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# Pyrazinium polyoxometalate tetrakaidecahedron-like crystals esterify oleic acid with equimolar methanol at room temperature



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## ABSTRACT

lonic-liquid-modified polyoxometalate was prepared by self-assembly of Keggin-type heteropolyacids and sulfonated pyrazinium-IL, in which no template, surfactant, or organic solvent was used. The obtained ionic hybrid exhibits uniform morphology of cubic tetrakaidecahedron-like crystals and possesses a larger number of strong acid sites with narrower dispersion of acid strength than its analogues with similar chemical composition but different morphology. Catalytic activity tests reveal its high conversion, stable recycling, and good substrate compatibility for esterification of free fatty acids (FFA) with methanol into biodiesel at room temperature and over a wide range of molar ratios of methanol to FFA (10–50). Even under the ideal stoichiometric conditions (methanol:FFA = 1:1, a viscous solution), it converts 83% of oleic acid in 24 h. Morphology and performance are discussed, suggesting that the uniform crystals translate into high activity due to improved accessibility of the strong acid sites on the smooth external surface of the catalyst.

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#### 1. Introduction

Acid catalysis is widely applied in the production of biodiesel fuel and various other industrially important chemicals. The urgency of green and sustainable approaches to chemical processes stimulates the requirement for recyclable solid acids as alternatives to commercially used environmentally unfavorable liquid acid catalysts [1-5]. Though numerous solid acid materials have been investigated, their applications usually suffer from inferior performance due to disadvantages such as declining acid strength, nonuniform dispersion of acid sites on the solid surface, inhibited mass transfer at the interface, or overlapped exposure of the acid sites [6-13]. To overcome this shortfall, many approaches have been proposed to improve the performance of solid acids by adjusting the chemical composition, crystallinity, porosity, topology, and morphology [14-24]. Among these studies, one focus toward efficient solid acids is to create uniform strong acid sites on the surfaces of solids through morphology and porosity control, because they benefit facilely adjusting the dispersion, exposure, and accessibility of the acid sites.

Acidic polyoxometalates (POMs), typically Keggin-type heteropolyacids (HPAs) such as H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (H<sub>3</sub>PW), have been implemented as catalysts for acid-catalyzed reactions due to high thermal stability and strong acidity [25]. Owing to their high solubility in polar solutions, it is difficult to direct use pure HPAs as solid acids. Normally, heterogeneous POM catalysts can be achieved by "immobilization" or "solidification" of the catalytically active POMs [26–28]. The latter method offers a facile preparation process and high-density acidic sites. In the solidification of POMs, ionic liquids (ILs) have demonstrated powerful functions in adjusting the solubility, acid/base properties, and pore structure of POM materials, fabricating a family of IL-POM hybrids with potential applications in electrochemistry, catalysis, materials science, etc. [29-31]. In the field of catalysis, a series of "Brønsted-acidic task-specific" IL-POMs exhibited superior catalytic performance in liquid-phase organic reactions [32-35]. However, no regular morphology has been observed over IL-POM materials, let alone morphology-performance study being performed.

Biodiesel is typically defined as alkyl esters of long-chain fatty acids that occur naturally in renewable resources such as vegetable oil or animal fats. Compared with petroleum-based diesel, biodiesel has several advantages, such as being biodegradable and cleanburning [36–38]. Biodiesel can be synthesized through either transesterification of triglycerides or esterification of free fatty



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acids (FFAs) with short-chained alcohols (mainly methanol). Esterification of FFAs is attractive in the production of biodiesel, especially for low-cost feedstock containing large amounts of FFAs (e.g., industrial sludge, inedible oil, or waste oil) and as a pretreatment to prevent saponification between FFAs and bases in transesterification reactions (saponification will produce soap that hinders further purification and reduces the biodiesel yield). Esterification of FFAs is usually carried out at a high temperature using hazardous H<sub>2</sub>SO<sub>4</sub>; catalyst separation from the reaction mixture is a very complicated process [4–8,13]. Recently, green processes for biodiesel production via sustainable heterogeneous acid catalysts have attracted significant attention. Nevertheless, virtually all of the reactions are carried out at high temperatures (>60 °C) and/ or high molar ratios of methanol to FFA (>10) [39-45]. It remains a huge challenge and becomes highly desirable to design efficient solid acids that are active at a lower molar ratio of methanol to FFA (down to stoichiometric conditions, methanol/FFA = 1:1) at a low temperature (down to room temperature).

In this work, we trigger the morphology control of IL-POM materials and report a new family of IL-POM materials with uniform morphology such as cubic tetrakaidecahedra. No template agent, surfactant, or organic solvent is required in the synthesis, making the preparation process facile and environmentally friendly. Acidic IL-POM with uniform morphology of cubic tetrakaidecahedron-like crystals (PzS-PW) results from the selfassembly of H<sub>3</sub>PW and sulfonic acid-functionalized pyrazinium (PzS-Cl) by adjusting synthesis parameters such as reaction temperature, crystallization time, solvent, and initial concentration of raw materials. The uniform morphology creates narrowly dispersed strong acid sites for PzS-PW, as demonstrated by a narrow strong peak in its NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub> TPD) curve. Catalytic tests indicate that the obtained PzS-PW acts as a highly efficient heterogeneous catalyst for esterification of FFA with methanol at room temperature with a very low substrate molar ratio. Even at the ideal equimolar ratio methanol:FFA = 1:1, it can convert 83% of oleic acid in 24 h. The morphology-performance relationship is investigated by comparing the tetrakaidecahedron-like PzS-PW with several analogues having the same chemical composition and acid strength but different morphology.

### 2. Materials and methods

#### 2.1. Materials

All the reagents used in the experiment were of analytical grade and used without further purification. Pyrazine (Pz, 99.5%), piperazine (99.5%), chlorosulfonic acid (99.5%), hydrochloric acid (HCl, 38.0%), sodium hydroxide (NaOH, 97%), sodium tungstate (NaWO<sub>4</sub>, 99.5%), and the polyoxometalates H<sub>3</sub>PW (AR), H<sub>3</sub>PMo<sub>12</sub>-O<sub>40</sub> (H<sub>3</sub>PMo, 98%), and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (H<sub>4</sub>SiW, AR) were purchased from Sinopharm Chemical Reagent Co. 1,3-Propanesultone (99%), Amberlyst-15 (AR), and NaPW<sub>12</sub>O<sub>40</sub> (NaPW, AR) were bought from Aladdin Co. The double V-containing POM H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> (H<sub>5</sub>PMoV) was prepared according to the procedure described in our previous report [46]. Purified water for the preparation of solutions was from the Membrane Science and Technology Research Center of this university.

# 2.2. Synthesis of catalysts

The sulfonic acid-functionalized pyrazinium IL monomer PzS-Cl was prepared according to the literature [47]. The main procedure is as follows. Chlorosulfonic acid (1.18 g) was added dropwise to a 50 mL round-bottomed flask containing pyrazine (0.40 g) in

anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at room temperature within 30 min. The reaction mixture was then stirred and heated under reflux conditions for 24 h. Upon completion of the reaction, CH<sub>2</sub>Cl<sub>2</sub> was decanted. The solid residue was washed with dry CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 30$  mL) and dried under vacuum to give PzS-Cl as a white solid powder in 98% yield. <sup>1</sup>H NMR (300 MHz, D<sup>6</sup>-DMSO, TMS)  $\delta$  13.23 (s, 1H), 9.45 (d, 2H), 9.17 (m, 2H), 8.80 (s, 1H). <sup>13</sup>C NMR (300 MHz, D<sup>6</sup>-DMSO, TMS)  $\delta$  144.26, 150.75. The synthesis of the other sulfonic acid-functionalized piperazinium IL (PiS-Cl), is described in the Supplementary Material.

Polyoxometalate-based ionic salts were prepared, referring to the reported procedures in a precipitation process [48]. For the synthesis of PzS-PW (Scheme 1), 25 mL aqueous solution of H<sub>3</sub>PW (1.00 g) was added dropwise within 1 min to 25 mL aqueous solution of PzS-Cl (0.12 g), followed by stirring at room temperature for 24 h. The created precipitate was filtered, washed with water, and dried under vacuum at 80 °C to obtain the final product. PzS-PW: <sup>1</sup>H NMR(300 MHz, D<sup>6</sup>-DMSO, TMS) 13.32 (s, 1H), 9.39 (d, 2H), 9.21 (m, 2H), 8.85 (s, 1H); <sup>13</sup>C NMR (300 MHz, D<sup>6</sup>-DMSO, TMS);  $\delta$  144.33, 150.02. The samples prepared at 25 °C in methanol and ethanol are designated as PzS-PW(MeOH) and PzS-PW(EtOH), respectively. The samples prepared at 0, 50, and 100 °C in H<sub>2</sub>O are designated as PzS-PW(0), PzS-PW(50), and PzS-PW(100), respectively.

Other PzS-Cl derived PzS-NaW, PzS-NaPW, PzS-PMo, PzS-SiW, and PzS-PMoV<sub>2</sub> hybrids were prepared similarly using different anion precursors NaWO<sub>4</sub>, NaPW, H<sub>3</sub>PMo, H<sub>4</sub>SiW, and H<sub>5</sub>PMoV, respectively. Several control catalysts were synthesized according to our previous work [32,34]. Briefly, PiS-PW, Pz-C<sub>3</sub>S-PW, Pz-C<sub>3</sub>S-Cl-PW, and Pz-PW were synthesized by respectively reacting PiS-Cl, Pz-C<sub>3</sub>S (1-propylsulfonic pyrazinium), Pz-C<sub>3</sub>S-Cl (1-propylsulfonic pyrazinium chloride), and Pz with H<sub>3</sub>PW. Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> was prepared by adding the aqueous solution of Cs<sub>2</sub>CO<sub>3</sub> dropwise to the aqueous solution of H<sub>3</sub>PW. The Supplementary Material includes the details of the synthesis.

#### 2.3. Characterization

Field emission scanning electron microscopy (FESEM; Hitachi S-4800, accelerating voltage: 5 kV) accompanied by energydispersive X-ray spectrometry (EDS; accelerating voltage: 20 kV) was utilized to study the morphology and the elemental distribution. The powder X-ray diffraction (XRD) patterns of the samples were recorded using a Smart Lab X-ray diffractometer from Rigaku. Fourier transform infrared (FT-IR) spectra were registered on an



**Scheme 1.** Synthesis of sulfonic acid-functionalized pyrazinium phosphotungstate, PzS-PW.

Agilent Cary 660 FT-IR instrument. The C, N, H, S elemental analysis was conducted on a Vario EL cube elemental analyzer. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a PHI 5000 Versa Probe X-ray photoelectron spectrometer with Al Ka radiation (1486.6 eV). Thermogravimetric (TG) analysis was carried out with an STA409 instrument in dry air at a heating rate of 10 °C min<sup>-1</sup>. The acidity of the solid samples in aqueous solution was measured by potentiometric titration with an automatic potentiometric titrator using a pH composite electrode. The solid was titrated with a solution of 0.05 mol  $L^{-1}$  *n*-butylamine in acetonitrile. Liquid-state <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were measured with a Bruker DPX 500 spectrometer at ambient temperature in MDSO using TMS as internal reference. A solid state <sup>31</sup>P NMR spectrum was originally recorded in a Bruker Avance III 400 M spectrometer at a magnetic field strength of 9.4 T corresponding to the Larmor frequency of 162 MHz with a cross-polarization (CP)/magic-angle-spinning (MAS) unit at room temperature. The spinning rate and contact time were 10 kHz and 5.0 ms. A <sup>1</sup>H NMR spectrum was obtained at 400 MHz using the Hahn echo at room temperature. The spinning rate was 10 kHz. A <sup>13</sup>C NMR spectrum was performed at 400 MHz using high-powered decoupling at room temperature. The spinning rate and contact time were 10 kHz and 2.5 ms. Scan numbers were 20, 1.2, and 2 for <sup>31</sup>P, <sup>1</sup>H, and <sup>13</sup>C, respectively. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 (200 kV) TEM instrument. NH<sub>3</sub> TPD curves were recorded on a BELCAT-B temperature-programming unit equipped with a thermal conductivity detector (TCD). The sample was first pretreated in He at 300 °C for 2 h. After cooling down to 60 °C in He flow, it was saturated with ammonia (5% NH<sub>3</sub> balanced with He) at 60 °C for 30 min. Next, the sample was exposed to He for 45 min to remove the physically adsorbed ammonia. Finally, the TPD profile was recorded while the sample was heated at a rate of 10 °C min<sup>-1</sup> up to 400 °C. Nitrogen (N<sub>2</sub>) adsorption isotherms and Brunauer-Emmett-Teller (BET) surface areas were measured using a BELSORPMINI analyzer. Before measurement, the samples were degassed at 30 °C for 3 h under high vacuum. Electrospray ionization mass spectrometry (ESI-MS) was recorded on a Finnigam Mat APISSQ 710 mass spectrometer. Single-crystal diffraction analysis was measured by a Bruker Apex II CCD. Inductively coupled plasma spectroscopy (ICP) was performed on a Jarrell-Ash 1100 ICP-AES spectrometer.

#### 2.4. Catalysis tests

Catalytic activity of different IL-POM hybrids in the esterification of oleic acid with methanol was evaluated. Taking the major catalyst PzS-PW as an example, in a typical batch experiment, 25 mg of PzS-PW was added into a mixture of oleic acid (1 mmol, 0.28 g) and anhydrous methanol (10 mmol, 0.32 g) in a 25 mL round-bottom flask equipped with a magnetic stirrer and a water condenser system. At the end of the reaction, the catalyst was separated by filtration.

FFA conversion can be evaluated using standard base-solution titration. The acid value (AV) was calculated using the equation

$$AV = V_{NaOH} \times C_{NaOH}, \tag{1}$$

where  $V_{NaOH}$  (mL) was the consumed volume of standard NaOH (in ethanol) in every titration and  $C_{NaOH}$  (mol L<sup>-1</sup>) was the concentration of standard NaOH (in ethanol).

Oleic acid conversion ( $X_{\text{ffa}}$ ) in the corresponding esters was estimated by calculating the product of an acid by titration with NaOH (0.01 mol L<sup>-1</sup>), according to the following equation:

$$X_{\rm ffa} = (AV_i - AV_f) / AV_i \times 100, \tag{2}$$

where  $AV_i$  and  $AV_f$  were the initial and final acid value of the mixture, respectively.

After reaction, the solid catalyst was separated and washed with methanol to remove absorbed oil and water prior to drying in the oven at 80 °C for 2 h. The obtained catalyst was reused in the next run to investigate its reusability.

The turnover number (TON) was based on the esterification product (mol) produced per molar acid site on the respective catalysts [49,50]. TON = (mmol of oleic acid × conversion of oleic acid)/(µmol of acid sites/1000). For PzS-Cl, PzS-PW, Amberlyst-15, PzS-PW(EtOH), PzS-PW(0), PzS-PW(50), and PzS-PW(100), each sulfonic acid group provides one acid site; thus the TON = (mmol of oleic acid × conversion of oleic acid)/(µmol of S/1000). For the two S-free catalysts (H<sub>3</sub>PW and Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>), each H<sup>+</sup> equals one acid site; thus TON = (mmol of oleic acid × conversion of oleic acid)/(µmol of H<sup>+</sup>/1000).

#### 3. Results and discussion

#### 3.1. Formation of crystal-like IL-POM hybrids

Scheme 1 illustrates the synthesis procedure for PzS-PW. The asymmetrical sulfoacid ionic liquid PzS-Cl is obtained from the precipitation of pyrazine and chlorosulfonic acid in the solution of anhydrous dichloromethane at 0 °C. Elemental analysis (wt.%) of PzS-Cl finds C 21.2, N 11.8, H 3.4, and S 13.9, in good accordance with Calcd: C 20.6, N 12.0, H 2.6, and S 13.8. The IL-POM hybrid sample PzS-PW is obtained by slowly dropping aqueous H<sub>3</sub>PW into the aqueous solution of PzS-Cl (PzS-Cl to  $H_3PW$  molar ratio = 1.5). The preparation, carried out at room temperature without using any seeds, surfactants, or templates, is a slow precipitation process, possibly because both the organic cation and inorganic anion have large volumes, similar to an ionic self-assembly process [51]. The cubic tetrakaidecahedron-like crystals for PzS-PW are achieved after stirring for 24 h. Elemental analysis (wt.%) of PzS-PW finds C 2.38, N 1.31, H 0.48, and S 1.49, which is very close to Calcd: C 2.31, N 1.35, H 0.29, and S 1.54. The calculated data are based on the suggested chemical composition for PzS-PW in Scheme 1, where the molar ratio of organic cation to inorganic anion is 1.5. As shown in the positive-ion and negative-ion ESI-MS spectra of PzS-PW (Fig. S1 in the Supplementary Material), the base peak at m/z 81.0 is due to the twofold charged PzS<sup>2+</sup> cation and the one at m/z 958.80 reveals the triply charged PW<sub>12</sub>O<sup>3-</sup><sub>40</sub>, indicating that PzS-PW is composed of organic IL cations (PzS<sup>2+</sup>) and inorganic heteropoly anions  $(PW_{12}O_{40}^{3-})$  through ionic linkage.

Fig. 1A shows the XRD patterns of PzS-PW and its precursors H<sub>3</sub>PW and PzS-Cl. PzS-Cl exhibits diffraction lines of a highly crystalline structure (curve a). H<sub>3</sub>PW displays a set of well-resolved sharp diffraction peaks for a HPA crystal, an index of the typical secondary cubic structure of Keggin anions (curve b). The crystal phase of H<sub>3</sub>PW is taken from the JCPDS powder diffraction file (Card 50-0304). The resultant PzS-PW sample exhibits X-ray diffraction peaks different from those of raw H<sub>3</sub>PW and PzS-Cl. revealing the formation of a crystal structure for PzS-PW (curve c). Only the major peak at 9.60° is tentatively assigned to the [110] phase, located at 10.44° for parent H<sub>3</sub>PW. This shift of the [110] phase reflects an expanded unit cell due to the replacement of protons with the bulky organic cation [52]. Single-crystal analysis is performed; however, PzS-PW demonstrates no definite single-crystal structure. The results of XRD and single-crystal diffraction indicate that PzS-PW is polycrystalline in structure rather than being a single crystal. The reason is that the arrangement of ion pairs in PzS-PW presents a certain regularity but is not as regular as the form of a single crystal. Based on these characterizations, PzS-PW is composed of IL cations (PzS<sup>2+</sup>) and



Fig. 1. (A) XRD patterns of (a) PzS-Cl, (b) H<sub>3</sub>PW and (c) PzS-PW; (B) FESEM image and (C) SAED pattern of PzS-PW; (D) elemental (N, O, S, P, and W) mapping of PzS-PW; FESEM images of (E) PzS-Cl and (F) H<sub>3</sub>PW.

 $PW_{12}O_{40}^3$  anions with a cation/anion molar ratio of 1.5. The IL cations are ionic bonded to the  $PW_{12}O_{40}^3$  anions, reaching a certain polycrystalline structure.

The FESEM image indicates that PzS-PW is composed of uniform freestanding microcrystal-like particles with the shape of cubic tetrakaidecahedra at the micrometer level (Fig. 1B). Selected-area electron diffraction (SAED) of the microcrystallites shows discrete spots, additionally confirming the crystalline structure (Fig. 1C). Elemental mapping images present homogeneous dispersion of N, O, S, P, and W throughout the whole crystal with the same shape, an index of the homogeneity of the obtained PzS-PW sample (Fig. 1D). To the best of our knowledge, no such morphology is observed over POM materials, and this is the first time uniform crystal-like morphology has been seen in IL-POM hybrids. In contrast, the parents PzS-Cl and H<sub>3</sub>PW are microsized disordered particles (Fig. 1E and F).

Further characterizations are performed on PzS-PW. Fig. 2A illustrates its FT-IR spectrum. A parallel test is also conducted on the parent samples PzS-Cl and H<sub>3</sub>PW. PzS-Cl shows a broad peak at 2650–3500 cm<sup>-1</sup>, which contains the overlaid  $-NH^+Cl^-$  stretching peak and the O—H stretching of  $-SO_3H$ . The two peaks at 1069 and 1174 cm<sup>-1</sup> correspond to vibrational modes of N–SO<sub>2</sub> and O–SO<sub>2</sub> bonds. Another peak at 1010 cm<sup>-1</sup> could be correlated with

S=O bonds (curve a) [47]. In the wavenumber region 800–1100 cm<sup>-1</sup> (curve b), H<sub>3</sub>PW gives four featured peaks (1080 (P–O<sub>a</sub>), 984 (W=O<sub>d</sub>), 889 (W–O<sub>b</sub>–W) (corner-sharing), and 806 cm<sup>-1</sup> (W–O<sub>c</sub>–W) (edge-sharing)), assigned to the Keggin structure. For the hybrid sample PzS-PW (curve c), in spite of the decrease in peak intensities and the slight shift in peak positions, these four peaks still appear distinctly, suggesting preservation of the Keggin structure for heteropolyanions. In addition, PzS-PW exhibits featured bands for organic groups, in which S=O stretching vibrations are detected to verify the presence of sulfonic groups in the hybrid. These observations reveal the existence of the organic group and Keggin-structured PW<sub>12</sub>O<sub>40</sub><sup>3</sup> anions in the hybrid.

TG analyses (Fig. 2B) show that the starting decomposition temperature of PzS-PW is about 350 °C (curve a), remarkably higher than 280 °C for PzS-Cl (curve b). The drastic weight loss of nearly 8% in the temperature range 350–600 °C corresponds to the thermal decomposition of the organic moiety PzS in the hybrid. This phenomenon reveals high thermal stability of PzS-PW due to the formation of ionic crystals [32,34].

The XPS spectrum of PzS-PW (Fig. 2C) presents five dominant peaks centered at 283.8, 399.6, 529.9, 231.6, and 167.6 eV, corresponding to the presence of C1s, N1s, O1s, S2s, and S2p, respectively. The observed S2s and S2p signals confirm the



Fig. 2. (A) FT-IR spectra of (a) PzS-Cl. (b) H<sub>3</sub>PW, and (c) PzS-PW; (B) TG curves of (a) PzS-PW and (b) PzS-Cl. (C) XPS survey; (D) <sup>13</sup>C MAS NMR; (E) <sup>1</sup>H MAS NMR and (F) <sup>31</sup>P CP MAS NMR spectra of PzS-PW.

presence of sulfonic groups. Signals of W4 $p_{1/2}$  (493.9 eV), W4 $p_{3/2}$  (426.4 eV), W4 $d_{3/2}$  (260.2 eV), W4 $d_{5/2}$  (247.0 eV), and P2p (132.5 eV) correspond to the presence of PW<sub>12</sub>O<sub>40</sub><sup>3–</sup> anions. These results prove the structure of the hybrid, matching the FT-IR and elemental analysis results.

The chemical structure of PzS-PW is further investigated by solid NMR analyses. As shown in the <sup>13</sup>C NMR spectrum (Fig. 2D), two peaks present at 159.99 and 124.99 support the proposed asymmetric structure, as shown in Scheme 1. <sup>1</sup>H (Fig. 2E) and <sup>31</sup>P (Fig. 2F) NMR spectra are also performed to give more structural information. The peaks of hydrogen are observed at 9.40, 9.18, 8.89, and 7.75 ppm, respectively. Two signals at -14.99 and -16.51 ppm for <sup>31</sup>P correspond to the distorted PW Keggin structure due to the strong intramolecular electron transfer from the organic moiety to the POM anions [53,54].

# 3.2. Insight into morphology formation

As noted above, a uniform cubic tetrakaidecahedron-like morphology is observed over the IL-POM hybrid PzS-PW. In order to understand the morphology formation process, various synthesis parameters, including the reaction temperature, crystallization time, solvent, and initial concentration of raw materials, are explored to investigate their influence on the product morphology. The obtained materials are characterized by XRD and SEM (Figs. S2A and S3 in the Supplementary Material). By fixing the initial composition and reaction temperature, SEM images of the intermediates involved in the formation are collected at reaction times of 1, 6, 24, and 48 h. Only irregular particles with a wide size dispersion at the micrometer level form within a short reaction time of 1 h, while increasing the reaction time to 6 h results in defective cubic particles with rough surfaces. Uniform cubic tetrakaidecahedra appear at 24 h. Further elongating the time to 48 h causes slightly cracked cubic tetrakaidecahedra with a wide size dispersion. These results indicate that the morphology formation of PzS-PW undergoes dissolution and reprecipitation of the nanocrystallites [55-58].

Reaction temperature also influences the entire nucleation, formation, and growth rate [59,60]. Low (0 °C) or high (50 and 100 °C) temperatures were tested in the precipitation of PzS-Cl and H<sub>3</sub>PW (Fig. S4 in the Supplementary Material). Cubic tetrakaidecahedra with cracked surfaces appear at 0 °C. In contrast, large and small particles with disturbed cubic shapes are observed at 50 °C. Irregular formless particles appear at a high temperature of 100 °C. Such phenomena show that only room temperature is suitable for the formation of PzS-PW with uniform cubic tetrakaidecahedron-like morphology.

Further, the solvent amount determines the concentration of raw materials and significantly influences the nucleation step and the following aggregation/growth process [61]. Different solvent dosages would influence the ultimate morphology of the product. Fig. S5 in the Supplementary Material shows the SEM images of the products prepared with different water amounts. The particles are of various sizes and random shapes as a result of using a small amount of water (5 mL). Distorted cubes appear when a large amount water is used (30 mL) and become more irregular with a larger water amount (50 mL). The solvent viscosity affects the diffusion rate of the formed nanocrystallites in the solution. Two other different solvents, methanol (MeOH) and ethanol (EtOH), with viscosity of 0.58 and 1.10 mPas, lower and higher than H<sub>2</sub>O (0.89 mPa s), are used in the precipitation of PzS-Cl and H<sub>3</sub>PW. The sample obtained using EtOH exhibits an XRD pattern similar to that of PzS-PW (Fig. S2D in the Supplementary Material), but presents a different morphology of uniform micrometer-sized cuboid particles with length  $\sim$ 30  $\mu$ m and width  $\sim$ 10  $\mu$ m (Fig. 3A and B). In contrast, no uniform morphology, but irregular randomly packed particles, is observed by using MeOH as the solvent (Fig. 3C and D).

Generally, IL-POM hybrids can be regarded as POM anions linked by IL cations in a periodic structure. In similar works, the used IL precursors usually possessed a soft molecular structure with a freely rotated C—C bond, thus resulting in random directions in cross-linking the POM anions and ultimately in a formless crystal or amorphous structure [62,63]. Here, IL PZS-Cl is of a rigid structure without any freely rotated C—C bond, inhibiting random cross-linking. Therefore, uniform crystals are obtained by utilizing PZS-Cl to modify H<sub>3</sub>PW. The behavior of rigid PZS cations is similar to that of inorganic cations, by using which various uniform crystal-like morphologies are attained on POM salts [55]. For direct comparison, several other IL precursors and pyrazine are used to pair with H<sub>3</sub>PW, as shown in Scheme S1 in the Supplementary Material. SEM images (Fig. S6 in the Supplementary Material) indicate that soft IL precursors all cause formless morphology in spite of these ILs possessing a structure similar to that of PzS-Cl. These phenomena further confirm that the special IL precursors are crucial for the formation of uniform cubic tetrakaidecahedron-like crystals of PzS-PW. The rigid organic compound pyrazinemodified IL-POM is also composed of angular particles, but with a wide size dispersion. This confirms that rigid structure in organic cations benefits the angular morphology in organic-groupmodified POMs; on the other hand, it suggests that acidic groups may be useful in the formation of regular morphology, in accordance with a previous report [64] that the carboxy groupcontaining rigid organic compound PA-HPW-3 also causes uniform cubelike morphology for POM.

In order to investigate the impact of POM anions on the morphology, various IL-POM hybrids are prepared using PzS-Cl to modify different POM anions. All these IL-POM materials possess polycrystal structure and retain the Keggin structure as their parent POM anion (Fig. S7 in the Supplementary Material). Nonetheless, they exhibit different morphologies, as depicted in Fig. 4. The primary particles of PzS-NaW are thin and uniform cycloidal slices (Fig. 4B) and are loosely packed. Uniform square slices can be achieved on PzS-NaPW (Fig. 4C) and these particles are about 15-20 µm in length. When the counteranion is changed to PMo<sup>3-</sup>, the primary particles of the obtained sample PzS-PMo are rhombic decahedral microcrystals with a size of about 10 µm (Fig. 4D). When the counteranion is replaced with  $SiW^{4-}$  (Fig. 4E), agglomerated particles are observed and accompanied by small cubic blocks with length varying from hundreds of nanometers to  $1-2 \mu m$ . The morphology of PzS-SiW is not as regular as that of other molecules because the solid is obtained by evaporating the water rather than by direct precipitation. Varying the anion to be PMoV<sub>2</sub><sup>5-</sup>, unusual rhombic tetrakaidecahedral microcrystals are obtained (Fig. 4F). These results demonstrate that various angular morphologies over IL-POM materials can be achieved utilizing PzS-Cl, though the exact shape depends on the POM anions, further supporting our speculation that a rigid organic modifier favors the production of angular morphology. These morphologies are never observed for organic-group-modified POMs, revealing



Fig. 3. FESEM images of PzS-PW synthesized in different solvents at 25 °C: (A, B) ethanol and (C, D) methanol.



Fig. 4. FESEM images of (A) PzS-PW, (B) PzS-NaW, (C) PzS-NaPW, (D) PzS-PMo, (E) PzS-SiW, and (F) PzS-PMoV<sub>2</sub>.

the distinctive role of PzS-Cl in controlling the morphology of the resultant IL-POM hybrid.

# 3.3. Catalytic activity

The catalytic activity of PzS-PW is evaluated at room temperature for esterification of oleic acid with methanol, one important reaction toward biodiesel. We start the test at a relatively low substrate molar ratio of 10 (methanol/oleic acid). The reaction results obtained with control catalysts are listed in Table 1. Esterification hardly occurs without a catalyst under the employed conditions, with oleic acid conversion of only 3.5% (entry 1). The IL precursor PzS-Cl gives a low conversion of 41.5% with TON 35.8 (entry 2), while the neat H<sub>3</sub>PW shows a high conversion of 85.2% with TON 73.4 (entry 3), agreeing with the previously reported good activity of H<sub>3</sub>PW [65]. Nonetheless, both IL PzS-Cl and H<sub>3</sub>PW are homogeneous catalysts due to their good solubility in the reaction media, making catalyst recovery impossible. In contrast, PzS-PW leads to a liquid–solid heterogeneous reaction system and demonstrates superior conversion of 88% with a high TON of 75.9% (entry 4). Such activity is not only as high as for the homogeneous parents PzS-Cl and H<sub>3</sub>PW, but also much better than the traditional inorganic POM salt solid acid Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> (conversion 62.5% and TON 53.9, entry 5) and the commercial polymeric solid acid Amberlyst-15 (conversion 29.2% and TON 25.2, entry 6). The comparison reveals the unique and interesting heterogeneous performance of PzS-PW in this reaction.

Parallel tests are performed on several control samples with the same composition as PzS-PW but different morphologies. These controls include PzS-PW(EtOH), PzS-PW(0), PzS-PW(50), and PzS-PW(100). PzS-PW(EtOH) prepared using EtOH as the solvent exhibits inferior conversion of 80.8% (entry 7), due to the bulky

#### Table 1

Catalytic performance of different catalysts in the esterification of oleic acid with methanol.<sup>a</sup>



| Entry | Catalyst             | Catalyst weight (mg) <sup>b</sup> | Catalysis type | $S_{BET}(m^2g^{-1})^c$ | Potentiometric titration (Ei) | Con. (%) | TON <sup>d</sup> | TOF $(h^{-1})^{e}$ |
|-------|----------------------|-----------------------------------|----------------|------------------------|-------------------------------|----------|------------------|--------------------|
| 1     | Without              | -                                 | -              | -                      | _                             | 3.5      | -                | -                  |
| 2     | PzS-Cl               | 2.8                               | Homo           | -                      | -                             | 41.5     | 35.8             | 1.8                |
| 3     | H₃PW                 | 11.1                              | Homo           | 8.0                    | 319                           | 85.2     | 73.4             | 3.7                |
| 4     | PzS-PW               | 25.0                              | Hetero         | 3.5                    | 308                           | 88.0     | 75.9             | 3.8                |
| 5     | $Cs_2HPW_{12}O_{40}$ | 12.2                              | Hetero         | 62                     | 217                           | 62.5     | 53.9             | 2.7                |
| 6     | Amberlyst-15         | 2.8                               | Hetero         | 45                     | -                             | 29.2     | 25.2             | 1.3                |
| 7     | PzS-PW(EtOH)         | 25.4                              | Hetero         | 3.5                    | 309                           | 80.8     | 69.7             | 3.5                |
| 8     | PzS-PW(0)            | 24.8                              | Hetero         | 7.2                    | 306                           | 77.8     | 67.1             | 3.4                |
| 9     | PzS-PW(50)           | 24.7                              | Hetero         | 8.2                    | 305                           | 79.9     | 68.9             | 3.4                |
| 10    | PzS-PW(100)          | 24.7                              | Hetero         | 8.8                    | 301                           | 73.3     | 63.3             | 3.2                |

<sup>a</sup> Reaction conditions: oleic acid 1 mmol, methanol 10 mmol, 25 °C, 20 h.

<sup>b</sup> For PzS-Cl, PzS-PW, Amberlyst-15, PzS-PW(EtOH), PzS-PW(0), PzS-PW(50) and PzS-PW(100), the S amount is 11.6 μmol; for the two S-free catalysts (H<sub>3</sub>PW and Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>), the amount of proton acid sites is 11.6 μmol, equal to the S amount above.

<sup>c</sup> BET surface area.

<sup>d</sup> The turnover number (TON) is based on the esterification product (mol) produce per molar acid site in the catalyst.

<sup>e</sup> The turnover frequency (TOF) is based on the esterification product (mol) produced per hour and per molar acid site in the catalyst.

block morphology that hinders the dispersion and access of the acid sites. The latter three, obtained using water as the solvent but at different synthesis temperatures of 0, 50 and 100 °C, possess morphologies of cracked cubes and irregular particles. They result in a desirable liquid-solid biphasic esterification process but exhibit inferior activity (entries 8-10) compared with the lead catalyst PzS-PW with uniform morphology. PzS-PW(0) and PzS-PW(50) possess the morphology of small crystals with cracked surfaces that complicate the surface state, thus exhibiting inferior conversion of 77.8 and 79.9%, respectively. PzS-PW(100), with the morphology of irregular particles, presents a much lower conversion of 73.3%. These results indicate that uniform crystals with a smooth surface for PzS-PW attain higher activity than those analogues with less regular or irregular morphology. Furthermore, catalytic kinetics tests are performed over the selected samples PzS-PW, PzS-PW(EtOH), and PzS-PW(100) with significant differences in morphology (Fig. 5A). They are assessed with the same S/C ratio for comparison. It is seen that PzS-PW with uniform cubic tetrakaidecahedron-like morphology exhibits a conversion rate of 0.057 s<sup>-1</sup> in the early reaction period, much higher than those over PzS-PW(EtOH) with the morphology of bulky block and PzS-PW (100), composed of irregular particles (Table 2). Such differentiation in the initial reaction rates further reflects morphologyrelated catalytic improvement over PzS-PW.

Various other PzS-Cl derived IL-POM materials with different POM anions are assessed in the esterification of oleic acid with methanol under the same reaction conditions. Though these materials also exhibit relatively uniform morphology, their catalytic performance dramatically varies with the POM precursors, especially their acidic properties (Table S1 in the Supplementary Material). Low conversion of oleic acid is observed over the samples derived from neutral NaWO<sub>4</sub> and NaPW. For example, the conversion is only 36.5% for PzS-NaW and very low for PzS-NaPW (7.7%). PzS-PMo and PzS-PMoV<sub>2</sub> prepared from the corresponding acidic POMs result in the conversion of 63.1% and 77.5%, respectively. PzS-SiW, obtained from more acidic H<sub>4</sub>SiW, demonstrates a higher conversion of 83.4%. Briefly, the catalytic activities of these sulfonated PzS-HPA catalysts are in the sequence PvS-PW > PzS-SiW > PzS-PMo, which is consistent with the order of acid strength for their parent HPAs:  $H_3PW > H_4SiW > H_3PMo$ . The above phenomena imply that the superior activity of PzS-PW is strongly related to the HPA anions, which have a strong electronwithdrawing capacity that can greatly enhance the acid properties of counter protons in sulfonic groups [34,63,66,67].

Further catalytic assessment of PzS-PW is performed by optimizing the reaction conditions under different molar ratios of methanol to oleic acid at room temperature (Table 3). High conver-

#### Table 2

Esterification of oleic acid with methanol in a batch reactor.<sup>a</sup>

| Catalysts    | Initial TOF (s <sup>-1</sup> ) <sup>b</sup> |
|--------------|---------------------------------------------|
| PzS-PW       | 0.057                                       |
| PzS-PW(EtOH) | 0.017                                       |
| PzS-PW(100)  | 0.006                                       |

 $^{\rm a}$  Conditions: oleic acid 1 mmol, methanol 10 mmol, catalyst 25 mg, 7.7  $\mu$ mol.  $^{\rm b}$  Calculated by the limiting reagent according to Fig. 5A; oleic acid conversion <10%.

sions of 95.6-97.4% can be obtained at high molar ratios of methanol to oleic acid (10–50) under optimized conditions. Even at low molar ratios of methanol to oleic acid of 5 and 3, PzS-PW still can efficiently catalyze the reaction, giving conversions of 91.8% and 90.7%, respectively. Unprecedentedly, more than 80% of the substrates can be converted at a stoichiometric ratio of 1. In previous work, excess methanol was required to allow efficient conversion of FFA in the esterification of FFA with methanol to produce biodiesel, even under high-temperature reaction conditions (Table S2 in the Supplementary Material). Efficient conversion usually happened with a molar ratio of methanol to FFA above 10. Only a few reports were related to conversion at a low molar ratio of methanol to FFA, and these reactions were normally carried out at high temperature. In this work, PzS-PW demonstrates high activity in this reaction at room temperature with a much low molar ratio of methanol to oleic acid. The reaction conditions are milder than for the previous catalysts, achieving esterification of FFA with methanol under ideal stoichiometric conditions.

To investigate the scope of PzS-PW catalyst for esterification, other long-chain fatty acid and short-chain alcohol substrates were tested, with results shown in Table 4 and Table S3 in the Supplementary Material. It converts >90% FFAs to corresponding esters in all cases at both high (20) and low (3) molar ratios of methanol to FFA at both high (60 °C) and low temperature (25 °C). These results demonstrate that the hybrid crystal catalyst PzS-PW can be applied to a variety of long-chain fatty acids and short-chain alcohols for production of biodiesel. An amplification experiment at large scale was performed in the esterification of oleic acid with methanol at a low substrate molar ratio of 10 (methanol/oleic acid) by increasing all raw materials to 400 times the previous amounts. Reaction conditions: oleic acid (0.4 mol, 113 g), methanol (4 mol, 128 g), 25 °C, 24 h, catalyst amount 5.04 mmol, 16 g. PzS-PW converts 90.3% of oleic acid into biodiesel, demonstrating the potential importance of this catalyst for practical application.

Reusability of PzS-PW in the esterification of oleic acid and methanol at room temperature is investigated in a five-run recy-



Fig. 5. (A) Time course of esterification of oleic acid with methanol catalyzed by (a) PzS-PW, (b) PzS-PW(EtOH), and (c) PzS-PW(100). Reaction conditions: oleic acid 1 mmol, methanol 10 mmol, catalyst 11.6 µmol S (25.0 mg of PzS-PW, 25.4 mg of PzS-PW(EtOH), 24.7 mg of PzS-PW(100)), 25 °C. (B) NH<sub>3</sub> TPD patterns of (a) PzS-PW, (b) PzS-PW (EtOH), and (c) PzS-PW(100).

 Table 3

 Catalytic performance of PzS-PW with different molar ratios of methanol to oleic acid.<sup>a</sup>

| Entry | Catalyst               | Catalyst<br>weight<br>(mg) <sup>b</sup> | Alcohol/acid<br>(mol/mol) | Con.<br>(%) | TON <sup>c</sup> | ${{TOF}\atop{(h^{-1})^d}}$ |
|-------|------------------------|-----------------------------------------|---------------------------|-------------|------------------|----------------------------|
| 1     | PzS-PW                 | 20                                      | 50                        | 97.4        | 104.7            | 4.4                        |
| 2     | PzS-PW                 | 20                                      | 20                        | 96.7        | 104.0            | 4.3                        |
| 3     | PzS-PW                 | 40                                      | 10                        | 95.6        | 51.7             | 2.2                        |
| 4     | PzS-PW                 | 70                                      | 5                         | 91.8        | 28.2             | 1.2                        |
| 5     | PzS-PW                 | 100                                     | 3                         | 90.7        | 19.5             | 0.8                        |
| 6     | PzS-PW                 | 200                                     | 1                         | 83.3        | 9.0              | 0.4                        |
| 7     | Amberlyst-             | 22                                      | 1                         | 40.3        | 4.3              | 0.2                        |
| 8     | 15<br>Amberlyst-<br>15 | 200                                     | 1                         | 54.5        | 0.65             | 0.03                       |

<sup>a</sup> Reaction conditions: oleic acid 1 mmol, 25 °C, 24 h.

<sup>b</sup> The amounts of the catalyst PzS-PW are respectively the optimal ones for the employed alcohol/acid molar ratios. The catalyst Amberlyst-15 is compared with PzS-PW in two ways: entries 7 and 6 have a similar S amount of 92.8 μmol, while entries 8 and 6 possess the same weight of 200 mg.

<sup>c</sup> The turnover number (TON) is based on the esterification product (mol) produced per molar acid site in the catalyst.

<sup>d</sup> The turnover frequency (TOF) is based on the esterification product (mol) produced per hour and per molar acid site in the catalyst.

cling test. PzS-PW catalyst can be reused steadily with negligible loss in activity, which is true at both relatively high (20) and low (3) molar ratios of methanol to oleic acid (Fig. 6A), reflecting good catalyst reusability. The organic elements (C, N, H, S) and inorganic element (W) of the recycled PzS-PW were measured by elemental analysis and ICP-AES, respectively, giving the composition (wt.%) C 2.35, N 1.35, H 0.54, S 1.49, and W 70.7, very close to that of the fresh catalyst (C 2.38, N 1.31, H 0.48, S 1.49, and W 70.6). ICP analysis of the reacted liquid mixture (after removal of solid catalyst) reveals that only 0.064 wt.% of the W in fresh PzS-PW has leached into the reaction media. These results suggest that the catalyst is stable during the recycling test. After the fifth recycling run, the recovered PzS-PW catalyst is analyzed by FESEM, XRD, and FT-IR (Fig. 6B–D). Almost identical FESEM images and XRD patterns are observed for the fresh and reused catalyst, suggesting that there is no noticeable change in the structure of the catalyst during the esterification of oleic acid and methanol. In the FT-IR spectra, the reused catalyst still exhibits the four characteristic Keggin adsorption peaks in the range 700–1100 cm<sup>-1</sup>, indicating that the Keggin structure is maintained well. Compared with the FT-IR spectrum of the fresh one, the reused catalyst demonstrates some additional adsorption bands at 2925 and 2855 cm<sup>-1</sup>, which can be assigned to the characteristic absorption of adsorbed methyl oleate [45,64]. Simply washed with methanol and water, these adsorbed species can be facilely removed and enable good reusability.

### 3.4. Understanding the catalytic process

Acid strength and surface exposure density of acid sites both affect the activity of a solid acid catalyst. The superior performance of acidic IL-POM PzS-PW in the esterification of FFA with methanol can be assigned primarily to the preservation of the acid strength of its parent H<sub>3</sub>PW, which is the strongest acid in POM materials. This is why PzS-PW attains higher conversion than other PzS-Cl-derived IL-POMs. Further, uniform morphology improves the dispersion and accessibility of acid sites. Therefore, PzS-PW with regular cubic tetrakaidecahedral crystal-like morphology exhibits performance superior to that of its analogues with the same chemical composition but less regular or irregular morphologies.

To support this speculation, two characterizations related to the acid properties are performed: potentiometric titration and NH<sub>3</sub> TPD. Acid properties of H<sub>3</sub>PW, PzS-PW, PzS-PW(EtOH), PzS-PW (0), PzS-PW(50), and PzS-PW(100) are compared by means of potentiometric titration with *n*-butylamine (Table 1), in which

Table 4

| Entry | Fatty acid | Alcohol | Conversion/%      |
|-------|------------|---------|-------------------|
| 1     | 0          | ОН      | 96.2ª             |
|       | ОН         |         | 90.2 <sup>b</sup> |
| 2     | O<br>II    | _OH     | 95.4ª             |
|       | ОН         |         | 90.4 <sup>b</sup> |
| 2     | 0<br>      | ОН      | 97.1 <sup>a</sup> |
| 3     | ОН         |         | 90.1 <sup>b</sup> |
| 4     | 0          | он      | 96.5 <sup>a</sup> |
|       | ОН         |         | 90.5 <sup>b</sup> |
| 5     | 0<br>      | ∧ OH    | 92.7 <sup>a</sup> |
|       | ОН         |         | 89.7 <sup>b</sup> |
| 6     | 0          | ОН      | 95.3 <sup>a</sup> |
|       | ОН         |         | 88.3 <sup>b</sup> |

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<sup>a</sup> Reaction conditions: oleic acid 1 mmol, methanol 20 mmol, catalyst 20 mg, 6.2  $\mu$ mol, 25 °C, 20 h. <sup>b</sup> Reaction conditions: oleic acid 1 mmol, methanol 3 mmol, catalyst 100 mg, 31  $\mu$ mol, 25 °C, 24 h.



**Fig. 6.** (A) Recyclability of PzS-PW in the esterification of oleic acid with methanol. (a) Reaction conditions: oleic acid 1 mmol, methanol 20 mmol, catalyst 25 mg, 7.7 µmol, 25 °C, 20 h. (b) Reaction conditions: oleic acid 1 mmol, methanol 3 mmol, catalyst 100 mg, 31 µmol, 25 °C, 24 h. (B) FESEM image of reused PzS-PW, (C) FT-IR spectra, and (D) XRD patterns of (a) fresh and (b) reused PzS-PW.

the initial electrode potential  $(E_i)$  indicates the maximum acid strength of the sites. PzS-PW and its analogues demonstrate more or less similar  $E_i$  values (301–309 mV), very close to the  $E_i$  of raw H<sub>3</sub>PW (319 mV). This result confirms that PzS-PW largely remains the acid strength of H<sub>3</sub>PW. On the other hand, the result implies that the acid strengths of PzS-PW and its analogues are close to each other. N<sub>2</sub> sorption experiments reveal the nonporous structure of these IL-POM materials with surface areas less than  $10 \text{ m}^2 \text{g}^{-1}$  (Table 1 and Fig. S8 in the Supplementary Material). Since PzS-PW and its controls possess very similar composition, nonporous structure, and acid strength, the difference in their activity can mostly be assigned to their morphology variation. NH<sub>3</sub> TPD curves are collected to understand their acid features in more detail (Fig. S9 in the Supplementary Material). The number of acid sites can be estimated from the peak area for the desorbed ammonia, and the acid strength is reflected by the desorption temperature at which the ammonia molecule is released. Further, the peak width implies the uniformity of the acid strength (a broad or sharp peak is an index of wide or narrow dispersion of acid strength), while the temperature for the maximum point of the desorption peak  $(T_{max})$  is indicative of the average value of the acid strength. The acid amounts for different samples are listed in Table S4 in the Supplementary Material, obtained by integrating NH<sub>3</sub> TPD traces. Fig. 5B shows the NH<sub>3</sub> TPD curves of the selected samples PzS-PW, PzS-PW(EtOH), and PzS-PW(100), which have significant differences in morphology. PzS-PW(100), composed of irregular particles, exhibits a broad peak that has partial acid sites with relatively high acid strength (155 °C), but it possesses fewer acid sites overall (0.738 mmol  $g^{-1}$ ). Its much broader peak is an index of wide dispersion of acid strength. PzS-PW(EtOH), with bulky blocks, exhibits a relatively narrow peak at 140 °C, suggesting that the dispersion of acid strength becomes more uniform due to improved uniformity in morphology. The number of acid sites for PzS-PW(EtOH) is 0.903 mmol  $g^{-1}$ , larger than for PzS-PW (100), an index of more acid sites due to variation in morphology.

Noticeably, PzS-PW, composed of small crystals with smooth surfaces, demonstrates a much narrower peak at 145 °C, confirming the uniform morphology-derived narrow dispersion of acid strength. The larger peak area observed over PzS-PW than over PzS-PW(EtOH) suggests that the small crystals with smooth surfaces also benefit from the exposure of more acid sites (0.965 mmol g<sup>-1</sup> for PzS-PW). PzS-PW has more exposed surface acid sites than PzS-PW(EtOH) and PzS-PW(100), thus leading to high catalytic activity. This result suggests that the morphological variation of these materials with the same chemical composition causes the different acid sites that affect their activity. Aiming to acquire additional evidence, NH<sub>3</sub> TPD curves of other solid samples, PzS-PW(50), PzS-PW(0), and Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>, are listed in Fig. S9 and their acid amounts are summarized in Table S4 in the Supplementary Material. The sample PzS-PW(50), which is also composed of irregular particles, displays a TPD curve similar to that of PzS-PW(100), suggesting that this irregular morphology will cause a wide dispersion of acid strength. The sample PzS-PW (0) having the same particle size and shape as PzS-PW but with a cracked surface demonstrates a TPD curve similar to that of PzS-PW, further illustrating the close association of the narrow dispersion of acid strength with regular crystal particles. The lower peak area for PzS-PW(0) than for PzS-PW shows the smaller number of acid sites for PzS-PW(0) (0.867 mmol  $g^{-1}$ ), again implying that the more acid sites on the smooth surface of PzS-PW account for its enhanced activity. All of these analyses support the influence of morphology, in which uniform small crystals provide a narrow dispersion of acid strength and expose a large number of acid sites, thus promoting catalytic activity.

Supporting suitable acid sites on porous carriers is a widely studied approach to enabling the high dispersion of active acid sites, aiming to improve mass transfer for both substrates and products [11,15,17–21]. Nevertheless, dispersion of acid sites on a large surface leads to a low concentration of acid sites, which would cause a decline of the acid strength and a lack of the cooperative



Fig. 7. Schematic representations of the effects of dispersion and exposure of acid sites on catalytic efficiency for the equimolar esterification of oleic acid with methanol at room temperature: (A) nonporous PzS-PW with uniform external surface; (B) a conventional porous solid acid with enriched internal surface.

effect among acid sites found in liquid acids. In contrast, nonporous solid acids provide high a density of active sites, but suffer from limited exposure and accessibility of the active sites.

Here, an ionic crystal IL-POM is synthesized by assembling strong acidic H<sub>3</sub>PW with an in situ sulfonated IL precursor. Potentiometric titration with *n*-butylamine (Table 1) indicates that PzS-PW well retains the strong acidity of H<sub>3</sub>PW. NH<sub>3</sub> TPD results reveal a large number of surface-exposed acid sites over PzS-PW, which exceeds the samples without this uniform morphology. Further, its acidity features a narrow dispersion of acid strength, and the density of acid sites is high due to its much lower surface area. Therefore, it is owing to the promotion effect of the unique morphology of PzS-PW that a high density of strong acid sites is preserved on its nonporous outer surface. These strong acid sites are easily accessible to the bulky substrate molecules, which may improve the catalytic performance [68]; as a result, PzS-PW as a recyclable heterogeneous catalyst demonstrates high activity for this reaction that even exceeds the parent catalyst H<sub>3</sub>PW, though the latter is homogeneous.

It is well accepted that porous solid acid catalysts with an enriched internal surface loaded with acid sites would display superior activity for numerous acid-catalyzed reactions to that of nonporous ones. However, this is not true for the nonporous PzS-PW in this work, which heterogeneously catalyzes the bulky and viscous substrate FFA toward production of biodiesel with an ideal equimolar ratio of methanol/FFA at room temperature. As compared in Table 3, the commercial solid acid Amberlyst-15 possesses a considerable surface area of 45 m<sup>2</sup> g<sup>-1</sup>, but shows a low conversion (40.3%) for the room temperature equimolar esterification of oleic acid with methanol (Table 3, entry 7), only half as much as for PzS-PW (83.3%). This comparison is based on the same amount of sulfonate acid sites in the two catalysts. Even with an enhanced amount of Amberlyst-15 up to the value of PzS-PW (200 mg). Amberlyst-15 still shows inferior conversion of 54.5% (Table 3, entry 8). We sketch and compare the effects of dispersion and exposure of acid sites on catalytic efficiency for the equimolar esterification of oleic acid with methanol at room temperature over nonporous PzS-PW with uniform external surface and a conventional porous solid acid with enriched internal surface (Fig. 7). Under such mild conditions, the reaction medium is a quite ropy

solution due to the high-viscosity FFA (e.g., CP : 26 mPa s for oleic acid), and in case of a very low ratio of methanol to FFA, dilution of FFA by methanol could make little contribution to lowering the viscosity of the overall medium. Moreover, the room temperature employed intensifies the viscosity (higher viscosity occurs at lower temperature). Therefore, the uniform smooth external surface of PzS-PW with narrowly dispersed strong acid sites would provide easily accessible active sites for the bulky substrate FFA in viscous reaction media, showing minimum mass transfer limitation (Fig. 7A); in clear contrast, high mass transfer resistance is encountered under similar conditions for the internal surface-acid sites over a porous catalyst (Fig. 7B). This may be an explanation for the much lower activity of Amberlyst-15 than of PzS-PW. Indeed, we note that some conventional porous solid acid catalysts showed good to excellent activities for esterification of FFA with methanol; however, they were, without exception, evaluated at a much high molar ratio of methanol to FFA (typically higher than 10) and/or at a higher reaction temperature (Table S2 in the Supplementary Material). In that case, the large amount of highly polar methanol dilutes the viscous FFA solution and the higher temperature also decreases the viscosity, thus promoting mass transfer in the internal surface pores. To the best of our knowledge, no roomtemperature equimolar esterification of oleic acid with methanol has been reported over porous solid acid catalysts as yet, let alone one getting a high conversion.

In brief, this is the first time that a nonporous solid acid catalyst has demonstrated considerable activity for room-temperature equimolar esterification of bulky and viscous FFA with methanol, even better than the porous solid acid. The superior performance can be attributed to the high density of strong acid sites with a narrow dispersion of acid strength on the smooth external surface; such acid sites are easily accessible to the bulky substrate in the viscous reaction medium.

#### 4. Conclusions

An IL-POM hybrid with uniform morphology is achieved by controlling the self-assembly process of acidic pyrazinium-based IL precursor and POM in aqueous solution without using any template, surfactant, or organic solvent. The task-specific in situ sulfonated pyrazinium salt with rigid molecular structure and -SO<sub>3</sub>H group contributes the regular crystal morphology of the obtained IL-POM hybrid. The Keggin HPA-derived PzS-PW hybrid composed of uniform cubic tetrakaidecahedron-like crystals acts as an efficient heterogeneous acid catalyst in the roomtemperature synthesis of biodiesel through esterification of free fatty acids with methanol, exhibiting an activity equal to 83% conversion in 24 h under the ideal equimolar ratio of FAA to methanol. The acid sites feature high and narrowly dispersed acid strength on the nonporous solid surface, which provides a high density of accessible acid sites. The uniform crystal morphology promotes the dispersion and exposure of acid sites, contributing to much superior performance.

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### **Appendix A. Supplementary material**

Supplementary information associated with this article, including detailed experimental procedures and additional characterization and catalytic data. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.jcat.2016.03.036.

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