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Zr-Containing Pillared Interlayer Clays

I. Preparation and Structural Characterisation

R. BURCH[1] AND C.I. WARBURTON

Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 2AD, United Kingdom

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Zr-Containing pillared interlayer clays have been prepared from montmorillonite by reaction with zirconyl chloride solutions. The method of preparation has been varied to investigate the effect on the surface area and stability of the interlayered clays of changing the degree of polymerisation of the Zr tetramers present in the fresh zirconyl chloride solution. The structure of the materials has been investigated by XRD and by detailed analysis of N_2 adsorption isotherms. The thermal stability and degradation of the samples have been investigated by DTA, TGA, and surface area measurements. The results show that the surface areas obtained are critically dependent on the method of preparation. Parameters such as the concentration of the Zr chloride solution, the temperature, and the time of contact with the clay all affect the structure and properties of the pillared clays. For samples prepared from an unwashed montmorillonite it is found that as the degree of polymerisation of the Zr tetramers is increased there is a gradual expansion of the interlayer spacing and a parallel increase in the apparent surface area. In contrast, the samples derived from a washed montmorillonite generally have much lower surface areas and smaller interlayer spacings. The differences are attributed to the variations in the extent of dispersion of the clay in the two cases. The thermal stability of the various pillared clays was investigated by following the changes in surface area after heating the samples in air at temperatures up to 1073 K. Zr-pillared clays are more stable than equivalent Al-pillared clays.

INTRODUCTION

It has been known for about 40 years that interlayering of smectite clays can occur naturally. Since the early 1950's many attempts have been made to develop artificial methods of introducing interlayers into expandable silicates (*1*). In the first instance the objective was to determine how interlayering occurred in nature, so inorganic interlayers based on Al, Mg, and Si hydroxy compounds were investigated. Subsequently, it was realised that organic molecules could be used to prop open a layer structure and provide a semipermanent pillar of moderate thermal stability. Early work by Barrer and others (*2*) had involved the use of small, relatively unstable cations, such as $(CH_3)_4N^+$. Recently, molecules, such as 1,10-phenanthroline (*3, 4*), bipyridyl (*4, 5*), or 1,4, diazobicyclo - (2,2,2) octane (*6*), have been used with varying degrees of success. The latter compound provides pillars stable to about 800 K.

The continuing quest for higher thermal stability has led to a reinvestigation of inorganic pillars. Several inorganic hydroxy compounds have been considered, including Al (*7–17*), Zr (*8, 9, 17, 18*), Si (*19*), Bi (*20*), and Ni (*21*). Of these, only Al and Zr appear to be worthy of further examination. Al has been investigated in some detail already.

Almost no research has been done on the corresponding Zr-pillared clays (Zr-PILC) (*8, 9, 17, 18*). There are likely to be some similarities between Al- and Zr-PILC. However, there are also good reasons to expect that pillars derived from a transition metal ion will have different characteristics to those produced from Al. In catalytic reactions it may be possible to utilise the Zr to

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[1] To whom correspondence should be addressed.

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develop unique properties, either by its action as a redox site, as an acidic site, or as a co-catalyst, for example, in synthesis gas reactions. Moreover, there is some evidence in the literature (*22*) that zirconia can stabilise oxide structures against sintering. This makes Zr-PILC of special interest for use as catalysts and adsorbents under extreme conditions, such as are experienced in hydrotreating of residual oils. In this paper we describe the preparation and structural characterisation of Zr-PILC. In a companion paper (Part II, Ref. (*23*)) we describe the properties of some of these Zr-PILC as catalysts in the conversion of methanol to olefins.

EXPERIMENTAL METHODS

1. Materials

The clay used (Fulbent 570) was a partially Na-exchanged form of a natural Ca montmorillonite supplied by Laporte Industries. The chemical analysis was: SiO_2, 56.0%; Al_2O_3, 15.0%; Fe_2O_3, 6.5%; Na_2O, 5.0%; MgO, 3.5%; CaO, 2.5%; TiO_2, 0.5%; K_2O, 0.5%, by weight. The cation-exchange capacity was 88 meq/100 g. For most experiments no attempt was made to refine the clay into finer fractions which would exclude grit and large clay fragments. The as-received clay contained excess Na_2CO_3 used in the exchange and so on contact with water the clay did not disperse totally. For some preparations a preliminary washing of the clay was performed. These samples will be indicated by the prefix W.

The zirconium was supplied, by Alcan International, as solid zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) which on dissolution produces the tetrameric ion $(Zr_4(OH)_8(H_2O)_{16})^{8+}$. This quickly hydrolyses to form cations with lower charge. These cations polymerise slowly at room temperature, and quite rapidly at higher temperatures, eventually resulting in the formation of hydrous zirconia (*24*). The degree of polymerisation may be controlled by varying the temperature or time of ageing of the Zr solution, and the pH of the solution.

2. Preparation of Pillared Interlayer Clays

Several different procedures were used to prepare Zr-PILC, in order to obtain information on the effect of temperature, time, and Zr concentration on the properties of the samples.

Method A. Dry clay (8.3 g) was added to 250 cm^3 of a 0.1 *M* solution of zirconyl chloride which had previously been refluxed for 5, 10, or 24 h. The resultant mixture was refluxed for a further hour, after which it was filtered, and washed free from chloride with warm deionised water (2 × 100 cm^3). The PILC was dried overnight at 380 K. Similar preparations were performed in which the concentration of zirconyl chloride was increased to 0.2 or 0.3 *M*. Samples will be referred to using the code AR/*x*/*y*, where R indicates that the zirconyl chloride was refluxed before the clay was added, *x* is the time of reflux, and *y*/10 is the molarity of the zirconyl chloride solution.

Method B. In this procedure the clay was dispersed in water or a 50/50 acetone/water mixture prior to the addition of the zirconyl chloride. Dry clay (5 g) was dispersed in water for 15 min and then 500 cm^3 of 0.1 *M* zirconyl chloride solution was added and the mixture aged at room temperature for 1 h. The solid was washed and centrifuged repeatedly to remove free chloride, and dried overnight at 380 K. This sample is referred to as B/0.

To ascertain the effect of refluxing the zirconyl chloride solution prior to addition to the clay, one sample was prepared by dispersing the clay in a 50% acetone/50% water mixture and then adding a solution of zirconyl chloride which had been refluxed for 24 h. Washing and drying was performed as before. This sample is labelled BR/50. A further sample (BR/0) was prepared in the same way but using water in place of the 50% acetone/50% water mixture.

TABLE 1

Preparative Details for Pillared Clays Obtained Using Washed Clay

Sample	State of Zr solution[a]	Ageing temperature (K)	Ageing time (h)
W2	U	290	1
W3	U	340	1
W4R	R	290	1
W5	U	290	24

[a] U indicates unrefluxed 0.1 *M* zirconyl chloride solution; R indicates 0.1 *M* zirconyl chloride solution refluxed for 24 h.

Method W. A sample of the as-received clay was washed free of excess ions. Samples of washed clay (5 g) were dispersed in 330 cm^3 of water and used to prepare PILCs. Further preparative details are given in Table 1.

3. *Characterisation of Pillared Clays*

Surface areas were determined by N_2 adsorption at 77 K using a Cahn microbalance. Samples were ground to mesh size -425 to $+250$ μm, and dried overnight at 380 K. Once loaded into the balance the samples were degassed for 1 h at 383 K. For most samples a complete adsorption/desorption isotherm was measured, from which a surface area was calculated using the BET equation, over the range $0.05 < P/P_0 < 0.20$ where there was good linearity. Changes in surface area and structure were followed by heating the same sample at temperatures up to 1073 K. The procedure was to heat the sample to the required temperature (over an 8-h period) and then to hold at this temperature for a further 8 h. In addition to using the BET method, the adsorption data were analysed using the α_s method (*25*). The reference material chosen was Al_2O_3 of surface area 162.5 m^2 g^{-1}. This is a suitable sample because although this alumina is porous (mesoporous) it contains no micropores, and it is microporosity which is the main feature of the structure of the PILC.

X-Ray diffraction measurements were performed on acetone smear samples using a Philips horizontal diffractometer and Cu radiation. Chemical analysis of the clay was performed by X-ray fluorescence and Zr analysis of the PILC by plasma spectroscopy. Thermal analysis (DTA and TGA) was performed using a Stanton Redcroft STA-780 thermal analyser. Sample pretreatment involved grinding to mesh size <250 μm and drying overnight at 380 K. The sample was then placed in a relative humidity meter (37.1% R.H.) at room temperature to standardise the degree of hydration of the various samples before thermal analysis. The analysis was performed at a heating rate of 10 K/min, using Al_2O_3 as a standard.

RESULTS AND DISCUSSION

Adsorption Isotherms

Figure 1 shows adsorption isotherms for a typical PILC prepared by Method A, after drying and calcining at progressively higher temperatures, and compares these with the isotherm for the original clay. Similar sets of isotherms were obtained for all other samples. The isotherms for the PILC sam-

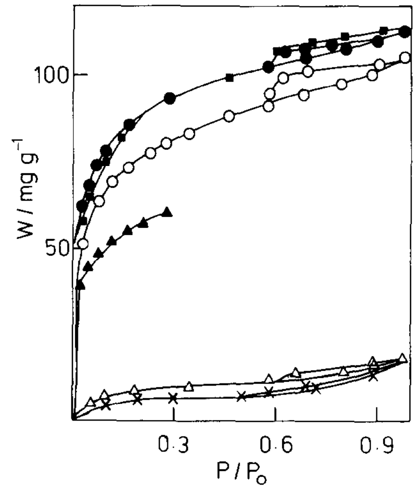

FIG. 1. BET sorption isotherms for sample AR/24/3 after calcination in air at various temperatures. ●, 378 K; ■, 573 K; ○, 773 K; ▲, 973 K; △, 1073 K; ×, original clay dried at 378 K.

TABLE 2

Surface Area Data from BET and α_s-Plots

Sample	Surface area (m^2 g^{-1})		
	S_{BET}	S_{α}	S_{EXT}
AR/24/1	214	259	21.1
B/0	212	323	25.7
BR/0	276	333	29.9
BR/50	305	362	30.0
W2	138	206	24.0
Clay	21.4		

ples are almost Type I, indicating that the solid is largely microporous. Some mesoporosity is indicated by the occurrence of a hysteresis loop at higher relative pressures. However, only a small fraction of the surface resides in mesopores. The shape of the desorption curve is Type B in the de Boer classification. This is believed to occur for slit-shaped pores witn parallel walls, which is consistent with the structure to be expected for materials prepared by expanding a layer structure. The high degree of microporosity is indicative of a material consisting mainly of pores <2 nm in diameter. This is consistent with the interlayer spacing observed by XRD, 0.3–1.0 nm (see below).

The general shape of the isotherms changes only slightly as the temperature of calcination is increased to 773 K, although there is a progressive decrease in the amount of N_2 adsorbed as the temperature is raised. Normalising these isotherms to take account of the different surface areas shows that they are all essentially equivalent across the whole range of P/P_0 values. This shows that the loss of surface area arises from complete closure of some pores, but that those remaining are hardly altered. When the calcination temperature is raised to 1073 K, however, we observe a sharp decrease in surface area, and a fundamental change in the shape of the isotherm. (This is the temperature at which the structure of the clay itself begins to collapse.) After this 1073 K treatment the surface area is almost identical to that of the original clay (23.3 vs 21.4 m^2 g^{-1}). However, the two materials do not have identical structures. The isotherms show significant differences, which indicate that even after the surface area has collapsed to its original value the PILC still retains the remnants of a microporous structure. Note, for example, the larger relative adsorption at low values of P/P_0, and the absence of an upswing in the isotherm at high values of P/P_0.

Superficially, there is a similarity between the isotherms (not shown) for the other PILC. All show a large uptake of N_2 at low relative pressures because of microporosity. However, it is found that refluxed samples are less microporous than unrefluxed samples. The pattern is the same whichever method of preparation is used, and whether the clay is in the original or in the washed form. PILC prepared from refluxed Zr solutions have a different distribution of pore sizes, with a greater fraction of pores in the larger size range (see also the XRD data later).

Table 2 gives the values of surface area calculated from the BET equation, from the slope of the initial linear branch of the α_s plots (the microporous region), and from the slope of the α_s plots in the linear multilayer region (*25*). The α_s plot for the original clay hardly deviates from linearity showing that this is essentially a meso/macroporous material. No N_2 can penetrate between the layers in the unexpanded clay. The α_s plots for all the PILC lie above the line for the reference material, which is evidence for a high degree of microporosity. The α_s plots for samples BR/50 and BR/0 have a greater slope in the mesopore region (α_s = 0.6) showing that these samples contain a proportionately larger fraction of mesopores. These two samples were prepared using refluxed solutions of zirconyl chloride. The longer hydroxy Zr polymers produced during refluxing would be expected to create larger pillars and hence a more expanded structure. The final, linear portions of the α_s

TABLE 3

XRD Results for PILC Prepared in Different Ways

Sample	Interlayer spacing (nm)
AR/5/1	0.30
AR/5/2	0.30
AR/5/3	0.30
AR/10/1	0.36
AR/24/1	0.40, 1.05
AR/24/2	0.40, 1.05
AR/24/3	0.40, 1.05
BR/0	0.38, 0.65
BR/50	0.44, 0.81
B/0	0.02, 0.65
W2	0.63
W3	0.40, 0.74
W4R	0.40, 0.96
W5	0.72

plots correspond to multilayer adsorption on a small external surface.

Table 2 shows that the BET surface areas are consistently lower, sometimes markedly so, than the total surface area obtained from α_s plots. This merely underlines the difficulty of determining accurate surface areas for microporous materials. The problem arises because of condensation of N_2 in very small pores at relative pressures where the BET method assumes only multilayer adsorption will occur. However, the trends in apparent surface area are similar, so we can compare relative changes in apparent surface area in order to obtain information on the effect of the preparative procedure on the structure of the PILC. The external surface area of all samples is comparable to that of the original clay.

XRD measurements

XRD patterns have been obtained on most samples and the results are summarised in Table 3. With few exceptions the lines are broad, indicative of heterogeneity or disorder in the layer structure. The unexpanded clay has an apparent basal spacing of about 0.95 nm which corresponds to the distance between two adjacent sheets. When there is no preliminary refluxing of the Zr solution a considerable fraction of the clay remains in its original state (compare B/0 and BR/0). When a refluxed solution is used most of the clay is converted into PILC and the average interlayer spacing is increased. Table 3 shows the effect of varying the time of reflux of the Zr solution before addition of the clay (samples AR/5/1, AR/10/1, and AR/24/1). After a 5-h reflux the sample contains none of the original clay, and the PILC has an interlayer spacing of 0.30 nm. Increasing the time of reflux results in an increase in the interlayer spacing. After a 24-h reflux spacings up to 1.05 nm are observed.

Comparison of samples BR/0 and AR/24/1 shows the effect of aging temperature on the interlayer spacing. AR/24/1 was aged at 373 K for 1 h, whereas BR/0 was aged at room temperature for 1 h. The material aged at the higher temperature has a larger interlayer spacing. Possibly there is a diffusional limitation on the rate of pillaring, so that the rate at which the larger polymers can penetrate between the layers determines the type of pillaring which will be observed.

When the clay is washed free of residual Na^+ ions prior to adding the Zr solutions there is a smooth increase in the maximum interlayer spacing as the degree of polymerisation of the Zr species is increased (i.e., $W2 < W5 < W3 < W4$). These samples also gave much sharper XRD patterns, indicating that the PILC were much more homogeneous than those prepared from unwashed clay.

Thermal Analysis

DTA curves for the original clay and the PILC prepared from the washed clay are shown in Fig. 2, which also includes a DTA curve for hydrous zirconia (*24*). The large endothermic peak around 370 K is due to the dehydration of the clay, and seems to be little affected by forming the pillared product. Above 420 K, where TGA shows a

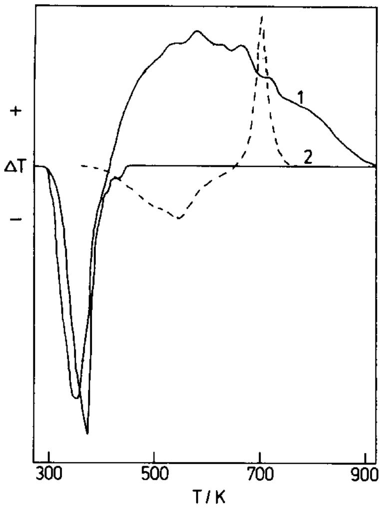

FIG. 2. DTA curves for sample W2 (curve 1), original clay (curve 2), and hydrous zirconia (broken line, after Ref. (*24*)).

loss of weight due to dehydroxylation of the hydroxy Zr species, the DTA shows a very broad exotherm. The DTA for pure hydrous zirconia is quite different, showing only a very sharp exotherm at about 700 K. In the pure material this exotherm occurs as the amorphous zirconia recrystallises into the tetragonal form of ZrO_2. It is thought that the broad exotherm for the PILC arises because as soon as the pillars begin to dehydroxylate they interact chemically with the clay layers to form a stable, covalent bond. At higher temperatures there may be some recrystallisation of the zirconia. However, the shape of the exotherm seems to indicate that there is a gradual and continuous chemical interaction over the whole range of temperature from 420 to 900 K. Presumably the pillars are fairly stable over this range and little or no crystalline ZrO_2 is formed.

Surface Area Data

The exchange capacity of the clay is 88 meq/100 g and assuming that the average charge on a Zr ion is 0.5 (*18*), the Zr content of a fully exchanged clay would be about 16%. It might be expected that the surface area would increase with Zr content up to this limit, and then remain constant, or decline, depending on whether the excess Zr was deposited as debris external to, or within the layer structure. In fact, as Table 4 shows, there is only a poor correlation between surface area and Zr content.

The surface area of the PILC is affected, however, by a number of experimental parameters, as follows.

(*a*) *Polymerisation of the Zr is beneficial.* When samples are prepared using fresh, unrefluxed Zr solutions, the surface area is markedly lower than when refluxed solutions are used (compare W2 and W4). Similarly, raising the ageing temperature to 340 K increases the surface area to 269 (W3) from 138 $m^2 g^{-2}$ (W2). Increasing the ageing time at room temperature to 24 h raises the surface area from 138 (W2) to 193 $m^2 g^{-1}$ (W5).

(*b*) *Dispersing the clay prior to the addition of the Zr solution has a large beneficial effect on the surface area.* At first sight this seems an obvious effect. If the clay is dispersed in water prior to the addition of the Zr solution the interlayer spacing will be

TABLE 4

BET Surface Areas and Zr Contents of Various PILC

Sample	Surface area ($m^2 g^{-1}$)	Zr (wt%)
AR/5/1	205	17.0
AR/5/2	194	20.5
AR/5/3	173	20.3
AR/10/1	216	—
AR/24/1	214	14.5
AR/24/2	196	22.4
AR/24/3	217	18.9
BR/0	263, 267, 276[a]	9.8
BR/50	305, 309, 325[a]	20.6
B/0	216	10.2
W2	138	8.6
W3	269	13.6
W4R	227	13.2
W5	193	9.2

[a] Separate repeat preparations.

increased, and diffusion of Zr ions between the layers will be facilitated. However, even in experiments where dry clay is added directly to the Zr solution there is ample time for the clay to be wetted and for the Zr ions to penetrate the interlayer regions. That this appears not to happen implies that there is a preemptive attack of the Zr ions on the peripheries of the clay particles, which prevents subsequent expansion and/or penetration of Zr ions into the interlayer regions of the clay.

When the clay is dispersed in a 50/50 acetone/water mixture and then a refluxed Zr solution is added, a PILC (BR/50) with a very large surface area is produced (305–325 $m^2 g^{-1}$). A similar preparation but using water rather than the acetone/water mixture produces a PILC (BR/0) having a lower surface area (263–276 $m^2 g^{-1}$).

(*c*) *The degree of swelling of the clay seems to affect the nature of the PILC.* Table 4 shows that when a washed clay is dispersed in water and then pillared with an unrefluxed Zr solution the surface area is very low (sample W2, compare sample B/0). Similarly, when a refluxed Zr solution is used the washed clay gives a lower surface area PILC than the unwashed clay (compare W4 and BR/0). The main difference between the two forms of the clay is that the unwashed sample contains excess Na^+ ions which on addition of water dissolve to produce an ionic solution. Under these conditions the clay will swell to a lesser degree.

Thermal Stability of PILC

The thermal stability of the PILC was determined by heating over a 16 h-period at successively higher temperatures, up to a limit of 1073 K. Figure 3 shows some typical data. The PILC show a gradual loss in surface area when the temperature is taken above 573 K. However, at 773 K the surface area has only decreased by 5–10%, and at 973 K by only 20–30%. It is only when the temperature is increased to 1073 K that the surface area declines rapidly. However, even then the surface area of sample BR/50 is over 100 $m^2 g^{-1}$. Yamanaka and Brindley (*18*) have reported a few results on the stability of Zr PILC. They heated samples for 24 h at various temperatures and observed a rapid loss in surface area at temperatures above only 673 K. Our PILC appear to be significantly more stable. For example, after heating for 24 h at 873 K, Yamanaka and Brindley observed a decrease in surface area of 50%, whereas even after heating at 973 K for 8 h we observe a decrease in surface area of only about 25%.

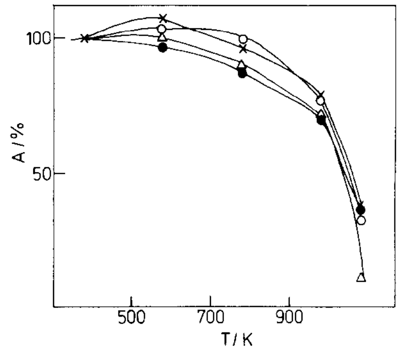

FIG. 3. Percentage change in surface area with temperature of heating in air. ×, AR/24/1; ○, AR/24/2; △, AR/24/3; ●, BR/50.

Comparison of the stability of our Zr-PILC with the Al-PILC prepared by Occelli (*13*) shows that the Zr-PILC appear to be more stable. This improved stability may reflect differences in the clay used in each case. However, ZrO_2 is known (*22*) to stabilise oxides against sintering so Zr-PILC may actually be inherently more stable than other types of PILC.

Effect of Type of Pillaring Species on Interlayer Spacings

Our XRD data show that as the degree of polymerisation of the Zr tetramers is increased there is a gradual increase in the interlayer spacings. It appears that insertion of single tetramers between the layers produces an expansion of only 0.3–0.4 nm. Since the tetramer has dimensions of 0.46 × 1.0 × 1.0 nm, we conclude that single tetramers are exchanged parallel to the layer surface, and that tetramers on opposite faces do not overlap. This conclusion may be contrasted with that arrived at by Yamanaka and Brindley (*18*). They pillared a Na-exchanged montmorillonite and obtained interlayer spacings of up to 1 nm even when using unrefluxed Zr solutions and ageing at room temperature. Under these conditions only tetramers will be present in any significant amount. Yamanaka and Brindley suggested that even tetramers could produce large interlayer spacings, either by standing perpendicular to the clay layers or by stacking on top of each other. We do not find this with our samples. One possible reason may be that when we have prepared PILC from Zr tetramers the amount of Zr taken up by the clay is quite low (see Table 4) and less than the 10.2% reported by Yamanaka and Brindley. The chance of tetramers overlapping to give large interlayer spacings will be less in our case. However, there does not seem to be any evidence that tetramers are positioned perpendicular to the clay layers.

By refluxing the Zr solutions to produce larger cations we have been able to produce interlayer spacings of about 1 nm. It is not possible to say whether these spacings originate because the polymeric cations are large enough by themselves or because of overlap due to a mismatch between cations adsorbed on opposite clay layers. It is clear, however, from our results that a much higher thermal stability is obtained when the pillaring species is a polymeric Zr ion.

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