

Structural, Catalytic, and Intercalation  
Chemistry of Clay Minerals

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Chemical processes involving clay minerals are of vital importance in such fields as petroleum engineering, refining, waste disposal, and the paper industry.[1] Despite the importance of clay minerals, only recently with the advent of new and improved spectroscopic techniques, has the complex chemistry of clay minerals begun to be understood. The present study was undertaken in an effort to understand more fully three aspects of clay chemistry. These three areas are: 1) the oxidation-reduction reactions of structural iron in high iron containing clays; 2) the use of clay minerals as supports for catalytic reactions; and 3) the effect of intercalation on the electronic structure of transition metal complexes.

Ballet and coworkers[2] have determined that the 1:1 clay mineral greenalite is highly two dimensional in regards to its magnetic properties. They determined that the iron atoms within the plane of the clay crystallite order ferromagnetically at 24K, and then adjacent sheets order antiferromagnetically at lower temperatures. The magnetic properties of a series of lepidomelanites with structural  $\text{Fe}^{2+}$  ranging from 95 to 7 percent of the total iron, indicate that the ferromagnetic character of this clay is directly related to the  $\text{Fe}^{2+}$  content. The value of  $(\text{XT})_{\text{max}}$  varies linearly with percent  $\text{Fe}^{2+}$  suggesting that the oxidation of  $\text{Fe}^{2+}$  ions in the clay layers proceeds from the edges of the crystallites inward, as contrasted with an oxidation that occurs randomly throughout each layer.

The use of clay minerals as supports for transition metal catalysts has been receiving much attention in the last decade.[3] Cation exchanged Cu(II)-clays with various amine ligands were found to catalyze the oxidative coupling of 2,6-dimethylphenol, leading to the quinone dimer or the polyphenylene oxide polymer, depending on the reaction conditions. The reaction rate is dependent on the phenol's ability to diffuse into the interlamellar region of the clay as determined by X-ray diffraction and  $\text{O}_2$  uptake experiments

Ferrocene can be intercalated and oxidized via electron transfer by the layered material  $\text{FeOCl}$ .[4] Clay minerals with exchangeable cations have been found to oxidize and intercalate a variety of ferrocene monomers and dimers. Dimers such as biferrocene and bis(fulvalene)diiron are intercalated into the clay as the mixed valent monocations. The clay environment seems to have no effect on the electron transfer rate of biferrocene and bis(fulvalene)diiron as judged by  $^{57}\text{Fe}$  Mössbauer spectroscopy. The biferricenium-clay sample has an outer quadrupole-split doublet of 2.15 mm/sec and an inner doublet of 0.49 mm/sec. This compares to 2.12 mm/sec and 0.38 mm/sec for biferricenium  $^+\text{I}_3^-$ . [5] The bis(fulvalene)diiron clay sample has a quadrupole splitting of 1.77 mm/sec as compared to 1.76 mm/sec for bis(fulvalene)diiron  $^+\text{I}_5^-$ . From X-ray diffraction data and orientation studies using EPR, it is suggested that the bis(fulvalene)diiron molecule is intercalated into the clay so that the fulvalene planes lie perpendicular to the clay layers.

References

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