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Preparation and Thermal Properties of Zr-Intercalated Clays

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Montmorillonites intercalated by zirconium macrocations have been prepared. Diffusion of the Zr cations within the particles of clay controls the rate of ion exchange, and hence the distribution of the Zr pillars. This effect accounts for the influence of particle size on the degree of exchange, the surface area, and the thermal stability of the pillared clay. The thermal stability of the Zr clays prepared under these conditions is limited to 973 K in dry air. The changes in microporosity, evaluated from nitrogen adsorption using the equation of Dubinin, show that collapse of the structure occurs by sintering of the pillars. This sintering can be decreased by doping the pillars with rare earth cations. The resulting material then retains a surface area of 180 m^2/g after calcination at 1023 K in dry air, and is more acidic than the corresponding Zr–clay. © 1989 Academic Press, Inc.

INTRODUCTION

Various reports in recent years have attracted attention to a new class of catalysts prepared by exchanging the ions of expandable clay minerals, such as montmorillonites, with macrocations obtained by the controlled hydrolysis of aluminium, zirconium, or chromium salts (*1–9*). This subject has been recently reviewed by several authors (*10–12*). According to Shabtai *et al.* (*6*), these interlayered clays are more active than Y-zeolites as catalysts for converting heavy oil fractions, and could therefore be attractive materials.

If these clays are to be used as cracking catalysts, they must have good thermal and hydrothermal resistance. In the patent literature, Vaughan *et al.* (*2*) described the preparation of montmorillonites intercalated by Al and Zr hydroxy cations, which are stable up to 973 K in steam. In the open literature Occelli (*9*) reported a poor stability in steam for an Al-pillared clay. These differences in stability are most probably related to details of the preparation.

In the case of Zr-pillared clays (Zr-PILC) Yamanaka and Brindley (*13*) described the preparation of a material showing a (001) spacing of 1.8 nm after calcination at 673 K, but it was unstable above this temperature. They concluded that the Zr cations were hydrolyzed to a large extent, since the charge per Zr ion in the solid was 0.5. Burch and co-workers (*14, 15*) have investigated the influence of several parameters of the preparation related to the chemistry of the Zr cations in solution. Upon refluxing the Zr solution they observed a notable influence on the porosity and stability of the resulting PILC. Refluxing was a requisite for good thermal stability.

The influence of the method of preparation of Zr–montmorillonites is also clear from the results reported by Occelli (*16a*); in that case the Zr-PILC was X-ray amorphous because of delamination, but was as active and selective as an Al-PILC for the cracking of gas oil. The catalytic properties were determined by the BET surface area of the PILC, whatever the pillars. The stability of the Zr-PILC was lower than that of the Al-PILC. An important point in the preparation was drying: the stability of the PILC was much higher when the clay was dried in the form of small grains. In the case

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of hectorite, however, the Zr form was more stable than the Al-PILC (*16b*). The influence of the method of preparation on the properties of the final product is therefore not clear.

Most authors have focused on the chemistry of the solution, but the influence of the clay itself is less documented. We present here some results obtained by changing the particle size of the original clay and adding promoters to the solution of zirconium. It has been reported previously that the thermal stability of Al-PILC was significantly increased by using a clay in the form of very small particles (*17*), and it appeared interesting to us to study this effect in the case of Zr–clays.

EXPERIMENTAL

Catalyst Preparation

Two different clays were used as starting materials.

(i) A Wyoming montmorillonite of the Volclay type was purchased from Wards National Science Establishment, Inc. From X-ray analysis this sample contained quartz and cristobalite; the impurity level was estimated to be 5–10% after sedimentation.

(ii) A second Wyoming montmorillonite was obtained from CECA (Honfleur) in the form of a suspension of clay in water. This material had been refined by the manufacturer and contained less than 1% of impurities. It was a homoionic Na^+ montmorillonite, with a particle size of 0.5 μm. The samples prepared from the powder will be designated *V* and those obtained from the suspensions *S*.

The chemical compositions of the original materials and of two representative samples are reported in Table 1. The clay was first exchanged to the Na form by four successive exchanges in a 1 *M* NaCl solution, followed by centrifugation. The solid was then washed until chlorine free, and then exchanged if necessary to the Ca form using 1 *M* $CaCl_2$ solutions and successive exchanges, followed by thorough washing until Cl ions were eliminated. The intercalation of the clay was performed using the method described by Yamanaka and Brindley (*13*): 10 g of montmorillonite was dispersed in 1 liter of distilled water; then 250 ml of a 0.1 *M* solution of $ZrOCl_2 \cdot 8H_2O$ was added dropwise. The addition took approximately 1 h. The slurry was kept under stirring for 24 h, and was then centrifuged, washed until chlorine free, filtered, and dried in thin layers < 1 mm. For doping of the Zr pillars by Ce^{3+} ions, a mixture of zirconium chloride and cerium chloride was used in a similar manner for the intercalation.

Thermal Treatments

The sample was placed in a thin bed configuration in a quartz tube swept by air (flow: 100 ml per minute). The temperature was raised 50 K h^{-1} and maintained 5 h at the desired level. In order to avoid cumulative effects, a fresh sample was used for each experiment.

Characterization Techniques

The solids were characterized by their basal spacings, surface areas, and microporosity.

Basal spacings were determined by X-ray powder diffraction from the position of the (001) peak. XRD patterns were recorded on a CGR Theta 60 instrument using Cu$K\alpha$ radiation. The precision of the values of $d(001)$ was estimated to be ±0.05 nm.

Surface areas were calculated from BET isotherms determined using N_2 as adsorbate at liquid nitrogen temperature. Although not without question when applied to microporous solids, this is a convenient characterization, adopted also by others (*14*). A good linearity of the BET plots was usually observed in the range of relative pressures below 0.3. The micropore volume (pores <1 nm) was determined by the application of the equation of Dubinin,

$$\mathrm{Log}\, v = \log v_m - K(\mathrm{Log}\, P_s/P)^2,$$

where v is the volume adsorbed at the equilibrium pressure, P, P_s the saturation pressure, v_m the volume of the micropores, and K a constant. The total pore volume was estimated by the extent of adsorption at $P/P_s = 0.95$.

RESULTS AND DISCUSSION

1. Chemical Composition of the Zr-PILC

The chemical compositions of the initial clays and of the solids fully saturated with zirconium are reported in Table 1. The relative amounts of aluminium, magnesium, and iron remain constant after intercalation. It can therefore be concluded that the composition of the clay sheet is preserved after ion exchange, in spite of the acidity generated by the hydrolysis of the chloride. The powder V was sedimented into two fractions: the first consisted of particles in the range 1–10 μm, and the second of particles smaller than 1.5 μm. Both were converted to the calcium form, and then intercalated by Zr. The smaller fraction exchanged 12.2 wt% ZrO_2, whereas the coarser fraction fixed 10.7 wt%. This influence of the size of the particles of the starting material, when using the same parent clay, shows that diffusion controls the rate of ion exchange.

TABLE 1

Chemical Compositions of the Original Clays and of Two PILC Fully Saturated with Zirconium Ions

Component (wt%)	Vol clay (v)	PILC V-7	Suspension (S)	PILC S-7
SiO_2	57.35	41.62	58.62	42.71
Al_2O_3	20.02	14.42	20.45	14.48
MgO	2.49	1.58	1.88	1.62
Fe_2O_3	3.93	2.69	3.35	2.78
TiO_2	0.30	0.35	0.33	1.06
Na_2O	1.27	0.17	3.06	0.11
CaO	0.07	—	0.20	0.04
BaO	—	—	0.02	—
ZrO_2	—	13.27	—	13.1
H_2O	13.4	25.2	12.8	23.95

2. XRD Patterns

The original clay in the Na form shows a (001) basal spacing of 1.28 nm. After ion exchange, a broad line centered at 1.6–1.7 nm is observed for the sample, as illustrated in Fig. 1. After a first washing this line splits into two lines, with the appearance of a line at 2.2 nm. A second washing provokes an increase in this line, which is observed at 2.2–2.3 nm. This behavior is also characteristic of a slow diffusion of the Zr polycations into the bulk of the material, as previously reported by Burch and Warburton (*14*).

3. Texture of the Zr-PILC

The values obtained for the micropore and total pore volumes are reported in Table 2. The original material shows no microporosity. The micropore volume is thus a measure of the porosity created by intercalation. After calcination at 523 K, the Zr-PILC show an important fraction of the pore volume to be contained in micropores < 1 nm, in agreement with the observation of a (001) spacing of 1.7–1.8 nm after this treatment, corresponding to pores of 0.8–0.9 nm in size. The micropore volume increases with the degree of exchange as expected. It is lower on the samples prepared

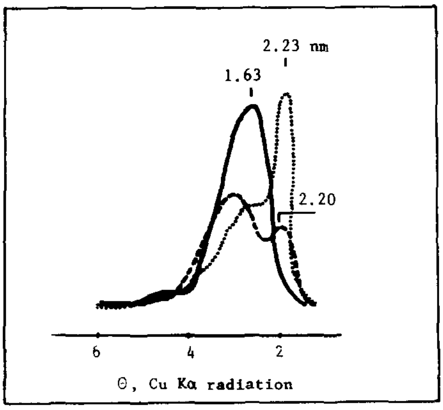

FIG. 1. X-ray diffraction pattern of a Zr-montmorillonite, prepared from sample S, just after intercalation (—), after a first washing (---), and after a second washing (. . .).

TABLE 2

BET Surface Areas (S), Total Pore Volumes (v_t) and Micropore Volumes (v_m) for Some Pillared Clays Calcined at Different Temperatures

Sample	% ZrO_2	v_m (cm^3/g)	v_t (cm^3/g)	S (m^2/g)	Calcination temp (K)
S-1	7.1	0.08	0.11	184	523
S-2	8.5	0.13	0.17	245	523
S-4	11	0.13	0.17	330	523
S-5	11.6	0.15	0.26	360	523
S-5	11.6	0.12	0.21	260	773
S-5	11.6	0.10	0.17	205	973
V-2	8	0.13	0.20	248	523
V-4	10.5	0.10	0.17	261	523

Note. Samples prepared from the Ca form of the clay and intercalated at room temperature.

from the powder, which is consistent with the proposal of diffusional limitations in ion exchange.

4. *Thermal Stability of the Zr-PILC*

When the samples are calcined in dry air at increasing temperatures the basal spacing decreases first from 2.1–2.2 nm at room temperature to 1.75 nm at 773 K, and then remains practically constant. The only modification above 773 K is a decrease in the intensity of the diffraction lines. The decrease in the (001) spacing between room temperature and 773 K simply reflects the dehydroxylation of the Zr–hydroxy cations. The micropore volume decreases continuously between 523 and 973 K (Table 2). Since microporosity is introduced by pillaring, this decrease reflects the sintering of the pillars. The total pore volume decreases simultaneously, but remains appreciable after calcination at the higher temperature. There is a parallel variation in micropore volumes and surface areas. The BET surface area can thus be used to evaluate the thermal stability of the PILC.

An interesting point is that the samples prepared from the larger clay particles appear to be less thermally stable, as can be seen in Table 3. The retention of specific surface area after calcination at 973 K reaches 56% for sample *S* compared to 42% for sample *V*-5 at a similar percentage of Zr. This influence of the particle size of the original clay on the thermal stability of the PILC is consistent with the observed influence of diffusion on ion exchange. It must be considered that, when diffusion limits the process, gradients of concentration exist within the clay particle. A homogeneous distribution corresponds to a larger distance between the pillars, and hence to a greater resistance to sintering.

5. *Influence of Additives to the Solution of $ZrOCl_2$*

A better homogeneity in the distribution of the pillars has little effect on the stability of the texture above 973 K when the solid is prepared by the present method. This temperature is not so far from that at which bulk ZrO_2 suffers a phase transition which is known to be blocked by the addition of trivalent oxides (*18*). An attempt was then made to add rare earth ions to the pillars. An exchange of the Zr-PILC by Ce^{3+} ions, corresponding to a loading of 2.3 wt% Ce does not improve the stability of the texture (Table 4). Most probably the sites for this cation exchange are localized on the clay sheet and cerium introduced by this procedure cannot diffuse in the ZrO_2 pillars. A second possibility is to cohydrolyze the chlorides, and then use a mixture of $ZrOCl_2$ and $CeCl_3$ for the intercalation. This procedure was tried and 30% of the Zr atoms of the solution were substituted for Ce. It

TABLE 3

Surface Areas (m^2/g) Retained by Zr–Montmorillonites Prepared from Small or Large Particles, after Calcination at Different Temperatures

Sample	Size particles	Temp (K)		
		523	773	973
S-4	(11% ZrO_2) 0.5 μm	330	260	205
V-5	(10.7% ZrO_2) 1–10 μm	260	180	110
V-7	(12.2% ZrO_2) 1.5 μm	280	210	130

Note. The three samples have been prepared from the Ca form of the clay and intercalated at 300 K.

therefore appears that the PILC retains only a small amount of Ce, 0.85 wt%. However, the results of this procedure (reported in Table 4) show that doping by cerium clearly stabilizes the structure: the residual surface area after calcination at 1023 K is twice that without cerium and reaches that retained by Al-PILC (*17*). The micropore volume measured after calcination at this temperature is 0.135 cm^3/g compared to 0.16 cm^3/g at 523 K, which also reflects a good stability of pillaring. The hydrothermal stability, evaluated after a treatment in a 50% steam–air atmosphere for 6 h, is also satisfactory. The accessibility of these solids to large molecules is illustrated by the adsorption of perylene from benzene solution. The adsorption of polyaromatics at the acid sites of the PILC yields a charge transfer complex which can be detected by ESR. On the sample prepared by cohydrolysis, calcined at 773 K, a number of sites was determined to be 2.10^{19}/g (*19*), which is comparable to the number of sites on amorphous silica–aluminas. Refluxing the slurry (clay + pillaring solution) has no positive effect in that case (Table 4). Changing the Ca form for the Na form yields comparable results with surface areas of 344, 279, and 146 m^2/g for a Zr–Ce PILC prepared from Na–montmorillonite, after treatments at 673, 873, and 973 K, respectively.

TABLE 4

Surface Areas (m^2/g) Retained after Calcination at Different Temperatures, Showing the Influence of Ce^{3+} Addition on the Stability of Zr-PILC

Sample	Calcination temp (K)					
	673	773	873	973	1023	1073
S-5, no Ce	280	260	260	250	80	30
S-5 exchanged by Ce (2.3 wt% Ce)	218	200	—	130		
Zr + Ce PILC-A[a] (cohydrolysis, 298 K)	265	260	252	234	180	
PILC-A steamed (50% water)	260	260	202	130	128	80
Zr + Ce PILC-B[a] (cohydrolysis, 350 K)	323	284	243	176	—	—
Zr + Ce PILC-C[b] (cohydrolysis, 350 K)	344	—	279	146	—	—

[a] Prepared from Ca–montmorillonite.

[b] Prepared from Na–montmorillonite.

TABLE 5

Influence of the Addition of Lanthanides on the Texture of Zr–Montmorillonites Prepared from the Suspension Na Form, Slurry (Clay + Pillaring Solution) Heated 2 h at 350 K

Additive (wt% fixed)	Temperature of calcination (K)	Surface area (m^2/g)	*d*(001) (nm)
La (0.16)	523	250	2
	773	220	2(weak)
Nd (0.61)	523	272	2
	873	212	1.91
Sm (0.26)	523	370	1.92
	873	—	1.84
	973	180	1.71

Different rare earths have been compared for this process (Table 5). Ce^{3+} and Nd^{3+} give the better stabilization, whereas La surprisingly gives worse results. It appears from Table 5 that these two elements are retained to a greater extent by the PILC. The stabilizing effect of the lanthanides seems to be correlated with the degree of hydrolysis of the chloride under the conditions of intercalation: those cations which can hydrolyze at the pH of the $ZrOCl_2$ solution are more retained by the clay and give positive results. This suggests that these ions are indeed introduced into the pillars, and can then show a stabilizing effect at high temperature. The catalytic properties of these pillared clays prepared from the suspension (size of the particles: 0.5 μm) have been determined for the dehydration of isobutyl alcohol, at low conversion. The temperature was 423 K and the partial pressure of alcohol 1.3 kPa. Dehydration of alcohols is an acid-catalyzed reaction which can be used to determine acidity. The activities of the Zr–Ce and Zr–Nd PILC are equivalent (6.10^{-6} mol s^{-1} g^{-1}) and higher than those of the Zr-PILC by a factor of 5. This higher activity is also consistent with the proposal of an incorporation of the rare earth into the pillars since the substitution of a quadrivalent by a trivalent cation should result in an increase in acidity.

In conclusion, the results reported here reproduce on Zr-PILC those reported elsewhere for Al-PILC (*17*) and illustrate the importance of diffusional limitations in pillaring on the properties of the resulting PILC. This influence of diffusion accounts for the lower stability of the samples prepared from large particles. The texture of the pillared clay can be stabilized by adding lanthanide ions to the pillaring solution. In that case, the positive effect of the rare earth is determined by its ability to hydrolyze under the conditions of intercalation. The observation of larger spacings and higher acidity on the resulting PILC suggests that the additive is located in the pillars.

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