Factors Affect on the Synthesis of Silica-Pillared Zirconium Phosphate with Template-Directing Self-Assembly Method and its Epoxidation Catalytic Performance

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Abstract A series of silica-pillared zirconium phosphate materials with ordered structure were synthesized using hexadecylamine (HDA) as expanding agent, dodecyl dimethyl benzyl ammonium chloride (DDBAC) as template agent and tetraethyl orthosilicate (TEOS) as silica source. The textural properties of the materials can be effectively controlled by adjusting the dosage of HDA, DDBAC and TEOS. Furthermore, a template-directing self-assembly mechanism was proposed based on the synthesis. In the epoxidation of methyl soyate, the prepared materials showed excellent performance with 95.9 % conversion of double bonds and 84.7 % epoxy selectivity. This result is determined by the large surface area and the ordered interlayer structure.

Keywords Controllable synthesis · Silica-pillared · Nanostructure · Self-assembly · Epoxidation

1 Introduction

Pillared layered materials represent a remarkable class of materials which with regular pore sizes and ordered layer structure, showing great advantages in many molecule-selective catalysis [1]. In the last decade, the self-assembly method using the template agent and functional guest had been successfully used in the preparation of porous clay heterostructure (PCH), permitting series applications in heterogeneous catalysis [2–4]. However, the disadvantages

of PCH include its poor thermal stability, weak acidity and fast inactivation in reaction [5, 6]. Those features restrict its application. In recent years, *α*-zirconium phosphate $(\alpha$ -Zr(HPO₄)₂·H₂O, α -ZrP) has been extensively studied as an ideal precursor for the preparation of pillared layered materials due to its typical layered structure and outstanding cation exchange capacity (6.67 mmol/g, which is $7 \sim 15$ times of that of clay compounds [7]). However, due to the large charge density between layers, it cannot swell in aqueous solution as clay does. Therefore, it could be difficult to expand the layers for pillaring. This issue was first solved by the insertion of polyhydroxy cations into interlayer of α -ZrP and different types of pillared zirconium phosphate materials were obtained and applied to catalytic reactions [8–12]. Nonetheless, this method has the following disadvantages such as unmanageable pillared structure and wide pore size distribution, which limited the applications in shape-selective adsorption and selective catalysis.

In 2005, the self-assembly effect of template agent was first utilized in the preparation of pillared zirconium phosphate by Jimenez-Lopez [13]. Acetyltrimethyl ammonium bromide (CTMA) expanded zirconium phosphate (CTMA-ZrP) was taken as raw material and the hexadecylamine (HDA) was intercalated as template agent. Then, the tetraethyl orthosilicate (TEOS) was intercalated and hydrolyzed to form interlayer gallery. Finally, the porous phosphate heterostructures (PPH) were obtained after calcinations. Compared with the traditional pillaring method using polyhydroxy cations, this method gives full play to the self-assembly effect of template agent. It achieves the controllable synthesis of PPH materials. A high specific surface area is obtained as well. Based on the methodology, a series of functional applications of PPH materials were developed [14-19] and the properties of

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acid site of PPH materials were also been investigated [20]. Furthermore, this method is still imperfect since the preparation of CTMA-ZrP provokes a worse orderliness than that of the layered zirconium phosphate. The abundant interlayer acid sites have not been fully exposed. This might due to the regularity of the pore structures is deficient. α-ZrP is composed of zirconium atoms in a semiplanar arrangement bridged by phosphate groups above and below the zirconium atom plane, which possess an integral structure and high stability of layer. The interlayer electrostatic interaction could be weakened by using some alkyl-amine. Thus a starting material with appropriate interlayer spacing and ordered layer structure could be obtained. Then, the pillared zirconium phosphate with uniform structure and more abundant acid sites would be expected to be synthesized by interlayer molecular selfassembly using suitable template agent and functional guest, permitting potential applications in adsorption and catalysis.

In this paper, a controllable synthesis of silica-pillared zirconium phosphate is achieved by adjusting the dosage of each reaction species. Alkylamine expanded zirconium phosphate is first prepared and used for the intercalation of surfactant and silica source. After adjusting the solution pH, the silica galleries are formed via interlayer molecular self-assembly. Based on the synthesis, a probable formation mechanism of the silica-pillared zirconium phosphate is proposed. As for the catalytic performance, the epoxidation of methyl soyate was chosen as probe reaction to evaluate the effective acid-base and structure properties of silica-pillared zirconium phosphate. It is an important approach to obtain industrial products whit high commercial significance [21]. Moreover, as a typical acid catalytic reaction, it could distinguish the Lewis sites and Bronsted sites of the catalyst sensitively [22] and the steric effect arising from the long carbon chain of methyl soyate also produces some structural requirements to the catalysts [23].

2 Experimental

2.1 Catalysis Synthesis

2.1.1 Hexadecylamine Intercalated *α*-ZrP

The synthesis of α -ZrP was performed with the methodology as described in the Ref. [24]. The hexadecylamine (HDA) intercalated α -ZrP were prepared via the following steps according to the published procedure [25]. First, α -ZrP was suspended in a 50:50 mixture of H₂O and ethanol and the mixture was sonicated for about 10 min to obtain well-dispersed colloidal suspensions. Second, various amounts of HDA dissolved in ethanol were added dropwise to the colloidal suspensions containing α -ZrP powders and the liquid solid ratio of the final suspensions was about 5 L/g. The resulting mixtures were stirred at 50 °C for about 24 h until HDAs were fully intercalated into the α -ZrP inter-galleries. At last, the HDA intercalated α -ZrP suspensions were filtered and subsequently washed with plenty of distilled water and ethanol to remove HDA molecules not intercalated. The obtained solid were dried at 60 °C and denoted HDA-n-ZrP, where n is the molar ratio of hexadecylamine/ α -ZrP.

2.1.2 Silica-Pillared Zirconium Phosphate

The HDA-n-ZrP was first suspended in water. Then a certain amount of 0.1 mol/L Dodecyl dimethyl benzyl ammonium chloride (DDBAC) water solution was added. Meanwhile tetraethyl orthosilicate (TEOS) was also dropped slowly into the suspensions. The liquid–solid ratio of the final mixtures was about 30 mL/g. After 2 h stirring, the pH of the gel mixture was adjusted by ammonia solution to 10 and continued stirring for other 2 h at room temperature. The product was recovered by filtration, dried in oven at 60 °C. Subsequently it was calcined at 550 °C for 6 h using programmed furnace in air (with increasing temperature rate of 2 °C/min). The prepared solids were denoted x-SPZHD-y, where x and y are the DDBAC/HDA–ZrP and TEOS/HDA–ZrP molar ratios used in the synthesis, respectively.

2.2 Characterization

The obtained solid products were characterized by X-ray diffraction (XRD) on a Rigaku D/Max 2,500 VBZ+/PC diffractometer using Cu Ka radiation (40 kV, 50 mA) in the range between 0.5° and $10^{\circ} 2\theta$ (low-angle range) and Cu Ka radiation (40 kV, 200 mA) in the range between 3° and 90° 2 θ (high-angle range). N₂ adsorption isotherms were obtained using a Micromeritics ASAP 2000 instrument. The samples were outgassed at 200 °C for 8 h before measurements. The specific surface area (SBET) was estimated by the Brunauer-Emmett-Teller (BET) equation, and the mesopore size distribution and mesopore analysis were obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda method. Scanning electron microscopy (SEM) micrographs were obtained on a HitachiS-4700 microscope operated at 30 kV. The transmission electron microscopy (TEM) was done using JEOL-2100 transmission electron micro-scope with an accelerating voltage of 200 kV. Ammonia thermal programmed desorption (NH₃-TPD) was used to determine the total acidity of the samples. Measurement was carried out by a ASAP2920 (Thermo Electron Corporation). About 100 mg of sample was treated at 600 °C in He for 1 h, cooled to



M ethyl palm itate

373 K and then exposed to a 1 vol% NH₃/He stream for 20 min. Weakly adsorbed NH₃ was removed by flushing with He at 100 °C for 10 min. Finally, the treating temperature was increased from 100 to 800 °C at a rate of 10 °C/min in a He flow of 20 cm³/min. Pyridine adsorption coupled to FT-IR spectroscopy was employed to determine the nature of the acid centres of the catalysts. The samples were evacuated (380 °C, 10^{-2} Pa overnight), exposed to pyridine vapour at room temperature, and then out-gassed between 200 °C and 450 °C. FT-IR spectra were recorded on a PROTÉGÉ 460 spectrometer.

2.3 Catalytic Reaction

Methyl soyate was prepared by transesterification of refined soybean oil with methanol by a standard procedure using an alkali catalyst [26]. In a typical epoxidation reaction, 10 g of methyl soyate was taken in a threenecked, glass round-bottom flask (50 ml) fitted with a water-cooled condenser and thermometer, then 1 g of methanoic acid, 0.1 g of catalyst and 6.5 g of hydrogen peroxide 30 wt% was added successively. The flask was placed in a water-bath maintained at about 55 °C and the reaction was conducted under reflux with magnetic stirring for 5 h. The final solution was transferred to a separating funnel and the aqueous layer was removed. The organic layer was washed with 0.1 mol/L Na₂CO₃ solution three times and then washed with distilled water until the pH was 7. Then the epoxidation of methyl soyate was obtained from the supernatant after centrifugation.

The representatives of methyl soyate are shown in Fig. 1 (left panel) and the possible epoxy products of methyl soyate are depicted in Fig. 1 (right panel). The epoxy products were analyzed to evaluate the double bond conversion, through the determination of the Iodine Number, and the epoxy selectivity, through the evaluation of the Oxirane Number, according to the analytical methods

reported by the literature [27]. Corresponding computational formulas are listed as follows:

Conversion (%)

$$= \frac{[\text{Iodine Number}]\text{initial} - [\text{Iodine Number}]\text{final}}{[\text{Iodine Number}]\text{initial}} \times 100$$
(1)

Yield (%) =
$$\frac{[\text{Oxirane Number}] \times \text{PMI2}}{[\text{Iodine Number}] \times \text{PMO}} \times 100 \quad (2)$$

Selectivity (%) =
$$\frac{\text{Yield}}{\text{Conversion}} \times 100$$
 (3)

where Iodine Number is the grams of I_2 that is taken up by 100 g of the oil; Oxirane Number is the grams of epoxydic oxygen per 100 g of the oil; PM_{I2} is the molar weight of I_2 (g/mol); PM_O is the molar weight of O (g/mol).

3 Results and Discussion

3.1 The Controllable Synthesis of SPZHD Analysis

3.1.1 The Effect of HDA upon the Morphology and Structure of SPZHD

First, several HDA-n-ZrP materials are obtained by adjusting the dosage of HDA (Fig. 2). As shown in the XRD patterns, when the molar ratio of HDA/ α -ZrP is 0.2, a relative weak peak at $2\theta = 2.95^{\circ}$ ($d_{001} = 3.00$ nm) grows out, it indicates HDA has been intercalated but the intercalated amount is small. As the ratio increases to 0.7, the diffraction peak at $2\theta = 2.95^{\circ}$ ($d_{001} = 3.00$ nm) becomes sharp and it indicates an interdigitated layers structure of intercalated HDAs occurs. Further increase the molar ratio of HDA/α-ZrP to 2, a new distinct peak located at $2\theta = 2.05^{\circ}$ ($d_{001} = 4.30$ nm) appears. It indicates the formation of a well-ordered bilayer structure of intercalated HDAs [21]. Using these HDA-n-ZrP and α -ZrP as starting



Fig. 2 The small angle XRD patterns for HDA-n-ZrP

materials, series 0.2-SPZHD-3 materials are synthesized via templating self-assembly method and examined by SEM (Fig. 3). Different amount of co-precipitated silica are observed on the surface or around the sheets of the synthesized silicon pillared material. Dramatically, silicon pillared material synthesized from HDA-0.7-ZrP exhibits a clear layer morphology and the least co-precipitated silica. In the corresponding XRD patterns (Fig. 4), each sample exhibits different layer structural ordering. Among them, silicon pillared material synthesized from HDA-0.7-ZrP also presents the best layer structure and the least co-precipitated silica (the weakest diffraction at $2\theta = 20 \sim 25^{\circ}$ [28])

The results of SEM and XRD could be explained by the expanding effects of HDA. When HDA is not used or its intercalated amount is relative small, the subsequent intercalation of DDBAC cationic and TEOS would be hindered by the intense electrostatic interaction between layers and the confined hydrophilic interlayer space also goes against the penetrate of TEOS, provoking a



Fig. 3 SEM images for 0.2-SPZHD-3 obtained from a α-ZrP, b HDA-0.2-ZrP, c HDA-0.7-ZrP, d HDA-2-ZrP



Fig. 4 The small angle XRD patterns for 0.2-SPZHD-3 obtained from $a \alpha$ -ZrP, b HDA-0.2-ZrP, c HDA-0.7-ZrP, d HDA-2-ZrP. The wide angle XRD patterns are shown in the *insets*

tagraggery of co-precipitated silica and α -ZrP (Fig. 3a, b). In this case, the amount of interlayer TEOS is insufficient for the adequate formation of the galleries, leading to the collapsed or disordered structure after calcinations (Fig. 4a, b). If the amount of the interlayer HDA is relatively large, most P-OH groups locating on the layers of zirconium phosphate are neutralized while the retained free P-OH are insufficient for the subsequent ion exchange with DDBAC, TEOS also fail to intercalate with DDBAC cationic by salvation [29]. Thus, large number of TEOS hydrolysis on the layer surface after adding ammonia solution (Fig. 3d) and a collapsed interlayer structure is provoked after calcinations (Fig. 4d). As the starting material is HDA-0.7-ZrP, the amount of interlayer HDA is suitable. In this situation, all the sheets of zirconium phosphate are expanded and the electrostatic interaction between the layers is weakened substantially. In addition, sufficient free P-OH groups are retained, it ensures the ion exchange between DDBAC cationic and H⁺ of the P-OH. Thus, the prepared pillared presents well-ordered interlayer structure material (Fig. 3c) and clear layer morphology (Fig. 4c). Consequently, it is deduced that the introducing of HDA improves the intercalation of DDBAC cationic and TEOS with ordered interlayer structure. One more thing to be noted is that the intercalated amount of HDA must be controlled to retain sufficient free P-OH groups as they are keys of the intercalation of DDBAC cationic and TEOS.



Fig. 5 The small angle XRD patterns for *a* 0.2-SPZHD-2, *b* 0.2-SPZHD-3, *c* 0.2-SPZHD-4, *d* 0.4-SPZHD-2, *e* 0.4-SPZHD-3, *f* 0.4-SPZHD-4. The wide angle XRD patterns are shown in the *insets*

3.1.2 The Effect of Surfactant upon the Layer Structure of SPZHD Using HDA-0.7-ZrP as starting material, several SPZHD materials are synthesized by adjusting the molar ratios of DDBAC/HDA-ZrP and TEOS/HDA-ZrP. Almost all the prepared solids exhibit diffraction peaks with different intensity at low angle and typical diffraction peaks of α-ZrP at wide angle (Fig. 5). It indicates that interlayer

prepared solids exhibit diffraction peaks with different intensity at low angle and typical diffraction peaks of α -ZrP at wide angle (Fig. 5). It indicates that interlayer silica gallery with various structural ordering has formed and the crystalline structure of the α -ZrP has not been destroyed after calcinations. In addition, the co-precipitated silica material was also obtained and it reflects a disordered crystal structure which completely different from the typical pillared-layer structure of the pillared materials. This fact assures the co-precipitated silica would not cause interference to the structural characterization of pillared materials. The interlayer spacing of all samples has been calculated out and it is found that all of them fluctuate at around 2.40 nm. Furthermore, several x-SPZHD-3 materials are synthesized by adjusting the molar ratio of DDBAC/HDA-ZrP from 0 to 0.6. Corresponding behavior of interlayer spacing is shown in Fig. 6. It can be seen that the pillared structure doesn't form until the molar ratio of DDBAC/HDA-ZrP achieves 0.2. When the ratio exceeds 0.2, the interlayer spacing fluctuates at around 2.40 nm. Thus it is possible to deduce that once the surfactant is elected and the critical amount is achieved, the interlayer spacing of SPZHD is stabilized. Otherwise, it should be noted that the interlayer spacing of each sample is bigger



Fig. 6 The relationship between molar ratio of DDBAC/HDA–ZrP and interlayer spacing. *a* 0-SPZHD-3, *b* 0.1-SPZHD-3, *c* 0.2-SPZHD-3, *d* 0.3-SPZHD-3, *e* 0.4-SPZHD-3, *f* 0.6-SPZHD-3

than length of DDBAC long chain (1.60 nm) and smaller than the double of that (3.20 nm). By considerations similar to those reported for the amine arrangements in zirconium phosphate [30, 31], it can be inferred that the interlayer DDBAC cationic molecules are arranged as molecular lamellar bi-layers with an oblique angle to the layer plane, and the carbon chains of DDBAC cationic molecules formed an inter-penetration phase [32]. To further verify this conclusion, two more materials are synthesized by using benzyl dimethyl hexadecyl ammonium chloride (BCDAC) and octadecyl dimethyl benzyl ammonium chloride (ODBAC), when the molar ratio of surfactant/HDA-ZrP is 0.2 and TEOS/HDA-ZrP is 3. Low-angle XRD patterns for the prepared solids show a single peak corresponding to the d_{001} diffraction at 3.00 nm (Fig. 7b) and 3.37 nm (Fig. 7c). Consistently, the interlayer spacing of corresponding samples is still between the length of long chain and double of it (the length of BCDAC long chain is 2.20 nm and the length of ODBAC long chain is 2.50 nm). Interestingly, the relationship between the interlayer spacing and the length of surfactants long chain is similar to linearity.

The preceding behaviors of the surfactant indicate that the layer structure of silicon pillared materials can be controlled directly by choosing the surfactant with required length of long chain and adjusting the dosage of surfactant. In this work, the 0.2-SPZHD-3 material synthesized from HDA-0.7-ZrP exhibits ordered interlayer structure and the largest interlayer spacing (2.52 nm).



Fig. 7 The small angle XRD patterns for silicon pillared materials synthesized by a DDBAC, b BCDAC, c ODBAC. Relationship between the interlayer spacing and the length of surfactants long chain is shown in the *insets*

3.1.3 The Effect of Tetraethyl Orthosilicate upon the Porous Structure of SPZHD

Using HDA-0.7-ZrP as starting material, several SPZHD materials are synthesized by adjusting the molar ratios of DDBAC/HDA-ZrP and TEOS/HDA-ZrP. As can be seen from the N₂ adsorption-desorption isotherms and pore size distributions (Fig. 8), all the samples are characterized as hybrid type IV according to the BDDT (Brunauer-Deming-Deming-Teller) classification with a hysteresis loop, whose features correspond to type B in Boer's five types representing the presence of open slit-shaped or cylindrical pores formed in gallery regions [33–35]. From the pore size distributions, it can be seen that the SPZHD materials possess a relatively narrow pore size distribution, which is typical for a well-ordered meso-structured material. The interlayer spacing, pore size, pore volume and S_{BET} of each sample are summarized in Table 1. It can be seen that the interlayer spacing of each sample is stabilized around 2.40 nm and it indicates that the effect of TEOS upon the interlayer spacing of SPZHD is insignificant. However, all the porous properties increases at first and then decreases with the increasing of the dosage of TEOS. When the molar ratio of TEOS/HDA-ZrP is 2, the relative small amount of interlayer TEOS would provoke a low distribution density of interlayer silica gallery and weak walls of interlayer pores. In this case, a partial collapse of the interlayer porous structure occurs throughout the



Fig. 8 The N₂ adsorption-desorption isotherms for SPZHD (*Left*) and the pore size distributions (*Right*). a 0.2-SPZHD-2, b 0.2-SPZHD-3, c 0.2-SPZHD-4, d 0.4-SPZHD-2, e 0.4-SPZHD-3, f 0.4-SPZHD-4

Material	Interlayer spacing (nm)	Pore diameter (nm)	Pore volume (cm ³ /g)	S _{BET} (m ² / g)
0.2-SPZHD- 2	2.36	1.49	0.22	285.2
0.2-SPZHD- 3	2.52	1.55	0.28	357.1
0.2-SPZHD- 4	2.41	1.40	0.21	303.6
0.4-SPZHD- 2	2.37	1.24	0.17	269.0
0.4-SPZHD- 3	2.43	1.29	0.31	480.5
0.4-SPZHD- 4	2.40	1.26	0.29	459.3

 Table 1
 Textural properties of SPZHD

calcinations and therefore the prepared silicon pillared material exhibits less S_{BET} and smaller pore size. When the molar ratio of TEOS/HDA-ZrP is 4, the amount of interlayer TEOS is relatively large, provoking a filled interlayer space and tightly arranged interlayer micelle molecules. This leads to the decrease in S_{BET} and pore size of the prepared silicon pillared material. As the molar ratio of TEOS/HDA-ZrP is 3, the suitable amount of interlayer TEOS is achieved and it results a well distribution of interlayer silica gallery, giving rise to a well-ordered interlayer porous structure and the largest S_{BET} and pore size. It should be noted that the interlayer porous structure also relates with the dosage of HDA closely, due to the distribution of interlayer silica gallery depends on the amount of available P-OH groups which participate the ion exchange with DDBAC cationic. On the basis of preceding facts, it is clear that the porous structure of SPZHD can be controlled by adjusting the dosage of TEOS. In this work, using HDA-0.7-ZrP as starting material, silicon pillared material with the highest S_{BET} and the largest pore size could be synthesized when the molar ratio of TEOS/HDA-ZrP is 3 and the molar ratio of DDBAC/HDA-ZrP is 0.2.

3.1.4 Proposed Formation Mechanism of SPZHD

Based on the synthesis, a possible formation mechanism of SPZHD is proposed and shown in Fig. 9. In the first step, HDA molecules are inserted into the interlayer by protonation, holding the zirconium phosphate sheets apart, weakening the interlayer electrostatic interaction and building a hydrophobic interlayer space. It would help to improve the subsequent intercalation of DDBAC cationic and TEOS. In the second step, the DDBAC cationic molecules intercalate into the interlayer by ion exchange, and TEOS also intercalates with DDBAC cationic by solvation. As the amount of intercalated DDBAC cationic increases to the critical amount, HDA and DDBAC cationic molecules in the gallery are arranged as molecular lamellar bilayers with an oblique angle, forming the interlayer micelle. After adding ammonia solution, the interlayer TEOS hydrolyzes quickly and assembles around interlayer micelle, provoking an ordered pillared structure. As shown in the formation mechanism, several factors are combined such as the expanding effects expressed from HDA, ion exchange property of α -ZrP, template-directing function of DDBAC and solvation mechanism of TEOS. Above all, the insertion of HDA significantly affects the morphology, pore size and SBET of SPZHD material and the length of DDBAC long chain directly controls the interlayer spacing



Fig. 9 Models of formation mechanism of SPZHD materials



Fig. 10 SEM and TEM images for the 0.2-SPZHD-3 material. a, b SEM images for the 0.2-SPZHD-3 material; c, d TEM images for the 0.2-SPZHD-3 material

of SPZHD material. Therefore, the controllable synthesis of SPZHD material could be achieved by regulating the dosage of HDA, choosing suitable surfactant with expected length of long chain and adjusting the dosage of surfactant and TEOS. It gives rise to a chance for SPZHD material to be used as a designable catalytic material which could be adjusted according to the size of reactant molecules. In this work, using HDA-0.7-ZrP as starting material, silicon pillared material 0.2-SPZHD-3 has been synthesized. It exhibits the largest interlayer spacing and the best porous structure among the x-SPZHD-y series. From the SEM and TEM images of 0.2-SPZHD-3, uniform ordered stacking of disk-shaped platelets are observed (Fig. 10a, b) and the

distinct layered crystalline phases are also observed from the edge of the sheets (Fig. 10c, d).

3.2 Evaluation of the Acidity and Catalytic Performance

3.2.1 Evaluation of the Acidity

The 0.2-SPZHD-2 material, the 0.2-SPZHD-3 material and α -ZrP are selected to examine the distribution of surface acidity in SPZHD material by using NH₃-TPD. According to the profiles it can be seen that each sample shows two desorption peaks placed at about 300 and 550 °C (Fig. 11).



Fig. 11 The NH₃–TPD patterns for *a* α -ZrP, *b* 0.2-SPZHD-3, *c* 0.2-SPZHD-2

The peaking temperature of silicon pillared material is slightly lower than the peaking temperature of α -ZrP, which indicates the acid strength is reduced after pillaring. This is because the interlayer silicon gallery would neutralize or cover some interlayer P-OH groups providing most acidity of zirconium phosphate and its derivatives [36]. In addition, the silicon pillared materials with variant pore structures and layer structures present similar behaviors in peaking temperature and peaking intensity. It indicates that the total acid content of SPZHD material is similar. Further characterization of α -ZrP and the 0.2-SPZHD-3 material was carried out by FT-IR spectra of adsorbed pyridine at 200 and 450 °C, respectively. Figure 12 shows the IR spectra in the $1,400-1,700 \text{ cm}^{-1}$ region, it can be seen that α -ZrP shows no bands at both temperature and it indicates that the pyridinium ion is not formed on the acid centre. At 200 °C, 0.2-SPZHD-3 material shows a characteristic band at $1,450 \text{ cm}^{-1}$ corresponds to pyridine coordinated to Lewis acid sites. When the temperature is raised up to 450 °C, the band at $1,450 \text{ cm}^{-1}$ still retains, it proposes a strong bonding between pyridine molecules and acid centre [37]. Additionally, it should be noted that no bands are observed at $1,540 \text{ cm}^{-1}$, it indicates that the Bronsted sites do not exist in the SPZHD material [38, 39]. It is interesting that α -ZrP exhibits a stronger acid strength in NH₃-TPD test but behaves oppositely in FT-IR spectra of adsorbed pyridine. This result can be explained by the difference in adsorption performance: the narrow interlayer spacing and low S_{BET} of α -ZrP leads to difficulty for pyridine molecules in accessing large number of interlayer acid sites. After



Fig. 12 FT–IR spectra of adsorbed pyridine on a α -ZrP and b 0.2-SPZHD-3 at 200 and 450 °C, respectively

pillaring, the layers are expanded and the porous system with large S_{BET} is obtained. It generates a better adsorption performance and provokes the accessible interlayer acid sites for pyridine molecules. The result from the IR spectra indicates that SPZHD material is a typical Lewis acid with enhanced adsorption performance.

3.2.2 Evaluation of Catalytic Performance

Table 2 lists the conversions of double bonds and the selectivity of epoxy over the SPZHD material, α -ZrP and the co-precipitated silica material. As can be seen, the silica material shows a conversion of double bonds of 70.9 % and selectivity of epoxy of 62.5 %. α-ZrP shows a conversion of double bonds of 77.8 % and selectivity of epoxy of 68.7 %. In contrast, SPZHD materials exhibit a substantially increase on catalytic effects: all conversions of double bonds over SPZHD are more than 90 % and the epoxy selectivities are more than 80 %. In parallel with other solid acids, SPZHD material also exhibits an excellent catalytic performance (the conversion of double bonds reaches 95.9 % and the epoxy selectivity reaches 84.7 % in 5 h reaction time). Epoxy selectivity over hydrotalcite-like compounds intercalated by 12-phosphorus tungsten heteropoly acid was only 59.4 % [23]. Ti grafted on silica exhibited 80 % of epoxy selectivity [40]. Ti-MCM-41 was reported to show better performance (both the conversion of double bonds and the epoxy selectivity are more than 90 %), but it requires long reaction time of 25 h [41]. Same level can be achieved over the sol-gel synthesized alumina, which requires 20 h reaction time [42]. On the other hand, the catalytic performance of each SPZHD material presents

Table 2 Catalytic performance over α-ZrP and SPZHD materials

Materials	Double bond conversion (%)	Epoxy selectivity (%)
co-precipitated silica	70.9	62.5
α-ZrP	77.8	68.7
0.2-SPZHD-2	91.0	80.4
0.2-SPZHD-3	95.9	84.7
0.2-SPZHD-4	93.5	82.6
0.4-SPZHD-2	91.9	81.2
0.4-SPZHD-3	93.0	82.2
0.4-SPZHD-4	94.6	83.5



Fig. 13 The relationship between interlayer spacing and the epoxy selectivity

some difference, 0.2-SPZHD-3 shows a maximum epoxy selectivity of 84.7 % and 0.2-SPZHD-2 exhibits a minimum epoxy selectivity of 80.4 %. Combining with the results of the NH₃-TPD (the total acid content of SPZHD material with different layer structure is similar), it is possible to deduce that the difference in catalytic performance is provoked by the different layer structure of each material. Based on this, the relationship between the interlayer spacing and the epoxy selectivity is summarized and shown in Fig. 13. It can be seen that with the increasing of interlayer spacing, the epoxy selectivity keeps improving. A rapid rise of epoxy selectivity is obtained through the increasing of interlayer spacing from 0.76 to 2.52 nm, further increase the interlayer spacing to 3.37 nm, the rising of epoxy selectivity flattens out gradually. This result is consistent with the more accessible diffusion pathway for the relatively large reactants and product



Fig. 14 The relationship between reaction time and the epoxy selectivity

molecules, which is provoked by the larger interlayer spacing.

Generally in the epoxidation of methyl soyate, an intermediate peroxy acid is first obtained and then the oxygen transfer from the peroxy acid to an olefin [43]. Based on this mechanism, a possible scheme of this epoxidation is proposed. Performic acid is generated from H₂O₂ and formic acid at first and then adsorbed into interlayer. Meanwhile, the methyl soyate molecules are also adsorbed into interlayer. With the catalyzing of basic hydroxyl function locating on the layers of SPZHD, epoxidation of the unsaturated carbon bonds occurs at around the basic hydroxyl function. As can be seen in Fig. 14, a rapid rise of epoxy selectivity is obtained in a short time and then the rising of epoxy selectivity flattens out gradually. It implies that an effect contact between the catalysts and reactants is achieved quickly. The epoxy selectivity is decreased as the reaction time is longer than 300 min because of the ring-opening of the epoxy products. Based on these facts, it can be inferred that the chemical step controls the reaction process and not the diffusion step, because macromolecular reactants can be effectively adsorbed into interlayer and well diffused to the basic hydroxyl function. The activation energy of reaction is also calculated to be 30.1 kJ/mol, which is significantly decreased compared with other catalytic system [44, 45]. Therefore, with the large surface area and the ordered interlayer structure of SPZHD material, reactants and active sites contact with each other adequately and a higher catalytic performance is expressed over the SPZHD material.

4 Conclusions

A series of SPZHD materials with ordered structure were successfully synthesized and the morphology, structure and acidity of SPZHD were systematically studied. It was found that the morphology, layered structure and porous structure of SPZHD can be effectively controlled by adjusting the dosage of HDA, DDBAC and TEOS, permitting the use of designable material with potential applications in adsorption and catalysis. Based on the synthesis, a probable formation mechanism of the template-directing self-assembly silicon gallery was described. As a typical Lewis acid, SPZHD shows a maximum conversion of double bonds of 95.9 % and epoxy selectivity of 84.7 % in the epoxidation of methyl soyate. Such an excellent catalytic performance in parallel with other solid acids may be consistent with the advantage of its structure.

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