

BOOK REVIEW

Pillared Clays, R. Burch, ed., *Catalysis Today*, Vol. 2, nos. 2-3, 185-366, 1988, Elsevier, Amsterdam, \$86.50, soft-bound. ISSN 0920-5861.

Pillared clays are smectites in which some of the charge-balancing cations of the interlamellar space have been exchanged with positively charged polymeric hydroxy-cations. Upon dehydroxylation, these polymeric species transform into the corresponding oxidic forms, the pillars. The clay layers are therefore propped apart, exposing the internal surface to all kinds of adsorbates. Pillars of different natures have been investigated, mainly those which contain Al, Zr, Cr, Fe, and Ti as the metal element. These intercalation compounds, due to the size and distribution of the pillars, form a 'bidimensional' porous system in which large molecules can diffuse and, eventually, react on proton sites created by the pillaring process. The main incentive for studying these interlayered pillared clays (PILCs) has come from the catalysts manufacturers and petroleum companies who, in order to treat heavy crude oils, are searching for porous catalytic systems having pores larger than those of the known synthetic zeolite molecular sieves used in fluid cracking catalysts.

This issue of *Catalysis Today*, edited by R. Burch, is the only book presently available dealing exclusively with these new types of solids, their preparation, characterization, and application in heterogeneous catalysis. It is divided into 14 chapters. The first chapter, by D. E. W. Vaughan, gives a historical review of his pioneering work and some perspective of pillared clays. Chapter 2, by C. J. B. Mott, is a brief introduction to the structure of clay minerals and the classification of swelling clays (namely those that can be pillared). Some insight is also given for the determination of their surface charge density. The next two chapters consider the pillaring solutions. S. L. Jones (Chapter 3) examines the properties and solution chemistry of Al and Zr pillaring species, and J. Sterte (Chapter 4) is chiefly concerned with the effect of temperature on the formation, shape, and properties of the resulting PILCs.

The next four chapters describe specific pillared clay systems. Chapter 5, by G. J. J. Bartley, is devoted to zirconium-pillared clays, and Chapter 6, by M. S. Zhou and T. J. Pinnavaia, to chromium PILCs. Iron-pillared clays and iron oxide-iron sulphide pillared clays are handled by S. Yamanaoka and M. Hattori (Chapter 7) and C. I. Warburton (Chapter 8). These four chapters yield information, to various degrees of detail, on the influence of several preparation parameters, on the structure and/or thermal stability of PILCs, and on the adsorption capacities for a few organics. They also provide catalytic results, to illustrate the potential of PILCs as catalysts. In particular, the iron sulphide interlayered clays are specifically envisaged as possible sulfur traps.

In Chapter 9, J. J. Fripiat discusses the nature and structure

of the Al species in Al-pillared clays in the light of magic angle spinning-nuclear magnetic resonance (MAS-NMR) results, and gives partial answers to questions on the structural modifications and cross-linking between the pillars and the clay layers which occur on calcination. Chapter 10, by E. Kikuchi and T. Matsuda, is a brief review on the adsorption capacities and catalytic activities, mainly, of Al and Zr pillared clays.

M. L. Occelli and R. J. Rennard, in Chapter 11, report on the effect of using pillared clays as cracking agents or as metal-support components in composite catalysts for the hydro-treatment of vacuum gas-oil feedstocks. The relationship between acidity, stability, and catalytic activity of various types of PILCs is briefly summarized in Chapter 12 by He Ming-Yuan, Liu Zhonghui, and Min Enze. In Chapter 13, M. L. Occelli compares the activities for gas-oil cracking of delaminated Al-pillared hectorite, Al-pillared bentonite, noncrystalline silica-alumina, and synthetic zeolite H-1 in terms of structural, textural, and acid properties. W. Jones, in the last chapter, provides additional information on the nature of the Al pillars, their link with the clay layers, and their distribution based on observations made with various techniques, including pore volume and surface measurements, neutron diffraction, MAS-NMR, and infrared spectroscopy.

To date, the principal area of application in which pillared clays have been investigated has been heterogeneous catalysis and, more precisely, for the reasons recalled earlier, the hydro-treatment of heavy crude oils. Such catalysts quickly revealed their weaknesses, which are basically of two types: the poor stability of the proton acidity at operational or regeneration temperatures, and the moderate thermal resistance of the clay structure itself. Even if the former limitation can be resolved through possible new preparation methods or appropriate treatments, the second one is inherent to all layered silicates and will be more difficult to overcome. Perhaps the future of pillared clays in catalytic applications (provided that the criteria for making industrial catalysts at competitive prices as put forward by D. E. W. Vaughan are met) will be restricted to processes which do not require simultaneously high reaction temperature and strong acidity and stability of the catalyst. Such processes might, e.g., include the synthesis of fine chemicals and mild oxidation. Other areas of potential uses of such materials should be considered, such as separation processes, chromatography, and, perhaps, electronic (semi-)conductors.

This book should be in the library of those who are working in the field of PILCs. To newcomers, it will constitute an invaluable source of references on the subject and provide a good picture of the state of the art and a basis for reflections for new developments.

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