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Isobutane alkylation with C_4 olefins on a sulfonic solid acid catalyst system based on laminar clays

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Abstract

Natural clays were modified by means of the controlled attack of strong Brönsted acids in aqueous solution. The variations of the surface acidity of the solids, followed by IR of adsorbed pyridine and hammett indicators, indicated a population of Brönsted type sites above 800 μ mol/g, while the surface area increased from 23 up to 105 m^2/g. A series of solids (ATZ-L, ATZ-A and ATZ-G) was activated using trifluoromethanesulfonic acid (CF_3SO_3H), then evaluated at the bench scale in a fixed bed reactor, both in liquid and gas phase, using an $iC_4/C_4^=$ molar ratio, which led to 5.5% trimethylpentanes (TMP) against 35.9% of $C_8^=$ and 53.4% of heavier C_9^+ products for the catalysts (ATZ-L) having higher acid strength, i.e. Ho ≈ -9.3. For the solids having a moderate surface acid strength (Ho ≈ -4.4) the activation rate after 12 h runs was about 70%, but the solids having a higher acid strength, i.e. Ho $= -5.6$ and -9.3, showed a deactivation rate almost null after 24 h runs.

Keywords: Brönsted acids; Trimethylpentanes; Activation rate; Deactivation rate

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1. Introduction

Clays are laminar phyllosilicates that represent a low-cost, accessible alternative for catalytic supports, which are susceptible of being modified for obtaining improved properties. In particular, the microporous structure and surface acidity of those materials is of great interest for carrying out reactions such as alkylation, polymerization and isomerization of light paraffins. The surface acid properties of those clays may be enhanced by the addition of inorganic acids and bases, for example BF_3, SbF_3 and sulfonic acids [1]. On the other hand, the increasing demand of clean fuels with high octane numbers (RON ≥ 94), makes it that some processes such as the alkylation of isobutane with olefins takes greater importance in the general reformulation scheme. In this respect, the gradual phase out of the corrosive liquid catalysts (HF, H_2SO_4) used in the traditional alkylation process [2–5], has motivated an intensive research for alternate heterogeneous processes and solid acid catalysts. Then, the main purpose of the present work was to explore the catalytic properties of the acidic clays for the alkylation reaction, searching for a correlation with the surface properties of the solids, such as surface area and acidity, before and after modifying them by the chemical attack with triflic acid. The surface property variations were characterized by means of IR spectroscopy and physical adsorption of N_2 (BET), while the structural features were followed

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Table 1
Chemical composition and surface properties of the starting clayey materials

Support	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	K_2O	Na_2O	AA[a] (wt.%)	CEC[b] (meq/g)	AT[c] (meq KOH/g)
DAZ	70.09	17.67	4.17	0.63	2.72	0.62	4.06	85	106	5.2

[a] Water adsorption capacity.
[b] Cationic exchange capacity (method: methylene blue).
[c] Total acidity (method: titration with KOH).

by means of ^{27}Al-NMR and X-ray diffraction (XRD) methods.

2. Experimental

The starting materials were mineral clays (DAZ) from Durango, Mexico, which were purified by sedimentation in distilled water, thus eliminating quartz and other impurities. The clay suspension was titrated with a solution of NH_4OH, then were centrifuged and submitted to washing with demineralized water. The acid sulfonic clays were prepared by means of two methods, one in the gaseous phase and the other in liquid phase. The former procedure consisted in saturating the system with a flow of N_2 passing through a saturator containing triflic acid (CF_3SO_3H, 98%), samples ATZ-G. In contrast to this, the solids ATZ-A were prepared using a solution of triflic acid in acetone, followed by drying at room temperature, then drying further at 120°C for 12 h in air flow [6]. The second catalyst was synthesized in liquid phase (ATZ-L), starting with the suspension of the original clayey material in water, then submitting it to a constant agitation for 4 h, while adding triflic acid. The resulting suspension was aged 24 h and finally submitted to drying [7].

The physicochemical properties of these catalysts were determined before and after the acid attack, the composition and structural variations being determined by means of the atomic absorption (AA) and XRD, respectively, while the surface area, volume and diameter of pore were determined by means of the BET method and molecular configuration made use of nuclear magnetic resonance (^{27}Al-RMN-MAS); the surface acid strength and acid type sites were determined by means of hammett indicators and IR spectroscopy of adsorbed pyridine. The catalytic behavior was evaluated in a fixed bed reactor, both in liquid and gaseous phase, using an isobutane/olefin molar ratio of 3. The reaction conditions (P, T) used in this work were established after a preliminary study. A GC-Varian 3400 fitted with an FID detector was used, together with a capillary injector and capillary columns of 50 m (PONA, for liquid products) and a GC with alumina–megaboro column was used for analysis of the reactants and the light compounds.

3. Results and discussion

The chemical composition, total acidity (meq/g) and exchange capacity (CEC) of the natural clays are reported in Table 1 while Table 2 displays the main surface properties of the catalysts. A change of the surface area of the natural clays was observed after the acid attack, resulting in an increase of about four

Table 2
Textural and acid properties of the initial and modified clays

Catalyst	TFA[a] (mmoles/g)	Acid strength Ho	H_2SO_4[b] (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)	d_{001} (Å)
DAZ	0	+1.1	1	23.0	0.14	22	12.3
ATZ-G	7	−4.4	63	52.0	0.16	58	12.5
ATZ-A	7	−5.6	74	78.0	0.17	65	14.3
ATZ-L	7	−9.3	98	105.0	0.20	77	12.9

[a] Trifluoromethanesulfonic acid.
[b] Equivalent H_2SO_4 concentration.

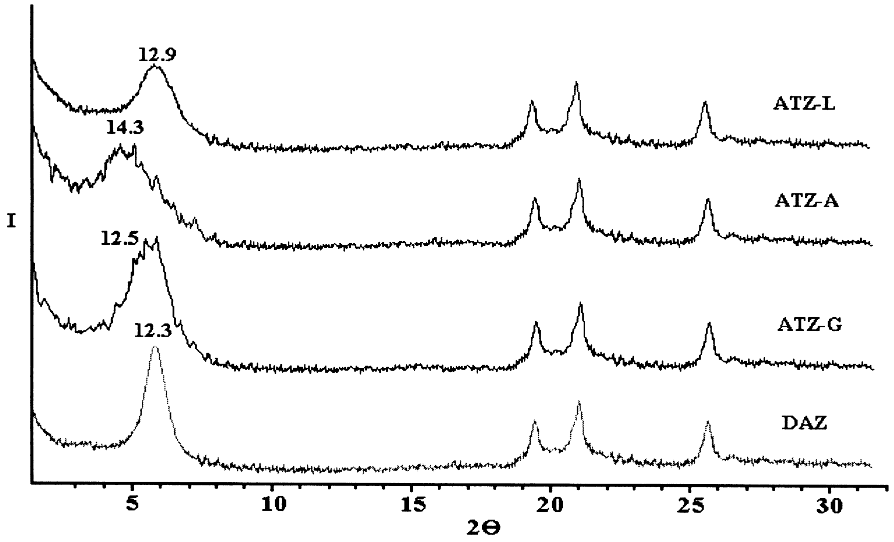

Fig. 1. X-ray diffraction of the clayey materials.

times. The acid strength measured by hammett indicators was different for each solid, being greater for the solids prepared in the liquid phase that used water as a dispersant agent (Ho ≅ −9.3).

The diffractograms in Fig. 1 show the (0 0 1) peak corresponding to montmorillonite clays, indicating their interlayer distances.

The analysis by pyridine adsorption (FTIR, Fig. 2) showed the presence of acid sites of Brönsted type (characteristic band in 1545 cm^{-1}) and Lewis type (band in 1455 cm^{-1}), the latter ones tending to disappear at 300°C; the sites of Brönsted type on the other hand, are favored with the increase in temperature reaching a maximum of 876 μmol pyridine/g of catalyst at 200°C. In the Fig. 3 the spectra of ^{27}Al-RMN-MAS was shown, where dealumination clay due to clay–acid attack was observed. The more firmly bound TFA species might be sorbed on loci which are close to the Al sites. Results obtained from FTIR and ^{1}H solid state NMR [6] are also in

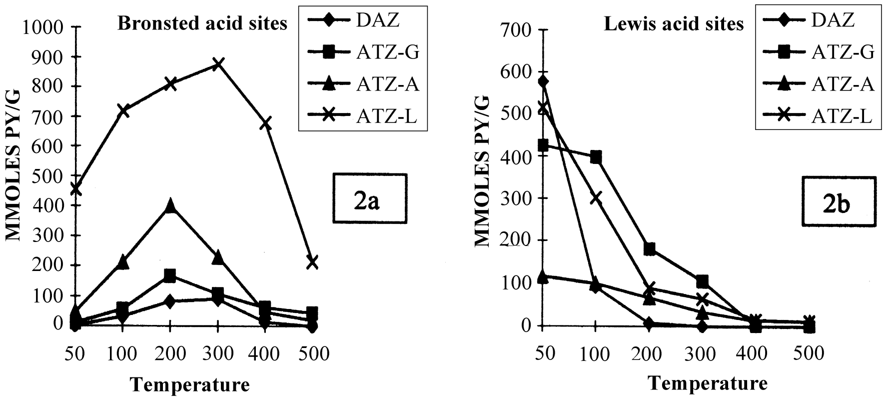

Fig. 2. Influence of the temperature on the surface acidity: (a) Brönsted, (b) Lewis.

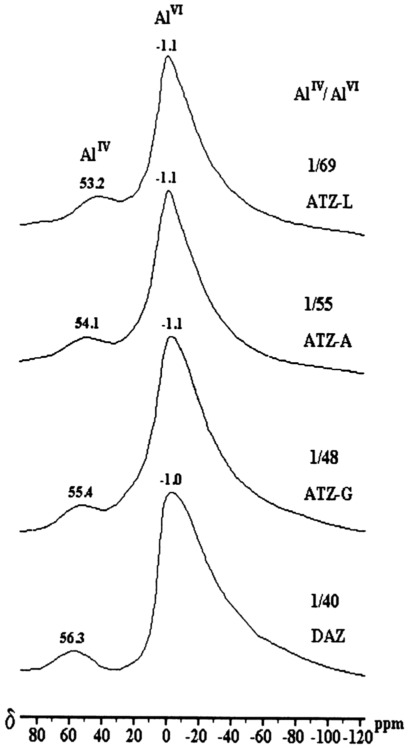

Fig. 3. Spectra of ^{27}Al-RMN-MAS of the natural and modified clays.

Table 3
Operation conditions and products distribution with ATZ-G, ATZ-A and ATZ-L

Conditions	Catalysts		
	ATZ-G	ATZ-A	ATZ-L
Acidity (Ho)	−4.4	−5.6	−9.3
H_2SO_4 (%)	63.5	74.2	98.5
Pressure (Kg/cm^2)	20	20	20
Temperature (°C)	100	100	100
Contact time (h)	36	36	36
Weight cat. (g)	2.5	2.5	2.5
Isoparaffine/olefin (I/O)	3	3	3
Products			
Light	–	0.5	–
C_7	–	0.29	0.24
C_8	–	6.28	0.98
TMP	1.85	3.36	5.52
DMH	2.24	5.53	3.27
$C_8^=$	25.33	29.62	35.92
TMH	4.68	4.42	0.68
C_9^+	65.91	49.98	53.39

agreement with such a conclusion.The results of the catalytic evaluation of the whole catalysts series are presented in Table 3.

The natural clay does not show catalytic activity. The catalysts prepared in liquid phase presented distinct catalytic properties with respect to materials prepared in the gas phase, i.e. higher selectivity towards TMP and dimethylhexanes (DMH), but a significant proportion of the products are in the range of the heavy products C_9^+. On the other hand, the ATZ-L catalyst promoted the formation of a higher proportion of TMP, but the olefin proportions of C_8 and C_9^+ increase, while the C_9^+ fraction diminishes. The selectivity towards TMP of the solid ATZ-A is lower than ATZ-L, so the ratio TMP/DMH is favored. In addition, the stability of the catalyst prepared in the gas phase ATZ-G is smaller, and after 12 h of reaction there is a 70% loss of activity compared with the initial activity. The ATZ-L and ATZ-A prototypes maintained their activity by more than 24 h, without apparent change; the analysis were accomplished each within 4 h.

4. Conclusions

There is an increase in the population of Brönsted acid sites as well of acid strength with respect to the initial clayey material, ATZ-L (prepared in aqueous phase) showing the greater acidity. The action of the triflic acid seems be the mineralization of octahedric and tetrahedric aluminium, giving the relaxation of the layers crystalline structure and the increase of the materials porosity. According to these results, ATZ-L catalysts showed a catalytic activity for isoparaffins alkylation with olefins, presenting a little higher selectivity towards TMP with respect to the catalysts prepared by means of alternative techniques, both in the gas phase and liquid phase (acetone). However, there exists a marked trend towards the formation of olefinic products, i.e. $C_8^=$. This effect has been reported [8,9] also for the alkylation C_4 fractions with solid acid catalysts. The preparation of catalysts based in the clayey materials as reported here but having the right combination of acid sites distribution (Brönsted–Lewis) and basic sites might improve still the selectivity towards the desired paraffinic products (TMP). The prototypes prepared in this study were based on the hypothesis of the mechanism that the proton insertion plays an important role (transfer of H^+ of the catalyst to the molecule of iC_4). The materials prepared in this work present a pore size sufficiently large so as to facilitate the desorption of the carbenium ions and that a high population of strong Brönsted acid sites could transfer the hydride towards the isobutane, but the obtained results do not comply with the established hypothesis, but show an activity decrease for the alquilation, while the great quantity of olefines in the products is prevailing. However, there exists the potential possibility of affecting the hydrogenation of the olefinic products obtained $C_8^{=}$, what would have been a product with similar characteristics to the alquilation gasoline.

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