Mesoporous Silicoaluminum Pillared Clays with High Thermal Stability and Brønsted /Lewis Acidity by One-pot Synthesis

Chun Hui ZHOU∗, Xiao Nian LI, Dong Sheng TONG, Yi Fen ZHU, Zhong Hua GE

College of Chemical Engineering and Materials Science, Zhejiang University of Technology,
Hangzhou 310032

Abstract: Mesoporous silicoaluminum pillared clays have been synthesized by one-pot gallery-templated synthesis using organomontmorillonite, tetraethyl orthosilicate and alumina isopropoxide as precursor. According to the characterization by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), N_2 adsorption isotherms and pyridine adsorption infrared (IR) techniques, the synthetic silicoaluminum pillared clays possess regular porosity with high thermal stability up to 750 ℃ and Brønsted /Lewis acidity.

Keywords: Pillared clays, mesoporous materials, acidity, solid acid catalysts.

The intercalation of polynuclear hydroxy metal cations in smectites affords porous pillared clays which show great potential applications involving separations, adsorption and catalysis [1]. Though the range of pillared agents has been considerably enlarged since its invention, aluminum Keggion ions $[Al_{13}O_4 (OH)_{24}]^{7+}$ and silicon cations are still often used as pillaring species. Pinnavaia reported that introduction of silica into interlayers by ion exchange of swollen clays with silicon acetylacetonate cation Si $(acac)_3^+$, followed by hydrolysis. Calcination of resulting Si $(acac)_3^+$-exchanged clays resulted in the formation of monolayer siloxane chain between the layers with a maximum d_{001} value of 1.26 nm and BET surface area 200 m^2/g [2]. Ge *et al*. successfully synthesized Al-pillared clays with bimodal pore distribution by improved pillaring methods[3]. To date, the application of pillared layered clays is severely limited by their lower thermal stability (usually < 500℃), acidity and broad pore size distribution. Many previous studies suggested that the introduction of the second component to pillars can overcome such problems [4]. Zhao *et al*. reported the preparation of hydroxylsilico-aluminum pillared clays with increased acidity using mixed polynuclear hydroxy silica and alumina sol as pillaring agents [5]. But the pore size distribution and thermal stability is still unsatisfactory. Recently, silica pillared clays with well-defined mesopores have been successfully prepared by gallery-emplated synthesis method which is based on the intercalation of quaternary ammonium cations and neutral amines as templates to direct the interlamellar hydrolysis and condensation polymerization of neutral inorganic

precursor within the galleries of an ionic lamellar solid [6-8]. This novel technique offered an effective pathway of preparation of mixed oxides pillared clays with regular pores by post-synthesis techniques [9]. In the present paper, instead of tedious post-synthesis, the one-pot synthesis of silicoaluminum pillared clay materials with larger pores using gallery templated techniques is explored.

The synthesis procedure is as follows. The organic clay was prepared by ion-exchange reaction between sodium montmorillonite (source clays, from Ningan Zhejiang, China) and 0.1 mol·L^{-1} solution of cetylmethylammonium bromides as our previous work [10]. 2 g of organic clay was added to the solution of dodecyl amine (7.12 g). The mixture was stirred for 25 min. Then 60.0 g of tetraethyl orthosilicate (TEOS) and alumina isopropoxide (0.588 g) in benzene (11.6 mL) were added with vigorous stirring for 8 h at room temperature. After that, the solid was separated by filtration, aged and finally dried in air and then calcined at 540℃ in air for 4 h to removed the template and surfactant to yield silicoaluminum pillared clays (denoted SiAl-PILCs). The pore structure and surface acidity of SiAl-PILCs are characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), nitrogen adsorption-desorption, infra red (IR) techniques and probe acid-catalyzed alkylation reaction.

As shown in **Figure 1**, the basal spacing d_{001} of starting clay is 12.9 Å (2θ=7.24°), and after calcined at 500℃ the d_{001} value decreased to 9.86 Å (2θ=8.96°) which is approximately equal to the thickness 9.6 Å of each layer of montmorillonite (Philips X'Pert diffractometer, Cu Kα radiation). After the gallery-templated intercalation of Si and Al precursors followed by calcinations at 540℃, the d_{001} value of SiAl-PILCs increased to 34.5 Å (2θ=2.56°), which is greatly larger than that of pristine clay. Thus it has been confirmed that a certain Si-Al mixed oxide form is present within gallery. After calcinations at 600℃ and 700℃, the strong reflections of basal space kept well in PXRD patterns. More importantly, the SiAl-PILCs still remain layer structure with basal spacing of 31.7 Å (2θ= 2.78°) after calcined at 750℃, indicating the maintenance of pillared structures. After calcination at 800℃ the d_{001} diffraction peak can not be detected owing to completely layer collapsing. The results suggested that SiAl-PILCs show better thermal stability than that reported previously [4,5]. The shape of nitrogen adsorption-desorption isotherms (Mocromeritics ASAP 2010C) for SiAl-PILCs has a hysteresis loop, which belongs to type-Ⅳ isotherms, according to the BDDT classification and to the type B in Bores five types [11]. The results indicated that the open slit-shaped pores with parallel walls exists in SiAl-PILCs. The BET specific surface area of the SiAl-PILCs reaches 502 m^2/g, with an average pore diameter of 20 Å. If the dense silica-alumina phase completely filled the interlayer region, the high surface area would not be observed. This phenomena reveal that the structure of SiAl-PILCs by *in situ* self-assembly and pillaring have different pillars from those of PILCs by traditional synthetic method. The detailed mechanism is not clear and need to be investigated. Based on these facts, a new type of porous SiAl-PILCs was formed by one-pot silica-alumina intercalation and assembly.

The TGA curve (Shimadzu TG-50 thermal analyzer) of as-synthesized SiAl-PILCs sample revealed about 43.3% total weight loss on heating temperature ranges of 125-900 ℃, which can be divided into four main parts, as shown in **Figure 2**. The signal before

Figure 1 PXRD patterns of pristine clay (a-b) SiAl-PILCs (c-g)

Figure 2 TG-DTG curves of as-synthesized SiAl-PILCs sample
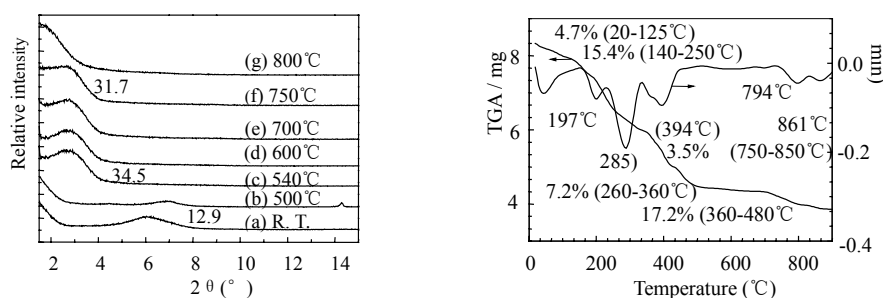
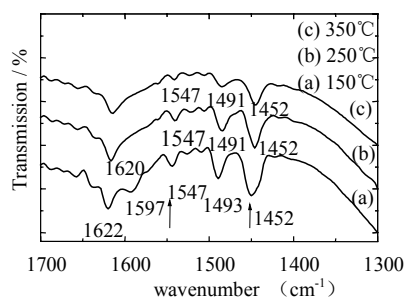**Figure 3** FT-IR spectra of pyridine adsorbed on samples at elevated temperature

Table 1 The acidity and catalysis of alkylation on samples

Catalysts	acid sites [a] (mmol/g)			Activity [b](%)	Selectivity (%)		
	Weak	Medium	Strong		4-TBC	3-TBC	3,5-DTBC
SiAl-PILCs	0.083	0.630	0.158	76.8	85.2	8.6	6.2
H-Clay	0.176	0.092	1.101	56.7	56.5	18.4	25.1

a) Determined by weight loss of ammonia (w_1)/ ammonia molecular weight /weight of catalyst sample (w_2).
b) 135℃; 8 h; TBA:CAT (molar ratio) = 2:1; solvent: *m*-xylene; catalysts: 220 mg; 3,5-DTBC: 3,5-di-*tert*-butyl catechol; 3-TBC: 3-*tert*-butyl catechol.

250℃ is attributed to the release of adsorbed water, the signal in the ranges of 260-360 ℃ attributed to the elimination and decomposition of neutral amine and C_{18} surfactant, the intensity of peak after 360℃ decreased slowly, due to desorption of organic species and dehydroxylation of silica and silicoaluminum within gallery.   The result showed that nano scale porous SiAl-PILCs with gallery height 23.9 Å (=34.5-9.6 Å) were obtained after calcination at 540℃. Up to 750℃, clay layer itself would dehydro- xylized, leading to the collapse of pillared structure.   The results are in good agreement with PXRD patterns, confirming the high thermal stability of SiAl-PILCs.

The acidity of SiAl-PILCs was characterized by adsorption of pyridine monitored by IR spectroscopy shown in **Figure 3** (Digilab FTS-2SPC). For calcined samples of SiAl-PILCs, the ring stretching frequencies characteristics of pyridine chemisorbed on Lewis acid sites (*ca* 1452 cm^{-1}) and on Brønsted acid sites (*ca* 1547 cm^{-1}) are obviously

observed.   Lewis pyridine sites is predominately more than BrØnsted sites at all elevated temperature.   The acidity of SiAl-PILCs was checked by ammonia adsorption TGA and probe acid catalyzed alkylation of catechol(CAT) with tertbutyl alcohol (TBA) to produce 4-*tert*-butylcatechol (4-TBC), as depicted in **Table 1**.   The total number of acid sites on SiAl-PILCs were less than H^+ exchanged clays (obtained by HCl exchanged pristine clay), but the SiAl-PILCs possess more medium acid sites than H-clay.   Over SiAl-PILCs catalyst the reaction showed the better conversion of CAT and better selectivity to 4-TBC than those of H-clay.   Compared with the H-clay, SiAl-PILCs possess larger mesopores than H-clays do (gallery height less than 5 Å) so that the efficiency of acidity is better than microporous H-clay, in which acid sites within gallery can not be penetrated by larger molecular like catechol (larger than 5 Å).   The meso-pores of SiAl-PILCs facilitate the acid catalysis, leading to better conversion and selectivity of 4-TBC.

In conclusion, the SiAl-PILCs was prepared through gallery-template methodology in one-pot.   Upon calcinations at 540℃ the hybrids exhibit a basal spacing 34.5 Å, gallery height 23.9 Å, and a BET surface area of 502 m^2/g and silt width 20 Å. Together with regular porosity the SiAl-PILCs offer high thermal stability up to 750℃ and BrØnsted/Lewis acidity, showing it can be used as environmentally friendly solid acid catalysts.

Acknowledgments

References

1. A. Vaccari, *Appl. Clay Sci.*, **1999**, *14*, 161.
2. T. J. Pinnavaia, *Science*，**1983**, *220*, 365.
3. Z. H Ge, T. J. Pinnavaia, *Chin. J. Catal.* (*Cuihua Xuebao*, (in Chinese)*)*, **1995**, *16*, 222.
4. A. Gil, M. L. Gandia, M. A. Vicente, *Catal. Rev. Sci. Eng.*, **2000**, *42*, 145.
5. D. Y. Zhao, Y. S. Yang, X. X. Guo, *Inorg. Chem.*, **1992**, *31*, 4727.
6. A. Galarneau, A. Barodawalla, T. J. Pinaavaia, *Nature*, **1995**, *375*, 529.
7. H. Y. Zhu, Z. Ding, C.Q. Lu, G. Q. Lu, *Appl. Clay Sci.*, **2002**, *20*(4-5), 165.
8. C. H. Zhou, Q. W. Li, Z. H. Ge, X. N. Li, Z. M. Ni, *Chem. J. Chin. Univ. (Gaodeng Xuexiao HuaXue Xuebao*, (in Chinese)*)*, **2003,**2*4*(12)**,** 1351.
9. M. Polverejan, Y. Liu, T. J. Pinnavaia, *Chem. Mater.*, **2002**, *14*(5), 2283.
10. C. H. Zhou, Z. H. Ge, X. N. Li, H. Q. Guo, J. Sun, *Chin. Chem. Lett.*, **2003,** *14*(12)**,**1285.
11. J. R. Anderson, K. C. Pratt, *Introduction to characterization and testing of catalysis*. Academic press, Australia, **1985**. p113.