

Porous clay heterostructures (PCH) as acid catalysts

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Porous clay heterostructures formed by surfactant assembly of open framework silica in the galleries of a smectite clay represent a new family of solid acid catalysts, as evidenced by the selective dehydration of 2-methylbut-3-yn-2-ol to 2-methylbut-3-yn-1-ene.

Pillared interlayered clays have been extensively studied as promising solid-state alternatives to traditional acid catalysts, such as aluminium trichloride, sulfuric acid and hydrofluoric acid.^{1,2} We recently reported a new type of clay intercalate with high surface area and a structural porosity substantially larger than pillared clays. These new derivatives, which we call porous clay heterostructures (PCH) are formed by surfactant-directed assembly of open-framework silica in the galleries of smectite clays with high charge density.³ In contrast to microporous pillared clays with pore sizes typically below 10 Å, PCH materials exhibit regular porosity in the supermicropore to small mesopore range (15–25 Å).

PCH synthesis makes use of the micellar ordering of silicate species and surfactants in a manner not unlike the supramolecular ordering processes for mesoporous MCM-41 molecular sieves.^{4,5} However, as shown in Fig. 1, PCH assembly differs from MCM-41 chemistry insofar as framework organization occurs in the restricted two-dimensional gallery region of the clay rather than in the three-dimensional bulk phase. Because PCH design combines the open framework structure of the gallery silica with the chemistry of the clay layer, new properties for selective heterogeneous catalysis may be anticipated. Using the dehydration of 2-methylbut-3-yn-2-ol (MBOH) as a probe reaction, we demonstrate in the present work the acid catalytic activity of PCH materials relative to alumina-pillared clays and related catalysts.

Cetyltrimethylammonium (CTMA) exchange cations and decylamine were used as co-surfactants to form a PCH with fluorohectorite as the clay host. Synthetic lithium fluorohectorite (Li-FH) with the unit cell composition $\text{Li}_{1.12}[\text{Li}_{1.12}\text{Mg}_{4.88}](\text{Si}_8\text{O}_{20})\text{F}_4 \cdot x\text{H}_2\text{O}$ (Corning, Inc.) was allowed to react at 50 °C with 0.3 M aqueous $[(\text{C}_{16}\text{H}_{33})\text{NMe}_3]\text{Br}$ in twofold excess of the clay cation exchange capacity. After a reaction time of 24 h, the product was washed with ethanol and water to remove the excess surfactant and air dried. The clay then was added to the decylamine in the molar ratio CTMA-FH : decylamine = 1 : 20, and the resulting suspension was stirred for 30 min. Sufficient tetraethylorthosilicate (TEOS) was added to achieve a final molar ratio of CTMA-FH : decylamine : TEOS = 1 : 20 : 150. After a reaction time of 4 h at room temp., the

reaction product was recovered by centrifugation, air-dried and calcined at the desired temperature for 4 h using a temperature ramp rate of 2 °C min⁻¹. The calcined products were denoted FH-PCH-X where X is the calcination temperature in °C. Chemical analyses indicated the presence of 10.4 moles of gallery Si per fluorohectorite O_{20}F_4 unit cell.

Table 1 provides the basal spacings, BET surface areas, and Horvath–Kowazoe pore sizes for FH-PCH samples calcined in the range 300–550 °C. Three orders of 00l X-ray reflection are observed in accord with a lamellar structure. Although the basal spacing decreases from 38.1 to 33.5 Å with increasing temperature, there is a general increase in the BET surface areas to a maximum value of 790 m² g⁻¹ at 500 °C where the removal of gallery surfactant (< 1 mass% C) and the dehydroxylation of the gallery silica become more complete. The lamellar structure is retained even at 700 °C, but the basal spacing begins to decrease more rapidly at this temperature. At 800 °C the PCH structure degrades substantially with the formation of quartz as a decomposition product. Clearly, the thermal stability of the PCH structure degrades substantially with the formation of quartz as a decomposition product. Clearly, the thermal stability of the PCH structure is sufficient to conduct a wide range of acid catalyzed conversions.

Table 1 also includes the results for the catalytic conversion of MBOH over calcined FH-PCH samples. This probe reaction is sensitive to the presence of acid-base sites on the catalyst surface.⁶ Acidic sites result in the dehydration of MBOH to 2-methylbut-3-yn-1-ene (MByne), whereas basic sites cause cleavage to acetone and acetylene. As indicated by the high selectivity to MByne, particularly for FH-PCH-350, the surfaces of FH-PCH contain mainly acidic sites. In contrast, pristine Li⁺ fluorohectorite is highly basic, affording primarily acetone and acetylene as reaction products. Thus, the intercalation of surfactant-assembled silica and the subsequent calcination of the heterostructure imparts acidic surface functionality.

The results given in Table 1 further show that FH-PCH-350 is a much more active acid catalyst than either mesoporous MCM-41 silica or microporous alumina pillared fluorohectorite (APF-350). The latter intercalate is an especially active alkylation catalyst among pillared clays.⁷ The reactivity of FH-PCH-350 even approaches that of K-10 montmorillonite, a commercially available acid-restructured clay. This latter material, however, lacks framework porosity and is incapable of shape selective catalysis.

The FH-PCH materials reported here are hybrid structures of the smectite clay fluorohectorite, which is basic, and weakly acidic MCM-41 silica (*cf.* Table 1). Some Brønsted acidity is expected for PCH materials, however, because the initial gallery cations (*i.e.* Li⁺) are replaced first by surfactant cations and then by protons upon destruction of the surfactant through calcination. Also, fluorohectorite is known⁸ to undergo hydrolysis of lattice fluorine at temperatures above 250 °C. Proton dissociation from the resulting hydroxyl groups also can contribute to Brønsted acidity. In addition, the silicate layers of fluorohectorite can undergo local restructuring upon calcination at elevated temperatures, giving rise to Lewis-acid sites in the gallery region.⁸

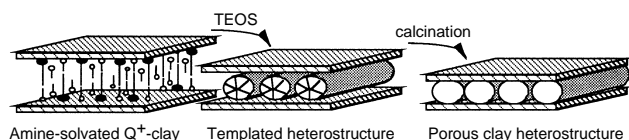


Fig. 1 Schematic illustration of porous clay heterostructure (PCH) formation through surfactant-directed assembly of open framework silica in the galleries of a layered silicate co-intercalated by a quaternary ammonium ion surfactant (filled head groups) and a neutral amine co-surfactant (open head groups)

Table 1 Physical and acid catalytic properties of calcined FH-PCH derivatives and related solids

Sample	$d_{001}/\text{\AA}$	Surface area/ $\text{m}^2 \text{g}^{-1}$	HK pore size/ \AA	MBOH conv. (%)	MBOH product selectivity ^a		
					Basic ^b		Acidic MByne
					Acetylene	Acetone	
FH-PCH-300	38.1	575	18.9	47.0	0	0	100
FH-PCH-350	38.7	555	19.6	52.7	0	0.1	99.9
FH-PCH-450	37.1	630	22.3	32.9	0.2	0.2	99.6
FH-PCH-500	35.3	790	22.6	23.6	0.4	0.8	98.9
FH-PCH-550	33.5	750	21.7	19.0	2.9	3.4	93.8
Li-FH	10.5	50	0	5.0	36.2	46.5	17.3
K-10 ^c	—	250	0	67.9	0	0.1	99.9
APF-350 ^d	18.9	214	< 10	16.4	3.6	3.6	92.9
MCM-41 ^e	—	1100	22.0	11.0	8.0	7.0	85.0

^a Reactions of MBOH were carried out over 150 mg quantities of catalyst at 180 °C in a packed-bed reactor linked to an on-line Perkin-Elmer 8500 gas chromatograph equipped with FID detection and a packed column of 3% SP-1500 on Carbowax B. The catalysts were activated at 200 °C for 2 h prior to testing under a helium flow of 20 ml min⁻¹. MBOH in the gas phase (0.35 mmol h⁻¹) was diluted to 2.5% in helium. ^b Basic active sites afford acetone and acetylene as reaction products, whereas acid sites afford exclusively MByne. ^c A commercial acid-treated clay (Aldrich) calcined at 350 °C. ^d Alumina-pillared fluorohectorite, prepared according to ref. 8 and calcined at 350 °C. ^e Mesoporous silica molecular sieve assembled from cetyltrimethylammonium bromide according to ref. 4 and calcined at 350 °C.

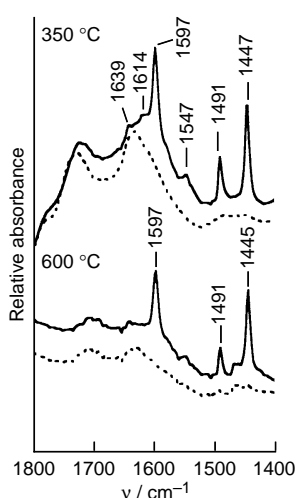


Fig. 2 IR spectra of pyridine chemisorbed at 150 °C on FH-PCH samples calcined at 350 and 600 °C (solid lines). The dashed lines are spectra for the pristine FH-PCH samples prior to pyridine adsorption.

FTIR spectra for pyridine chemisorbed at 150 °C on FH-PCH-350 and -600 provide insights into the nature of the acid sites in PCH materials (Fig. 2). The C–C ring stretching frequencies near 1445 and 1547 cm⁻¹ are diagnostic of the bonding of pyridine to Lewis and Brønsted sites,⁹ respectively. The relative intensities of these bands are very similar to those observed for APF. This similarity in acid functionality is somewhat surprising, because the Lewis acidity of alumina pillared clays normally is associated with the presence of coordinatively unsaturated sites on the alumina pillars. FH-PCH, however, contains no aluminium.

To better understand the origin of the observed acidity for FH-PCH materials and the relationship of the acidity to APF, we carried out ¹⁹F and ²⁹Si MAS NMR studies for materials calcined to 550 °C. ¹⁹F NMR showed that the fluorine sites associated with the negatively charged octahedral triads of the silicate layers ($\delta -16$) diminish to ca. 25% of the initial intensity when calcined at 350 °C. This latter result is in accord with the previously observed hydrolysis chemistry of fluorohectorite (APF-350).⁸ Also, ²⁹Si MAS NMR showed that the silicate layers in FH-PCH are locally restructured in a manner

analogous to APF-350. Upon layer restructuring at calcination temperatures up to 350 °C, the Q³ resonance of the clay broadens and shifts progressively from $\delta -93.3$ to -96.6 signifying an increase in the Si–O–Si bond angle of the tetrahedral sheet. The Q³ ($\delta -103$) and Q⁴ ($\delta -110$) resonances of the assembled gallery silica, however, are not affected by calcination over this temperature range. Inversion and grafting of the clay tetrahedral sheet to the gallery silica, as evidenced by a new resonance at $\delta -99.7$, does not occur until the FH-PCH is calcined in the range 450–550 °C. Such local restructuring of the silicate layer also occurs for APF over the same temperature range.

On the basis of the above FTIR and MAS NMR results we conclude that FH-PCH-350 and APF-350 share the same type of acid functionality and layered structural features. The important difference, of course, is that FH-PCH-350 is a surfactant-assembled supermicroporous to mesoporous intercalate, whereas APF-350 is exclusively a microporous pillared derivative. The enhanced access to the framework gallery sites in FH-PCH-350 most likely contributes greatly to the superior catalytic activity of this intercalate.

The partial support of this research by the National Science Foundation through CRG grants CHE-9224102 and -9633798 is gratefully acknowledged.

Footnote and References

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Received in Columbia, MO, USA, 6th May 1997; 7/03101G