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Hydroconversion of heptane over a Colombian montmorillonite modified with mixed pillars of Al–Zr and Al–Si

M.F. Molina, R. Molina, S. Moreno *

Centro de Catálisis Heterogénea, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia,
Carrera 30 No. 45-03, Bogotá, Colombia

Abstract

A Colombian montmorillonite was successfully pillared with solutions of Al, Al–Zr, Zr and Al–Si polyhydroxocations to obtain active catalysts for the hydroconversion of *n*-heptane. The catalysts were characterised by X-ray diffraction, N_2 adsorption and heptane hydroconversion tests. The catalysts modified by mixed pillaring (Al–Zr and Al–Si) showed a favourable effect on the activity, selectivity and stability, leading to an increase in heptane isomer products.

Keywords: Heptane hydroconversion; Mixed pillared clays; Montmorillonite

1. Introduction

Pillared clays (PILCs) are porous solids that are commonly used as catalysts because they have good textural properties, such as high surface area and substantial micropore content [1]. Modification by pillaring is carried out by intercalation of hydroxymetallic cations between the clay sheets, which when treated thermally generate pillars of the corresponding metal.

Pillared clays with Al (Al-PILC) are the most extensively studied, but commercial applications in catalysis are limited due to their low thermal stability. The introduction of mixed pillars in the clays presents two advantages: (i) it creates a two-dimensional porosity in the interlaminar spacing of the clay and (ii) it generates thermal stability, increasing the application range of such solids to high temperatures [2,3]. Depending on the final properties of the materials, they can be used in catalytic cracking reactions and the isomerisation of paraffin, among others.

On the other hand, using elements, such as Zr for pillaring is important for two reasons: clays pillared with Zr show comparable qualities to those pillared with Al, and Zr oxides possess good catalytic properties in acid catalyst reactions [4]. It is equally interesting to use mixes of Al–Zr, because Al polycations are easily formed without damaging the clay structure and serve as a mould for the incorporation of Zr. Moreover, with Zr in small quantities, an intermediate acidity is achieved, making the solid very selective towards isomerisation and introducing improvements in the thermal stability of the material [5].

Another mixed system involves intercalation with silicium–aluminium solutions. The addition of Si as a dopant is interesting due to the fact that it produces solids with high surface area, substantial thermal properties and better acid properties. Wada and Wada proposed the partial substitution of hydroxyl groups in Al_{13} polycations by –$Si(OH)_3$ groups. They correlated the higher acidic properties of hydroxyl-silico-alumina-pillared clays compared to the alumina-pillared clay to the presence of these groups [3,6].

More direct evaluation of the acid surface of a solid catalyst can be carried out by analysis of the distribution of product of any model reaction [7]. In this case, the hydroconversion of heptane is the reaction used to characterise acid catalysts.

Hydroisomerisation of heptane is a typical reaction that uses acid catalysts and its conversion is limited by an

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* Corresponding author. Fax: +57 1 3165220.
E-mail address: smorenog@unal.edu.co (S. Moreno).

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equilibrium that is favoured at low temperatures, with products of higher octane number. This is carried out without variation of the number of moles and is accompanied by weak exothermicity (1–5 kcal/mol). Thus, a decrease in reaction temperature favours the formation of branched isomers, which are interesting because of their higher octane number [8]. According to the thermodynamics of the isomerisation reaction, which indicates a higher octane number for lower reaction temperature, the best catalysts will be those that operate at the lowest temperatures.

In this study, the main textural, structural and acidic properties of Zr-, Al–Zr- and Al–Si-pillared clays were compared with those of Al-pillared analogues. The influence of mixed pillars combining Zr or Si with Al on the thermal stability of catalytic performance was examined in the hydroisomerisation of heptane.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Starting material

The starting material was a montmorillonite from the Valle del Cauca in Colombia (MV). This material, which is classified as a sodium bentonite, contains small amounts (<5% in each case) of quartz and feldspar as the main impurities.

2.1.2. Modification with Al

For modification with Al, a solution of 0.2 M $AlCl_3$ and 0.5 M NaOH was prepared at a constant ratio of OH/Al = 2.2. The suspension was aged at 80 °C for 2 h with agitation. This was added dropwise to a 2% clay suspension until 5 mmol Al/g clay was achieved [9]. The resulting material was kept for 2 h at 60 °C with agitation and was then left to rest overnight. The resulting suspension was washed by dialysis until the conductivity of the dialysate was the same as for distilled water. It was dried at 60 °C for 16 h and then calcined at 400 °C for 2 h. Material thus obtained is denoted as Al-MV.

2.1.3. Modification with Zr

A solution of 0.1 M $ZrOCl_2{\cdot}8H_2O$ was prepared and then aged for 2 h at 80 °C. The solution was then added dropwise to a 2% clay suspension until 5 mmol Zr/g clay was achieved. It was then kept at 60 °C for 2 h with constant agitation and left to age for 16 h. It was washed by dialysis, dried at 60 °C for 16 h and then calcined at 400 °C for 2 h. This procedure yielded solid Zr-MV.

2.1.4. Modification with Al–Zr

Pillared clays were synthesised with 4 mmol Al/g clay and 1 mmol Zr/g clay, for which a solution of 0.2 M $AlCl_3$ and 0.1 M $ZrOCl_2{\cdot}8H_2O$ was used, with a constant ratio of OH/Al = 2.2. This solution was aged for 2 h at 80 °C and then added slowly to a 2% suspension of clay in water until 5 mmol metal/g clay was achieved. It was then kept at 60 °C for 2 h with constant agitation and left to age for 16 h. It was then washed by dialysis, dried at 60 °C for 16 h and calcined at 400 °C for 2 h. This yielded Al–Zr-MV material.

2.1.5. Modification with Al–Si

To a solution of tetraethylorthosilicate (TEOS) in 50 ml of 96% ethanol aged for 2 h was added a solution of 0.2 M $AlCl_3$ until a relation of 4 mmol is reached of Al by 1 mmol of Si. Then 0.5 M NaOH was added until the ratio OH/Al = 2.2 was reached and the solution was aged for 2 h at 60 °C with constant agitation. This pillaring solution was added dropwise to a 2% clay suspension and kept at 60 °C for 2 h with constant agitation, then rested for 16 h. It was then washed by dialysis, dried at 60 °C for 16 h and calcined at 400 °C for 2 h. This methodology yielded solid Al–Si-MV.

2.1.6. Bifunctional catalyst

The reaction of heptane hydroconversion is a bifunctional acid-catalysed reaction. Based on previous studies of the ideal metal content (Pt) for this reaction [5], in this work a charge of 1% metal mass was used on the clays.

2.2. Characterisation of the catalysts

X-ray diffraction (XRD) was carried out using the powder method on a Bruker D8 Advance instrument.

Adsorption isotherms for N_2 were measured at liquid nitrogen temperature using a Micromeritics ASAP 2000 instrument. The samples were previously calcined for 2 h at 400 °C and outgassed for 4 h at 200 °C.

The acid content of the samples was determined by isothermic adsorption (200 °C) of ammonia followed by temperature programmed desorption. The following procedure was used: 200 mg of pillared material were treated in a U-shaped fixed-bed reactor for 2 h at 400 °C under a flow of helium. At the end of the pre-treatment, the temperature was lowered to 200 °C and stabilised by means of a temperature controller. Successive pulses of pure ammonia were injected over the solid. After saturation of the solid with ammonia, the reactor temperature was linearly increased up to 400 °C at a rate of 10 °C under stream of helium, and the final temperature was maintained for 14 h. The total amount of ammonia evolved and collected in boric acid was back-titrated. Prior to ammonia adsorption, the samples were heated for 2 h at 400 °C in flowing helium.

2.3. Catalytic activity

The catalytic activity was measured in a unit containing a fixed-bed microreactor at atmospheric pressure.

Once the bifunctional catalyst was loaded into the reactor (200 mg), activation was carried out as follows. The catalyst was heated at a rate of 7 °C/min under a dry air flow to 400 °C and then kept at that temperature for 2 h. The circuit was then purged with N_2 and the metal was subsequently reduced with a flow of H_2 crossing the catalytic bed for 2 h at 400 °C.

After the activation period, the reactor was cooled to 200 °C and stabilised at that temperature. H_2 flow saturated with heptane was generated by passing the gas through a thermostatted glass saturator containing heptane at a constant temperature of 27 °C. Evolution of the reaction was followed as a function of the temperature.

The total flow (H_2–heptane) was 12 ml/min and the weight hourly space velocity (WHSV) was 1.2 g heptane per gram catalyst per hour.

In-line gas-phase GC analysis was carried out on a HP 5890 Series II chromatograph equipped with a HP-1-(methyl silicone) capillary column (5 m × 0.53 mm, 2.65 mm thickness) and a flame ionisation detector.

3. Results and discussion

3.1. Characterisation

After the pillaring processes, XRD diffractograms showed peaks in the low 2θ region, as shown in Table 1. A successful pillaring process caused a gradual peak shift to the left; this is a clear indication of an increase in the basal spacing of the clay.

As listed in Table 1, the diffractograms showed differences for the three metals used to modify the clay (data not shown). The sample modified with only Al has a well-defined peak with an appreciable intensity. In the case of clay pillared with Zr, the d0 0 1 signal is very irregular, suggesting the presence of pillared and non-pillared fractions in the material, which could be due to the effect of the extreme synthesis conditions, such as pH of close to 2.1 [10].

For the clays modified with mixed pillars, the increase in basal spacing observed implies that species were effectively introduced within the sheets. The increase is somewhat greater for Al–Si mixed pillars.

The BET surface area and micropore volume obtained are shown in Table 1. For the natural clay MVn, the BET surface area corresponds to the typical values reported for totally collapsed montmorillonites, which are in the range 30–70 m^2/g. The micropore volume is very small, which is consistent for a clay with a very close interlayer spacing.

Values for the surface area and micropore volume in the pillared clays are within the range of expected values and the results agree with the XRD results. For example, Al-MV, which has the greatest micropore volume, also has a well-defined d0 0 1 signal, which reflects a more regular distribution of the pillars in this clay.

Table 1
Characterisation of clays

Solid	d0 0 1 (Å)	BET area (m^2/g)	Micropore volume (cm^3/g)	Acid contents (mmol/100 g)
MVn	14.8	52	0.021	30
Al-MV	17.7	181	0.091	38
Zr-MV	16.7	114	0.046	46
Al–Zr-MV	17.0	171	0.062	41
Si–Al-MV	17.3	192	0.077	42

On the other hand, the solid with the greatest BET surface area is that with mixed Al–Si pillars, while the simple Al-pillar samples show the greatest microporosity. Analysis of the evolution of the micropore volume suggests that the addition of a second cation affects the quality of pillars that are formed, deviating from "ideal pillaring". However, it is evident from the catalytic properties that the benefits are greater than the disadvantages for mixed pillars.

The acid content values established by isothermal adsorption of ammonia and subsequent temperature-programmed desorption are given in Table 1. In all cases, the pillared clays exhibited higher acid content than the starting MV. The values obtained show that the number of acid sites varied according to the nature of the pillaring species.

The Zr-pillared sample was substantially more acid than the Al-pillared form. The enhanced acid content of the Zr-pillared clay compared with the Al-pillared clay is due to the nature of the metal. Indeed, Miehé-Brendlé et al. [11] inferred from ZrK extended X-ray absorption fine structure (EXAFS) results that the pillars formed upon contacting a 0.1 M $ZrOCl_2$ solution consisted of nearly square Zr_4 zirconyl units standing perpendicular to the clay sheets in pillared beidellites, with spacing of 16.5 Å after calcination at 500 °C. These units are clearly more acid in character than Al_2O_3.

In this study, a zirconyl chloride solution was used and similar spacings to those obtained by Miehé-Brendlé et al. were observed for the Zr-pillared clay, which may indicate that such units are well formed. On the other hand, Zr-MV exhibited the lowest BET surface area and micropore volume, but the highest acid content (Table 1), suggesting that the most important contribution to the acid sites comes from Zr-pillaring species.

Pillars obtained from solutions containing two or more cations greatly influence the properties of the solid. Usually, the first cation polymerises easily (Al is the most studied), whereas the addition of small molar fractions of a second cation is used to improve the thermal, adsorptive and/or catalytic properties of the final solid.

In this work, the acid content (Table 1) found for the Al–Zr- and Al–Si-pillared clays exhibited similar trends to the Zr-pillared form, but there was less improvement compared to results for the Al-pillared sample.

In Al–Zr-MV the acid sites generated can be associated with the enhanced acid strength of Brönsted sites, whereas in the Al–Si-pillared clay the acid properties are probably generated by $-Si(OH)_3$ groups [12].

3.2. Catalytic activity in the hydroconversion of heptane

Balancing of the two catalytic functions and reaction mechanisms for skeletal isomerisation and hydrocracking of

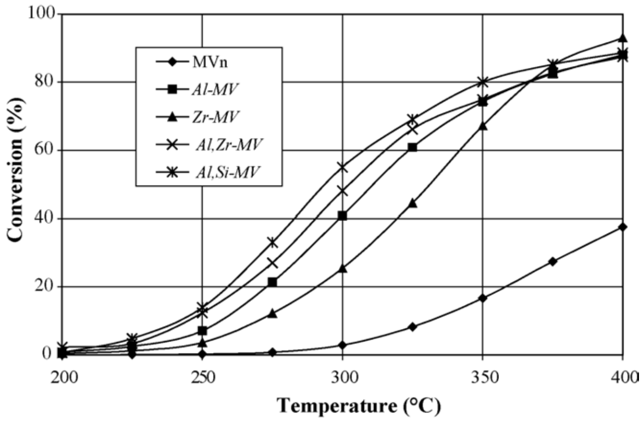

Fig. 1. Hydroconversion of heptane as a function of the temperature.

alkanes in the presence and absence of molecular shape selectivity are well understood [13].

Indeed, isomerisation and hydrocracking of alkanes on bifunctional catalysts require cooperation between noble metal particles and the Brönsted acid sites [14]. The noble metal catalyses hydrogenation–dehydrogenation reactions, while isomerisation and cleavage of the hydrocarbon skeleton occur over Brönsted acid sites. When the two functions are well balanced, the rearrangement of alkenes on the Brönsted acid sites is the rate-limiting step of the conversion [15].

Based on previous studies [5] that identified the ideal metal content (Pt) for this reaction, a charge of 1% metal mass was used on the clays in our study.

Study of the evolution of the catalytic behaviour was based on the percentage total conversion, the content of cracking and isomerisation products (selectivity), and evaluation of $T_{10\ \mathrm{Iso.}}$, the temperature at which 10% of the reaction products are heptane isomers. This conversion zone demonstrates the acid function of the catalysts [5,7].

The curves in Fig. 1 show the evolution of total conversion as a function of the reaction temperature for both natural and modified MVs. There is notable change in catalytic behaviour between the starting material and the pillared clays, which are enormously more active. This increase is greater for the MV samples modified with mixed pillars than for clays pillared with Al or Zr alone.

For the starting clay, MVn, the conversion curve gradually increases with increasing temperature. At the maximum reaction temperature (400 °C) only 37% conversion was achieved.

Above 250 °C, the increase in activity is steeper for the samples modified with mixed pillars. At 400 °C, Zr-MV reached 93% conversion, with 90% for Al–Zr-MV, and 88% for Al- and Al–Si-MV.

It is clearly evident from the conversion curves that the catalytic performance of the mixed-pillar-modified MVs was very similar. High conversion percentage for these materials depends on good formation of pillars, development of microporous structures, substantial acidity and, most importantly, a increase in acid strength compared to the samples modified with only Al. For Zr-MV, an significant increase in activity at high temperatures was observed. The apparently greater stability of this material compared to the other solids could be a result of collateral ‘‘acid treatment’’ of the clay during the pillaring process, which would increase the stability of the final solid.

Table 2 summarises the following parameters for the catalytic performance of these solids in the hydroconversion of heptane: $T_{10\ \mathrm{Iso.}}$, $T_{\mathrm{Max\ Iso.}}$ (temperature for maximum isomerisation), at which we also measured the total conversion, the yield of isomers (Y Iso.) and of cracking products (Y Cra.), and the selectivity for heptane isomers (Sel. Iso.). In addition, the final two columns contain relative percentages of mono- and dibranched isomers.

The results shown in Table 2 illustrate the effects of MV clay modification. The best results (maximum activity), measured as the lowest $T_{10\ \mathrm{Iso.}}$, were achieved with the mixed-pillar MVs. Thus, the Al–Zr- and Al–Si-pillared clays were not only the most active catalysts, but also produced more heptane isomers, with values of 51 and 55%, respectively, at a temperature of 325 °C.

It is clear that selection of the ‘‘best’’ catalyst should balance a series of characteristics and, in this particular case, the catalytic properties. Therefore, the catalyst should show the lowest $T_{10\ \mathrm{Iso.}}$, which reflects greater isomerisation activity, and the lowest $T_{\mathrm{Max\ Iso.}}$. Moreover, at $T_{\mathrm{Max\ Iso.}}$, the catalyst should show greater conversion, greater yield and selectivity for isomers, the lowest yield of cracking products and the greatest selectivity for dibranched isomers.

Taking into account these criteria, it is evident that the best catalysts for the hydroconversion of heptane are the Al–Si- and Al–Zr-pillared clays.

It is important to emphasise the fact that despite the good conversion for Zr-MV over the entire temperature range

Table 2
Catalytic activity in the hydroconversion of heptane

Pt/catalyst	$T_{10\ \mathrm{Iso.}}$ (°C)	$T_{\mathrm{Max\ Iso.}}$ (°C)	Values to the temperature of maximum isomerisation					
			Conversion (%)	Y Iso. (%)	Y Cra. (%)	Sel. Iso. (%)	Mono (%)	Di (%)
MVn	340	400	38	24	5	63	94	6
Al-MV	257	350	74	60	14	81	84	16
Zr-MV	288	350	67	24	42	36	87	13
Al–Zr-MV	245	325	71	51	19	72	86	14
Al–Si-MV	245	325	69	55	14	80	86	14

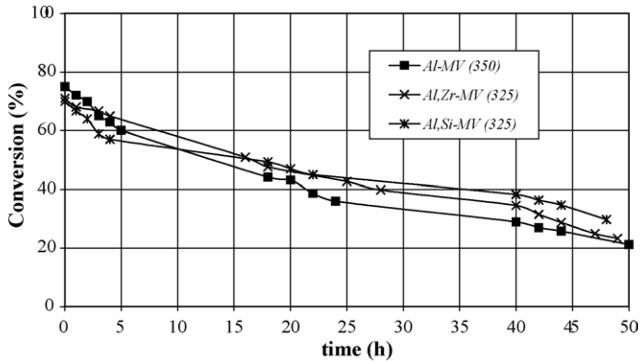

Fig. 2. Activity in time of function to the temperatures of maximum isomerisation.

(Fig. 1), its selectivity was principally towards cracking products (42% at $T_{\text{Max Iso.}}$), which could be due to its greater acid strength compared to the other materials.

To evaluate the effect of the nature of the pillars on stability during catalysis, clays modified with Al, Al–Zr and Al–Si were used for long-term reactions under the most drastic evaluation conditions (typical $T_{\text{Max Iso.}}$ temperature for each solid). The results in Fig. 2 show that after 45 h of reaction, Al–Si-MV activity decreased by 37%, Al–Zr-MV activity by 50% and Al-MV activity by 55%. This result is very important, because it leads to the conclusion that the incorporation of Si in the pillars considerably improves the thermal and catalytic stability of the final catalyst.

Replacement of the –OH groups in Al pillars by the more bulky $-OSiO(OH)_3$ groups decreased the inter-pillar spacing, which affected the micropore volume but increased the interlayer spacing. This can generate better control by diffusion, which in this case is beneficial for catalyst selectivity.

The Al–Zr-MV catalyst showed better catalytic stability compared to Al-MV, which indicates the beneficial effect of Zr in this solid. The pH of the pillaring solution for this sample was 3.7. According to some authors, including Farfán-Torres [4], pH 1.9 leads to greater intercalation of Zr in the clay structure, which improves the pillar distribution and induces thermal stability, thus promoting a microporous structure and creating strong interactions between the pillars and the silica layers. Indeed, after 20 h of reaction, this catalyst shows a considerable loss of activity; this could be correlated to its greater acid strength, which generates greater production of coke and consequently a loss in stability of the material.

4. Conclusions

The addition of a second metal (Zr or Si) to pillars modifying the clay structure affects the efficiency of the pillaring process. This is manifest in an increase in acid properties of the solid and in the generation of more active, selective and stable catalysts for the hydroconversion of heptane.

The most active, selective and stable modified clay for the isomerisation of heptane was Al–Si-MV ($T_{10\ \text{Iso.}} = 245\ ^{\circ}\text{C}$; 50% of the initial activity and 80% selectivity for isomers retained after 40 h), followed closely by Al–Zr-MV.

Zr-PILC showed the greatest selectivity for cracking (42%), possibly due to the generation of acid sites.

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