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NEW TRIPHASE CATALYSTS FROM MONTMORILLONITE[1]

Key Words—Catalyst, Montmorillonite, Onium salts, Phase transfer, Quaternary ammonium salts.

Quaternary ammonium salts immobilized on insoluble synthetic polymers and inorganic oxides, such as silica and alumina, have been widely explored as triphase catalysts (Deschler *et al.*, 1986; Tundo and Venturello, 1979; Ford, 1984). Inherent disadvantages, such as low physical strength, alkali instability, and acid instability, respectively, with polymers, silica, and alumina (Ford, 1984), render these catalysts unsuitable for many reactions. Montmorillonite is the support of current interest for pillared (Figueras, 1988), immobilized (Pinnavaia, 1983), and anchored catalysts (Choudary *et al.*, 1989; Sharma *et al.*, 1989). In view of the natural abundance of montmorillonite, an inexpensive material can be obtained that has high physical strength and relatively high resistance towards acid and alkali treatment.

In an earlier study, onium salts were intercalated by exchange in montmorillonite (Cornelis and Laszlo, 1982), but their applicability was limited to a few reactions in phase-transfer catalysis. Possible desorption of exchanged onium salts with cationic impurities preclude their wide use. Montmorillonite is known to participate in Friedel-Crafts reactions, esterification, etherification, and arylation to form stable, covalently bonded organic moieties in the interlamellar region (Gentili and Deuel, 1957; MacEwan and Wilson, 1984). In the present paper the novel synthesis of covalently bound onium salts in the interlamellar region of montmorillonite is described and the application of these products as phase-transfer catalysts in triphase catalytic nucleophilic substitution reactions is presented.

EXPERIMENTAL

Materials

Natural montmorillonite (SWy-1, from the Source Clay Repository of The Clay Mineral Society) (chemical composition, SiO_2, 55.6; Al_2O_3 20.1; Fe_2O_3, 3.7; CaO, 0.5; MgO, 2.5; Na_2O, 2.8; K_2O, 0.6; cation-exchange capacity = 1.2 meq/g) was allowed to sediment for 24 hr as a 1 wt. % aqueous slurry to remove dense impurities, such as quartz. The clay was then treated with excess aqueous NaCl solution and with 0.1 N HCl at room temperature for 24 hr to produce a H-montmorillonite. The material was thoroughly washed free of chloride and dried at 65°C and under a 0.01 mm vacuum. The reagents 3-aminopropyltriethoxysilane, 3-chloropropyltrimethoxysilane, and octylbromide, obtained from Fluka, were used without purification. Tributyl-amine and pyridine were purified prior to use. Freshly dried solvents were used. All experiments leading to the preparation of montmorillonite onium salts were conducted under a nitrogen atmosphere.

Fourier-transform infrared (FTIR) spectra were recorded on a Bomem Michelson-100 grating spectrophotometer. X-ray powder diffraction (XRD) patterns were recorded in the 0–10 Å region on thin films on a Philips PW 1051 diffractometer using Ni-filtered CuKα radiation (λ = 1.54138 Å). Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 80 A instrument using tetramethylsilane as an internal reference. Gas chromatographic (GC) analysis of products was performed with a CIC column chromatograph, India, equipped with a flame ionization detector (FID), and a 10% Carbowax column.

Methods

Preparation of amino- and chlorofunctionalized montmorillonite. H-montmorillonite (10.0 g) was refluxed with 3-aminopropyltriethoxysilane (1.55 g, 7.0 mmole) and 3-chloropropyltrimethoxysilane (1.39 g, 7.0 mmole) separately in dry toluene for 48 hr, followed by filtration, washing with toluene and dry ether, and drying at 65°C and 0.01 mm vacuum to produce amino-functionalized (A) and chloro-functionalized (B) products, respectively. Product A contained 0.56 meq N/g; product B contained 0.51 meq Cl/g. The ammonia adsorption capacity was considerably reduced to 0.30 and 0.31 mmole/g for the A and B products, respectively, compared with H-montmorillonite, which adsorbed 0.85 mmole/g ammonia. These smaller NH_3 adsorption capacities correspond approximately to the involvement of one hydroxyl of the montmorillonite with each silyl group in the condensation reaction.

Preparation of montmorillonite-silylpropyl trimethyl ammoniumiodide. Product A (3.0 g) was suspended in 30 ml of ethanol and cooled to 0°C. Ten milliliters of methyl iodide was added, allowed to attain room temperature, and refluxed for 5 hr. The mixture was then diluted with ether and filtered, washed twice with methanol and ether, and dried at 65°C and 0.01 mm vacuum for 10 hr to yield catalyst 1. The iodide content of this catalyst was 0.5 meq/g.

Preparation of montmorillonite-silylpropyl tributyl ammonium chloride. Product B (5.0 g) was suspended in 10 ml of tributylamine and heated at 90°C for 7 days

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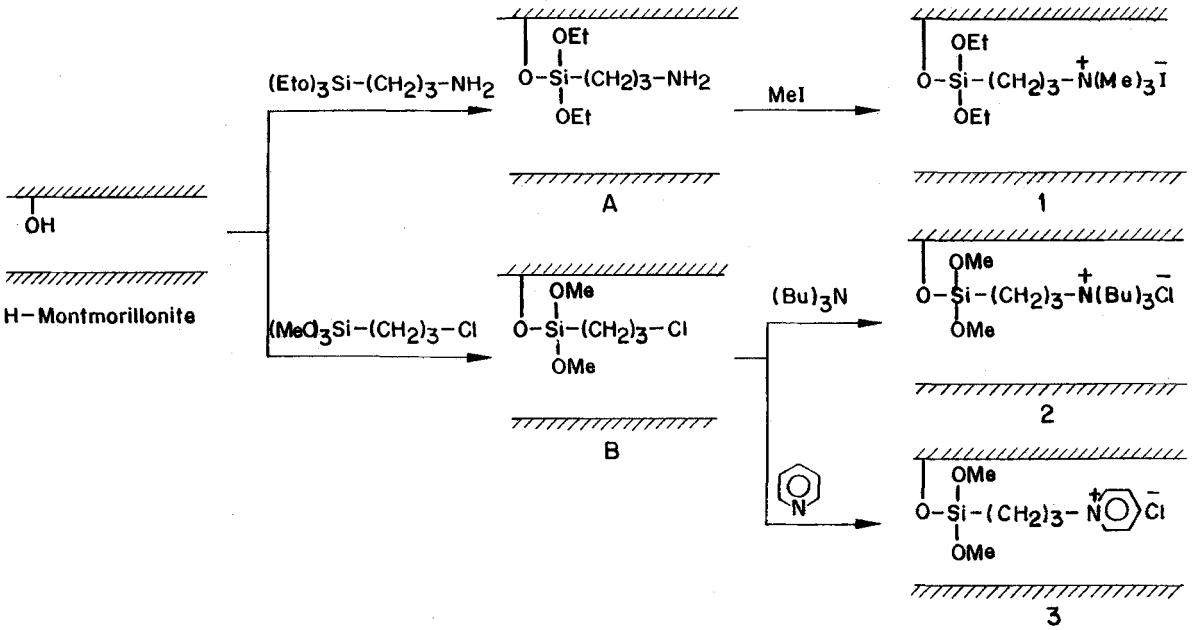


Figure 1. Synthesis mechanism of new triphase catalysts from montmorillonite.

with occasional stirring. After cooling, it was recovered with ether, filtered, and washed three times with methanol and twice with dry ether and dried to produce catalyst 2. The ionic chloride content of this catalyst was 0.132 meq/g, as determined gravimetrically by precipitation with silver nitrate solution.

Table 1. Infrared stretching frequencies for onium montmorillonite samples.

Sample	Name	Frequency (cm^{-1})[1]
A	Amino-functionalized montmorillonite	2860–3000s, 3020s, 1450m, 1390s, 1300s, 1200s, 1050–1120s, 950s, 750–820s
B	Chloro-functionalized montmorillonite	2850s, 1460s, 1350m, 1300s, 1240m, 840s, 860w, 790s, 730s
Catalyst 1	Trimethylonium	3060m, 3040s, 2940s, 2813w, 1440s, 1420s, 1350m, 1340m, 950s, 900s, 720s
Catalyst 2	Tributylonium montmorillonite	2965s, 2945m, 2885s, 1740s, 1555s, 1485s, 1470s, 740m
Catalyst 3	Pyridinium montmorillonite	3134w, 3080s, 2965s, 2960m, 1635m, 1580w, 1485s, 1410w, 1345w, 1300m, 1250m, 905s, 850w, 770s, 685s, 610w, 570w

[1] s = strong; m = medium; w = weak.

Preparation of montmorillonite-silylpropyl pyridinium chloride. Product B (2.0 g) was suspended in 8 ml of pyridine and heated at 100°C for 8 hr. After cooling, it was diluted with ether, filtered, washed twice with methanol and dry ether, and dried to produce catalyst 3. The chloride content of this catalyst was 0.432 meq/g.

Nucleophilic substitution. Typically, a flask was charged with 3.5 ml of water, 5.0 g of KI, catalyst 1 (114 mg, 0.057 mmole), and octylbromide (1 ml, 5.7 mmole). The reaction mixture was heated at 90°C under stirring (200 rpm) for 24 hr and filtered. The filtrate was extracted with ether, dried over anhydrous Na_2SO_4, and concentrated. The product was analyzed by GC and NMR. For recycling, the filtered catalyst was washed with water and ether before reuse.

RESULTS

The silyl moieties present in products A and B were 0.56 and 0.51 mmole/g, respectively, as calculated from the nitrogen and chloride contents of the respective samples. The FTIR spectra of the onium salts showed all the bands corresponding to the respective onium salts (Table 1). XRD of thin films showed a basal expansion for catalyst 1 to 19.5–19.7 Å; for catalyst 2, 20.0–20.2 Å; and for catalyst 3, 15.0–15.2 Å, compared with dehydrated montmorillonite, at 9.4 Å (Figure 2). The halide content in the ionic state of catalysts 1–3 were 0.50, 0.132, and 0.432 meq/g, respectively. Nucleophilic substitution reactions of octylbromide with iodide, thiocyanate, and cyanide ions in presence of

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Table 2. Nucleophilic substitution reaction of 1-bromooctane.

Reagent	Catalyst[1]	Product	Yield[2] (%)
Potassium iodide	1	$C_8H_{17}I$	86
	2	$C_8H_{17}I$	96
	2[3]	$C_8H_{17}I$	94
	H-montmorillonite[4]	$C_8H_{17}I$	9
Potassium thiocyanate	1	$C_8H_{17}SCN$	92
	2	$C_8H_{17}SCN$	97
	H-montmorillonite[4]	$C_8H_{17}SCN$	12
Potassium cyanide	1	$C_8H_{17}CN$	89
	2	$C_8H_{17}CN$	92
	H-montmorillonite[4]	$C_8H_{17}CN$	11

[1] See Table 1 for descriptions.
[2] Yields based on gas chromatography and nuclear magnetic resonance spectra.
[3] Yield in fourth recycle.
[4] Same time.

catalytic amounts of onium salts (catalysts 1 and 2) gave yields of 86–97% (Table 2); in contrast, 12% yields were obtained in the control experiments conducted with H-montmorillonite. The reactions were conducted in the absence of solvent 1.0 mole % of catalyst. All the nucleophilic substituted products were well characterized by NMR and compared with the spectra of the authentic samples (Pouchert, 1983a, 1983b). Analysis of either organic or aqueous layers described in the experimental section indicated the absence of silyl moiety.

DISCUSSIONS

The content of silyl moieties in products A and B were 0.56 and 0.51 mmole/g, respectively. The ammonia adsorption capacity was reduced to 0.30 and 0.31 meq/g for products A and B respectively, compared with the starting material, H-montmorillonite, which had adsorbed 0.85 meq/g ammonia. Hence, the decrease in ammonia adsorption capacity for products A and B was probably due to utilization of –OH sites for condensation with alkoxy of silyl group and corresponded to the loss of about one OH group for each silyl group depicted in Figure 1.

The presence of all the bands corresponding to the quaternary onium salts in their FTIR spectra (Table 1) and the expansion of the XRD basal spacings (Figure 2) demonstrate the formation and intercalation of the quaternary onium salts in the interlayers of montmorillonite.

The intercalation usually is determined by XRD expansion, as recorded for the oriented film (Pinnavaia and Farzanch, 1983). The expansion apparently dependent upon the size, orientation, and extent of crosslinking of onium salts in interlayers. The smaller onium salt content of catalyst 2 compared with analogous pyridinium salt 3 was probably due to the lower nucleophilicity of tributylamine.

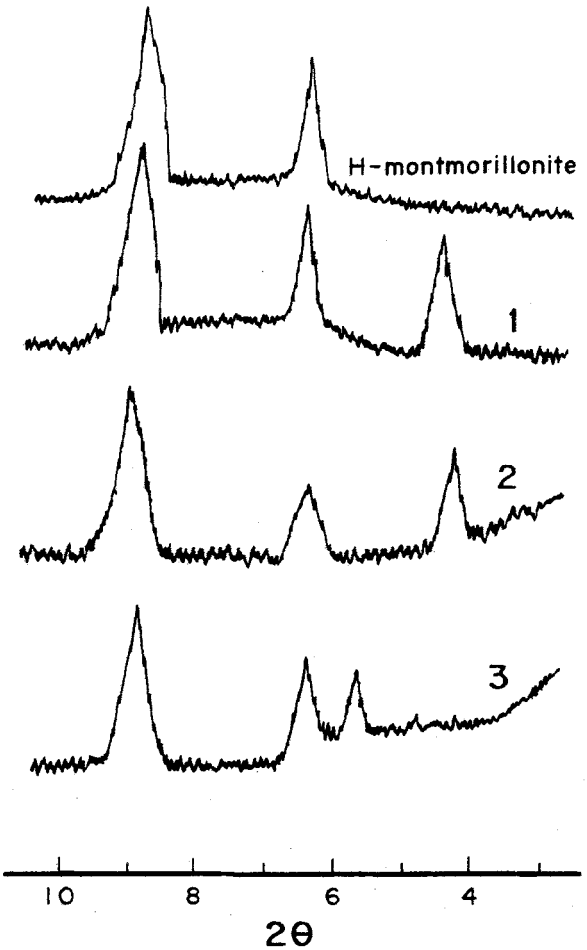


Figure 2. X-ray powder diffraction patterns (CuKα radiation) of onium montmorillonite: 1, trimethylonium; 2, tributylonium; 3, pyridinium montmorillonite.

Nucleophilic exchange reactions of octylbromide with iodide, thiocyanate, and cyanide in the presence of catalytic amounts of catalysts 1 and 2 gave yields of 86–97% (Table 2). The control experiment conducted under identical conditions in presence of H-montmorillonite gave only <12% yields. Thus, the nucleophilic substitution reactions demonstrated the utility of anchored onium salts as phase-transfer catalysts in the triphase system. The trimethylonium salt (catalyst 1) showed an unusually large exchange capacity, very close to its tributylonium salt (catalyst 2), compared with analogous onium salts (homogeneous) and immobilized on resin and silica which are nearly inactive (Molinari *et al.*, 1979; Rolla *et al.*, 1977).

The consistent activity of catalyst 2 displayed in iodide exchange reactions for four recycles and the absence of silyl moiety either in aqueous or organic layers

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indicate the stability and reusability of the anchored montmorillonite. The catalyst was stable even for use in concentrated KCN solution (alkaline in nature), unlike silica, which is soluble in this medium (Ford, 1984).

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