JOURNAL OF MATERIALS SCIENCE 31 (1996) 1255–1259

Intercalation of kaolinite under hydrothermal conditions

R. K. VEMPATI*, M. Y. A. MOLLAH‡, G. R. REDDY, D. L. COCKE
Gill Chair of Analytical Chemistry, Lamar University, Beaumont TX 77710, USA
H. V. LAUER Jr‡
Lockhead Science and Engineering Co., Houston, TX 77058, USA

Intercalation of kaolinite with dimethylsulphoxide (DMSO) was carried out under hydrothermal conditions using a Parr bomb. The intercalated complex has been characterized by X-ray diffraction (XRD), Fourier transform–infrared spectroscopy (FT–IR) and thermogravimetric analysis techniques. It was found that the intercalation reaction is completed in 20 min and a high yield, ~90%, of kaolinite/DMSO intercalate was obtained. An expansion of the original *c*-axis spacing of 0.714 nm in kaolinite to 1·124 nm, as a result of incorporation of DMSO molecules into the kaolinite interlayers, has been observed by XRD studies. FT–IR analyses of the intercalated complex have established the nature of interactions between the host structures and the incoming DMSO molecules. The hydrothermal method of intercalation developed in this study can also be used for other systems.

1. Introduction

The phenomenon of intercalation refers to chemical incorporation of a foreign molecule into the structural moiety of a crystalline substance. Intercalation is a reversible process and may involve (i) exchange of cations from interlayer, (ii) adsorption of polar molecules through ion–dipole interactions, (iii) hydrogen bonding, and (iv) protonation. The kaolinite group of minerals have been intercalated by a variety of polar compounds because these complex materials possess unique rheological, surface and structural properties. These modified clays have wide applications as catalysts, catalyst supports, adsorbents, ion exchangers, fillers, etc. [1].

The layered structure of kaolinite consists of silica tetrahedral [SiO_4] units stacked together with alumina octahedral [AlO_6] units. In kaolinite mineral, the sheets of silica tetrahedral units share a common oxygen plane with one of the alumina octahedral surface. The layers are held together by hydrogen bonds between the oxygens in one layer and the hydroxyl groups in the next layer [2]. The hydrogen bonding between adjacent layers prevents expansion (swelling) of kaolinite beyond its basal spacing of 0.714 nm. However, this basal spacing can be expanded by incorporating polar organic compounds under different experimental conditions. The extent of interlayer spacing depends upon the size and arrangement of the incoming molecules. Dimethylsulphoxide (DMSO), formamide, hydrazine, potassium acetate and urea are known to intercalate into kaolinite directly from either the liquid or the melt (acetamide) or concentrated aqueous solution (>10 M) [3–6]. Nitrobenzene, acetonitrile, glycol, and long-chain alkyl amines have also been intercalated by displacement reactions in which a previously intercalated compound was substituted by the compound of interest [7]. Acetone has been incorporated into the interlamellar space of kaolinite by displacement reactions [3]. Other compounds which have been intercalated into kaolinite include dimethylselenoxide [8], *N*-methylformamide [9], salts of fatty acids [10], hydrazine [11, 12], pyridine *N*-oxide [3], alkali halides [13], pyridine [14], etc. In a recent review article, Bruce and O'Hare [15] have compiled a large number of inorganic intercalation compounds and discussed their physico-chemical properties. Table I shows a list of compounds with varying dipole moments and the basal spacings of kaolinite intercalates.

However, a considerable amount of information is available in the literature on the structure and spectroscopic properties of kaolinite/DMSO complex. A number of techniques, e.g. X-ray diffraction (XRD) [3, 8, 10, 12, 19–21], infrared (IR) [4, 8, 10, 22–24], solid-state nuclear magnetic resonance (NMR) (^{29}Si, ^{27}Al and ^{13}C) [11, 19, 25], neutron diffraction [19], attenuated total reflectance [8] and Raman spectroscopy [12] have been used to monitor the progress of intercalation and characterization of the orientation of the intercalated molecules into the kaolinite

---

* Author to whom all correspondence should be addressed.
‡Visiting Professor, Department of Chemistry, Dhaka University, Bangladesh.

TABLE I Basal spacing of kaolinite intercalates obtained after treating with compounds having varying dipole moments

Serial no.	Compound	Basal spacing, [3] $d(001)$ (nm)	Dipole moment (Debye Unit)
1	Formamide	1.012	3.71 [16]
2	*N*-methylformamide	1.070	3.83 [16]
3	Dimethylformamide	1.212	3.82 [16]
4	Acetamide	1.090	3.76 [16]
5	*N*-methylacetamide	1.130	3.73 [16]
6	Dimethylacetamide	1.230	3.81 [16]
7	Pyridine *N*-oxide	1.252	4.28 [18]
8	Acetone	1.118	–
9	Dimethylsulphoxide	1.183	4.31 [17]

interlayer. The intercalation of kaolinite by these compounds was generally accomplished after prolonged contact, sometimes over a period of many days, with the substrate at ambient as well as elevated temperatures.

The present study was undertaken to re-investigate the intercalation of DMSO into kaolinite under hydrothermal conditions in a closed system using a Parr bomb. The primary objectives of this work were to (i) find reaction conditions to increase the rate of synthesis of the kaolinite/DMSO complex, (ii) increase the yield of the intercalation reaction, and (iii) analyse the resultant complexes using X-ray diffraction (XRD), Fourier transform–infrared spectroscopy (FT–IR) and thermogravimetric analysis (TGA) techniques to gain a better understanding of the mechanism of such an intercalation process.

2. Experimental procedure

2.1. Materials

Kaolinite was obtained from the Ward's Natural Science Establishment, Inc., 46E 0995, kaolinite (China clay) powdered, Twiggs County, GA, USA. Analytical grade dimethyl sulphoxide (DMSO) (Fisher Chemical, USA) and methyl alcohol (99%, Aldrich Chemical Company Inc., USA) were used.

2.2. Synthesis of the DMSO/kaolinite intercalate

The DMSO/kaolinite intercalates were synthesized at constant temperature and pressure using a Parr bomb (Parr Instrument Company, IL, USA). In the Parr Bomb, 10 ml DMSO was added to 1 g kaolinite. The Parr bomb was tightly closed and placed in an oven at 423 K for a definite period of time. After a given time period, the Parr bomb was removed from the oven and immediately cooled under tap water. Subsequently, the sample was filtered using a Whatman no. 42 filter paper. The residue was washed two or three times with methyl alcohol to remove excess DMSO. The clay was air-dried for 24 h. The dried samples were ground with a mortar and pestle and stored in a glass vial for analysis.

3. Characterization

3.1. XRD

XRD analyses were carried out using a CuK_α radiation (35 kV and 25 mA) on a Scintag XDS 2000 diffractometer equipped with a graphite monochromator. The sample was filled into a circular hollow aluminum holder. The XRD scans were run at 0.05° steps, and with a 1 s counting time, or 10 000 counts, whichever came first.

3.2. FT–IR

Diffuse reflectance–infrared spectroscopy of the powdered sample was recorded using a Perkin–Elmer 2000 FT–IR instrument. After mixing 10 mg of the samples with 300 mg FT–IR-grade KBr, the mixture was filled into a hollow steel holder. The samples were scanned 25 times in the region 4000–450 cm^{-1} and then averaged. The average spectrum was then corrected using the reflectivity spectrum of KBr powder run under identical conditions. The band positions were determined by fitting the Kubelka–Munk function.

3.4. TGA

Thermogravimetric analysis of intercalated samples was performed using a Dupont 990 thermal analyser. Dry helium was used as a stripping gas and the sample was heated at the rate of 0.5 °C min^{-1}. The sample was heated from ambient to ~1273 K.

4. Results and discussion

4.1. XRD results

Typical XRD patterns of the kaolinite/DMSO intercalates are shown in Fig. 1 and the corresponding basal spacings obtained after intercalation of kaolinite by DMSO are given in Table II. The peak at 1.124 nm is due to kaolinite/DMSO intercalate, and the remnant peak at 0.714 nm corresponds to the unintercalated kaolinite. These results indicate the formation of kaolinite/DMSO intercalate with basal spacing increasing from 0.714 nm to 1.124 nm. From calculations based on the formula given by Theng [26] as shown below

$$\text{intercalation ratio} = \text{intensity }(001)\text{intercalate}/[\text{intensity }(001)\text{kaolinite} + \text{intensity}(001)\text{intercalate}] \quad (1)$$

about 90% of the compound has been intercalated in an hour and ~10% of kaolinite layers has not been expanded. Similar calculations based on the areas under the 001 peaks also agree with the per cent intercalation.

The per cent intercalated remains fairly constant even after 24 h reaction. This is a significant result, because intercalation was achieved in an hour, while others have reported a much longer reaction time for the same purpose [4, 10, 11, 19]. The rate of intercalation of DMSO into kaolinite under the present

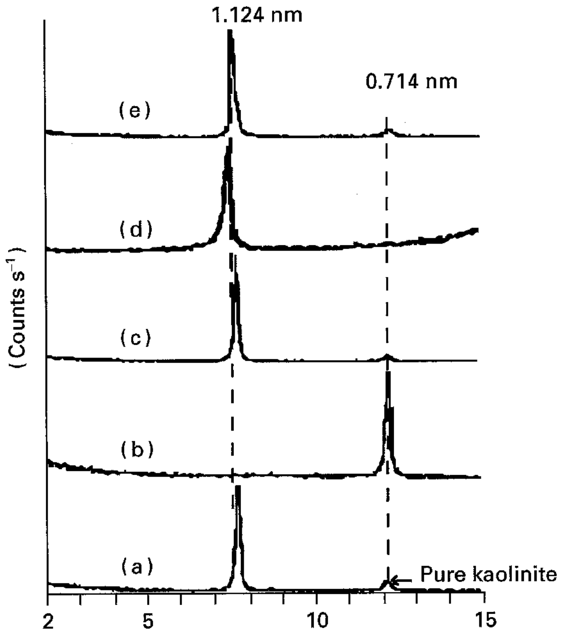

Figure 1 XRD patterns of kaolinite/DMSO intercalates obtained under different reaction conditions. (a) 373 K, 1 d; (b) 423 K, 30 min; (c) 423 K, 1 min; (d) 423 K, 4 h, and (e) 423 K, 18 h.

TABLE II Basal spacing of kaolinite/DMSO intercalates under different reaction conditions

Serial no.	Temperature (K)	Time (h)	Basal spacing, (001) (nm)	Intercalation (%)
1	423	1	1.112	88
2	423	2	1.120	90
3	423	4	1.113	90
4	423	6	1.116	90
5	423	12	1.113	90
6	423	18	1.125	90
7	423	24	1.119	90

hydrothermal conditions has been considerably enhanced, although it has been previously reported that direct intercalation of most molecules may often be very slow [4]. The higher rate of the reaction is attributed to the presence of larger proportions of "free" substrate molecules under the applied hydrothermal conditions, because the DMSO aggregates in liquid state are transformed into a more disordered state at higher temperature [27]. The large dipole moment of DMSO causes association of the molecules in the liquid state, thereby hindering the insertion of these aggregates into the kaolinite interlamellar spaces. A rise in temperature is expected to bring more "free" DMSO molecules in contact with kaolinite due to higher frequency of collisions, and thus facilitate their insertion into the lattice space by increasing the rate of diffusion.

4.2. FT–IR results

The FT–IR data of kaolinite/DMSO complex, together with the spectral data of DMSO [4] and pure kaolinite [27] are presented in Table III. The corresponding FT–IR spectra of the kaolinite/DMSO complexes obtained after a varying period of contact time are shown in Fig. 2. The vibrational band assignments of the kaolinite/DMSO complex are in good agreement with those reported by others [4, 25]. For kaolinite, the band assignments are: 3690–3620 cm^{-1} (O–H stretching vibration), 1117–1016 cm^{-1} (Si–O in-plane vibration), 941–917 cm^{-1} (Al–OH vibration), 797–693 cm^{-1} (gibbsite-like layers of kaolinite vibrations) and 542–421 cm^{-1} (Si–O–Al skeletal vibrations). The band at 3965 cm^{-1} has been assigned to stretching vibration of two coupled inner-surface hydroxyl groups lying almost perpendicular to the (001) plane [5].

The bands for DMSO have been attributed to asymmetric CH stretching (2994 cm^{-1}), symmetric CH stretching (2913 cm^{-1}), asymmetric CH_3 deformation (1445–1414 cm^{-1}), symmetric CH_3 deformation (1320–1288 cm^{-1}), SO stretching (1057 cm^{-1}), CH_3 rocking (953–896 cm^{-1}), asymmetric CS stretching (699 cm^{-1}) and symmetric CS stretching (669 cm^{-1}) vibrations [4]. Close examination of the FT–IR results presented in Fig. 2 as well as in Table III reveal that with the exception of the 24 h sample there is no discernible difference between the other three samples, where the hydrothermal reactions were carried out for 45, 60 and 360 min duration at 423 K.

The O–H stretching band at 3621 cm^{-1} is due to an inner hydroxyl group in kaolinite [4], and it is unlikely to be significantly affected by the inclusion of DMSO molecules in the interlamellar layers, because of its presence within the bulk of kaolinite structure. The relative intensity of this particular band remained unchanged upon intercalation and is unaffected when kaolinite is subjected to DMSO treatment (spectrum) at 423 K. The 3690 cm^{-1} band in kaolinite upon intercalation has apparently been perturbed by the presence of the DMSO guest molecules. The perturbation the 3690 cm^{-1} band in kaolinite by about 5 cm^{-1} unit is due to the close approach of the S=O linkage of the DMSO molecule towards kaolinite molecule [8]. The two bands at 3540 and 3505 cm^{-1} are due to the formation of moderately strong H–bonding between some of the inner-surface hydroxyls of the kaolinite and the sulphonyl oxygen [11, 12]. The 3646 cm^{-1} band in kaolinite is absent from the kaolinite/DMSO intercalates. The absence (or drastic reduction in intensity) of this particular band with time of intercalation has been related by Johnston *et al.* [24] to the extent of intercalation. The present study clearly shows that the intercalation was complete even after 1 h, and is in good agreement with the XRD result presented above. The Al–OH vibrational bands appear at 941 and 917 cm^{-1} [4] and their intensities are significantly reduced with intercalation, and the 941 cm^{-1} band decreased more significantly than the 917 cm^{-1} band. The increased intensity and sharpness of the band at 1099–1114 cm^{-1} and gradual reduction in intensity of the band at ~608 cm^{-1} also indicate enhanced intercalation [4]. This is due to the bonding between the DMSO and the hydroxyl surface of the kaolinite sheets. The 941 cm^{-1} band is absent in the present experiment and the 917 cm^{-1} band appears at

TABLE III FT–IR data of pure kaolinite, pure DMSO and kaolinite/DMSO complex

Band assignment in kaolinite	Kaolinite [28]	DMSO [4]	KD[a], 423 (K)			
			45 m	1 h	6 h	24 h
OH-stretching	–	–	3955	3955	3955	–
	3690					
	3664	–	3695	3695	3695	3694
	3646	–	3664	3664	3664	3653
	3621	–	–	–	–	–
	–	–	3621	3621	3621	3621
	–	–	3540	3540	3540	–
	–	–	3505	3505	3505	–
	–	2994	3022	3022	3022	–
	–	–	2937	2937	2937	–
	–	2913	2919	2919	2919	–
	–	1445	1428	1428	1428	–
	–	1414	1408	1408	1408	–
	–	–	1393	1393	1393	–
	–	1320	1318	1318	1318	–
	–	1303	–	–	–	–
	–	1288	–	–	–	–
Si–O in-plane vibration	1117	1057	1099	1099	1116	1114
	1035	–	1031	1032	1030	1019
	1016	953	959	959	–	–
Al–OH vibration	941	929	–	–	–	–
	917	896	907	912	914	916
Gibbsite-like vibration	797	–	789	789	789	789
	780	–	–	–	–	–
	751	–	744	744	747	754
	693	699	687	687	688	695
Si-O-Al	542	669	557	553	556	544
	476	–	471	469	476	476
	434	–	436	435	436	432
	421	–	388	388	387	–

[a] KD: kaolinite/DMSO complex.

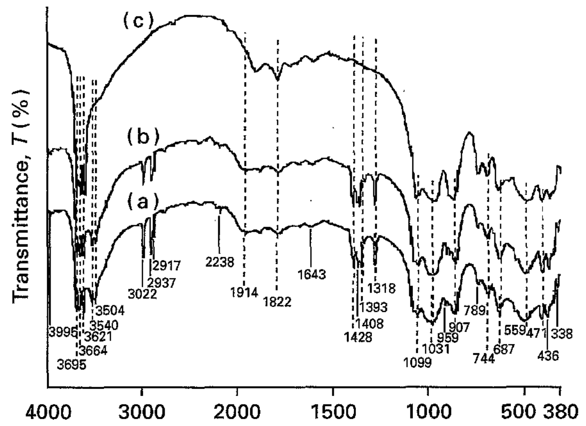

Figure 2 FT–IR spectra of kaolinite/DMSO complex obtained under different reaction conditions. (a) 423 K, 45 min; (b) 423 K, 1 h, and (c) 423 K, 24 h.

907, 912, 914 and 916 cm^{-1} in the 45 min, 1, 6 and 24 h, samples, respectively. These results clearly indicate the incorporation of DMSO into the layered structure of kaolinite. However, the shifting of the 917 cm^{-1} peak to the lower frequency region is due to the nature of hydrogen bonding in the kaolinite/DMSO complex. The absence of the bands in the region 3000–1100 cm^{-1} from the kaolinite/DMSO complex obtained after 24 h reaction is likely from the decomposition of DMSO adsorbed on the surface of kaolinite due to longer exposure.

4.3. TGA analysis

TGA analysis of the kaolinite/DMSO complex under flowing helium at 2 °C min^{-1} showed a stepwise decomposition of the intercalated compound. A loss of $\sim 64\%$ occurs at temperature > 873 K due to complete dehydroxylation resulting in the breakdown of kaolinite layered structure (Fig. 3). A net weight loss of $\sim 20\%$ at ~ 473 K is due to the removal of intercalated DMSO from the interlamellar spaces in the kaolinite moiety. The weight loss corresponds to the formula, $Al_2Si_2O_5(OH)_4(DMSO)_{0.78}$, for the intercalate which is in agreement with the formula $[Al_2Si_2O_5(OH)_4(DMSO)_{0.74}]$ reported by Adams and Watl [6] from similar analysis. The TGA results thus establish the stabilization of DMSO into the kaolinite layered structure.

4.4. Effect of washing the kaolinite/DMSO complex

The DMSO guest species was removed from inside that lattice by washing ten times with excess water and the *d*-spacing in kaolinite structure was practically restored, indicating that the DMSO/kaolinite intercalate unstable.

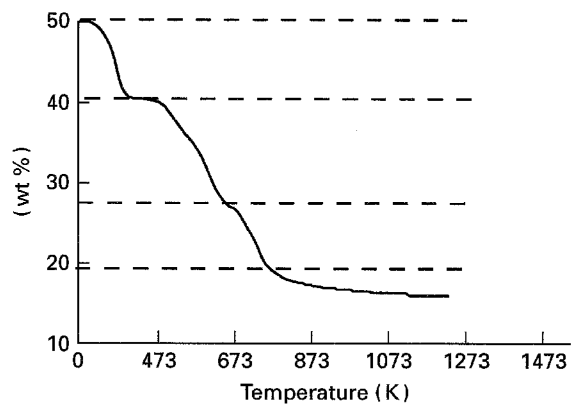

Figure 3 TGA profile of kaolinite/DMSO complex.

5. Conclusion

The primary purpose of this work was to determine suitable experimental conditions to enhance the rate and yield of intercalation of kaolinite. The present results clearly indicate that the application of hydrothermal conditions enhance the rate as well as the yield of kaolinite/DMSO complex. More than 90% of the treated kaolinite was intercalated, and all the intercalated sample exhibited a residual 0.714 nm reflection in the XRD pattern. This is an important observation, because all previous works reported a much longer time to achieve reasonably high yield of the intercalation reactions. However, the kaolinite/DMSO complex was found to be unstable, because repeated washings with water removed DMSO from inside the interlamellar space of kaolinite. This observation led us to believe that DMSO may be used as an entraining agent for intercalation of other compounds which cannot otherwise be easily intercalated into kaolinite or any other clay minerals. The potential uses of these modified clays as sinks for immobilization of organic pollutants may be justified by their unique adsorption properties and exchange properties.

Acknowledgements

We thank the Texas Advanced Technology and Research Program and the Texas State Coordinating Board for supporting this work. We also acknowledge partial financial support from the Welch Foundation. Special thanks go to Mr Gopal R. Erusu for technical assistance.

References

1. M. KOWALSKA, HULYA GULER and D. L. COCKE, *Sci. Total Environ.* **141** (1994) 223.
2. A. WEISS, "Organic Geochemistry" (Springer, Berlin, 1969) p. 737.
3. S. OLEJNIC, A. M. POSNER and J. P. QUIRK, *Clays Clay Mineral.* **8** (1970) 421.
4. S. OLEJNIC, L. A. G. AYLMORE, A. M. POSNER and J. P. QUIRK *J. Phys. Chem.* **72** (1968) 241.
5. O. ANTON and P. G. ROUXHET, *Clays Clay Mineral.* **25** (1977) 259.
6. J. M. ADAMS and S. WALTL, *ibid.* **28** (1980) 130.
7. A. WEISS, W. THIELEPAPE and H. ORTH, *Proc. Int. Clay Conf.* **1** (1966) 277.
8. M. RAUPACH, P. F. BARRON and J. G. THOMSON, *Clays Clay Mineral.* **35** (1987) 208.
9. S. OLEJNIC, A. M. POSNER and J. P. QUIRK, *J. Coll. Interface Sci.* **37** (1971) 536.
10. P. SIDHESWARAN, S. V. RAMMOHAN, P. GANGULY and A. N. BHAT, *Ind. J. Chem.* **26** (1987) 994.
11. J. G. THOMSON, *Clays Clay Mineral.* **33** (1985) 173.
12. C. T. JOHNSTON and D. A. STONE, *ibid.* **38** (1990) 121.
13. J. G. THOMSON, N. GABBITAS and P. J. R. UWINS, *ibid.* **41** (1993) 73.
14. Y. SUGAHARA, S. SHIGEO, K.-I. YOSHIOKA, K. KURODA and C. KATO, *ibid.* **37** (1989) 143.
15. D. W. BRUCE and D. O'HARE, "Inorganic Materials" (Wiley, New York, 1992).
16. R. M. MEIGHAN and R. H. COLE, *J. Phys. Chem.* **68** (1964) 503.
17. E. P. LINTON, *J. Am. Soc.* **62** (1940) 1945.
18. H. L. SCHLAFER and W. SCHAFFERNICHT, *Angew. Chem.* **72** (1960) 618.
19. J. G. THOMPSON and C. CUFF, *Clays Clay Mineral.* **33** (1985) 490.
20. P. M. COSTANZO, R. F. GIESE, Jr. and M. LIPSICAS, *ibid.* **32** (1984) 419.
21. T. J. BANDOSZ, J. JAGIELLO, K. A. G. AMANKWAH and J. A. SCHWARZ, *Clay Mineral.* **27** (1992) 435.
22. R. L. LEDOUX and J. L. WHITE, *J. Coll. Interface Sci.* **21** (1966) 127.
23. P. M. COSTANZO and R. F. GIESE, Jr, *Clays Clay Mineral.* **38** (1990) 160.
24. C. T. JOHNSTON, G. SPOSITO, D. F. BOCIAN and R. R. BIRGE, *J. Phys. Chem.* **88** (1984) 5959.
25. J. G. THOMPSON, P. J. R. UWINS, A. K. WHITTAKER and I. D. R. MACKINNON, *Clays Clay Mineral.* **40** (1992) 369.
26. B. K. G. THENG, "The chemistry of clay-organic reactions" (Wiley, New York, 1974).
27. A. J. PARKER, *Q. Rev.* **16** (1962) 163.
28. V. C. FARMER, "The infrared spectra of minerals", Mineralogical Society monograph **4** (Mineralogical Society of America, Washington, DC, 1974) (1974).

Received 8 February
and accepted 8 September 1995