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One-pot synthesis and characterization of a dual-function hierarchical multiporous composite $H_3PW_{12}O_{40}$ @HKUST-1/ γ -Al₂O₃ with enhanced performance in adsorptive desulfurization and acid catalysis

Libo Qin^{a,b}, Yang Zheng^a, Zipeng Zhao^a, Yunshan Zhou^a, Lijuan Zhang^a, Zareen Zuhra^a, Fang Tang^a and Chao Li^a

^aState Key laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing, P. R. China; ^bDepartment of Chemistry, Changzhi University, Changzhi, P. R. China

ABSTRACT

A hierarchical multiporous ternary composite HPW@HKUST-1/y-Al₂O₃ (HPW = phosphotungstic acid) is prepared, in which the nanosized HPW@HKUST-1 is formed on both the external and internal surface of mesoporous γ -Al₂O₃ beads due to the confinement effect of internal pores/channels of the γ -Al₂O₃ beads. The composite not only possesses excellent adsorptive desulfurization capacity (e.g. 65.3 mg S/g MOF for dibenzothiophene; the adsorption capacities decreased in the order of dibenzothiophene > benzothiophene > 3methylthiophene > 4,6-dimethyldibenzothiophene) superior to HKUST- $1/\gamma$ -Al₂O₃ beads due to the significant role of the favorable acid-base interaction between acidic HPW and slightly basic sulfurcontaining compounds, but also exhibits super acid catalytic activity for hydrolysis of ethyl acetate (325.6 mmol mol_{acid}⁻¹ min⁻¹) and for synthesis of ethyl acetate (75.4 mol mol_{acid}⁻¹ min⁻¹) and *n*-butyl acetate (13.2 mol mol_{acid}⁻¹ min⁻¹) with selectivity of 100%, due to high dispersion and free access of the HPW in the composite which features high surface area and more easily accessible active sites of HPW and HKUST-1. Besides, the composite features remarkable mechanical strength, chemical/thermal stability, being friendly to the environment, and low cost, can easily be regenerated and reused many times for both acid catalysis reactions and adsorptive desulfurization without observable HPW leaching or material dissolution/decomposition.

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CONTACT Yunshan Zhou Zhouys@mail.buct.edu.cn State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, P. R. China; L. Zhang Ijzhang@mail.buct.edu.cn State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, P. R. China



1. Introduction

Polyoxometalates (POMs) owing to excellent chemical stability, super acidity, extraordinary redox performance, and other remarkable features [1-3] have attracted increasing attention for many catalyzed organic transformations and industrial applications [3–9]. For example, as homogeneous catalysts, POMs are applied for the epoxidation of olefins [8, 9], hydration of alkenes and esterification [4–6]. The experimental results showed that the molar catalytic activities of POMs in organic media are usually 100–1000 times higher than that of H_2SO_4 [6], meantime POMs do not enter into side reactions by virtue of the inertness of the anion with organic reagents such as sulfonation, chlorination, nitration, etc., that occur in the presence of mineral acids [6]. Although the homogeneous catalyzed reactions by POMs show high activity/selectivity, are friendly to the environment, and have mild operating conditions, they have very high solubility in polar solvents, such as water, lower alcohols and ketones, etc. that lead to difficulty for separation and recycling, while pure solid POMs have surface areas less than $10 \text{ m}^2 \text{ g}^{-1}$ [4] which limits their catalytic activity in practical applications due to less exposed active sites. Thus, it is necessary to disperse POMs on supports possessing high surface areas to increase recovery, recycling, and catalytic performance.

Metal-organic frameworks (MOFs), a new type of porous crystalline material with periodic multidimensional networks, are composed of a central metal and organic ligands through covalent-bonding. MOFs possess wide potential applications in adsorption [10], separation [11], catalysis [12], etc. in contrast to active carbon, silicates, and zeolites [10–12] owing to the high specific surface area and rich surface chemistry via varying the type of organic ligands and active metal sites. Especially, MOFs are investigated as sulfur absorbers at mild environmental conditions, demonstrating that MOFs possess excellent desulfurization capability with high selectivity as compared to traditional adsorbents [13-20]. In addition, the notable extra-large pore cavities in some MOFs enable them to encapsulate nano-sized POM clusters [21-26]. The resulting composite POM@MOFs do not merely improve the adsorptive desulfurization performance for Lewis base compounds by acid-base interactions, such as organosulfurs [23], but also overcome generally the drawbacks such as low quantity of loading, leaching, irregular active centers, aggregation, and the deactivation of acid sites encountered in the case of dispersion of POMs on traditional supports, such as silica [27], active carbon [28], TiO₂ [29], and zeolites [30]. However, the following tiresome problems exist in the POM@MOFs composite: MOFs have low thermal stability due to their low coordination bond energy, thus MOFs cannot be used in high temperature water and other harsh conditions because the coordination bonds can partially or wholly crack. Usually, the outer surface of powdered POM@MOFs are assessable by smaller molecules, but the inner pores/surface and the POMs therein are not assessable to others, leading to low utilization of pore volume, surface area of MOFs and active sites of the POMs therein. The mechanical strengths of POM@MOF materials are usually poor, limiting recovery and recycling in industrial operation.

In this work, on the basis of the above consideration, the Keggin-type phosphotungstic acid (denoted HPW) which has been explored for different types of catalysis due to their advantageous properties, and the rigid metal carboxylate HKUST-1 which possesses stable framework, are deliberately integrated by using a simple one-step hydrothermal technique on the surface of the millimeter-sized mesoporous γ -Al₂O₃ beads with numerous advantages, such as fine pore structure [31, 32], high specific surface area, low price, and excellent chemical stability [33], through interactions between hydroxyl groups of the carrier and carboxylic groups of the organic ligand 1,3,5-benzenetricarboxylic acid [34, 35]. Importantly, the resulting composite POM@MOFs/ γ -Al₂O₃ exhibits both superior adsorptive desulfurization and excellence in the hydrolysis of ethyl acetate, synthesis of ethyl acetate and n-butyl acetate, due to the confined environment of nano-sized channels/pores of γ -Al₂O₃beads which can effectively avoid aggregation of MOFs and the rich mesoporous structure of γ -Al₂O₃ beads which can decrease the mass transfer resistance and enhance the diffusion rate of reactants, can be conveniently separated, recovered and recycled attributed to its enhanced mechanical strength and millimeter size, therefore has great potentials in industrial applications.

2. Experimental

2.1. Materials and methods

 γ -Al₂O₃ beads were homemade by the State Key Laboratory of Chemical Resource Engineering (Beijing University of Chemical Technology, China) and were washed three times with distilled water and pre-treated at 200 °C for 2 h before use. All other reagents and solvents were commercially available and used as received. HKUST-1 and HKUST-1/ γ -Al₂O₃ were prepared following literature procedures [36].

The Fourier transform infrared (FT-IR) spectroscopy was carried on a Nicolet FTIR-170SX spectrometer with mixed powdered materials and KBr pellets from 400 to 4000 cm⁻¹. Ultraviolet–visible spectroscopy (UV-vis) was recorded on a UV-2500 spectrophotometer to estimate the leakage of Keggin POM species by monitoring the characteristic adsorption at 260-270 nm. Powder X-ray diffraction (XRD) data were recorded on a Rigaku D/max 2500 X-ray diffractometer using graphite-monochromatic Cu K α radiation ($\lambda = 0.15405$ nm) from 20 of 5° to 70° with a scanning rate of 10°/min. Scanning electron microscope (SEM) images and energy dispersive X-ray (EDX) mapping data were collected on a Zeiss Supra55 scanning electron microscope at an accelerating voltage of 20 kV. High Resolution Transmission Electron Microscopy (HRTEM) images were obtained using a JEOL JEM2100 transmission electron microscope at an accelerating voltage of 200 kV. Elemental analyses were recorded on a Perkin-Elmer 240 C analytical instrument for C, H, N and the SPECTRO ARCOS type inductively coupled plasma spectrometer (ICP) for Al, Cu. Thermogravimetric Analysis-Differential Thermal Analysis (TG-DTA) curves were carried out using a Netzsch STA449 analyzer from 25 °C to 800 °C with a rate of 10 °C min⁻¹ under air flow. The NH₃ temperatureprogrammed desorption (NH₃-TPD) was carried out on an Autochem 2920. Samples were first pre-treated at 300 °C at a ramp rate of 10 °C min⁻¹ in helium flow for 1 h and then cooled to 40 $^{\circ}$ C. Ammonia (10% NH₃/He) was introduced at a flow rate of 30 mL min⁻¹ for 1 h at 40 °C and then blown by helium for 1 h at 40 °C; the reactor temperature was increased to 600 °C at a ramp rate of 10 °C min⁻¹, and the amount of ammonia in effluent was measured. The nitrogen adsorption and desorption isotherms were carried out on an ASAP-2020 at 77 K. The specific surface area (SBET) was determined from the linear part of the BET equation at a relative pressure of 0.05-0.3. The pore size distribution was calculated using the Barrett-Joyner-Halenda method. The total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of ca. 0.99. The mechanical strength of the sample was measured on a YHKC-2A particle strength tester. High performance liquid chromatography (HPLC) equipped with a C18 column (length 250 mm, diameter 4.6 mm, diameter of filler $5 \,\mu$ m) was used for the quantitative assay of sulfur content. The mobile phase changed from 10% water and 90% methanol gradient elution to 100% methanol in 10 min with flow rate of 1.0 mL min^{-1} . The ester contents were analyzed by a SP-6890 GC instrument with a PEG-20M capillary column and *n*-tridecane was used as internal standard. The GC operating conditions were as follows: the temperatures for injector and detector were 240 °C and 220 °C, respectively, and the oven temperature was programmed from 50 °C (hold for 0.5 min) to 60 °C at 2 °C min⁻¹, then raised to 150 °C (hold for 2.5 min) at 2° C min⁻¹ for ethyl acetate and from 60 to 150° C (hold for 3.5 min) at 20 °C min⁻¹ for *n*-butyl acetate.

2.2. Preparation of the composite material HPW@HKUST-1/ γ -Al₂O₃

In a typical synthesis, $Cu(NO_3)_2 \cdot 3H_2O$ (1.8 mM), H_3BTC (1.0 mM) and HPW (0.04 mM) were added into the H_2O :ethanol (V:V = 1:1) solution (50 mL) and stirred magnetically for 20 min at room temperature. Then the mixture and γ -Al₂O₃ beads (1.0 g) were loaded in an autoclave (100 mL) and heated at 110 °C for 20 h. After the reaction, the autoclave was cooled to room temperature, the products were recovered by decanting and washing three times with deionized water (10 mL). The obtained composite was dried at 150 °C overnight to remove water and other contaminants and then stored in vacuum. The loading of HPW and HKUST-1 on the basis of elemental analysis (Al 38.82, Cu 5.02, C 5.70, P 0.11, W 7.21, and H 0.36%) are 9.4 and 17.3 wt% in the composite, respectively.

2.3. Adsorptive desulfurization

The model oil of S-containing compounds (dibenzothiophene (DBT), benzothiophene (BT), 3-methylthiophene (3-MT), 4,6-dimethyldibenzothiophene (4,6-DMDBT)) (250, 500

and 1000 ppmw_s) was prepared by dissolving S-containing compounds in *n*-octane, which were used directly in the following adsorptive experiments. The model oil was mixed with the adsorbent into a conical flask using a water bath under stirring at atmospheric pressure, and the adsorptive performance was tested by HPLC. After the adsorption, the HPW@HKUST-1/ γ -Al₂O₃ was separated by decantation, washed with acetone overnight to remove adsorbed S-containing compounds by using a Soxhlet extractor and then dried at 150 °C overnight in the oven. The performance of the regenerated composite was tested as the fresh. The adsorptive desulfurization capacity of the adsorbents was calculated by

$$Q_i = \frac{W}{M} (C_0 - C_i) \times 10^{-3}$$
 (1)

where Q_i is the adsorptive desulfurization capacity of the adsorbents (mg S g⁻¹ MOF); W and M are the mass of model oil (g) and the absorber added (g), respectively; C_o and C_i are the initial and final sulfur concentrations in the model oil (ppmw_s), respectively.

2.4. Hydrolysis of ethyl acetate

Hydrolysis of ethyl acetate was carried out using 0.20 g HPW@HKUST-1/ γ -Al₂O₃ as catalyst with 5 wt% ethyl acetate aqueous solution (40 mL) in a 150-mL three-neck flask with a Teflon stirrer, a water cooler condenser, and a thermometer (scheme S1, supplementary material). The reaction temperature was raised immediately to 65 °C with controlled conditions using an oil bath under stirring for 2 h. After the reaction, the catalyst was separated by decantation, washed three times with deionized water (10 mL) and then dried at 150 °C overnight in the oven for the next recycling experiments. The catalytic activity of HPW@HKUST-1/ γ -Al₂O₃ for the hydrolysis of ethyl acetate was estimated by conversion of ethyl acetate at 2 h and normalized by the unit time (k_1 , µmol g_{cat} .⁻¹min⁻¹) and catalyst amount (k_2 , mmol mol_{acid}.⁻¹min⁻¹). The k_1 and k_2 could be calculated by

$$k_1 = (CN)/(tm_{cat}) \tag{2}$$

$$k_2 = k_1 / acid amount \tag{3}$$

where *C*, *N*, *t* and m_{cat} are the conversion of ethyl acetate, the molar amount of ethyl acetate added (mmol), the reaction time (min), and the weight of the HPW@HKUST-1/ γ -Al₂O₃ (g), respectively.

2.5. Synthesis of ethyl acetate and n-butyl acetate

2.5.1. Synthesis of ethyl acetate

The synthesis of ethyl acetate was carried out using 0.6 mol of glacial acetic acid and 0.3 mol of absolute ethyl alcohol in a 100-mL three-neck flask with a thermometer, a Teflon stirrer, and a glass tube arranged by a water cooled condenser and a connecting glass tube to collect the product (Scheme S2). The catalyst (0.10–0.35 g) was added when the reaction temperature was raised to 75 °C to initiate the reaction.



Figure 1. IR spectra of the γ -Al₂O₃ beads (a), the composite (b), HPW (c) and HKUST-1 (d). Symbols Δ and * highlight the characteristic vibration bands from HKUST-1 and HPW, respectively.

2.5.2. Synthesis of n-butyl acetate

The synthesis of *n*-butyl acetate was carried out using 0.6 mol of glacial acetic acid, 0.3 mol of *n*-butyl alcohol, and 15 mL of toluene as water-carrying reagent in a 150-mL three-neck flask with a Teflon stirrer, a thermometer, and a water segregator added 4/ 5 volume of distilled water arranged by a water cooled condenser (scheme S3). The reaction temperature was raised to 110 °C and then the HPW@HKUST-1/ γ -Al₂O₃ as catalyst (0.20–0.50 g) was added to initiate the reaction.

The reaction temperature of the systems for the synthesis of ethyl acetate and *n*butyl acetate was controlled by an oil bath under stirring. After the reaction, the catalyst was separated by decantation, washed with water and then dried at 150 °C overnight in the oven in order to do the next recycling experiments. The catalytic activity of the HPW@HKUST-1/ γ -Al₂O₃ for the synthesis of ethyl acetate and *n*-butyl acetate was estimated from the conversion of alcohols calculated according to the change in amount of ethyl and butyl alcohol by

$$X_{\text{ester}} = \left[(m_i - m_t) / m_i \right] \times 100\% \tag{4}$$

where X_{ester} , m_i and m_t represent the conversion of alcohol, the initial amount of alcohol (unit: g) and the amount of alcohol (unit: g) at a given time.

3. Results and discussion

3.1. Characterization of the composite HPW@HKUST-1/γ-Al₂O₃

Comparing IR spectra of the composite HPW@HKUST-1/ γ -Al₂O₃ with that of γ -Al₂O₃ support, HPW and HKUST-1 (Figure 1) showed characteristic vibration bands of the composite at 1084 cm⁻¹, 894 cm⁻¹ from the P-O and W-O_b-W of HPW [37], bands at



Figure 2. SEM images of the external surface of γ -Al₂O₃ (a), external (b) and inner cross-sectional (c) surface of the composite. The photographs of the γ -Al₂O₃ beads (a), the composite (b (overview), c (inner cross-section)) are also shown as insets highlighting color change from white to blue. The EDX mapping of W (in green) (d) and Cu (in red) (e) of cross-section of the composite, SEM-EDX cross-sectional line scans of W (f), and HRTEM images of the cross-section of the composite highlighting the lattice fringe (g, h). [Inset: highlighting the spherical appearance and color change from white to blue].



Figure 3. XRD patterns of the simulated γ -Al₂O₃ beads (a), the prepared γ -Al₂O₃ beads (b), HPW (c), HKUST-1 (d), and the composite (e).

1650 cm⁻¹ (v_{C=O}), 1564 cm⁻¹ (v_{asCOO}), 1457 cm⁻¹ (v_{sCOO}) and 1379 cm⁻¹ (δ_{C-H}) from HKUST-1 [38] and bands at 3455 cm⁻¹ (v_{O-H}), 1632 cm⁻¹ (δ_{H-O-H}) [39], 950 cm⁻¹ (v_{AlO6}) and 450 cm⁻¹ (δ_{AlO6}) [40] from γ -Al₂O₃ support. The results indicate that the composite HPW@HKUST-1/ γ -Al₂O₃ was synthesized by loading HPW and HKUST-1 with their original structures in the γ -Al₂O₃ support, further confirmed by the elemental analysis data (P:W = 1:11.44 corresponding to the formula of PW₁₂O₄₀³⁻; the loading amount of HPW is calculated to be 9.4%) as well.

The observed color change from white for γ -Al₂O₃ beads (Figure 2(a)) to preserved duck eggs-like blue for the composite (Figure 2(b,c)) further confirm the HPW@HKUST-1 loading on γ -Al₂O₃ beads. Apart from above, there is no visible size change (Figure 2(a,b): insert) observed with respect to their diameter (ca. 2 mm) between the γ -Al₂O₃ and the composite. To study distribution of the HPW and HKUST-1 of the composite, the beads were sliced into equal parts for cross-sectional EDX mapping. It can be clearly found that HPW and HKUST-1 are distributed uniformly in sub-micrometer scales within the γ -Al₂O₃ beads (Figure 2(d,e)). W (tungsten) penetration depth in the composite beads was more than 445 µm (Figure 2(f)), i.e. HPW@HKUST-1 penetration depth is about half of the diameter of the composite. Moreover, another substantial evidence for loading of the HKUST-1 on γ -Al₂O₃ beads is the presence of the lattice fringe distance of 0.2297 nm corresponding to (880) crystal surface of HKUST-1 (Figure 2(g)). According to the discontinuously lattice diffraction fringes of HKUST-1 (Figure 2(h)), it can be speculated that discontinuous nanoparticles of HKUST-1 are formed/ deposited on the inner surface of pores/channels within γ -Al₂O₃ beads due to fast nucleation of HKUST-1. In addition, the XRD pattern of the composite (Figure 3) shows the relatively strong peaks at 2 θ values about 46.6 and 66.7° corresponding to (400) and (440) reflections of γ -Al₂O₃ (JCPDS 10-0425) [41]. The appearance of a few weak peaks at 2θ values in 7.3°, 9.6°, and 13.7° (the gray dashed lines) are ascribed to the



Figure 4. Low-temperature nitrogen adsorption-desorption isotherms of γ -Al₂O₃ beads (in black) and the composite (in red). Inset is pore size distribution of γ -Al₂O₃ beads and the composite.

formation of nano-sized HKUST-1 of the composite [38] that is consistent with the TEM and SEM results. The characteristic peaks of HPW phase (PDF#50-0657) does not appear in the composite in the high-angle region indicating the high dispersion of HPW in the composite [42].

The N_2 adsorption isotherm of the composite (Figure 4) reveals a combination of the typical I and IV type isotherms [43, 44], corresponding to the presence of both the microporous and mesoporous structures, confirming formation of a hierarchical multiporous composite. Meanwhile, the hysteresis loops of the composite are superposition of H1 type and H3 type representative of tubular capillaries and parallel slit shaped pores that are caused by the granular particles of HPW@HKUST-1 that is confirmed by the results of HRTEM [44]. The BET surface area for the composite (354.6 m²/q) is larger than that of carrier γ -Al₂O₃ beads (216.5 m²/g), and the pore volume changes from 0.68 cm³/g for γ -Al₂O₃ to 0.386 cm³/g for the composite (Table 1), due to the HKUST-1 occupying inner spaces of γ -Al₂O₃ bead has large BET surface area of 1601.4 m²/g. For comparison, it should be pointed out that the BET surface area for the composite $(354.6 \text{ m}^2/\text{g})$ is larger than that of HKUST-1/ γ -Al₂O₃ (320.1 m²/g), while the pore volume for the composite (0.39 cm³/g) is a little bit smaller than that of HKUST-1/ γ -Al₂O₃ (0.40 cm³/q) because of the contribution coming from HPW molecule of about 1 nm in diameter with high surface area and spatial volume. The comparison of pore size distributions of γ -Al₂O₃ and the composite (Figure 4, inset) shows decreases in mean pore size of 13.9 nm for γ -Al₂O₃ to broader region of 3 \sim 12 nm for the composite. The composite shows a sharp peak of pore diameter (3.9 nm) followed by a broader one reflecting the behavior of confinement-effect exertive internal pores/channels of γ -Al₂O₃ bead on anchoring HPW@HUST-1 nanoparticles with penetration depth being almost half of the diameter of γ -Al₂O₃ beads, as shown by the EDX mapping (Figure 2(f)).

Samples	S _{BET} (m²/g)	Pore volume (cm ³ /g)	Pore size of maximum possibility (nm)	HKUST-1 (%)	HPW (%)	Mechanical strength (N/grain)
γ -Al ₂ O ₃	216.5	0.68	13.9			62.2
HKUST-1	1601.4	0.79	0.6			
HKUST-1/γ-Al ₂ O ₃	320.1	0.40	5.1	18.7		96.1
HPW@HKUST-1/γ-Al ₂ O ₃	354.6	0.39	8.7	17.3	9.4	99.5

Table 1. Texture of γ -Al₂O₃, HKUST-1, HKUST-1/ γ -Al₂O₃ and the composite.



Figure 5. NH₃-TPD profiles of HKUST- $1/\gamma$ -Al₂O₃ (a) and the composite (b).

Figure 5 shows the NH₃-TPD profiles of HKUST-1/ γ -Al₂O₃ and the composite. Three main NH₃ desorption peaks about 190 °C, 467 °C and 532 °C are detected, corresponding to desorption of NH₃ from weak, middle and strong acid sites, respectively [45, 46]. Compared to the NH₃-TPD curve of HKUST-1/ γ -Al₂O₃, a peak at 532 °C for the composite could be assigned to NH₃ that strongly adsorbed on the Brønsted acid sites of HPW [47]. According to the desorbed amount of NH₃, the total acid amount increases from 6.16 mmol/g for HKUST-1/ γ -Al₂O₃ to 7.20 mmol/g for the composite. The HPW has 97.9 µmol/g_(HPW) of acidic protons corresponding with three acidic protons per polyanion calculated by the loading amount of HPW (9.4%). Considering the fact that HPW can only stay inside type A pores of HKUST-1 [48] and the ratio of Cu/P/W determined by ICP analysis is 48:2.2:23.8, it is concluded that nearly half of type A pores of HKUST-1 are occupied with HPW in the composite.

Remarkably, the composite not only has enhanced thermal stability as compared to HKUST-1 (decomposition temperature 505 °C for the composite vs. 488 °C for HKUST-1/ γ -Al₂O₃ and 316 °C for HKUST-1) (Figure S1, supplementary material) because of the formation of the secondary bonding, such as Van der Waals interactions or hydrogen bonds with the support [34, 35], but also enhanced mechanical strength (62.2 N/grain for γ -Al₂O₃ and 99.5 N/grain for the composite) (Table 1). The composite has other advantages such as low price, impact resistance, crush resistance, abrasion resistance



Figure 6. Effect of time on adsorptive desulfurization capacity of γ -Al₂O₃ (a), HKUST-1 (b), HKUST-1/ γ -Al₂O₃ (c), and the composite (d) for DBT at optimum reaction conditions.

and low coefficient of friction. All these merits are important and guarantee the potential of the composite for practical application.

3.2. Study on adsorptive desulfurization performance

The reduction of sulfur-containing compounds in commercial gasoline and diesel fuels is a major concern of automotive and power generation industries [49, 50]. Among many desulfurization technologies, adsorptive desulfurization attracts extensive attention owing to advantages such as low cost, mild operation conditions and no requirement of hydrogen. MOFs showed superior adsorption capacities in contrast traditional adsorbents due to the porous structure and extraordinary specific surface area [49, 50]. The composite HKUST- $1/\gamma$ -Al₂O₃ that we previously reported showed higher desulfurization performance, especially with convenience in separation, recovery, and recycling [36], however, the composite still has low pore utilization and desulfurization selectivity.

The optimum reaction time (Figure 6, Figure S2, 60 min; supplementary material), reaction temperature (Figure S3, 30°C; supplementary material), and mass ratio of oil to HKUST-1 (Figure S4, m(oil)/m(HKUST-1; supplementary material) = 40:1) are investigated in this work. As shown in Figure 6, the adsorptive desulfurization capacity and adsorption rate of HPW@HKUST-1/ γ -Al₂O₃ are higher than those of γ -Al₂O₃, HKUST-1 and HKUST-1/ γ -Al₂O₃, indicating efficient utilization of the surfaces/pores in the composite HPW@HKUST-1/ γ -Al₂O₃; the corresponding adsorptive desulfurization rate is reduced over time because the DBT concentration around adsorbent molecules decreases. Specifically, the adsorptive desulfurization capacity for HPW@HKUST-1/ γ -Al₂O₃ at optimum reaction conditions is 65.3 mg S g⁻¹ MOF. There is significant increase of 9.4% in the desulfurization efficiency compared to 59.7 mg S g^{-1} MOF for HKUST-1/ γ -Al₂O₃. According to the dynamic diameter of the DBT molecule (5.97 Å), the dynamic molecular size of the DBT molecule (0.26 nm²), and BET surface area of the HKUST-1 (1601 m^2/q), it can be calculated that the DBT molecules occupy 19.9% of total surface area of HPW@HKUST-1/ γ -Al₂O₃. The surface area utilization dramatically increased by 9.3% compared to 18.2% for HKUST-1/ γ -Al₂O₃. The fact that the surface

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Adsorbent	Solvent	C ₀ (ppmw _s) / system	Q ₀ (mg S/g MOF)
MIL-101 [23]	n-octane	\sim 714/batch	28.9
Cr-BDC [15]	n-octane	1000/batch	41.0 ^c
Cr-BTC [15]	n-octane	1000/batch	30.7 ^c
MOF-5 [50]	iso-octane	300/fixed bed	12.7
MOF-505 [50]	iso-octane	300/fixed bed	20.5
UMCM-150 [50]	iso-octane	300/fixed bed	66.3
MOF-5 [50]	iso-octane:toluene (85:15)	300/fixed bed	9.1
MOF-505 [50]	iso-octane:toluene (85:15)	300/fixed bed	14.9
UMCM-150 [50]	iso-octane:toluene (85:15)	300/fixed bed	66.6
ZIF-8-derived [51]	n-hexane	<160/batch	26.7
ZIF-8-derived [51]	n-hexane:para-xylene (9:1)	<174/batch	22.2
CMK-3 [52]	n-hexane	<261/batch	10.9
CMK-5 [52]	n-hexane	<261/batch	21.7
Activated Al ₂ O ₃ [53]	n-hexane	<174/batch	21.0
Activated carbon [54]	n-octane	300/batch	28.9
Carbon aerogel [55]	n-hexadecane	<696/batch	15.1
Cu(I)-Y zeolite [56]	n-octane	\sim 690/batch	32.6
Co-Y zeolite [56]	n-octane	\sim 690/batch	29.4
Activated carbon spheres [57]	n-octane	<124/batch	17.6
AC loaded Na, Co, Ag or Cu ^a [58]	n-hexane	178/batch	65-115
Ce/Ni-Y zeolite [59]	n-octane	\sim 124/batch	22.2
PT-Ag-MASN ^b [60]	n-decane	500/batch	15.0 ^c
MC-Z(Cu, Co or Fe) [61]	n-hexane	178/batch	51.4-75.5
HKUST-1 [36]	n-octane	1000/batch	59.6, 49.5 ^c
HKUST-1/γ-A _{I2} O ₃ [36]	n-octane	1000/batch	76.1, 59.7 ^c
HPW@HKUST-1/γ-Al ₂ O ₃	n-octane	1000/batch	84.7, 65.3 ^c

Table 2.	Comparison	of	adsorptive	desulfurization	capacity	of	reported	adsorbents	and	the	com-
posite for	r DBT.										

^aMesoporous carbons with dispersed metal.

^bMesoporous aluminosilicate nanoparticle with dispersed Ag.

^cEquilibrium adsorption.

area and pore volume are $320.12 \text{ m}^2/\text{g}$ and $0.403 \text{ cm}^3/\text{g}$ for HKUST- $1/\gamma$ -Al₂O₃, and 354.60 m^2 /g and 0.386 cm^3 /g for the composite, respectively, indicate slight increase in surface area and slightly decrease in pore volume after the incorporation of HPW into HKUST-1/ γ -Al₂O₃. This means that the enhancement in the adsorptive desulfurization capacity and adsorption rate for the composite, compared with HKUST-1/ γ -Al₂O₃, cannot be simply explained with the porosity. In order to understand the role of the HPW in the adsorptive desulfurization, a control experiment was done by using NaPW@HKUST-1/ γ -Al₂O₃ where sodium phosphotungstate (NaPW) was used to replace HPW. The adsorptive desulfurization performance of NaPW@HKUST-1/ γ -Al₂O₃ was tested at same optimum reaction conditions and the adsorptive capacity was 38.2 mg S g^{-1} MOF, which was much lower than 65.3 mg S g^{-1} MOF of HPW@HKUST-1/ γ -Al₂O₃ and even lower than 49.5 mg S g^{-1} MOF of HKUST-1 and 59.7 mg S g^{-1} MOF of HKUST-1/ γ -Al₂O₃. The NaPW is thought to just occupy the pores of HKUST-1 leading to the inferior adsorptive desulfurization capacity of NaPW@HKUST-1/ γ -Al₂O₃. In turn this result proves the significant roles of Brønsted acidic centers of HPW in HPW@HKUST- $1/\gamma$ -Al₂O₃ for adsorptive desulfurization. It is clear that the introduction of HPW not only enhances adsorptive desulfurization capacity, but also increases the adsorptive desulfurization selectivity due to the acid-base interaction between acidic HPW and slightly basic sulfurcontaining compounds. Impressively, the composite HPW@HKUST-1/y-Al₂O₃ showed superior adsorptive desulfurization compared to reported adsorbents, such as traditional zeolites, activated carbons, and MOFs listed in Table 2.

		Pseu constan	do-second-orde ts (<i>k₂</i> ,10 ⁻³ g mir	er rate 1 ⁻¹ mg ⁻¹)	Maximum adsorption		
Adsorbent	T (°C)	250 ppmw _s	500 ppmw _s	1000 ppmw _s	(mg S g^{-1} MOF)	(mol/mol)	
HPW@HKUST-1/γ-Al ₂ O ₃	10	2.46 (2.44)	2.51 (2.48)	2.68 (2.51)	70.12 (62.13)	0.47 (0.42)	
(HKUST-1/ γ -Al ₂ O ₃)	20	2.51 (2.50)	2.65 (2.59)	2.73 (2.68)	76.34 (70.47)	0.52 (0.48)	
	30	2.74 (2.63)	2.84 (2.66)	2.90 (2.78)	84.64 (76.10)	0.58 (0.52)	

Table 3. Pseudo-second-order rate constants (k_2) of HKUST-1/ γ -Al₂O₃ and the composite with various DBT concentrations. The maximum adsorptive desulfurization capacities (Q₀) and the molar ratios of DBT to metal ion are also presented.^a

^aThe values for HKUST-1 are in brackets.

In view of practical applications, investigation of the adsorptive kinetics and thermodynamics are necessary to understand enhanced desulfurization performance of the composite HPW@HKUST-1/ γ -Al₂O₃. The changes of adsorbed amount over the composite versus time match well with the pseudo-second-order kinetic model (Supporting Information), meanwhile, the adsorption rate constants (k_2 , Table 3) for DBT adsorption are calculated and the constant order is HKUST-1/ γ -Al₂O₃ <HPW@HKUST-1/ γ -Al₂O₃. The greater DBT adsorption can be attributed to HPW@HKUST-1/ γ -Al₂O₃ with shorter diffusion channels and lower diffusion resistance. The adsorption isotherms of DBT (Figure S5, supplementary material) show that the maximum adsorptive desulfurization capacity Q_0 of the composite is higher than that of HKUST-1/₂-Al₂O₃ because of acid-base interactions. The molar ratios of the adsorbed DBT to metal site are 0.58 for the composite and 0.52 for HKUST- $1/\gamma$ -Al₂O₃ at 30 °C, respectively. Table S4 (supplementary material) shows the Gibbs free energy (ΔG) , enthalpy (ΔH) , and entropy (ΔS) change. The ΔG is negative, implying feasible and spontaneous adsorption. The calculated ΔH (Figure S6, supplementary material) of the DBT adsorption for HKUST- $1/\gamma$ -Al₂O₃ and the composite is 4.08 and 5.73 kJ mol⁻¹, respectively, indicating an endothermic adsorption. Because the adsorption process is a combination of two processes, desorption of the pre-adsorbed solvent molecules and adsorption of the adsorbate species, the DBT molecules have to displace more than one *n*-octane molecule for their adsorption. This results in endothermic adsorption owing to a stronger interaction between *n*-octane and the composite than the interaction between DBT and the composite [52, 62]. The positive ΔS indicated the increased randomness during the adsorptive process due to the number of desorbed solvent molecules being larger than that of the adsorbed adsorbate species [52, 62].

Adsorptive desulfurization experiments and corresponding kinetic and thermodynamic studies for 3-MT, BT, and 4,6-DMDBT were carried out (Supporting Information) and the adsorptive desulfurization performances are in the same order: HKUST-1/ γ -Al₂O₃ < HPW@KUST-1@ γ -Al₂O₃, implying the composite can be widely used to adsorb different kinds of S-containing compounds (Table 4).

3.3. Study on hydrolysis of ethyl acetate

The Keggin type HPW with strongest Brønsted acidity shows promising applications as solid-acid catalysts in industry, thus, the hydrolysis of ethyl acetate is chosen as a probe reaction to assess the acid activity with rates based on catalyst weight and acid amount of the composite. Table 5 lists the comparison of catalytic activities of the

Table 4.	The thermody	ynamic param	eters of adsorpt	tion of HKUST	$-1/\gamma$ -Al ₂ O ₃ and	the composite ^a .
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Adsorbent	T (°C)	ΔG (kJmol $^{-1}$)	Δ H (kJmol $^{-1}$)	$\Delta {\sf S}$ (Jmol $^{-1}$ K $^{-1}$)
HPW@HKUST-1/γ-Al ₂ O ₃	10	—11.56 (—11.36)	5.73 (4.08)	60.96 (54.40)
$(HKUST-1/\gamma-AI_2O_3)$	20	-12.14 (-12.01)		
	30	-12.74 (-12.41)		

^aThe values for HKUST-1 are in brackets.

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	Acid amount	<i>k</i> ₁	k ₂
Catalyst	$(mmol g^{-1})$	(μ mol g _{cat.} ⁻¹ min ⁻¹)	$(mmol mol_{acid}^{-1} min^{-1})$
(Solid Oxides)			
PW/C ₈ -AP-SBA [63]	0.091	25.1	275.0
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [64]	0.15	30.1	200.6
Cs ₃ PW ₁₂ O ₄₀ [64]	0.0	0.0	0.0
SO ₄ ²⁻ /ZrO ₂ [64]	0.20	25.5	127.5
H-ZSM-5 [64]	0.39	27.6	70.8
Nb ₂ O ₅ [64]	0.31	4.0	12.9
HY zeolite [64]	2.60	0.0	0.0
(Organic Resins)			
Nafion-H resin [64]	0.80	161.9	202.3
Amberlyst –1564	4.70	193.6	41.2
(Liquid Acids)			
H ₃ PW ₁₂ O ₄₀ [64]	1.0	70.4	70.3
H ₂ SO ₄ [64]	19.8	911.9	46.1
(MOF)			
NENU-3 [26]	0.18	49.3	273.9
NENU-3a [26]	0.57	178.9	313.8
HKUST-1	0.0	0.0	0.0
HKUST-1/γ-Al ₂ O ₃	6.16	0.0	0.0
HPW@HKUST-1/γ-Al ₂ O ₃	0.0979	31.7	325.6

composite and other acid catalysts. The 3.4% conversion of ethyl acetate was obtained after 2 h reaction using catalyst dosage of 0.2 g. Catalytic activity per acid amount k_2 was calculated as 325.6 mmol mol_{acid}⁻¹ min⁻¹ for HPW@HKUST-1/ γ -Al₂O₃. As shown in Table 5, the activity per acid amount of HPW@HKUST-1/ γ -Al₂O₃ is the highest among all of the inorganic and organic solid acids and even exceeds the best former result of 313.8 mmol mol_{acid}⁻¹ min⁻¹ for NENU-3a. The reason to this excellent performance is the formation of nano-sized HPW@HKUST-1 possessing shorter diffusion channels, larger specific surface area, and more exposed active sites on the external and internal surface of γ -Al₂O₃ due to confinement effect of γ -Al₂O₃ pores and channels. Only ethanol and acetic acid are produced during that reaction, indicating no sub-reactions occur. In addition, the reaction cannot occur in the presence of only HKUST-1, or only HKUST-1/ γ -Al₂O₃ nor in absence of catalysts, so it can be concluded that a reaction can be assigned to the homogenous catalysis caused by HPW. In summary, HPW@HKUST-1/ γ -Al₂O₃ shows high catalytic activity, and there was no deactivation of acid sites by water.

3.4. Study on synthesis of ethyl acetate and n-butyl acetate

Esters are an important class of organic compounds used as plasticizers, perfumes, artificial spices, etc. [65], and also as essential raw materials for production of fine chemicals and pharmaceuticals [66]. Especially, ethyl acetate and *n*-butyl acetate are important chemicals, environment-friendly organic solvents and diluents, widely



Figure 7. Effect of reaction time on the esterification for ethyl acetate (a) and *n*-butyl acetate (b) over the composite. Reaction conditions: (a) $acid_{mol}$: $alcohol_{mol}$, 2:1; catalyst, 0.25 g; temperature, 75 °C; (b) $acid_{mol}$: $alcohol_{mol}$, 2:1; catalyst, 0.4 g; temperature, 110 °C.



Figure 8. Effect of catalyst amount on the esterification for ethyl acetate (a) and *n*-butyl acetate (b) over the composite. Reaction conditions: (a) $acid_{mol}$: $alcohol_{mol}$, 2:1; time, 2.5 h; temperature, 75 °C; (b) $acid_{mol}$: $alcohol_{mol}$, 2:1; reaction time, 8 h; temperature, 110 °C.

applied in synthesis of dyestuffs, drugs and perfumes. Demand for ethyl acetate and *n*-butyl acetate has increased. Thus, synthesis of ethyl acetate and *n*-butyl acetate is chosen to assess the acid activity and selectivity of HPW@HKUST-1/ γ -Al₂O₃.

The effect of the reaction time (Figure 7) and catalyst dosage (Figure 8) on the esterification is tested under the same conditions. As shown in Figures 7 and 8, ester conversions increased gradually with the increase in reaction time and catalyst dosage. The 92.3% and 82.7% conversions were obtained at 2.5 h and 8 h using catalyst dosage of 0.25 g and 0.4 g for ethyl acetate and *n*-butyl acetate, respectively. When the time was extended to 3.5 h and 10 h, the ester conversions increased only by 0.3% and 0.2% for ethyl acetate and *n*-butyl acetate, correspondingly. The ester conversions are increased only by 0.1% for both ethyl acetate and *n*-butyl acetate, when the catalyst dosage was increased further to 0.35 and 0.5 g, respectively. Thus, 2.5 h, 0.25 g for the esterification for ethyl acetate and 8 h, 0.4 g for the esterification for *n*-butyl acetate are optimal for catalysis. The specific activity per acid amount is 75.4 and

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	_	acid _{mol} :	Temperature	Reaction	Ester
Catalyst	Esters	alcohol _{mol}	(°C)	time (h)	conversion (%)
HPW/K10 [67]	Ethyl acetate	2:1	100	8	89.8
Melm-PMo [68]		1:4	60	8	15.5
Melm-PW [68]		1:4	60	20	36
Melm-SiMo [68]		1:4	60	20	45
Bulm-PMo [68]		1:4	60	20	29
Bulm-PW [68]		1:4	60	20	73
Bulm-SiMo [68]		1:4	60	20	68
HPW@HKUST-1/γ-Al ₂ O ₃		2:1	75	2.5	92.3
AI-MCM-41 [69]	n-Butyl acetate	1:2	125	6	75.5
H ₃ PW ₁₂ O ₄₀ [69]		1:2	125	6	79.0
HY [69]		1:2	125	6	53.5
HZSM-15 [69]		1:2	125	6	42.7
H ₄ SiW ₁₂ O ₄₀ /ZrO ₂ [70]		1:2	80	4	81
HPW@HKUST-1/ γ -Al ₂ O ₃		2:1	110	8	82.7

Table 6. Activity of catalysts for synthesis of ethyl acetate and n-butyl acetate.



Figure 9. Recyclability of HKUST-1, HKUST- $1/\gamma$ -Al₂O₃ and the composite for adsorptive desulfurization of DBT at optimum reaction conditions.

13.2 mmol mol_{acid}⁻¹min⁻¹ for ethyl acetate and *n*-butyl acetate, respectively. Notably, there is no sub-reaction in this esterification and the selectivity is 100%. Table 6 lists the catalytic activities with ester conversions of HPW@HKUST-1/ γ -Al₂O₃ and other acid catalysts for comparison. As shown in Table 6, the conversion of ethyl acetate and *n*-butyl acetate is 92.3% and 82.7% catalyzed by the composite, respectively, and the results are superior to other solid acids under optimal conditions.

3.5. Regeneration performance of the composite HPW@HKUST-1/ γ -Al₂O₃

There is no doubt that regeneration and stability of the composite as adsorbent and catalyst are exceedingly important factors in term of industrial applications. The recyclability of the regenerated HPW@HKUST-1/ γ -Al₂O₃ as adsorbent is tested in the S-



Figure 10. Recyclability of the composite on hydrolysis of ethyl acetate (a), synthesis of ethyl acetate (b) and *n*-butyl acetate (c). Reaction conditions: (a) 40 mL 5 wt% ethyl acetate; catalyst, 0.2 g; reaction time, 120 min; temperature, 65 °C, (b) $acid_{mol}$: $alcohol_{mol}$, 2:1; catalyst, 0.25 g; reaction time, 2.5 h; temperature, 75 °C; (c) $acid_{mol}$: $alcohol_{mol}$, 2:1; catalyst, 0.4 g; reaction time, 8 h; temperature, 110 °C.

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containing model oil at the same optimum conditions. As shown in Figure 9 for DBT model oil and Figure S7 (supplementary material) for 3-MT, BT, and 4,6-DMDBT model oils, the reusable efficiency of HPW@HKUST-1/ γ -Al₂O₃ decreased very slightly after the 6th cycle, obviously better than HKUST-1 and HKUST- $1/\gamma$ -Al₂O₃. The insignificant loss of the adsorptive desulfurization performance may be assigned to the chemisorption caused by Lewis acid-base interactions of direct sulfur-metal bonds. The regenerated HPW@HKUST-1/ γ -Al₂O₃ is also recyclable as acid catalyst under the same reaction conditions up to six cycles without any change in reactivity and selectivity (Figure 10). Moreover, no HPW leaching was observed in the product solution under subsequent recycling by UV-vis spectrum. The IR spectra (Figure S8, supplementary material) and XRD spectra (Figure S9, supplementary material) of the fresh and sixth regenerated HPW@HKUST-1/ γ -Al₂O₃ after both adsorptive desulfurization and acidic catalysis are almost the same so that it can be concluded that the composite possesses high stability and immobility. The regeneration efficiency is due to the formation of secondary bonding, such as hydrogen bonding between hydroxyl groups of γ -Al₂O₃ and carboxvlic groups of BTC3⁻ or Van der Waals interactions [36, 37], which prevent aggregation and deletion of nano-sized HPW@HKUST-1. In addition, the HKUST-1/ γ -Al₂O₃ composites can be easily recovered by simple decantation due to its millimeter size and enhanced mechanical strength.

4. Conclusion

We prepared a hierarchical multiporous composite HPW@HKUST-1/ γ -Al₂O₃ in which HPW is included in the host matrix of HKUST-1 loaded on the γ -Al₂O₃ beads through one-step hydrothermal reaction. The composite HPW@HKUST-1/ γ -Al₂O₃ not only shows excellent adsorptive desulfurization performance owing to the beneficial acidbase interaction between acidic HPW and slightly basic sulfur-containing compounds, but also shows high acidic activity in hydrolysis of ethyl acetate and synthesis of ethyl acetate and *n*-butyl acetate owing to the high dispersion and easy access of HPW in the composite. The composite material can be easily regenerated by acetone washing and reused for many times with small decrease in adsorptive desulfurization capacity and acid catalytic activity, suggesting potential as adsorbent and acid catalyst in practical applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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