
Use of Competitive Ion Exchange for Intercalation of Montmorillonite with Hydroxy-Aluminum Species

F. Figueras, Z. Klapysa, P. Massiani, Z. Mountassir, D. Tichit, F. Fajula, C. Gueguen, J. Bousquet and A. Auroux

Laboratoire de Chimie Organique Physique et Chimie Appliquées UA 418 du CNRS, ENSCM, 8 rue de l'Ecole Normale, 34075 Montpellier Cedex 2, France
(Centre de Recherches ELF, Solaize, 69360 St. Symphorien d'Ozon, France
Institut de Recherches sur la Catalyse, CNRS, 2 av. A. Einstein 69626 Villeurbanne, France

Abstract: Three montmorillonite samples, from Wyoming (particle size $<0.2 \mu\text{m}$, 4.6 wt. % Fe_2O_3), Greece ($<14 \mu\text{m}$, 6.5 wt. % Fe_2O_3), and Poland (0.5 wt. % Fe_2O_3 , two fractions $<2 \mu\text{m}$ and 2–10 μm) were intercalated with hydroxy-Al species. The amount of hydroxy-Al cations exchanged by the clays depended on the particle size: it decreased from 31 wt. % Al_2O_3 for 0.2 μm in size to 22.6 wt. % for $>2 \mu\text{m}$. The X-ray powder diffraction (XRD) pattern showed that most of the material was not intercalated after refluxing at 80°C for 2 hr; several redispersions of the pillared clay in hot water were required to obtain a single sharp XRD line at 18.6 Å. The diffusion of the Al cations therefore limited the cation-exchange process. The addition of NH_4^+ to the pillaring solution decreased the amount of Al fixed by the clay from 31 (no NH_4^+) to 26 wt. % ($\text{NH}_4^+/\text{Al} = 10$), but increased slightly the microporous volume of the resulting pillared material from 0.13 to 0.14 ml/g. The competition between NH_4^+ and Al-hydroxy cations for ion-exchange sites forced the Al species into the interlayer space and increased the homogeneity of the resulting pillared material. The influence of particle size on the amount of Al exchanged was then reduced. After calcination in air at 700°C the pillared Wyoming clay retained a microporous volume of 0.09 ml/g if no NH_4^+ was added, compared with 0.11 ml/g for a NH_4^+/Al ratio of 10. The Fe content of the clay affected the thermal stability of pillared clays at 800°C : for two samples prepared by competitive ion exchange ($\text{NH}_4^+/\text{Al} = 10$) the microporous volume increased from 0.06 ml/g for 6.4 wt. % Fe_2O_3 to 0.08 ml/g for 0.5 wt. % Fe_2O_3 . The acidity of the pillared clay was determined by calorimetric adsorption of ammonia at 150°C , on samples calcined at 500°C . Pillared montmorillonite prepared using noncompetitive intercalation showed a weak acid strength: most sites adsorbed ammonia with an enthalpy of 65 kJ/mole. The intercalation of the same original clay using competitive ion exchange yielded a solid that possessed both weak (heat = 60 kJ/mole) and strong (120 kJ/mole) acid sites. Competitive ion exchange appears to be a simple means of preparation of large quantities of pillared clays of reasonable thermal stability and higher acidity than those obtained by conventional methods.

Key Words: Competitive ion exchange • Hydroxy-Al • Intercalation • Montmorillonite • Pillared clays • Thermal stability • X-ray powder diffraction

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