

## Aluminium–Gallium Pillared Montmorillonite with High Thermal Stability

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The preparation and characterization of a novel pillared clay material (montmorillonite pillared with aluminium–gallium) which shows a particularly high thermal stability is described.

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Layered clays, such as montmorillonite, are the focus of considerable current attention in the field of shape-selective catalysis. By intercalating in organic polyoxy cations (*e.g.* Al, Cr, Zr)<sup>1–6</sup> between the silicate layers, it is possible to obtain materials with permanent porosity and high surface area. The

activity and selectivity of these materials make them suitable for use as cracking catalysts. However, they show little resistance to the high-temperature thermal treatment which is used to regenerate catalysts after their deactivation by coke formation. By using Al and Ga polyoxy cations in the pillaring

**Table 1** Percentage of Ga and basal spacing (Å) in samples

Sample	mequiv. Ga (%)		g Ga per 100 g clay	$d/\text{Å}$	
	Pillaring solution	Pillars			
				25 °C	500 °C
A	0	0	0	18.9	17.5
B	25	70.4	9.3	18.7	17.7
C	50	87.4	16.2	19.6	17.6
D	75	98.3	28.2	19.9	17.7
E	100	100	23.9	19.2	17.7

**Table 2** Specific surface area and area percentage of the samples treated at 700 °C

Sample	$S_{\text{BET}}^a/\text{m}^2 \text{g}^{-1}$		Area at 700 °C (%)	
	25 °C	700 °C		
			PILC, 25 °C	M-Na
A	384	117	30	134
B	288	204	71	234
C	227	161	71	185
D	136	65	48	75
E	107	45	42	51

<sup>a</sup> By Brunauer–Emmett–Teller method.

of montmorillonite, we have obtained a novel pillared clay (PILC) whose thermal stability is greater than PILC materials synthesized previously, making it more resistant to thermal processes.

The clay used was the Na-exchanged form of a natural Spanish bentonite with a specific surface area of  $87 \text{ m}^2 \text{ g}^{-1}$  and a cation exchange capacity of 59 mequiv. per 100 g clay. Its basal spacing of  $15.4 \text{ Å}$  decreased to  $9.9 \text{ Å}$  when the sample was heated at  $500 \text{ °C}$ . The Al–Ga–PILC was synthesized by adding solutions of the pillaring agent to specific volumes of the clay slurry so as to adjust the (aluminium + gallium) contents to the desired values. The resulting system used in all the experiments had 20 mequiv. (Al + Ga) per g clay. The different Ga/Al ratios used are shown in the first column of Table 1. For comparison, samples with pillars of only hydroxyaluminium (A) and hydroxygallium (E) are also considered. The method of preparation of the pillaring agent was the same as described by Shabtai *et al.*<sup>7</sup> Appropriate volumes of  $0.5 \text{ mol dm}^{-3}$  NaOH were gradually added to stirred  $0.2 \text{ mol dm}^{-3}$   $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} + \text{GaCl}_3$  solutions with the desired Ga/Al proportion in order to obtain an OH/(Al + Ga) ratio of 2.0. The resulting solutions were then aged at  $60 \text{ °C}$  for 2 h before being used in the pillaring process. The second column of Table 1 gives the proportion of Ga/Al intercalated in the pillared product. These values were obtained by

chemical analysis of the Ga remaining in the liquid after centrifugation of the reaction mixture. In corroboration of the former values the solid pillared samples were analysed by EDXRA (energy dispersive X-ray analysis). These results are shown in the third column of Table 1, expressed as g of Ga incorporated in each 100 g of original clay.

Expansion of the montmorillonite basal spacing by exchange of oligomeric species was followed by X-ray powder diffraction of thin layers of the clay on glass slides (Table 1). The values of  $d(001)$  varied between  $18.7$  and  $19.9 \text{ Å}$  with the different Ga/Al percentages. After heating at  $500 \text{ °C}$  the basal spacing was still  $17.5$ – $17.7 \text{ Å}$ . All the diffractograms of Al–Ga–montmorillonite samples show a second peak between  $10.6$  and  $11.5 \text{ Å}$ , which is shifted to  $9.9 \text{ Å}$  at  $500 \text{ °C}$ . This could be due to a fraction of the clay that remains unpillared.

Table 2 shows the evolution of the specific surface area ( $S_{\text{BET}}$ ) for untreated PILC samples and PILC samples treated for 2 h at  $700 \text{ °C}$ . These data were obtained from  $\text{N}_2$  adsorption–desorption isotherms at liquid nitrogen temperature. Table 2 also summarizes the area percentages of the samples treated at  $700 \text{ °C}$  with respect to the untreated PILC samples and, in the last column, with respect to the original homoionic–montmorillonite (M-Na).

Samples B and C, with 70.4 and 87.4% of Ga respectively (Table 1), still have large surface areas ( $204$  and  $161 \text{ m}^2 \text{ g}^{-1}$ ) at  $700 \text{ °C}$ . These areas represent 71% of their untreated values in both cases, and 234 and 185% with respect to homoionic montmorillonite (M-Na). In contrast, when samples A and E, whose pillars were only Al or Ga, were heated to  $700 \text{ °C}$ , their surface area decreased considerably ( $117$  and  $45 \text{ m}^2 \text{ g}^{-1}$ ). In the case of sample E (100% Ga) the surface area reached values even lower than that of the homoionic montmorillonite sample. Sample D, with 98.3% Ga, shows a similar behaviour to the sample E.

In conclusion, pillaring with mixtures of Al and Ga in determined proportions allows us to obtain PILC-materials whose thermal stability is higher than that observed for Al-pillared clays.

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