

# Activity–acidity relationship in zeolite Y Part 1. Transformation of light olefins

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## Abstract

Reactions of ethene, propene, 1-butene and *iso*-butene over two series of catalysts, HNaY (prepared from NaY zeolite) and HNaUSY (prepared from NH<sub>4</sub>USY zeolite), were studied. The catalytic activity for the transformation of these olefins follows the expected order according to the ease of formation of the respective carbocations: ethene < propene < 1-butene < *iso*-butene, for all the samples that were studied. The catalytic results obtained over the HNaUSY series of catalysts are compatible with what was expected for light olefin transformation over acid catalysts. The catalytic activity of HNaY series of catalysts, however, does not follow a regular trend with the protonic content, showing a decrease when the protonic content is high. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Zeolites; Y zeolite; Olefins transformation; Acidity

## 1. Introduction

Zeolites are catalysts widely used in hydrocarbons transformation, being their largest application the catalytic cracking.

Light olefins have an important role in the methanol-to-gasoline process [1–3], in the production of aromatic compounds [4], in the production of oxygenated compounds, like methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME) and ethyl *tert*-butyl ether (ETBE), which are used as gasoline additives in order to

reduce toxic emissions from vehicle exhausts as well as to boost the octane number of lead-free gasoline [5–9], and in the production of isoprene and methacrylic acid which are used in polymer synthesis [10].

The study of olefin transformation, particularly light olefins, which are important products of catalytic cracking, is far from being complete. It is remarkable the reduced number of scientific works performed about olefins reactivity, as compared with the equivalent works done using paraffins as reactants. However, the importance of this study lies not only on the understanding of the reaction mechanism of olefins transformation over zeolites and the mechanism of coke formation, but also on its relevance in detailing the cracking mechanism

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of paraffins. In fact, it is commonly accepted that the intermediate species involved in the cracking mechanism are the same for both paraffin and olefin transformation.

In this paper, we will present a systematic study of ethene, propene, 1-butene and *iso*-butene transformation over Y zeolite in two different forms: HNaY and HNaUSY. This study will be performed in order to analyse, for each olefin reaction, the influence of the time-on-stream and of the number of acid sites on catalytic activity, on molar distribution of products and on coke content.

## 2. Experimental

### 2.1. Catalysts

Two series of catalysts, based on two different forms of zeolite Y, were prepared. The HNaY series of catalysts was obtained from the NaY zeolite (LZ-Y52—Union Carbide) by successive ion-exchange with  $\text{NH}_4\text{NO}_3$  solutions and the HNaUSY series of catalysts were obtained from the  $\text{NH}_4\text{USY}$  zeolite (LZ-Y82—Union Carbide) by successive ion-exchange with  $\text{NaNO}_3$  solutions. Ion-exchanges were performed with solutions of different concentration (between 0.25 M and 2 M) depending on the degree of exchange desired. Mechanical agitation and a solution volume (ml) to catalyst mass (g) ratio of 4 was used. Most of the ion-exchanges were done at room temperature, but in order to obtain high exchange rates, some of them were performed at 100°C under reflux conditions. After exchange, all samples were washed with deionized water, dried at 100°C and calcined at 480°C in a low flow of dry air (0.5 l/h g) for 8 h using a deep bed approach, to prevent the degradation of the structure.

The chemical compositions and protonic contents of zeolites are presented in Table 1.

Table 1

Chemical composition and protonic content of the zeolites used in this work

Catalyst	Chemical composition	H <sup>+</sup> (%)
<i>HNaY series</i>		
NaY	$\text{Na}_{55} [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	0.0
HNaY25	$\text{H}_{14}\text{Na}_{41} [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	25.0
HNaY40	$\text{H}_{22}\text{Na}_{33} [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	40.0
HNaY56	$\text{H}_{31}\text{Na}_{24} [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	56.4
HNaY73	$\text{H}_{40}\text{Na}_{15} [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	72.7
HNaY80	$\text{H}_{44}\text{Na}_{11} [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	80.0
HNaY85.5	$\text{H}_{47}\text{Na}_8 [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	85.5
HNaY87	$\text{H}_{48}\text{Na}_7 [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	87.3
HNaY91	$\text{H}_{50}\text{Na}_5 [\text{Al}_{55}\text{Si}_{137}\text{O}_{384}]$	90.9
<i>HNaUSY series</i>		
HNaUSY3	$\text{H}_1\text{Na}_{34} [\text{Al}_{35}\text{Si}_{157}\text{O}_{384}]$	2.9
HNaUSY71	$\text{H}_{25}\text{Na}_{10} [\text{Al}_{35}\text{Si}_{157}\text{O}_{384}]$	71.4
HNaUSY83	$\text{H}_{29}\text{Na}_6 [\text{Al}_{35}\text{Si}_{157}\text{O}_{384}]$	82.6
HNaUSY94	$\text{H}_{33}\text{Na}_2 [\text{Al}_{35}\text{Si}_{157}\text{O}_{384}]$	94.3
USHY	$\text{H}_{35} [\text{Al}_{35}\text{Si}_{157}\text{O}_{384}]$	100.0

The crystallinity of the samples was checked by X-ray diffraction.

### 2.2. Catalytic experiments

The catalytic activity measurements for the transformation of ethene, propene, 1-butene and *iso*-butene were carried out in a fixed bed reactor at 350°C and atmospheric pressure. A 60 ml/min flow of dry nitrogen was used, and the reactants were fed with a partial pressure of 12%. An amount of 200 mg of catalyst was used in the reactor. In all the cases, before the olefins were fed to the reactor, the catalysts were pre-treated in situ at 450°C during 12 h under a flow of dry nitrogen.

To analyse the products of the reaction, samples of the effluent were injected in a gas chromatograph (Perkin Elmer 8420) equipped with a 50 m PLOT column coated with alumina deactivated with potassium chloride and a flame ionization detector. Reactant feeding was interrupted during chromatographic analysis in order to minimise the deactivation of the catalyst.

To ensure the reproducibility of the data obtained, several catalytic tests were performed

more than once, precisely in exactly the same experimental conditions.

Blank experiments were carried out under the same experimental conditions for all olefins, but in absence of catalyst. We were able to verify that the amount of products formed by thermal transformation is negligible.

After the reaction (approximately 1 h on stream), the amount of coke retained on the catalysts was determined by combustion using a Setaram CS92 DSC. The coke was burned in a flow of air (30 ml/min) and the change in sample weight was measured as a function of the temperature. A heating rate of 10°C/min was used.

### 3. Results and discussion

The experimental catalytic data obtained were analysed in order to study, for each olefin reaction, the influence of the:

- time-on-stream on catalytic activity and on molar distribution of products; and
- number of acid sites of each catalyst on catalytic activity and on coke content.

For the analysis of the results of 1-butene transformation, the fact that the double bond isomerisation to 2-butenes involves a very easy protonation so that the thermodynamic equilibrium is rapidly reached, was taken into account. However, the isomerisation of 1-butene to *iso*-butene is much more difficult, since it involves a skeletal alteration. The thermodynamic equilibrium data for the four isomers of butene were computed using the values of  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$  [11,12]. The thermodynamic ratios of *iso*-butene to 1-butene, *trans*-2-butene to 1-butene and *cis*-2-butene to 1-butene at 350°C are 4.3, 2.0 and 1.5, respectively [13].

Experimental data showed that the equilibrium between 1-butene and 2-butenes was always reached for all the catalysts that were used, that the equilibrium with *iso*-butene was never reached, and that it was not affected by

coke deposition. This behaviour had already been observed by Szabo et al. [14] for the isomerisation of *n*-butenes catalysed by fluorinated alumina.

In conformity with this, when the experimental data for the transformation of 1-butene were processed, the three *n*-butenes (1-butene, *trans*-2-butene and *cis*-2-butene) were grouped together, treated and considered as the reactant. This had already been done by other authors [8,15,16].

#### 3.1. Influence of time-on-stream on the catalytic activity

As expected, the transformation of all olefins induce coke deposition, thus leading to a catalytic activity decrease with time-on-stream, going from a relatively high value at the beginning to a residual activity in a quasi-steady-state at the end. This decrease is sharper for catalysts with higher protonic content, in each series of catalysts.

In Fig. 1, the deactivation of some zeolites on transformation of different reactants as a function of time-on-stream is shown as an example.

The activity vs. time-on-stream fitted well with the semi-empirical model described by Eq. (1) [17–19]. The parameters, for each reaction, were computed by a non-linear least-squares minimisation method using a commercial spreadsheet. This equation was used to compute the initial activity values ( $A_i + A_f$ ) and was integrated, for the overall time of reaction, to compute the total amount of reactant transformed into products detectable in the gas phase ( $A_{\text{cumulative}}$ ):

$$A(t) = A_i \exp(-\alpha_d t) + A_f \quad (1)$$

( $A_i$  is the initial value of the time-dependent component of the activity,  $\alpha_d$  is the deactivation factor and  $A_f$  is the residual value of catalytic activity).

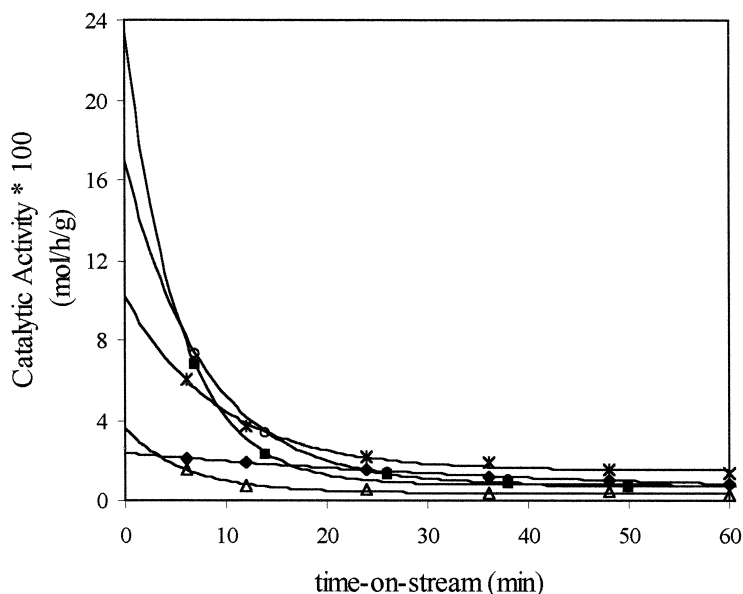


Fig. 1. Catalytic activity for the following transformations: (◆) propene over HNaY40; (\*) 1-butene over HNaY87; (○) *iso*-butene over HNaY80; (Δ) ethene over USHY and (■) *iso*-butene over HNaUSY83. Experimental values and correspondent fittings using a semi-empirical model.

### 3.2. Influence of the time-on-stream on the molar distribution of products

In Fig. 2, examples of the molar distribution of products are shown.

The formation of considerable amounts of products with molecular weight higher than the reactant is evidence that the main reaction is the oligomerization, involving probably the formation of a carbocation by protonation of a reactant molecule and the reaction of this carbocation with another reactant molecule. These heavier products subsequently take part in other reactions, namely scission, cyclization and aromatisation, leading to the existence of a wide variety of products including light hydrocarbons and aromatic compounds.

As it would be expected, the amount of secondary products formed decreases with the time-on-stream due to the catalysts progressive deactivation by coke deposition, leading to a gradual rise of the relative amount of primary products—oligomers and direct scission products.

In the catalytic experiments using 1-butene as reactant, the molar distribution of products practically does not change with time-on-stream (Fig. 2e and f) because this olefin is so reactive that the activity is not very sensitive to the catalyst deactivation.

The formation of *iso*-butene from 1-butene decreases with time-on-stream; nevertheless, the selectivity towards this product increases. Thus, *iso*-butene is produced from 1-butene mainly by the monomolecular mechanism and not by secondary reactions of oligomers scission. As the catalyst becomes more deactivated, the probability that bimolecular reactions (leading to products of oligomerization, cracking, cyclization, etc.) took place is lower. Moreover, olefin isomerization can occur in acid sites that are weaker than those needed for the formation of the other products, the latter being the first to be deactivated. On the other hand, the coke deposited in the zeolite channels decreases the free space near the acid sites, leading to a decrease in the effective channel size, defavouring reactions involving larger molecules. These consid-

erations are in agreement with data obtained by other authors [5,16,20,21].

In the catalytic experiments that were carried out using *iso*-butene as reactant (Fig. 2g and h),

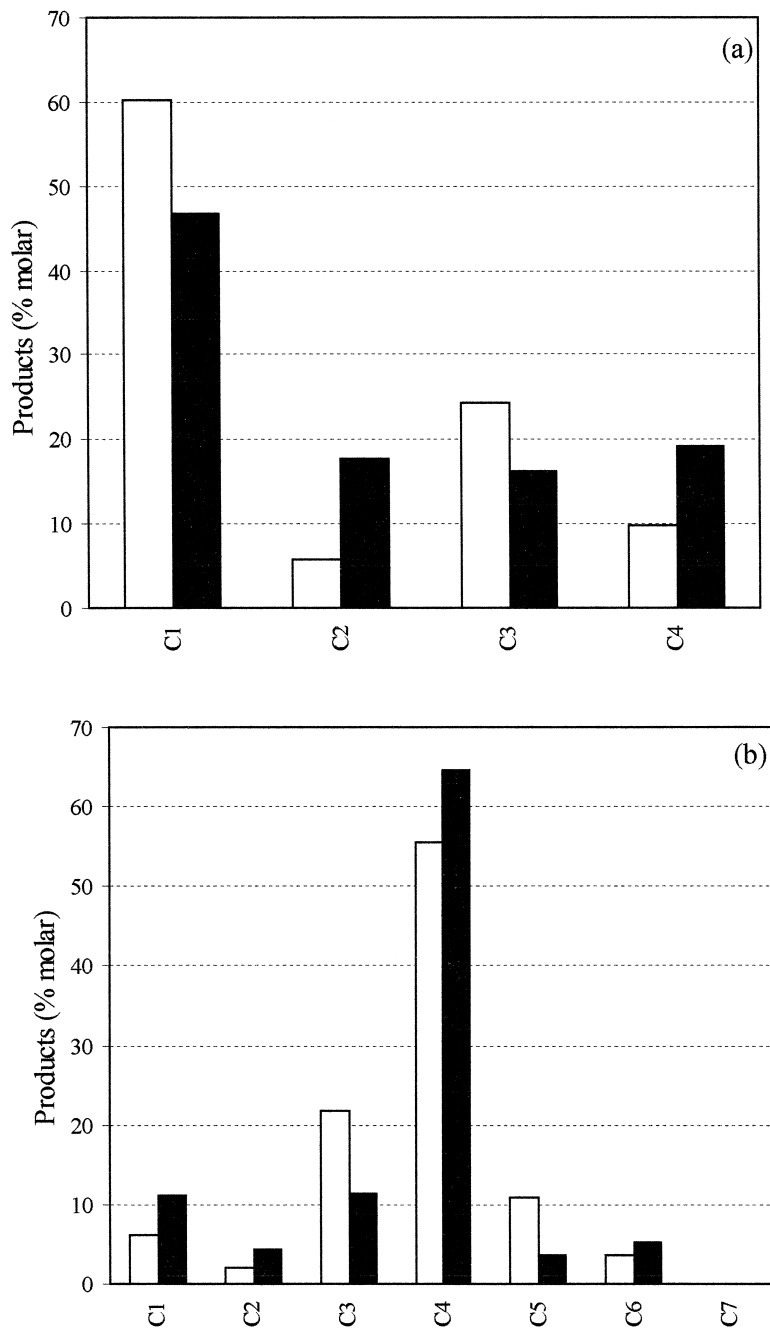


Fig. 2. Molar distribution of products (%) as a function of the number of carbon atoms, at the beginning ( $\square$ :  $t = 6$  min) and at the end ( $\blacksquare$ :  $t = 60$  min) of the catalytic experiments for the following transformations: (a) ethene over HNaY91; (b) ethene over HNaUSY83; (c) propene over NaY; (d) propene over HNaUSY3; (e) 1-butene (excluding linear isomerisation) over HNaY87; (f) 1-butene (excluding linear isomerisation) over HNaUSY71; (g) *iso*-butene over HNaY87 and (h) *iso*-butene over USHY.

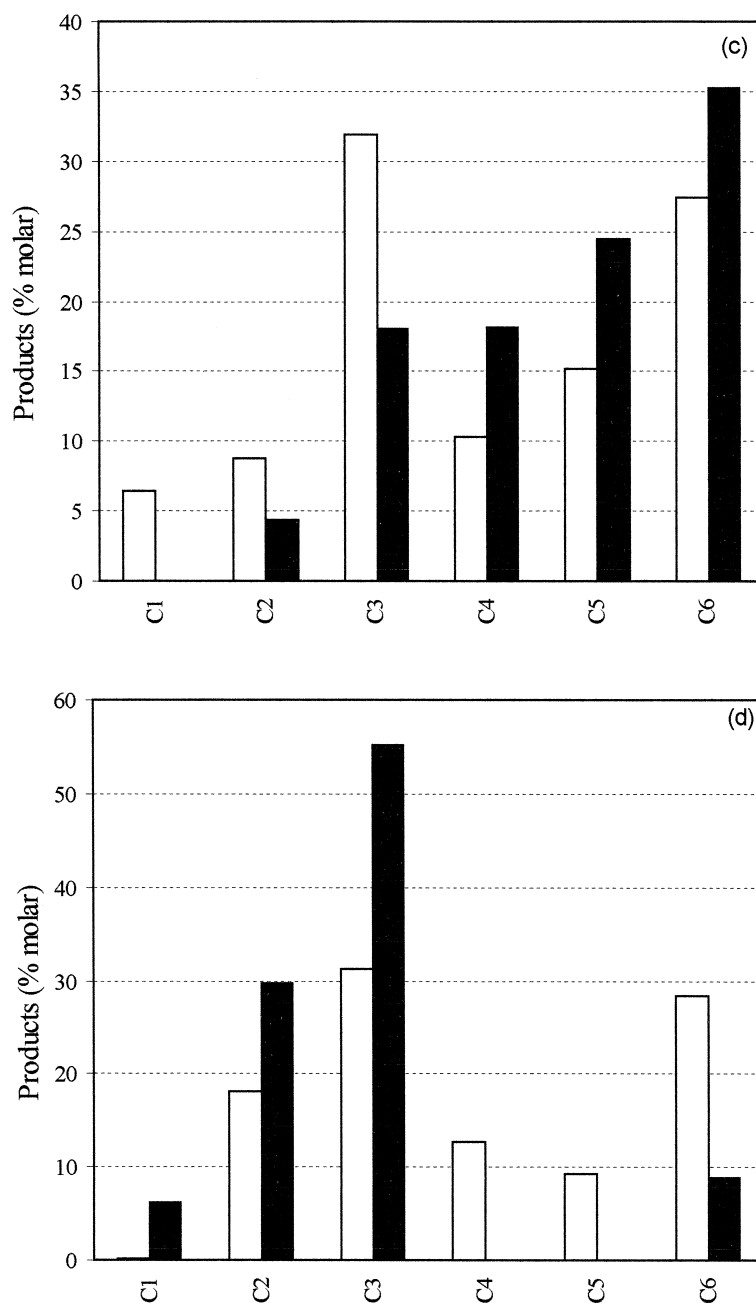


Fig. 2 (continued).

there is a significant decrease in C4 products and an increase in C8 products fraction, with time-on-stream. This seems to indicate that a significant portion of the C4 products are produced by scission reactions of oligomers formed,

competing with the direct isomerization reaction of *iso*-butene, which should not be very quick since it involves the conversion of a very stable tertiary carbocation into a secondary one.

It has been reported in the literature that

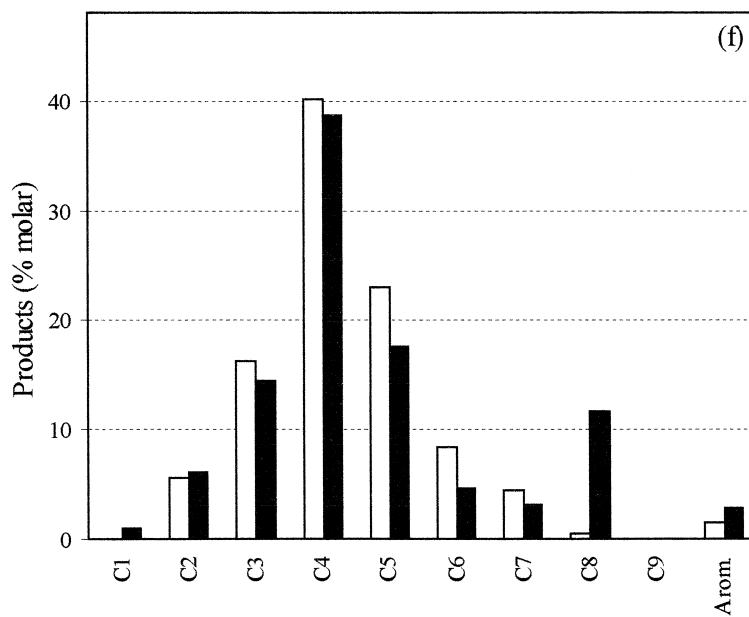
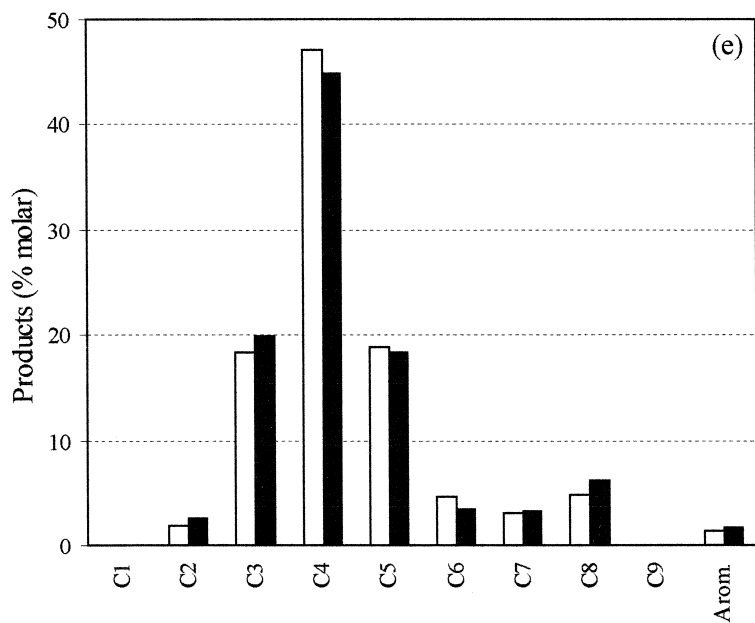


Fig. 2 (continued).

some catalysts (MCM-22 and ZSM-23) lead to the same molar distribution of products regardless of the fact that 1-butene or *iso*-butene are used as reactants, under the same experimental conditions [5,6]. However, there are other zeolites, such as borosilicate [21], over

which *n*-butenes and *iso*-butene present very different product distribution.

For the catalysts under study in this work, the molar distribution of products using 1-butene is clearly different from the one obtained with *iso*-butene.

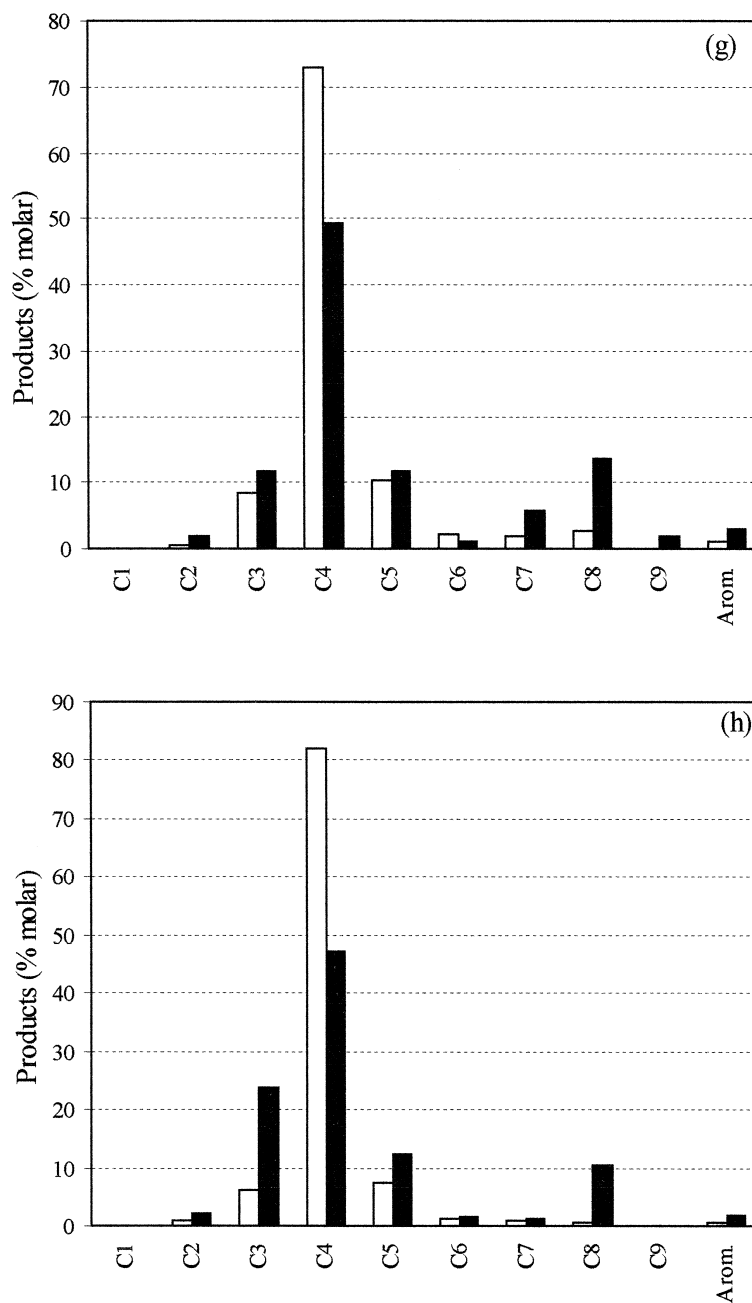


Fig. 2 (continued).

### 3.3. Influence of the number of acid sites on the catalytic activity

In Fig. 3, the global catalytic activity at the beginning of the transformation of olefins over the catalysts of HNaY and HNaUSY series is

plotted as a function of the number of acid sites per unit cell.

The catalytic activity of olefins transformation over the catalysts under study follows the expected order: ethene < propene < 1-butene < *iso*-butene. This is the behaviour expected for



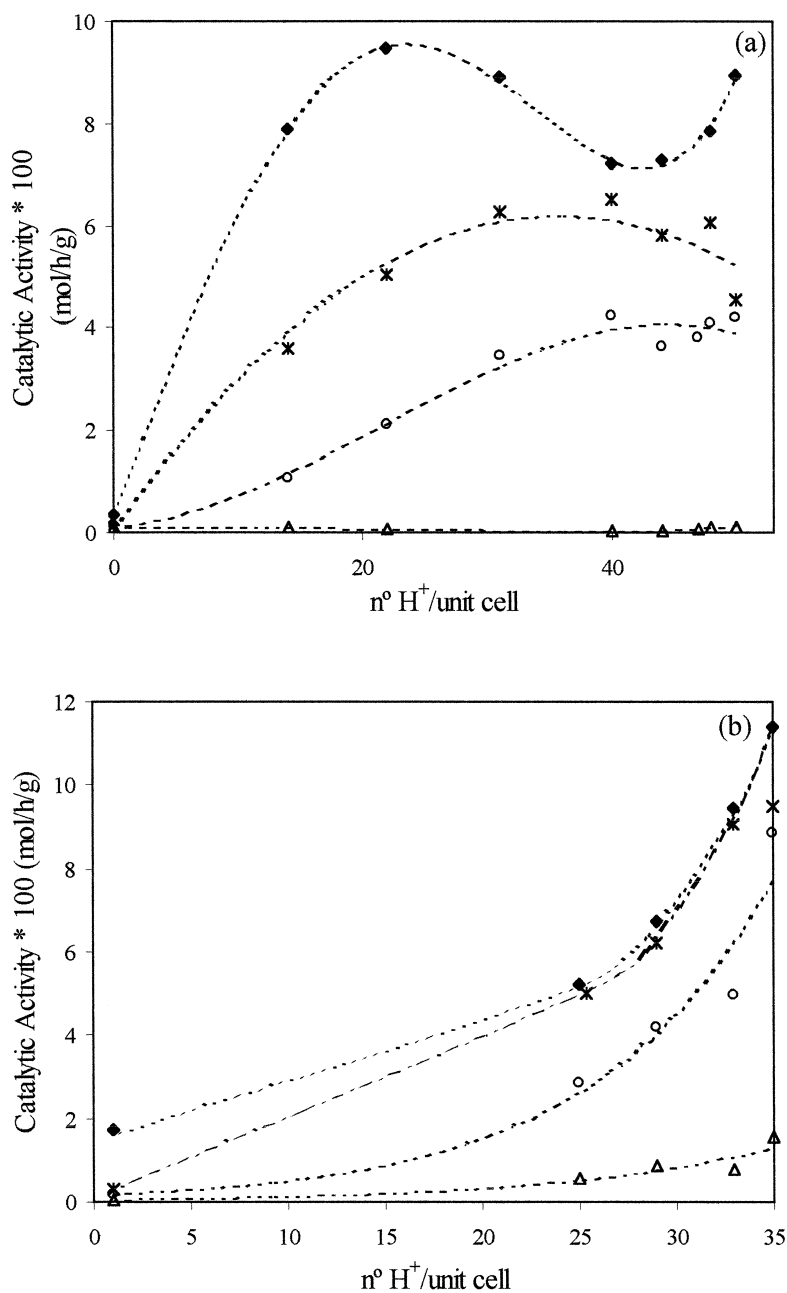


Fig. 3. Catalytic activities at the beginning of transformation reactions ( $t = 6$  min) of ( $\Delta$ ) ethene, ( $\circ$ ) propene, ( $*$ ) 1-butene (excluding linear isomerization) and ( $\blacklozenge$ ) *iso*-butene over the zeolites belonging to the (a) HNaY series and (b) HNaUSY series, as a function of the number of acid sites per unit cell.

the catalytic activity over acid catalysts since as the carbocation formation becomes easier because they are more stable, the reactivity of the respective olefin increases [22].

The catalytic activity of the zeolites belonging to HNaUSY series increases approximately in an exponential way with the number of acid sites per unit cell for each of the olefins. In fact,

when the number of acid sites increases, their strength also increases, leading to a rise in the transformation rate of the olefins. Nevertheless, it is curious to observe that there is no significant difference in reactivity between 1-butene

and *iso*-butene over the zeolites of this series, although it is clear that *iso*-butene produces very stable tertiary carbocations more easily.

Relative to the HNaY series of catalysts, there is a more complex trend in the catalytic

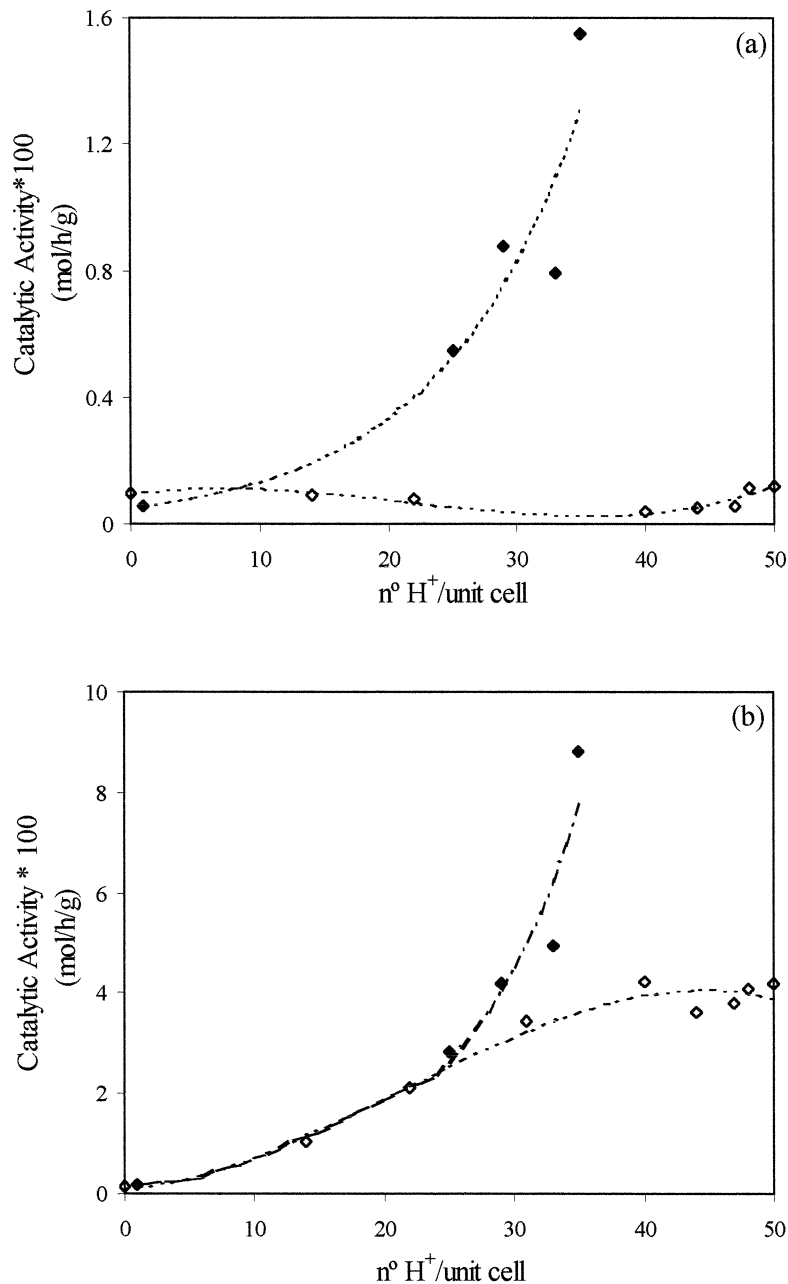


Fig. 4. Catalytic activity at the beginning of the transformation reactions ( $t = 6$  min) of (a) ethene, (b) propene, (c) 1-butene (excluding linear isomerization) and (d) *iso*-butene as a function of the number of acid sites, over the catalysts belonging to the (◇) HNaY series and (◆) HNaUSY series.

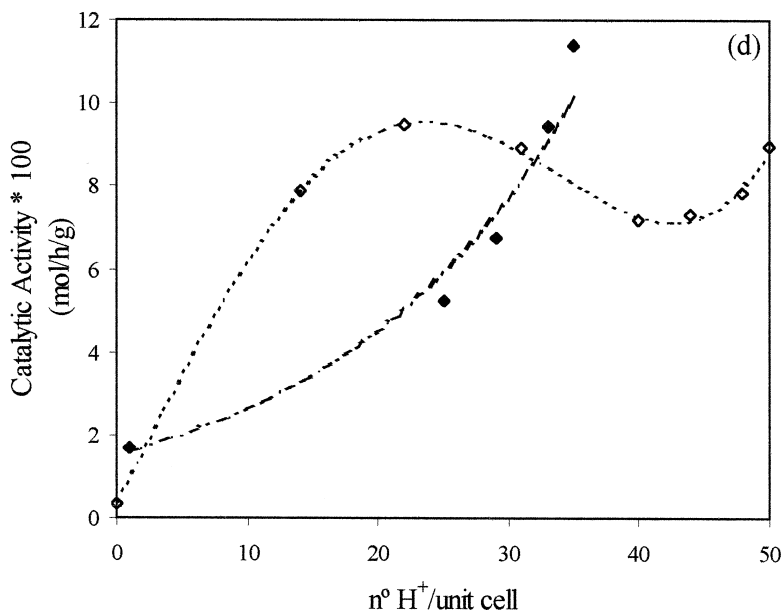
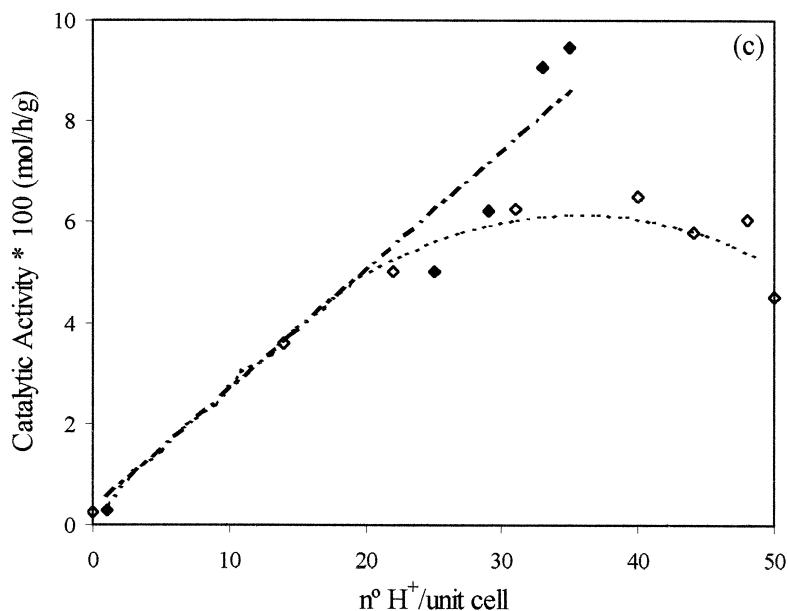


Fig. 4 (continued).

activity values as a function of the number of acid sites per unit cell and particularly, a decrease in the transformation rate for high content of protons is observed. This behaviour could not be related with acid catalysis alone. In fact, one could speculate that over these zeolites, in which the acidity is not so strong, there could

be a synergetic interaction between the Brønsted acid sites and the residual Na<sup>+</sup> cations or other types of sites that could interfere with the processes.

Some other authors have already referred that the Na<sup>+</sup> cations can be active sites in adsorption and oligomerization of olefins, par-

ticularly in the transformation of 1-butene [23–25].

To completely understand the catalytic activity as a function of the number of protonic sites,

in the zeolites of HNaY series for these olefins transformation, additional work will have to be done to identify and quantify the additional effects that are observed.

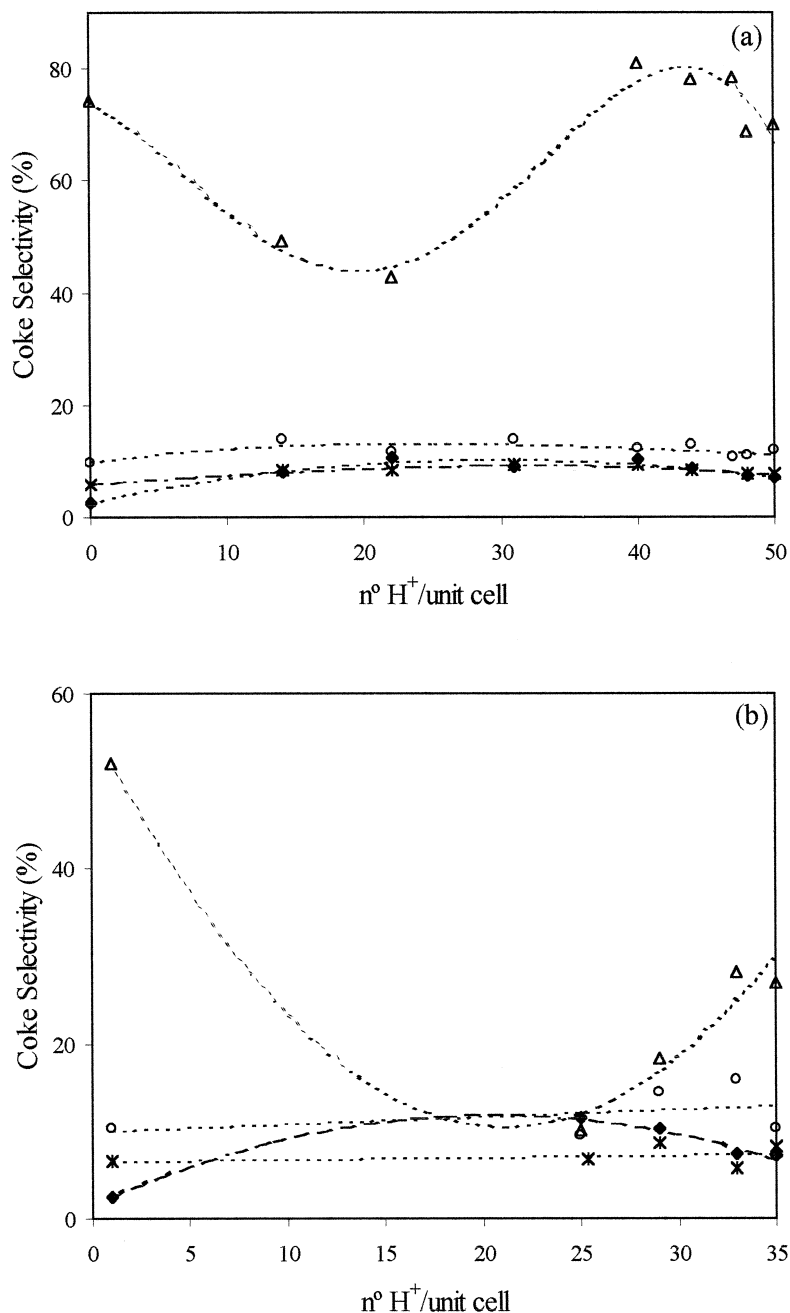


Fig. 5. Coke selectivity obtained in the catalytic experiments for ( $\Delta$ ) ethene, ( $\circ$ ) propene, ( $*$ ) 1-butene and ( $\blacklozenge$ ) *iso*-butene transformation, over the catalysts belonging to the (a) HNaY series and (b) HNaUSY series.

In Fig. 4, a comparison of the catalytic activity between the catalysts belonging to the two series is depicted.

When the number of acid sites per unit cell is low, the catalytic activity for ethene, propene and 1-butene transformation is similar in both series of catalysts that were used. Nevertheless, when the number of acid sites per unit cell increases, the catalytic activity of HNaUSY series of catalysts for these olefins transformation becomes much higher than the catalytic activity of HNaY series of catalysts. This is certainly due to the fact that the zeolites belonging to the HNaUSY series have a higher Si/Al ratio and have extra-frame cations,  $Al^{3+}$ , leading to stronger Brönsted acid sites.

Comparing the catalytic activity of both catalysts series for *iso*-butene transformation, one can observe a completely different behaviour relative to the others olefins used. Since it had already been seen that the catalytic activity trend, for the *iso*-butene transformation, as a function of protons content is similar to the others olefins over the HNaUSY series of catalysts, the behaviour of the HNaY series of catalysts seems to be very peculiar.

### 3.4. Influence of the number of acid sites on coke content

The total amount of reactant transformed into gas phase products ( $A_{\text{cumulative}}$ ) was estimated for all the catalytic experiments, as it is explained above. The total amount of reactant transformed into coke during all the reaction time was also estimated by determining the coke retained in the catalysts by the method described above. With these values, it is possible to compute the selectivity towards the coke formation by Eq. (2):

Coke selectivity

$$= \frac{n \text{ of reagent moles which give coke}}{A_{\text{cumulative}} + n \text{ of reagent moles which give coke}} * 100. \quad (2)$$

In Fig. 5, the coke selectivity values for the four olefins under study over the catalysts of

HNaY and HNaUSY series are plotted against protonic content.

The selectivity towards the coke formation is higher for ethene transformation than for the others olefins, and this difference is more significant for the catalysts with weaker acid sites.

## 4. Conclusions

Light olefins transformation over Y zeolite seems to follow a mechanism involving the formation of carbenium ions leading to the oligomerization. The oligomers will then undergo secondary reactions of scission, cyclization and aromatization.

The catalytic activity for olefin transformation, for each of the catalysts that was used, follows the expected order according to the facility of formation of relating carbocation: ethene < propene < 1-butene < *iso*-butene.

For HNaUSHY series, the increase of activity follows as expected the increase in number and strength of the acid sites of the catalysts.

For catalysts belonging to HNaY series, the results are somewhat different and a non-monotone trend for the catalytic activity as a function of the number of acid sites is observed. This is possibly related to the composition of these zeolites and is certainly not related to acid catalysis alone. A definitive explication of this behaviour demands additional work to be confirmed.

For all olefins under study, excluding *iso*-butene, there is an overlap in the curves of catalytic activity at the beginning of reaction as a function of number of protonic sites for both catalysts series. This indicates that for low density and weak acid strength, the structural differences between the two series of catalysts is not very significant.

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