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Catalysis Today 133–135 (2008) 223–230

CATALYSIS TODAY

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Alkylation of benzene with olefins in the presence of zirconium-pillared clays

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Abstract

Purified Brazilian montmorillonite and Wyoming clays intercalated with zirconium acetate solutions with different Zr/clay ratios were pillared and characterized by X-ray fluorescence and diffraction (XRF, XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), N_2 adsorption and temperature-programmed desorption (TPD) of NH_3. The intercalation time was followed by XRD analysis. The pillarization resulted in the displacement of the low-angle diffraction pattern, indicating structural modification of the samples. The Wyoming clay presented a significant increase of the surface area for the ratio of Zr/clay = 10 (from 29 to 217 m^2/g). The Brazilian clay, under the same pillarization conditions as the Wyoming clay, showed an increase of the surface area from 108 to 206 m^2/g. As a result of the thermogravimetric analysis, the Brazilian clay showed a smaller thermal stability than the Wyoming natural clay. The TPD of NH_3 analyses showed similar amounts of acid sites for K10 commercial acid clay, Brazilian and Wyoming-pillared clays with Zr/clay ratio of 10. The K10 commercial clay had greater activity and stability for the isomerization of 1-butene than the Brazilian and Wyoming-pillared clays. The alkylation reactions of benzene with 1-hexene, 1-octene and 1-dodecene showed greater selectivity for monoalkylated products for K10, and similar selectivities for the Brazilian and Wyoming-pillared clays, when using the olefin with longer hydrocarbon chain. As the hydrocarbon chain length was decreased, the selectivity for monoalkylated products was increased when using the Wyoming clay as compared to the Brazilian clay.

Keywords: Zr-pillared clays; K10; 1-Butene isomerization; Alkylation; 1-Hexene; 1-Octene; 1-Dodecene

1. Introduction

The search for catalysts that present high activity, low deactivation and thermal stability have motivated the study of new materials using natural clays. In some cases the clays present activity in their raw form, but it is usually necessary to perform a chemical activation step, based upon their ionic exchange capacity. Among the predominantly used natural clays, the smectites are useful for producing active materials with interesting physico-chemical properties, due to their potential for modifying the interlayer distance through the exchange of compensating cations (Na^+, Ca^{2+} and others) by hydroxonium ions (as in the case of K10 and other commercial acid clays), or cations and polyoxocations (intercalated and pillared clays).

Pillared clays are layered materials prepared by the exchange of compensating cations for oligomeric or polymeric hydroxymetals, followed by calcination. The calcination promotes the dehydration and dehydroxylation of the polycations, with the formation of metal oxides that act as pillars, maintaining the separation between the layers with the appearance of interlayer and interpillar spaces with molecular dimensions. Reviews on the subject have been published by several authors [1–4]. The literature describes the use of various cations as intercalation agents: Al, Ti, Zr, La and others. Zirconium compounds have been used to form stable pillars in smectite interlayers, resulting in an increase of the surface area, stability, acidity and shape selectivity comparable to zeolite structures [5–9]. Nickel catalysts supported on zirconium-pillared clays were tested in catalytic reforming reactions [10], while copper catalysts supported on those clays were employed for methanol dehydrogenation [11]. In addition, the alkylation of phenol with methanol using zirconium-pillared clays, by using clays doped with Ni^{2+} was studied [12].

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doi:10.1016/j.cattod.2007.12.094

The alkylation of aromatic hydrocarbons with olefins is an important industrial process for the production of ethylbenzene, cumene and linear alkylbenzenes (LABs). In a previous study, Guarino [13] indicated the importance of the zirconium cation in the intercalation of clays in order to obtain monoalkylated benzene products. However, when the results were compared to those obtained with aluminum, the catalytic performance with zirconium was lower. Furthermore, a dealumination was observed when zirconium chloride or zirconium oxychloride solutions were employed as the zirconium source. The low selectivity noticed for zirconium-intercalated clays was attributed to the microporosity, which may have hampered access of the olefin to the active sites [14].

The purpose of the present work is to prepare and characterize Brazilian and Wyoming zirconium-pillared clays, by using zirconium acetate as Zr precursor, in order to minimize dealumination of the clay structure. In addition, the work also intends to compare the properties of the active sites to the catalytic performance of these materials for the alkylation of benzene with olefins of different chain lengths, in order to evaluate the effect of microporosity on the activity and selectivity.

2. Experimental

2.1. Preparation

Two sodium montmorillonites were used: the Brazilian bentonite from Campina Grande, Paraíba (named F), with a cationic exchange capacity (CTC) of 106 mequiv./100 g of clay; and a clay from Wyoming (named W), USA (CTC = 76 mequiv./100 g and 4.3% Fe_2O_3). The Brazilian clay was fractionated by sedimentation (<2 μm), purified (named FAP) for the elimination of organic matter, and carbonates, and also for the reduction of no structural iron content, which decreased from 14.2 to 12.7% Fe_2O_3. The aqueous suspensions with 1% solid content were treated with a solution of zirconium acetate (0.1 mol L^{-1}) at 298 K, where the Zr/clay ratio was varied: 1, 5 and 10 mmols of zirconium per gram of clay. The intercalation time was studied, for the Zr/clay ratio of 10, from 2 h to 6 days. After the intercalation period, the samples were dried at 333 K and pillared at 773 K for 2 h. The K10 commercial acid clay was used as a reference.

2.2. Characterization

The chemical analyses were determined by X-ray fluorescence (XRF) using a Rigaku RIX 3100 equipment.

The X-ray diffraction (XRD) was used to follow the $d_{0\,0\,1}$ basal spacing after intercalation and pillarization. The analyses were performed on a Rigaku equipment, DMax and Miniflex (fix gap) models, equipped with a copper tube. The X-ray slides were prepared by oriented slide and powder methods. The oriented slide method is recommended when one intends to obtain rising values of the $d_{0\,0\,1}$ main peak and $d_{0\,0\,2}$ and $d_{0\,0\,3}$ secondary peaks, and consists of preparing a varnish of the suspension in the slide. The powder method is the most traditional used for the X-ray diffraction of solid samples, by which the material is macerated in a grail and dispersed on a glass slide with the proper furrow.

The decomposition of the Zr polycation precursor inside the interlayer space of the clays and the thermal stability of the F and W raw samples were analyzed by TGA/DTG methods using a Rigaku Thermal Analysis Station TAS100 equipment. The samples were heated from 298 to 900 K (rate 10 K/min) under a 17% O_2/N_2 (60 cm^3/min) mixture flow. A sample of γ-Al_2O_3 was used as reference.

The textural characterization was performed by an accelerated surface Area and porosity (ASAP) equipment from Micromeritcs (model 2000) for the determination of surface area (BET), microporous and the total porous volume. The samples were pre-treated in situ under vacuum at 373 K for 24 h. After the vacuum treatment the analysis was performed through adsorption and desorption isotherms of N_2 at 77 K.

X-ray photoelectron spectroscopy (XPS) of the Zr-pillared clays was performed with a PHI (model 1257) spectrometer using Al Kα (1486.6 eV). The pressure in the analysis chamber was kept at 10^{-9} Torr. A hemispheric analyzer PHI model 10-360 was used to select the energy of the electrons (46.95 eV). The binding energies of O 1s, Al 2p, Si 2p and Zr 3d were referred to the C 1s peak, established at 284.6 eV. The XPS atomic ratios (Zr/Si + Al) were calculated by using Zr 3d, Si 2p and Al 2p peak areas considering the sensitivity factors.

The NH_3 desorption analyses were performed with a Micromeritcs equipment (model 2900), connected to a mass spectrometer with a Balzers quadrupole. The procedure consisted of drying the sample under helium at 453 K for 1 h. The NH_3 adsorption was performed in a flow of 4% NH_3/He at 423 K followed by He flow at the same temperature for 30 min. The NH_3 desorption was performed by heating the sample to 873 K (12 K/min) and following the mass signal of NH_3 (m/e) = 15 until complete desorption.

2.3. Catalytic tests

The pillared clays and the commercial acid were tested in the isomerization of 1-butene and also in the alkylation of benzene with 1-hexene, 1-octene and 1-dodecene. The experimental conditions of the reactions were adjusted to eliminate diffusional effects.

The isomerization of 1-butene was performed at 573 K, at atmospheric pressure, with a pre-treatment of 100 mg of catalyst at 623 K for 2 h under a flow of N_2. A mixture of 5.2% 1-butene/N_2 with a spatial velocity of 0.08 h^{-1} was used. The activity and selectivity were evaluated for time of stream of reactant up to 20 h. The products were analyzed in line by an INTRALAB gas chromatograph (model 3300) equipped with a flame ionization detector and a capillary column of Al_2O_3/KCl (60 m length, 0.32 mm diameter).

The benzene alkylations with 1-hexene, 1-octene and 1-dodecene were performed in a glass batch-slurry reactor at 353 K, at atmosphere pressure, with magnetic stirring for a reaction time of 6 h. The reactions used 100 mg of catalyst previously dried for 22 h at 353 K and a mixture of 10 mL of

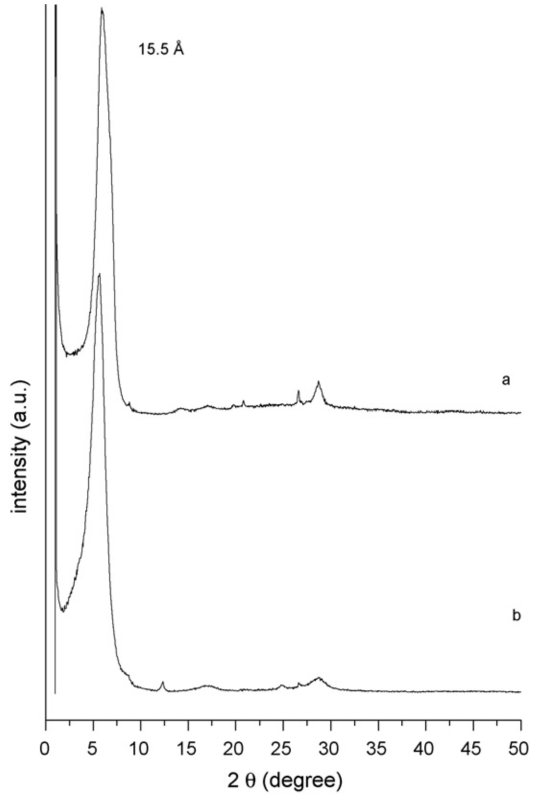

Fig. 1. XRD patterns (oriented slide) of the natural clays: (a) Wyoming and (b) purified Brazilian.

benzene and olefin with a molar ratio of benzene/olefin = 8. Samples were analyzed on a Varian gas chromatograph (model 3350) equipped with a flame ionization detector and an SE-54 column (30 m length, 0.20 mm internal diameter).

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns obtained for the Wyoming raw clay and also for the Brazilian clay after the purification procedure. Both diffractograms are very similar, which suggests that the purification procedure did not change the structure of the Brazilian clay. The values obtained for the $d_{0\,0\,1}$ (15 Å) are in accord with the literature: Singh et al. [15] and Carvalho et al. [16] observed this diffraction line at 15.3 and 15.0 Å, respectively, whereas Agashe et al. [17] obtained this line at 13 Å.

Brazilian and Wyoming clays were intercalated at different time lapses (2, 24, and 48 h, 4 and 6 days) by using in situ XRD with the oriented slide method, in order to estimate the intercalation performance. The Wyoming clay presented the maximum intensity for 4 and 6 intercalation days as shown in Fig. 2. Two peaks were observed at low diffraction angles at all the intercalation times. The first one is related to the $d_{0\,0\,1}$ from the intercalated clay at 23.2 Å, and the second at 12.4 Å that could be due to non-intercalated clay or the $d_{0\,0\,2}$ from the intercalated clay [18]. The diffractograms obtained for the Wyoming-intercalated clay revealed a good structural organization of these materials and the values for $d_{0\,0\,1}$ are in accord with the literature data for zirconium-intercalated clays [14,15,17]. The Brazilian clay presented maximum intensity of the peaks at low diffraction angles after 24 and 48 h as shown in Fig. 2. The shoulder next to the line at 23 Å refers to the $d_{0\,0\,1}$ of the intercalated clay. The low resolution of the diffractograms for the Brazilian-intercalated clay is due to the structural change as a result of the intercalation process.

The pillarization of the Wyoming clay samples generated diffractograms where the displacement at low diffraction angles and the shoulder at 19.6 Å were greatest after 4 and 6 days (Fig. 3). The pillarization process resulted in structural change and permitted the visualization of a shoulder at 19.6 Å, consistent with the $d_{0\,0\,1}$ main reflection. The $d_{0\,0\,1}$ value was close to that obtained by Singh et al. [15] for the zirconium-pillared clay.

The pillarization of the Brazilian clay samples generated diffractograms with displacement at low diffraction angles, that was greatest after 24 and 48 h (Fig. 3). Brazilian and Wyoming-pillared clays presented a low intensity diffraction at 10 Å, which corresponds to the collapsed clay. The low intensity observed for this peak suggests that most of the samples were intercalated. The low intensity of the diffraction at 10 Å indicates that the peak at 12.4 Å, observed in Fig. 2, is not due to the non-intercalated fraction of clay. Further studies are in

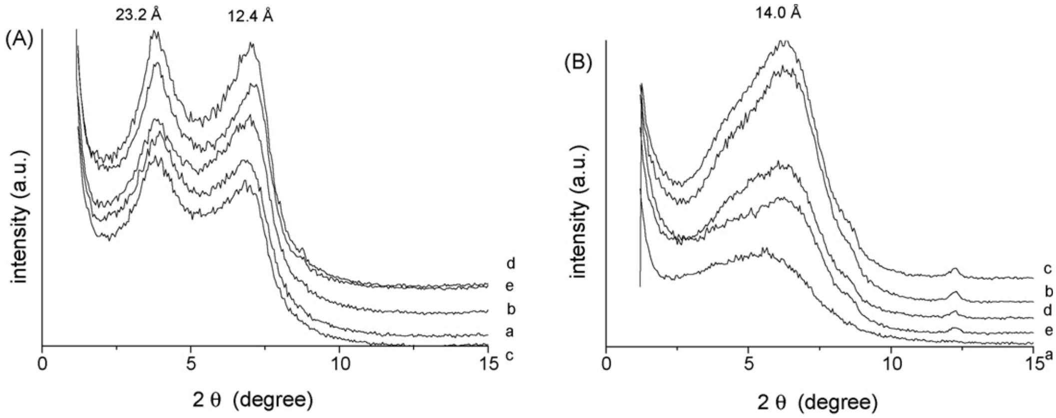

Fig. 2. XRD patterns (oriented slide) of the Wyoming (A)- and Brazilian (B)-intercalated clays for different intercalation times: (a) 2 h, (b) 24 h, (c) 48 h, (d) 4 days, and (e) 6 days.

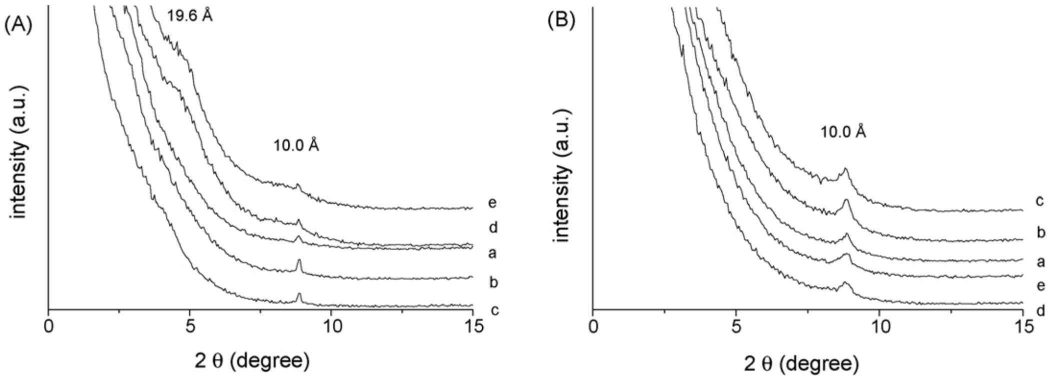

Fig. 3. XRD patterns (oriented slide) of the Wyoming (A)- and Brazilian (B)-pillared clays for different intercalation times: (a) 2 h, (b) 24 h, (c) 48 h, (d) 4 days, and (e) 6 days.

progress in order to confirm this diffraction peak as being the $d_{0\ 0\ 2}$.

The stability of the raw clays was monitored by TGA/DTG analysis and is presented in Figs. 4 and 5. For the Wyoming clay the DTG showed an exothermic peak at 950 K due to structural dehydroxylation. For the Brazilian clay this exothermic peak was observed at 759 K. This result is consistent with the lesser quantity of structural iron in the Wyoming clay compared to the Brazilian clay. An exothermic peak at around 620–640 K due to the decomposition of the zirconium acetate was observed for both samples. Wyoming and Brazilian clays after intercalation with Zr presented weight losses of 24.3 and 21.8%, respectively.

The intercalated and pillared clays were submitted to XRF and XPS analyses. One can notice that the intercalation with zirconium acetate did not promote dealumination of the clays, as indicated in Table 1. For a Zr/clay = 10 the XPS results revealed that the Zr is preferentially located inside the clay structure (Table 2). On the other hand, for the Wyoming-pillared clay with a Zr/clay = 5, the Zr is more dispersed and also preferentially located on the surface of the clay. The binding energies (BE) of Zr $3d_{5/2}$ are close to the value of 183 eV reported in the literature [17] and also to the values presented in the NIST database for ZrO_2. The Zr $3d_{5/2}$ binding energies for zirconium acetate and zirconium oxide are 182.8 and 182.2 eV, respectively. Because of this small difference it is not easy to determine which Zr species are present in the intercalated and pillared clays prepared in this work. The Brazilian Zr-pillared clay showed a reduction in the binding energy compared to the Brazilian Zr-intercalated clay. This effect is in accordance with the decomposition of zirconium acetate and formation of ZrO_2. However, for the Wyoming Zr-pillared clay the binding energy is close to the value for zirconium acetate.

Table 3 presents the results for surface area and total and microporous volumes for the acidic and natural clays (K10, FAP, W) and the pillared clays with different Zr/clay ratios. The Wyoming-pillared clay presented a significant increase of the surface area when compared to the natural sample (about seven times greater). The surface area and microporous values are maximized in the sample with a Zr/clay ratio of 10. Even though the Brazilian clay presents a discrete increase of the area compared with the natural sample (about two times greater), for the same intercalation and pillarization conditions, the surface area was similar to that obtained for the Wyoming clay.

The purified Brazilian clay (FAP) presented a ratio of microporous volume/total volume (V_{μ}/V_t) of 15%. After the

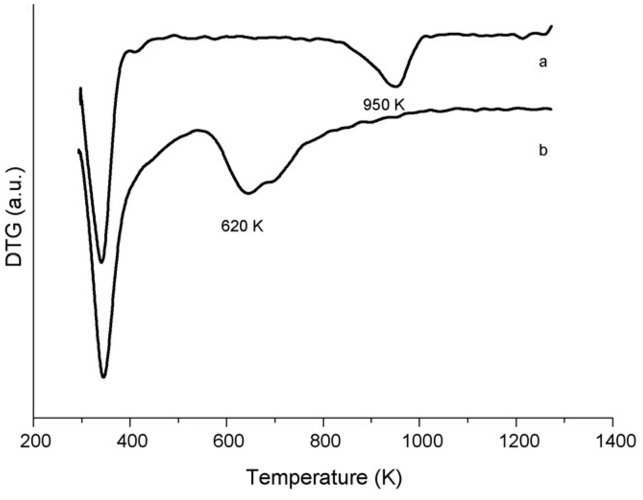

Fig. 4. DTG curves of the Wyoming clay: (a) natural and (b) intercalated with Zr/clay = 10.

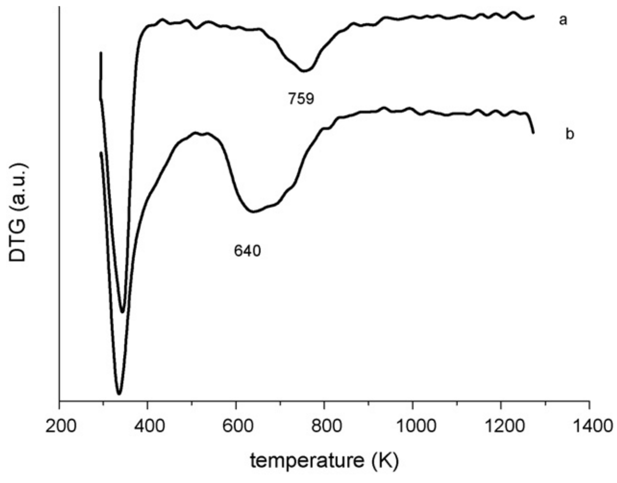

Fig. 5. DTG curves of the Brazilian clay: (a) natural and (b) intercalated with Zr/clay = 10.

Table 1
Chemical analysis (XRF) of the purified Brazilian (FAP), natural Wyoming (W) and Zr-pillared clays

Clay	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	Fe_2O_3 (%)	CaO (%)	Na_2O (%)	K_2O (%)	ZrO_2 (%)	SAR (%)
FAP	56.8	23.5	3.4	12.7	0.5	2.7	0.5	0.0	2.4
10ZrF	29.2	11.7	1.5	7.6	0.0	0.1	0.4	49.4	2.5
10ZrF[a]	57.7	23.2	3.0	15.1	0.1	0.2	0.7	0.0	2.5
W	66.3	21.7	2.6	4.3	1.1	3.2	0.5	0.0	3.1
10ZrW	22.5	8.5	1.0	2.2	0.2	0.1	0.1	65.3	2.7
10ZrW[a]	66.3	23.4	2.8	6.2	0.6	0.4	0.4	0.0	2.8

[a] Results adjusted to 100% after excluding the fixed ZrO_2.

Table 2
XRF and XPS results of the Wyoming (W) and Brazilian (F) intercalated (int) and pillared clays

Clay	$(Zr/Si + Al)_{XPS}$	$(Zr/Si + Al)_{XRF}$	XPS/XRF	Zr $3d_{5/2}$ (eV)
$ZrAc_4$[a]	–	–	–	182.8
ZrO_2[a]	–	–	–	182.2
5ZrW(int)	0.60	0.40	1.50	183.0
10ZrW(int)	0.32	1.00	0.32	182.6
10ZrW	0.54	1.00	0.54	183.2
10ZrF(int)	0.80	1.29	0.62	183.0
10ZrF	0.70	1.30	0.54	182.6

[a] Bulk reference.

pillarization of the sample (Zr/clay = 10), this ratio increased to 33%. In a similar manner, the Wyoming clay which initially presented a V_μ/V_t ratio of 11% changed to 55% after the pillarization procedure (Zr/clay = 10). The results reveal the increase in the fraction of microporous volume after the pillarization with zirconium and also as a function of the Zr/clay ratio (10ZrW > 5ZrW > 1ZrW). Gandía et al. [19] after intercalation and pillarization of Gador clay with Al and Zr polycations observed type I isotherms, indicating the formation of microporosity, as well as an increase in surface area (from 144 to 283 m^2/g) after intercalation and drying at 323 K, and an increase in the microporous volume. Our results on the textural analyses indicate that the increase of the surface area is due to a significant increase of the microporosity. The results of the textural characterization for the K10 clay are similar to those reported in the literature. Kawi and Yao [20] obtained a surface area of 197 m^2/g for this clay. The K10 clay has a low microporosity and a V_μ/V_t ratio of just 2%, but has a surface area similar to those of the pillared clays with Zr/clay = 10.

Table 3
Textural characteristics of the natural, K10 acid and zirconium-pillared clays

Clay	BET area (m^2/g)	V_t[a] (cm^3/g)	V_μ (cm^3/g)	V_μ/V_t (%)
K10	212	0.301	0.006	2
FAP	108	0.098	0.015	15
1ZrF	143	–	–	–
5ZrF	205	–	–	–
10ZrF	206	0.147	0.049	33
W	29	0.079	0.009	11
1ZrW	144	0.138	0.047	34
5ZrW	183	0.132	0.065	42
10ZrW	217	0.154	0.086	55

[a] $p/p_0 = 0.98$.

Table 4
TPD of NH_3 of the purified Brazilian, K10 acid and zirconium-pillared clays

Clay	Acid sites (μmol NH_3/g_{cat})
FAP[a]	155
1ZrF	630
10ZrF	780
10ZrW	839
K10	833

[a] Treated at 773 K/2 h.

The results for the NH_3 thermodesorption (Table 4) indicate that the pillarization with zirconium increases the quantity of acidic sites, in the following order: FAP < 1ZrF < 10ZrF. The same amount of acidic sites for the K10 commercial clay and Wyoming-pillared clay (10ZrW) were observed, both being slightly greater than the Brazilian-pillared clay with a ratio of 10 (10ZrF). The desorption profile of the Wyoming-pillared clay presented two peaks (Fig. 6d). The peak at high temperature (780 K), also present in the K10 clay, demonstrates the presence of more strongly acidic sites than those present in the Brazilian-pillared clays (1ZrF and 10ZrF). On the other hand, the peak at low temperature (600 K) was the same for all the samples. The characterization of the acidic sites by use of trimethylphosphine (TMP) as a probe [21] showed the presence of Brönsted sites for K10 and Brazilian Zr-pillared clays. ^{31}P MAS NMR spectra of K10 showed three types of Brönsted

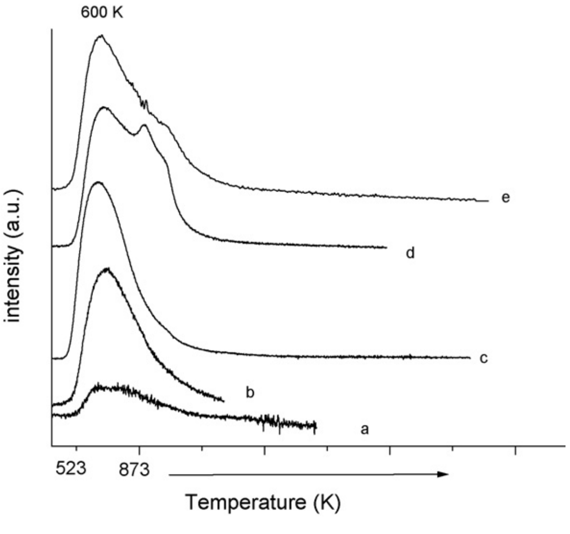

Fig. 6. TPD of NH_3 of the samples: (a) FAP, (b) 1ZrF, (c) 10ZrF, (d) 10ZrW, and (e) K10.

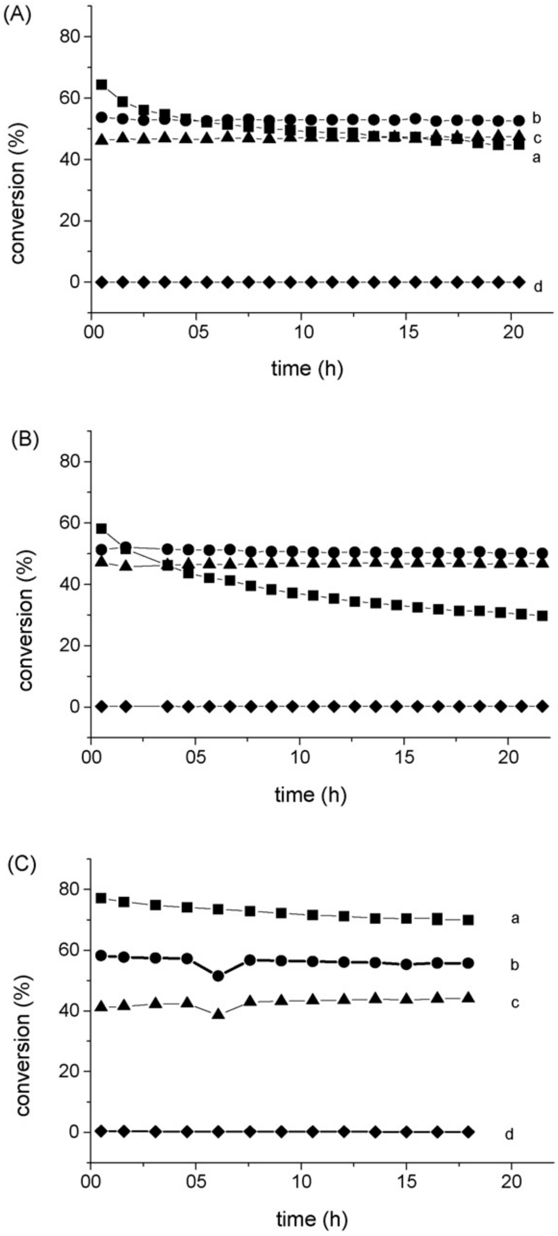

Fig. 7. Results of 1-butene isomerization for the samples: Brazilian-pillared clay with Zr/clay = 10 (A), Wyoming-pillared clay with Zr/clay = 10 (B) and K10 (C): (a) conversion, (b) *trans*-2-butene, (c) *cis*-2-butene, and (d) isobutene.

sites, but only one is present in the case of the Brazilian Zr-pillared clay. The difference in the ^{31}P MAS spectra would indicate that K10 has a larger number of acidic sites and a greater distribution of acidic site strength than zirconium-pillared clay, consistent with the NH_3 TPD results.

The catalytic tests for 1-butene isomerization evidenced the difference in activity, selectivity, and stability, between the Brazilian Zr-pillared and the reference clays, K10 acid and Wyoming Zr-pillared. The Brazilian clay presented greater initial activity and stability than the Wyoming (Fig. 7A and B). The K10 commercial acid clay presented greater activity and stability when compared to both pillared clays (Fig. 7C).

The formation of isobutene, as the result of a skeletal isomerization that occurs within strongly acidic sites, was negligible for all the samples. The distribution of products was similar, thus indicating the similarity of the nature of the acidic sites for all the samples. The K10 commercial clay gave a *cis*/*trans* relation of 0.76, while the pillared Brazilian clay (F), Zr/clay = 10, gave a *cis*/*trans* ratio of 0.89, and the Wyoming clay (W), pillared in an identical manner to the Brazilian clay gave a ratio of 0.92.

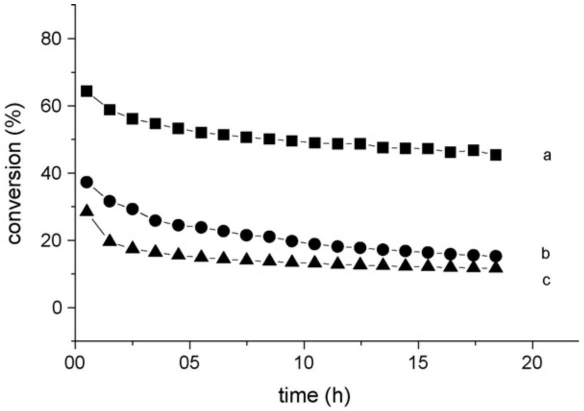

Fig. 8. Conversion vs. reaction time in the 1-butene isomerization for the Brazilian-pillared clay with different zirconium contents: (a) Zr/clay = 10, (b) Zr/clay = 5, and (c) Zr/clay = 1.

The Brazilian clay presented variations in the conversion of 1-butene as a function of the zirconium content. The conversion increased with the increase of the Zr/clay ratio (Fig. 8). This result is consistent with the variation observed for total acidity (Table 4).

Reactions of benzene with primary linear olefins, with different hydrocarbon chain lengths (1-dodecene, 1-octene and 1-hexene), were evaluated using the Brazilian-pillared and Wyoming clays with Zr/clay = 10 and the K10 acid clay. The products of the reaction were olefin isomerization and monoalkylation of benzene. Dialkylated products and olefin dimers or oligomers were not detected. The conversion was expressed as a percentage of the olefin converted to isomerized and monoalkylated products. The selectivities for the monoalkylation of benzene and for olefin isomers were compared in isoconversion conditions.

The Brazilian-pillared clay showed greater conversion of 1-dodecene than the Wyoming (Fig. 9A and Table 5). However, for shorter reaction times the conversions were similar. The K10 commercial clay presented the greatest conversion among the samples studied.

The Brazilian clay showed lower selectivity for monoalkylated products when compared to the Wyoming clay (Table 5). These results are in accord with the data obtained by Guarino et al. [14], who also obtained low selectivity for benzene monoalkylation using clays intercalated with zirconium. The K10 presented higher selectivity for benzene monoalkylation in comparison with the pillared clays (Table 5), despite the later presenting microporosity in the range of 30–50% in relation to the total porous volume (Table 3) while for K10 the microporosity is negligible. The results suggest that access to acidic sites in the clays that present microporosity is more hindered for longer olefin chains (C12).

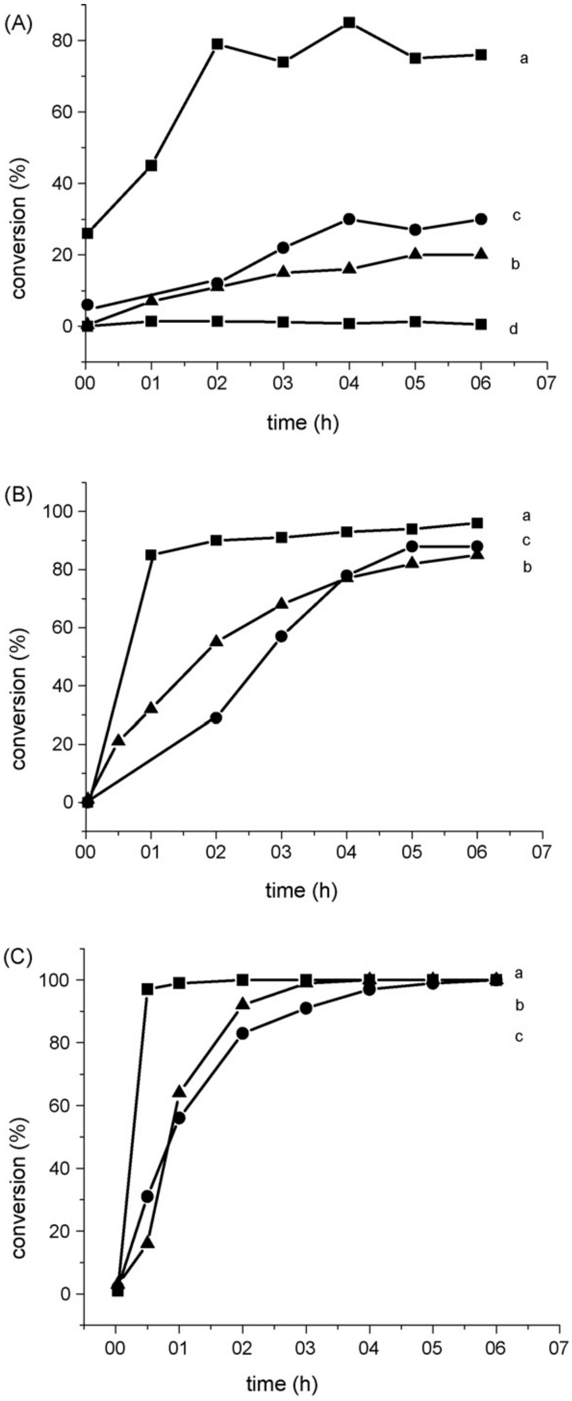

Fig. 9. Conversion in the benzene alkylation with 1-dodecene (A), 1-octene (B) and 1-hexene (C) for the samples: (a) K10, (b) Wyoming-pillared clay with Zr/clay = 10, (c) Brazilian-pillared clay with Zr/clay = 10, and (d) Brazilian natural clay treated at 773 K.

Table 5
Catalytic activity and selectivity towards benzene alkylation with 1-dodecene for the samples indicated

Clay	Reaction time (h)	Conversion (%)	Selectivity (%)	
			Monoalkylation	Isomerization
K10	1	45	24	76
	3	74	34	66
10ZrF	3	22	7	93
	4	30	14	86
10ZrW	5	16	13	87
	6	20	12	88

Table 6
Catalytic activity and selectivity towards benzene alkylation with 1-octene for the samples indicated

Clay	Reaction time (h)	Conversion (%)	Selectivity (%)	
			Monoalkylation	Isomerization
K10	2	90	85	15
	6	96	93	7
10ZrF	2	29	10	90
	4	78	15	85
10ZrW	1	32	15	85
	4	77	17	83

Table 7
Catalytic activity and selectivity towards benzene alkylation with 1-hexene for the samples indicated

Clay	Reaction time (h)	Conversion (%)	Selectivity (%)	
			Monoalkylation	Isomerization
K10	0.5	97	61	39
10ZrF	0.5	31	15	85
	1.0	56	17	83
10ZrW	0.5	16	17	83
	1.0	64	30	70

The Brazilian clay showed lower conversion of 1-octene for shorter reaction times in comparison with the Wyoming (Fig. 9B). For similar conversions, the Brazilian clay showed lower selectivity for monoalkylated benzene products than that presented by the Wyoming clay (Table 6). The K10 presented greater 1-octene conversion and also a higher selectivity for monoalkylated products in comparison to the others. The values obtained were similar to those reported by Devasy et al. [22] for a zirconium catalyst supported on phosphomolibdic acid, which confirms the acidic character of the commercial K10 clay used as a reference in the present work.

The K10 clay presented greater 1-hexene conversion than all the other clays. The Brazilian clay showed greater conversion at the initial stage of reaction than the Wyoming clay (Fig. 9C and Table 7). The K10 also showed a remarkable increase in the selectivity for monoalkylated products compared to the Brazilian clay for olefin conversion in the range of 60% (Table 7).

The increase of activity for the reaction of benzene with 1-dodecene (Fig. 9: K10 > 10ZrF > 10ZrW) reflects the presence of microporosity in the Zr-pillared clays compared with K10 acid clay (Table 3). For all the samples, an increase of conversion was obtained when olefins with lower hydrocarbon chain lengths were used (Fig. 9).

The K10 showed greater selectivity for monoalkylated products for all the olefins, probably due to stronger acid sites as evidenced in the NH_3 TPD analysis. It was also noticed that a high accessibility to the active sites, due to the negligible microporosity, and an equivalent value of surface area when compared to the other clays was tested. Among the pillared clays, the Wyoming presented greater selectivity for mono-alkylated products for the reactions with 1-dodecene, 1-octene and with 1-hexene. As the olefin carbon chain length decreases, the restriction to accessibility becomes less important and the presence of stronger acid sites (Fig. 6), which benefits the alkylation, increases the selectivity.

4. Conclusions

The X-ray diffraction oriented slide technique allowed the characterization of the effect of intercalation time upon the structure of the pillared clays. The textural analysis showed that the increase of the surface area of the pillared clays is due to the increase of the microporosity of the samples. The acidic sites were quantified by TPD of NH_3 and revealed that the K10 commercial clay and Wyoming pillarized have an equivalent number of sites where the Zr/clay ratio equals 10. For the Brazilian clay the total amount of acidic sites was a little less, though the acidity increased with the increase of the zirconium content. The benzene alkylation with olefins of smaller carbon chain length showed greater selectivity for monoalkylated products for the Wyoming-pillared clay than for the Brazilian-pillared clay.

Acknowledgements

The authors would like to express their thanks to CNPq for financial support, to Dr. Arnaldo Alcover Neto (CETEM, Brazil) for the clay sample used in this work, and to Prof. Simon John Garden (IQ-UFRJ, Brazil) for detailed reading of the work.

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