



Note from the field

Turning phosphatizing wastewater into zinc-incorporated aluminophosphate molecular sieve with an enhanced catalytic performance



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ABSTRACT

Zinc-incorporated aluminophosphate molecular sieve (ZnAPO-34) has been successfully synthesized from Zn-contained phosphatizing wastewater. More than 90% of Zn and P were removed from wastewater after synthesis. The synthesized materials were characterized by X-ray diffraction, small angle X-ray diffraction and ammonia temperature programmed desorption. As a result, these samples were proven to be typical ZnAPO-34, which possessed mesoporous structure together with a great number of Brønsted and Lewis acid sites. Furthermore, the synthesized ZnAPO-34 showed 80% catalytic activity and 80% selectivity in cyclohexane oxidation to cyclohexanol. The higher activity and selectivity could be ascribed to the incorporation of Zn in the aluminophosphate molecular sieve.

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1. Introduction

There is a huge amount of phosphatizing wastewater generated every year from metal polishing and coating industry. For example, Shanghai Baosteel Group Corporation yearly produces more than 4000 ton of phosphatizing wastewater, which contains high concentrations of phosphate and zinc. However, phosphatizing wastewater is usually treated by coagulation method using ferric chloride or lime, and resulted in great amount of secondary waste, such as hydroxyapatite (Lee et al., 2009).

Aluminophosphate molecular sieve (APO) is a class of microporous or mesoporous catalyst with high surface area (Gencel et al., 2013; Park et al., 2011). In order to enhance its catalytic activity, zinc is usually incorporated in APO (Concepción et al., 1996) to form ZnAPO, in which zinc and phosphate coordinate tetrahedrally to oxygen, and generate Brønsted and Lewis acidity (Zhao and Zhao, 1993). ZnAPO had high activity in p-cresol (Anand et al., 2013)

and benzene hydroxylation (Sreenivasulu et al., 2013a, b), acetophenone alkylation (Sreenivasulu et al., 2013a, b), and cycloalkanes oxidation because of its abundant Brønsted sites (Yang et al., 2012). In particular, some products from cyclohexane catalytic oxidation (such as cyclohexanol and cyclohexanone) are often utilized in the production of ϵ -caprolactam, which was a key intermediate in synthesis of polyamide fibers and plastics (Toberer et al., 2005).

Therefore, in the present research, the feasibility of producing high value-added ZnAPO by zinc and phosphate from phosphatizing wastewater was tested. The compositional, structural and acidic features of as-prepared ZnAPO were investigated. Especially, synthesized ZnAPO was further applied to oxidize cyclohexane.

2. Materials and methods

2.1. Synthesis procedures

Phosphatizing wastewater was supplied by Shanghai Baosteel Co., Ltd, and mainly contained 1786 ppm P, 2431 ppm Zn, 52.5 ppm Fe, 62.3 ppm Ca and 19.0 ppm Cu. ZnAPO with various Zn/(Al + Zn) molar ratios were synthesized by hydrothermal process (Zhao et al., 1998b). In detail, phosphatizing wastewater was added with pseudo-boehmite (p-BM) ($\text{Al}_2\text{O}_3 \geq 60.0\%$) and heated at 60 °C under stirring for 2.5 h. Subsequently, Triethylamine (TEA) and acetic acid (AA) were added into the mixture at 60 °C for another

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2 h. Molar ratio of Zn:P:TEA:H₂O:AA was 1.54:1:0.75:20:0.35. Initial pH of the mixture was 3.0 ± 0.7 . The obtained gel was then sealed in an autoclave and kept at 105 °C for 48 h. The product was collected via centrifugation and washed with distilled water, followed by calcination at 550 °C for 7 h. Zn/(Al + Zn) (x) molar ratio was designed from 0.2 to 0.7, and the corresponding sample was denoted as ZnAPO n ($n = 2, 4, 6$ and 7). AlPO₄ and simulated ZnAPO (ZnAPOs) were synthesized by the same method.

2.2. Catalytic test

Cyclohexane oxidation was performed at 20–90 °C in N₂ under atmospheric pressure. In each reaction, 0.45 g catalyst was added into a mixture solution containing 2 mL cyclohexane, 18 mmol H₂O₂ (~1.5 mL), 10 mL acetic acid (as solvent) and 5 mmol 2-butanone (~0.4 mL, as the reaction initiator). After reaction, the mixture was analyzed by gas chromatograph (GC-MS 6890N/5975/CI, Agilent) to estimate the conversion and selectivity of cyclohexane. Prior to the catalytic investigation, it was confirmed that no cyclohexane oxidation occurred, if there was no catalyst added into the solution.

2.3. Characterization

Solids were characterized by powder X-ray diffraction (XRD, Siemens D 2200, CuK α radiation, Rigaku), which operated at a voltage of 40 kV and a current of 30 mA. Scans were conducted from 5 to 40° (2 θ) at a scanning rate of 3°/min. In small angle X-ray diffraction, the collection was conducted in the 2 θ range from 0.5 to 5° at a rate of 0.6°/min. Transmission electron microscopy (TEM) image was obtained on a JEOL 1010 electron microscope. Scanning electron microscopy (SEM) image was obtained on a JSM 6700F electron microscopy. JSM 6700F was also equipped with energy dispersive spectrometry (EDS) for elemental analysis. Zn and Al concentrations were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Prodigy, Leeman) after sample digestion. P concentration was determined in a UV-2450 spectrophotometer (SHIMAZD) at 700 nm. Acidity was evaluated through ammonia temperature programmed desorption (NH₃-TPD) on TPD-5080 (Xianquan, Tianjin).

3. Results and discussions

3.1. Zn and P utilization efficiency

Zn and P from wastewater precipitated with p-BM, and their utilization depended on the amount of added p-BM, i.e. Zn/(Zn + Al) molar ratio (x). Table 1 shows that when x varied between 0.2 and 0.6, 90–94% of Zn and P was removed. However, at $x = 0.7$, the percentage of precipitated Zn dropped to 80%. In particular, at $x = 0.4$, 91.7% Zn and 94.1% P incorporated with p-BM to form

synthesized materials. EDS result of ZnAPO₄ showed that zinc had incorporated into p-BM matrix (Fig. 1B). Elemental analysis revealed that the molar ratio of Zn:Al:P was 0.36:0.57:1 (Fig. 1B and Table 1), which was close to the designed ratio (0.4:0.6:1). Therefore, treatment of Zn-containing phosphatizing wastewater was fairly efficient (90–94%), when $x = 0.2$ –0.6.

Furthermore, there were C, Fe, and Ca peaks in Fig. 1B, where C could be residual carbons. Fe and Ca might come from phosphatizing wastewater. Morphology of the precipitation was rhombohedral-like particles, which aggregated into flakes with size of 1–5 μ m (Fig. 1A). The morphology was probably due to preferred orientation of crystals after hydrothermal treatment, similar to the situation of CoAPO reported elsewhere (Anand et al., 2013).

3.2. Structural characteristics of ZnAPO n

Fig. 2 exhibits that diffraction of AlPO₄ was located at 6.0, 21.2, 22.4 and 25.9°. Thus the prepared sample obviously contained AlPO₄-5 (Kim et al., 2009) and AlPO₄ phases. Peaks of ZnAPOs at 9.5, 12.8, 16, 20.5, 25 and 31° were identical to reported ZnAPO-34 (Tusar et al., 1995). Diffraction patterns of ZnAPO₂~ZnAPO₇ were complicated, including main characteristic peaks of AlPO₄-5 and ZnAPO-34, together with other crystalline phases. For example, in ZnAPO₄, peaks of ZnAPO-34 were detected at 9.5, 16, 20.5 and 31°. The peaks of AlPO₄ could be recognized at 21 and 25°. In addition, there were some impurities detected. For example, crystalline boehmite and cordierite in ZnAPO₂; zinc phosphate (ZnPO₄) in ZnAPO₄~ZnAPO₇.

During the heating process, added p-BM was expected to first dissolve in acidic solution (pH 3.0) and then precipitate with Zn²⁺ as well as phosphate to form ZnAPO-34. While at a small Zn/(Zn + Al) ratio, e.g. ZnAPO₂, p-MB (13.6 g in 135 mL) could not be completely dissolved. Thus, the crystalline boehmite was still detected by XRD (Fig. 2). At a large Zn/(Zn + Al) ratio, i.e. ZnAPO₇, p-MB (1.8 g in 135 mL) could be all dissolved. Therefore, XRD only indicated ZnAPO-34, AlPO₄ and ZnPO₄ (where Al was not enough) (Fig. 2).

3.3. Mesoporous feature of ZnAPO n

ZnAPO n had a significant mesoporous feature, as showed by the small angle XRD pattern (Subrahmanyam et al., 2003) and TEM images (Zhao et al., 1998a). Small angle X-ray diffraction patterns of ZnAPOs (Fig. 3) exhibited characteristic mesoporous structure of ZnAPO-34 at ~0.7°. The samples ZnAPOs, ZnAPO₄ and minority of ZnAPO₂ showed the small angle XRD, which meant that they were amorphous and only the mesopores were uniformly organized. The peak at 0.7° was corresponding to a d-spacing of 14.1 nm in ZnAPO₄, similar to that of ZnAPOs. The mesoporous structure could be clearly observed in the TEM image of ZnAPOs (Fig. 1C). By

Table 1
Properties and selective catalytic activities of as-synthesized samples in oxidation of cyclohexane.

Sample	Utilization (%)		Zn:Al:P (digested)	Specific acidity (NH ₃ -TPD)		Catalytic activity (%)	Selectivity (%)	
	P	Zn		Total acid site (a.u.)	W/S		C1 ^a	C2 ^b
ZnAPOs	–	–	0.41:0.58:1	1	0.65/0.35	67.2	80.4	15.3
AlPO ₄	–	–	–	0.20	0.16/0.04	6.0	15.9	5.07
ZnAPO ₂	94.3	93.8	0.22:0.81:1	0.56	0.42/0.14	81.2	74.4	23.7
ZnAPO ₄	94.1	91.7	0.36:0.57:1	1.29	0.84/0.45	79.8	83.9	14.1
ZnAPO ₆	89.5	90.2	0.67:0.45:1	0.65	0.45/0.20	83.3	82.9	13.9
ZnAPO ₇	92.3	80.9	0.70:0.33:1	0.25	0.19/0.06	80.7	79.3	18.9

^a Selectivity to cyclohexanol.

^b Selectivity to cyclohexanone; W/S stands for weak and strong acid site amount ratio.

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