

## REACTIVITY OF ANISOLES ON CLAY AND PILLARED CLAY SURFACES

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**Abstract**—Pillared bentonites were found to be efficient catalysts for the O-methyl bond cleavage of anisoles (e.g., *m*-methylanisole, guaiacol, and creosol) under very mild, static conditions (150°C, a few hours, inert atmosphere). The O-methyl bond cleavage led to phenolic products. Gas chromatography-mass spectrometry and solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) techniques used to probe <sup>13</sup>C-labeled anisoles revealed that dealkylation and transalkylation reactions occurred to a large extent, and that conversion was efficient at >95% after two days. Ortho- and para-isomers were observed exclusively, without any evidence of meta-substitution. Volatile products were determined by mass spectrometry to be <sup>13</sup>CH<sub>3</sub>OH and (<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>O. Magic-angle spinning <sup>13</sup>C NMR experiments showed that the molecules were fairly mobile in the clay micropores prior to catalysis. After catalysis, cross-polarization NMR showed that molecular motion had decreased markedly. Ultraviolet-visible spectroscopy of the colored complexes suggested some quinone formation. The trend of clay reactivity was found to be: pillared bentonite ≫ acid-washed montmorillonite > untreated bentonite > pillared fluorhectorite ≈ untreated fluorhectorite.

**Key Words**—Anisoles, Bentonite, Catalysis, Fluorhectorite, Montmorillonite, Nuclear magnetic resonance, Pillared clay, Quinones.

### INTRODUCTION

The advent of metal oxide pillared clays (PILCs) (Vaughan and Lussier, 1980; Pinnavaia, 1983; Lahav *et al.*, 1978; Vaughan, 1988) has renewed interest in clays as heterogeneous catalysts, especially for the shape-selective cracking of heavy residual crude oils to transportation fuels (Shabtai *et al.*, 1981; Ocelli, 1983; Lussier *et al.*, 1980). Studies of PILCs have revealed the existence of both Brønsted and Lewis acidity (Poncelet and Schutz, 1986) and that these materials are thermally stable to 540°C (Ocelli and Tindwa, 1983). In addition, the internal surface areas of PILCs (200–300 m<sup>2</sup>/g) (Ocelli and Lester, 1985) are considerably greater than those of untreated smectite clays (50–80 m<sup>2</sup>/g).

The unique properties of PILCs may find use in the catalytic process developed by Hayatsu *et al.* (1984) to simulate the formation of coal. During this process, lignins are transformed in the presence of clays into a material resembling coal. Recently, solid-state <sup>13</sup>C NMR of [<sup>13</sup>C]lignins has been used to probe coalification reaction pathways, with the <sup>13</sup>C isotope at the β-position in the propyl side chain or at the methoxyl carbon of synthetic lignins (Botto, 1987). In the present investigation, similar techniques were applied to compounds that model the lignin structure using pillared clays as the catalysts. The objectives were (1) to examine the reactivity of different clays under simulated coalification conditions and (2) to elucidate clay-organic reactions responsible for bond cleavage and rearrangement processes in these systems.

Softwood lignin (MW > 10,000) has a typical mo-

nomeric unit shown in Figure 1. Inasmuch as this structure contains many reactive ether linkages (Adler, 1977), the model compounds examined in the present study contained some combination of methoxyl and phenolic groups. These include *m*-methylanisole (mMA), guaiacol, 4-hydroxy-3-methoxytoluene (HMT or creosol), and 4-phenoxy-3-methoxytoluene (PMT), also shown in Figure 1. In addition, isotopically <sup>13</sup>C-labeled derivatives were synthesized and reacted to trace reaction pathways specifically involving the methoxyl carbon.

### EXPERIMENTAL

#### Materials

Bentolite L (abbreviated BENT), a Ca<sup>2+</sup>-bentonite specially treated to remove Fe, was supplied by E.C.C. America Inc., a Southern Clay Products subsidiary. The cation-exchange capacity (CEC) given by the supplier was 80 meq/100 g. Acid-washed montmorillonite (commercial name K10) was purchased from Aldrich. Li-fluorhectorite (LFH) was synthesized by a sintering reaction at 800°C according to Barrer and Jones (1970), who reported a CEC of 90 meq/100 g for this preparation. About 10% impurities were estimated by X-ray powder diffraction (XRD); they were removed by sedimentation prior to all pillaring experiments. The aluminum pillaring solution, Chlorhydrol, was supplied by Reheis Chemical Company, New Jersey. The synthesis of the pillared clays has been described in detail elsewhere (Carrado *et al.*, 1986b). During the preparation, the pH was kept near 5.5 by adding dilute NH<sub>4</sub>OH. PILCs were calcined at 400°C in air for 4 hr

in a muffle furnace and are herein denoted as P-BENT and P-LFH. *m*-Methylanisole (mMA) (Aldrich) was distilled prior to use; guaiacol (Sigma) and 4-hydroxy-3-methoxytoluene (HMT) (Pfaltz & Bauer) were used as received. 4-Phenoxy-3-methoxytoluene (PMT) was synthesized from HMT using the Ullman ether synthesis, following a method developed by Williams *et al.* (1967).

$^{13}\text{C}$ -*m*-methylanisole was synthesized from  $^{13}\text{CH}_3\text{I}$  (MSD Isotopes) and *m*-cresol (Aldrich). The starting materials were reacted with KOH (1:1:1 mole ratios) in refluxing ethanol/water (2.5/1 liter) as a 10% by weight solution for 6 hr. The reaction was quenched on ice, extracted with ether, and washed successively with dilute NaOH, water, and saturated NaCl solution.

### Catalysis

Reactants were combined with clay in a 4:1 weight ratio of clay : organic. Solids (e.g., PMT) were ground with the clay in a mortar. Liquid reactants were combined with clay by grinding in a mortar by means of an incipient-wetness technique. In some experiments, liquid reactants dissolved in  $\text{CH}_2\text{Cl}_2$  were slurried with clay, and the solvent was removed by evaporation. The results of the slurry technique were the same except that some starting material was lost. The batches were then separated into equal portions (250–400 mg) and loaded into  $\frac{1}{4}$ " i.d., 8" Pyrex tubes. The tubes were evacuated at  $-78^\circ\text{C}$  (dry ice) to prevent loss of the organic; about  $\frac{2}{3}$  atm helium or argon was then introduced before sealing. The catalysis reactions were carried out in an oven at  $150^\circ\text{C}$  for a period ranging from hours to weeks.

### Characterization

Solvent-extractable products were recovered by refluxing the clay-organic complex in  $\text{CH}_2\text{Cl}_2$  for 1 hr followed by filtration. Octafluoronaphthalene ( $\text{F}_8\text{-n}$ ) was added as an internal standard for gas chromatographic-mass spectrometric (GCMS) analysis of these soluble products. Spectra were obtained on a Kratos MS25 mass spectrometer. GC separations were made via splitless injection using a 30-m DBWax column temperature programmed from  $150^\circ$  to  $250^\circ\text{C}$  at  $8^\circ\text{C}/\text{min}$ . A Kratos MS50 mass spectrometer operating in the precise-mass measurement mode was used to obtain high-resolution MS (HRMS). Solids were evaporated in the source by using a direct-heating platinum-mesh filament probe designed in this laboratory. The volatile products of catalysis reactions were analyzed by gas-phase MS after breaking open specially designed tubes; no oxygen or nitrogen was detected.

Solid-state  $^{13}\text{C}$  NMR spectra were obtained at 25.18 MHz on a Bruker CXP-100 spectrometer equipped with a doubly tuned single-coil probe and a dual air-bearing spinning apparatus. Ceramic sample rotors (300- $\mu\text{l}$  internal volume) were packed with about 300

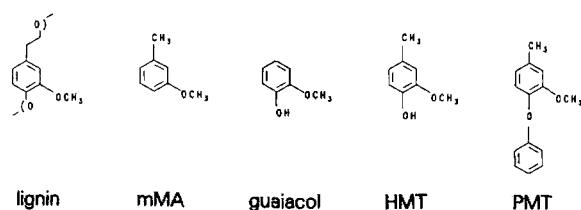


Figure 1. Softwood lignin monomer and model compounds: *m*-methylanisole (mMA), guaiacol, 4-hydroxy-3-methoxytoluene (HMT), and 4-phenoxy-3-methoxytoluene (PMT).

mg of clay-organic complex and spun at about 4 kHz. Cross-polarization (CP) experiments were performed using a contact time of 2 ms with a 2- or 3-sec pulse repetition time and a 67-kHz proton-decoupling field (3.75- $\mu\text{s}$   $90^\circ$  pulse width). Experiments without CP ( $90^\circ$  pulse – acquire) were performed using the same proton-decoupling field, a carbon-13 pulse width of 4.25  $\mu\text{s}$  and a pulse repetition time of 3 sec. Solution  $^{13}\text{C}$  NMR spectra of pure organic starting materials were obtained on either a Bruker AM-300 or a Nicolet NTC-200 in  $\text{CDCl}_3$  as solvent; spectroscopic data were referenced to an internal standard of tetramethylsilane (TMS).

The colored complexes were characterized by dissolving the clay matrix with HF and analyzing UV-visible absorption on a Shimadzu UV-160 spectrometer. Plastic 1-cm pathlength cuvettes were used to avoid leaching of glass by HF.

The samples were analyzed by X-ray powder diffraction using a Scintag PAD V instrument,  $\text{CuK}\alpha$  radiation, and a hyperpure germanium solid-state detector. Data were collected on a DG Desktop computer system. Bentonite samples were examined as loose powders in horizontally held trays using a scan rate of  $0.25^\circ 2\theta/\text{min}$ . Fluorhectorite materials were examined as oriented thin films on glass slides, also horizontally held, at scan rates of  $0.5^\circ$  or  $1^\circ 2\theta/\text{min}$ .

## RESULTS

The XRD patterns of the pillared bentonite, both alone and loaded with 4-hydroxy-3-methoxytoluene (P-BENT-HMT), as it was exposed to progressive thermal treatment are shown in Figure 2. Organic (e.g., HMT) loaded onto the clay and then extracted in a control experiment gave rise to an XRD pattern nearly identical with that in Figure 2a. The peaks at  $21.6^\circ 2\theta$  ( $4.11 \text{ \AA}$ ) and  $35.9^\circ 2\theta$  ( $2.50 \text{ \AA}$ ) are due to cristobalite impurities present in this clay (Carrado *et al.*, 1986a). A 002 reflection at  $9.42 \text{ \AA}$  was also present.

Figure 3 shows the XRD patterns of Li-fluorhectorite (LFH) before and after pillaring; the basal spacing increased from 12.2 to 18.0  $\text{ \AA}$ . These samples were analyzed as thin films on glass slides; therefore, the 001

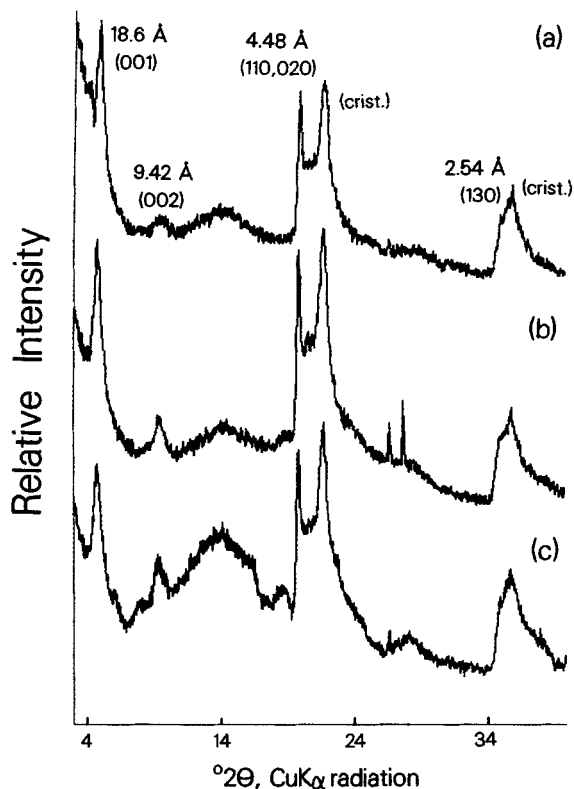


Figure 2. X-ray powder diffraction spectra of pillared bentonite (a) loaded with 4-hydroxy-3-methoxytoluene: (b) unreacted, (c) reacted at 150°C for 2 weeks.

reflections were enhanced. The pattern before pillaring was taken after impurities had been removed by sedimentation.

MAS  $^{13}\text{C}$ NMR spectra of all clay-organic complexes taken before reaction displayed strong, sharp resonances similar to spectra of the pure organic starting materials in solution. Figure 4 shows NMR spectra of the P-BENT-HMT complex before reaction and after 5 days at 150°C. Note the decrease in intensity of the resonance at 55 ppm for the methoxyl group. The latter spectrum (Figure 4b) was obtained under CP conditions; however, the unreacted sample (Figure 4a) would not cross-polarize, which is typical of the clay-organic complexes made from liquid starting materials (mMA, guaiacol, etc.). Spectra of complexes made with solid reactants (e.g., PMT) were obtained with CP conditions even before catalysis.

Table 1 lists  $\text{N}_2$ -BET surface areas of several clays. Reactivities of the clays as catalysts for demethoxylation are also listed in Table 1, expressed as conversion of mMA estimated from the % peak-area decrease of the 55-ppm NMR resonance due to  $-\text{OCH}_3$  methoxyl groups.

Typical results from a GCMS experiment are shown in Figure 5 for the solvent-extractable products from  $^{13}\text{C}$ -mMA (isotopically labeled with  $^{13}\text{C}$  at the meth-

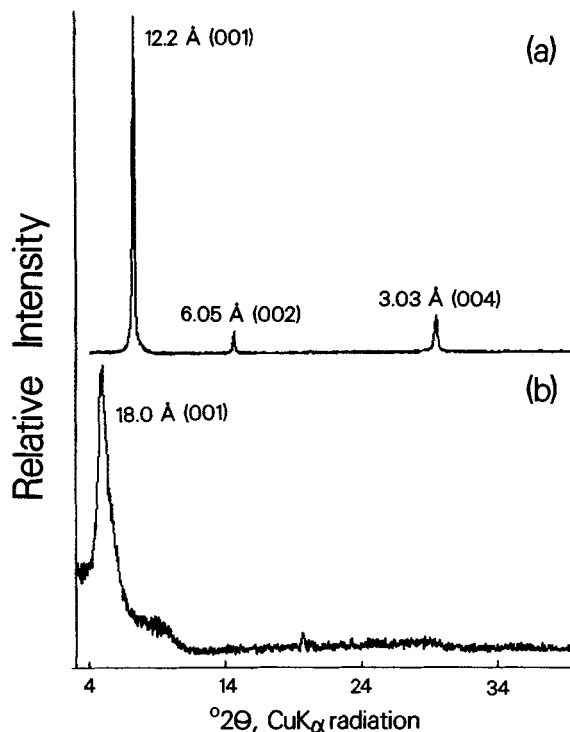


Figure 3. X-ray diffraction spectra of Li-fluorhectorite (a) after removal of impurities by sedimentation and (b) after pillaring; samples analyzed as oriented thin films, with 001 reflections indicated.

oxyl position) reacted with pillared bentonite for 3 days. Figure 6 shows  $^{13}\text{C}$  NMR spectra for  $^{13}\text{C}$ -mMA after one and six days of reaction. Standard methyl-substituted phenols and anisoles were examined to establish chemical shifts for the various methyl isomers (Table 2). MS analysis of the volatile products revealed the presence of  $^{13}\text{CH}_3\text{OH}$  and  $(^{13}\text{CH}_3)_2\text{O}$  exclusively.

The product distribution as estimated from GCMS analysis for mMA catalysis (Table 3) indicate the conversion of mMA to *m*-cresol (*m*-methylphenol), alkylated anisoles, and di- and tri-alkylated phenols. After extraction, clay- $^{13}\text{C}$ -mMA complexes contained <2% C, and only a very weak signal was seen by NMR.

The clay-organic complexes went through various color changes as the reaction progressed, usually from pink to green to black (an exception was clay-PMT which changed from pink to purple). The nature of these changes was examined by UV-visible spectroscopy; the methylene chloride extract of P-BENT-HMT reacted at 150°C for 14 hr, for example, exhibited absorption bands at 230 and 282 nm. After extraction the clay itself remained pink. Dissolution of the matrix with HF produced a pink solution that absorbed at 290, 383, and 542 nm. Table 4 summarizes these spectral data and absorption assignments for various standard compounds, as well as data from Sawhney *et al.* (1984).

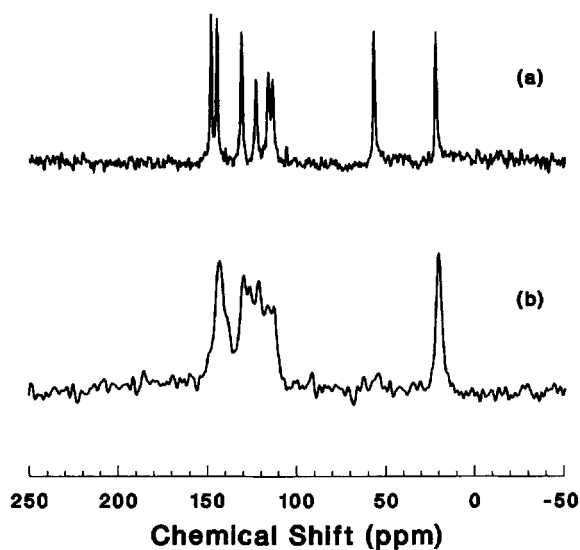


Figure 4. Magic-angle spinning  $^{13}\text{C}$  nuclear magnetic resonance spectra of pillared bentonite loaded with 4-hydroxy-3-methoxytoluene (a) before reaction (cross-polarization not used) and (b) after catalysis at  $150^\circ\text{C}$  for 5 days, obtained under cross-polarization conditions.

Using HF, the clay matrix was removed from a sample of P-BENT-HMT that had been reacted at  $150^\circ\text{C}$  for 2 wks and already extracted with  $\text{CH}_2\text{Cl}_2$ . This procedure left a black residue that was analyzed for precise mass measurement by HRMS. Most of the peaks corresponded to phenols, quinones, and benzo- and dibenzo-furans appearing in the  $\text{C}_{15}\text{-C}_{18}$ -mass range. Likely structures for the most intense ion observed at  $m/z = 240.1149$ ,  $\text{C}_{16}\text{H}_{16}\text{O}_2$ , are shown in Figure 7.

## DISCUSSION

### Clay reactivity

Pillared clays were stable during the mild catalytic reactions of this investigation. The XRD data in Figure 2 show that the interlayer spacing of  $18.6 \text{ \AA}$  for P-BENT was unchanged after being heated at  $150^\circ\text{C}$  for two weeks in the presence of organic material. In contrast, the interlayer spacing of un-pillared clays decreased gradually with thermal treatment (e.g.,  $15.6$  to about  $12 \text{ \AA}$  for bentonite). Thus, PILCs retained their internal surface area, providing an advantage over un-pillared clays and also the acid-activated, essentially noncrystalline materials, such as montmorillonite K10. A broad region centered at about  $14^\circ 2\theta$  ( $6.3 \text{ \AA}$ ) was present in the P-BENT pattern and increased in intensity with reaction time. Small peaks at  $7.8^\circ$ ,  $18.7^\circ$ , and  $28.0^\circ 2\theta$  ( $11.3$ ,  $6.32$ , and  $3.18 \text{ \AA}$ , respectively) were also present. These were not assigned, although the latter two peaks were at the expected values for the 004 and 006 reflections. The weak, narrow peaks present in the pattern of unreacted P-BENT-HMT, at  $26.7^\circ 2\theta$  ( $3.34$

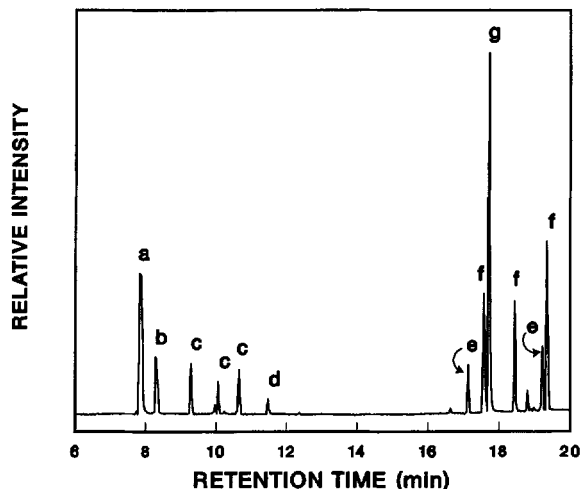


Figure 5. Gas chromatographic separation of solvent-extractable products from  $^{13}\text{C}$ -*m*-methylanisole ( $^{13}\text{C}$ -*m*-MA) catalysis by pillared bentonite at  $150^\circ\text{C}$  for three days. Assignments from mass spectrometric data are: (a)  $\text{F}_8$ -naphthalene internal standard; (b) starting material ( $^{13}\text{C}$ -*m*-MA); (c) isomers of alkylated starting material [ $(^{13}\text{CH}_3)_2$ -*m*-MA]; (d) dimethylated starting material [ $(^{13}\text{CH}_3)_3$ -*m*-MA]; (e) isomers of dialkylated *m*-cresol [ $(^{13}\text{CH}_3)_2$ -*m*-cresol]; (f) isomers of alkylated *m*-cresol [ $^{13}\text{CH}_3$ -*m*-cresol]; (g) *m*-cresol.

$\text{ \AA}$ ) and  $27.6^\circ 2\theta$  ( $3.23 \text{ \AA}$ ), are probably due to the organic material, because they disappeared after extraction.

As shown in Table 1 the least reactive complexes are, surprisingly, those involving synthetic Li-fluorhectorite. Because the surface area of P-LFH was high ( $403 \text{ m}^2/\text{g}$ ), and the XRD pattern showed a pillared crystalline material (see Figure 3), other factors must have contributed to the low activity of this clay. Urabe *et al.* (1988) recently demonstrated by  $\text{NH}_3$  temperature-programmed desorption that the surface acidity of a synthetic hectorite (Laponite) is lower than that of natural saponite and montmorillonite. Low surface acidity of LFH may therefore have been a factor contributing to its low catalytic activity. Poncelet and

Table 1. Clay surface areas and percent conversion of *m*-methylanisole.<sup>1</sup>

Clay	Surface area ( $\text{m}^2/\text{g}$ ) <sup>2</sup>	Conversion (%) <sup>3</sup>
LFH	17	0
P-LFH	403	5
BENT	76	10
K10	148	40
P-BENT	664	90

LFH = Li-fluorhectorite; BENT = bentonite; P = pillared; K10 = acid-washed montmorillonite.

<sup>1</sup> After catalysis at  $150^\circ\text{C}$  for 48 hr.

<sup>2</sup>  $\text{N}_2$ -BET surface areas by Particle Data Labs, Elmhurst, Illinois.

<sup>3</sup> Approximate results from nuclear magnetic resonance data, measured as % decrease of 55-ppm methoxyl resonance.

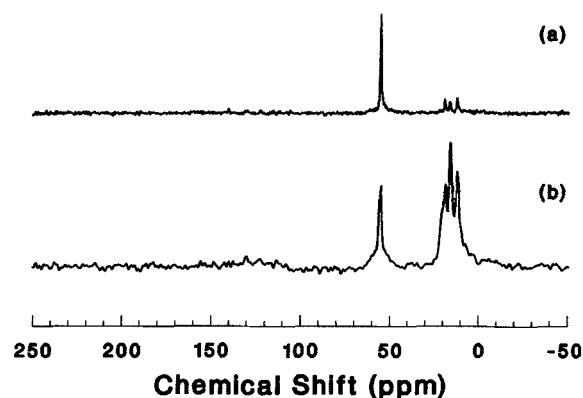


Figure 6. Cross-polarized magic-angle spinning  $^{13}\text{C}$  nuclear magnetic resonance spectra of  $^{13}\text{C}$ -*m*-methylanisole catalysis by pillared bentonite at  $150^\circ\text{C}$  after (a) 1 day and (b) 6 days.

Schutz (1986) attributed Lewis acidity in PILCs to sites on the alumina pillars, and Tichit *et al.* (1985) found these sites to be stronger than those in synthetic Y-zeolites. Inasmuch as the P-LFH clay was only marginally more active than unpillared LFH, the alumina pillars themselves were probably not catalytically active in these reactions. Thus, the high catalytic activity of the P-BENT was also not due to Lewis acid sites on the pillars, but instead to Brønsted acidity. This is not surprising, because reactions such as those reported in this work are typically catalyzed by protons. Whether the Brønsted acidity of Li-fluorhectorite is much lower than that of bentonite or negated by some structural or compositional factor, e.g., fluoride ions, is not known.

As can be seen from Table 1, the conversion of mMA using P-BENT was nine times greater than if unpillared bentonite had been used as the catalyst. This activity correlates with the increase in internal surface area due to pillaring (8.7 times increase) and accounts for the superior activity of P-BENT. The surface areas of these pillared clays were higher than values typically reported (400–600 vs. 200–300  $\text{m}^2/\text{g}$ ). A reference sam-

Table 2.  $^{13}\text{C}$  nuclear magnetic resonance chemical shifts of aromatic methyl groups in standard compounds and products from *m*-methylanisole-clay catalysis.

Compound	Chemical shifts (ppm)
2,3-dimethylphenol	19.9, 11.7
2,4-dimethylphenol	20.3, 18.3
2,5-dimethylphenol	20.1, 14.4
3,5-dimethylphenol <sup>1</sup>	21.8, 19.3
2,3,6-trimethylphenol	18.9, 15.2, 12.4
2,4,6-trimethylphenol	21.3, 16.1
3,5-dimethylanisole	20.9 <sup>2</sup>
$^{13}\text{C}$ - <i>m</i> -methylanisole	20.9
P-BENT- $^{13}\text{C}$ -mMA <sup>3</sup>	18.0, 15.0, 11.0

<sup>1</sup> Although only one peak is expected, two were observed.

<sup>2</sup> Salman and Kamounah (1987).

<sup>3</sup> mMA = *m*-methylanisole; P-BENT = pillared bentonite; this sample was reacted at  $150^\circ\text{C}$  for 6 days.

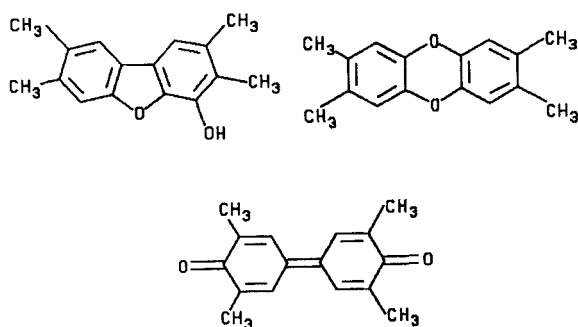


Figure 7. Possible structures for the most intense high-resolution mass spectrometric ion at 240.1149,  $\text{C}_{16}\text{H}_{16}\text{O}_2$ , identified from the residue of 4-hydroxy-3-methoxytoluene catalysis by pillared bentonite for 2 weeks, after solvent extraction and HF dissolution of the clay matrix.

ple of bentonite (Bentolite L), for which the supplier stated a surface area of  $80 \text{ m}^2/\text{g}$ , was concurrently analyzed to have a surface area of  $76 \text{ m}^2/\text{g}$ . All surface area measurements were therefore considered reliable. Although the internal surface area of sample K10 was only twice that of bentonite, its catalytic reactivity was about four times greater. This increase may be accounted for by the high acidity of this acid-washed montmorillonite.

Little use has been made of  $^{13}\text{C}$  NMR spectroscopy for the elucidation of the microenvironment of organic molecules in silicate structures. A few studies have demonstrated the potential for identifying species in zeolites (Aronson *et al.*, 1989) and the degree of molecular freedom in clays (Fyfe *et al.*, 1981). CP coupled with MAS has made possible the study of solids by  $^{13}\text{C}$  NMR spectroscopy. In this technique, the abundant  $^1\text{H}$  spin system is polarized, and this magnetization is transferred to the dilute  $^{13}\text{C}$  spin system. CP cannot be applied to samples possessing a large degree of mobility (e.g., liquids), because dipolar interactions are lost due to motional averaging. CP  $^{13}\text{C}$  NMR spectra of clay-organic complexes derived from model compounds that are liquids at room temperature are readily obtained only after catalysis. Figure 4 demonstrates this behavior for sample P-BENT-HMT. This result indicates that the mobility of the organic molecules decreased

Table 3. Distribution (mole %) of soluble products obtained from the reaction of *m*-methylanisole with pillared bentonite at  $150^\circ\text{C}$ .<sup>1</sup>

Time (hr)	mMA	Me-mMA	Me <sub>2</sub> -mMA	<i>m</i> -cresol	Me-cresol	Me <sub>2</sub> -cresol
0	100	0	0	0	0	0
22	69.2	3.3	0	27.7	0	0
49	9.4	9.8	1.8	33.2	24.5	21.3
72	4.9	10.1	1.0	34.8	41.4	7.8

mMA = *m*-methylanisole; Me = methyl.

<sup>1</sup> Based on gas chromatography/mass spectrometry analysis.

Table 4. Ultraviolet-visible data for clay-organic complexes.

Sample	Treatment	Absorption (nm)	Assignment
HMT	in CH <sub>2</sub> Cl <sub>2</sub>	225, 282	HMT
P-BENT-HMT/14 hr <sup>1</sup>	CH <sub>2</sub> Cl <sub>2</sub> extract	230, 282	HMT
2,6-dimethylphenol/clay/24 hr/50°C <sup>2</sup>	MeOH extract	269, 412	phenols + quinones
Bentonite	dilute HF	291, 297	clay
P-BENT-HMT/14-hr after extraction <sup>3</sup>	dilute HF	290, 383, 542	clay + quinones

HMT = 4-hydroxy-3-methoxy toluene; P-BENT = pillared bentonite.

<sup>1</sup> Complex reacted at 150°C for 14 hr.

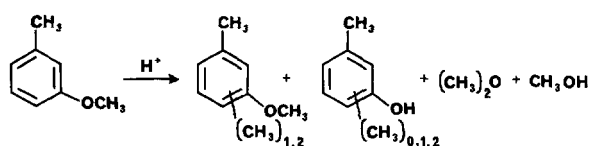
<sup>2</sup> Sawhney *et al.* (1984).

<sup>3</sup> Previously extracted with CH<sub>2</sub>Cl<sub>2</sub>.

significantly after reaction at elevated temperatures. Because the products were predominately phenolic in nature, it was probably the OH group that interacted with the clay surface. This interaction was, however, weak enough to allow products to be easily extracted with solvent.

### Catalysis

Major changes occurred after heating the clay-anisole complexes at 150°C for only a short period of time. Figure 4 shows the characteristic decrease of the methoxyl resonance at 55 ppm, which indicates extensive cleavage of the O-methyl bond. GCMS data of solvent-extractable products were consistent with O-methyl bond cleavage of anisoles and revealed phenols and a series of substituted methyl phenol products, as illustrated in Figure 5 for *m*-methylanisole. MS analysis of volatile products indicated the formation of methanol, which was the expected demethoxylation side-product. Large quantities of dimethyl ether were also produced as a result of further dehydration of methanol over the clay surface. The volatile products for the reaction of <sup>13</sup>C-MMA were found to be the labeled compounds <sup>13</sup>CH<sub>3</sub>OH and (<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>O, exclusively. In contrast, non-catalytic thermal decomposition of anisoles yields predominantly CH<sub>4</sub> and a mixture of C<sub>2</sub>H<sub>4</sub>/CO light gases resulting from O-methyl bond homolysis (Suryan *et al.*, 1989). The reaction scheme of MMA to produce alkylated anisoles, alkylated phenols, and volatile products is shown below.



Isotopically labeling MMA with <sup>13</sup>C provided insight into the extent to which dealkylation and transalkylation may have occurred. The NMR spectrum of <sup>13</sup>C-MMA after one and after six days of heating in the presence of bentonite (Figure 6) showed aromatic -<sup>13</sup>CH<sub>3</sub> resonances in the 10–18 ppm range increasing at the expense of the methoxyl-O<sup>13</sup>CH<sub>3</sub> resonance at 55 ppm. Pure compounds of the possible isomers were examined individually by <sup>13</sup>C NMR to compare chem-

ical shifts (see Table 2). Methyl groups in the meta-positions were not expected as products; these resonances occur at higher chemical shifts, about 20–22 ppm, and were indeed not observed. Ortho- and para-substituted products were the expected isomers, and reference compounds were found to exhibit chemical shifts identical to those of the observed products. Table 3 shows a concomitant decrease of MMA with an increase in alkylated anisoles (minor products) and *m*-cresol and alkylated cresols (major products). The amount of dialkylated products began to decline proportionally with time, as they were further cracked to simpler products.

### HRMS and ultraviolet-visible spectroscopy

Ultraviolet-visible data presented in Table 4 indicate that the phenolic products underwent further transformation to minor amounts of quinones, even in the absence of O<sub>2</sub>. Sawhney *et al.* (1984), investigating the polymerization of 2,6-dimethylphenol on smectites, also reported the formation of quinone products. Their results revealed the following order for phenol reactivity with exchangeable cations on homoionic clays: Fe > Al > Ca > Na. If transition metal ions were present, radical cations formed by electron transfer and reacted further to oligomers and quinones (Sawhney *et al.*, 1984; Mortland and Halloran, 1976). The BENT and LFH samples had extremely low iron contents (0.3 and <0.3% Fe<sub>2</sub>O<sub>3</sub>, respectively). The overall amount of quinones formed is therefore assumed to have been very low, which correlates with the observation that only about 2% C in non-extractable products remained on the catalyst.

Color changes were not observed for LFH and P-LFH in the presence of anisoles either before or after catalysis. This result is consistent with the low reactivity of LFH surfaces for the conversion of anisoles to phenols. Furthermore, phenolic species, such as guaiacol and HMT, did not oxidize to quinones on the surface of LFH even in the presence of oxygen.

An absorption band was noted at 542 nm (see Table 3) for a dissolved clay-organic complex from HMT that had been reacted with P-BENT. This band is in the 400–600-nm range characteristic of many diphen-quinones that contain no hydroxy substituents (Hor-

ner and Weber, 1967). Isaacson and Sawhney (1983) observed single absorption bands between 410 and 419 nm if phenols had been transformed on clay surfaces. The band at 383 nm for the dissolved P-BENT-HMT sample, however, may have been due to a quinone species that *does* contain hydroxyl groups. Figure 7 shows possible structures for the most intense molecular ion peak in an HRMS spectrum of non-extractable products from a sample of HMT reacted with P-BENT for two weeks. This  $C_{16}H_{16}O_2$  product could have been an extensively methylated quinone dimer, hydroxy-dibenzofuran, or dibenzodioxin.

Even in the absence of oxygen, some oxidation of phenols to quinones was indicated, suggesting some oxidation power of the bentonite surface. Fe(III), Cu(II), and other transition metal (TM) ions exchanged into clays should enhance this type of oxidation. Furthermore, selectivity effects using TM-PILCs should accompany this type of oxidation.

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