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Synthesis, stability and oxidative activity of polyoxometalates pillared anionic clays ZnAl-SiW$_{11}$ and ZnAl-SiW$_{11}$Z

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Abstract

Layered double hydrotalcites pillared by heteropolyoxometalates, ZnAl-SiW$_{11}$ and ZnAl-SiW$_{11}$Z (Z = Co^{2+}, Ni^{2+} and Cu^{2+}) have been synthesized by an anion-exchange reaction. The powder X-ray diffraction spectra and IR analysis show that the compounds are layered complexes with gallery heights of 0.99 nm and the anions entering the layer retain their Keggin structure. The decomposition temperatures of these complexes in air decrease in the following order: ZnAl-SiW$_{11}$Ni (620 K), ZnAl-SiW$_{11}$Co (614 K), ZnAl-SiW$_{11}$Cu (608 K), ZnAl-SiW$_{11}$ (602 K), ZnAl-NO$_3$ (563 K). The XRD patterns of the compounds treated in boiling solutions with different pH for 2 h reveal that the layer framework is stable in the pH range from 3.6 to 7.5. The synthesized materials, especially ZnAl-SiW$_{11}$Co, show high catalytic activities for the oxidation of benzaldehyde to benzoic acid using H$_2$O$_2$ in a liquid–solid biphase system.

Keywords: Heteropolyoxometalates; Pillared anionic clays; Synthesis; Stabilities; Oxidative activities

1. Introduction

Layered anionic clays are a class of layered materials of current interest because of their wide application in catalysis [1]. Recently, Pinnavaia et al. reported that $V_{10}O_{28}^{6-}$ pillared anionic clay was a microporous material with mesopores of around 2.0 nm in diameter and found that ZnAl-$V_{10}O_{28}$ was more active than the homogeneous catalyst for the photooxidation of isopropyl alcohol to acetone [2]. Xu et al. utilized polyoxometalates (POMs) pillared anionic clays for the alkylation of alkene and observed high activity and selectivity [3]. We also synthesized ZnAl-PW$_{11}$Z (Z = V, Ti and Cr) and proposed their orientational structures according to the result of ^{31}P MAS NMR [4]; their catalytic activities for the esterification of acetic acid with *n*-butanol were also studied [5]. Although the phenomenon of the intercalation of POMs has been established and several routes have been used for the synthesis of pillared materials [6,7], studies of their thermal stability and stability in acid/base solutions, which are important for catalysis, have rarely been reported [8]. Here, we report the synthesis, the thermal stability and the stability in acid/base solutions of new microporous materials ZnAl-SiW$_{11}$ and ZnAl-SiW$_{11}$Z (Z = Co^{2+}, Ni^{2+} and Cu^{2+}) by means of powder XRD, IR and DTA,

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and also their catalytic activities for the oxidation of benzaldehyde to benzoic acid in a liquid–solid biphase system.

2. Experimental

2.1. Reagents, apparatus and analytical measurements

All reagents used were of analytical grade. Powder XRD were taken on an automated D_{max}-IIIC X-ray diffractometer (nickel-filtered Cu K_α radiation). IR spectra were obtained on a PHA Centauri FT/IR spectrometer (KBr pellet). Differential thermal analysis (DTA) of the samples was carried out in a Perkin-Elmer DTA-1700; the heating schedule was 10 K/min in air from room temperature to 843 K. Elemental analyses were performed in an American Leeman Labs Inc. PLASMA-SPE ICP spectrometer.

2.2. Synthesis of ZnAl-NO_3 clay

The synthesis of ZnAl-NO_3 clay was carried out by a coprecipitation reaction of $Zn(NO_3)_2 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and NaOH in an aqueous solution according to a previously described method [4].

2.3. Synthesis of ZnAl-SiW_{11} and ZnAl-$SiW_{11}Z$ ($Z = Co^{2+}$, Ni^{2+} and Cu^{2+})

Potassium salts of $SiW_{11}O_{39}^{8-}$ and $SiW_{11}O_{39}Z(H_2O)^{6-}$ ($Z = Co^{2+}, Ni^{2+}$ and Cu^{2+}, abbreviated as SiW_{11} and $SiW_{11}Z$) were prepared according to the literature [9]. POMs intercalated clays were prepared by an ion-exchange reaction [4].

2.4. Measurements of thermal stability and acid / base stability

2.4.1. Thermal stability

After the samples were calcined at different temperatures for 2 h, XRD and IR spectra were then taken. The decomposition temperature of the layered structure was determined according to the XRD spectra; the stabilities of the layered anions were determined by IR spectroscopy.

2.4.2. Stability in acid / base solution

The samples were heated in boiling water at different pH for 2 h, then XRD and IR measurements were taken to determine the pH range in which they were stable.

2.5. Catalytic reaction

A 0.20 g catalyst sample, pretreated for 2 h at 423 K under a nitrogen flow, 5.0 ml benzaldehyde and 5.0 ml 30% H_2O_2 were added to a 100 ml three-necked flask, which was placed on a magnetic stirring heater. Under stirring and N_2 protection, the reaction was carried out at 323 K for 1.0 h, and then the product was separated. The catalytic activity was evaluated by the yield of benzoic acid.

3. Results and discussions

3.1. The structure of ZnAl-SiW_{11} and ZnAl-$SiW_{11}Z$

The layered structure of the synthesized materials was determined by XRD spectra. The

Table 1
Powder XRD parameters of the samples and the corresponding gallery heights

XRD parameter	Anion in the layer				
	NO_3^-	SiW_{11}	$SiW_{11}Co$	$SiW_{11}Ni$	$SiW_{11}Cu$
2θ (°)	9.92	6.08	6.02	6.06	6.06
Basal spacing (nm)	0.891	1.452	1.467	1.467	1.457
Gallery height (nm)	0.421	0.982	0.997	0.987	0.997

diffraction parameters and calculated gallery heights are listed in Table 1. The characteristic (001) harmonics of the clays appeared at 2θ of 9.6° indicates the clays basal spacing of 0.89 nm, which is in good agreement with the literature [10]. However, when polyoxoanions replace NO_3^-, the (001) harmonics of the synthesized materials shift ($2\theta = 6.0°$), showing that the corresponding basal spacings changed to 1.46 ± 0.01 nm. Gallery heights of 0.99 ± 0.01 nm were obtained if the thickness of the host sheet was subtracted from the basal spacings [10], indicating that the layers have been enlarged by the large polyoxoanions.

Similar gallery heights of the synthesized materials can be attributed to the nearly identical volumes of the lacunary and monosubstituted Keggin polyoxoanions.

Further evidence for the retention of Keggin polyoxoanions in the layer was provided by the IR spectra (Table 2). ZnAl-NO_3 has no absorption in the range 700–1100 cm^{-1}, where characteristic absorptions of polyoxoanions appear. After intercalation, the four groups of characteristic absorptions of vibrations of Si-O_d, W = O_d, W-O_b-W and W-O_c-W have no obvious change, showing the retention of the Keggin structure of the intercalated polyoxoanions. The results of elemental analyses indicate that the ratios between Zn and Al contents before and after the exchange are almost unaltered (2:1); the molar ratio of the three elements of the layered polyoxoanions was Si:W:Z = 1:11:1, which is further evidence for $SiW_{11}Z$ entering the galleries and maintaining the structural integrities.

Table 2
Characteristic IR data of the sample (in cm^{-1})

Sample	$\nu_{Si\text{-}Oa}$	$\nu_{W=Od}$	$\nu_{W\text{-}Ob\text{-}W}$	$\nu_{W\text{-}Oc\text{-}W}$
SiW_{11} [a]	1000	952	870	797, 725
ZnAl-SiW_{11}	997	945	897	792, 728
$SiW_{11}Co$ [a]	1001	950	907	794, 725
ZnAl-$SiW_{11}Co$	997	952	904	791, 717
$SiW_{11}Ni$ [a]	997	955	904	792, 731
ZnAl-$SiW_{11}Ni$	998	953	908	787, 715
$SiW_{11}Cu$ [a]	1009	954	902	795, 744
ZnAl-$SiW_{11}Cu$	999	950	901	798, 720

[a] Potassium salt

The new pillared materials can thus be represented by a simple structural model as shown in Fig. 1.

3.2. Thermal stabilities of the samples

Thermal stabilities of the samples were determined by means of DTA, XRD and IR. Fig. 2 shows DTA spectra of the samples. It can be seen that the clay precursor absorbs heat at 290 K and loses water at 437 K. The strong endothermic peaks at 540 K and 563 K represent, respectively, the dehydration of the layers and the loss of the layered NO_3^-, which indicate the destruction of the layered structure of the ZnAl-NO_3 clay. ZnAl-SiW_{11} and ZnAl-$SiW_{11}Z$ have similar DTA spectra, which all lose water at 313 K and the water loss peaks appear in the range from 478 to 483 K. The strong endother-

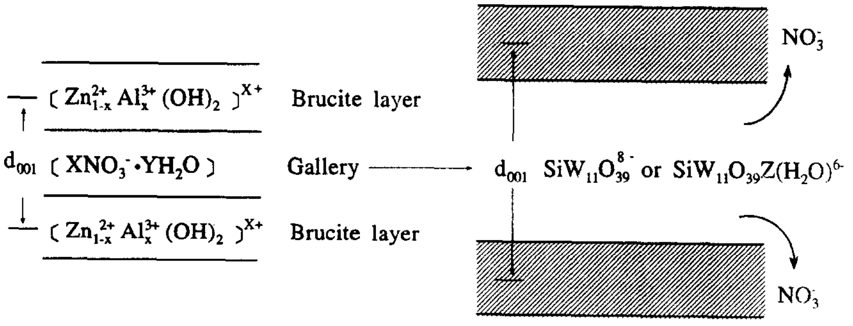

Fig. 1. Simple structural model for pillared clays.

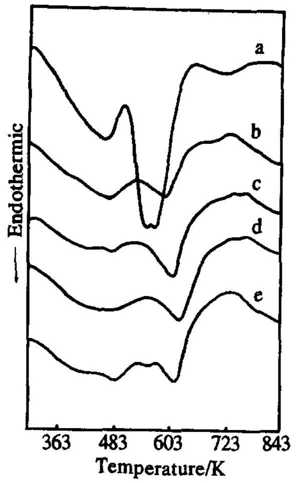

Fig. 2. DTA spectra of the samples: a, ZnAl-NO_3; b, ZnAl-SiW_{11}; c, ZnAl-SiW_{11}Co; d, ZnAl-SiW_{11}Ni; e, ZnAl-SiW_{11}Cu.

mic peaks from 601 to 620 K are indicative of the destruction of the pillared layered materials, which were caused by the strong interaction of the sheets and the pillared polyoxoanions at high temperatures. The decomposition temperatures decrease in the following order: ZnAl-SiW_{11}Ni (620 K), ZnAl-SiW_{11}Co (614 K), ZnAl-SiW_{11}Cu (608 K), ZnAl-SiW_{11} (602 K), ZnAl-NO_3 (563 K). This series indicates that the intercalated moieties have an effect on the stabilities of the pillared materials: the substituted Keggin polyanions pillared clays are more stable than the lacunary polyoxoanion pillared clays.

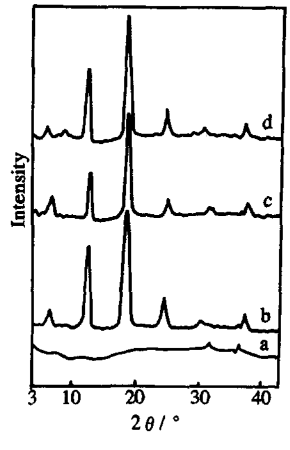

Fig. 3. Powder XRD spectra of the samples calcined at: a, 613 K; b, 478 K; c, 418 K; d, 298 K.

Figs. 3 and 4 illustrate the XRD and IR spectra of ZnAl-SiW_{11}Co which was heated in air at different temperatures for 2 h. There is no significant change in these spectra from room temperature to 478 K, indicating that the intercalated anions as well as the framework remain intact. For ZnAl-SiW_{11}Co heated up to 613 K, apparent changes can be noted in the XRD and IR spectra. The (001) reflection of XRD which was the characteristic peak of the pillared materials has disappeared; the flatting of fine absorption of IR spectrum also shows the decomposition of the pillared polyoxoanion.

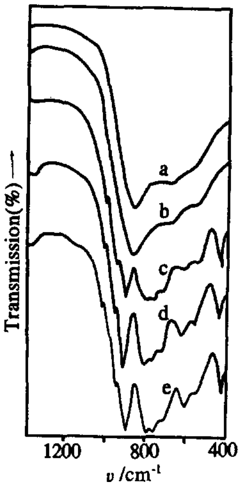

Fig. 4. IR spectra of the samples calcined at: a, 763 K; b, 613 K; c, 478 K; d, 418 K; e, 298 K.

3.3. *Stabilities of the samples in acid/base solution*

Different suspensions were obtained by adding ZnAl-SiW_{11}Co powder to different pH buffered aqueous solutions. The suspensions were heated to boiling (373 K) for 2 h. Then the samples were collected for XRD measurement. The results (Fig. 5) show that ZnAl-SiW_{11}Co is stable in the pH range of 3.6–7.5. When the pH was less than 3.5, the solid sample dissolved totally upon heating; when the pH was above

7.5, the IR spectra of the so-treated samples indicate that the pillared $SiW_{11}Co$ was destroyed. The conclusion that pillared materials in solution are stable in the pH range of 3.6–7.5, at least not destroyed in hot water for 2 h, is vital for the choice of catalytic reaction.

3.4. The catalytic activities for the oxidation of benzaldehyde

Our interest in POMs intercalated anionic clays is ultimately derived from the importance of POMs clays catalysis. Besides esterification [5], we were also interested in the oxidation aspect of these materials. We thus need an organic substrate that could be catalytically oxidized by oxidants with our catalysts at temperatures and pH values where gross decomposition was not prevalent. We chose benzaldehyde owing to the ease of detection of its oxidation product, benzoic acid. We note that oxidizing benzaldehyde is not especially challenging; however, we clearly demonstrated that some POMs pillared clays can be used in this oxidation reaction as catalysts.

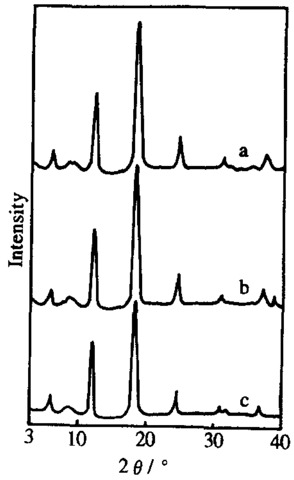

Fig. 5. Powder XRD spectra of $ZnAl\text{-}SiW_{11}Co$ after heating in solutions with different pH: a, heated in $NH_3\text{-}NH_4Cl$ solution ($pH = 7.5$); b, heated in HAc–NaAc solution ($pH = 3.6$); c, heated in distilled water.

Table 3
Catalysts and the corresponding yield of benzoic acid

Catalyst [a]	Yield of benzoic acid (wt%)	Catalyst [a]	Yield of benzoic acid (wt%)
$ZnAl\text{-}SiW_{11}Co$	73.2	$SiW_{11}Co$	43.9
$ZnAl\text{-}SiW_{11}Ni$	16.4	$SiW_{11}Ni$	12.2
$ZnAl\text{-}SiW_{11}Cu$	32.9	$SiW_{11}Cu$	34.9
$ZnAl\text{-}SiW_{11}$	11.8	SiW_{11}	52.6
$ZnAl\text{-}NO_3$	13.0		10.3

[a] Quantity of catalyst: 0.20 g.

The conversions of benzaldehyde to benzoic acid using 30% H_2O_2 and different catalysts are listed in Table 3.

From Table 3, it can be seen that new pillared anionic clays $ZnAl\text{-}SiW_{11}$ and $ZnAl\text{-}SiW_{11}Z$ show catalytic activities for the oxidation of benzaldehyde to benzoic acid in a liquid–solid biphase system. For $ZnAl\text{-}SiW_{11}Co$, the yield of benzoic acid is up to 73.2%. The catalytic activities of $ZnAl\text{-}SiW_{11}Ni$ and $ZnAl\text{-}SiW_{11}Cu$ are similar to that of the unintercalated polyoxoanions. The high catalytic activity of $ZnAl\text{-}SiW_{11}Co$ can be attributed to the easy variation of the oxidation number of cobalt [11], where the mechanism may be Co^{2+} oxidized to Co^{3+} by H_2O_2 and then benzaldehyde oxidized to benzoic acid by Co^{3+}. The same process is difficult for Cu^{2+} and Ni^{2+}. It thus can explain the low catalytic activities of $ZnAl\text{-}SiW_{11}Cu$ and $ZnAl\text{-}SiW_{11}Ni$. Further studies of oxidation reactions of other organic substrates and the evidence about the mechanism are still under investigation [12].

4. Conclusions

Polyoxoanions SiW_{11} and $SiW_{11}Z$ ($Z = Co^{2+}$, Ni^{2+}, and Cu^{2+}) can be intercalated into the layer of $ZnAl\text{-}NO_3$ clay via an ion-exchange reaction. The synthesized materials were characterized by XRD, IR and elemental analysis. The results show that the compounds are pillared complexes with gallery heights of 0.99 nm and the anions entering the layer retain their Keggin structure. The decomposition temperatures of these complexes in air determined by DTA and confirmed by XRD and IR, decrease in the following order: ZnAl-$SiW_{11}Ni$ (620 K), ZnAl-$SiW_{11}Co$ (614 K), ZnAl-$SiW_{11}Cu$ (608 K), ZnAl-SiW_{11} (602 K), ZnAl-NO_3 (563 K). The layer framework of the pillared clay is stable in the pH range of 3.6–7.5, at least in boiling water for 2 h. The pillared clays, especially ZnAl-$SiW_{11}Co$, show high catalytic activities for the oxidation of benzaldehyde to benzoic acid using H_2O_2 in a liquid–solid biphase system.

Acknowledgements

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