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Incorporation of Chelated Cobalt Complexes and Polyoxocations of Aluminum in Montmorillonite

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The thermal stability of montmorillonites, expanded with solutions of $Co_3(H_2NCH_2CH_2O)_6]$-$(ClO_4)_3$, can be drastically increased by introducing, together with the Co trimer, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions that upon calcination in air at 500 °C form stable alumina clusters. Several synthetic routes to the preparation of these bipillared interlayered clays (bi-PILC) have been studied. Best results have been obtained by first ion-exchanging the clay charge compensating Na and Ca cations with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions followed by a second ion exchange step to replace some of the Al_{13} clusters in the intermediate Al−PILC with $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions. Elemental analysis together with powder XRD results indicate that PILC composition and pore height can be manipulated by washing the intermediate Al−PILC in order to hydrolyze the Al oligomers believed to occupy exchange sites on the clay silicate layers. Formation of Keggin ions seems to facilitate the back-exchange reaction with the Co trimer. Pillared materials with a Si/Co molar ratio between 38.4 and 128.0 and *d* spacing in the 1.40−1.75 nm range stable to 500 °C in air can be obtained in this way.

Introduction

The low-temperature (T < 20 °C) liquid-phase synthesis of certain fine chemicals can be catalyzed by microporous solid acids such as clays and zeolites.[1] Examples of C−C bond forming reactions catalyzed by clays include Diels−Alder,[2] Fridel−Craft,[3] and a variety of Michael addition reactions.[4−8] Catalytic activity and selectivity can be influenced by the choice of the cations used to charge compensate the negative layer charge on the clay silicate layers.[1] The yields of *N*-silyldihydropyridine from the direct addition of silyl ketene acetals to pyridine derivatives[9] depend on the clay interlamellar cations in the following manner: Fe(III) > Co(II) >Cu(II) > Zn(II) > Al(III) > Ni(II) > Sn(IV).[9] In addition, Fe−montmorillonite has a unique catalytic activity for the addition of silyl ketene to α,β-unsaturated imines,[4] and Al−montmorillonites are the catalysts of choice for several other Michael addition reactions.[4]

The use of clays such as montmorillonites to catalyze the synthesis of the aforementioned organic compounds offers advantages over traditional homogeneous catalysts that include easy catalyst recovery and, possibly, shape selectivity effects dictated by the microporous catalyst unique architecture. Problems associated with the handling of moisture sensitive homogeneous catalysts such as $TiCl_4$ and Ph_3CCl_4 are also avoided.[1] In another publication,[10] it was shown that montmorillonites, pillared with $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions in acetonitrile, lack the proper stability for high-temperature (T > 400 °C) applications. However, partial decomposition of the trimeric complex can be achieved while a 0.45 nm layer expansion is still maintained, indicating that these materials could be considered for low-temperature (T < 200 °C) applications.

It is the purpose of this paper to extend the stability of these Co−clays by introducing, together with the Co trimer, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions that on calcination at 500 °C form heat stable alumina clusters. As a result, the clay silicate layers are permanently open and therefore remain available to sorption and catalysis at temperatures as high as 500 °C.

Experimental Section

Pillared Interlayered Clays (PILC) Preparation. All PILC were prepared using a sample of bentolite-H, (Na−bentonite) obtained from the Southern Clay Products, Inc. of Gonzales, TX. The sample contains >90% of the clay mineral montmorillonite; quartz is the main impurity; its *d* spacing is 0.96 nm. Chemical analysis gave a unit cell composition of $[(Si_{8.0})(Al_{3.02}Mg_{0.50}Ca_{0.06}Fe_{0.18}Ti_{0.02}Na_{0.22})O_{20}(OH)_4]Na_{0.97}K_{0.01}$. This clay was expanded with $[Co_3(OC_2H_4NH_2)_6]^{3+}$ and $[Al_{13}O_4(OH)_{24}$-$(H_2O)_{12}]^{7+}$ ions using several synthesis procedures including the following: (1) secondary pillaring of Co−PILC with

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Table 1. Bi-PILC Elemental Analysis (in wt %) Results

sample	% Co	% C_{corr}	% N	% Si	% Al	% Na
1	0.72	0.34	0.34	22.7	13.7	
2	0.96	0.37	0.43	25.7	10.8	
3	0.36	0.12	0.21	21.9	12.5	
4	0.49	0.14	0.10	23.6	10.8	
10	0.58			25.6	14.6	
17	1.60			29.3	12.3	0.06
18	0.56	0.21	0.35	24.8	13.0	0.05

$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions (samples 1 and 2, Table 1); (2) secondary pillaring of Al_{13}−PILC with $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions, without washing (samples 3 and 10, Table 1) and with washing (samples 17,18, Table 1) the Al_{13}−PILC; and (3) one-step pillaring of montmorillonite with a mixture of chlorhydrol and $Co_3(H_2NCH_2CH_2O)_6](ClO_4)_3$ (sample 4, Table 1).

In all cases, 0.557−1.11 g of the $[Co_3(H_2NCH_2CH_2O)_6](ClO_4)_3$ salt (that is 0.40−0.80 mequiv/g of clay) was added by Soxhlet extraction to the reaction mixture over a 12 h period. The Co trimer has limited stability in hot aqueous solutions.[12] However, it is stable in acidic aqueous solutions at room temperature.[12] The pillaring reactions of montmorillonites with solutions of aluminum chlorhydrate (ACH) containing $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions (Rheis's chlorhydrol)[11] or with solutions of $Co_3(H_2NCH_2CH_2O)_6](ClO_4)_3$[10] have been discussed in detail elsewhere.

Elemental Analysis. Determination of metal content was performed by Applied Technical Services, Inc., in Marietta, GA, and Galbraith Laboratories, in Knoxville, TN, using atomic absorption and (ICP) atomic emission techniques. Amounts of trace metal (<0.01%) were not reported. Carbon, nitrogen, and halide analyses were performed by Atlantic Microlab, Inc., in Norcross, GA. Carbon and nitrogen analyses were obtained using combustion methods and reported to have an uncertainty of ±0.3 wt %. Quantitative analysis for ClO_4^- on the bipillared clay materials was accomplished using the procedure of Geilmann and Voight[13] as modified by Beckler.[14]

Powder X-ray Diffraction (XRD). Powder X-ray data was collected on a Scintag X1 diffractometer with unfiltered Cu Kα radiation, fixed divergence slits, and a Scintag Peltier cooled solid-state detector. A convergent slit width of 1 mm and a scatter slit width of 2 mm were employed for the beam source; a receiving slit width of 0.3 and scatter slit width of 0.5 mm were used for the detector. Data were analyzed using version 1.12 DMSNT software. Scans were run in continuous mode at a rate of 2°/min or less.

BET Surface Analysis. Nitrogen sorption isotherms obtained at liquid nitrogen temperature were collected using a volumetric technique on a Micromeritics ASAP 2010 adsorption instrument equipped with version 3.0 software. Prior to analysis, samples weighing from 0.1 to 0.3 g were outgassed in a vacuum at their calcination temperature for at least 16 h. Six points of BET surface area were calculated from nitrogen uptake at relative pressures ranging from 0.05 to 0.30.

Results and Discussion

Bi-PILC Synthesis. The results of elemental analyses for the bi-PILC under study are summarized in Table 1; elemental molar ratios are listed in Table 2. In these tables, carbon loadings have been corrected to account for the parent montmorillonite carbon impurities. The absence of perchlorate confirms that solvent occlusion in the bi-PILC samples did not occur.

Table 2. Bi-PILC Elemental Molar Ratio Data

sample	C/Co	C/N	N/Co	Si/Al	Si/Co	Al/Co
1	2.3	1.2	2.0	1.6	66.1	41.5
2	1.9	1.0	1.9	2.3	56.2	24.5
3	1.7	0.7	2.4	1.7	128.0	75.8
4	1.4	1.6	0.9	2.1	101.0	48.1
10				1.7	92.6	54.9
17				2.3	38.4	16.8
18	1.8	0.7	2.5	1.8	92.9	50.7
Bent-H				2.6		

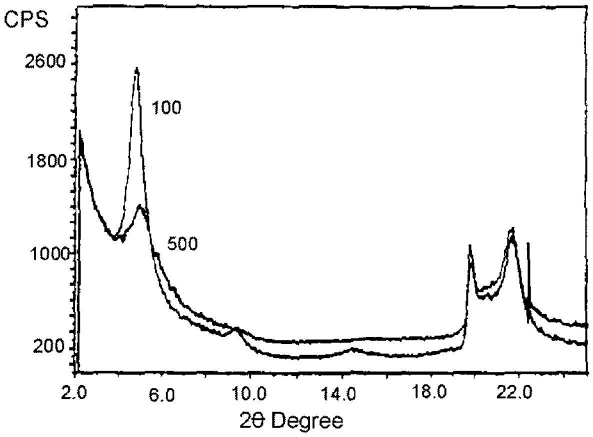

Figure 1. Powder XRD of bi-PILC sample 1 (Table 2), calcined at 100 and 500 °C, prepared by first introducing $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions into the clay silicate layers followed by addition of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions.

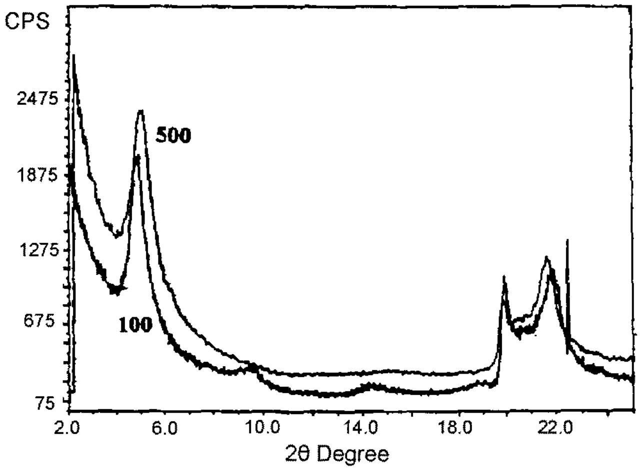

Figure 2. Powder XRD of bi-PILC sample 3 (Table 2), calcined at 100 and 500 °C, prepared by first introducing $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions into the clay silicate layers followed by addition of $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions.

The order and the manner of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ or $Co_3(H_2NCH_2CH_2O)_6]^{3+}$ addition seems to determine the resulting bi-PILC sample properties. If the trimer is added first, the bi-PILC obtained, after back-exchanging some of the Co complex with the Al_{13} cations, contained 0.72 wt % Co and exhibited, at 100 °C, a *d* spacing of 1.6 nm that drastically decreased in intensity at 500 °C (Figure 1). By inverting the order of complex addition, that is if the Keggin ions are added first, the bi-PILC obtained was found to contain 0.36−0.49 wt % Co. The powder XRD data for sample 3 clearly shows the Keggin ion to be the dominant pillar in the sample (Figure 2). In fact, the expanded clay exibited a sharp *d*(001) peak at 1.82 nm that decreased to 1.76 nm at 500 °C because of dehydroxylation of the Al_{13} cations; at 500 °C the sample surface area was 256 m²/g.

Co trimer concentrations in excess of 0.50 mequiv of trimer/g of clay were also used during synthesis. The intent was to maximize the amount of cobalt interca-

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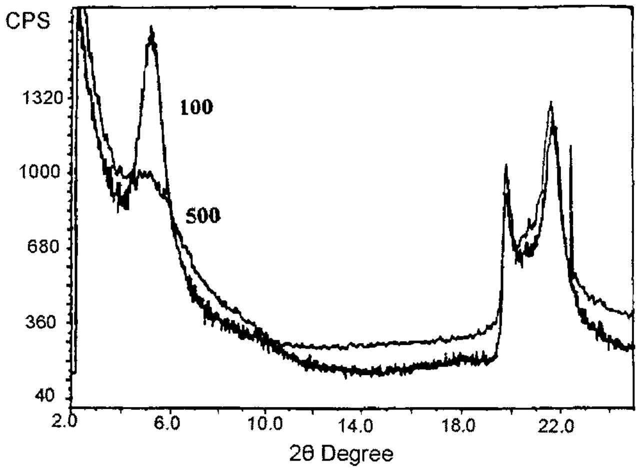

Figure 3. Powder XRD of bi-PILC sample 4 (Table 2), calcined at 100and 500 °C, prepared by introducing simultaneously $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions into the clay silicate layers.

lated while still retaining enough Al_{13} ions to ensure thermal stability at 500 °C. However, filtrates from these preparations were colored, indicating the presence of Co trimer in the bulk solution and that the desired ion exchange reaction did not go to completion. It appears that, at the synthesis condition used, the clay interlamellar space contains Al species (such as aluminum dimers, trimers, hexamers) that the cobalt complex cannot replace.

The simultaneous addition of ACH solution and Co trimer mixture produces a bi-PILC sample containing 0.49 wt % Co with the Keggin ion as the primary pillar (Figure 3). After drying, sample 4 possesses *d* spacing similar to sample 3, though the peak intensity is slightly lower. However this expanded structure is thermally unstable at 500 °C (Figure 3). The limited thermal stability is attributed to the low (0.00704 mol of Al_{13}/mol of Si) pillar density.[11] In Table 2, the N/Co molar ratios match what would be theoretically predicted for the cobalt trimer for every sample but sample 4. The cobalt complex does not appear to have survived the intercalation process intact when added to the ACH solution.

When preparing bi-PILC samples, the results in Tables 1 and 2 indicate that the Si/Co ratio increases from sample 1 (which introduces the trimer first in the synthesis) to sample 4 (which uses a simultaneous introduction of the two complexes) to sample 3 (which intercalates the Al_{13} ions prior to Co trimer addition).

Previous investigations[15−17] of hydrolysis in aqueous solutions of aluminum have revealed the existence of a complicated, pH-sensitive equilibrium among $Al(H_2O)_6{}^{3+}$, $[Al_2(OH)_2(OH_2)_4]^{4+}$, $[Al_3(OH)_4(OH_2)_9]^{5+}$, and the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. Furthermore, in another study,[11] it has been reported that initially, after the pillaring reaction is completed, the Keggin ion is not present and that it is formed in situ only after extensive washing of the pillared product with water. Thus the bi-PILC procedure that intercalates Al ions prior to Co trimer addition could be affected by the extent to which the intercalated Al species are hydrolyzed.

Table 3. Effects of Washing the Al−PILC Intermediate on Cobalt Incorporation in the Al_{13}−PILC Microporous Structure

no.	(mL of H_2O/g)	d(001), nm at 100 °C	d(001), nm at 500 °C	Si/Al	Si/Co
17	500	1.62	1.43	2.3	38.4
19	400	1.77	1.67		
20	300	1.72	1.64		
18	200	1.95	1.72	1.8	92.9
3	0	1.82	1.76	1.7	128.0

Effects of Al−PILC Hydrolysis on Co Addition. The effects of an intermediate washing step prior to back-exchange the Al species with the Co trimer are shown in Table 3. The various *d* spacing reduction on calcination shown in this table is attributed to the Al complex contraction due to dehydroxylation and to the rearrangement of the alumina particles in the pillars formed.

Washing with only 200 mL of H_2O/g of clay yielded a bi-PILC with only 0.56% Co and an XRD pattern typical of montmorillonites expanded with Al_{13} cations. In another work,[10] it was shown that a Al_{13}−PILC sample containing 0.0102 mol of Al_{13}/mol of Si collapsed upon calcination at 500 °C, while one containing 0.0121 mol of Al_{13}/mol of Si did not. Using the results in Table 2, the moles of Keggin ions in the washed bi-PILC sample can be estimated from the following identity

$$\text{mol of Al}_{13}\text{/mol of Si} = [\text{mol of Al}_{\text{PILC}}\text{/mol of Si}_{\text{PILC}} - \text{mol of Al}_{\text{clay}}\text{/mol of Si}_{\text{clay}}]/13 = 0.0131\ \text{mol of Al}_{13}\text{/mol of Si}$$

well in excess of the minimum pillar density required for stability at 500 °C. As a result, like the unwashed Al−PILC, the least-washed sample exhibits a layer expansion of 1.95 nm that decreases to 1.72 nm after calcination in air at 500 °C.

In contrast, in the most washed (500 mL of H_2O/g of clay) Al−PILC intermediate, the secondary exchange reaction introduced 1.6 wt % Co in the bi-PILC structure (sample 17, Table 1). The nearly colorless filtrates observed when preparing these samples indicated that the majority of the cobalt in solution was intercalated. Bi−PILC samples obtained in this way were observed to possess a 1.6 nm *d* spacing at 100 °C. This *d*(001) peak was seen in Co−PILC expanded only with Co trimer.[10] This layer expansion is not consistent with the incorporation of the pristine Keggin ions (0.82 nm in diameter) and suggests instead the possible presence of one of its hydrolysis products.[11,15−17] Calcination at 500 °C leaves an expanded clay with with a *d* spacing of 1.43 nm, indicative of the presence of an Al-pillar different from the dehydroxylated Keggin ion; see Table 3.

Shifting the aluminum equilibrium in the direction of the Keggin ion favors the ion exchange process that replaces Al species with the Co complex; see Table 2. As a result, not enough extraframework aluminum is left in the clay interlamellar space to produce a heat stable microspace. In fact, the results in Table 2 indicate that there are 0.00386 mol of Al_{13}/mol of Si, much less

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than the 0.0121 mol of Al_{13}/mol of Si required for thermal stability.

After the washing step, the Si/Al ratio of the bi-PILC increases and the Si/Co ratio decreases significantly (Table 3). The Na content in the two samples is identical and it is known that repeated washing of Al−PILC samples with water does not affect the amount of intercalated aluminum.[11] Therefore, the large decrease in aluminum content between the two samples is attributed to an ion exchange of interlamellar Al species with Co trimer cations. This replacement of Al with Co explains the large Si/Co molar ratio reduction reported in Table 3. In fact, the Si/Co ratio of the bi-PILC decreases to 38.4 from 92.9 after extensive washing of the intermediate Al−PILC, indicating that the more prevalent the Keggin ions are, the more Co is intercalated during the back-exchange reaction.

Summary and Conclusions

Synthesis conditions can be manipulated to generate bi-PILC materials containing different Co concentration and thermal stability. Best results have been obtained by exchanging the montmorillonite charge-compensating Na and Ca ions with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions and then by back-exchanging some of the clay extra-framework aluminum species with $[Co_3(OC_2H_4NH_2)_6]^{3+}$ ions. Thermally stable (to 500 °C) Co-containing microporous Al_{13}−PILC with $d(001) = 1.7$ nm and surface area of 256 m^2/g has been obtained in this way.

It appears that the clay interlamellar space contains Keggin ions and other Al species (such as aluminum dimers, trimers, hexamers) that the Co trimer cannot easily replace. One possible explanation is based on the different charge density that the different ions on the clay interlamellar space have. The charge per aluminum in the Keggin species is +0.54 and increases to +3 as and the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ion decomposes to $[Al_3(OH)_4(OH_2)_9]^{5+}$, $[Al_2(OH)_2(OH_2)_4]^{4+}$, and finally to $Al(H_2O)_6{}^{3+}$. The charge per Co could be +1 or +0.66 if the Co trimer ions were intercalating as the trivalent or as the divalent Co complex, respectively. XPS results[10] have shown that the air-dried (at 100 °C) Co−PILC, prepared from the trivalent Co trimer, contained Co(II) species, indicating that, during the pillaring reaction, the Co trimer was reduced to its divalent analogue. Since the smaller aluminum polyoxocations have higher per-metal charge than either the Keggin ion or the Co complex, in the intermediate Al−PILC Keggin ions will be preferentially replaced by Co trimer ions.

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