Effect of pillared clays on the hydroisomerization of *n*-heptane

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Abstract

Different montmorillonites and saponites were pillared with Al polyoxocations to obtain catalytic supports for the hydroisomerization of *n*-heptane. The catalysts were characterized by different techniques such as X-ray diffraction, elemental analysis and N_2 adsoprtion. The temperature-programmed desorption of ammonia indicated that pillared clays exhibited moderate and strong acid sites. The concentration of the acid sites depended on the starting clays as well as the type of the clays. The pillared saponites are more effective for the hydroisomerization of *n*-heptane at 300 °C, however, it decreased over the Al-pillared montmorillonites, and mainly cracking products were obtained.
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1. Introduction

The development of reforming catalysts that isomerizes straight chain alkanes with low octane numbers to their branched isomers with high octane numbers is in high demand [1]. These substances can replace the aromatics in gasoline without the compromise in fuel efficiency, are an environmentally more acceptable alternative, and cause less harm to human health, compared to other technologies such as blending with oxygenates and aromatics [2]. The most important reports concerning the hydroconversion of *n*-heptane use platinum (Pt)-supported zeolites or aluminosilicates [3–6]. Only few studies on *n*-alkane hydroisomerization over pillared clays are available in the literatures [7–9]. The pillared clay minerals (PILCs) have been extensively synthesized and characterized over the past three decades and evaluated as catalysts in wide range of reactions, mainly in acid catalysis [10–12]. The improvement of their properties such as acidity and hydrothermal stability has been extended to the possible use of these materials in the oil refining hydrotreating process [13,14]. The importance of the nature of the starting clay on the catalytic

performances of its Al-pillared form has been demonstrated in several reactions [15–17]. Indeed, Al-pillared saponites are more efficient than those of Al-pillared montmorillonites in the hydroisomerization–hydrocracking of decane, and cumene cracking. The difference in catalytic activities was attributed to the presence of stronger Si–OH–Al acid sites, which occurred only in smectites where lattice substitutions are mainly located within the tetrahedral layers. In montmorillonites, these substitutions took place principally in the octahedral layers, and therefore, sites with equivalent strength were absent [18,19]. In this study, the effect of the source and type of clay minerals on the physico-chemical properties of their pillared counterparts is investigated by means of different characterization techniques. The catalytic performance of these materials on the hydroisomerization of *n*-heptane is also investigated.

2. Experimental part

2.1. Catalyst preparation

Three different montmorillonite clays and two saponites were used, without further modification, respectively. Na-rich montmorillonite (SY-2) from USA with cation exchange capacity (CEC) of 76 mequiv. per 100 g was received from Source Clays Repository, Purdue University. A Na-cloisite

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(SY-3) with CEC of 84 mequiv. per 100 g was obtained from Southern Clay Products, Inc. (USA), and polymer grade montmorillonite (SY-6) with a CEC of 140 mequiv. per 100 g was purchased from Nanocor (USA). One natural saponite (SY-5) from Source Clays Repository, Purdue University, USA with CEC of 74 mequiv. per 100 g, and a synthetic saponite (SY-4) from Kunimine Industries Co., Japan, with CEC of 70 mequiv. per 100 g.

The preparation of the Al_{13} intercalated clays was carried out using a solution of aluminium chlorhydrate hydroxide (Chlorhydrol 50%) from Reheis as the source of pillaring agent, following the procedure described elsewhere [19]. The Al_{13} intercalated clay was prepared by adding the raw clay to pillaring solution which had been previously aged for 1 h at 80 °C. The resulting reaction mixture was then stirred at 80 °C for a further 1 h to allow the intercalation reaction to take place. The solid was filtrated and extensively washed with deionized water, then air-dried overnight. The obtained intercalated clays were calcined at 500 °C for 4 h in air atmosphere, to obtain the resulting pillared materials. The samples are assigned as following, SY2-500 and so on.

2.2. Catalytic test

The preparation of the bifunctional catalysts (with 0.5% Pd) was carried out by incipient-wetness impregnation. Then, the impregnated sample was dried at 110 °C for 24 h followed by calcination at 500 °C for 3 h.

The catalytic analysis of the hydroconversion of *n*-heptane was carried out at atmospheric pressure in a glass fixed-bed reactor. Before catalytic measurements, the 150 mg of catalyst were reduced at 400 °C using H_2 (30 ml/min) for 2 h. The *n*-heptane was introduced to the reactor by a carrying gas of H_2 flow through a saturator maintained at 16 °C. The flow rate was maintained at 30 ml/min with H_2/*n*-heptane molar ratio of 1:0.039. The product gas mixture was analyzed (one analysis every 35 min) on-line with HP 6890N gas chromatograph equipped with FID and HP-PONA (50 m × 0.2 mm) capillary column.

2.3. Catalysts characterization

Powder X-ray diffraction (XRD) patterns were carried out using a Bruker AXS D8 advance instrument to determine the *d* spacing of the pillared clays after calcination. The textural characteristics were determined from nitrogen absorption isotherms at liquid nitrogen temperature using a Quantachrome Autosorb 6B instrument. The samples were outgassed at 300 °C for overnight before being analyzed. The specific surface areas of the pillared clays were estimated from both BET and Langmuir equations, the micropore surface areas were deduced from the *t*-plot method of nitrogen. The chemical compositions of the clays before and after pillaring were performed using X-ray fluorescence (XRF) Bruker AXS S4 Explorer. The acidity contents of the pillared clays were measured by the isothermic absorption of cyclohexylamine (CHA) followed by a thermal gravimetric analysis (TGA) using a SDT 2960 simultaneous

DSC-TGA from TA instruments. The pillared clay was first immersed in excess of CHA at room temperature and allowed to fully absorb overnight. The suspension was then dried on a hot plate at 80 °C or at 250 °C prior the TGA analysis. The sample was then placed in the TGA and the mass changes were recorded over a linear increase of temperature up to 600 °C at a rate of 10 °C/min, under nitrogen atmosphere. The weight loss due to CHA desorption from acid sites between 290 °C and 420 °C was used to quantify the acidity in mmol of CHA. Since each cyclohexylamine molecule reacted with one proton (H^+), it can be assumed that each mmol of cyclohexylamine corresponds to one mmol of proton (H^+) [19]. To characterize the strength of the different acid sites of the pillared clays, temperature-programmed desorption (TPD) spectra of ammonia were recorded by Quantachrome Autosorb-1-C equipped with thermal conductivity detector. About 200 mg of the sample were heated in a stream of He for 1 h at 400 °C, then cooled till 100 °C. The ammonia adsorption was carried out for 30 min at 100 °C. The physisorbed ammonia was eliminated by purging out in a flow of He for 1 h. The measurement was carried out up to 800 °C at a heating rate of 10 °C/min and a He flow rate of 80 ml/min.

3. Results and discussion

3.1. Characterization of the catalysts

The powder XRD patterns of the pillared clays are illustrated in Fig. 1. The pillared clays exhibited similar shape and position, except for the SY4500 sample, where the reflection was broadened, due to the crystallinity of the starting synthetic saponite. The basal spacing of the clay layers increased from 0.96 nm to about 1.7 nm, and higher order reflections (at least 2nd) were observed, suggesting the pillaring species were intercalated in an order manner. The interlayer gallery was about 0.8 nm, and in good agreement with pillared alumina clays reported in the literature [12].

The intercalation of Al_{13} cations was confirmed by the chemical analysis data summarized in Table 1. The composition of the starting clays was assumed to be constant during the pillaring process. Table 1 indicates that the amount of intercalated Al was higher for the SY6 sample with the highest CEC value for the montmorillonite clays. The synthetic saponite (SYS4) contained also the highest content of Al compared to natural one (SYS5). This fact could be related to the chemical stability of the silicate layers of the synthetic saponite during the pillaring process. We noted that high content of MgO in the saponite samples was analyzed compared to the montmorillonite ones, due to their chemical nature and formulae.

The nitrogen adsorption isotherms (not shown) can be described as type I for low relative pressures (p/p_o), indicating the presence of micropores [20], except for SY4-500. At high relative values of p/p_o a type II isotherm is observed, corresponding to mesoporous materials. The hysteresis loops are of type H3 in the IUPAC classification [21], attributed to adsorbents having slit-shaped pores between parallel layers.
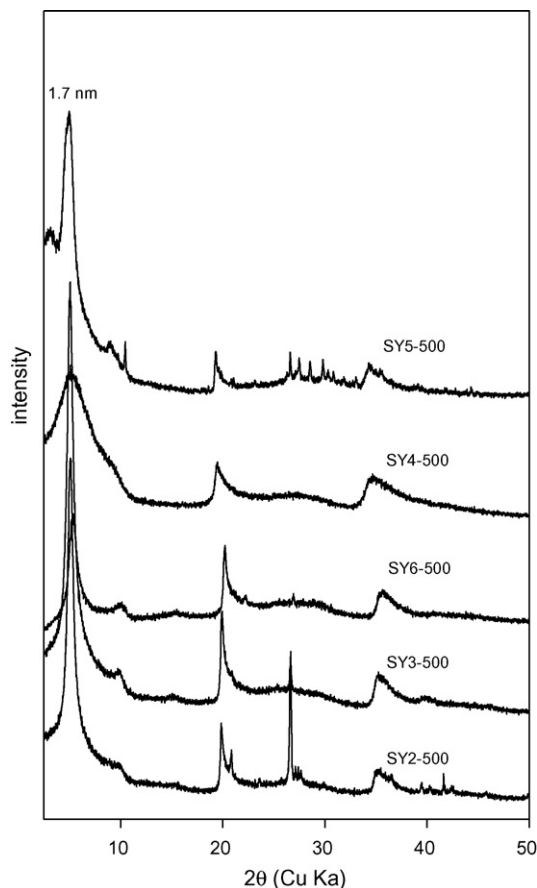
Fig. 1. Powder XRD patterns of the different pillared clays calcined at 500 °C.

The textural properties of the pillared clays are summarized in Table 2. A well-pillared sample is likely to give higher micropore content and that any mesoporosity is likely to be due to stacking disorder and/or platelet stacking effects. The surface area increased after the pillaring process, and they are much higher than those of the starting clays. Although the values obtained varied with the starting precursor, the SY4500 has a lower specific surface area and pore volume compared to the other materials. This fact might be related to the crystallinity of the material which affected the accessibility of nitrogen molecules to the pores. The SY5-500 has the highest surface area of 311 m^2/g. The proportion of the micropore surface area (70–73%) was not affected by the content of Al intercalated, but by the starting clays. On the other hand, the proportion of micropore volumes vary between 57–62% for pillared montmorillonites and 42–48% for pillared saponites. For the SY4-500 a low contribution of the micropore surface area and volume was observed, indicating the non-microporous character of this material. Overall, higher surface area and micropore volumes were obtained, although the basal spacing of the pillared clays remained almost unchanged, the porous structure of pillared clays depended on the interpillar spacing and not the interlayer distance (gallery height) [22]. The values of the average pore diameters indicated that alumina-pillared saponites have more mesoporous character than the alumina-pillared montmorillonites.

The ammonia temperature-programmed desorption (TPD) was used to probe the strength of the acid sites of the pillared materials, and the obtained profiles of the different pillared clays are plotted in Fig. 2. For all samples there are two desorption peaks centered around 250 °C and 500 °C, except for SY3-500 pillared clay where only one peak was observed at 245 °C. The first one corresponds to a moderate acidity, whereas the second one can be attributed to medium to strong acid sites. According to the literature, the pillared clays

However, the SY4-500 exhibited an isotherm adsorption of type II with hysteresis of type H4, characteristic of mesoporous materials, with lower nitrogen adsorbed amounts, especially at lower relative pressures.

Table 1
The chemical analysis data of the different pillared materials

Samples	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	Fe_2O_3 (%)	CEC mequiv./g	Intercalated Al[a]
SY2	43.1	23.6	1.51	3.57	0.76	2.13
SY3	42.2	27.6	2.58	2.17	0.84	2.12
SY6	44.7	27.8	2.05	4.15	1.40	2.66
SY4	39.4	13.0	18.4	1.00	0.70	2.43
SY5	31.1	14.3	14.2	0.01	0.74	2.17

[a] mmol per gram of clay.

Table 2
Textural properties of the calcined pillared clays

Pillared clays	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	S_{micro} (m^2/g)	T.P.V. (ml/g)	V_{micro} (ml/g)	A.P.S. (nm)
SY2-500	290 (34)[a]	438	213	0.184 (0.11)	0.114	2.53
SY3-500	268 (13)	411	190	0.212 (0.08)	0.102	3.16
SY6-500	281 (10)	430	202	0.191 (0.07)	0.110	2.72
SY4-500	170 (20)	267	29	0.154 (0.07)	0.015	3.63
SY5-500	311(10)	471	229	0.263 (0.02)	0.122	3.38

T.P.V. corresponds to total pore volume; A.P.S. stands for average pore size.
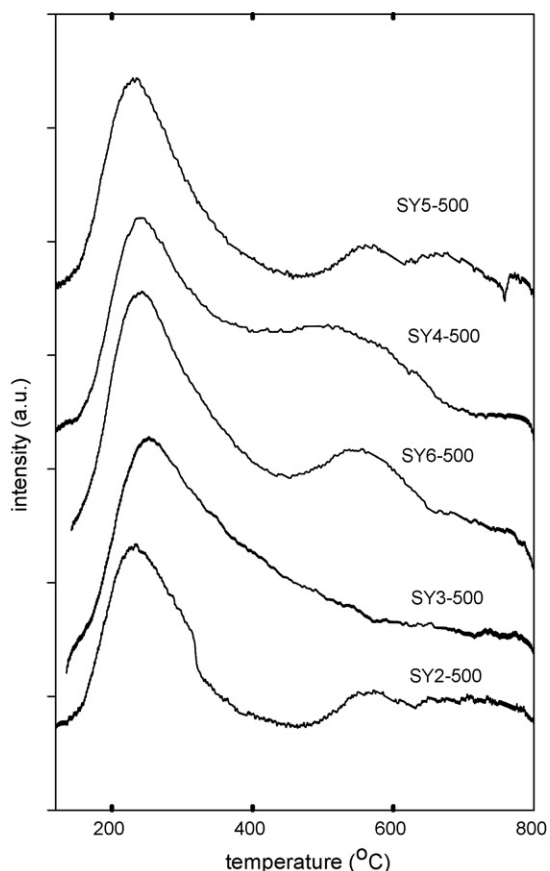[a] Corresponds to calcined starting clays.

Fig. 2. Ammonia TPD curves of the different pillared clays calcined at 500 °C.

molecules strongly decreased. This fact could indicate that the pillared samples exhibited a moderate strong acidic character. In the case of the SY4-500, surprisingly the acidity increased, this fact could not be an artefact, because we have repeated the analysis thrice, it might indicate that some of the acid sites in the interlayer region were not blocked by the pillaring species [26]. In overall, it was difficult to correlate the number of the acid site to the Al content in the pillared samples, and the chemical composition of the clay sheets could affect the acidic character as we have mentioned above.

3.2. Catalytic testing

The hydroisomerization of *n*-heptane requires bifunctional catalysts containing the noble metal for hydrogenation/dehydrogenation of paraffin and the olefin isomers, and molecular sieves with mild acidity for carbon–carbon bond rearrangements and shape selectivity [27]. Our bifunctional catalysts did show a very low conversion at temperature of 200 °C. So, we have performed the tests in the temperature range of 250–350 °C in step of 50 °C.

The percentage conversion of *n*-heptane over the different catalysts obtained at different temperatures is shown in Fig. 3. The *n*-heptane conversion (%) generally increased with increasing reaction temperature overall the catalysts. The

contained both Brönsted and Lewis acid sites at temperatures below 300 °C [23,24]. The Brönsted acid sites usually disappeared after being heated above 400 °C [25]. Thus second peak in the ammonia TPD profile might be originated from Lewis acid sites rather Brönsted acid ones. In general, the peak at higher temperature is less intense compared to the one at lower temperature. The acid sites in the montmorillonite-pillared clays exhibited stronger acid sites compared to saponite-pillared clays. Although the same content of Al intercalated aluminium was estimated. In our case, the chemical composition of the clay sheets affected the strength of acid sites of the resulted pillared materials.

The concentration of Brönsted acid sites was obtained by TPD of cyclohexylamine. The values are expressed in mmol of protons per weight of pillared clay at 290 °C (Table 2). The results indicated that the pillaring process indeed increased the acidity of the pillared clays. The number of the acid sites in the pillared samples depended on the nature of the starting clays and the temperature of the pre-treatment of the adsorbed cyclohexylamine–Al-pillared clays. The SY3500 exhibited the highest acidity of 0.68 mmol of H$^+$/g amongst the pillared montmorillonite clays, while the natural saponite exhibited slightly less acidity of 0.66 mmol of H$^+$/g. The number of acid sites was very low for the case of the synthetic saponite, this could be related to the reduced accessible acid sites for the probe molecule [25].

At higher pre-treatment temperatures of 250 °C prior TGA measurements, the number of the adsorbed cyclohexylamine
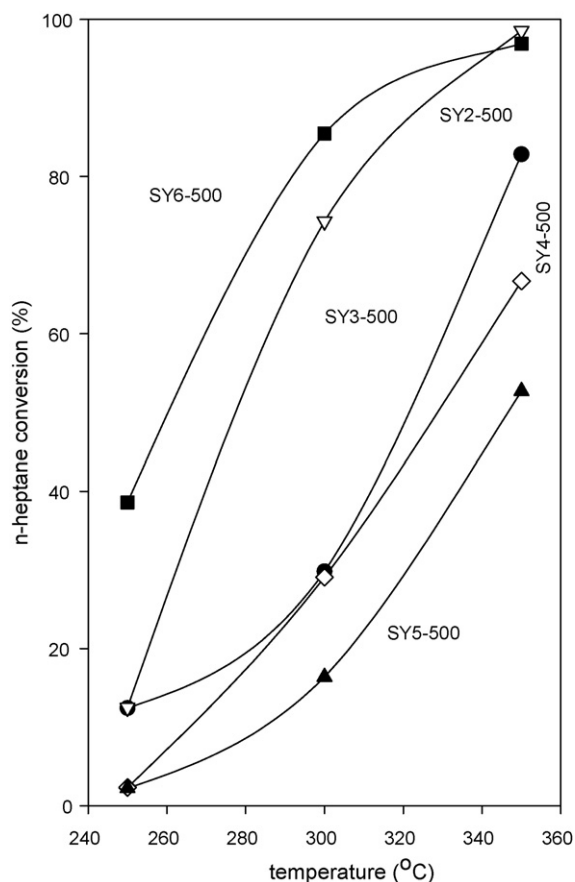

Fig. 3. Variation of *n*-heptane conversion vs. reaction temperature over the different pillared clays calcined at 500 °C.

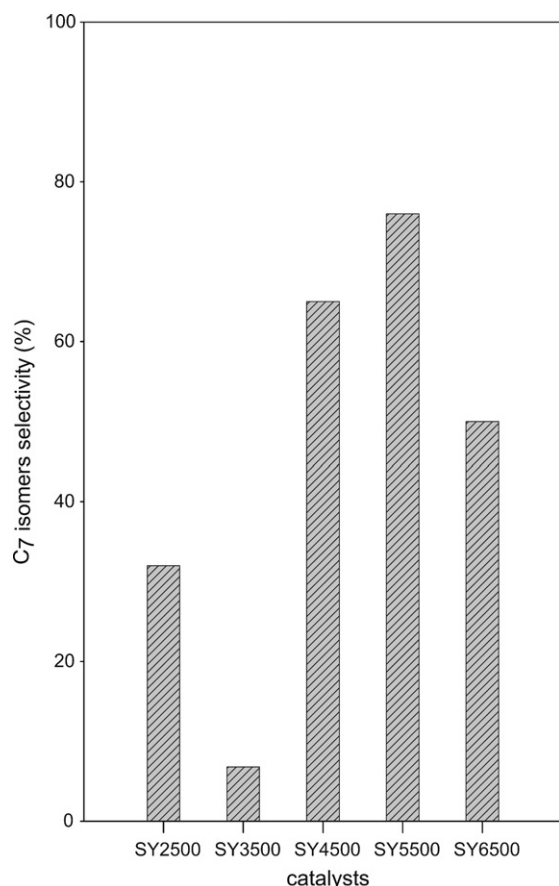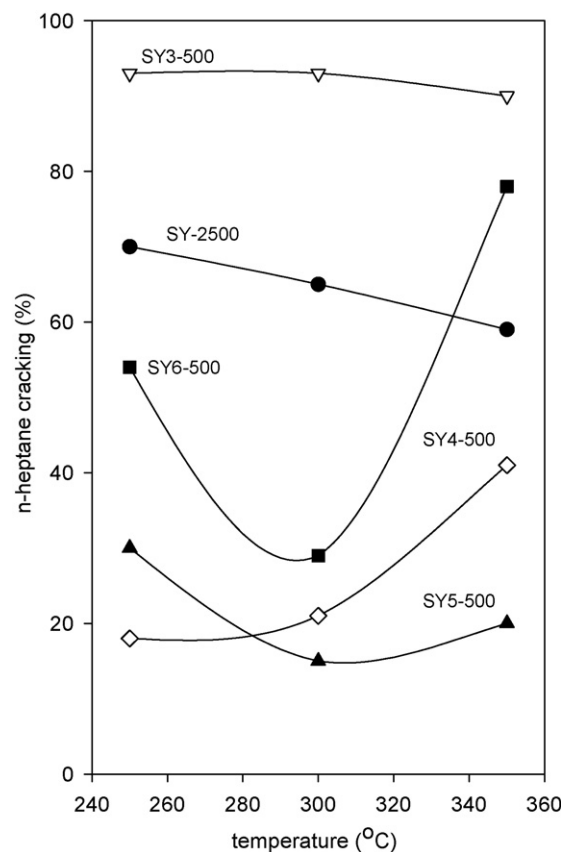Fig. 4. C7 isomers selectivity of different pillared clays at the same level of 50% of conversion.

Fig. 5. Variation of *n*-heptane cracking (%) vs. reaction temperature over the different pillared clays calcined at 500 °C.

increase of the temperature was related to the activation of the catalytic sites in the different catalysts. The pillared montmorillonites clays show considerably lower selectivity to isomers (Fig. 4) with higher selectivity to cracked products compared to pillared saponites (Fig. 5). The initial increase in hydroisomerization selectivity with decreasing cracking products is due to more availability of metallic sites in the vicinity of the acid sites enabling rapid hydrogenation of the carbenium and desorbing them as alkane before they undergo cracking reaction.

The SY3-500 pillared clay showed the low activity to isomers with the highest cracking selectivity even at 250 °C. This fact could be explained by the absence of the necessary acid sites for the isomerization reaction, as shown in the TPD profile. We noted that the Brönsted acid site content is quite higher (Table 3), indicating the existence of acid sites strong

enough to bind CHA, but too weak to catalyze the hydroisomerization or other type of reactions [28]. Meanwhile, the SY6-500 exhibited the highest isomer selectivity, at reasonable conversion percentage. The selectivity of *n*-heptane isomers was affected by the starting clays, and it could be related to the surface area and the acidity of the resulting pillared materials.

The isomerization/cracking (I/C) ratio of hydroisomerization catalyst is an indication of its suitability to isomerization reactions. A good hydroisomerization catalyst must have very high I/C ratio. In Table 4, the I/C ratio of pillared montmorillonite clays was always lower than the ratios of pillared saponites. This fact could be related to the different nature of the acid sites in the catalysts. An increasing trend in I/C ratio is observed up to 300 °C for SY6-500 and SY5-500

Table 3
Acidity measurements of different pillared clays

Pillared clays	Acidity at 80 °C (mmol of H$^+$/g)	Acidity at 250 °C (mmol of H$^+$/g)
SY2-500	0.58	0.21
SY3-500	0.68	0.30
SY6-500	0.55	0.21
SY4-500	0.15	0.25
SY6-500	0.66	0.24

Table 4
Catalytic activity of the pillared clays at 300 °C

Pillared clays	Conv.	Yield sel.	Yield crack.	I/C ratio
SY2-500	29.8	10.2	19.5	0.52
SY3-500	74.3	4.6	69.5	0.06
SY6-500	85.4	60	25.1	2.39
SY4-500	29.1	22	6.2	3.54
SY5-500	16.3	13.4	2.4	5.58

Conversion (conv.), selectivity (sel.) and cracking (crack.) yields are expressed in %. I/C (sel. isomers/sel. cracking ratio).
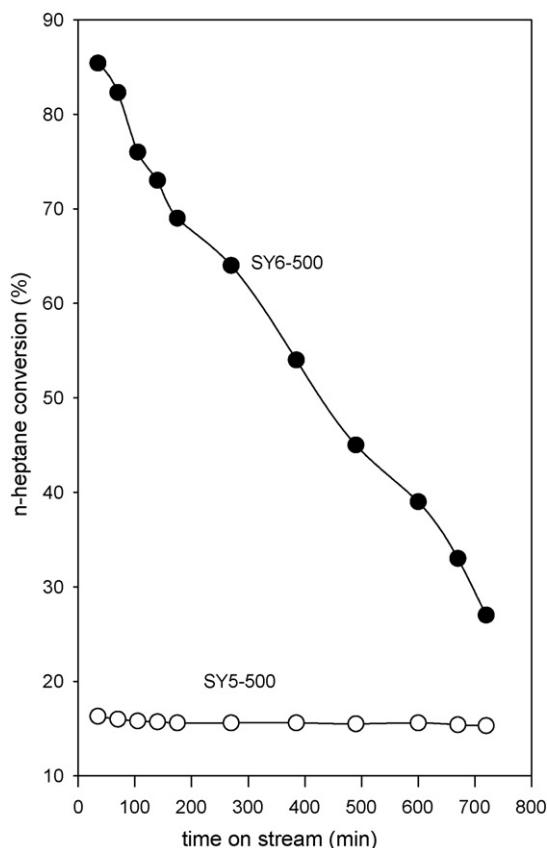
Fig. 6. Variation of *n*-heptane conversion (%) vs. time on stream for different pillared clays at 300 °C.

samples. Further increase of temperature decreased the I/C ratio for all the catalysts, indicating that high temperature favored cracking process. The higher values were obtained for the pillared montmorillonite catalysts. This fact could be related to acidic character of the different catalysts at 350 °C.

The sustainability of SY6-500 andSY5-500 was studied by expanding the time on stream for 24 h (Fig. 6). The temperature reaction of 300 °C was selected, due to the maximum value of I/C ratios for these two catalysts. The activity showed a fall in conversion when the time was increased. The SY5-500 showed the minimum fall in its activity, and could be explained by better balance between the Pd and the acid sites. The SY6-500 exhibited the maximum fall in its activity after 12 h of stream. This fall could be accounted in terms of coke formation due to the cracking reaction which blocked the active acid sites of the catalysts. The rate of the coke formation was related to the starting clay materials, but in general the montmorillonite clays exhibited good environment for the coke formation compared to saponite ones. Similar results were also reported elsewhere [18].

4. Conclusion

The catalytic activity of different pillared clays has been tested in the hydroisomerization of *n*-heptane. The pillared saponites have a higher catalytic activity than pillared montmorillonites for the isomer selectivity. However, the selectivity for the cracking products was higher for the pillared montmorillonite clays. The content of Al did not affect the catalytic properties of the obtained materials, however, the type of starting clay and its chemical composition affected the overall the physical and chemical properties. The suitability of the aluminium-pillared saponites could be envisaged as a reforming catalysts.

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