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Al-, Al,Zr-, and Zr-Pillared Montmorillonites and Saponites: Preparation, Characterization, and Catalytic Activity in Heptane Hydroconversion

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Zr- and Zr,Al-pillared smectites have been prepared and characterised by X-ray diffraction and nitrogen sorption measurements. The residual cation exchange capacities and the acid contents have been determined. Hydroconversion of heptane over Pt-impregnated samples was used to evaluate their catalytic properties. The results were compared with those obtained over Al-pillared forms of the same smectites. For the Zr-pillared clays, mixtures of pillared and unpillared fractions were obtained in proportions depending on the preparation conditions. The pillared fractions exhibited poorer thermal resistance than the corresponding Al-pillared forms. Mixed Al,Zr-pillared clays behaved much like Al-pillared clays. The conversion of heptane over the Zr-pillared montmorillonites was substantially enhanced with respect to the Al-pillared analogues, due to the enhanced hydrogenolysis on platinum. Isomerisation activity at the opposite drastically decreased. These changes were less pronounced in the case of the pillared saponites. Zr-pillared saponite with low tetrahedral charge showed an intermediate behaviour. © 1999 Academic Press

Key Words: **Al-pillared clays; Zr-pillared clays; Al,Zr-pillared clays; pillared montmorillonites; pillared saponites; hydroconversion of heptane.**

INTRODUCTION

Clays pillared with Al–polyhydroxy cations have been amply investigated and the influence of the preparation parameters on the textural, structural, and acidic properties is well documented. $ZrO_x \cdot H_2O$ pillar precursors have also been introduced in the interlamellar space of smectites. The chemistry of zirconium in aqueous medium and the factors ruling the species in equilibrium appear somewhat more constraining than for aluminum. The effects of pH, concentration, and aging time and temperature on the degree of polymerisation of the hydroxy-zirconium species in $ZrOCl_2$ solutions have been discussed by Jones (1), Bartley (2), and Figueras (3). Most Zr-pillared clays described in the literature were prepared, indeed, from diluted zirconium oxychloride solutions, with changes of the aging conditions of both pillaring solutions and final suspensions, essentially room (4), medium (60°C) (5), and reflux temperature (6–8).

Ohtsuka *et al.* (9) obtained Zr-pillared materials with gallery heights of 7, 12, and 14 Å depending on the degree of polymerisation of the zirconium species. The 7 Å type was obtained from solutions aged at room temperature, where the tetrameric form is the dominant species. Addition of NaOH (10) and cerium (11) to the pillaring solution was found to improve the thermal stability of Zr-pillared clays.

Enhanced acid contents and/or strength in Zr-pillared clays could be achieved, e.g., by addition of a lanthanide (11), treatment with ammonium bifluoride (12), or introduction of sulfate (13) with, for this last approach, a detrimental effect on the spacings and specific surface area. Pillaring of tetrasilicic fluromica with zirconyl acetate solutions provided materials with improved textural characteristics, hydrothermal stability, and enhanced acidity for the sulfated form (14). As for the other pillared clays, the catalytic activity of Zr-pillared smectites has been investigated in view of potential applications.

In this study, the textural, structural, and acidic properties of Zr- and mixed Al,Zr-pillared clays have been compared with those of Al-pillared analogues. Hydroisomerisation of heptane on platinum-loaded samples was used to investigate the influence of the nature of the pillars and type of clay on the catalytic properties.

EXPERIMENTAL

Materials

Different smectites were used in this study: two montmorillonites, one from Chile (Minclay W-140, Deltamat-Paquet, Belgium) and the other from Spain (Serrata Blanca); a magnesian smectite, probably a saponite-type with few tetrahedral Al for Si substitutions (Volclay,

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TABLE 1

Chemical Compositions of the Starting Clays (wt%)

Clay	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	CaO	Na_2O	K_2O	MnO
M1	73.94	14.55	1.92	3.29	0.33	0.22	1.68	0.11	0.026
M2	63.31	19.95	3.43	4.26	0.13	0.24	3.00	0.58	0.026
H	48.13	2.46	0.99	20.56	0.20	2.73	3.13	0.31	—
S2	48.87	5.03	1.52	24.09	0.20	1.80	0.19	1.00	—
S3	55.29	5.40	1.43	25.23	0.15	0.41	0.75	0.30	0.026

American Colloid Co.); and two saponites, Esmectita de Yunclillos (EY) and Vicalvaro (V), provided by Tolsa S.A., Madrid. Montmorillonites (dioctahedral clays) have structural substitutions in the octahedral layer, while in saponites (trioctahedral clays) substitutions occur mainly in the tetrahedral layer. A minor amount of cristobalite was identified by XRD in the Chilean montmorillonite and both montmorillonites contained traces of nonclay contaminants. The saponites contained nonnegligible quantities of sepiolite, 10–20% in Vicalvaro, and about 10% in Yunclillos (15). A small amount of calcite was detected in the Volclay sample. The different clays will be referred to hereafter as M1 (Chilean mont.), M2 (Serrata Blanca), H (Volclay sample), S2 (Vicalvaro saponite), and S3 (Yunclillos saponite).

The $<2\ \mu$m fractions separated by the usual sedimentation in Atterberg cylinders were used for the pillaring experiments. The chemical compositions established by inductively coupled plasma emission spectroscopy are given in Table 1. The high silica content of M1 is, of course, related to the presence of cristobalite. For the H clay, assuming that CaO is totally associated to calcite, this phase would represent at most 5 wt%. The presence of Al in this latter clay (only Al in fourfold coordination was shown by ^{27}Al MAS-NMR spectroscopy) indicated a saponite-type smectite, with low tetrahedral charge.

Pillaring Procedures

Zr-pillared clays were prepared from zirconyl chloride or zirconyl nitrate solutions. In a first set of preparations, 10 mequiv. Zr g^{-1} clay of 0.1 *M* solution of $ZrOCl_2$ aged at room temperature for 24 h were added dropwise to 2 wt% suspensions of the different clays, pH being adjusted to 1.9. The final suspensions were stirred for 24 h at room temperature. Suspensions of montmorillonite M1 containing 10 and 20 mequiv. Zr g^{-1} clay were aged for 8 days. One of these samples was thereafter refluxed for 3 h. The clays were subsequently washed by dialysis or centrifugation, renewing the water until the conductivity of the wash was reduced to the initial value, and the solids were oven-dried. This method is essentially similar to that of Yamanaka and Brindley (4), with some difference in the aging time and washing method.

In a different approach, 0.1 *M* $ZrOCl_2$ solution was previously refluxed at 95°C for 5 and 24 h. The solution refluxed for 5 h remained limpid, but it turned turbid after refluxing for 24 h. The solutions were added dropwise to 2 wt% suspensions of M1 montmorillonite at a rate of 10 mequiv. Zr g^{-1} clay. The final suspensions were stirred for 24 h at room temperature. One sample was further aged for 8 days. In another set of preparations, the final suspension (containing 10 mequiv. g^{-1} of clay, 0.1 *M* $ZrOCl_2$ solution refluxed for 5 h) was refluxed for 1, 5, and 24 h. The pillared clays were washed by dialysis and oven-dried. The refluxing procedure was previously employed by Burch and Warburton (7) and more recently by Cool and Vansant (8).

Pillaring was also achieved using 0.1 *M* solution of zirconyl nitrate aged at room temperature for 24 h and added to 2 wt% suspensions of the different clays with a supply of 10 and 20 mequiv. g^{-1} clay. The clay concentration of the final suspensions was either 0.5 or 1 wt%. Washing and drying were done as above.

Mixed Al–Zr pillared clays were prepared from a commercial solution (pH 4.5) containing 15% Zr and 85% Al (REZAL from Reheis Chem. Co., Ireland), by dropwise addition of a sufficient volume of the diluted solution in order to bring 20 mequiv. (17 mequiv. Al, 3 mequiv. Zr) per gram of clay. The final suspensions were stirred for 24 h at room temperature, washing and drying of the solid being as above.

For comparison purposes, Al-pillared clays were prepared with solutions of Al–chlorhydrol (Reheis), using the conditions reported in a previous study (16). After standing for 2 h at 60°C, adequate volumes of the pillaring solution (0.1 *M* in Al) were slowly added to 2 wt% clay suspensions at a rate of 20 mequiv. Al g^{-1} clay. The final suspensions were maintained at 80°C for 2 h followed by an aging period of 16 h at room temperature, with stirring during the exchange process. The pillared clays were oven-dried after removal of the excess salts by dialysis.

Characterisation

X-ray diffraction (XRD) patterns of samples dried at room temperature and after calcination for 2 h at increasing temperatures (separate preparations, oriented films) were recorded with a Philips PW01150/90 instrument provided with copper anticathode and Ni filter.

The initial and residual cation exchange capacities (CECs) were determined over ammonium-exchanged samples (with 2 *M* ammonium acetate solution, room temperature). The ammonium contents were determined by the micro-Kjeldahl method. The pillared clays were heated for 2 h at 500°C prior to ammonium exchange.

The textural characteristics were determined from the nitrogen sorption isotherms measured at liquid nitrogen temperature with an ASAP 2000 sorptometer (Micromeritics) on samples outgassed *in situ* for 6–8 h at 200°C, preceded or not by a calcination step for 2 h at 500°C. The micropore volumes and external surface areas of the pillared clays were established following a method recently proposed (17), while for the starting collapsed clays, the "*t*-plot" method of de Boer and Broekhoff was adopted (18).

The acid contents were established from the amounts of ammonia adsorbed at 250°C (pulse method), followed by temperature-programmed desorption (TPD) between 250 and 400°C with a plateau of 16 h at 400°C. Prior to ammonia adsorption, the samples were heated for 2 h at 400°C in flowing helium. The procedure has been detailed elsewhere (19).

Catalytic Evaluation: Hydroconversion of Heptane

Hydroisomerisation–hydrocracking of heptane, a reaction requiring both protonic and metal functions, was used as test reaction. The clay catalysts were previously calcined at 500°C and impregnated with a 5×10^{-3} *M* solution of tetrammineplatinum(II) chloride. The metal loading was 1 wt%, unless otherwise specified. The reaction was carried out in a U-shaped fixed bed glass microreactor operated at atmospheric pressure. The catalyst (typically 0.2 g) was sandwiched between pure fine-grained quartz layers and heated for 2 h at 400°C at a rate of 7°C/min in flowing dry air. After purging the reactor with helium, the metal reduction was achieved at 400°C in flowing hydrogen for 2 h. At the end of the activation treatment, the reactor was cooled at 150°C. Heptane vapour was generated by flowing hydrogen through a glass saturator thermostated at 27°C (partial pressure: 56.9 Torr; 7.584×10^3 N m^{-2}). The total flow (hydrogen–heptane) was 10 ml min^{-1}. These conditions defined a WHSV of 0.9 g heptane g catalyst^{-1} h^{-1}. The reaction was performed in temperature-programmed mode between 150 and 400°C using a ramp of 1.5°C min^{-1}. On-line gas phase analysis was carried out in an H.P. 5880 gas chromatograph fitted with FID and CPSil-5 capillary column (Chrompack). Data were treated as detailed in (19).

RESULTS

Characterisation of the Starting Clays

The *d* spacings (001 reflections) of the Na clays dried at room temperature and after heating at 200 and 500°C are given in Table 2. One clay (H) collapsed at 10.3 Å after heating at 200°C. All the samples calcined at 500°C showed interlamellar distances characterizing fully collapsed monoionic clays.

The initial CECs of the ammonium-exchanged clays (<2 μm fractions) (Table 2) were above 0.80 mequiv. g^{-1} for the two montmorillonites (M1 and M2) and the low-charge saponite (H), and substantially lower for the two other saponites (S2 and S3). As shown previously, these saponites also exhibited a poor stacking order compared with the montmorillonites (16).

TABLE 2

Initial CEC and *d* Spacings of the Starting Clays after Heating at Different Temperatures

Clay	CEC (mequiv. g^{-1})	*d* Spacings (Å) Room temperature	200°C	500°C
M1	0.81	12.6	11.6	9.6
M2	1.10	12.8	12.3	10.2
H	1.03	12.8	10.3	9.6
S2	0.56	14.2	12.4	10.0
S3	0.61	14.7	12.8	10.2

The textural data obtained from the N_2 adsorption–desorption isotherms over samples submitted to the pretreatment conditions indicated under Experimental are given in Table 3. The saponites S2 and S3 exhibited higher BET surface areas and micropore volumes, even after a calcination at 500°C. As mentioned above, these saponites contained sepiolite. Considering a surface area of about 320 m^2 g^{-1} for sepiolite outgassed at 200°C (20), the contribution of this fraction to the S_{BET} of sample S2 (assuming 20 wt% sepiolite) would amount to 64 m^2 g^{-1}, and 32 m^2 g^{-1} for S3 (with 10 wt% sepiolite). After calcination at 500°C, these contributions would be reduced to 25 and 12.5 m^2 g^{-1} for, respectively, S2 and S3. Assuming that fully collapsed clays (interlayer distance of 9.8 Å) develop surface areas of around 60–70 m^2 g^{-1}, the values found for the two saponites can only partly be accounted for by the respective sepiolite contents. In the case of the H clay, at the opposite, an abnormally low surface area (isotherms repeated in triplicate)

TABLE 3

Textural Characteristics of the Starting Clays

Clay	S_{BET} (m^2 g^{-1})	S_{ext} (m^2 g^{-1})	V_μ (cm^3 g^{-1})
M1	82	72	0.005
M1[a]	86	78	0.004
M2	97	68	0.014
M2[a]	83	53	0.014
H	4	3	0.001
H[a]	36	18	0.009
S2	185	74	0.058
S2[a]	158	117	0.020
S3	147	85	0.030
S3[a]	138	97	0.020

[a] Precalcined at 500°C.

TABLE 4

X-Ray Diffraction Data of Al-; Al, Zr-; and Zr-Pillared Clays: Basal Spacings Observed after Calcination at Increasing Temperatures

	Basal spacings (Å)			
Clay	Room temperature	200°C	500°C	700°C
AlP-M1	21.5	18.8	18.4	18.0
AlP-M2	19.9	18.8	17.7	17.3
AlP-H	19.2	18.4	18.4	18.8
AlP-S2	20.1	18.8	18.8	18.0
AlP-S3	19.2	18.4	18.0	16.7
Al,ZrP-M1	20.1	17.9	17.0	15.8
Al,ZrP-M2	19.6	19.5	18.2	17.7
Al,ZrP-H	19.6	18.4	17.7	16.2
Al,ZrP-S2	19.8	18.4	17.0	15.5
Al,ZrP-S3	19.2	18.0	17.3	17.0
ZrP-M1	**19.2**–( )	17.0	16.5	15.1
ZrP-M2	**20.1**–( )	17.7	16.4	14.0
ZrP-H	**19.2**–10.2	17.0–9.8	16.5–( )	15.0–( )
ZrP-S2	**19.6**–12.3	(17.7)–12.8	(i.d.)–10.2	(i.d.)
ZrP-S3	**19.2**–12.1	17.0–12.1	16.4–( )	17.7–( )

Note. i.d., ill-defined reflection; ( ), shoulder.

was found, which increased after calcination at 500°C. Microporosity in this clay outgassed at 200°C was absent. The S_{BET} and $V\mu$ of the montmorillonites were in the normal range of values.

Characterisation of the Pillared Clays

X-ray diffraction data. The interlayer distances of the Al-, Al,Zr-, and Zr-pillared clays are compiled in Tables 4 and 5. The spacings observed after heating at increasing temperatures constitute one of the main criteria which assess adequate pillaring.

The Al-pillared clays (Table 4) exhibited *d* spacings in the range of values usually found for these microporous materials. The decreasing spacings (height of the pillars) after heat treatment result from the transformation of the pillar precursors to the dehydroxylated (oxide) forms. The mixed Al,Zr-pillared samples as well showed stable spacings up to 500°C. Three samples exhibited a lesser thermal stability, with interlayer distances between 15.5 and 16.2 Å after calcination at 700°C.

For the series of Zr-pillared clays (oxychloride and oxynitrate solutions), the X-ray patterns showed different features according to the pillaring method and solution. In general, two reflections were observed between 2° and 10° 2θ, indicating heterogeneous pillaring (mixture of non-pillared and pillared fractions). Pillaring with zirconium oxychloride solutions (series with 10 mequiv. g^{-1}, aged for 24 h at room temperature) provided materials with interplanar distances of about 10–12 and 19–20 Å (room temperature dried samples). The fraction with 20 Å spacings (boldface characters in Table 4) was dominant in this series. The second peak appearing in most samples as more or less distinct shoulders progressively vanished as calcination

TABLE 5

X-Ray Diffraction Data of Zr-Pillared Clays Obtained under Different Conditions: Basal Spacings Observed after Calcination at Increasing Temperatures

		Basal spacings (Å)			
Pillaring conditions	Clay	Room temperature	200°C	500°C	700°C
$ZrOCl_2$	ZrP-M1 (10-8d)	**19.4**–10.6	17.4	16.8	14.7
	ZrP-M1 (20-8d-3R)	**20.1**–10.3	18.3	16.8	15.6
	ZrP-M1 (20-8d-3R)	**20.1**–10.8	17.4–10.3	16.8	15.6
	ZrP-M1 (10-A-1d)	**20.9**–10.8	31.1–18.3	36.6–16.3	14.7
$ZrOCl_2$ reflux	ZrP-M1 (R5-8d)	21.8–**12.5**	28.5–20.9–10.8	29.3–19.4	16.3
	ZrP-M1 (R24-1d)	21.0–**13.6**	19.6–11.6	17.7–10.0	9.4
	ZrP-M1 (R24-R1)	23.2–**13.7**	(20.1)–11.5	(20.1)–10.3	i.d.
	ZrP-M1 (R5-1R)	24.5–**14.3**	22.1–11.5	20.1–10.3	16.4–9.3
	ZrP-M1 (R5-5R)	24.5–**14.7**	(21.9)–11.3	31.5–20.5–10.0	12.3–9.8
	ZrP-M1 (R5-24R)	(25.2)–**14.0**	(22.9)–11.5	28.5–10.4	i.d.
$ZrO(NO_3)_2$	ZrP-M1 (10-1%)	**20.1**–10.4	17.3	16.1	13.6
	ZrP-M1 (10-0.5%)	**19.6**–( )	17.7–( )	16.1	14.7
	ZrP-M1 (20-0.5%)	**19.2**–( )	17.0–( )	15.8	16.1
$ZrO(NO_3)_2$	ZrP-M1 (20-0.5%)	**18.8**–( )	18.0–( )	16.7	15.0
	ZrP-M2 (20-0.5%)	**19.6**–( )	17.7–( )	17.0	14.7
	ZrP-H (20-0.5%)	**20.1**–( )	18.0–( )	17.9–( )	17.7–( )
	ZrP-S2 (20-0.5%)	**17.7**–12.6	17.7–12.6	17.7–( )	i.d.
	ZrP-S3 (20-0.5%)	**17.7**–12.6	17.7–12.4	18.0 (br)	18.0 (br)

Note. i.d., ill-defined reflection; br, broad; ( ), shoulder.

temperature increased. The temperature effect on the interlayer distances and peak intensities was more pronounced for the Zr-pillared samples than for either the Al- or Al,Zr-pillared samples.

The pillaring trials with the Chilean montmorillonite (M1) with 10 and 20 mequiv. of $ZrOCl_2$ solution and aged for 8 days [M1(10-8d) and M1(20-8d)] as well as refluxing for 3 h the suspension aged for 8 days [M1(20-8d-3R)] or using acetone as a solvent [M1(10-A-1d)] (Table 5) did not lead to a significant improvement of the spacings of the calcined samples.

Pillaring with refluxed solutions (5 and 24 h) and aging the final suspension either at room temperature for 1 and 8 days, or under reflux for 1, 5, and 24 h, gave materials exhibiting as well two reflections, but different from the previous series, the most intense reflection (Table 5, series $ZrOCl_2$ reflux) corresponded to the nonpillared fraction with *d* values at around 14 Å (room temperature drying), collapsing at 10 Å after calcination. The minority fraction exhibited rather high interlayer distances, even after calcination at 500°C, but dramatic collapses and ill-defined reflections were noticed after treatment at 700°C. Only one sample, ZrP-M1(R5-8d), showed improved spacings. Thus, supplying more zirconium per gram of clay (20 instead of 10 mequiv. Zr g^{-1}) did not result in pillared materials with enhanced thermal resistance. Only a prolonged aging period appeared to be somewhat beneficial.

Using zirconium oxynitrate solutions apparently had some positive effect on the thermal stability (at 500°C) of the pillared fraction with respect to the results obtained with zirconyl chloride solutions (compare with the values in Table 4). Partial collapse occurred after calcination, with interlayer distances near 17–18 Å after heating at 500°C, and near 15 Å at 700°C. Two clays (ZrP-H and ZrP-S3) showed improved stability at 700°C. Nevertheless, as for the samples prepared with zirconyl chloride, pillaring was heterogeneous.

Textural Properties

The textural characteristics (S_{BET}; external surface area, S_{ext}; and micropore volumes, V_μ) of the Al-, Al,Zr-, and Zr-(oxychloride, 10 mequiv. g^{-1}, room temperature method) pillared clays precalcined at 500°C are given in Table 6. The large values of S_{ext} of the S2- and S3-pillared samples have been commented on elsewhere (16). In general, greater surface areas were obtained for the Al-pillared samples. For each type of clay, the micropore volume of samples calcined at 500°C decreased in the sequence: AlP → Al,ZrP → ZrP clays. The Al-pillared clays also exhibited higher *d* spacings at 500°C, and the lower values of V_μ and S_{BET} of the mixed Al–Zr and Zr-pillared clays may be related to the smaller interlayer distances noticed after calcination at 500°C, except for Al,ZrP-S2 and -S3, which had significantly lower V_μ than one would expect from their *d* spacings (at 500°C). There was a further but less marked decrease of microporosity for the series of Zr-pillared clays, probably in relation to the presence of unpillared (minority) fraction and the smaller spacings in the samples calcined at 500°C.

TABLE 6

BET Specific Surface Area (S_{BET}), External Surface Area (S_{ext}), and Micropore Volume (V_μ) of the Al-; Al, Zr-; and Zr-Pillared Clays

Clay	S_{BET} ($m^2\ g^{-1}$)	S_{ext} ($m^2\ g^{-1}$)	V_μ ($cm^3\ g^{-1}$)
AlP-M1[a]	212	62	0.071
AlP-M2[a]	304	76	0.110
AlP-H[a]	304	135	0.080
AlP-S2[a]	303	155	0.071
AlP-S3[a]	320	151	0.081
Al,ZrP-M1	269	85	0.090
Al,ZrP-M1[a]	192	96	0.046
Al,ZrP-M2	348	99	0.117
Al,ZrP-M2[a]	238	92	0.069
Al,ZrP-H	307	80	0.105
Al,ZrP-H[a]	214	68	0.071
Al,ZrP-S2	294	161	0.064
Al,ZrP-S2[a]	206	154	0.025
Al,ZrP-S3	348	120	0.114
Al,ZrP-S3[a]	239	174	0.031
ZrP-M1	198	87	0.053
ZrP-M1[a]	171	81	0.042
ZrP-M1 (10-8d)[a]	173	94	0.040
ZrP-M1 (20-8d)[a]	176	71	0.050
ZrP-M1 (20-8d-3R)[a]	184	77	0.051
ZrP-M2	275	86	0.090
ZrP-M2[a]	216	86	0.062
ZrP-H	197	51	0.069
ZrP-H[a]	165	60	0.051
ZrP-S2	279	174	0.050
ZrP-S2[a]	198	145	0.023
ZrP-S3	295	143	0.074
ZrP-S3[a]	262	175	0.042

[a] Precalcined at 500°C.

Residual Cation Exchange Capacities

The residual CEC provides an estimation on the fraction of the layer charge which is not compensated by cationic pillaring species. It has been shown in the case of Al- and Al,Zr-pillared taeniolite (a synthetic lithium-type F-hectorite) that the pillars could be protonated and deprotonated according to pH (21), hence changing the acid contents. Since the pillared clays were all exchanged with ammonium acetate solution (pH at which the amphoteric charater would play a limited role), it may be assumed that the residual CECs have a comparable value and that most of the ammonium ions occupy the accessible exchange positions. During the exchange process, some monomeric forms of the pillaring species could as well be exchanged.

TABLE 7

Residual CECs

Clay	CEC (mmol g^{-1})	(Res. CEC/init. CEC) × 100 (%)
AlP-M1	0.27	33.3
AlP-M2	0.33	30.0
AlP-H	0.28	27.3
AlP-S2	0.21	37.6
AlP-S3	0.23	37.6
Al,ZrP-M1	0.16	19.7
Al,ZrP-M2	0.18	16.4
Al,ZrP-H	0.15	14.6
Al,ZrP-S2	0.20	35.8
Al,ZrP-S3	0.22	35.9
ZrP-M1	0.27	33.3
ZrP-M1 (10-8d)	0.28	34.5
ZrP-M1 (20-8d)	0.24	29.6
ZrP-M1 (20-8d-3R)	0.22	27.1
ZrP-M2	0.31	28.2
ZrP-H	0.36	35.1
ZrP-S2	0.20	35.5
ZrP-S3	0.32	52.3

The values obtained for representative samples are compared in Table 7. The residual CECs of the Al,ZrP-M1, -M2, and -H were systematically lower than for the corresponding Al- and Zr-pillared clays for a reason which has not been clarified. Al,ZrP-S2 and -S3 exhibited values comparable to those of the Al forms (and of the Zr-form in the case of S1). AlP- and ZrP-M1 and -M2 as well had similar CECs. Except for the samples mentioned above, the fraction of exchange positions not occupied by pillar species was around 30%.

Acid Content

The acid contents established by isothermal adsorption of ammonia at 250°C (IA) and subsequent TPD are given in Table 8. For the reasons discussed elsewhere (19) for Al-pillared clays, at this temperature ammonia principally interacts with the Brønsted acid sites and therefore the amounts adsorbed (IA) or desorbed (TPD) provide a reasonable estimation of the proton contents. Except for a few samples, the agreement between the two sets of values was acceptable. Regardless of the pillar nature, the pillared saponites (S2 and S3) exhibited higher acid contents than the pillared montmorillonites. These differences have been accounted for in the case of the Al-pillared clays in recent articles (16, 19, 22). The acid contents (IA values) found for the saponites S2 and S3 were similar to the residual CECs (Table 7), whereas noticeable differences were obtained for the other clays. For each type of clay, the nature of the pillars had a limited effect on the acid contents.

Catalytic properties. The variation of heptane conversion, of the yields of C7 isomers, and of the cracked products (expressed in mole%) vs reaction temperature are shown in Figs. 1 to 5, each figure comparing for a given clay the effect of the pillar species on the catalytic properties. For the Zr-pillared clays, the catalytic results refer to the series of samples prepared with zirconyl chloride solutions (10 mequiv. g^{-1}, aged at room temperature for 1 day). The Zr-pillared clays prepared with zirconyl nitrate solutions did not show significant differences compared with the series obtained with zirconyl chloride and therefore have not been included.

Under the temperature-programmed conditions used for the catalytic tests, together with its influence on the conversion, temperature has a more or less pronounced negative effect on the acidity of the catalysts (migration of protons to the octahedral layers, particularly for the pillared montmorillonites, and deactivation due to coke formation), and this effect will be increasingly more important as temperature increases. Therefore, beyond a certain temperature threshold (depending on clay type and pillar nature), the conversions will in fact represent the resultant of these opposite influences. For the reasons given under Discussion, the acid sites of pillared montmorillonites are more sensitive to temperature than in pillared saponites. An illustration is shown in some curves of Figs. 1–3 where conversion keeps low figures (total conversion is not reached) and even decreases above a certain temperature. Similar observations have been made for Al-pillared montmorillonites from various origins (16).

As shown in Figs. 1–5, the nature of the pillaring species on the conversion of heptane had a more or less pronounced influence according to the type of clay. The Zr-pillared montmorillonites were substantially more active

TABLE 8

Amounts of Ammonia Adsorbed at 250°C (IA) and Desorbed under Temperature-Programmed Conditions (TPD)

Clay	IA (mmol g^{-1})	TPD (mmol g^{-1})
AlP-M1	0.16	0.14
AlP-M2	0.14	0.14
AlP-H	0.14	0.10
AlP-S2	0.23	0.22
AlP-S3	0.24	0.24
Al,ZrP-M1	0.15	0.12
Al,ZrP-M2	0.13	0.13
Al,ZrP-H	0.14	0.13
Al,ZrP-S2	0.19	0.16
Al,ZrP-S3	0.20	0.20
ZrP-M1	0.15	0.13
ZrP-M2	0.15	0.15
ZrP-H	0.14	0.13
ZrP-S2	0.21	0.19
ZrP-S3	0.26	0.23

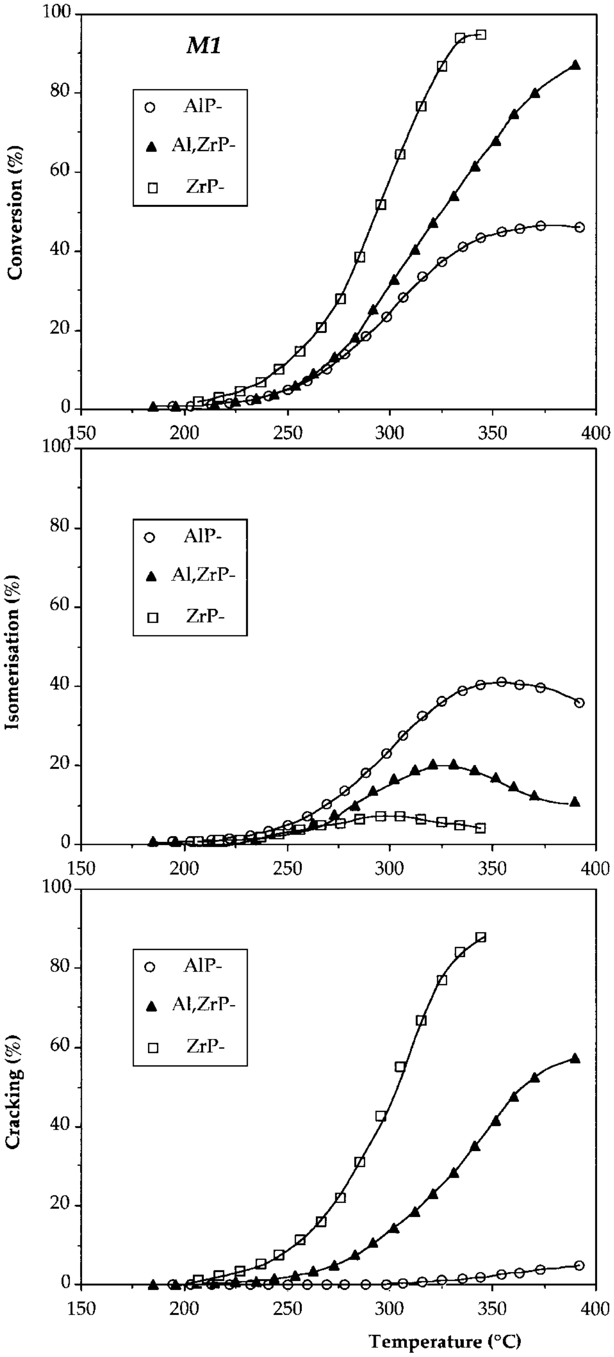

FIG. 1. Variation of total conversion (top), of the yield of C7 isomers (middle), and of the cracked products (bottom) vs reaction temperature over pillared M1 montmorillonites.

than their Al-pillared forms (Figs. 1 and 2). Enhanced activities were also observed for the mixed Zr,Al-pillared montmorillonites. The pillared-H samples (Fig. 3) exhibited similar trends, but the improvement was less important. For the two series of pillared S2 and S3 saponites (Figs. 4 and 5), the conversion curves were only slightly affected by the nature of the pillars compared with the other clays, except above 300°C. For both ZrP-S2 and ZrP-S3, total conversion was achieved below 350°C.

Considering the reaction products, the main feature was the lower yields of C7 isomers (central curves in Figs. 1 to 5) produced over the Zr-pillared clays, independent of the

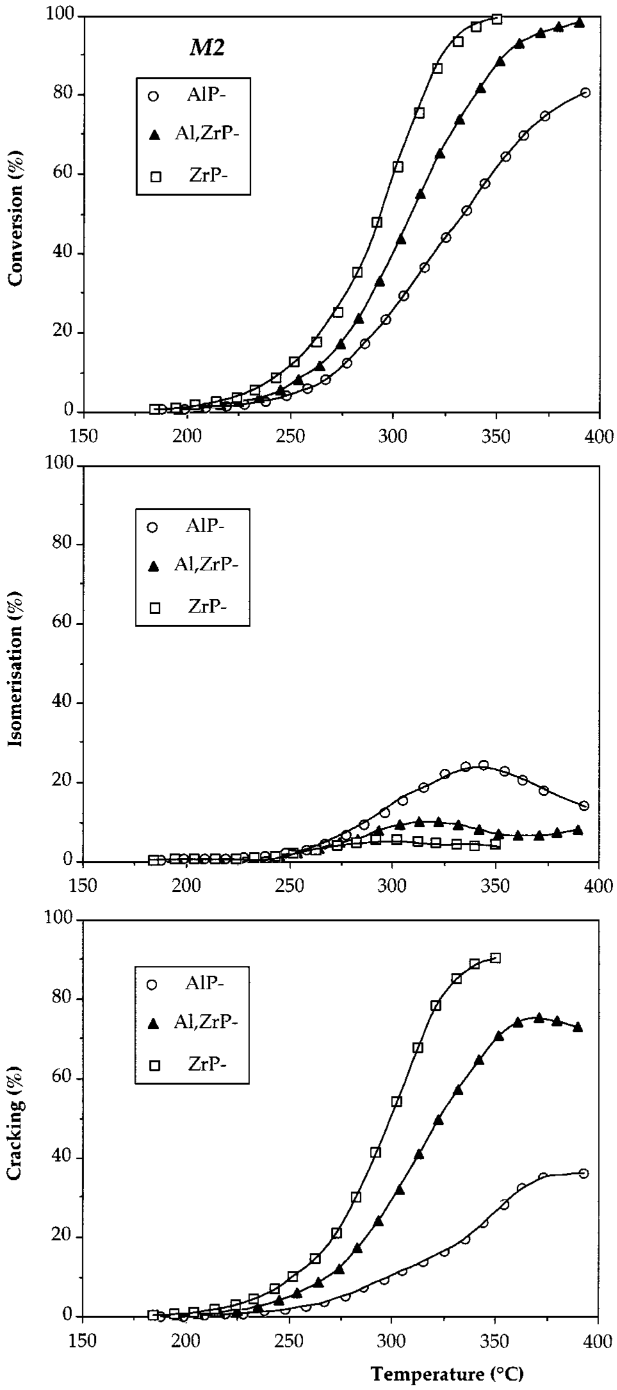

FIG. 2. Variation of total conversion (top), of the yield of C7 isomers (middle), and of the cracked products (bottom) vs reaction temperature over pillared M2 montmorillonites.

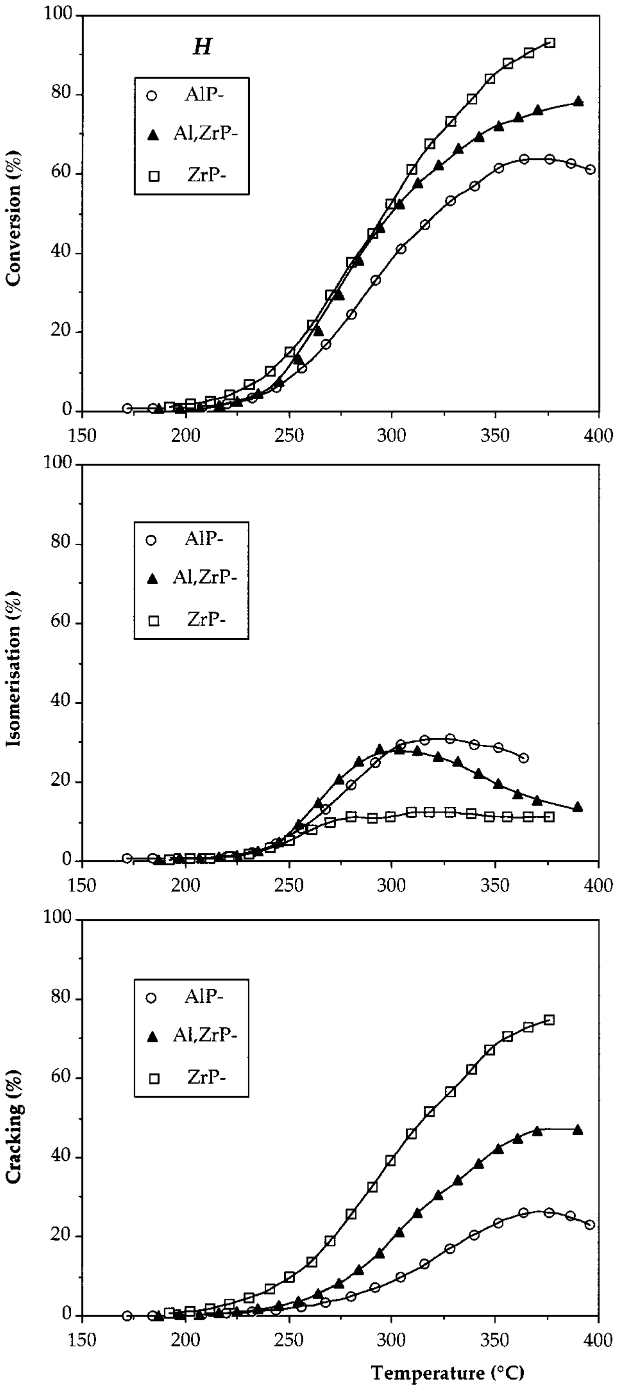

FIG. 3. Variation of total conversion (top), of the yield of C7 isomers (middle), and of the cracked products (bottom) vs reaction temperature over pillared H clays.

type of clay, compared to their Al analogues. The changes were relatively more pronounced for the pillared montmorillonites than for the pillared saponites. Intermediate results were obtained on the mixed Zr,Al-pillared samples. At the opposite, all the Zr-pillared clays showed increased cracking activities (bottom curves in Figs. 1 to 5), this increase being more spectacular for ZrP-M1 and -M2 than for the ZrP saponites.

In the course of this study, heptane tests were run again on the same samples which had been stored for a period of 2 years in closed recipients. The Zr samples had lost their catalytic activity. XRD controls showed completely

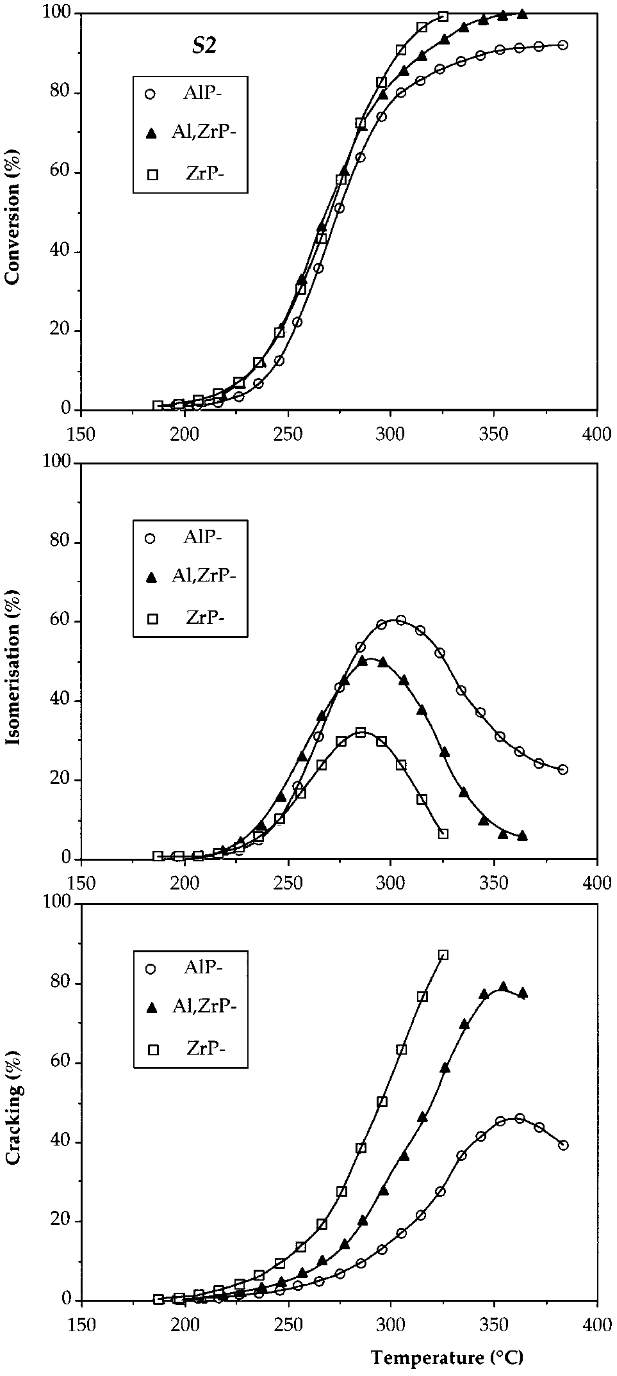

FIG. 4. Variation of total conversion (top), of the yield of C7 isomers (middle), and of the cracked products (bottom) vs reaction temperature over pillared S2 saponites.

silent patterns. A loss of activity was also found for the Al-pillared samples, but it was by far much less dramatic. For those samples, the intensity of the 001 reflection was somewhat reduced and peak broadening was noticed. New samples were pillared with $ZrOCl_2$ solutions and tested under the same experimental conditions. The catalytic results are indicated in Table 9 (samples marked with a superscript "*a*"). Comparable data were obtained, thus establishing the reproducibility of the preparation method.

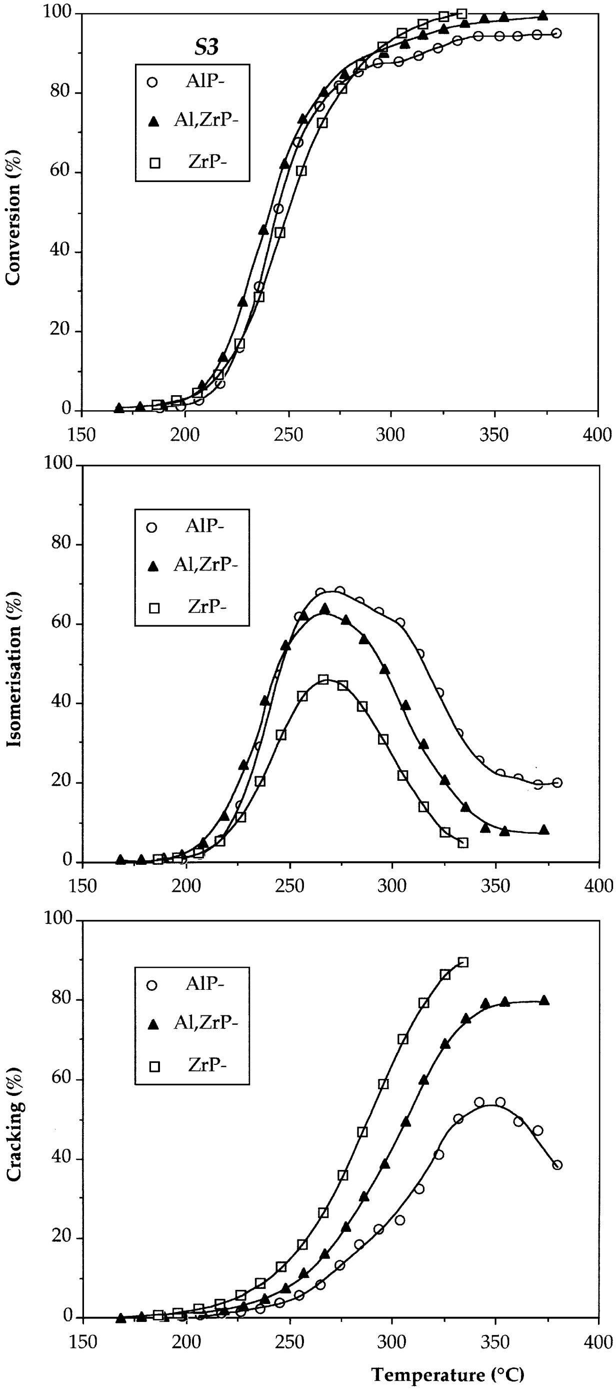

FIG. 5. Variation of total conversion (top), of the yield of C7 isomers (middle), and of the cracked products (bottom) vs reaction temperature over pillared S3 saponites.

TABLE 9

Results Obtained at 20% Conversion of Heptane: Yields of Isomers (Y_{iso}, %), Yields of Cracked Products (Y_{cr}, %), and Selectivities to C7 Isomers (%)

Sample	*T* (°C)	Y_{iso} (%)	Y_{cr} (%)	Sel. (%)
AlP-M1	291	19.5	0.3	97.5
AlP-M2	290	10.5	8.5	52.5
AlP-H	273	15.5	4.5	77.5
AlP-S2	253	16.5	3.5	85.5
AlP-S3	229	17.5	2.5	87.5
AlP-S3[a]	224	16.1	5.0	80.5
Al,ZrP-M1	285	10.4	8.6	52.0
Al,ZrP-M2	278	5.0	14.5	25.0
Al,ZrP-H	263	14.0	5.8	70.0
Al,ZrP-S2	246	14.5	5.5	72.5
Al,ZrP-S3	223	17.0	3.0	85.0
ZrP-M1	265	4.5	15.5	22.5
ZrP-M1[a]	262	5.3	14.7	26.5
ZrP-M2	267	3.2	16.8	16.0
ZrP-H	258	7.0	13.0	35.5
ZrP-S2	246	10.0	9.8	50.0
ZrP-S3	229	13.0	7.0	65.0
ZrP-S3[a]	226	12.5	7.5	62.5

[a] Duplicate on new preparation.

DISCUSSION

Al-pillared clays with heat-resistant basal spacings of 17–18 Å, surface areas in excess of 200 $m^2\ g^{-1}$, and micropore volumes above 0.05 $cm^3\ g^{-1}$ are easily obtained with base-hydrolyzed Al solutions or commercial Al–chlorhydrol solutions. Pillaring with an element other than aluminum needs to adapt the pillaring procedure according to the chemical specificities of the element, in particular to its hydrolytic behaviour. Zirconium is one such case. From a literature survey, it appears that most of the pillaring methods using zirconyl chloride solutions have not reached the same level of reliability and reproducibility as those currently employed for the preparation of Al-pillared smectites, perhaps because Zr pillaring has been much less investigated than Al pillaring, and perhaps also because zirconyl chloride may not be the most favorable compound to start with, as the pillaring solution requires low pHs (1.9) to avoid the formation of colloids or precipitation. At this pH, the clay structure and the exchange process may be perturbed, especially when pillaring is performed in refluxing conditions and/or when long contact periods are employed, due to factors inherent in the chemical stability of the clay in acidic medium, which differs according to its dioctahedral or trioctahedral character.

The changes occurring upon aging zirconyl chloride solutions as well as the drastic effect of pH and temperature on the hydrolysis rate have been addressed by several authors. According to pH, no fewer than five different species with various complexity have been shown by Raman spectroscopy in diluted zirconyl chloride solutions (23). Partial or unsuited pillaring shown by the presence of clay fractions with different interlayer spacings in calcined samples has been observed by several authors (e.g., (7, 24, 25)). Burch and Warburton (7) obtained pillared clays with high spacings from refluxed solutions in which the formation of larger polymerised cationic species is favored. Pillaring with such solutions, however, introduces diffusional limitations, the importance of which was underlined by, e.g., Figueras *et al.* (11). For Katoh *et al.* (26), aging $ZrOCl_2$ clay suspension under refluxing conditions had a "fatal" importance on the specific surface area and *d* spacing.

The results obtained in this study are thus consistent with those of the cited authors. Indeed, the minority pillared fraction obtained with refluxed solutions exhibited rather high spacings stable up to 500°C, the main clay fraction with unstable spacings of 13–14 Å being intercalated by smaller hydrated cationic species (Table 5). This partial pillaring thus could be well accounted for by a restricted diffusion of the larger polymeric species (possibly in limited amount).

Pillaring with unrefluxed solutions gave different results, the majority fraction exhibiting spacings similar to those found in the literature. Using diluted clay suspensions (0.5 wt%) and higher amounts of Zr (20 mequiv. g^{-1}) apparently contributed to a slight improvement of the thermal stability of the pillared fraction.

The pillaring trials performed with Zr oxynitrate solutions were too fragmentary to allow one to conclude on a significant improvement of the characteristics of the pillared materials (Table 5). Johnson *et al.* (14) obtained well-pillared material from a synthetic Na–fluoromica and zirconyl acetate solutions. The fact that synthetic clays often have smaller particle sizes than their natural counterparts could perhaps contribute to these successful results (less diffusional restrictions). But, as underlined by these authors, a major advantage of zirconyl acetate probably resides in the higher pH (3.9) of the pillaring solutions and perhaps, also, in the selective uptake of the bigger Zr_{18} (and probably more abundant) polyoxocationic species. The relatively higher amounts of Zr g^{-1} clay (23 mmol g^{-1} vs 5 mmol g^{-1} in this work) and especially the effect of a postcalcination (400°C) washing step, as shown in the study referred to, are probably related to the improved characteristics (spacings, surface areas, and micropore volumes) compared with calcined but unwashed samples. However, Miehé-Brendlé *et al.* (27) obtained homogeneously pillared beidellites with 16.5 Å spacing after calcination at 500°C (18.2 Å for uncalcined samples) upon contacting a 0.1 *M* $ZrOCl_2$ solution (2.375 mmol Zr g^{-1} clay) for 15 min. The authors inferred from ZrK EXAFS results that the pillars consisted of nearly square frame Zr_4 zirconyl units standing perpendicular to the clay sheets, in both uncalcined and calcined samples. The similar spacings observed in this study for the clays pillared with zirconyl chloride solutions may indicate that such units are as well formed.

With respect to the catalytic properties, the results obtained on the different pillared materials at 20% conversion have been compiled in Table 9. The columns refer to, successively, the temperature, the yields of heptane isomers (Y_{iso}, %) and of cracked products (Y_{cr}, %), and the selectivities to the C7 isomers (Sel., %). At this conversion, cyclization products (benzene and mainly toluene) are absent, and the temperature effect on the acid sites and deactivation are still limited.

The higher activity of the Al-pillared saponites relative to the Al-pillared montmorillonites may be appreciated by the temperature required to reach 20% conversion, and has been accounted for in previous studies by the respective location of the structural substitutions in the different smectites and its impact on the nature and relative strength of the acid sites (16, 19). The changes of the reaction products with the nature of the pillars are less drastic for the S2- and S3-pillared saponites than for the montmorillonites. Of course, the selectivities to the C7 isomers vary accordingly, the losses noticed between the AlP forms and the ZrP forms amounting to 75, 36.5, 42, 32.5, and 22.5% for M1, M2, H, S2, and S3 clays, respectively.

The substantial increase of the cracking activity of the Zr-pillared clays relative to the Al analogues (particularly for the montmorillonites) can hardly be accounted for by differences of their respective acid contents, as it is inferred from the ammonia adsorption–desorption measurements (Table 6), but by the nature of the pillars (Zr, Al). Indeed, the isomerisation conversions of both Zr-pillared montmorillonites and saponites are significantly depressed.

On the other hand, the information available in the literature does not provide a clear indication of the strength of the Brønsted acid sites of Zr-pillared montmorillonites relative to Al-pillared montmorillonites. Indeed, IR spectroscopic studies of pyridine adsorbed on Zr-pillared montmorillonites (and hectorite, another clay with octahedral substitutions) showed the presence of both Lewis and Brønsted acidities, Lewis acidity being dominant (12, 28), as in the case of their Al-pillared analogues (29–33). Weak acidity (mainly Lewis) was concluded by Zhonhui and Guida on ZrP materials (34). Johnson *et al.* (14) observed by ammonia TPD measurement that even for a well-Zr-pillared tetrasilicic fluoromica, most of the ammonia desorbed between 300 and 400°C. Several authors noticed a drastic diminution (in some cases, the total disappearence) of the pyridinium IR band at 1545 cm^{-1} upon outgassing

Al-pillared montmorillonites in the same temperature range (12, 35–38). Similar observations were reported in previous work (39).

Among possible explanations for the increased cracking activity in ZrP clays, one could be the change of balance between the metal and acid functions, hydrogenolysis on Pt becoming more important. Differences in platinum dispersion according to the type of clay and nature of the pillar can probably be excluded. Chemisorption of CO on prereduced samples gave dispersions of 31, 28, and 30% for ZrP-M1, ZrP-S3, and AlP-S3, respectively. In a separate trial on ZrP-M1 with 0.6% Pt instead of 1%, both conversion and cracking activity were reduced with, at maximum isomerisation, heptane conversion of 51% (vs 67% for 1 wt% Pt), yield of cracked products of 27% (vs 46%), and yield of C7 isomers of 22% (vs 16%), and thus with a selectivity to the isomers of 43% (vs 24%). In the absence of platinum, the catalyst was inactive. This seems to indicate that lowering the Pt content improves the balance of the functions, enhancing the isomerisation conversion. It may also be inferred that the average strength of the acid sites is weaker in ZrP clays than in the corresponding AlP clays. The imbalance between the catalytic functions is less accentuated in the ZrP saponites than in the ZrP montmorillonites for at least two reasons: (i) ZrP saponites have higher proton contents, and (ii) the average intrinsic strength of the Brønsted sites is higher and the acid sites are more stable than in Zr-pillared montmorillonites.

It has been shown, indeed, that in Al-pillared saponites (as in pillared beidellites, another clay with tetrahedral substitutions), in addition to the acid sites generated by the pillaring process, protonic sites are associated to bridging hydroxyls (Si–OH $\cdots$ Al groups) formed by proton attack of Si–O–Al bonds of the tetrahedral layers. This was shown by a new IR band in the OH stretching region (at 3595 cm^{-1}), which disappeared upon pyridine adsorption and reappeared upon removal of pyridine (19, 39, 40). Such acid sites are absent in pillared montmorillonites because the substitutions occur in the octahedral layers. In these latter clays, migration of the protons (formed at the pillaring step) to the octahedral layers with heat treatment is generally admitted (19, 38, 39, 41–44).

With respect to this, the similar CEC and NH_3 TPD values mentioned earlier for the pillared saponites and the differences observed for the pillared montmorillonites are consistent with the different nature of the acid sites in both types of clays.

Due to the different strength, stability, and content of the Brønsted sites, one may expect the out-of-balance of the catalytic functions to be more pronounced in montmorillonites than in saponites, and to be more accentuated as reaction temperature increases with, as a result, a higher contribution of hydrogenolysis on Pt particles in the former ones. The large excess of the C4 fraction over the iso-C4 for these clays also points to the hydrogenolysis route.

In addition to these observations, the textural properties (in particular the micropore volumes) also have to be considered. Indeed, as shown in Tables 6 and 9, Zr-pillared clays generally exhibit lower V_μ than the corresponding Al-pillared clays, and also lower yields of C7 isomers (higher yields of cracking products). When the two sets of values are plotted against each other, although a straight relation could not be drawn for each clay, the tendencies existed. It must be emphasized that in the case of the Zr-pillared clays, the V_μ values correspond essentially to the pillared fraction, the contribution of the unpillared fraction (or poorly pillared) to V_μ being negligible (of the order of the values given in Table 2).

The higher activity of the pillared saponites and other clays with structural substitutions in the tetrahedral layers (beidellite) compared with pillared montmorillonites has also been established in the hydroisomerisation–hydrocracking of octane (45), decane (46), and heptadecane (47), and in other reactions (48–51). In this study, an illustration is given by the conversions obtained, e.g., at 250°C, namely the same temperature at which the adsorption of ammonia was carried out and where the temperature effect on acidity should be relatively limited (all the catalysts were previously heated at 400°C at the activation step). The conversions obtained on the different types of pillared clays were in the following ranges: 5–15% for M1 and M2; 8–17% for H; 16–30% for S2; 58–72% for S3. Therefore, despite the “nonsteady” conditions under which the catalysts were evaluated, the results have a meaningful comparative value. Clearly, the Zr-pillared clays are poorer isomerisation catalysts than the Al-pillared analogues.

It may also be mentioned that in preparing Zr-pillared clays it is not known whether all the Zr left on the solids after the washing step is located in the interlamellar space, as chemical analysis does not allow us to discriminate the part which is interlayered from that at the external surface. It may thus well be that partial deposition of polymeric Zr species occurs on the external surface. At the calcination step, some form of amorphous zirconia islands could be formed and, in the presence of Pt, this “clay-supported zirconia” could be converted to an active cracking catalyst. Although this possible contribution has not been experimentally verified, it could not account for the differences observed between the two types of clays, as there is no obvious reason that it should drastically change the cracking activity of ZrP montmorillonites and have a restricted effect in the case of the ZrP saponites.

CONCLUSIONS

Pillaring of clays with zirconyl chloride and nitrate solutions gave materials consisting of a mixture of unpillared and pillared fractions, the pillared fraction exhibiting poorer thermal stability compared with Al-pillared analogues. Pillaring with refluxed $ZrOCl_2$ solutions was less efficient, whereas using mixed Al, Zr solutions had no detrimental effect on the textural characteristics or on the thermal stability of the clays. Zr-pillared clays and, to a lesser extent, mixed Al,Zr-pillared clays were poorer isomerization catalysts than the corresponding Al-pillared clays. The cracked products were formed in larger amounts on the ZrP clays and were by far dominant on the ZrP montmorillonites relative to the saponites, probably due to the enhancement of hydrogenolysis on the metal, as a consequence of a greater imbalance between metal and acid functions in the former ones (with smaller proton content, weaker and less stable acid sites). The results confirm the influence of the nature of the starting clay on the catalytic properties of their pillared forms.

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