Zirconia-Pillared Tetrasilicic Fluoromica

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Zirconia-pillared tetrasilicic fluoromicas are prepared from sodium tetrasilicic mica, Na-$[Mg_{2.5}Si_4O_{10}F_2]$, using a commercial zirconyl acetate solution as the source of the zirconium polyoxocation pillars. Reproducible results are conveniently obtained without any preliminary heating of the pillaring solution, and the pillaring reaction is performed at ambient temperature. The resulting zirconia-pillared mica has a consistently higher crystallinity and layer spacing than pillared clays prepared from zirconyl chloride solutions and shows significantly higher thermal stability, an important factor in potential catalytic applications. Zirconia-pillared tetrasilicic fluoromica is a microporous material containing two-dimensional galleries with a height of 11 Å. The surface area is high, about 300 m^2/g. After treatment in steam at 760 °C for 17 h, the surface area is reduced only to ~200 m^2/g. Thus, very small particles of ZrO_2 dispersed between 10-Å-thick mica layers have been stabilized.

Introduction

Pillared clays are currently of interest for a variety of applications in adsorption and catalysis due to the two-dimensional microporous galleries that are formed when the clay layers are propped apart by thermally stable oxide pillars.[1,2] Most of the work to date on pillared clays has employed materials from the smectite group of clay minerals such as montmorillonite, hectorite, and beidellite. Sodium tetrasilicic mica (NaTSM), with formula $Na[Mg_{2.5}Si_4O_{10}F_2]$, is a mica. Micas are distinguished from smectites by their higher layer charge density. Due to this higher layer charge density, naturally occurring micas do not normally swell in water and other polar solvents, and as a result, exchange reactions with the interlayer cations do not readily occur. In contrast to most micas, NaTSM swells in water and can be pillared with inorganic polyoxocations.[3] Alumina-pillared tetrasilicic mica (Al-TSM) has been studied as a catalyst for olefin isomerization,[4] toluene alkylation by methanol,[5,6] and cumene cracking.[7,8] To further explore the synthetic chemistry of pillared micas, we have investigated the introduction of zirconia pillars into tetrasilicic mica to form Zr-TSM.

Zirconia-pillared smectites have been known for over a decade. The original reports of the pillaring of smectite clays with polyoxozirconium cations appeared at the about the same time as the description of thermally stable oxide-pillared clays formed with polyoxoaluminum cations.[9,10] Since that time zirconia-pillared clays have been studied extensively, with the amount of effort devoted to them second only to that devoted to clays with alumina pillars. A number of studies have concentrated on the preparation and characterization of the physical properties of zirconia-pillared clays,[3,10-20] while others have investigated their use in catalytic cracking of hydrocarbons,[13,14,16,21] as catalysts for the conversion of methanol to hydrocarbons,[22,23] trimethylbenzene disproportionation,[24] propene oligomerization,[25] and syngas conversion to methanol and hydrocarbons.[26] Zirconia-pillared clays have been investigated as sorbents for gas separation.[27] A recent review covering zirconia-pillared clays has appeared.[28] In all the work reported thus far, the zirconia polyoxocation solutions used to pillar the smectite clays employed have been prepared from zirconyl chloride, $ZrOCl_2$. The zirconyl chloride solutions have been treated in various ways to optimize the properties of the resulting pillared clays, including refluxing the solution either before or after

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Table I. Preparation and Characterization of ZrTSM Samples with Varying Zr/TMS Ratios

mL of ZrOAc/g of TSM	1	2	4	6	8	10	15	20
mmol of Zr/g of TSM	2.3	4.6	9.3	13.9	18.6	23.2	34.8	46.4
g of ZrO_2/g of TSM	0.3	0.6	1.1	1.7	2.3	2.9	4.3	5.7
surface area (m^2/g)	184	308	319	301	294	290	313	311
micropore volume (mL/g)	0.057	0.102	0.111	0.105	0.110	0.107	0.117	0.109
%Zr	16.24	21.32	19.28	19.62	18.20	17.88	17.66	17.72
%Si	20.54	16.82	18.70	20.42	19.12	20.06	19.96	22.14
%Na	1.14	0.99	1.18	1.01	1.14	1.00	1.19	1.03
mol of $Zr/O_{10}F_2$	0.97	1.56	1.27	1.18	1.17	1.10	1.09	0.99
mol of $Si/O_{10}F_2$	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
mol of $Na/O_{10}F_2$	0.27	0.29	0.31	0.24	0.29	0.24	0.29	0.23

mixing with the clay[9,11,12,17,21,26,29] and predrying the $ZrOCl_2 \cdot 8H_2O$ in an oven at 260 °C to form $ZrOCl_2 \cdot 4H_2O$ before dissolving it in water to form the pillaring solution.[9] Treating the zirconyl chloride solution with bases such as sodium carbonate has also been reported.[9]

In our attempts to prepare zirconia-pillared tetrasilicic mica using polyoxocation solutions derived from zirconyl chloride, the pillared micas produced have had crystallinities, layer separations, surface areas, and thermal and hydrothermal stabilities that were inferior to those we were able to obtain routinely in parallel work on alumina-pillared micas. We have found an improved method of preparing zirconia-pillared clays that avoids the use of zirconyl chloride in the preparation of the pillaring solution. This method is more convenient than those using zirconyl chloride; reproducible results are easily obtained without any preliminary heating of the pillaring solution, and the pillaring reaction is performed at ambient temperature. The resulting pillared mica has a consistently higher crystallinity and layer spacing than most of the materials prepared using zirconyl chloride and shows significantly higher thermal stability, which is important for potential catalytic applications.

Experimental Section

Materials. Synthetic tetrasilicic fluoromica (NaTSM) with a nominal formula of $Na_2[Mg_5Si_8O_{20}F_4]$ was obtained from Topy Industries. An aqueous suspension of NaTSM was adjusted to pH 5 with HCl, size-fractionated by conventional sedimentation techniques to isolate the <2-μm fraction, and spray dried. The refined NaTSM contained only trace amounts of impurities, such as cristobalite. The zirconium pillaring reagent employed in this work was an aqueous zirconyl acetate solution (ZAA) supplied by Magnesium Elektron, Inc. of Flemington, NJ. According to information supplied by the manufacturer its nominal formula is $ZrO(OH)_{0.5}(CH_3COO)_{1.5}$ and it contains 22% ZrO_2 by weight. The pH of the solution is 3.3, and its specific gravity is 1.30. Mixed hydroxy acetates of zirconium have been reported in the literature,[30] but none have been structurally characterized. When the zirconyl acetate solution was heated to reflux for 2 h, it polymerized to an opaque white gel. Pillaring experiments were performed at room temperature to avoid excessive polymerization of the zirconyl acetate reagent.

Characterization. Surface areas were calculated from the nitrogen adsorption isotherms measured on an Omnisorp 360 continuous-flow instrument at 77 K using the multipoint BET method. X-ray powder diffraction (XRD) analysis was performed using a Siemens D-500 diffractometer equipped with Cu Kα radiation. Elemental analyses were determined by plasma emission spectroscopy using a Leeman Labs Plasma-Spec 2.5 ICP. Samples for elemental analysis were dissolved by means of a lithium tetraborate fusion method. Infrared spectra were measured on samples in dilute KBr pellets using a Mattson FTIR 5000. Transmission electron micrographs were taken using a Philips CM-12 operating at 100 keV.

Preparation of Zirconia-Pillared TSM. NaTSM was pillared with zirconia by means of a modification of the technique employed for pillaring smectites with alumina. Two series of experiments were performed:

(a) *Effect of the Ratio of Zirconium to TSM in the Pillaring Step.* A series of eight samples were prepared in which the Zr/TSM ratio was 2.3, 4.6, 9.2, 13.8, 18.4, 23, 34.5, and 46 mmol of Zr/g of TSM. The amount of zirconyl acetate solution (ZAA) required to obtain the desired Zr/TSM ratio was added to 100 mL of distilled water and stirred at room temperature for 10 min. NaTSM (1 g) was added, and the resulting milky-white dispersion was stirred for 3 h at room temperature and then separated by centrifugation. The solid product was washed by redispersion in 1 L of distilled water and separated by centrifugation. The washing procedure was repeated until the acetic acid odor in the decantates was no longer noticeable, requiring from four to eight washes. The first wash produced a great deal of foam which takes approximately 0.5 h to settle. The foaming disappears after the second wash. The samples were filtered and dried at 120 °C overnight. The samples were then calcined in air at 200 °C for 2 h, heated to 400 °C at 50 °C/h, and held at 400 °C for 2 h. Results from this series of experiments are listed in Table I.

(b) *Hydrothermal Stability of the Most Crystalline Products.* The amount of ZAA required to obtain Zr/TSM ratios of 11.6, 23.2, and 34.8 mmol of Zr/g TSM was added to 750 mL of distilled water and stirred at room temperature for 10 min. NaTSM (10 g) was added, and the resulting milky-white dispersion was stirred for 3 h at room temperature. The products were isolated and calcined as described above. Results from this series of experiments are listed in Table II.

Preparation of Washed ZrTSM. Half portions of each of the three calcined ZrTSM products in (b) above were stirred in 700 mL of distilled water at room temperature for several hours and then separated by centrifugation. This procedure was repeated three times over 24 h. The samples were filtered and dried at 120 °C overnight. The samples were then calcined in air at 250 °C for 2 h and then heated to 400 °C for 2 h.

Steaming Procedure. A series of three steaming experiments were conducted at temperatures of 650, 700, and 760 °C. Fresh 0.5-g samples of unwashed and washed ZrTSM prepared with Zr/TSM ratios of 11.6, 23.2, and 34.8 mmol of Zr/g of TSM were spread in shallow layers inside quartz tubes and inserted into a steaming apparatus designed for deactivating cracking catalysts. The samples were exposed to pure steam flowing at approximately 1200–1400 cm^3/min for 17 h at the temperatures indicated.

Results

After preliminary experiments showed that zirconyl acetate was an effective pillaring agent for tetrasilicic mica, a series of experiments were conducted to ascertain the affect of the ratio of zirconium to NaTSM in the pillaring step. All reactions in this series were carried out at room temperature for 3 h. The Zr/TSM ratio was varied from 2.3 to 46 mmol of Zr/g of TSM, which corresponds to a range of ZrO_2/NaTSM weight ratios from 0.3 to 5.7. The resulting zirconia-pillared tetrasilicic mica samples were washed thoroughly and dried at 120 °C. Examination of

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Table II. Preparation and Characterization of ZrTSM Samples at Three ZrTSM Ratios

	unwashed	washed	unwashed	washed	unwashed	washed
mL of ZrOAc/g of TSM	5	5	10	10	15	15
mmol of Zr/g of TSM	11.6	11.6	23.2	23.2	34.8	34.8
g of ZrO_2/g of TSM	1.4	1.4	2.9	2.9	4.3	4.3
surface area (m^2/g)	308	332	328	339	311	339
micropore volume (mL/g)	0.109	0.120	0.113	0.118	0.104	0.119
%Zr	23.20	24.00	21.75	22.15	21.60	22.22
%Si	19.35	20.10	20.35	20.30	20.45	20.75
%Na	0.77	0.15	0.61	0.25	0.75	0.20
mol of $Zr/O_{10}F_2$	1.48	1.47	1.32	1.34	1.30	1.32
mol of $Si/O_{10}F_2$	4.00	4.00	4.00	4.00	4.00	4.00
mol of $Na/O_{10}F_2$	0.19	0.04	0.15	0.06	0.18	0.05

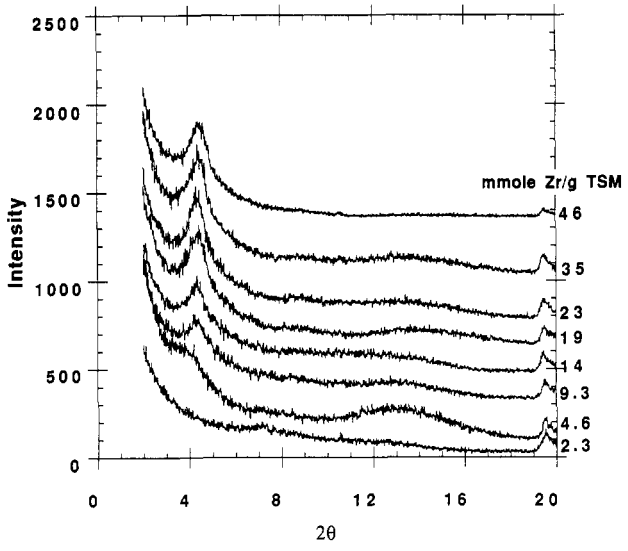

Figure 1. X-ray powder diffraction patterns (Cu Kα radiation) of zirconia-pillared micas prepared with varying amounts of zirconyl acetate solution, after 400 °C calcination.

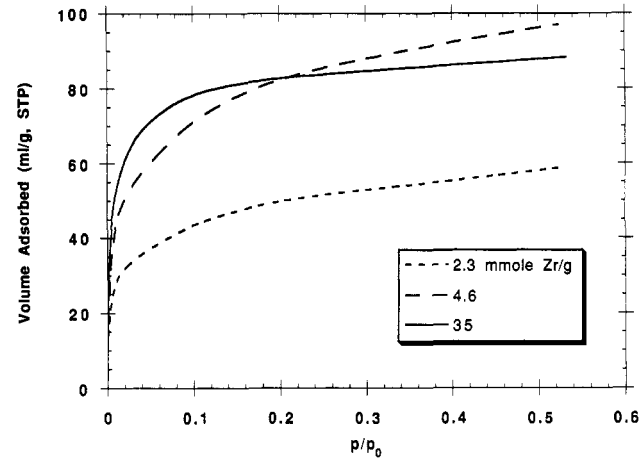

Figure 2. Nitrogen adsorption isotherms (77 K) of zirconia-pillared micas prepared with varying amounts of zirconyl acetate solution, after 400 °C calcination.

the pillared micas by X-ray diffraction at this point in the preparation showed that there was not a high degree of order in the interlayer spacings. Two broad, weak peaks at about 20 and 10 Å were usually present on a high background in the low-angle region of the diffraction patterns. When the samples were calcined at 400 °C, the resulting diffraction patterns had significantly sharper and stronger peaks at 20.1–20.6 Å, depending on Zr/TSM ratio. The X-ray diffraction patterns in the low angle region of the samples after 400 °C calcination are presented in Figure 1. It can readily be seen that an excess of zirconyl acetate solution in the pillaring step is beneficial in enhancing the crystallinity of the zirconia-pillared mica. When only 2.3 mmol of Zr/g of TSM is used, no diffraction maximum corresponding to an expanded interlayer spacing is observed. Zirconia polyoxocations must be entering the interlayer space, because the diffraction maximum for unpillared clay is not present, but the layer-to-layer distance must vary from layer to layer so that no coherent diffraction is observed. As the amount of zirconyl acetate is increased, a peak in the diffraction pattern appears at slightly greater than 20 Å. The intensity of this 20-Å peak is maximized at a ratio of 23 mmol of Zr/g of TSM, although it clearly appears at all ratios from 9.3 to 46 mmol of Zr/g of TSM.

The surface areas of the Zr-pillared micas in this series are not as sensitive to the Zr/TSM ratio as are the X-ray crystallinities. As shown in Table I, the surface area of the sample prepared with the lowest amount of zirconyl acetate is only 184 m^2/g, but the rest of the samples have surface areas between 290 and 319 m^2/g. The shape of nitrogen uptake isotherms approaches ideal type 1 behavior as the crystallinity of the samples increases. Figure 2 shows the isotherms for three representative samples prepared at Zr/TSM ratios of 2.3, 4.6, and 35 mmol of Zr/g of TSM. The isotherms for the samples prepared with ratios from 9 to 46 mmol of Zr/g of TSM were very similar in shape to that of the 35 mmol of Zr/g of TSM sample. Type 1 isotherms indicate the presence of micropores (R_p < 20 Å)[31] and are characteristic of zeolites and well-ordered pillared clays.

The excess zirconyl acetate solution in the pillaring reactions does not result in increased zirconia incorporation in the pillared mica. The analytical results show a maximum in zirconium content in the sample prepared with 4.6 mmol of Zr/g of TSM and a slight decrease in the amount of zirconium incorporated as the amount of zirconyl acetate used in the pillaring increases. The formula of the starting NaTSM is $Na[Mg_{2.5}Si_4O_{10}F_2]$. As can be seen from the molar ratios calculated from the results of the elemental analysis at the bottom of Table I, approximately three-fourths of the sodium in the interlayer space of the NaTSM is exchanged by the zirconium polyoxocations.

A crucial property of pillared clays, if they are to be considered for applications in catalytic cracking, is hydrothermal stability. Temperatures in the regenerator of a commercial fluid catalytic cracking unit can be as high as 750 °C, and steam is present. To test the effect of high-temperature steam treatment on the crystallinity and surface area of zirconia-pillared tetrasilicic mica, larger samples were prepared using 12, 23, and 35 mmol of Zr/g

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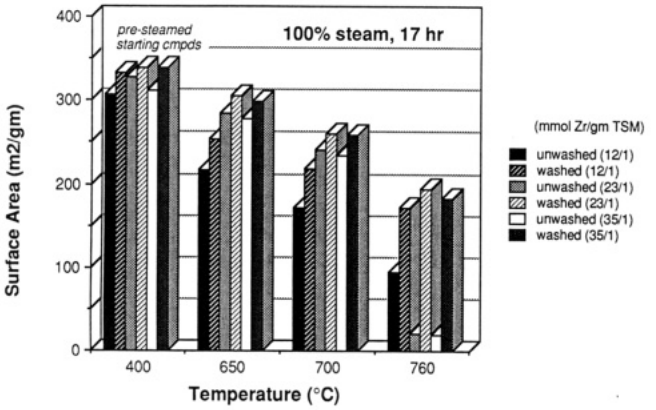

Figure 3. Surface areas of Zr-TSM samples after heating for 17 h in 100% steam at the indicated temperature.

of TSM. In previous experiments with alumina-pillared tetrasilicic mica,[3] we have shown that after calcination of the pillared mica at 400 °C, some of the residual sodium that was not removed by the pillaring cations during the initial exchange is labilized and can be removed by a postcalcination washing step. The removal of this labilized sodium results in an increase in the acidity[4] and the thermal stability of alumina-pillared tetrasilicic mica. To see if a similar sodium labilization effect is present in zirconia-pillared tetrasilicic mica, each of the three samples above was calcined at 400 °C, washed with distilled water, and recalcined. As the data in Table II show, the washed and recalcined samples have significantly lower sodium contents than their unwashed precursors. The form of the sodium removed is unknown at present, but elemental analyses show that the Zr/Si ratio and the fluoride content of the pillared mica are not changed significantly after calcination and washing. The surface areas and micropore volumes of the washed samples are also slightly higher in all three cases. The sample prepared with 12 mmol of Zr/g of TSM had a slightly higher zirconium content than the two samples prepared at higher Zr/TSM ratio, confirming the trend shown in the first series of experiments, but little variation was detected in the three samples by X-ray diffraction. All six samples had low-angle diffraction maxima of similar intensity corresponding to a layer separation of 22 Å. The nitrogen adsorption data show that the surface area and micropore volume are highest in the sample prepared with 23 mmol of Zr/g of TSM.

Samples of zirconia-pillared tetrasilicic mica were heated in flowing steam for 17-h periods at 650, 700, and 760 °C. The results of surface area measurements on the steamed samples are presented in Figure 3. As the steaming temperature is increased, the difference in surface area between unwashed and washed samples becomes more pronounced. For example, after steaming at 760 °C the sample with the highest surface area is the one that was prepared with 23 mmol of Zr/g of TSM and washed after calcination. This sample had a surface area of 194 m^2/g, a loss of only 43% from its original surface area before steaming of 339 m^2/g. In contrast, the same sample when steamed at 760 °C before washing lost 94% of its surface area, retaining only 20 m^2/g. The deleterious effect of small amounts of sodium on the hydrothermal stability of zirconia-pillared tetrasilicic mica becomes increasingly more important as the temperature of the steam treatment increases.

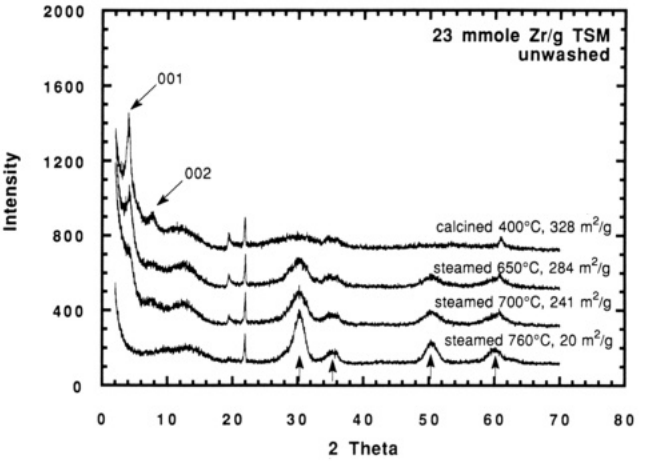

Figure 4. X-ray powder diffraction patterns (Cu Kα radiation) of zirconia-pillared mica prepared with 23 mmol of Zr/g of TSM, after steaming at various temperatures. The layer lines 001 and 002 are indicated. Vertical arrows mark the lines of ZrO_2 that appear after steam treatment.

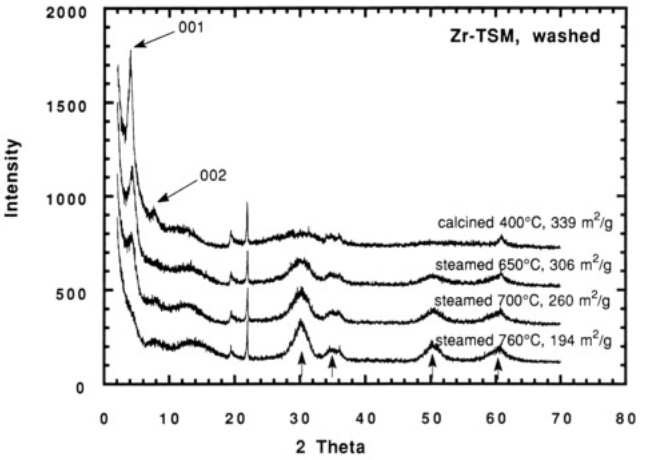

Figure 5. X-ray powder diffraction patterns (Cu Kα radiation) of zirconia-pillared mica prepared with 23 mmol of Zr/g of TSM and washed after calcination, after steaming at various temperatures. The layer lines 001 and 002 are indicated. Vertical arrows mark the lines of ZrO_2 that appear after steam treatment.

The X-ray powder diffraction patterns of pillared clays give an indication of their crystallinity. The d spacing of the first low-angle line corresponds to the layer repeat distance. If the layer spacing is uniform for many layers in the pillared mica microcrystallite, one expects a sharp intense line at a d value equal to the layer repeat distance, followed by higher orders of the layer spacing line at $d/2$, $d/3$, etc. As the crystallinity is lowered, that is, as the distance from layer to layer begins to vary and as the number of layers stacked in each coherently diffracting crystallite diminishes, the higher order peaks disappear and the low-angle peak becomes weaker and broader. A series of X-ray powder diffraction patterns of zirconia-pillared tetrasilicic mica samples prepared with the optimum amount of zirconium in the pillaring solution, 23 mmol of Zr/g of TSM, that have been steamed at 650, 700, and 760 °C are displayed in Figure 4. Similar data for the same sample that had been washed after calcination to remove sodium is displayed in Figure 5. Again the enhancement of hydrothermal stability by the removal of sodium by the postcalcination wash is evident, as the intensities of the 001 diffraction maxima are greater for the washed samples of Figure 5. This is particularly

Table III. Line Widths (fwhm) and Crystallite Diameters (d) Calculated from the Scherrer Equation, $d = 0.9\lambda/(\text{fwhm}\cdot\cos\theta)$, Using the 111 Line of Tetragonal ZrO_2 at $2\theta = 29.1°$ for Zirconia-Pillared Tetrasilicic Mica Prepared with 23 mmol Zr/g of TSM, and for Bulk Zirconia Prepared from Zirconyl Acetate

		fwhm(°)	d (Å)			fwhm(°)	d (Å)
unwashed ZrTSM	400 °C calcined	4.92	17	washed ZrTSM	400 °C calcined	5.1	16
	650 °C steamed	3.08	27		650 °C steamed	3.3	25
	700 °C steamed	2.62	31		700 °C steamed	2.72	30
	760 °C steamed	1.83	45		760 °C steamed	2.23	37
bulk ZrO_2	400 °C calcined	1.43	58				
	650 °C steamed	0.64	135				

noticeable in the samples steamed at 700 °C. One aspect of the behavior of zirconia-pillared tetrasilicic mica is qualitatively different from that we have previously observed in alumina-pillared tetrasilicic mica. After steaming at 760 °C, the washed sample of zirconia-pillared tetrasilicic mica still has a surface area of 194 m^2/g and a micropore volume of 0.073 mL/g, although the layer spacing line is no longer detectable in the X-ray powder diffraction pattern. In contrast, loss of the X-ray crystallinity in alumina-pillared tetrasilicic mica coincides with collapse of the layers and almost complete loss of the surface area and micropore volume.

In the X-ray diffraction patterns of zirconia-pillared tetrasilicic mica shown in Figures 4 and 5, broad new lines at approximate diffraction angles $2\theta = 30, 35, 50$, and 60° appear and grow larger with increasing temperature of the steam treatment. These lines are in the positions expected for the tetragonal phase of zirconium dioxide, although the resolution of this data does not make it possible to distinguish this phase from the related cubic phase of zirconia.[32,33] There is no significant difference in the line widths of these ZrO_2 lines for the unwashed and washed samples before steaming or after steaming at 650 and 700 °C, but after steaming at 760 °C the ZrO_2 lines in the diffraction pattern of the unwashed sample are sharper (see Table III and Figures 4 and 5), demonstrating that the removal of sodium retards the growth of ZrO_2 microcrystallites during the steam treatment. When bulk zirconia is formed by evaporating the zirconyl acetate solution and calcining it to 400 °C, tetragonal zirconia with surface area of 78 m^2/g is formed. The crystallite size as determined from the X-ray diffraction pattern is larger than that of the zirconia associated with the pillared mica. When the bulk sample is steamed at 650 °C, the resulting product sinters to surface area of 10 m^2/g, and the X-ray diffraction pattern shows much larger crystallites and the onset of the formation of the more stable monoclinic phase of ZrO_2. (Figure 6 and Table III).

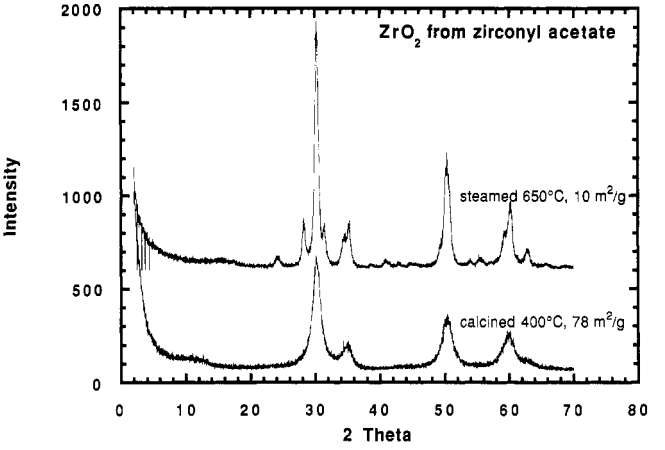

Figure 6. X-ray powder diffraction patterns (Cu Kα radiation) of bulk zirconia prepared from zirconyl acetate after calcination at 400 °C and after steaming at 650 °C.

Discussion

Previous work on zirconia-pillared clays employed $ZrOCl_2$ as the source of the zirconia polyoxocations that serve as the pillars. The zirconia-pillared tetrasilicic fluoromica of this report, prepared from zirconyl acetate, has higher crystallinity and surface area than pillared micas prepared from $ZrOCl_2$. Diffraction patterns of zirconia-pillared TSM prepared using a solution of $ZrOCl_2 \cdot 4H_2O$ that had been refluxed 24 h before pillaring at room temperature show a layer spacing of ca. 21 Å, but the peak in the diffraction pattern is only a shoulder on the low-angle scattering.[3] The surface area of the $ZrOCl_2$-prepared sample was 231 m^2/g, while the zirconyl acetate-prepared samples have surface areas above 300 m^2/g (see Table II). We have found the zirconyl chloride preparations difficult to reproduce in detail. In preparing a larger batch of ZrTSM pillared by zirconyl chloride, we saw no 21-Å shoulder in the X-ray diffraction pattern of the product after calcination at 400 °C, and the surface area of the material was 108 m^2/g. After steaming at 700 °C, the surface area of the zirconyl chloride pillared TSM fell to 48 m^2/g and to 31 m^2/g after steaming at 760 °C.

Solutions of $ZrOCl_2$ are quite acidic, with pH values <2. Trioctahedral clays such as hectorite that have magnesium in the octahedral sheet are more susceptible to attack by acid than are clays like montmorillonite with aluminum in the octahedral sheet.[34] Thus it is not surprising that the less acidic zirconyl acetate solution used in this work is more suitable than is zirconyl chloride for pillaring tetrasilicic mica, which contains only magnesium in the octahedral sheet. Some workers have recognized that the acidity of the pillaring solution is important in determining the distribution of the polyoxocations present and have modified it by adding basic reagents such as Na_2CO_3[9] or NaOH[27] in order to produce pillared clays with enhanced properties. A few of the previous reports describe pillared clays with layer spacings higher than 20 Å,[3,9,17,19,27] but none describe their thermal or hydrothermal stability at temperatures above 400 °C. The zirconyl acetate solution used in this study has a lower acidity than that of zirconyl chloride solutions, and this as well as the presence of acetate ions must result in a different distribution of polyoxozirconium cations than is found in the zirconyl chloride solutions after various heat treatments. The distribution of cations in the zirconyl acetate solution is favorable for the synthesis of well-ordered, pillared clays with gallery heights of 20–22 Å. The use of zirconyl acetate solution is also more convenient and reproducible than the methods employing zirconyl chloride, in that the commercial

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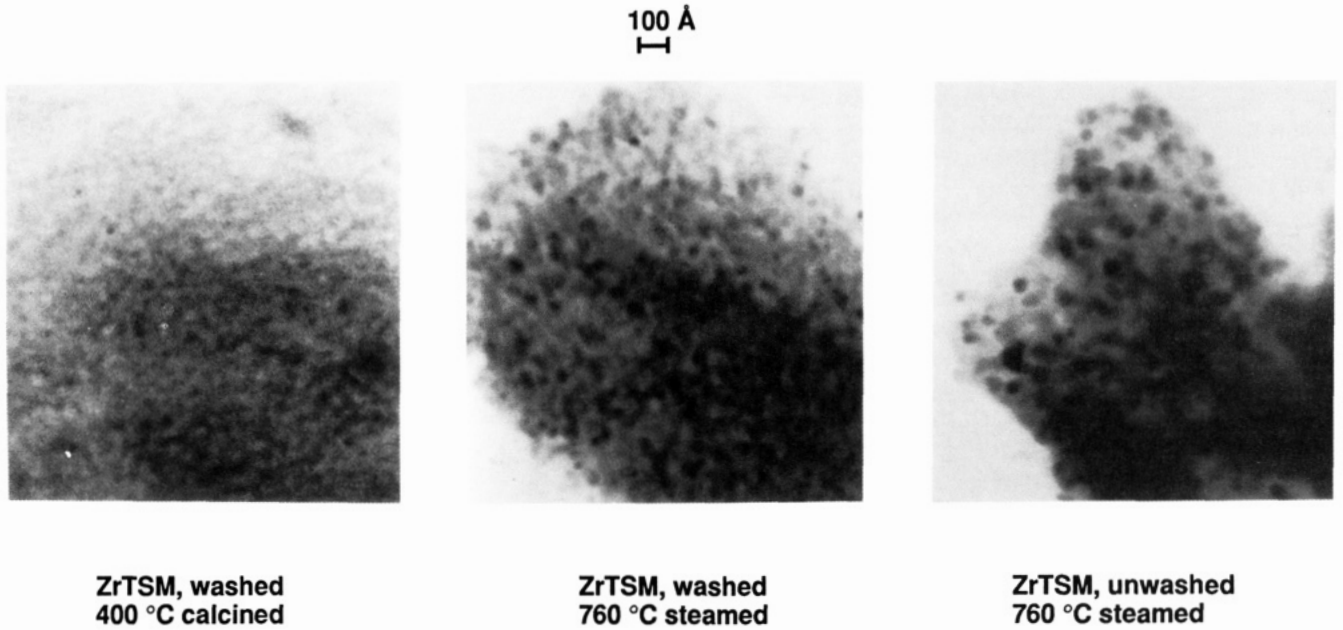

Figure 7. Transmission electron micrographs of zirconia pillared-mica prepared with 23 mmol/g of TSM.

solution is used directly. No heat treatment of the solid zirconyl chloride or high-temperature aging of the pillaring solution is necessary.

To form crystalline zirconia-pillared micas, an excess of the zirconyl acetate pillaring agent is beneficial. The optimum amount found in this study was 23 mmol of Zr/g of TSM. This amounts to almost 3 g of ZrO_2 in the pillaring solution per gram of TSM. Most of this excess zirconia is removed in the washing step, because the Zr-TSM product contains only about 20% Zr by weight. The most likely explanation for this effect lies in the composition of the zirconyl acetate solution. There must be a single polyoxozirconium cation which is a minor component of the solution that is being selectively extracted by the tetrasilicic mica. When enough of the solution is used to supply the entire cation exchange capacity of the mica with this favored cation, a regularly pillared 22-Å phase is produced after calcination. If less zirconyl acetate pillaring solution is used, a variety of the polyoxozirconium cations present in the pillaring solutions are intercalated, and the resulting product has an irregular layer repeat distance after washing and calcination. This presents a problem for a practical, economic synthesis of large quantities of zirconia-pillared mica, because of the excess zirconyl acetate required. More study of the zirconyl acetate pillaring solution to identify the key pillaring species and to maximize its presence would reduce the need to use excess zirconia and make the preparation more economically attractive. A benefit of large excesses of pillaring solution has been observed in the synthesis of titania-pillared montmorillonites,[35,36] in which the polyoxotitanium cations were produced by peptizing $TiCl_4$ or $Ti(OC_2H_5)_4$ with HCl.

In earlier work on zirconia-pillared clays, it was suggested that the polyoxocation present in zirconyl chloride solutions that was responsible for the pillaring upon ion exchange and the subsequent generation of zirconia pillars during calcination was the $Zr_4(OH)_8(H_2O)_{16}^{8+}$ cation that had been characterized in solid $ZrOCl_2$ by single-crystal X-ray diffraction[37] and identified in aqueous solutions by small-angle X-ray scattering.[38] Using modern interactive molecular modelling, we find that placing $Zr_4(OH)_8(H_2O)_{16}^{8+}$ cations between mica layers at van der Waals contacts results in layer spacings of 16–17 Å, agreeing with the spacings observed in much of the work on zirconyl chloride pillared clays. These tetrameric cations are unable in a reasonable way to prop the layers far enough apart to form a 21–22-Å layer spacing, as is observed in some of the zirconyl chloride work mentioned in the Introduction, and in the present examples of tetrasilicic mica pillared with zirconyl acetate derived polyoxocations. A better model for the type of polyoxocation that must be present in these pillared materials can be found in a more recent report of the crystal structure of a complex basic zirconium sulfate that contains idealized $Zr_{18}O_4(OH)_{36}(SO_4)_{14}(H_2O)_{16}$ molecules.[39] By dissociating a portion of the sulfate groups, the resulting Zr_{18} polyoxocation when placed between mica layers using molecular graphic techniques results in a layer spacing of 21–22 Å. A polynuclear cation containing zirconium atoms, oxide, hydroxyl, and acetate groups of a size similar to that of the Zr_{18} polyoxocation must be present in the zirconyl acetate solution, and this cation is selectively exchanged into the tetrasilicic mica. The infrared spectrum of zirconyl acetate exchanged tetrasilicic mica after drying at 120 °C shows strong adsorption maxima at 1561 and 1448 cm^{-1}, corresponding to the C=O strectching vibrations of acetate groups, as well as a weak C–H stretching absorption at 2952 cm^{-1}. These bands are no longer present in the spectrum of the sample after calcination at 400 °C, due to the loss of the acetate groups from the pillar precursor by combustion.

When zirconia-pillared tetrasilicic mica that has been prepared using zirconyl acetate is heated in steam, the intensity and definition of the low-angle peak in the X-ray

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diffraction pattern corresponding to the 22-Å layer spacing decreases, while peaks at higher angle corresponding to those of the tetragonal phase of ZrO_2 grow in (see Figures 4 and 5). The line widths of the emerging ZrO_2 peaks become narrower with increasing temperature of the steam treatment as the zirconia particles between the clay layers grow. As these interlayer zirconia particles grow, the layer spacing becomes irregular, but significant surface area is maintained even after all evidence of an ordered layer spacing is gone from the diffraction pattern. The particle sizes estimated from the Scherrer equation and given in Table III should be regarded as estimates because of the assumptions involved, but the trend that they point out is clear. The removal of sodium by a postcalcination wash is important, as the sodium enhances the rate of growth of the zirconia particles and the collapse of the pillared clay. After steaming at 760 °C, the surface area of the unwashed sample is only 20 m^2/g while that of the washed sample is 194 m^2/g. High-resolution transmission microscopy confirms the growth of the zirconia particles upon steaming. In Figure 7 a micrograph of zirconia-pillared TSM after calcination at 400 °C is displayed. The view is perpendicular to the layer surface of an oriented small particle of pillared mica. The mottled contrast is due to the presence of the zirconia pillars within the clay layers, with sizes that are at approximately the resolution limit of the micrograph (10–20 Å). After the sample has been washed and steamed at 760 °C, clusters of zirconia are clearly present, with diameters up to ca. 40 Å. Omitting the wash step before the steaming results in even larger zirconia clusters, in agreement with the X-ray line width data. An interesting aspect of this work is the ability of the pillared clay structure to retard the sintering of these small particles of zirconia and their transformation to the monoclinic phase. When small particle zirconia is produced by heating the zirconyl acetate solution, washing the resulting product and heating it to 400 °C, a tetragonal zirconia of larger crystallite size is produced. When this material is steamed, it sinters more readily than do the zirconia particles between the layers of the pillared mica. Concomitant with this enhanced sintering of the unintercalated zirconia is its partial transformation to the monoclinic phase.

Zirconia-pillared tetrasilicic micas are models for potential cracking catalyst components. The large pores present in materials of this type allow molecules larger than those that can fit into the micropores of faujasite zeolites to access the micropore space. There these molecules can crack into smaller, fuel size molecules on the acid sites present on the surface of the zirconia pillars. The high hydrothermal stabilities of these materials are impressive when compared to conventional pillared smectites. A disadvantage of these materials that may prevent their eventual commercial application is the presence of fluoride in the mica layers. In the presence of steam at high temperature, some of the lattice fluoride is lost, presumably as HF, and this can present corrosion problems in steel equipment. The fluoride loss is probably due to OH^- for F^- exchange, because it can occur without loss of surface area or crystallinity. For example, when Zr-TSM is heated in 20 Torr of steam at 740 °C for 2 h, 30% of the fluoride is lost, although surface area and X-ray diffraction measurements show negligible loss of crystallinity. Under more severe steaming conditions, most of the fluoride can be lost. When a washed sample of Zr-TSM was treated in pure flowing steam for 17 h at 760 °C, 27% of its fluoride was retained, while the unwashed sample retained only 9% of its fluoride when steamed under the same conditions.