Review of the Diffusion of Water and Pyridine in the Interlayer Space of Montmorillonite: Relevance to Kinetics of Catalytic Reactions in Clays

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Abstract: With the current interest in the use of transition metal-exchanged phyllosilicates as catalysts for novel organic syntheses, investigations into the factors which affect the movement of reactant, product, and solvent molecules into and out of their interlamellar region are of considerable importance. Mixed organic-water intercalates of a Wyoming montmorillonite, exemplified by the Na-montmorillonite-pyridine-water system which can form four different intercalates exhibiting basal spacing of 29.3, 23.3, 19.4, and 14.8 Å depending on the pyridine: water ratio, have been used as a model system. X-ray and neutron diffraction and quasielastic neutron scattering data relating to the interconversion of interlayer species indicate that access to and exit from the interlayer space is hindered at high partial pressures of water by a water-film diffusion barrier in the interparticulate voids which exist between the aggregated silicate layers. At lower water vapor pressures the rate-limiting step for interconversion from one intercalate to another is the rate of transport of reagents and products to and from the clay particles. Under conditions where these rates are fixed, the rate-limiting step is the rate of diffusion of the pyridine molecule in the lower-spacing intercalate. Processes which involve a change in basal spacing do not necessarily proceed via a single discrete step, but are also affected by the amount of water made available to the system. In organic reactions catalyzed in the interlamellar space of various cation-exchanged montmorillonites (e.g., the conversion of alk-l-enes to di-2,2′-alkyl ethers and the reaction of alcohols to form ethers), rate-determining steps similar to those found above are likely to be operative. In particular, for reactions carried out in the liquid phase, where mass transport is facile and where phase-transfer problems are avoided, such reactions are likely to be diffusion controlled.

Key Words: Catalysis • Diffusion • Interlayer space • Kinetics • Montmorillonite • Pyridine • Water

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