

Effect of rare-earth nature on the basic properties of zeolite NaX containing occluded rare-earth species

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Abstract

The acid–base properties of a series of zeolite NaX samples, impregnated with several rare-earth nitrates (Ce, Nd, Eu, Dy, Er, Tm, Yb and Lu) and thermally treated under air, have been tested on the model reaction of 1-butene double bond position isomerization at different temperatures (200–300 °C).

The activity rises with the reaction temperature increase and the participation of the basic mechanism decreases, while that of the acidic process increases. At 250 °C, the initial catalytic activities do not present significant differences among the rare-earth series (0.5–1.5 mmol/(h g)) with the exception of Yb; in this case, the total activity is quite higher (11.5 mmol/(h g)). The basic character of the transformation, evaluated from the *cis/trans*-2-butene ratio, is superior for part of the impregnated samples than for the rare-earth-free NaX sample, which presents a value of 0.94 for this parameter. The nature of the rare earth does not induce important changes in the basicity among the series, the *cis/trans* ratio decreasing from 1.9 (Ce) to 1.3 (Lu), with the same exception of the Yb impregnated sample (*cis/trans* = 2.4); the basic character of this sample is higher than the other one. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

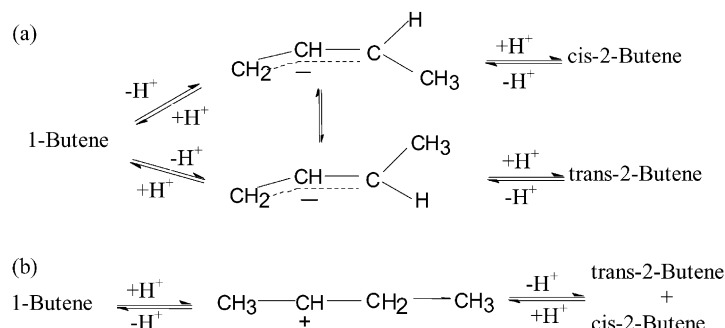
The use of heterogeneous basic catalysts in organic synthesis and industrial processes has been increased recently [1]. Despite this some of the most common features of zeolite materials are related to the possibility of generation of high strength acid sites; zeolites can also present some basic character [2,3]. In fact, alkali metal ion exchanged zeolites presents relatively weak basic sites, which are the framework oxygens bearing the negative charge; the compensating cation inductive effect is dependent on the cation nature and

can induce some modifications in the basic character of the oxygen [3,4]. Another possibility that results in higher basic strength is to impregnate the zeolite pores with particles of strongly basic materials as alkaline oxides [5–8], alkaline earth oxides [9,10]; in these cases, the effectiveness of shape selectivity in base-catalyzed reactions is another source of interest [11].

Alkaline earth oxides possess strong basic sites, presenting a high ability to abstract a H⁺ from an allylic position [2]. Rare-earth oxides have been tested less extensively than alkaline earth oxides for the promotion of basic catalyzed transformations [2].

The objective of this paper is not to prepare zeolite samples with interesting absolute basic properties when compared to other zeolite-based basic

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Scheme 1. 1-Butene double bond migration via: (a) basic and (b) acidic mechanisms.

catalysts, but to evaluate the influence of the rare-earth nature among the lanthanide series, in the basic properties of NaX zeolite samples containing rare-earth oxide species dispersed within the porous network. This is a contribution to the study of the behavior of compounds containing block f elements, searching the understanding of the influence of the electronic configuration, size, electronegativity, etc. particularly among the lanthanide series in that chemical behavior. The basicity is evaluated by testing these samples on the double bond migration of 1-butene.

Double bond position isomerization of 1-butene to 2-butene is one of the most extensively used model reaction for basicity evaluation [2]. This reaction can proceed both through an acidic or a basic mechanism, as illustrated in Scheme 1. In the basic mechanism, the transformation is initiated by the abstraction of an allylic hydrogen by the basic site to form *cis*- or *trans* allyl anion forms which are stabilized by the cations present on the zeolite surface; being the allyl *cis* form more stable than the *trans* form, the *cis*-2-butene is predominantly formed at the initial stage of the reaction. In the acidic process, the initial protonation of the double bond generates carbenium cations that can be transformed indistinctly to *cis*- or *trans*-2-butene. The ratio *cis/trans* of the 2-butene products expresses the effectiveness of the basic versus acidic catalytic ways.

2. Experimental

The sodium form of X zeolite, NaX (13X) was obtained from Aldrich. Modified samples of this zeolite were obtained by impregnation to the incipient

wetness point through slow addition, under constant mixing action, of each rare-earth nitrate aqueous solution from the series: Ce, Nd, Eu, Dy, Er, Tm, Yb and Lu. The salt solutions concentrations were calculated so that the rare earth loadings lie between 1 and 4 rare-earth species per zeolite supercavity. After impregnation, the samples were dried at 100 °C.

The nitrate salts, occluded inside the zeolite porosity, were then decomposed by calcination of the impregnated samples at 500 °C for 8 h under a flow of dry air with a slow heating rate in order to generate basic rare-earth oxide species [12]. This thermal treatment did not induce a collapse of the zeolite structure, as concluded from the X-ray diffraction characterization of the calcined samples; the crystallinity level of all the impregnated and thermally treated samples is quite similar.

Previous to the reaction, each zeolite sample was submitted to an in situ pre-treatment at 450 °C for 12 h under a flow of dry nitrogen. The samples mass ranged from 0.05 to 0.3 g so that low and similar levels of conversion are obtained lower than 10%. The activity was obtained from the calculation: activity = $(F_b \chi / W)$, where F_b is the molar debit of 1-butene feed to the reactor, χ the conversion and W the mass of catalyst.

The 1-butene isomerization was carried out in a fixed bed, vertical, down flow tubular reactor, with an online gas chromatograph at 200, 250 and 300 °C. The reagent was diluted in nitrogen with partial pressure of 0.1 atm nitrogen flow of 3.6 l/h and the total pressure was 1 atm. Periodically, a sample of the reactor effluent was analyzed in the gas chromatograph using a 50 m × 0.32 mm ID fused-silica plot Al₂O₃ deactivated with KCl.

3. Results and discussion

3.1. Rare earth loading

Fig. 1(a) and (b) presents the 1-butene isomerization activity and the 2-butene *cis/trans* ratio, respectively, for the samples impregnated with 1, 2 and 4 species of Yb per zeolite supercavity (Yb–NaX(1, 2 and 4)), as a function of time-on-stream at 250 °C. Both the activity and the *cis/trans* parameter are higher for the sample with the four rare-earth species per supercavity loading, clearly expressing higher basicity for this sample than for the other Yb loadings. This loading was

chosen for the study of the rare-earth nature influence on the resulting basicity.

Considering that Yb oxide clusters are the basic active sites for the reaction and more basic than the framework zeolite oxygen, increasing the amount of oxide clusters increases the activity and the *cis/trans* ratio. In the most active sample, the oxide clusters will be poisoned more rapidly decreasing their contribution to activity and *cis/trans* ratio along time-on-stream; it is deactivated more rapidly and the *cis/trans* ratio becomes close to 1. Only 2-butene products were detected for all the catalytic tests at 200 and 250 °C.

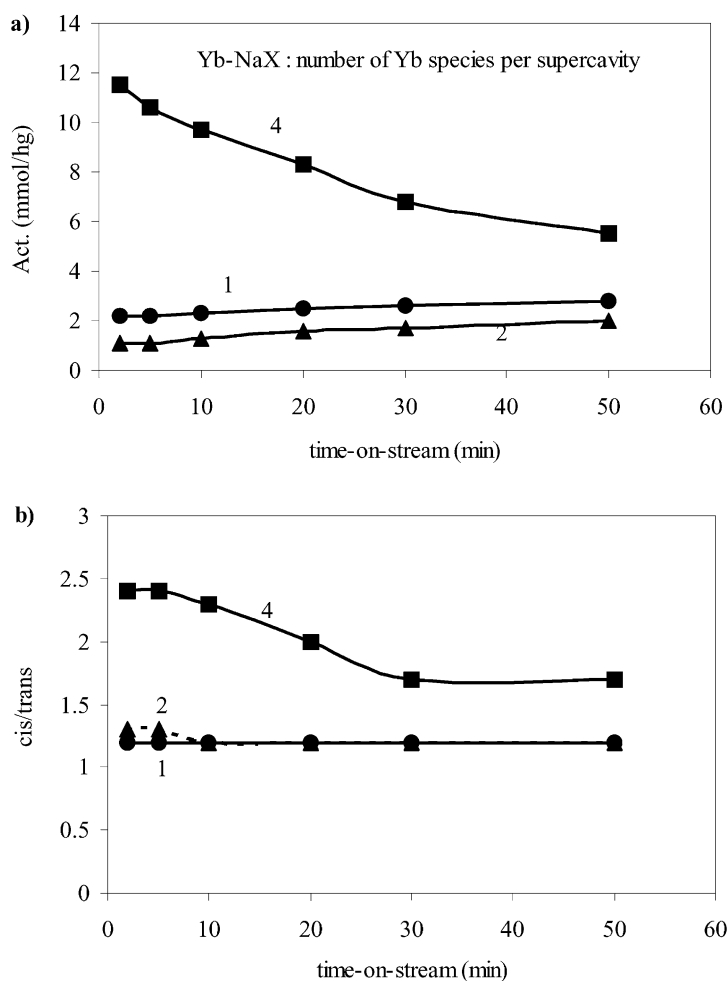


Fig. 1. Activity of the NaX samples impregnated with Yb (a), and *cis/trans* ratio in the isomerized 2-butene products (b), as a function of time-on-stream for different rare earth loadings (1, 2 and 4 Yb species per supercavity) at 250 °C.

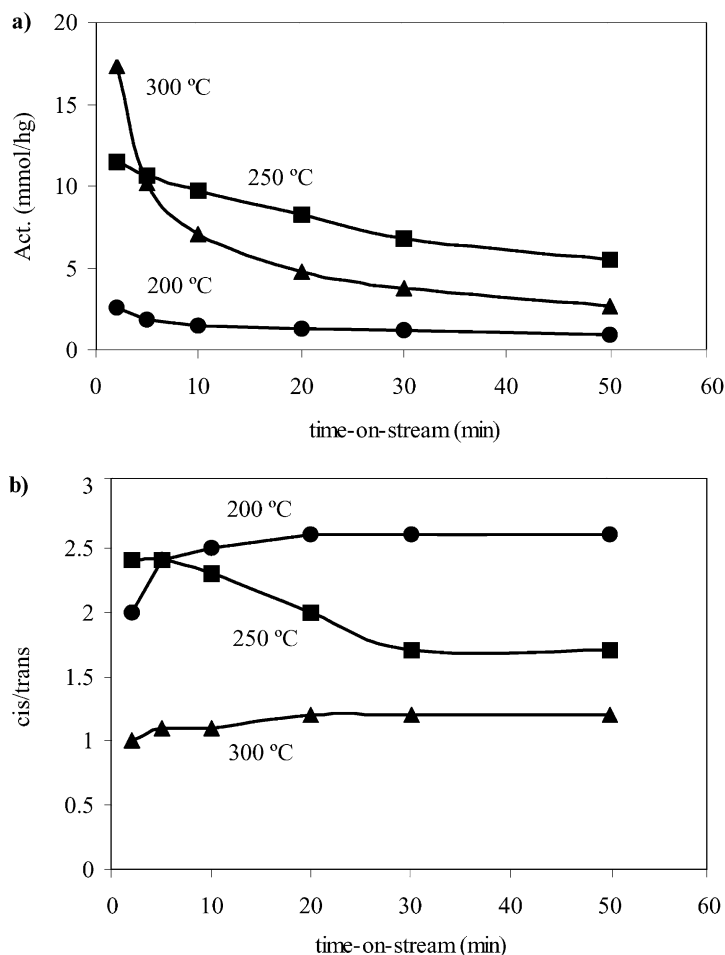


Fig. 2. Isomerization activity of Yb–NaX(4) (a), and *cis/trans* 2-butene ratio (b), for different reaction temperatures.

3.2. Reaction temperature

Higher reaction temperature induces an increase in the isomerization activity simultaneously with a reduction in the *cis/trans* parameter (Fig. 2), which reaches values close to unity for 300 °C, thus expressing a reduction in the contribution of the basic mechanism. At 300 °C, the higher proximity to the equilibrium will contribute to the observed decrease in the *cis/trans* ratio relative to lower temperatures; the deactivation with time-on-stream is also more important at this temperature, probably as a result of active sites poisoning by butene oligomers. The chosen temperature for the continuation of the study was 250 °C.

3.3. Rare-earth nature

Fig. 3(a) and (b) presents the dependence of the initial isomerization activity and of the initial *cis/trans* ratio for the 2-butene products, respectively, on the rare-earth nature. At 250 °C, there is not a clearly defined trend in the influence of the rare-earth nature on the activity; only slight oscillations are observed among the studied series, with the exception of the sample impregnated with Yb, which is much more active than the other one. This sample also presents the highest value for the *cis/trans* parameter.

The activity of the non-impregnated NaX zeolite (22 mmol/(h g)) is higher than all the activities

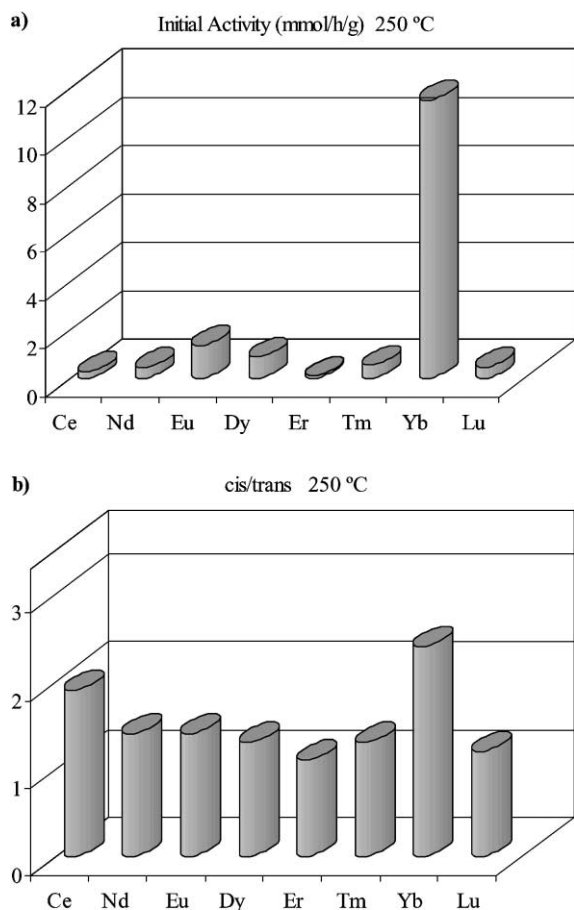


Fig. 3. Initial activity (a), and initial *cis/trans*-2-butene ratio (b), for the impregnated samples with the different rare-earth species at 250 °C for loading level of four species per supercavity.

presented in Fig. 3(a) for the impregnated samples as a probable consequence of an increased reactant transport limitations inside the porous network of the modified zeolite samples due to the presence of the extra-framework species. Nevertheless, the basic character of the transformation, expressed in the *cis/trans* ratio of the products, is higher for some of the impregnated samples than for NaX; a value close to 1 was obtained in the isomerization over the rare-earth-free NaX zeolite.

In the preparation procedure, it is possible that some ion exchange occurred leading to the presence of some trivalent rare-earth cations as compensating cations; these species are able to hydrolyze water molecules producing some weak Brönsted acidity [13–15],

additionally to the already existing weak acidity from the silanol groups. This represents the acid contribution to the reaction, while the basic contribution will result essentially from the occluded species. The catalytic behavior in the double bond isomerization will then result from the balance of the participation of the acidic and basic mechanisms, which will be expressed in the *cis/trans* ratio of the products, higher than one values corresponding to some participation of the basic process.

The impregnated samples for which values of *cis/trans* ratio close to 1 were obtained present quite low activities, when compared to the Yb-modified sample; the only products are the *cis*- and *trans*-2-butene, as for all the samples tested at 250 °C, which means that the final acidity is quite weak. In fact, this reaction is very sensible also to the acidity and a skeletal 1-butene isomerization is usually observed when a moderate acidity is produced [16,17].

Several factors are important in the definition of the resulting basicity of the impregnated samples, such as the dimensions and localization of the rare-earth oxide, the adsorption interaction between the zeolite heterogeneous negatively charged surface and the rare-earth species, geometric factors, etc. Anyway a certainly important property in the determination of the resulting basicity among the series of the studied impregnated samples is the rare earth electronegativity, since it will significantly contribute to the negative charge density on the oxygen of the oxide and, thus, to the ability to abstract the allylic hydrogen of 1-butene. Considering the electronegativity values among the rare-earth series obtained from Sargent–Welch periodic table of the elements, presented in Fig. 4, it is clearly detached the lower value of this property for Yb; this can be a positive contribution to the corresponding higher Lewis basic strength of the Yb oxide, which will be the important source of basicity in the impregnated NaX sample. A similar qualitative correlation between the decreasing basicity of the bulk alkaline earth oxides BaO > SrO > CaO > MgO [2] and the corresponding alkaline earth increasing electronegativity can be observed.

3.4. Pure rare-earth oxide

The results obtained with the pure Yb oxide (Yb₂O₃) are compared to those of the most basic

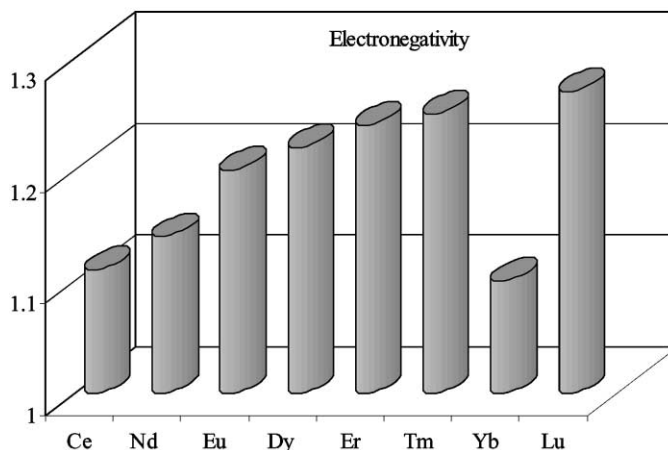


Fig. 4. Electronegativity of the tested rare earth elements.

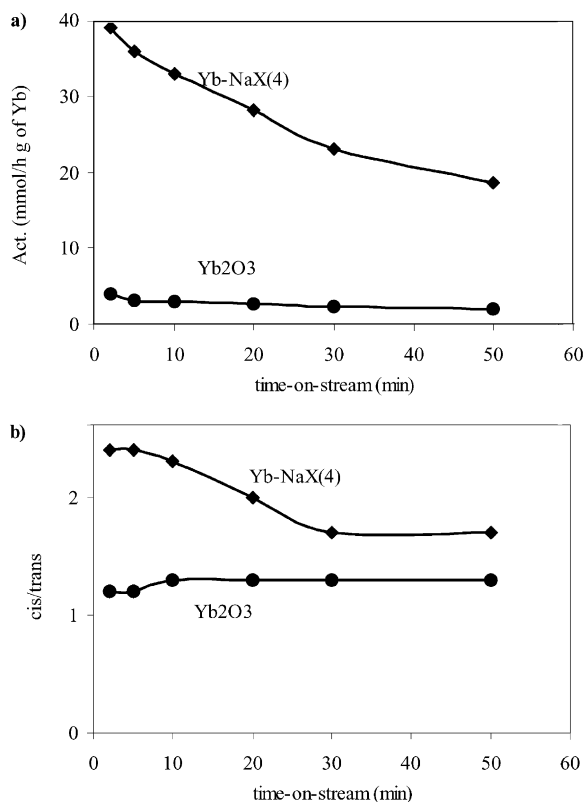


Fig. 5. Activity expressed per mass of Yb (a), and *cis/trans*-2-butene ratio (b), of NaX impregnated with 4 Yb species per supercavity and pure Yb₂O₃ at 250 °C.

sample, the NaX impregnated with Yb, in Fig. 5. Expressing the activities per mass of rare earth, the sample Yb–NaX(4) is much more active than the pure oxide, and the *cis/trans* ratio is also higher for the zeolite impregnated sample. The same kind of differences in the 1-butene isomerization activity and *cis/trans* ratio were observed in a related study performed with CsX zeolite containing occluded CsO_x species and with the pure oxide, Cs₂O, probably expressing different nature between the occluded species dispersed inside the porosity network and the bulk oxide [7].

4. Conclusions

The catalytic activities of the prepared samples do not present significant differences among the rare-earth series with the exception of Yb impregnated one; in this case, the total activity is quite higher. Considering the selectivity of the 1-butene transformation, the nature of the rare earth does not induce important changes in the basicity among the series, with the same exception holding for the Yb impregnated sample; the basic character of this sample is clearly higher. The basic character of the transformation for part of the impregnated samples is higher than that for the rare-earth-free NaX sample.

Acknowledgements

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