

CHEMISORPTION OF BENZENE ON CU-MONTMORILLONITE AS CHARACTERIZED BY FTIR AND ^{13}C MAS NMR

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Abstract—Sorption of benzene onto Cu-montmorillonite was characterized by Fourier transform infrared (FTIR) spectroscopy and ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR). Under anhydrous conditions, chemisorption of benzene in the interlamellar region of Cu-montmorillonite led to the formation of a dark red surface complex that exhibited a vibrational spectrum similar to that of doped poly-p-phenylene. When the benzene sorption reaction was carried out under high relative humidity conditions, polymerization of benzene did not occur. The FTIR spectrum of the surface complex formed under wet conditions exhibited vibrational bands that could not be assigned to those of the parent benzene molecule or to those of previously observed chemisorbed Type I or Type II complexes. ^{13}C MAS NMR spectra of ^{13}C -enriched benzene sorbed onto Cu-montmorillonite powder showed the presence of two groups of peaks that could be assigned to aromatic and aliphatic carbon respectively.

Key words—Benzene chemisorption, ^{13}C MAS NMR, Cu-montmorillonite, FTIR, Poly-p-phenylene.

INTRODUCTION

Sorption of benzene onto transition metal exchanged montmorillonite results in the formation of chemisorbed surface complexes that have characteristic UV-visible, vibrational, and ESR spectra (Pinnavaia and Mortland, 1971; Van de Poel *et al.*, 1973; Soma *et al.*, 1983). Vibrational spectroscopy has provided valuable information to differentiate physisorbed and chemisorbed surface complexes. The infrared spectrum of benzene physisorbed on Cu-montmorillonite is characterized by a 13 cm^{-1} shift to higher frequency in the C-H out of plane ν_{11} mode compared with its position in liquid benzene (Pinnavaia and Mortland, 1971). Depending on the water content of the clay, two types of chemisorbed benzene complexes were observed. Partial dehydration of the clay prior to exposure to benzene vapor results in the formation of a green surface complex designated as the Type I complex by Doner and Mortland (1969) and Pinnavaia *et al.* (1974). Benzene sorption onto strongly dehydrated Cu-montmorillonite, however, leads to the formation of the Type II complex with characteristic vibrational and UV-visible spectra (Doner and Mortland, 1969; Pinnavaia *et al.*, 1974).

Eastman *et al.* (1984) did not distinguish between a simple Type I or Type II scheme but found that the reaction products of benzene chemisorbed on Cu-montmorillonite depended on the reaction time and the concentration of water in the reaction medium. They proposed that hydrogen and oxygen from water were incorporated into the reaction products. In addition to the Lewis acid character of the Cu-montmorillonite, they proposed that the hydration sphere

of the exchangeable cation could act as a source of Bronsted acidity in the chemisorption reaction due to hydrolysis. Based on infrared evidence, Pinnavaia and Mortland (1971) proposed that the benzene ring was edge-bonded to Cu^{+2} in a manner similar to that in $\text{Cu}(\text{C}_6\text{H}_6)\text{AlCl}_4$ complexes.

The nature of the Type II complex was less evident from infrared spectroscopic characterization (Pinnavaia *et al.*, 1974). A very broad absorption band centered $\approx 2000\text{ cm}^{-1}$ was attributed to a low-energy electronic transition (Pinnavaia and Mortland, 1971).

Soma *et al.* (1984) observed a correspondence between IR spectra of Type I and Type II chemisorbed complexes and those of poly-(p-phenylene) and the poly-(p-phenylene) cation, respectively. They concluded that the chemisorption of benzene onto Cu-montmorillonite resulted in the polymerization of benzene in the interlamellar region of the clay. Supplementing their IR data with Resonance Raman (RR) measurements, Soma *et al.* (1984) observed that in the spectra of the Type I complex, the 1283 cm^{-1} (inter-ring CC stretching) and the δ_{CH} in-plane bending at 1240 cm^{-1} bands underwent blue shifts to 1324 and 1271 cm^{-1} , respectively, when the Type II complex was formed. The assignment of the bands was in accordance with the Raman bands of biphenyl and biphenyl anion radical.

Higher molecular weight species were detected by mass spectral analysis of methanol extracts of Cu-smectite-benzene (Mortland and Halloran, 1976). When the mineral matrix in the benzene-Cu-montmorillonite system was dissolved by acid digestion, the IR spectrum of the residue was similar to that of poly-p-phenylene with two new bands at 805 cm^{-1} attributed to

$\gamma(\text{CH})$ out-of-plane deformation and at 1002 cm^{-1} attributed to $\delta(\text{CH})$ in-plane deformation previously obscured by absorption of the clay matrix in that region (Stoessel *et al.*, 1977; Walter *et al.*, 1990). A net darkening of the red Type II complex was observed (Stoessel *et al.*, 1977) after several cycles of hydration/dehydration and was attributed to polymerization favored by reoxidation of Cu^{+1} into Cu^{+2} . In addition to the three major vibrational bands (at 810 , 1005 , and 1485 cm^{-1}), Walter *et al.* (1990) observed less intense bands (705 and 770 cm^{-1}) that the authors attributed to monosubstitutions at the end of the polymer chain. Based on the ratio of the Σ mono ($705 + 770\text{ cm}^{-1}$)/para (810 cm^{-1}), the authors estimated that there were nine benzene rings in the poly-*p*-phenylene formed in the interlamellar region of Cu-montmorillonite. The relative intensities of the mono and para bands of the first cycle diminishes as compared with those of the 20th and 40th cycles, suggesting a reticulation process. In the infrared spectra of the Type II surface complex acquired in the presence of the mineral matrix, the 1005 cm^{-1} band is masked by overlapping clay bands while the 1485 (common to benzene) and the 810 bands of poly-*p*-phenylene are observed. While high molecular weight reaction products were detected by mass spectral analysis of methanol extracts of Cu-smectite-benzene (Mortland and Halloran, 1976), the extracted species were not rational multiples of benzene.

The available spectroscopic evidence regarding the chemisorption of benzene in the interlamellar region of the clay shows the formation of one or more new chemical species that have a higher molecular weight and are characterized by different vibrational spectra than the parent benzene molecule. The objective of this study is to identify the sorbed species at different water contents using FTIR and ^{13}C MAS NMR.

MATERIALS AND METHODS

Preparation of self-supporting-clay films of homoionic montmorillonite

The SAz-1-montmorillonite used in this study was obtained from the Source Clays Repository located at the University of Missouri. Ten grams of montmorillonite were allowed to equilibrate in 1 liter of 0.5 M NaCl ($\text{pH} = 6$) for 24 hr. The NaCl supernatant was discarded from the flocculated clay suspension. The clay was repeatedly washed with deionized water and centrifuged until the supernatant tested negative for Cl^- using the standard AgNO_3 test. The Na-montmorillonite suspension was size-fractionated by centrifugation, and the fraction having an e.s.d. of $< 2\ \mu\text{m}$ was collected and flocculated with $0.05\ \text{M CuCl}_2$ ($\text{pH} = 4.36$). Aliquots of Cu-montmorillonite were washed with deionized water and $1\ \text{ml}$ suspensions ($2.5\ \text{mg clay/g}$ of the suspension) were deposited onto polyethylene sheets and allowed to dry overnight. The self-

supporting clay films were peeled off by running the sheet over the edge of a glass slide. Powdered copper montmorillonite was prepared by dialyzing the homoionic clay in deionized water until it tested negative for Cl^- using the AgNO_3 test. The salt-free Cu-montmorillonite was frozen in an ethanol-dry ice bath (-117°C). The samples were lyophilized on a Virtis freeze-dryer for 24 hr.

FTIR experiment

The FTIR spectra were obtained using a Bomem DA 3.10 FTIR spectrometer controlled by a Digital Equipment Corporation Vaxstation-II computer. The Bomem spectrometer incorporates a Michelson interferometer with a KBr beamsplitter and a mercury-cadmium-telluride (MCT) detector. The mirror velocity was set to $1\ \text{cm s}^{-1}$, and the temperature of the ceramic source was estimated to be $1200\ \text{K}$.

In the first set of FTIR experiments, one clay film was equilibrated with water vapor at 100% relative humidity for 24 hr in a desiccator. After 24 hr, liquid benzene was placed into the desiccator and this film was exposed to benzene and water vapor for 24 hr. The clay film resulting from the first set of experiments will be referred to in the Results and Discussion sections as the partially hydrated clay film. In the second set of experiments, a clay film was exposed to benzene and water vapors for 24 hr, and the clay was desiccated using P_2O_5 . The clay film turned dark red within 24 hr, and it was kept under P_2O_5 until it was characterized by FTIR. The clay film resulting from the second set of experiments will be referred to in the Results and Discussion sections as the strongly dehydrated clay films. During the transfer operation from the desiccator to the gas cell, the clay film was exposed to the atmospheric moisture and almost instantaneously turned green.

The clay films were mounted in a $10\ \text{cm}$ pathlength gas cell fitted with two ZnSe windows using Viton-O-rings. Benzene along with P_2O_5 or water were present in the cell depending on the desired moisture conditions. The clay film was held in place in the gas cell between a magnetic and stainless steel plate that had an ID of $1.0\ \text{cm}$. The clay holder was positioned perpendicular to a stainless steel base plate. The pressure in the cell was kept at 1 atmosphere, and the interferometer and sample compartment were evacuated to $0.02\ \text{Torr}$.

A combined gravimetric-FTIR experiment was conducted using an FTIR-gravimetric cell (Johnston *et al.*, 1991). The Cu-clay film self-supporting clay film was left to equilibrate under P_2O_5 . When an equilibrium weight was reached, the electrobalance was evacuated to $10^{-2}\ \text{Torr}$ using the gas manifold and vacuum pumping station. The benzene was degassed separately before being introduced to the cell under a pressure equivalent to 3 Torr. When the gravimetric data indicated

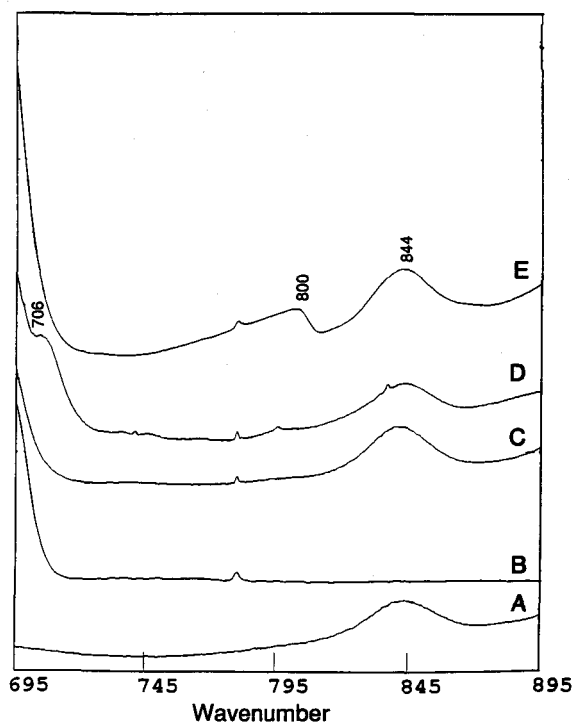


Figure 1. FTIR spectra of benzene sorbed onto Cu-montmorillonite (695–895 cm^{-1} region): A) Cu-montmorillonite; B) benzene vapor; C) physisorbed benzene (partially hydrated clay film); D) Type I complex (partially hydrated clay film); and E) Type II complex (strongly dehydrated clay film).

equilibrium condition, the system was rehydrated. The spectra were run at optical resolutions of either 1 or 2 cm^{-1} . Typically, 250–500 scans were co-added for the sample and reference scans. A Hamming apodization function was used to transform the interferograms.

Sorption of $^{13}\text{C}_6\text{H}_6$ onto Cu-SAz-1 for solid state NMR analysis

A glass apparatus was designed to study the vapor phase sorption of labeled benzene ($^{13}\text{C}_6$) onto Cu-montmorillonite for solid-state NMR analysis. Three hundred and thirty milligrams of the freeze-dried clay were placed under P_2O_5 in a 25 ml round-bottom flask and evacuated for 2 hr at 10^{-2} Torr. The Cu-montmorillonite was then exposed to $^{13}\text{C}_6\text{H}_6$ vapors (in equilibrium with 0.5 g $^{13}\text{C}_6\text{H}_6$) for 72 hr, yielding the characteristic reddish Type II complex. The red complex was heated at 110°C for 24 hr, which prevented it from changing to the green Type I complex when exposed to atmospheric moisture. The sample was ground to pass through a 100 mesh sieve.

Solid state NMR experiments

The sample was packed in a 5 mm Maycor rotor and spun at 3.3–3.5 KHz. The magic angle was set using ^{79}Br spectrum of KBr. The ^{13}C MAS and CP

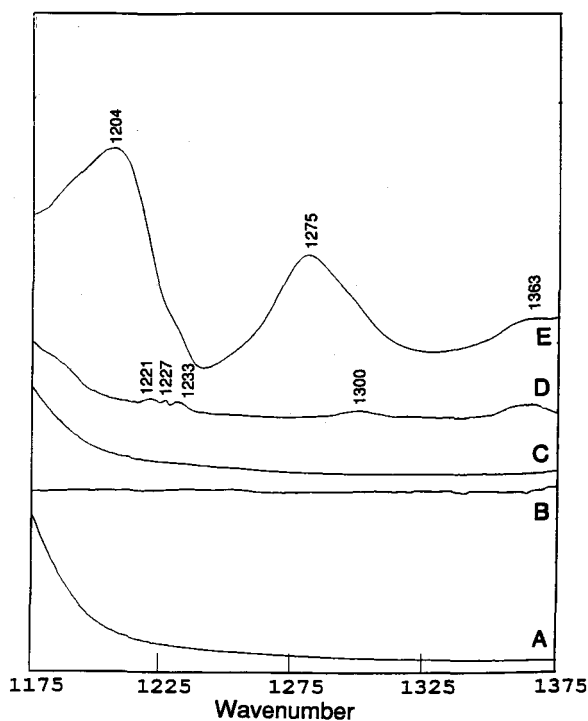


Figure 2. FTIR spectra of benzene sorbed onto Cu-montmorillonite (1175–1375 cm^{-1} region): A) Cu-montmorillonite; B) benzene vapor; C) physisorbed benzene (partially hydrated clay film); D) Type I complex (partially hydrated clay film); and E) Type II complex (strongly dehydrated clay film).

MAS NMR spectra were collected at 75.45 MHz using a Nicolet NT-300 spectrometer controlled by a Nicolet 1280 computer. Chemical shifts were measured relative to tetramethylsilane (TMS) using hexamethylbenzene (HMB) as a secondary reference ($\delta = 132.3$ ppm assigned to aromatic carbon and 16.9 ppm assigned to aliphatic carbon). A delay time of 25 s was chosen in both the single-pulse and the cross-polarization experiments. The single-pulse experiment was conducted under continuous proton decoupling conditions to reduce linebroadening due to ^1H - ^{13}C dipolar coupling. In the cross-polarization experiment, a 90° pulse of 14 μs and a contact time of 1 ms were used.

RESULTS

Vibrational data

FTIR spectra of benzene, Cu-montmorillonite, and benzene sorbed on montmorillonite at different water contents are shown in Figures 1–3.

695–895 cm^{-1} region. FTIR spectrum of benzene physisorbed on a hydrated Cu-montmorillonite clay film is shown in Figure 1C. The broad band at 844 cm^{-1} corresponds to the OH deformation frequency of Al-(O-H)-Al structural moiety in montmorillonite (Farmer, 1974; Figure 1A). The ν_{11} ($\delta_{\text{oop}}(\text{C-H})$) deformation

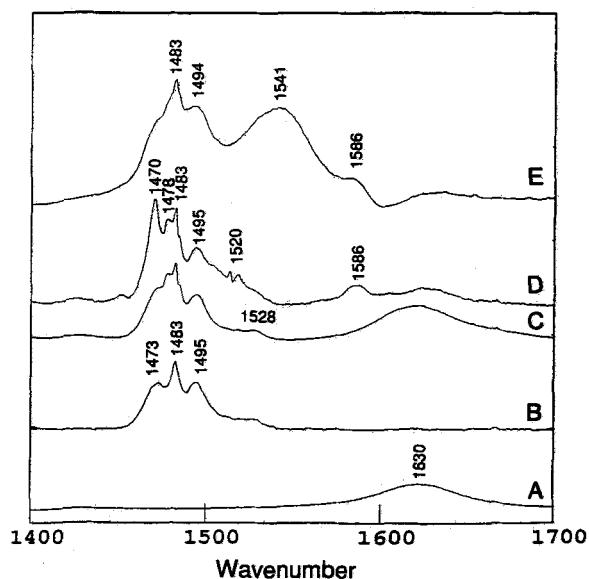


Figure 3. FTIR spectra of benzene sorbed onto Cu-montmorillonite (1400–1700 cm^{-1} region): A) Cu-montmorillonite; B) benzene vapor; C) physisorbed benzene (partially hydrated clay film); D) Type I complex (partially hydrated clay film); and E) Type II complex (strongly dehydrated clay film).

band centered at 674 cm^{-1} was optically saturated in this study. Consequently, only the high-frequency shoulder starting at 695 cm^{-1} is shown (Figure 1B). With further desiccation of the benzene-Cu-montmorillonite complex on the partially hydrated clay film, the spectrum shows the presence of a shoulder at 706 cm^{-1} (Figure 1D). The sorption reaction of benzene on strongly dehydrated Cu-montmorillonite produced a rapid darkening of the clay film. The vibrational spectrum of the strongly dehydrated clay film was characterized by the appearance of a new band at 800 cm^{-1} (Figure 1E).

1175–1375 cm^{-1} region. The vapor phase and the physisorbed benzene spectra (Figures 2B and 2C) do not show any absorption bands. The partially hydrated clay film (Figure 2D) exhibits absorption bands at 1221, 1227, 1233, 1300 and 1363 cm^{-1} . The vibrational spectrum of the strongly dehydrated clay film exhibits a band at 1275 cm^{-1} (Figure 2E) within less than 5 min after benzene is introduced into the system following extensive desiccation. The 1204 cm^{-1} band (Figure 2E), by contrast, forms after the first hydration-dehydration of the Type II complex and increases in intensity with repeated hydration-dehydration.

1400–1700 cm^{-1} region. This vibrational region is free from absorption bands from the clay (Figure 3A). The vapor phase spectrum of benzene (Figure 3B) is characterized by three bands at 1473, 1483 and 1495 cm^{-1} that correspond to P, Q, and R of the ν_{19} mode. A shift of 5 cm^{-1} and 13 cm^{-1} to lower frequency for benzene sorbed on the clay was observed relative to the vapor

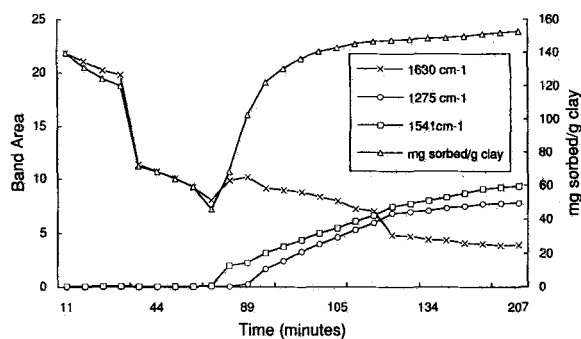


Figure 4. Combined gravimetric-vibrational measurements of benzene sorbed onto Cu-montmorillonite.

phase spectrum of the Q branch of the ν_{19} mode as illustrated in Figures 3C and 3D, respectively. An additional band in Figure 3D is observed at 1586 cm^{-1} . A new band is also observed at 1541 cm^{-1} .

The results of the combined gravimetric-FTIR experiments are shown in Figure 4 on a double Y axis plotted as a function of exposure time to P_2O_5 . The combined effect of the total amounts (mg/g of clay) of benzene sorbed and water desorbed on the weight of the self-supporting clay film is plotted on the right Y-axis. The left Y-axis shows the area of the characteristic water and chemisorbed benzene bands. The rate of increase in the intensity of the 1275 cm^{-1} and the 1541 cm^{-1} bands attributed to chemisorbed benzene reaches a plateau at the same time as the 1630 cm^{-1} band attributed to water of hydration of the $\text{Cu}^{+2}(\text{H}_3\text{O})_x$ has reached its lowest intensity.

^{13}C MAS and CP MAS NMR

The ^1H T_1 spin-lattice relaxation times for poly-p-phenylene and other oligomers that are suspected to form when benzene is sorbed onto Cu-montmorillonite vary between 910 s for biphenyl to 21 s for p-sexiphenyl and 0.48 s for poly-p-phenylene (Murray *et al.*, 1984). The presence of paramagnetics (i.e., doping with $\text{Cr}^{\text{III}}(\text{acac})$), has been found to reduce both the ^1H and ^{13}C T_1 relaxations for polystyrene by about 400 fold (Sullivan and Maciel, 1982). A delay time of 25 s was chosen for this study, and two ^{13}C solid-state NMR experiments were run under magic angle spinning (MAS) conditions. The single pulse spectrum (in Figure 5A: 3240 accumulations over 22 hr) shows two broad resonances one in the 130–140 ppm region and another at 60 ppm. Under cross-polarization conditions (in Figure 5B: 8472 accumulations over 58 hr), only the peak in the 130–140 ppm region is observed.

DISCUSSION

Vibrational characterization

695–895 cm^{-1} region. The initial interaction of benzene with the partially hydrated Cu-montmorillonite

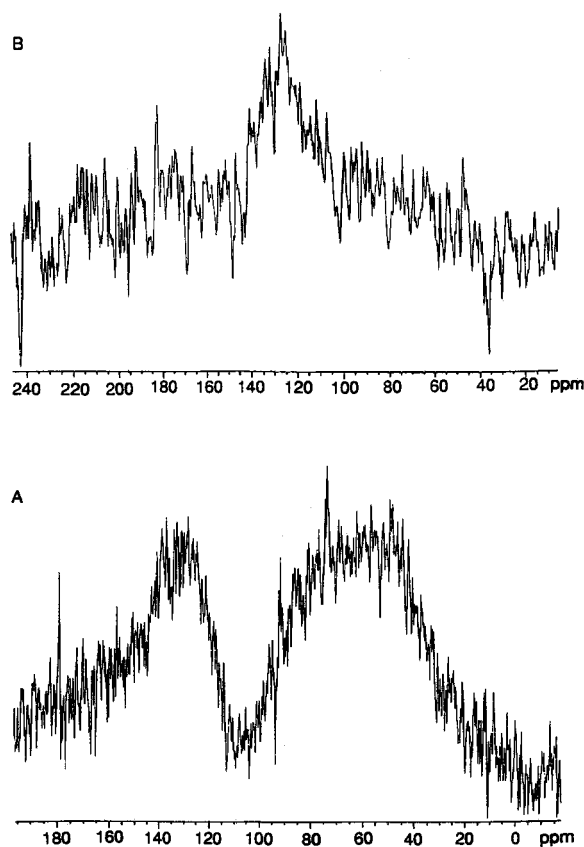


Figure 5. ^{13}C MAS NMR spectra of benzene sorbed onto Cu-montmorillonite: A) single pulse; and B) cross polarization.

is due to physisorption where no change occurs in the 685–885 region of the vibrational spectrum of the vapor phase parent benzene (Figure 1C). With further desiccation of the partially hydrated clay film, a 32 cm^{-1} blue shift of the ν_{11} C-H deformation band is observed in the form of a shoulder at 706 cm^{-1} (Figure 1D), which is characteristic of the Type I complex detected in previous studies (Pinnavaia and Mortland, 1971). Comparable blue shifts ranging in magnitude from 2 cm^{-1} in the case of Ag(111) to 157 cm^{-1} for Pt(111) have been observed when benzene was chemisorbed onto different metal surfaces (Koel *et al.*, 1984). The magnitude of the shift of the CH out-of-plane bending mode has been used as a means of evaluating the metal-ring bond-strength for arene-metal complexes (Koel *et al.*, 1984). The sorption reaction between benzene and strongly Cu-montmorillonite leads to the formation of the Type II complex as a result of a single electron transfer (SET) reaction. The Type II complex is characterized by a band at 800 cm^{-1} (Figure 1E), which has been attributed to the formation of poly-p-phenylene (Stoessel *et al.*, 1977). In the polymer literature, the IR absorption band at $803\text{--}805\text{ cm}^{-1}$ is

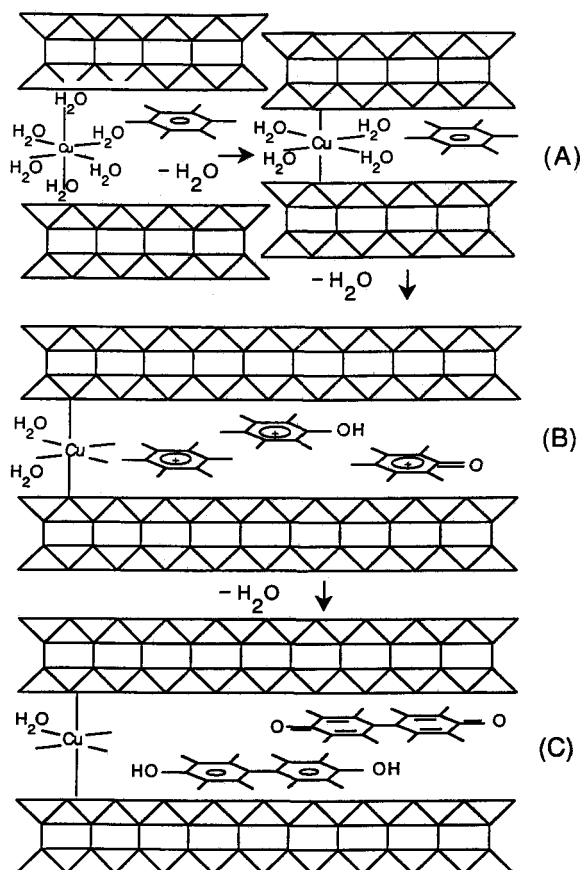


Figure 6. Reaction scheme of benzene with partially hydrated clay film.

indicative of parasubstitution in poly-p-phenylene (Kovacic and Jones, 1987).

1175–1375 cm^{-1} region. The presence of water molecules during the equilibration of benzene with the partially hydrated clay film may have contributed to the formation of bands attributable to oxygen and/or hydrogen containing surface species (Kovacic and Jones, 1987; see Figures 6A and 6B). The cation radical can also be subject to fragmentation resulting in the formation of aliphatic reaction products. Mass spectral data (Mortland and Halloran, 1976) showed that extracted reaction products of the Type II complex were not rational multiples of benzene, which supports the theory of fragmentation and the possibility that some of the unassigned bands (see Figure 2D: 1221 , 1227 , 1233 , 1300 , and 1363 cm^{-1}) could correspond to lower molecular weight hydrocarbons (Figure 6B). When multilayers of water are present, the nucleophilicity of the water may prevent the formation of the reaction product that gave rise to the 1275 cm^{-1} band. The presence of water at concentrations higher than $5 \times 10^{-2}\text{ M}$ was found to prevent the polymerization of benzene by electro-synthesis on a Pt electrode (Aeiych

and Lacaze, 1989), presumably because of the nucleophilicity of water, which causes it to react with cation radicals as soon as they formed. The formation of substituted biphenyls where the para positions are occupied by O/OH groups would explain why further polymerization would not have occurred (Figure 6C).

1400–1700 cm^{-1} region. The equilibration of benzene with strongly dehydrated Cu-montmorillonite is propitious to the formation of poly-p-phenylene (Figures 7A–C). Soma *et al.* (1984) compared the spectra of the Type I and Type II complexes with those of poly-p-phenylene and doped poly-p-phenylene and found that there was good agreement. The 1280 and 1530–1541 cm^{-1} IR bands (Soma *et al.*, 1984; this study) observed in spectra of the Type II complex are two out of four bands that show in the spectra of poly-p-phenylene when poly-p-phenylene are doped and become conducting. The 980 and 1180 cm^{-1} bands in doped poly-p-phenylene would be masked by those of the clay matrix in the benzene-Cu-montmorillonite system. The doping of poly-p-phenylene using an electron acceptor (e.g., AsF_5) has been shown to result in further polymerization (Shacklette *et al.*, 1980) of parent oligomers. In a photoacoustic infrared study of doped and undoped poly-p-phenylene, Yaniger *et al.* (1984) suggested that the Raman-active 1598 and 1216 cm^{-1} modes in undoped poly-p-phenylene become IR active in doped poly-p-phenylene as a result of symmetry breaking. The authors hypothesized that the 1216 cm^{-1} band would undergo a blue shift and show at 1280 cm^{-1} when the electronic structure of the poly-p-phenylene changes from benzoidal to quinoidal upon doping (Figures 7B and 7C). The dopant causes conjugational defects to form in the polymer chain (Zannoni and Zerbi, 1985). The likely electronic structure of the doped poly-p-phenylene is thought to consist of a sequence of paraquinoid benzene rings intercalated between benzenoid rings, thereby forming a bipolaron (Figure 7B). The formation of the chemisorbed complex in the interlamellar region of Cu^{+2} saturated smectites (Doner and Mortland, 1969), recently attributed to doped poly-p-phenylene (Soma *et al.*, 1984), has since been recognized as one of the more novel ways of synthesizing poly-p-phenylene by Kovacic and Jones (1987).

The weight gained/lost of the self-supporting clay film, measured along with the formation of new vibrational bands in the combined gravimetric-vibrational experiment, is more difficult to interpret because of occurrence of several concomitant processes (e.g., dehydration, chemisorption, etc.; see Figure 4).

¹³C MAS and CP MAS NMR

In the ¹³C MAS and CP MAS NMR spectra (Figure 5), the resonance between 130 and 140 ppm is assigned to aromatic (the ¹³C NMR signal of liquid benzene is

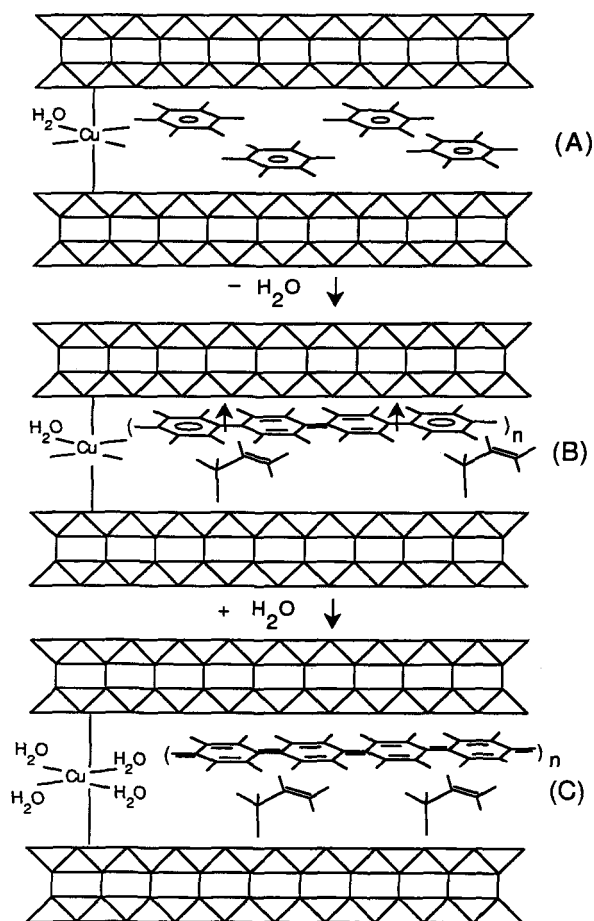


Figure 7. Reaction scheme of benzene with strongly dehydrated clay film (for accepted electronic structures of poly-paraphenylene, see Zannoni and Zerbi, 1985).

128.5 ppm downfield from MeSi_4), possibly polymeric, surface species (the ¹³C CP MAS NMR signal of biphenyl is at 128 ppm for ortho C, 131 ppm for meta C, 139 ppm for unprotonated para C, in Murray *et al.*, 1984). The presence of the resonance at 60 ppm is an indication that other surface species are present that seem to have aliphatic character (Wilson, 1987). The presence of aliphatic surface species, conceivably resulting from fragmentation of the benzene ring, corroborates the mass spectral findings by Mortland and Halloran (1976) that the reaction byproducts of benzene adsorbed onto Cu-montmorillonite are not necessarily rational multiples of benzene. The broad linewidth caused by paramagnetic Cu in the system precludes further identification of surface species beyond the aromatic and aliphatic assignment. Theoretical (Nayeem and Yesinowski, 1988) and experimental (Walter and Oldfield, 1987) MAS NMR studies of paramagnetic solids have provided insight into characteristic effects such as linebroadening, enhanced side-

Table 1. Listing of vibrational bands of benzene in the vapor phase, Ar matrix, physisorbed, and chemisorbed onto Cu-montmorillonite.

ν Lit. ¹	C ₆ H ₆ vapor lit. ²	Assignment	C ₆ H ₆ in Ar matrix	Phys. lit. ³	Phys. lit. ⁴	Type I lit. ³	Type I lit. ⁴	Type II lit. ³	Type II lit. ⁴
6 (R)	608	C-C-C bend							
11 (IR)	674	C-H bend		688	684	706	686 706	780 800	801
1 (R)	993	C-C stretch							
18 (IR)	1038	C-H stretch	1040						
9 (R)	1178	C-C bend	1180					1195	1204
							1221 1227 1233		
								1277	1275
5 + 16			1388		1388	1360	1300 1363		1364
					1472	1470	1388 1470		1388 1470
19 (IR)	1484	C-C bend	1483	1478	1478		1478	1480	1483
					1483		1483		1483
10 + 11			1522		1495		1495		1495
			1574		1520		1520		1520
						1586	1585	1540	1541
8 (R)	1609	C-C stretch							1585
10 + 17			1810		1811		1803 1812 1820		
5 + 17			1955						
20 (IR)	3048	C-H stretch	3048	3035	3035	3035	3036 3047		
7 (R)	3057	C-H stretch		3057			3057		
2 (R)	3074	C-H bend		3071	3071	3071	3073		
8 + 19	3079								
			3080						
1 + 6 + 19	3101		3100		3089	3089	3092 3101 3110		

¹ Wilson *et al.*, 1955.² Thakur *et al.*, 1986.³ Pinnavaia and Mortland, 1971.⁴ This study.

band intensities, and, sometimes, isotropic paramagnetic shifts. Magnetic properties can be changed from paramagnetic to diamagnetic by varying the temperature of a system. An antiferromagnetically coupled copper formate dimer showed a marked temperature-dependent linebroadening in magic-angle sample spinning nuclear magnetic resonance spectra (Walter and Oldfield, 1987). It has been suggested that the information gained studying the mechanisms causing linebroadening in MAS NMR spectra of paramagnetic solids would be applicable in the case of linebroadening in aluminosilicate mineral systems exhibiting the effects of the presence of random distributed paramagnetic or ferromagnetic impurities (Hartman and Sher-

iff, 1991; Nayeem and Yesinowski, 1988). Conceivably, the benzene-Cu-montmorillonite would be expected to exhibit narrower and better-resolved resonances if the experiment is run under low temperature.

CONCLUSIONS

1. The nature of the reaction products of the chemisorption of benzene in the interlamellar region of homoionic copper saturated montmorillonite is highly dependent on the hydration state of the Cu⁺² cation. When a multilayer of water is present during the early stages of the sorption process, this water can prevent the polymerization process by contrib-

uting to the formation of oxygen or OH p-substituted biphenyl.

2. Fragmentation of the radical cation is postulated based on the FTIR and solid-state NMR observation of aliphatic species in addition to the aromatic reaction byproducts.
3. Under exhaustive desiccation conditions, the chemisorption of benzene leads to the formation of poly-p-phenylene similar to those formed by electrochemical means. It remains to be seen whether the "doped" Type II poly-p-phenylene formed in the interlamellar region of the clay has the same conducting properties as the one synthesized by other catalyst-oxidant combinations.

ACKNOWLEDGMENTS

This work was supported in part by the Environics Laboratory, Air Force Engineering and Services Center, Tynall AFB, Florida, under Contract F08635-89-C 0152.

REFERENCES

- Aeiyaeh, S. and Lacaze, P. D. (1989) Electropolymerization of benzene and biphenyl in organic media: Influence of different parameters (solvent, water, acidity, salt) on the formation of polyparaphenylene films (PPP): *J. Polym. Sci. Part A. Polym. Chem.* **27**, 515-526.
- Doner, H. E. and Mortland, M. M. (1969) Benzene complexes with copper (II)-montmorillonite: *Science* **166**, 1406-1407.
- Eastman, M. P., Patterson, D. E., and Pannell, K. H. (1984) Reaction of benzene with Cu(II)- and Fe(III)-exchanged hectorites: *Clays & Clay Minerals* **32**, 327-333.
- Farmer, V. C. (1974) *The Infrared Spectra of Minerals*: 1st ed., V. C. Farmer, ed., Mineral Society; London, p 331-359.
- Hartman, J. S. and Sherriff, B. L. (1991) ^{29}Si MAS NMR of the aluminosilicate mineral kyanite: Residual dipolar coupling to ^{27}Al and nonexponential spin-lattice relaxation: *J. Phys. Chem.* **95**, 7575-7579.
- Johnston, C. T., Tipton, T., Stone, D. H., Erickson, C., and Trabue, S. L. (1991). Chemisorption of p-Dimethoxybenzene on Copper-montmorillonite: *Langmuir* **7**, 289-296.
- Koel, B. E., Crowell, J. E., Mate, C. M., and Somorjai, G. A. (1984) A high-resolution electron energy loss spectroscopy study of the surface structure of benzene adsorbed on the Rhodium (111) crystal face P: *J. Phys. Chem.* **88**, 1988-1996.
- Kovacic, P. and Jones, M. B. (1987) Dehydro coupling of aromatic nuclei by catalyst-oxidant systems: Poly(p-phenylene): *Chem. Rev.* **87**, 357-379.
- Mortland, M. M. and Halloran, L. J. (1976) Polymerization of aromatic molecules on smectite: *Soil Sci. Soc. Am. J.* **40**, 367-370.
- Murray, D. P., Dechter, J. J., and Kispert, L. D. (1984) Cross-polarization and magic angle sample spinning NMR of model organic compounds with extremely long ^1H T_1 's: *J. Polym. Sci., Polym. Lett. Ed.* **22**, 519-522.
- Nayeem, A. and Yesinowski, J. P. (1988) Calculation of magic-angle spinning nuclear magnetic resonance spectra of paramagnetic solids: *J. Chem. Phys.* **89**, 4600-4608.
- Pinnavaia, T. J. and Mortland, M. M. (1971) Interlamellar metal complexes on layer silicates. I. Copper (II) arene complexes on montmorillonite: *J. Phys. Chem.* **75**, 3957-3962.
- Pinnavaia, T. J., Hall, P. L., Cady, S. S., and Mortland, M. M. (1974) Aromatic radical cation formation on the intracrystal surfaces of transition-metal layer lattice silicates: *J. Phys. Chem.* **78**, 994-999.
- Shacklette, L. W., Eckhardt, H., Chance, R. R., Miller, G. G., Ivory, D. M., and Baughman, R. H. (1980) Solid-state synthesis of highly conducting polyphenylene from crystalline oligomers: *J. Chem. Phys.* **73**, 4098-4102.
- Soma, Y., Soma, M., and Harada, I. (1984) The reaction of aromatic molecules in the interlayer of transition-metal-ion-exchange montmorillonite studied by resonance Raman spectroscopy. 1 Benzene and p-Phenylenes: *J. Phys. Chem.* **88**, 3034-3038.
- Stoessel, F., Guth, J. L., and Rey, R. (1977) Polmerisation de benzene en polyparaphenylene dans une montmorillonite cuivrique. *Clay Miner.* **12**, 255-259.
- Sullivan, M. J. and Maciel, G. E. (1982) Spin dynamics in the carbon-13 nuclear magnetic resonance spectrometric analysis of coal by cross polarization and magic angle spinning: *Anal. Chem.* **54**, 1615-1623.
- Thakur, S. M., Goodman, L., and Ozkarak, A. G. (1986) The benzene ground state potential surface. I. Fundamental frequencies for planar vibrations: *J. Chem. Phys.* **84**, 6642-6656.
- Van de Poel, D., Cloos, P., Helsen, J., and Jannini, E. (1973) Comportement particulier du benzene adsorbe sur la montmorillonite cuivrique: *Bull. Gr. Fr. Agr.* **25**, 115-126.
- Walter, T. H. and Oldfield, E. (1987) Magic-angle sample spinning NMR spectroscopy of an antiferromagnetically coupled copper formate dimer: *J. Chem. Soc., Chem. Commun.*, 646-647.
- Walter, D., Saehr, D., and Wey, R. (1990) Les complexes montmorillonite(III)-benzene: Une contribution: *Clay Miner.* **25**, 343-354.
- Wilson, E. B., Decius, J. C., and Cross, P. C. (1955) *Molecular Vibrations*: McGraw-Hill, New York, 249-272.
- Wilson, M. A. (1987) *NMR Techniques in Geochemistry and Soil Chemistry*: Pergamon Press, Oxford, 353 pp.
- Yaniger, S. I., Rose, D. J., McKenna, W. P., and Eyring, E. M. (1984) Photoacoustic infrared spectroscopy of doped and undoped poly(p-phenylene): *Macromolecules* **17**, 2579-2583.
- Zannoni, G. and Zerbi, G. (1985) Lattice dynamics and vibrational spectra of undoped and doped polyparaphenylene: *J. Chem. Phys.* **82**, 31-38.

(Received 12 March 1992; accepted 19 February 1993; Ms. 2195)