Mesoporous zinc aluminate (ZnAl_2O_4) nanocrystal: synthesis, structural characterization and catalytic performance towards phenol hydroxylation

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Abstract:

Mesoporous zinc aluminate (ZnAl_2O_4) nanocrystal with rhombus-shaped morphology was for the first time synthesized by a vacuum-promoted self-assembly and alkaline hydrothermal approach. The obtained mesoporous ZnAl_2O_4 (Meso-ZA) was characterized by X-ray diffraction (XRD), nitrogen sorption, transmission electron micrograph (TEM), pyridine adsorbed infrared spectra (Pyridine-FTIR) and temperature-programmed desorption of ammonia (NH_3 -TPD). The characterization results indicate that the final Meso-ZA possesses rhombus-shaped morphology, worm-like mesoporous structure, crystalline framework, narrow pore size distribution, large surface area (up to $216 \text{ m}^2/\text{g}$) and rich surface Lewis acid sites. The catalytic test on phenol hydroxylation shows that the synthesized Meso-ZA exhibits a superior catalytic performances to titanium silicalite (TS-1) and bulk zinc aluminate.

Key words: rhombus-shaped nanocrystal, mesoporous zinc aluminate, self-assembly, hydrothermal treatment, catalytic hydroxylation

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1. Introduction:

Over the past twenty years, great advances have been gained in the design and synthesis of various mesostructured materials from silica/silicates [1, 2] to transitional metal oxides [3-5], metal phosphates [6-8], carbons [9-13] and so on. Hitherto, mesostructured metal oxides or composite metal oxides [14, 15] have long been a hot research topic due to their unique features of open mesoporous architecture, tunable pore size, large surface area, adjustable surface properties and potential applications in catalysis [16,17], energy storage [18, 19], sorption and separation [20]. Among composite metal oxides, spinel type zinc aluminate (ZnAl_2O_4) has a wide applications in catalysis as catalyst or catalyst supports [21-25]. Compared with the conventional catalyst supports, which are not thermally resistant, retain water and favor catalyst sintering, aluminates seem to be a good option as they are hydrophobic, mechanically resistant and present a surface acidity/basicity [26].

To date, various approaches including nanocasting [27, 28], self-generated template [29], solvothermal treatment [30] and self-assembly [31, 32] have been developed towards the fabrication of mesostructured spinel type composite oxides. However, most of the recent research on mesoporous zinc aluminate are mainly focused on constructing high surface area products for catalyst support application. Only a few research were conducted to explore its inherent catalytic performance as heterogeneous catalyst [33, 34] and thus there are plenty room for further explorations.

Herein, we developed a rhombus-shaped mesoporous zinc aluminate nanocrystal (Meso-ZA) by a vacuum-promoted self-assembly and basic hydrothermal approach, in which vacuum serves as an adjustor towards the acidity of the assembly system by fast evaporating the generated acid (HCl) so that an efficient assembly could occur, while, the following alkaline hydrothermal was utilized to further eliminate the influence of Cl^- ion towards the crystallization [35]. Moreover, the obtained Meso-ZA was investigated as heterogeneous catalyst for phenol hydroxylation, which is a useful reaction for the production of high value chemicals of catechol and hydroquinone (dihydroxybenzenes, DBs). To date, various catalysts including pure metal oxides [36-38] or composite oxides (e.g. Fe_2O_3 , Co_3O_4 , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, CuO/SiO_2 , MoO_3 , V_2O_5 ,

etc.) and heteropoly compounds [39] have been proved to be active for phenol hydroxylation, but neither the catalytic activity nor the selectivity of these catalysts is satisfactory. In the recent decade, increasing attention has been paid on the development of other metal-modified molecular sieves [40, 41] (e.g. Fe-SBA-15, Cu-MCM-41, Cu-ZSM-5, etc.) in order to acquire higher reaction rate and better selectivity of DBs since the finding of titanium silicalite (TS-1) molecular sieve for phenol hydroxylation. However, these metal-modified catalysts usually show considerable difference in phenol conversion or in product selectivity, depending on the chemical composition and preparation method. In this work, phenol hydroxylation with Meso-ZA, TS-1 and bulk zinc aluminate as catalyst were examined. The catalytic test results show that the synthesized Meso-ZA exhibits a superior catalytic performances to TS-1 and bulk zinc aluminate, attributing to its open-accessed structure and rich surface Lewis acid site.

Experimental section:

1.1 Synthesis

Synthesis of Meso-ZA. Typically, 3.0 g P123 (BASF) was dissolved in 60.0 ml anhydrous ethanol with magnetic stirring to get a template solution. Then, 1.36 g (1.0 mmol) ZnCl_2 and 2.66 g (2.0 mmol) anhydrous AlCl_3 were added to the template solution with magnetic stirring till a homogeneous mixed solution was obtained. The resulted mixed solution was dipped into a Petri dish and evaporated in a vacuum desiccator at 313 K first with low degree of vacuum (0.05 M atm) for 1 h then with high degree of vacuum (0.01 M atm) for 5 h to obtain a white gel. The obtained gel together with 50.0 ml aqueous ammonia (25 wt. %) was transferred into a steel autoclave to undergo a hydrothermal treatment at 453 K for 24 h. After hydrothermal treatment, the resulting gel was washed for several times and dried prior to calcination. The template was removed by calcinations in air with a rate of 1 K/min at 773~973 K for 4 h and the obtained products were denoted as Meso-ZA-T (T: calcination temperature/K). As a comparison, bulk zinc aluminate was synthesized by a co-precipitation method with aqueous ammonia as precipitate. After co-precipitation reaction, the obtained composite hydroxides were calcined at 773 K to get a bulk zinc

aluminate (denoted as Bulk-ZA-773). The crystallinity of Bulk-ZA-773 was confirmed by X-ray diffraction shown in supporting information (SI, Fig. S1).

1.2 Characterization

The X-ray diffraction (XRD) analysis was performed on a Philips X'Pert X-ray diffractometer with a Cu K α radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) measurements were conducted on JEM-2100 using an accelerating voltage of 200 kV. N₂ sorption isotherms were measured using a Micromeritics ASAP2020 analyzer at 77 K. Before measurements, all samples were degassed at 573 K for 4 h. The specific surface area is calculated by Brunauer-Emmett-Teller (BET) theory and the pore size distribution is determined by adsorption branch via Barrett-Joyner-Halenda (BJH) method. The nature of acid sites was investigated by Pyridine adsorbed Fourier transform infrared spectroscopy (Pyridine-FTIR), which was recorded at room temperature on Bruker Vertex 70 spectrometer. Self-supporting wafers of each sample (ca. 15.0 mg) were calcined under vacuum of 10⁻² Pa at 673 K for 1 h in the IR cell. The vacuum IR cell was cooled down to room temperature and exposed to pyridine vapor for 1h; thereafter wafers were evacuated at 473 K for 1 h and cooled down to room temperature to get the IR spectra. The temperature-programmed desorption of ammonia (NH₃-TPD) was recorded on a TP-5080 automatic multi-purpose adsorption apparatus with a thermal conductivity detector. The samples were pretreated at 823 K for 1 h in He (ultra-high-purity grade) flow and then cooled to 373 K for NH₃ adsorption, with subsequently purged in pure He at 373 K for 1 h and then raised to 823 K (10 K/min) for the desorption of NH₃.

1.3 Catalytic test

Phenol hydroxylation to dihydroxybenzenes (DBs) over various catalysts including mesoporous zinc aluminate (Meso-ZA-773), microporous titanium silicalite (TS-1, Si/Ti=75), bulk zinc aluminate (Bulk-ZA-773) and no catalyst was conducted in a 50.0 ml three neck flask with a magnetic stirring in batch mode using a reaction mixture of phenol/H₂O₂ of 2:1. Typically, 0.94 g (0.01 mol) phenol was dissolved in 10.0 ml distilled water and mixed with 80.0 mg catalyst. After the mixture was heated

to 353 K under vigorously stirring, 0.50 ml H₂O₂ (30 wt. %) was added. After reaction for 360 min, the products were centrifuged to remove the catalyst before analysis. Oxidation products were analyzed by a Shimadzu 2014 gas chromatography equipped with a FID detector. The GC was operated under programmed temperature conditions with the initial column temperature was kept at 413 K for 7 min and then increased to 473 K for 2 min at a rate of 5 K/min. Helium was used as the carrier gas with a constant velocity of 1.0 ml/min and the temperature of the injector was set at 553 K. The molecular formula of reaction products were determined using Agilent 5975 GC/MASS spectrometer.

2. Results and discussion

3.1 Structure and Morphology characterization

To investigate the mesoporous structure in the final products, a small angle X-ray diffraction (SAXRD) was measured as shown in Fig.1a and 1b. After calcination at 773 K, the SAXRD pattern (Fig.1a) of the obtained Meso-ZA-773 shows a single sharp diffraction peak around 1.0° indexed to the diffraction of (100) direction of mesoporous structure, illustrating the existence of mesoporous structure. After calcination at 973 K, the SAXRD pattern of the obtained Meso-ZA-973 (Fig. 1b) also exhibits a single diffraction peak around 1.2°, suggesting the mesoporous structure could be maintained upon high temperature calcination, which implies an excellent thermal stability of the mesoporous structure. The crystallinity of the final products were characterized by wide angle X-ray diffraction (WAXRD) shown in Fig. 1c and 1d. The WAXRD patterns of Meso-ZA-773 and Meso-ZA-973 both show six typical diffraction peaks that can be attributed to (220), (311), (400), (422), (511) and (440) diffractions of spinel-type zinc aluminate (JCPDS No. 01-1146), indicating that mesostructured spinel type Zn-Al composite (zinc aluminate) could be obtained by the presented method.

The morphology of the obtained mesoporous zinc aluminate was characterized by transmission electron microscopy (TEM) shown in Fig.2 and Fig. S2 (S: supporting information). The low magnification TEM image of Meso-ZA-773 (Fig. S2) shows that the obtained zinc aluminate possesses a rhombus-shaped morphology after

template removal. The gradually magnified TEM images of Meso-ZA-773 in Fig. 2a-2c further confirms the rhombus-shaped morphology and wormlike mesoporous structure with the pore size of ~ 3.3 nm. The high-resolution TEM image (Fig. 2d) of Meso-ZA-773 displays some visible lattice fringes with an equal interplanar distance of 0.243 nm, corresponding to (311) planes of ZnAl_2O_4 , indicative of a crystalline structure, which is consistent to the wide angle XRD results. The SAED pattern (Fig. 2d-inset) of Meso-ZA-773 shows five bright diffraction rings assigned to the (220), (311), (400), (511) and (440) reflections of ZnAl_2O_4 , further confirming the crystalline structure.

Nitrogen sorption isotherms (Fig. 3) was employed to further investigate the texture of the final products fabricated by the presented method. After template removal, both of the obtained zinc aluminate possess an IV-type isotherms with a clear condensation step in $P/P_0=0.4-0.6$ for Meso-ZA-773 and $P/P_0=0.6-0.8$ for Meso-ZA-973, indicating the existence of uniform mesopore in the obtained zinc aluminate. The pore size distributions curves (PSD Fig. 3-inset) show that the both zinc aluminates have a narrow pore size distributions with the pore size centered at 3.1 nm and 7.6 nm, respectively, which further confirms the existence of uniform pore size and in agreement with the TEM results. The detailed textual parameters listed in Table 1 reveal that the BET surface area and total volume for the both zinc aluminates are $216 \text{ m}^2/\text{g}$, $0.31 \text{ cm}^3/\text{g}$ (Meso-ZA-773) and $114 \text{ m}^2/\text{g}$, $0.27 \text{ cm}^3/\text{g}$ (Meso-ZA-973), respectively.

3.2 Surface acidic properties

To investigate the surface acidity, pyridine adsorbed infrared spectrum (Pyridine-FTIR) and temperature-programmed desorption of ammonia (NH_3 -TPD) were measured, respectively. The kind of surface acidity were indicated by pyridine characteristic adsorption bands at 1540 cm^{-1} (Brønsted acid sites) and 1450 cm^{-1} (Lewis acid sites), respectively [42]. Fig. 4 shows the Pyridine-FTIR spectra of the obtained Meso-ZA-773, Bulk-ZA-773 and TS-1, in which all the samples has a sharp adsorption peak around 1450 cm^{-1} , indicating the existence of Lewis acid site. However, there is no adsorption peak around 1540 cm^{-1} emerged in pyridine-FTIR

spectra of the three samples, indicative of the absence of Brønsted acid site. The strength and amounts of the surface acidity were studied by NH_3 -TPD as shown in Fig. S3. All the NH_3 -TPD profiles of the three samples exhibit a single peak around 360 K ascribed to weak adsorption center of ammonium on Lewis acidic site. The NH_3 -TPD measurements further confirm that the surface acidic centers of the samples exist in the form of Lewis acidic sites, which is in agreement with the pyridine FTIR results. The calculated acid amounts for the three samples are 0.036 mmol/g (Meso-ZA-773), 0.042 mmol/g (TS-1) and 0.015 mmol/g (Bulk-ZA-773) respectively. The acid amount difference between Meso-ZA-773 and TS-1 can be attributed to their different chemical compositions and microstructure. While for Meso-ZA-773 and Bulk-ZA-773, the specific area is the only reason leading to the difference of the acid amount since they have the same chemical composition.

3.3 Catalytic performances on phenol hydroxylation

Since the obtained mesoporous zinc aluminate nanocrystal possesses the similar surface acidity with titanium silicalite (TS-1), it can be expected that the obtained Meso-ZA-773 may act as an effective catalyst on those catalytic reactions using TS-1 as catalyst. Phenol hydroxylation was selected as model reaction to find the effect and merit of the obtained mesoporous zinc aluminate nanocrystal in catalytic application. The detailed catalytic performances on phenol hydroxylation over Meso-ZA, titanium silicalite (TS-1), bulk zinc aluminate and no catalyst were listed in Table 2. The reaction of phenol hydroxylation could occur without the aid of catalyst, but the conversion of phenol is very low and the major product is benzoquinone. Obviously, the conversion of phenol dramatically increases with the aid of catalyst. Among all the tested catalysts, TS-1 achieved higher conversion of phenol (49.04 %) than Meso-ZA-773 (43.16 %) and Bulk-ZA-773 (28.28 %) due to its large acid amounts and large surface area (387 m^2/g , listed in Table 1), providing more active sites. While, as shown in Fig. 5, Meso-ZA-773 attained higher selectivity (98.20 %) of DBs than TS-1 (75.81 %), Bulk-ZA-773 (76.09 %) and some reported metal oxides [36-38]. The detailed products distribution (listed in Table 2) shows that the low selectivity of DBs for TS-1 and Bulk-ZA-773 is mainly caused by the high yield of the byproduct

(benzoquinone). The high yield of benzoquinone can be attributed to the overoxidation of phenol resulted from diffusion resistance of substances in the limited pore volume of the catalysts. Since it is reported that the hydroxylation reaction on solid acid occurs by a electrophilic aromatic substitution mechanism, in which the surface Lewis acidic site could form a five-membered ring intermediate of metal peroxy species [43] with solvent molecules, leading to the reduction of the pore volume of the catalyst and thus would impose remarkable diffusion resistance of substances, resulting in a overoxidation of the phenol. Compared to some former reported metal oxide catalyst, the superior selectivity of DBs for Meso-ZA-773 may be attributed to its rich surface Lewis acid site resulted from the unique preparation procedure, i.e. alkaline hydrothermal treatment, implying that alkaline hydrothermal treatment favors the creation of Lewis acid site on metal oxides. Hence, it is can be concluded that the open-accessed mesoporous structure and the rich surface Lewis acid sites of Meso-ZA-773 accounted for its superior catalytic performance on phenol hydroxylation.

Conclusions

For the first time, rhombus-shaped mesoporous zinc aluminate (ZnAl_2O_4) nanocrystal was prepared by a vacuum-promoted self-assembly and alkaline hydrothermal approach. The obtained mesoporous ZnAl_2O_4 (Meso-ZA) possesses rhombus-shaped morphology, worm-like mesoporous structure, crystalline framework, narrow pore size distribution, large surface area ($216 \text{ m}^2/\text{g}$) and rich surface Lewis acid sites. The catalytic test on phenol hydroxylation shows that the synthesized Meso-ZA-773 exhibits a superior catalytic performances to titanium silicalite (TS-1) and bulk zinc aluminate. The presented method not only affords a simple approach for the synthesis of mesostructured Zn-Al composite oxides but also could be applicable to the fabrication of others mesostructured alumina-based composite oxides. Moreover, the obtained mesoporous zinc aluminate can also find applications in many other areas such as sorption, photocatalysis, sensors, etc.

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Figure captions:

Fig. 1. X-ray diffraction (XRD) patterns. Small angle XRD (SAXRD) patterns of Meso-ZA-773, a) and Meso-ZA-973, b); Wide angle XRD (WAXRD) patterns of mesoporous Meso-ZA-773, c) and Meso-ZA-973, d).

Fig. 2. TEM and Selected area electron diffraction (SAED, inset) images of Meso-ZA-773.

Fig. 3. N₂ sorption isotherms and pore size distribution curves (PSD, inset) of Meso-ZA-773 and Meso-ZA-973.

Fig. 4. Pyridine adsorbed infrared spectra (Pyridine-FTIR) of the obtained Meso-ZA-773, Bulk-ZA-773 and TS-1.

Fig. 5. Catalysis performance of phenol hydroxylation over no catalyst, TS-1, Meso-ZA-773 and Bulk-ZA-773.

Figures

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Table 1. Textural parameters of synthesized zinc aluminates,

Sample	S_{BET} (m^2/g)	Pore size (nm)	V_{Total} (cm^3/g)	S_{Micro} (m^2/g)	S_{Exter} (m^2/g)
Meso-ZA-773	216	3.1	0.31	10	206
Meso-ZA-973	114	7.6	0.27	2	112
Bulk-ZA-773	28	-	0.12	6	22
TS-1(Si/Ti=75)	387	-	0.21	323	64

S_{Exter} represents the surface area outside of microporosity.

Table 2. Comparison of phenol hydroxylation performance over different catalysts with the same reaction conditions after reaction for 360 min.

Catalyst	Conversion	Yield	Selectivity			
	PH ^a /%	DBs ^b /%	DBs/%	CT ^c /%	HQ ^d /%	BQ ^e /%
No catalyst	0.70	0.27	39.46	39.46	0	60.54
TS-1	49.04	37.18	75.81	43.91	31.90	24.19
Meso-ZA-773	43.16	42.38	98.20	67.26	30.94	1.79
Bulk-ZA-773	28.28	21.51	76.09	14.49	61.60	23.81

^a Phenol. ^b Dihydroxybenzenes. ^c Catechol. ^d Hydroquinone. ^e Benzoquinone.

Graphical abstract: