for 3 − 93 h at approximately 25 °C, a new ^{31}P NMR signal was observed at around − 11.46 ppm, a slight shift from those of as-prepared **TBA-P-Al-Zr** ($\delta = -12.25$ and -12.33), and no signal due to **TBA-P-Al** ($\delta = -12.5$) was observed (Fig. S4). The intensities of the signals did not change over 93 h. As a control experiment, we added 50 equiv. of benzoic acid to **HPW** and found that the signal ($\delta = -14.16$) did not shift, as shown in Fig. S5. This also suggests that the Lewis acid sites in **TBA-P-Al-Zr** interacted with benzoic acid. For the ^{13}C NMR spectrum in acetonitrile-d_3 of **TBA-P-Al-Zr** in the presence of 5 equiv. of benzoic acid, two new signals were observed at 130.91 and 129.33 ppm, which are likely due to the interaction of benzoic acid with the Lewis acid sites in **TBA-P-Al-Zr**, as shown in Fig. S6. When 100 equiv. of methanol was added to the mixture of **TBA-P-Al-Zr** and 5 equiv. of benzoic acid, followed by stirring at 60 °C for 72 h, a signal due to the methyl group of methyl benzoate was observed at 52.77 ppm. A signal due to the methyl group of methyl benzoate was also observed in the ^{1}H NMR spectrum at 3.87 ppm. In the ^{31}P NMR spectrum, the signal at −11.46 ppm completely disappeared, and a new signal at −12.10 ppm appeared; this was observed for a mixture of **TBA-P-Al-Zr** and methyl benzoate, as shown in Fig. S7. These results suggest that the signal observed at −11.46 ppm in the ^{31}P NMR spectrum was a reaction intermediate. In contrast, the signals in the ^{31}P NMR spectrum in acetonitrile-d_3 of **TBA-P-Al-Zr** did not shift in the presence of 100 equiv. of methanol, followed by 3 h stirring at approximately 25 °C (Fig. S8). These results suggest that the coordination of benzoic acid

11

to the Lewis acid sites in **TBA-P-Al-Zr** was more preferential than that of methanol. Thus, the esterification process is initiated by the interaction of Lewis acid sites in **TBA-P-Al-Zr** with carboxylic acids, thus generating the intermediate; subsequently, the nucleophilic attack of methanol on the intermediates resulted in the formation of the corresponding esters, as reported for Lewis acidic zirconium-containing metal organic frameworks [9] and layered zinc laurate and zinc stearate [10].

When excess water was added to a mixture of **TBA-P-Al-Zr** and benzoic acid (50 equiv.), a yellow solid was precipitated (the solid was abbreviated as **TBA-P-Al-Zr-S**). The ^{31}P NMR spectrum in acetonitrile-d_3 of **TBA-P-Al-Zr-S** contains signals at (−12.33 and −12.25 ppm) and −11.46 ppm, which were assigned to the original **TBA-P-Al-Zr** and the reaction intermediate, respectively (Fig. S9). Although the ^{13}C NMR spectrum in acetonitrile-d_3 of **TBA-P-Al-Zr-S** was quite noisy, some signals were observed at around 130 ppm due to benzoic acid, as shown in Fig. S10(a). In contrast, **TBA-Si-Al-Zr-S** prepared by the addition of excess water to a mixture of **TBA-Si-Al-Zr** and benzoic acid (50 equiv.) showed no signals in the ^{13}C NMR spectrum corresponding to benzoic acid (Fig. S10(b)). Thus, the interaction of benzoic acid with the Lewis acid sites in **TBA-P-Al-Zr** was stronger than that in **TBA-Si-Al-Zr**. These results indicate that Lewis acidity of **TBA-P-Al-Zr** was higher than that of **TBA-Si-Al-Zr**; this is consistent with the activities of the catalysts for the esterification reactions.

4. Conclusion

Organozirconium complexes with α-Keggin-type mono-aluminum-substituted polyoxotungstates, $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}PW_{11}Al(OH)O_{39}ZrCp_2]_2$ (**TBA-P-Al-Zr**) and $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}SiW_{11}Al(OH)_2O_{38}ZrCp_2]_2\cdot2H_2O$ (**TBA-Si-Al-Zr**), were used as

heterogeneous catalysts for the esterification of various FFAs 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**; thus, the internal atoms in the Keggin units affected the catalytic activities significantly. **TBA-P-Al-Zr** also exhibited 69 – 90% conversions for the esterification reactions of oleic acid, palmitic acid, myristic acid, and lauric acid with methanol at 80 ± 2 °C. The protons located at the oxygen atoms around the zirconium centers in **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** did not act as Brønsted acid sites, and **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** acted as Lewis acid catalysts. In the esterification reaction mechanism, the carboxylic acids interact with the Lewis acid sites in the organozirconium compounds, and the high catalytic activities of **TBA-P-Al-Zr** result from its Lewis acidity. **TBA-P-Al-Zr** is the first example of an effective, polyoxometalate-based Lewis acid catalyst for the esterification of FFAs with methanol in a heterogeneous system.

References

[1] For selected references, see: a) A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, Chem. Rev. 107 (2007) 2411 – 2502; b) G.W. Hubers, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, Chem. Rev. 106 (2006) 4044 – 4098; c) F. Su, Y. Guo,

Advancements in solid acid catalysts for biodiesel production, Green Chem. 16 (2014) 2934 – 2957.

[2] B. Banerjee, S. Bhunia, A. Bhaumik, Self-assembled sulfated zirconia nanocrystals with mesoscopic void space synthesized via ionic liquid as a porogen and its catalytic activity for the synthesis of biodiesels, Appl. Catal., A 502 (2015) 380 – 387.

[3] A. Patel, V. Brahmkhatri, N. Singh, Biodiesel production by esterification of free fatty acid over sulfated zirconia, Renewable Energy 51 (2013) 227 – 233.

[4] R. Liu, X. Wang, X. Zhao, P. Feng, Sulfonated ordered mesoporous carbon for catalytic preparation of biodiesel, Carbon 46 (2008) 1664 – 1669.

[5] X. Mo, E. Lotero, C. Lu, Y. Liu, J.G. Goodwin, A novel sulfonated carbon composite solid acid catalyst for biodiesel synthesis, Catal. Lett. 123 (2008) 1 – 6.

[6] J. Ni, F.C. Meunier, Esterification of free fatty acids in sunflower oil over solid acid catalysts using batch and fixed bed-reactors, Appl. Catal., A 333 (2007) 122 – 130.

[7] M. Toda, A. Takagaki, M. Okamura, J.N. Kondo, S. Hayashi, K Domen, M. Hara, Green chemistry: biodiesel made with sugar catalyst, Nature 438 (2005) 178.

[8] A. Takagaki, M. Toda, M. Okamura, J.N. Kondo, S. Hayashi, K. Domen, M. Hara, Esterification of higher fatty acids by a novel strong solid acid, Catal. Today 116 (2006) 157 – 161.

[9] F.G. Cirujano, A. Corma, F.X. Llabrés i Xamena, Zirconium-containing metal organic frameworks as solid acid catalysts for the esterification of free fatty acids: Synthesis of biodiesel and other compounds of interest, Catal. Today 257 (2015) 213 – 220.

[10] E.J.M. de Paiva, S. Sterchele, M. L. Corazza, D. Y. Murzin, F. Wypych, T. Salmi, Esterification of fatty acids with ethanol over layered zinc laurate and zinc stearate - Kinetic modeling, Fuel 153 (2015) 445 – 454.

[11] S.K. Kundu, A. Bhaumik, Pyrene-based porous organic polymers as efficient catalytic

support for the synthesis of biodiesels at room temperature, ACS Sustainable Chem. Eng. 3 (2015) 1715 – 1723.

[12] For selected references, see: a) M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Berlin, 1983; b) M.T. Pope, A. Müller, Chemistry of polyoxometallates. Actual variation on an old theme with interdisciplinary references, Angew. Chem. Int. Ed. Engl. 30 (1991) 34 – 48; c) Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity, in: M.T. Pope, A. Müller (Eds.), Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994; d) S.-S. Wang, G.-Y. Yang, Recent advances in polyoxometalate-catalyzed reactions, Chem. Rev. 115 (2015) 4893 – 4962.

[13] T. Okuhara, N. Mizuno, M. Misono, Catalytic chemistry of heteropoly compounds, Adv. Catal. 41 (1996) 113 – 252.

[14] For selected references, see: a) N. Narkhede, S. Singh, A. Patel, Recent progress on supported polyoxometalates for biodiesel synthesis via esterification and transesterification, Green Chem. 17 (2015) 89 – 107; b) F. Su, S. An, D. Song, X. Zhang, B. Lu, Y. Guo, Heteropoly acid and ZrO_2 bifunctionalized organosilica hollow nanospheres for esterification and transesterification, J. Mater. Chem. A 2 (2014) 14127 – 14138; c) J. A.-Monge, G. Trautwein, J.P. M.-Loza, Biodiesel production by acid catalysis with heteropolyacids supported on activated carbon fibers, Appl. Catal., A 468 (2013) 432 – 441; d) C. Baroi, A. K. Dalai, Esterification of free fatty acids (FFA) of green seed canola (GSC) oil using H-Y zeolite supported 12-tungstophosphoric acid (TPA), Appl. Catal., A 485 (2014) 99 – 107.

[15] L. Huang, S.-S. Wang, J.-W. Zhao, L. Cheng, G.-Y. Yang, Synergistic combination of multi-Zr^{IV} cations and lacunary Keggin germanotungstates leading to a gigantic Zr_{24}-cluster-substituted polyoxometalate, J. Am. Chem Soc. 136 (2014) 7637 – 7642.

[16] K. Stroobants, G. Absillis, E. Moelants, P. Proost, T.N. Parac-Vogt, Regioselective

hydrolysis of human serum albumin by Zr^{IV}-substituted polyoxotungstates at the interface of positively charged protein surface patches and negatively charged amino acid residues, Chem. Eur. J. 20 (2014) 3894 – 3897.

[17] G. Absillis, T.N. Parac-Vogt, Peptide bond hydrolysis catalyzed by the Wells-Dawson $Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2$ polyoxometalate, Inorg. Chem. 51 (2012) 9902 – 9910.

[18] Y. Kikukawa, S. Yamaguchi, Y. Nakagawa, K. Uehara, S. Uchida, K. Yamaguchi, N. Mizuno, Synthesis of a dialuminum-substituted silicotungstate and the diastereoselective cyclization of citronellal derivatives, J. Am. Chem. Soc. 130 (2008) 15872 – 15878.

[19] N. Mizuno, K. Yamagushi, K. Kamata, Molecular design of polyoxometalate-based compounds for environmentally-friendly functional group transformations: from molecular catalysts to heterogeneous catalysts, Catal. Surv. Asia 15 (2011) 68 – 79.

[20] M. Carraro, B.S. Bassil, A. Sorarù, S. Berardi, A. Suchopar, U. Kortz, M. Bonchio, A Lewis acid catalytic core sandwiched by inorganic polyoxoanion caps: Selective H_2O_2-based oxidations with $[Al^{III}_4(H_2O)_{10}(\beta\text{-}XW_9O_{33}H)_2]^{6-}$ ($X = As^{III}$, Sb^{III}), Chem. Commun. 49 (2013) 7914 – 7916.

[21] K. Nomiya, K. Ohta, Y. Sakai, T. Hosoya, A. Ohtake, A. Takakura, S. Matsunaga, Tetranuclear hafnium(IV) and zirconium(IV) cationic complexes sandwiched between two di-lacunary species of α-Keggin polyoxometalates: Lewis acid catalysis of the Mukaiyama–Aldol reaction, Bull. Chem. Soc. Jpn., 86 (2013) 800 – 812.

[22] Y. Kikukawa, S. Yamaguchi, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi, N. Mizuno, Synthesis and catalysis of di- and tetranuclear metal sandwich-type silicotungstates $[(\gamma\text{-}SiW_{10}O_{36})_2M_2(\mu\text{-}OH)_2]^{10-}$ and $[(\gamma\text{-}SiW_{10}O_{36})_2M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]^{8-}$ (M = Zr or Hf), J. Am. Chem. Soc. 130 (2008) 5472 – 5478.

[23] J. Zhao, H. Guan, W. Shi, M. Cheng, Z. Wang, S. Li, A Brønsted-Lewis-surfactant-combined heteropolyacid as an environmental benign catalyst

for esterification reaction, Catal. Commun. 20 (2012) 103 – 106.

[24] C.N. Kato, Y. Makino, W. Unno, H. Uno, Synthesis, molecular structure, and stability of a zirconocene derivative with α-Keggin mono-aluminum-substituted polyoxotungstate, Dalton Trans. 42 (2013) 1129 – 1135.

[25] C.N. Kato, W. Unno, S. Kato, T. Ogasawara, T. Kashiwagi, H. Uno, K. Suzuki, N. Mizuno, Organozirconium complex with Keggin-type mono-aluminum-substituted silicotungstate: synthesis, molecular structure, and catalytic performance for Meerwein-Ponndorf-Verley reduction, Catal. Lett. 146 (2016) 2119 – 2128.

[26] C.N. Kato, Y. Makino, M. Yamasaki, Y. Kataoka, Y. Kitagawa, M. Okumura, Synthesis and X-ray crystal structure of α-Keggin-type aluminum-substituted polyoxotungstate in: Y. Mastai (Ed.), Advances in crystallization processes, InTech, Croatia, 2012, p. 601 – 618.

[27] C.N. Kato, A. Shinohara, K. Hayashi, K. Nomiya, Syntheses and X-ray crystal structures of zirconium(IV) and hafnium(IV) complexes containing monovacant Wells-Dawson and Keggin polyoxotungstates, Inorg. Chem. 45 (2006) 8108 – 8119.

[28] C.F. Oliveira, L.M. Dezaneti, F.A. C. Carcia, J.L. de Macedo, J.A. Dias, S.C.L. Dias, K.S.P. Alvim, Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia, Appl. Catal., A 372 (2010) 153 – 161.

[29] H. Weiner, J.D. Aiken III, R.G. Finke, Polyoxometalate catalyst precursors. improved synthesis, H^+-titration procedure, and evidence for ^{31}P NMR as a highly sensitive support-site indicator for the prototype polyoxoanion-organometallic-support system [(n-C$_4$H$_9$)$_4$N]$_9$P$_2$W$_{15}$Nb$_3$O$_{62}$, Inorg Chem. 35 (1996) 7905 – 7913.

[30] T. Okuhara, C. Hu, M. Hashimoto, M. Misono, Acid strength of heteropolyacids and its correlation with catalytic activity, Bull. Chem. Soc. Jpn. 67 (1994) 1186 – 1188.

Figure captions

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.

Fig. 2. Time course for the esterification of linoleic acid with methanol catalyzed by (a) **TBA-P-Al-Zr** and (b) **TBA-Si-Al-Zr**. Reaction conditions: **TBA-P-Al-Zr** and **TBA-Si-Al-Zr** (19.1 μmol), linoleic acid (0.28 mmol), methanol (49.3 mmol), and reaction temperature 80 ± 2 °C.

Table 1 Esterification of linoleic acid with methanol catalyzed by various compounds[a]

Catalyst (μmol)	System	Selectivity of methyl linolate (%)	Conversion (%)[b]	TON[c]
TBA-P-Al-Zr (19.1)	heterogeneous	>99	83	12
TBA-Si-Al-Zr (19.1)	heterogeneous	>99	15	2
TBA-P-Al (19.1)	heterogeneous	>99	2.3	<1
TBA-Si-Al (19.1)	homogeneous	>99	1.9	<1
$Cp_2Zr(OTf)_2 \cdot THF$ (23.7)	homogeneous	>99	99	12
Cp_2ZrCl_2 (23.9)	homogeneous	>99	98	11
HPW (15.2)	homogeneous	>99	99	18
ZrO_2[d]	heterogeneous	>99	15	−
HPW/ZrO_2[d]	hetero- and homogeneous	>99	99	110[e]
no catalyst	−	>99	3.9	−

[a]Reaction conditions: catalyst (15.2 − 23.9 μmol), linoleic acid (0.28 mmol), methanol (49.3 mmol), 80 ± 2 ℃, and reaction time 6 h.

[b]Conversion (%) = {[mol of linoleic acid]$_0$ − [mol of linoleic acid]$_t$}/[mol of linoleic acid]$_0$ × 100.

[c]Turnover number (TON) = [mol of product]/[mol of catalyst].

[d]50 mg of sample was used as a catalyst.

[e]TON was calculated based on the number of moles of $H_3PW_{12}O_{40} \cdot 23H_2O$ (2.53 μmol) contained in **HPW**/ZrO_2 (50 mg).

19

Table 2 Esterification of various carboxyl acids with methanol catalyzed by **TBA-P-Al-Zr** in a heterogeneous system[a]

Substrate (mmol)	Selectivity of product (%)	Conversion (%)[b]	TON[c]
oleic acid (0.31)	methyl oleate (>99)	90	15
palmitic acid (0.28)	methyl palmitate (>99)	86	13
myristic acid (0.30)	methyl myristate (>99)	75	12
lauric acid (0.34)	methyl laurate (>99)	69	12
benzoic acid (0.41)	methyl benzoate (>99)	54[d]	11[d]
benzoic acid (0.82)[e]	methyl benzoate (>99)	83	99

[a]Reaction conditions: catalyst (19.1 μmol), substrates (0.28 – 0.34 mmol), methanol (49.3 mmol), 80 ± 2 ℃, and reaction time 6 h.
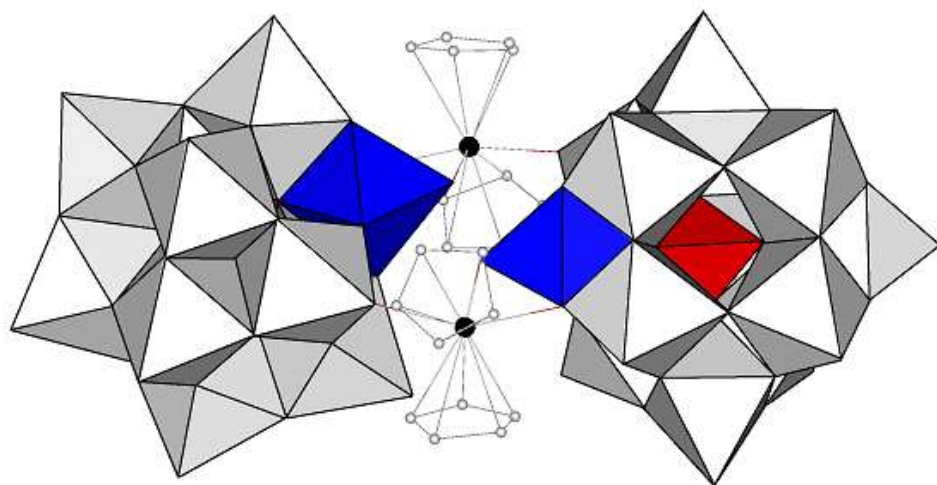
[b]Conversion (%) = {[mol of substrate]$_0$ − [mol of substrate]$_t$}/[mol of substrate]$_0$ × 100.

[c]Turnover number (TON) = [mol of corresponding product]$_t$/[mol of catalyst].

[d]Reaction time 69 h.

[e]This system is homogeneous. Reaction conditions: catalyst (6.8 μmol), benzoic acid (0.82 mmol), methanol (24.7 mmol), acetonitrile (4 mL), 80 ± 2 ℃, and reaction time 96 h.
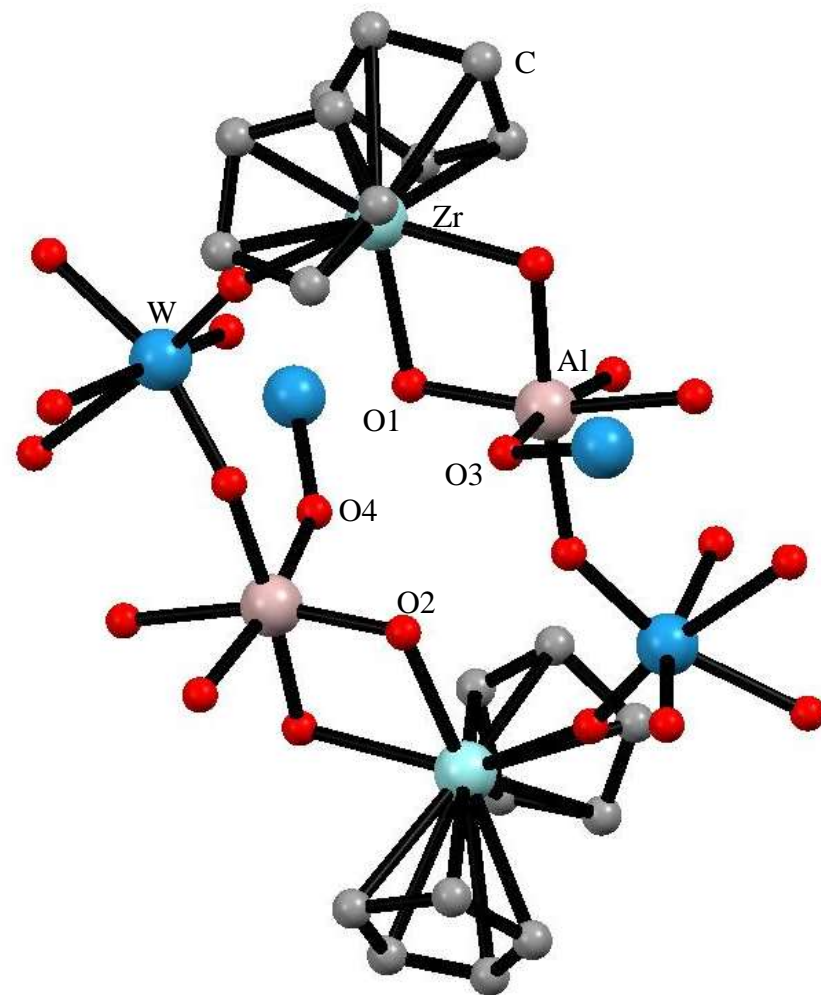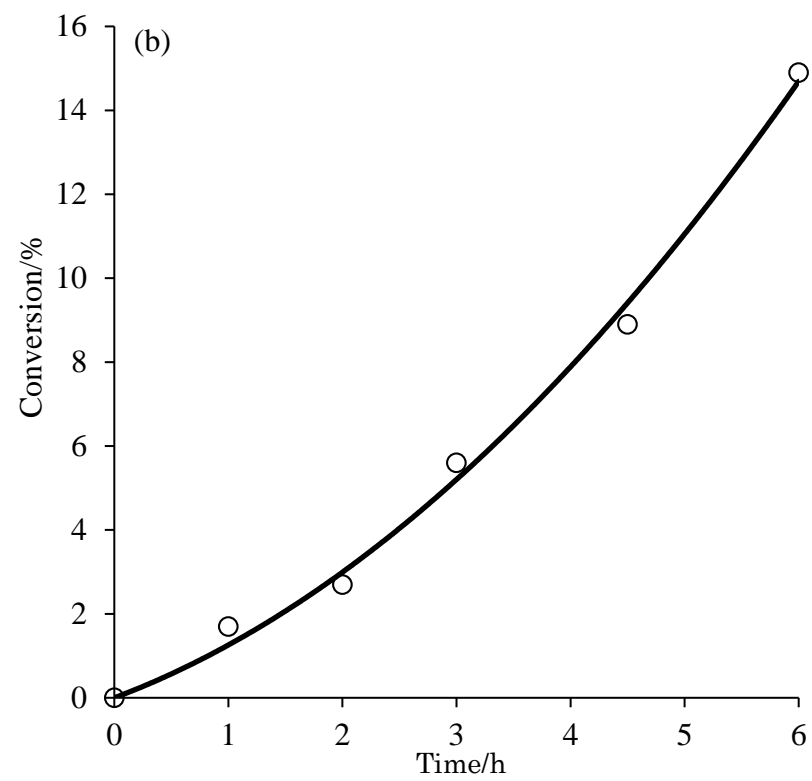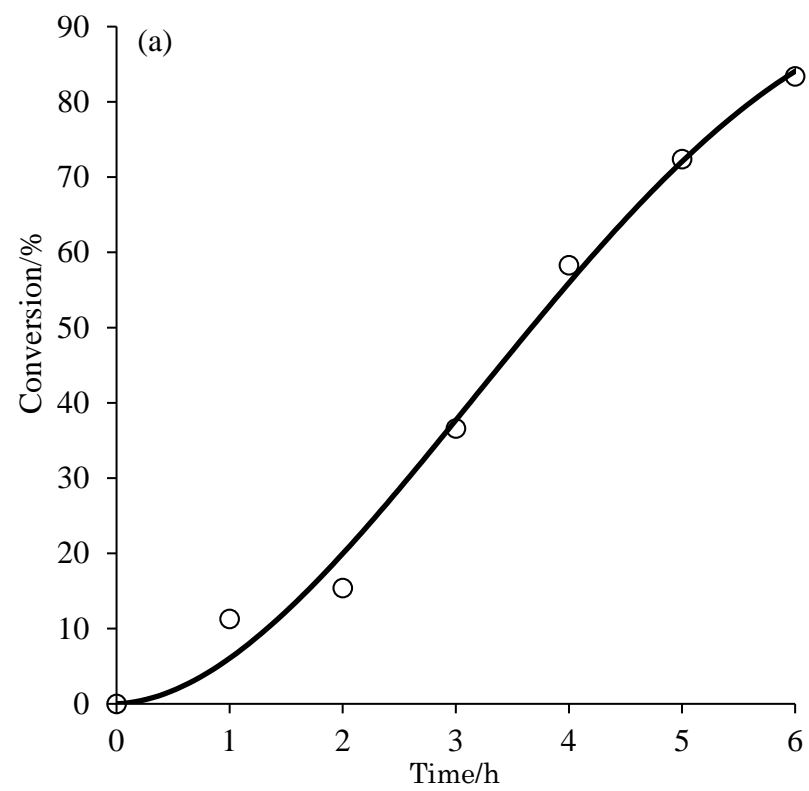
(a)

(b)

C

Zr

W

Al

O1

O3

O4

O2

Fig. 1

21

Fig. 2