

COMMENTS ON “ENHANCED THERMAL STABILITY OF Al-PILLARED SMECTITES MODIFIED WITH Ce AND La” BY J.L. VALVERDE, P. CAÑIZARES, M.R. SUN KOU, AND C.B. MOLINA

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Valverde *et al.* (2000) recently reported on the preparation and characterization of Al-pillared smectites modified with Ce and La. Pillaring of clays with Al polyoxocations (Keggin type Al_{13}) and a large variety of other complexing cations has been reported many times since the seventies. McCauley (1988) described in a patent the preparation of thermally stable pillared clays with large basal spacings of ~ 28 Å, followed by publications by Sterte (1991a, 1991b) and Booiij and coworkers (Booiij *et al.*, 1996a, 1996b). These authors used hydrothermally treated or refluxed solutions containing the Al polyoxocation and the rare earth elements in the form of their chloride salts. The presence of cerium or lanthanum seems to promote polymerization of the Al polyoxocation. Until now however, nobody has been able to assess the structure of the newly formed pillaring molecules. Although the interlayer spacing is about twice that of the normal Al-pillared clay, chemical analyses indicate smaller amounts of Ce and La than expected from polymerization of the Al polymer alone. Several other studies on the combination of Al pillars with Ce or La resulted in the formation of pillared clays with basal spacings characteristic of Al-pillared clays. However, catalytic activity is enhanced owing to Ce or La (*e.g.*, González *et al.*, 1992; Mendioroz *et al.*, 1993; Trillo *et al.*, 1993).

Unfortunately, Valverde and coworkers (Valverde *et al.*, 2000) missed most of the important publications on the thermally stable large-pore pillared clays based on Al pillars modified by Ce or La. The basal spacings reported by Valverde *et al.* (2000) are in a similar range to those reported by others for Al-pillared smectites (Kloprogge, 1998 and references therein), but ~ 6 – 7 Å smaller than those reported for the Al and rare-earth element (Al/REE) large-pore pillared smectites (McCauley, 1988; Sterte, 1991a, 1991b; Booiij *et al.*, 1996a, 1996b). This indicates that rare earth elements do not form an integral part of the pillars within the interlayer. Although the surface areas are in the order of what is expected for a pillared clay, the micropore volume is significantly lower as, for example, observed for Al-pillared montmorillonite SWy-1 (Klo-

progge *et al.*, 1994). However, their micropore volume is much higher than that of large-pore Al/REE pillared clays in which no micropores are present at all because the average pore diameter is ~ 60 – 70 Å (Booiij *et al.*, 1996b). The relatively low micropore volume can probably be explained by the incorporation of a relatively large amount of Ce or La in the interlayer between the pillars during the synthesis of the pillared clays where initial REE/Al ratios of ≤ 1.8 were maintained. Although the thermal stability of these pillared clays is enhanced, the access to the catalytically active sites in the pillared clays may be severely hindered. However, Valverde *et al.* (2000) did not report any catalytic testing on their materials.

Valverde *et al.* (2000) also reported on the infrared spectra of their pillared clays after calcination at various temperatures for 2 h. These spectra are quite different from those reported in other studies. Teagarden *et al.* (1981) and Kloprogge *et al.* (1992) reported the infrared spectra of the Al_{13} -sulphate salt with OH-stretching and bending modes of H_2O at ~ 3247 and ~ 1640 cm^{-1} , Al-OH stretching mode at ~ 3440 cm^{-1} , and the Al-O mode at ~ 713 cm^{-1} . Michot *et al.* (1993) described the infrared spectrum of the Al polyoxocation in solution with OH-stretching modes at ~ 3438 and ~ 3180 cm^{-1} ; OH-bending modes at ~ 1640 (H_2O), ~ 1085 , and ~ 979 cm^{-1} , and other OH-modes at ~ 772 , ~ 695 , ~ 582 , and ~ 530 cm^{-1} . In addition Kloprogge and Frost (1998) studied the structural changes of this salt by infrared emission spectroscopy. Kloprogge and coworkers (Kloprogge and Frost, 1999; Kloprogge *et al.*, 1999) also studied the thermal transformations of Al-pillared montmorillonite, saponite, hectorite, and beidellite by applying infrared emission spectroscopy. They observed that upon exchange of smectite with the Al polyoxocation, new infrared Al-OH and Al- H_2O OH-stretching modes became visible at ~ 3682 and ~ 3538 cm^{-1} . Brydon and Kodama (1966) described the formation of new OH-stretching bands at 3700 and 3480 cm^{-1} for Al-pillared montmorillonite, which disappeared after heating to 450 and 590°C. Similar bands were observed by Goh and Huang (1986) at 3695 and 3570 cm^{-1} . Chevalier *et al.* (1994) reported

for Al-pillared saponite a new band in the OH-stretching region at 3594–3597 cm^{-1} , which they interpreted as new OH configurations created by the pillaring process comparable to the band observed by Ocelli and Finseth (1986) for H-bonded OH groups in pillared hectorite. These bands however are not observed by Valverde *et al.* (2000). Upon transformation of Al_{13} , the Al-OH stretching band was not observed above 400°C. The Al-H₂O OH-stretching band was replaced by bands at ~3574 and ~3505 cm^{-1} , indicating structural rearrangement within the Al_{13} . Although the band intensities strongly diminished, they remain observable at 800°C, suggesting that the pillar retains some OH groups and incompletely converted to aluminum-oxide. This observation is supported by emanation thermal analysis of Al-pillared montmorillonite (Balek *et al.*, 1998), which showed a minor band at ~500°C for the calcined sample.

Below 1750 cm^{-1} , the Al_{13} -exchanged montmorillonite displays bands at 642, 1008, 1321, 1402, and 1512 cm^{-1} (Kloprogge *et al.*, 1999). The 1512- cm^{-1} band was not observable at ~500°C, followed by the loss of the 1402, 1321, and 1008- cm^{-1} bands above 600°C. The 642- cm^{-1} band diminished in intensity but was observable at 800°C. At 700°C, an additional band was observed at 722 cm^{-1} indicating the formation of an Al-O bond. Tichit *et al.* (1988) observed that exchange with Al_{13} had no effect on the tetrahedral sheet of the montmorillonite based primarily on the absence of changes in the 1125- cm^{-1} (Si-O^{apical} stretching mode), the 1035- cm^{-1} (combined stretching and bending modes Si-O^{basal}), and 935- cm^{-1} (Al-OH) bands. A slight shift of the 710- cm^{-1} band towards 735 cm^{-1} was the only change in the infrared spectrum. Valverde *et al.* (2000) however reported a broadening of the Si-O band at 1047 cm^{-1} , which they ascribed to the formation of Si-O-Al bonds. These authors did not observe the formation of a new Al-O band at ~722 cm^{-1} owing to the conversion of the Al polyoxocation to its oxide equivalent as indicated by Tichit *et al.* (1988) and by Kloprogge *et al.* (1999).

In conclusion, the publication by Valverde *et al.* (2000), although interesting, failed to adequately review the relevant literature on the application of rare-earth element modified Al-pillared clays and the effects on the thermal stability and pore structure. Their contribution also reports poor quality infrared spectra without proper interpretation. Also, the interpretations are different from the infrared spectra reported in many other publications.

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