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A COMPARISON OF THE THERMAL STABILITIES Ga_{13}, $GaAl_{12}$ AND Al_{13}-PILLARED CLAY MINERALS

Susan M. BRADLEY and Ronald A. KYDD *

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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A comparison has been made of the thermal stabilities of pillared clays prepared through the intercalation of Ga_{13}, Al_{13} and $GaAl_{12}$ polyoxocations by STx-1 montmorillonite. The stabilities, as revealed through differential thermal analyses, powder X-ray diffraction and surface area studies, were found to increase in the order Ga_{13}-PILC < Al_{13}-PILC < $GaAl_{12}$-PILC. This is in agreement with the order of the stabilities of these polyoxocations in solution, which also correlates with their relative degrees of symmetry, as previously revealed by NMR studies.

Keywords: Pillared clays, PILC, polyoxocations, tridecamers, catalysis, Al_{13}, $GaAl_{12}$, Ga_{13}

1. Introduction

Recently, a great deal of interest has been seen in the area of pillar interlayered clay minerals (PILC's), in terms of their potential as acid catalysts. The predominant polymeric species which has been employed as a pillar in this regard has been the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polyoxocation [1–3]. With this species, d_{001} basal spacings of ca. 18.5–19.0 Å have been achieved at room temperature, and surface areas of between approximately 200 and 300 m^2/g have been the most commonly reported [4–8], however values as high as 500 m^2/g have also been seen [9,10]. The exact values seemingly depend largely on the method of preparation of the intercalant solution (i.e. concentration, rate of addition of base, OH/Al ratio, aging time etc...), as well as the type of phyllosilicate used, its cation exchange capacity and on the degree of loading of the pillars. The reported thermal stabilities of these different PILC's have also varied widely, but unfortunately none have been adequate for surviving the high temperature treatments required to regenerate poisoned catalysts. This has led to a search for new pillaring agents with the potential for different types of catalytic activity, and higher thermal stabilities. We have recently characterized two new pillaring agents [11–13], the $GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and the $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polyoxocations (i.e. Ga_{13} and $GaAl_{12}$), which are analogous in structure to the Al_{13} species. Solution NMR of these ions [11,13] and solid state MAS NMR of their sulfate salts [14] have revealed, however, that they vary in terms of their degrees of symmetry, increasing in the order $Ga_{13} < Al_{13} < GaAl_{12}$. The increased symmetry of the latter species probably is a result of there being a better fit achieved by having the larger gallium in the central tetrahedral position. These species differ widely in terms of their stabilities in solution, also increasing in the order $Ga_{13} \ll Al_{13} \ll GaAl_{12}$ [13]. This has led to the important question of whether or not this stability sequence also will be maintained in the PILC's, with the $GaAl_{12}$ pillars perhaps affording a more stable structure. Studies of the thermal stabilities of PILC's utilizing these ions as intercalants were therefore undertaken.

2. Experimental

The Al_{13}, Ga_{13} and $GaAl_{12}$ solutions (which also are known to contain partially hydrolysed monomers) were prepared using $AlCl_3.6H_2O$ (Aldrich 99%) and $CaCl_3$ (Aldrich, 99.9^+%) solutions, the concentrations of which were determined by precipitation with 8-hydroxyquinoline. The Al_{13} ion was prepared by hydrolysing an $AlCl_3$ solution (ca. 0.1M) with 0.2M NaOH to an OH/Al mole ratio of 2.20. This solution was then heated at 70 ° C for 30 minutes, after which it was cooled. The Ga_{13} solution was prepared by hydrolysing a 0.1M $GaCl_3$ solution with 0.2M NaOH to an OH/Ga ratio of 2.0. This solution was then aged at 50 ° C for approximately 30 minutes, then quickly cooled in an ice bath. The $GaAl_{12}$ solution was prepared by hydrolysing a solution containing $GaCl_3$ and $AlCl_3$ mixed in a 1 : 12 mole ratio to an OH/M ratio of 2.20, and then refluxing at the boiling point (96 ° C at our altitude) for approximately 2 days. This step is required to ensure that any of the Al_{13} species which may have been formed upon hydrolysis is converted to the $GaAl_{12}$ species [13]. A suspension of < 2 μm STx-1 montmorillonite (Source Clay Minerals Repository, University of Missouri), which had been acid washed (2M HCl), neutralized and exchanged three times with 4M NaCl was used. This clay mineral has a cation exchange capacity of approximately 84 meq/100 g, and a surface area of about 83.3 m^2/g [15]. The hydrolysed metal solutions were added dropwise to vigorously stirred suspensions (ca. 1% w/w) of the Na-STx-1, to solution loadings of ca. 10 meq metal/g STx-1. The suspensions were then washed with distilled water by centrifugation until testing with silver nitrate revealed the supernatant fluid to be negative for chloride ions.

Differential thermal analyses of the PILC's were undertaken using a Shimadzu DT-2B thermal analyzer. Analyses were measured relative to an α-Al_2O_3 reference, and were carried out up to 1000 ° C.

X-ray powder diffraction patterns were recorded with a Norelco powder diffractometer, using FeK_α radiation. Oriented thin films of the three samples deposited on quartz slides were heated for 12 hour periods at incrementally

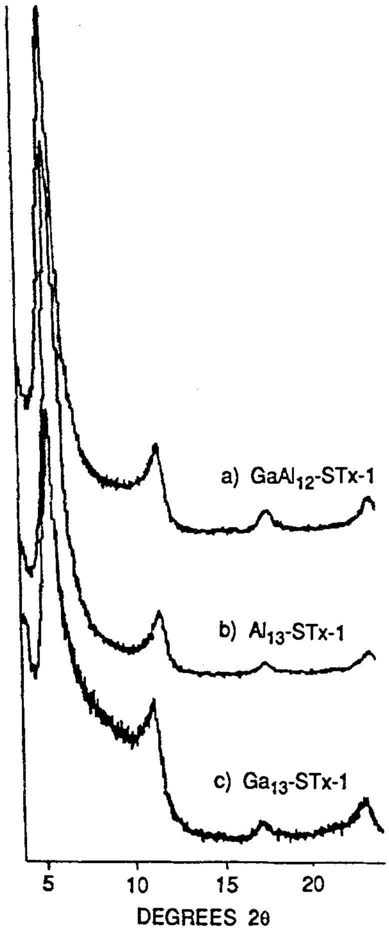

Fig. 1. Powder X-ray diffraction patterns (4–24° 2Θ) for the a) $GaAl_{12}$, b) Al_{13} and c) Ga_{13}-PILC's at room temperature.

increasing temperatures, and powder patterns were run from 4–24° 2Θ employing step widths of 0.02° 2Θ and scan times of 4 seconds.

Surface areas of samples also heated at incrementally increasing temperatures were determined using a Micromeritics model 2200 surface area analyzer.

3. Results

A comparison of the powder XRD patterns of the Ga_{13}, Al_{13} and $GaAl_{12}$ M-PILC's studied reveals d_{001} basal spacings of 19.38, 18.82 and 18.78 Å respectively, at room temperature. In all cases, the d_{001} peaks were quite sharp (fig. 1), indicating a relatively homogeneous pillar height. It should be noted that in the case of the $GaAl_{12}$ species, it is extremely easy to produce a very crystalline product, whereas in the case of Ga_{13} the time and temperature at which the solution is allowed to age before it is used for intercalation must be carefully controlled. The Al_{13} species is intermediate in this regard. These observations reflect the fact that all are metastable species in solution. The kinetics of the gallium system are the most rapid, and result very quickly in the precipitation of the $GaO(OH).H_2O$ phase. The hydrolysed Al solutions also eventually age to the point of having the $Al(OH)_3$ phase precipitate out, as does the $GaAl_{12}$ system, however the kinetics are vey much slower in the latter case. The surface areas of the samples after treatment at 200 ° C were found to increase in the order $Ga_{13} < Al_{13} < GaAl_{12}$ (vide infra). This could be an indication of there having been a greater number of tridecamers intercalated in the case of the $GaAl_{12}$-PILC, whereas the Al_{13}- and Ga_{13}-PILC's may have incorporated increasing amounts of partially hydrolysed monomers, as well as any other species (e.g. dimers, trimers etc...) which would have been present in the hydrolysed solutions. As such smaller species would be of lower charge, a greater number would have to be intercalated to achieve charge balance, and would therefore result in lower surface areas. This is in accord with NMR studies which found the hydrolysed $GaAl_{12}$ solutions to contain a larger amount of the tridecameric species than the Al_{13} solutions [13]. The hydrolysed Al and Ga solutions appeared to be comparable in the amounts of the M_{13} species formed, however the much lower stability of the Ga_{13} species could readily have resulted in a larger degree of dissociation [12].

Differential thermal analyses carried out for the three PILC's revealed no marked differences (e.g. no shifts in the positions of the peaks). In each case there was a strong endotherm occurring at ca. 140 ° C, corresponding to dehydration, another endotherm at ca. 620 ° C which probably is due to dehydroxylation, and finally an exotherm at ca. 870 ° C, which corresponds to recrystallization. In comparison, the untreated STx-1 is known to exhibit endotherms at 185 ° C (dehydration), 720 ° C (dehydroxylation), and exotherms at 1055, 1065 and 1135 ° C [15].

A comparison of the d_{001} basal spacings of the three species as a function of temperature is given in fig. 2. At 700 ° C, the d_{001} spacing of the $GaAl_{12}$-PILC had decreased to 85% of its value at room temperature, the Al_{13}-PILC to 82%, and the Ga_{13} to 81%. These variations are minor enough to suggest no apparent differences in thermal stabilities. A comparison of the widths of the d_{001} peaks of the powder diffraction patterns, however, (fig. 3) reveal the $GaAl_{12}$-PILC to have the most crystalline system after heating to 700 ° C. Unfortunately, as the thin films had a tendency to crack somewhat at high temperatures, the intensities of these peaks, relative to their intensities at room temperature, are not directly comparable.

The most dramatic result, however, is seen in the comparison of the surface areas (fig. 4). All of the samples exhibited marked drops in surface area between 500 and 700 ° C, as would be expected from the position of the dehydroxylation

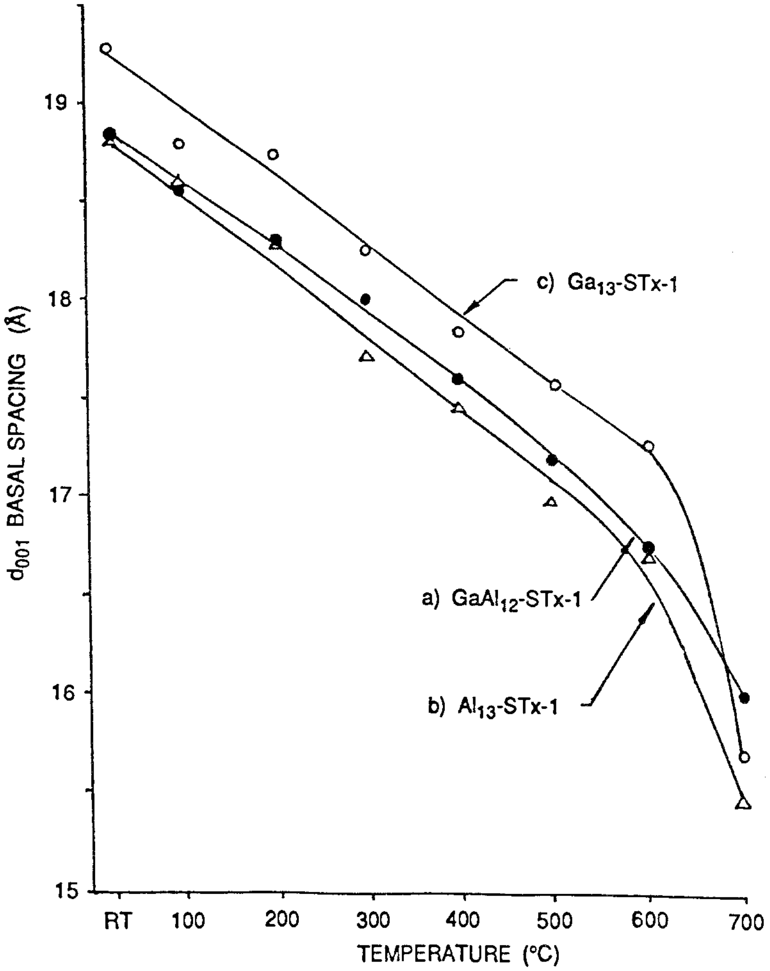

Fig. 2. X-ray diffraction d_{001} basal spacings (Å) as a function of increasing temperature (°C) for the a) $GaAl_{12}$, b) Al_{13} and c) Ga_{13}-PILC's.

endotherm in the DTA's. The fact that the Al_{13}-PILC is more stable than the Ga_{13}-PILC is obvious from the observation that on heating to 700 °C, the surface area of the Al_{13} species had dropped to 47% of its value at 200 °C (from 240 to 114 m^2/g) while that of the Ga_{13}-PILC had fallen to 37% (from 231 to 86 m^2/g). In marked contrast to either of these cases, however, the surface area of the $GaAl_{12}$-PILC was observed to drop to only 71% of its value at 200 °C (from 277 to 196 m^2/g). Thus the $GaAl_{12}$ pillared clay was observed to have a much higher thermal stability than the 'traditional' Al_{13} pillared clays. Clearly, the incorporation of a larger metal (gallium) into the central tetrahedral position has resulted in a significantly more stable structure.

In the case of Ga-PILC's, another group has looked at the surface areas from 200 to 500 °C, and has reported increases in surface area with an increase in

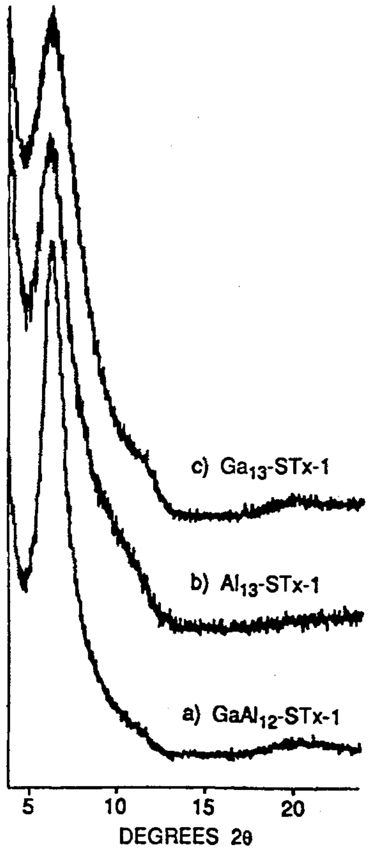

Fig. 3. Powder X-ray diffraction patterns (4–24° 2Θ) for the a) $GaAl_{12}$, b) Al_{13} and c) Ga_{13}-PILC's after heating to 700 °C.

temperature [16]. We saw no indication of this, and can offer no explanation for the difference. The degree of loss of surface area in each of the cases we examined was definitely a function of the length of time the sample was held at each temperature. This could explain different values being observed by different groups, but does not offer any explanation for a possible increase in surface area. These results clearly indicate an increased thermal stability in the order Ga_{13}-PILC < Al_{13}-PILC < $GaAl_{12}$-PILC, which correlates with the order observed for the polyoxocations in solution.

4. Conclusions

A comparison of the d_{001} basal spacings, peak widths, and surface areas of the pillared clays studied has revealed that the thermal stabilities increase in the order Ga_{13}-PILC < Al_{13}-PILC < $GaAl_{12}$-PILC. The surface area retained by the

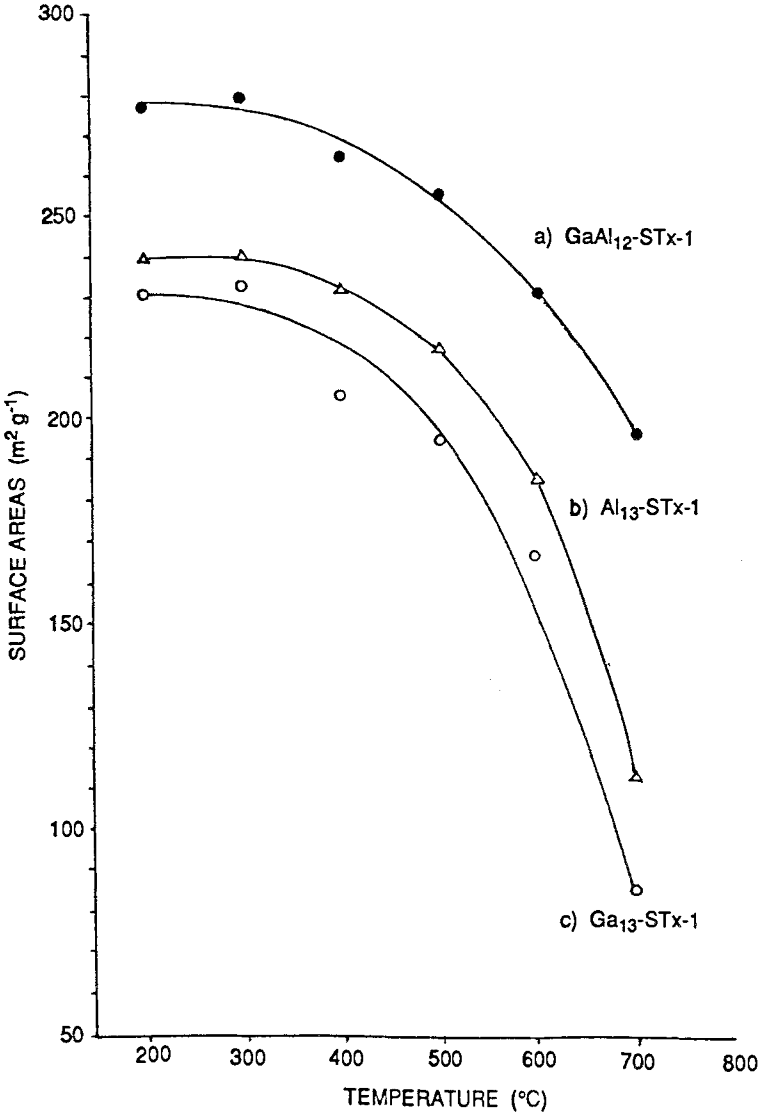

Fig. 4. Surface areas (m^2/g) as a function of incrementally increasing temperature (° C) for the a) $GaAl_{12}$, b) Al_{13} and c) Ga_{13}-PILC's.

$GaAl_{12}$-pillared clay after prolonged heating, culminating with 12 hours at 700 ° C, is substantially higher than that of the more common Al_{13}-pillared clay. This is in agreement with the stabilities of the respective ions in solution (e.g. the lifetimes of these metastable species in solution), which also correlates with their relative degrees of symmetry. This is an important observation in terms of the potential industrial applications of these species.

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