Cooperative Effect of Surface Sites on the Laser Flash Photolysis of 1,1-Diphenylacetone and 1,1,3,3-Tetraphenylacetone Adsorbed on Layered Clays. Generation of Radicals and Carbocations

Frances L. Cozens,[†] Hermenegildo García,[*,‡] F. Gessner,[†] and J. C. Scaiano[*,†]

Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5, and Instituto de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, 46071 Valencia, Spain

Received: January 28, 1994; In Final Form: May 19, 1994[®]

Laser flash photolysis of 1,1-diphenyl- and 1,1,3,3-tetraphenylacetone adsorbed onto a series of clays has been carried out under dry conditions. The photochemical behavior of the guests was investigated by using time-resolved diffuse reflectance techniques. Deposition of the organic compounds onto the solids was performed by slow removal of the solvent from dilute solutions at low temperature. Distinct transient spectra in the microsecond time domain were obtained for the guest–host composites. The formation of the diphenylmethyl radical ($DPM^\bullet$) was observed with montmorillonites SWy-1 (λ_{max} = 310 nm) and STx-1 (λ_{max} = 340 nm). The decay of $DPM^\bullet$ on the bidimensional geometry of the layered clays was found to be much slower than within a tridimensional large-pore zeolite. By contrast, in the case of the pillared Al_{13}SWy-1 and Al_{13}STx-1 clays, additional reflectance at 450 nm characteristic of the diphenylmethyl cation (DPM^+) was present. This intermediate presumably arises from the cooperative interaction with the acid sites of the clay. These results show that these ketones are convenient probes to report on the chemical and topological properties of solid surfaces.

Introduction

Adsorption of a guest molecule onto a solid surface has become a general methodology to alter and gain control of the photochemical behavior of the guest.[1,2] Differences in the photochemistry of substrates upon irradiation in solid systems from that obtained in homogeneous solutions can arise from both the confinement of the guest in the restricted spaces and the interaction of the substrate with the active sites of the solid.[3]

While the presence of acid sites in natural layered clays[4-6] has been widely exploited in their use as heterogeneous catalysts for thermal ground-state reactions,[7,8] and particularly for petrochemical processes,[9] their use as hosts to perform photochemical reactions under dry conditions has been uncommon compared with applications of other adsorbents. The vast majority of these studies has focused on the use of guests as photophysical probes and comparatively little attention has been paid to the study of the photochemical reactivity of organic compounds on these surfaces.[10-12]

Incorporation of nonpolar organic molecules within the highly hydrophilic interlayer regions of these solids has been found to be problematic, as only the external surfaces are generally accessible to the guests. Therefore, the bidimensional open topology characteristic of these montmorillonite guest-host systems can influence the course of the photochemical reaction in a distinctive way compared to other solid hosts exhibiting closed reaction cavities. Moreover, the possibility to prepare pillared clays[13,14] by ion exchange provides a smooth transition to zeolitic-like materials with increasing sieving capabilities and accessibility to the internal regions.

The photochemistry of 1,1-diphenylacetone (DPA) and 1,1,3,3-tetraphenylacetone (TPA) has been exhaustively studied in solution.[15] The diphenylmethyl radical ($DPM^\bullet$) generated by homolytic bond cleavage from the triplet excited state is the characteristic reaction intermediate. Recently, we reported that the photochemical behavior of DPA and TPA can be modified by inclusion within acidic zeolites[16] where, in addition to $DPM^\bullet$, the diphenylmethyl cation (DPM^+) was observed with time-resolved diffuse reflectance techniques. These types of guests are therefore convenient probes to investigate the influence of the host-guest interaction. In the present work, we report that the crystalline structure and active sites of clays also have a significant effect on the photochemistry of these ketones.

Results and Discussion

Two natural samples of smectites from Wyoming (SWy-1) and Texas (STx-1) were purified by treatment with aqueous acid, then neutralized with dilute NaOH, and treated with a saturated solution of aqueous NaCl. Adventitious salts were finally removed from the clay by dialysis and the aqueous suspension was submitted to freeze-drying. Deposition of DPA and TPA (1-3 wt %) onto the solids was carried out by slowly removing the solvent from a suspension of the clay in a solution of the organic compound in CH_2Cl_2 at 273 K under reduced pressure. In the case of the DPA–SWy-1 composite, exhaustive extraction led to a complete recovery of the unchanged organic compound. An alternative adsorption procedure based on the free diffusion of the guest from a CH_2Cl_2 solution onto the solids, followed by subsequent washing with fresh solvent, did not result in any appreciable incorporation of the aromatic ketones and unaltered DPA and TPA were completely recovered. In contrast, the free diffusion technique leads to extensive incorporation in the case of large-pore zeolites.[3]

The strength of the interaction between the ketones and the clays was determined by recording the diffuse reflectance and luminescence spectra of the composites. These spectra show a remarkable coincidence with those reported within the cavities of NaY, where it has been found that the host-guest interaction is weak.[16] In addition, the frequency of the C=O stretching band at 1705 cm^{-1} in the IR spectra of these composites is similar to that measured in a KBr disk.

The adsorption data together with the spectroscopic characterization of these composites suggests that the organic compounds are located on the externally accessible surface of the clays and that only a loose interaction is experienced.

Time-resolved diffuse reflectance experiments were carried out with the fourth harmonic (266 nm) of a Nd:YAG laser as the excitation source.[17,18] Representative decay traces of $DPM^\bullet$ generated upon photolysis of the DPA–SWy-1 and DPA–STx-1

[†] University of Ottawa.

[‡] Universidad Politécnica de Valencia.

[®] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

0022-3654/94/2098-8494$04.50/0

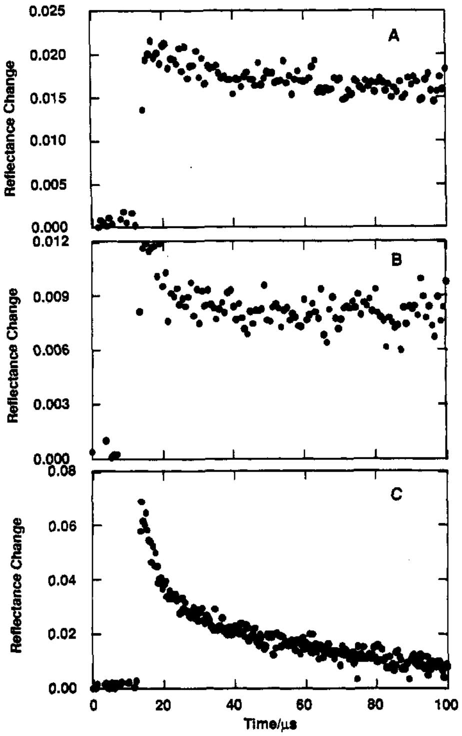

Figure 1. Decay traces monitored at 320 nm (A and B) and 330 nm (C) after 266-nm excitation of (A) DPA–SWy-1, (B) DPA–STx-1, and (C) DPA-NaY.

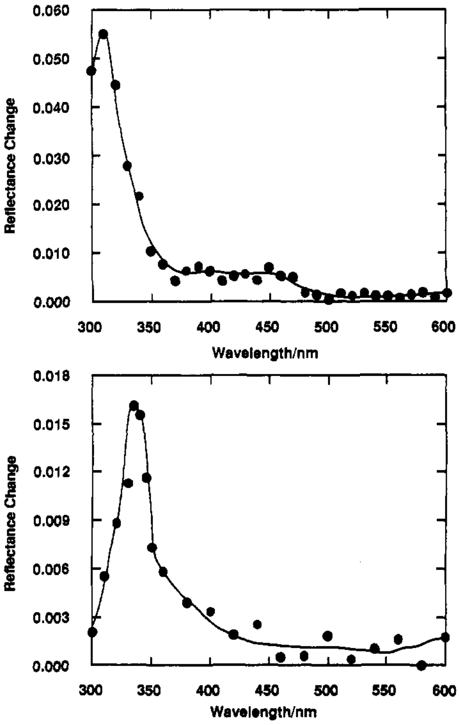

Figure 2. Transient spectra recorded 3 μs after 266-nm excitation of DPA–SWy-1 (top) and DPA–STx-1 (bottom) composites.

composites, eq 1, are shown in Figure 1. For the sake of comparison the 330-nm decay trace for DPM$^\bullet$ obtained upon photolysis of DPA hosted within NaY under the same conditions has also been included in Figure 1.

$$\mathrm{Ph_2CHCOCH_3 \xrightarrow{h\nu} Ph_2CH^\bullet + CH_3CO^\bullet} \qquad (1)$$

The relatively slower kinetics for the disappearance of DPM$^\bullet$ on the flat layers of the clay as compared with the large-pore zeolite is quite remarkable. The bidimensional topology of the clays, which allows one degree of translational freedom less than the tridimensional micropore structure of the faujasite, would impose more restriction on the mobility of the radicals and consequently slow down the rate constant for the reaction of the separated DPM$^\bullet$.

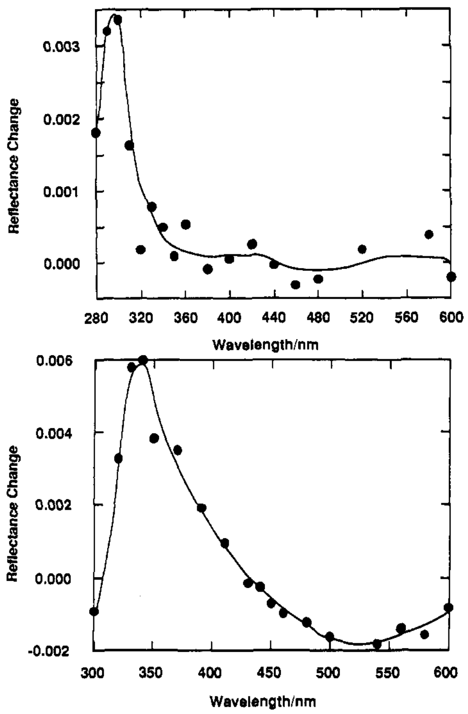

Figure 3. Transient spectra recorded 3 μs after excitation of TPA–SWy-1 (top) and TPA–STx-1 (bottom) composites.

The transient spectra recorded 3 μs after laser excitation of these composites, Figures 2 and 3, show differences in the position of the maximum attributed to DPM$^\bullet$. In STx-1 the maximum is 340 nm, close to the usual value of 330 nm,[19] while in SWy-1 the maximum is shifted by 20 nm to 310 nm. The broadness of the band in the case of STx-1, with appreciable reflectance above 350 nm, is worth noting. The same features were recorded for the transient spectra of the TPA–SWy-1 and TPA–STx-1 composites, Figure 3, showing that the differences are due to the specific properties of the two montmorillonites. Note the higher intensity of the SWy-1 system.

The above observation is particularly surprising taking into account that SWy-1 and STx-1 are the same type of materials.[20] They possess identical layered structures, are in their sodium forms, and have similar cation exchange capacities. Nonetheless, these two materials do originate from different geographic sites (Wyoming and Texas) and may differ in some of their physical properties (such as surface area) as well as chemical composition. For example, their iron contents are somewhat different (3.35% for SWy-1 versus 0.65% for STx-1).

We were therefore interested in examining the origin of the differences in transient spectra. In order to address this question polyhydroxyaluminum pillared clays of the two smectites ($\mathrm{Al_{13}}$-SWy-1 and $\mathrm{Al_{13}}$STx-1) were prepared by ion exchange using a solution of $[\mathrm{Al_{13}O_4(OH)_{24}(H_2O)_{12}}]^{7+}$ (abbreviated as $\mathrm{Al_{13}}$) obtained by basic hydrolysis of $\mathrm{AlCl_3}$ according to reported procedures.[21] After washing the resulting solids thoroughly, a final calcination at 723 K was carried out to ensure chemical bonding of the pillars to the clay sheets.

Free diffusion of the guests from a $\mathrm{CH_2Cl_2}$ to the solids did not result in any significant incorporation of the organic ketones. Deposition of DPA and TPA was performed by slow solvent removal from dilute solutions. No appreciable changes in the reflectance and emission spectra or the C=O region of the FT-

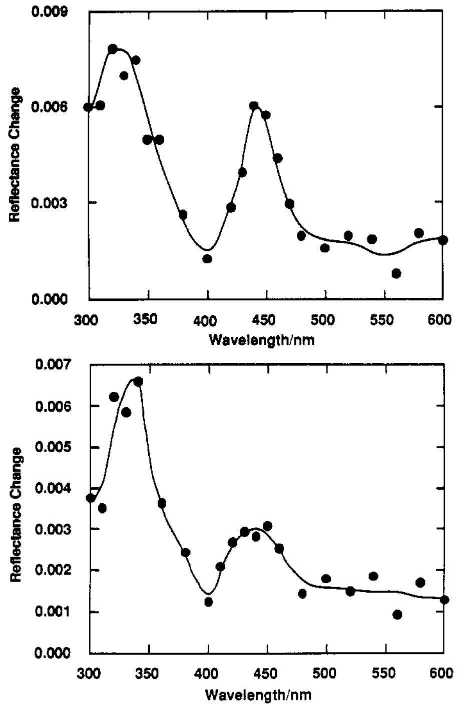

Figure 4. Transient spectra recorded 3 μs after excitation of DPA–Al_{13}SWy-1 (top) and DPA–Al_{13}STx-1 (bottom) composites.

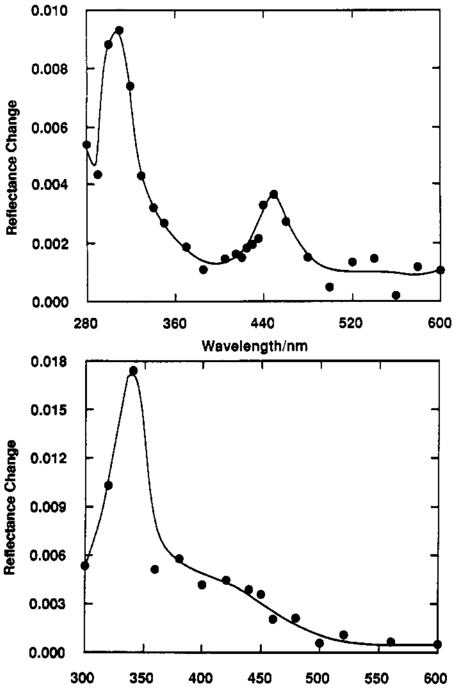

Figure 5. Transient spectra recorded 3 μs after excitation of TPA–Al_{13}-SWy-1 (top) and TPA–Al_{13}STx-1 (bottom) composites.

IR spectra of these four composites compared with the original smectites were observed. This indicates a weak interaction between the ground and excited states of the organic guests with the solid surfaces.

The transient spectra recorded 3 μs after 266-nm laser excitation of the pillared composites are presented in Figures 4 and 5. In addition to the reflectance corresponding to DPM•, a new band centered at 450 nm is present. In particular, a comparison between the spectra of the sodium and Al_{13} pillared forms of SWy-1 reveals how dramatically the course of the photochemical reaction has been altered. Based on the reported absorption spectrum in solution,[22] we assign this new transient to the diphenylmethyl cation (DPM^+).

It is well established that pillaring of layered clays increases the total number of acid sites measured by the pyridine vapor adsorption technique.[14,21,23–26] This is due to the combination of two factors, the increase in the surface area accessible to organic bases, and the new Brønsted acid sites introduced by hydrolysis of the polyoxyaluminum pillars in the calcination step. It has been reported that while STx-1 shows only a weak Lewis acidity, the corresponding Al_{13}STx-1 exhibits a much higher population of stronger Brønsted and Lewis sites.[27] Therefore, we ascribe the generation of DPM^+ to the interaction of the solid surface acid sites with DPA and TPA as indicated in eqs 2 and 3. The same cooperative effect of the acid sites on the photochemistry of these ketones has been observed in the case of acid faujasites.[16]

$$Ph_2CHCOCH_3 \xrightarrow[H^+\text{-clay}]{h\nu} Ph_2CH^+ + CH_3CHO \quad (2)$$

$$Ph_2CHCOCHPh_2 \xrightarrow[H^+\text{-clay}]{h\nu} Ph_2CH^+ + Ph_2CHCHO \quad (3)$$

From inspection of Figures 4 and 5 it is clear that the 330- and 450-nm signal intensities are more similar for DPA than for TPA, with the latter giving significantly more radical than cation. Moreover, for both guests cation formation is favored in the SWy-1 composite compared to the STx-1 composite. The efficiency of the proton-assisted fragmentation will depend on a combination of factors such as the acid strength distribution of the sites and the position of the ketone group with respect to the acidic protons. We have observed that in the case of DPA within a highly dealuminated acid Y faujasite (HYD), DPM^+ is almost exclusively generated. This higher efficiency of the HYD zeolite to promote DPM^+ formation reflects the higher acid strength of the zeolite acid sites[21,24] and/or the occurrence of a cage effect due to the closed reaction cavity provided by the faujasite crystalline structure.

In conclusion, we find that the photochemistry of 1,1-diphenylacetone and 1,1,3,3-tetraphenylacetone can be deeply influenced by deposition on natural and modified clays, making these compounds convenient probes to report on the chemical and geometrical characteristics of the surfaces. Even weak guest-host interactions, which do not produce significant changes of the guest as monitored by the electronic and IR spectra, can lead to distinctive transient spectra. Besides DPM•, generation of DPM^+ through the cooperation with the solid acid sites appears to be a general process.

While it is clear that ketone photochemistry is considerably more complex in clays and zeolites than in solution, it is precisely the ability of these materials to modify the substrate chemistry that makes clays and zeolites useful catalysts in industry. Our early attempts to study photoinduced carbocation formation in clays led to the observation that typical precursors gave carbocations spontaneously[28] and photoexcitation was not needed. Recent work in zeolites[16] and the current report in clays show that typical photochemical precursors of free radicals can yield carbocations on these acidic materials. These same clays and zeolites can be viewed as carbocation promoters, a characteristic well-known to industry. Laser techniques provide a direct approach to study these processes. Finally, this report leaves some questions unanswered, such as the origin of radical spectral shifts and the identity of weaker reflectance changes in the 380–400-nm region. Clearly further work will be required to elucidate these aspects.

Experimental Section

Materials. Purification of SWy-1 and STx-1. Natural samples of these two clays were purified by treating the solids (about 60

g) consecutively with dilute aqueous HCl solutions (1 L) of pH 2 and 3.5, respectively, according to report procedures.[28] The clays were then dispersed twice in dilute aqueous NaOH solutions (1 L, pH 8) and left undisturbed for 12 h. The clay sediment was treated with a saturated aqueous NaCl solution (300 mL) and submitted to dialysis using Millipore purified water that was frequently replaced for about 10 days. The final clay samples were recovered from the aqueous solution by freeze-drying for 4 days.

Preparation of Al$_{13}$SWy-1 and Al$_{13}$STx-1. A 0.5 M aqueous solution of NaOH (250 mL) was added to a 0.2 M solution of AlCl$_3$·6H$_2$O (200 mL) under vigorous magnetic stirring. The solution was heated at 333 K for 3 h and allowed to cool at room temperature. The corresponding clay (2 g) was added to the solution and the resulting suspension stirred at room temperature for 1 h. After this time, the suspension was centrifuged and subjected to several washing (100 mL of distilled water)–centrifugation cycles (typically 6), until a negative test for Cl$^-$ using a 0.1 M solution of AgNO$_3$ was obtained. The exchanged clays were dried at 378 K for 6 h and baked in the oven at 723 K for 8 h.

Deposition of the Organic Compounds onto the Solids. DPA was a commercial sample (Aldrich) and used as received. TPA was synthesized by condensation of ethyl diphenylacetate using sodium metal following the procedure described in the literature[29] and purified by flash column chromatography with silica gel using hexane as eluent. A solution of the corresponding organic material (between 10 and 30 mg) in CH$_2$Cl$_2$ (BDH, spectroscopic grade, <0.01% water) (50 mL) was poured onto the solid and the suspension was concentrated under reduced pressure at 273 K. Exhaustive extraction of the organic material from the composites was carried out by using a micro-Soxhlet equipment and CH$_2$Cl$_2$ as solvent. GC analysis using a Perkin-Elmer 8320 apparatus with a capillary column showed that only the unaltered starting compound was present in the recovered material.

Alternatively, a suspension of the ketone (about 20 mg) and the solid in CH$_2$Cl$_2$ (30 mL) was stirred for 2 h. After this time, the mixture was centrifuged and the solid washed with fresh solvent (10 mL) for 30 min. The amount of organic substrate adsorbed was calculated from the difference between the initial weight and the amount recovered in the combined CH$_2$Cl$_2$ solutions measured by UV absorption at 256 nm. However, this procedure did not lead to any appreciable incorporation of organic material onto the solids.

Reflectance and emission spectra of the guest-host composites were carried out with a Perkin-Elmer LS50 spectrophotometer. In the first case the spectra were obtained using the option of synchronous scanning of both monochromators. FT-IR spectra were recorded on a Bomen MB 100 spectrophotometer and wafers were prepared by pressing the composites.

Laser Flash Photolysis. The experimental setup for transient diffuse reflectance is similar to that described in detail previously.[17] The fourth harmonic (266 nm, ≤10 ns pulses, ≤10 mJ/pulse) from a Surelite Nd:YAG laser was used for sample excitation. Samples contained in 3 × 7 mm^2 quartz Suprasil cuvettes were purged with nitrogen for at least 30 min prior to photolysis. After acquisition of each data point the sample was shaken to ensure that a fresh surface was accessible to the laser beam.

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada for an operating grant (J.C.S.) and a post doctoral fellowship (F.L.C.) and the DGICYT of Spain (H.G., Grant PB90-0747) for financial support. H.G. also thanks to the DGICYT for a fellowship.

References and Notes

(1) Ramamurthy, V. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991.

(2) Gessner, F.; Scaiano, J. C. *J. Photochem. Photobiol. A: Chem.* **1992**, *67*, 91.

(3) Ramamurthy, V.; Eaton, D. F.; Caspar, J. V. *Acc. Chem. Res.* **1992**, *25*, 299.

(4) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.

(5) Ocelli, M. L.; Robson, H. E. E. *Expanded Clays and Other Microporous Solids*; van Nostrand Reinhold: New York, 1992.

(6) Suib, S. L. *Chem. Rev.* **1993**, *93*, 803.

(7) Cornélils, A.; Laszlo, P. *Synthesis* **1987**, 909.

(8) Adams, J. M. *Appl. Clay Sci.* **1987**, *2*, 309.

(9) Otterstedt, J. E.; Gevert, B.; Sterte, J. *ACS Symp. Ser.* **1988**, *375*, 266.

(10) Thomas, J. K. *Acc. Chem. Res.* **1988**, *21*, 275.

(11) Cenens, J.; Schoonheydt, R. A.; De Schryver, F. C. *ACS Symp. Ser.* **1989**, *415*, 378.

(12) Jones, W. In *Photochemistry in Organized and Constrained Media*; V. Ramamurthy, Ed.; VCH: New York, 1991; Chap. 9, p. 387.

(13) Pinnavaia, T. J. *Science* **1983**, *220*, 4595.

(14) Figueras, F. *Catal. Rev.-Sci. Eng.* **1988**, *30*, 457.

(15) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(16) Cozens, F. L.; García, H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 11134.

(17) Wilkinson, F.; Kelly, G. In *Handbook of Organic Photochemistry*; J. C. Scaiano, Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 293.

(18) Bohne, C.; Redmond, R. W.; Scaiano, J. C. In *Photochemistry in Organized and Constrained Media*; V. Ramamurthy, Ed.; VCH: New York, 1991; p 79.

(19) Kelly, G.; Willsher, C. J.; Wilkinson, F.; Netto-Ferrereira, J. C.; Olea, A.; Weir, D.; Johnston, L. J.; Scaiano, J. C. *Can. J. Chem.* **1990**, *68*, 812.

(20) van Olphen, H.; Fripiat, J. J. *Data Handbook for Clay Minerals and Other Non-Metallic Minerals*; Pergamon Press: Oxford, 1979.

(21) Schutz, A.; Stone, W. E. E.; Poncelet, G.; Fripiat, J. J. *Clays Clay Miner.* **1987**, *35*, 251.

(22) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918.

(23) Occelli, M. L.; Tindwa, R. M. *Clays Clay Miner.* **1983**, *31*, 22.

(24) Plee, D.; Schutz, A.; Poncelet, G.; Fripiat, J. J. In *Catalysis by Acid and Bases*; B. Imelik, C. Naccache, G. Coudurier, J. Ben Taarit and J. C. Vedrine, Ed.; Elsevier: Amsterdam, 1985; Vol. 20, p 343.

(25) Tichit, D.; Fajula, F.; Figueras, F. In *Catalysis by Acid and Bases*; B. Imelik, C. Naccache, G. Coudurier, J. Ben Taarit and J. C. Vedrine, Ed.; Elsevier: Amsteredam, 1985; vol. 20, p 351.

(26) Ming-Yuan, H.; Zhonghui, L.; Enze, M. *Catal. Today* **1988**, *2*, 321.

(27) Bradley, S.; Kydd, R. A. *J. Catal.* **1993**, *141*, 239.

(28) Cozens, F. L.; Gessner, F.; Scaiano, J. C. *Langmuir* **1993**, *9*, 874.

(29) Dean, D. O.; Dickinson, W. B.; Quayle, O. R.; Lester, C. T. *J. Am. Chem. Soc.* **1950**, *72*, 1740.