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The influence on selectivity of the aluminum content in the matrix of FCC catalysts

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Abstract

The influence that both the type of matrix and the interaction between zeolite and matrix have on the selectivity of FCC catalysts was studied by means of the conversion of cyclohexene at 300 °C on a large number of samples in which the matrix was changed. Silica/alumina matrices had 0, 12 and 25% of alumina, and catalysts were subjected to steaming of varying severity followed by acid extraction in some samples to remove extraframework aluminum species (EFAl). Resulting catalysts were characterized by various techniques. It was confirmed that hydrogen transfer does not depend directly on the type of coordination of the aluminum atoms in the sample, but rather on the density of paired sites in the zeolite component. It was possible to define the selectivity of reaction pathways (S_{RP}) as an index to describe the relative importance of the processes of desorption via hydride transfer to yield cyclohexane against retention of the cation cyclohexil via isomerization and further reaction. A high value of S_{RP} would mean that a given catalyst has a lower ability to retain adsorbed species that can be subjected to additional reactions like, in this particular reaction, isomerization and further proton transfer to the catalyst surface, or cracking. The index was shown to increase whereas the relative amount of octahedral aluminum atoms decreased, a fact that can be associated to the formation of a new silica/alumina phase. Such phase would be formed by means of the reaction of aluminum extracted from the zeolite upon steaming and silica present in the matrix.

Keywords: Cracking; Selectivity; Matrix; FCC; Cyclohexene; Y zeolite

1. Introduction

Product selectivity in the FCC process is the main topic to be understood and controlled in order to increase process benefits and comply with mandatory regulations about the composition of most important fuels [1,2]. In fact, even though the process technology can be considered established, it is certainly possible to optimize the catalysts, the reactor design or the operative approaches. The catalyst used in FCC is a very complex composite, with the main component, the Y zeolite, deposited on a matrix, binders and various additives being also present [3]. Matrices are of different types and they can be classified according to different criteria: the chemical composition, the origin of their components (synthetic, semi-synthetic or natural), or the catalytic role they play (inactive, or with low, medium or high activity). Most

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commercial catalysts have semi-synthetic matrices, consisting of a synthetic compound, usually amorphous silica, alumina or silica/alumina, and a natural component, usually clay. Inactive matrices often consist of amorphous silica and clay. In active matrices, the catalytically active component is usually alumina, silica/alumina or thermally and chemically modified clays. When amorphous silica/alumina is one of the components of an active matrix, the physical and catalytic properties of the catalyst are strongly affected by the composition and preparation conditions [4].

It is generally considered [3], that matrices play a very important role in supporting the Y zeolite, being also a carrier of heat from the regenerator to the riser reactor. Specially in the cracking of heavy feedstocks, matrices are also assumed to be important in providing a diffusion medium to reactant molecules and also performing as a precracking component [5–7].

However, not much has been published regarding the true role of the matrix in FCC, and particularly its impact on process selectivity. Cheng and Rajagopalan [8], and Otterstedt et al. [9,10], studied the activity and selectivity of silica/alumina matrices of different compositions in gas oil cracking. These samples were subjected to hydrothermal treatment that leads to different aluminum atoms' coordination: tetrahedral, octahedral and pentacoordinated, their relative amounts depending on the conditions of the treatment. Activity was observed to increase with aluminum content, while no particular correlation was found with the coordination of the aluminum atoms [8], suggesting that aluminum other than tetrahedral would be active as well. The existence of active aluminum atoms in the matrix, then, might also have consequences on other significant reactions occurring in FCC, like those of hydrogen transfer.

Another important issue concerning the role of the matrix is the potential interaction between the silica thereof and the aluminum species formed during dealumination of the zeolite due to the severe conditions of the riser– regenerator system. In that sense, there seems to be evidences of the formation of a new silica/alumina phase between them [11–13].

It is the objective of this work to study the influence of the composition of the matrix in FCC catalysts, as well as changes and interactions associated to the dealumination of the zeolitic component, on the catalytic performance, particularly on reaction selectivity. FCC catalysts prepared by spray drying, with matrices having different aluminum amounts and subjected to different dealumination and/or extraction treatments, were evaluated by means of the conversion of cyclohexene in a Riser Simulator reactor. This reaction is a very sensitive test when used under an optimized approach [14].

2. Experimental

The silica/alumina matrices, containing various amounts of Al_2O_3, were prepared based on the method described in Magee and Blazek [15], with minor modifications, using sodium silicate as the silica source and aluminum sulfate as the aluminum source. The Y zeolite was prepared according to [16] and calcined at 550 °C for 1 h to generate ultrastable Y zeolite (USY). Portions of this batch were extracted with 25% sulfuric acid for 1 h at 70 °C to remove extraframework aluminum species (EFAl) and to produce USY-A zeolite. The observed framework Si/Al ratio indicated that this acid treatment did not attack the zeolite structure. The catalysts were then prepared by adding 30% USY and USY-A zeolite on the three different silica/alumina matrices containing 0% Al_2O_3 (Series A, no zeolite; Series A1, USY; and Series A2, USY-A), 12% Al_2O_3 (Series B, no zeolite; Series B1, USY; and Series B2, USY-A) and 25% Al_2O_3 (Series C, no zeolite; Series C1, USY; and Series C2, USY-A). The catalysts were then spray dried and thoroughly washed with $(NH4)_2SO_4$ and NH_4OH to remove sodium and sulfate ions, and with decationized water until free of chloride ion; calcination was then performed at 550 °C during 4 h. Finally, the catalysts were dealuminated by steaming in a fluidized bed reactor with 100% steam at 788 °C during 1, 3 and 5 h, while other samples were kept unmodified. The catalysts containing USY-A were again extracted with acid to remove extraframework aluminum species. In this way, 30 different samples were produced. The samples were named according to *Xx-y*, where *Xx* indicates the series name (*X*, matrix; *x*, zeolite type (1: USY, 2: USY-A)), and *y* indicates the steaming time in hours. The physical properties of the catalysts were determined by means of nitrogen adsorption isotherms on a Micromeritics Accusorb 2100 apparatus and conventional techniques. The zeolite unit cell sizes were determined by

Table 1
Catalyst properties

Catalyst	UCS (nm)[a]	Framework mass Si/Al ratio[b]	Total mass Si/Al ratio[c]	Al_2O_3 Content (%)[d]	Specific surface area ($m^2\,g^{-1}$)[e]	Micropore volume ($cm^3\,g^{-1}$)[f]
A	–	–	–	0.00	387	0.0070
B	–	–	7.69	10.28	394	0.0040
C	–	–	2.94	23.07	390	0.0000
A1	2.454	3.762	26.44	3.23	344	0.0706
A1-1	2.425	26.776	26.44	3.23	193	0.0489
A1-3	2.424	32.331	26.44	3.23	192	0.0464
A1-5	2.423	40.664	26.44	3.23	156	0.0444
B1	2.454	3.762	5.83	13.13	378	0.0723
B1-1	2.428	17.517	5.83	13.13	142	0.0469
B1-3	2.427	19.832	5.83	13.13	127	0.0410
B1-5	2.427	19.832	5.83	13.13	115	0.0472
C1	2.454	3.762	2.30	27.71	374	0.0497
C1-1	2.428	17.517	2.30	27.71	166	0.0497
C1-3	2.427	19.832	2.30	27.71	148	0.0468
C1-5	2.427	19.832	2.30	27.71	139	0.0453
A2	2.452	4.050	29.51	2.90	402	0.0659
A2-1	2.428	17.517	109.30	0.80	230	0.0497
A2-3	2.426	22.808	87.27	1.00	189	0.0460
A2-5	2.428	17.517	54.21	1.60	194	0.0476
B2	2.452	4.050	6.86	11.39	386	0.0753
B2-1	2.430	14.151	–	–	238	0.0648
B2-3	2.429	15.666	–	–	177	0.0500
B2-5	2.429	15.666	–	–	161	0.0521
C2	2.452	4.050	2.8	23.94	423	0.0612
C2-1	2.430	14.151	–	–	265	0.0656
C2-3	2.428	17.517	–	–	289	0.0650
C2-5	2.427	19.832	–	–	218	0.0592
USY-A	2.452	4.050	3.21	21.52	–	–
USY	2.454	3.762	2.96	22.97	–	–

[a] ASTM D-3942-85.
[b] Breck, 1974 [17].
[c] X-ray fluorescence.
[d] Calculated from total Si/Al.
[e] BET method [18], from N_2 isotherms.
[f] *t*-curve method [18], from N_2 isotherms.

means of the ASTM D-3942-85 standard method, using a Shimadzu XD-1 apparatus. The catalysts were also analyzed by ^{27}Al MAS-NMR spectroscopy on a Varian VRX 300 equipment. The chemical composition of the various samples was determined by means of X-ray fluorescence (XRF, Philips PW-1480). The properties of the resulting catalysts are summarized in Table 1.

The relative amount of extraframework aluminum species (EFAl) was calculated in the following way:

$$\mathrm{EFAl} = \frac{1 - \mathrm{Al_F} - \mathrm{Al_M}}{1 - \mathrm{Al_M}}$$

where $\mathrm{Al_F}$ is the amount of aluminum atoms in the zeolite framework (calculated by means of the Breck's relationship [17]), and $\mathrm{Al_M}$ is the amount of aluminum atoms in the matrix (calculated with XRF data), both relative to the total amount of aluminum atoms.

The experiments of cyclohexene conversion were performed in a batch, internal recirculation fluidized bed reactor named Riser Simulator, which reproduces the conditions of commercial FCC units. The isothermal laboratory reactor unit has been described thoroughly elsewhere [19,20]. Runs were performed at 300 °C under short contact times between 1.5 and 12 s, the mass of catalyst being 0.8 g and the amount of reactant injected 0.2 ml. Cyclohexene (Fluka, > 99%) was used without further purification. The reaction products were analyzed by on-line gas chromatography, using a 60 m long, 0.25 mm i.d., methylsilicone capillary column. The mass balances in the experiments closed to more than 96% in all the cases. Results were evaluated following the approach developed by de la Puente and Sedran [14], using yield curves (yield was defined as the ratio between the masses of individual or group hydrocarbons and the initial mass of reactant) to assess the indexes that are described below.

3. Results and discussion

It can be seen in Table 1 that the starting unit cell size in the zeolite component of catalysts that contain USY and USY-A are essentially the same (2.452 and 2.454 nm, respectively), and the variations due to steaming are typical for this type of catalysts. Properties will be considered in the text in relation to the catalytic behavior of the various samples.

The conversion of cyclohexene was shown to be adequate to evaluate the properties of cracking catalysts in relation to some reactions [21]. Particularly, by making use of a simple kinetic model and the definition of the index named i_{HT}, that relates the most important reactions occurring on the methyl cyclopentyl ion in the reaction network [14], it resulted to be very sensitive to evaluate the ability of FCC commercial catalysts in the promotion of hydrogen transfer reactions. The same approach was also used to study the influence of various rare earths on Y zeolite [22].

Conversion experiments (refer to Table 2, where the conversions at 9 s contact time are shown) showed that for the same zeolite (USY or USY-A), the activity of the base catalysts, i.e. without steaming, followed the order SiO_2 (series A1 and A2) < 12% Al_2O_3 (series B1 and B2) < 25% Al_2O_3 (series C1 and C2). That is in accordance with the matrix type; i.e. the higher the aluminum content, the more active the catalysts. Moreover, it can be seen that the extraction of extraframework species produced more active catalysts; indeed, catalysts prepared with zeolite USY-A were more active than their homologous based on USY (compare series A1 and A2, B1 and B2, C1 and C2). This difference could be attributed to the fact that the process of extraction in the series with USY-A zeolite (series A2 to C2) yields higher micropore volumes (or zeolitic surface area) than those of their homologous series with non extracted USY zeolite (series A1 to C1). For each of the series, based either on USY or extracted USY-A, the steam treatment decreased activity significantly, as a consequence of the dealumination process. Moreover, the effect of steaming on the activity of series of catalysts with the same matrix (homologous series) seems to be somewhat less important on extracted samples.

Typical curves of product yields versus reaction time are shown in Fig. 1 (for the case of catalyst

Table 2
Catalyst activity. Cyclohexene conversion (%) at 9 s contact time

Steaming time (h)	Catalyst series					
	USY			USY-A		
	A1	B1	C1	A2	B2	C2
0	42.0	43.4	54.0	44.9	55.2	56.2
1	20.8	18.8	22.8	24.1	21.5	26.1
3	13.6	12.4	15.2	17.5	16.7	28.7
5	9.7	12.1	13.7	13.4	15.0	23.5

T = 300 °C.

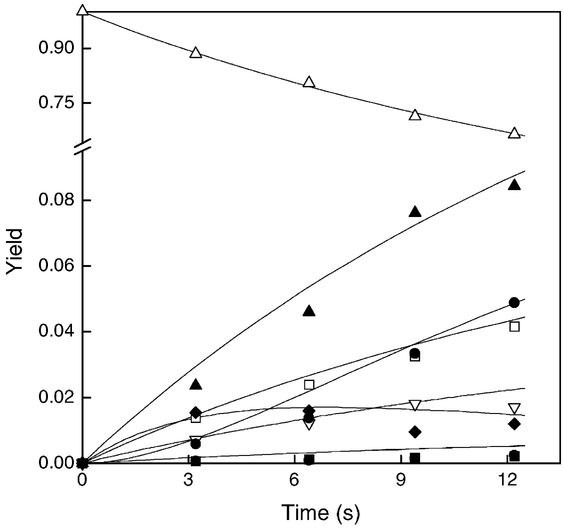

Fig. 1. Product yields and unconverted cyclohexene as a function of reaction time for catalyst C2-3. T: 300 °C. Symbols: MCPA, (▲); MCPE, (□); CHA, (▽); DIM, (●); C6DIE, (◆); Cr, (○); MCHA, (■); CHE, (△). Lines: model's response.

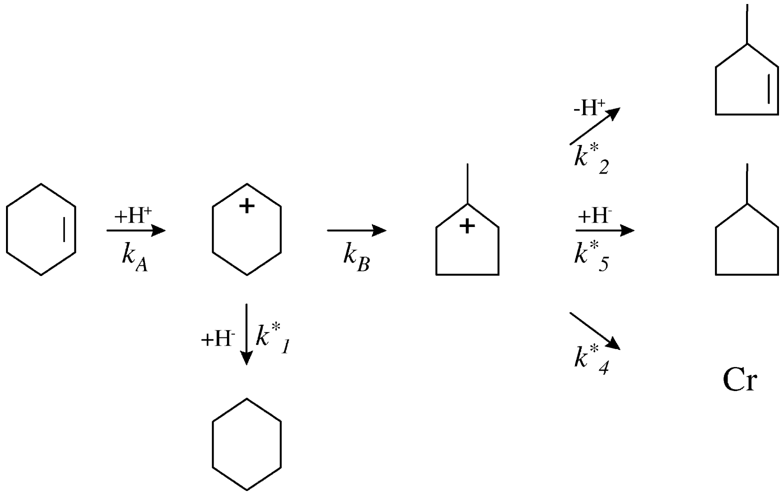

Fig. 2. Reaction scheme for cyclohexene conversion. Main branch of reaction.

C2-3) for the most important gas phase products: methylcyclopentane (MCPA), methylcyclopentenes (MCPE), cyclohexadienes (C6DIE), cyclohexane (CHA), dimeric products (DIM), and minor amounts of compounds with six or less carbon atoms per molecule (Cr), and methylcyclohexane (MCHA). The fraction of unconverted cyclohexene (CHE) is also included. For all the catalysts, these curves were qualitatively the same, differences being observed in the quantitative performances according to the catalysts properties, as it will be discussed later. The lines in the figure represent the corresponding model's response [14].

The index to assess catalysts' hydrogen transfer capabilities (i_{HT}) is defined below; it is the ratio between the kinetic constant for hydride transfer and the addition of those of proton transfer, cracking and hydride transfer, all occurring on the methyl cyclopentyl ion. This definition is based on the main branch (refer to Fig. 2) of the kinetic model described in [14], which is a simplified description of the reaction scheme for the formation of the products indicated. While it is recognized that there are other reaction pathways to form these products, the simplified scheme is used for the purpose of qualitative comparison among different catalysts and not for quantitative evaluation of the acid catalytic functions. It can also be easily shown that i_{HT} is fully equivalent to the slope of the curve of the yield of MCPA as a function of the total yield of MCPA, MCPE and Cr.

$$i_{\mathrm{HT}} = \frac{k_5^*}{k_2^* + k_4^* + k_5^*} = \frac{\mathrm{d}\,[\mathrm{MCPA}]}{\mathrm{d}\,[\mathrm{MCPE} + \mathrm{Cr} + \mathrm{MCPA}]} \quad (1)$$

The different values of the index can be analyzed in order to study the influence of the matrix composition on hydrogen transfer reactions. If the variation of the index is observed against the density of zeolite acid sites, the behavior of the various catalysts is consistent. Thus, as it can be seen in Fig. 3, all the series presented similar changes: the index increases as unit cell size—which is an indirect expression of the density of aluminum atoms and their associated acid sites [23]—increases, with two very different rates of change before and after approximately 2.430 nm. This behavior has been rationalized [14] considering that it is completely analogous to the change in the relative number of zeolite paired (1-NNN, [24]) aluminum sites for unit cell sizes in the approximate range from 2.420 to 2.460 nm, as predicted by site distribution models [24,25]. Only the series A1 (silica matrix, USY zeolite with no acid extraction) shows this particular point appearing at somewhat smaller UCSs. As it will be discussed later, the catalysts with silica matrix might form a silica alumina interphase by reaction with the aluminum extraframework species coming from the zeolite during dealumination, that may alter the catalyst properties and its catalytic behavior.

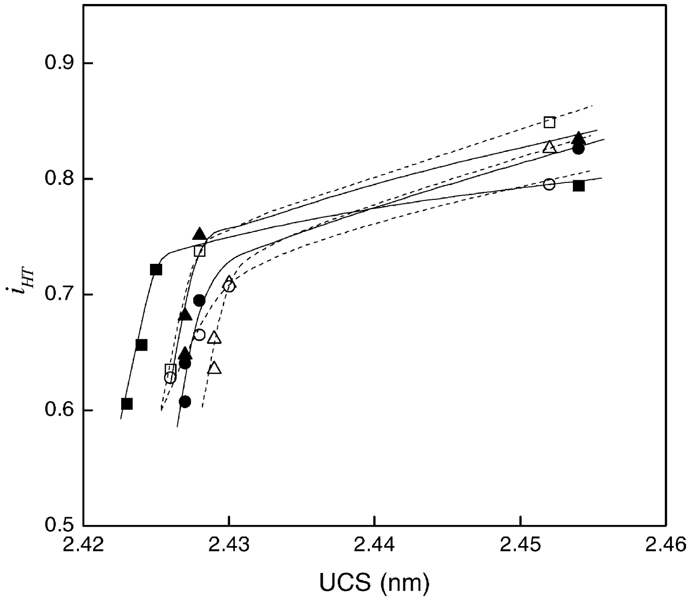

Fig. 3. Index i_{HT} as a function of zeolite unit cell size. Symbols: series A1, (■); B1, (▲); C1, (●); A2, (□); B2, (△); C2, (○).

The evidences shown in Fig. 3 point again to the importance of zeolite paired acid sites as the main factor controlling hydrogen transfer reactions, and a significant influence by the matrix composition is not observed. The index values for "fresh" matrices were about 0.40 in the case of SiO_2—and about 0.85 in the cases of the Al_2O_3—containing matrices; should the matrix have an important additive effect on the catalyst's index, then these widely differing values should reflect in the catalysts, which is certainly not the case. However, samples with the same UCS (for example, sets A1-0, B1-0, C1-0, or A2-0, B2-0, C2-0) indicate that some effect is exerted by the matrix, since their indexes are not the same as expected. This effect cannot be related only to the matrix composition, since each set, based on a different zeolite, shows a distinct behavior. These differences may be due to the fact that USY and USY-A, according to the various treatments, are indeed different materials, and they may react differently with the same matrix. This analysis does not take diffusional issues into account since it is to be expected that the molecular species of this reaction system, and particularly those involved in the index definition, are not subjected to important mass transfer limitations in these catalysts. It is to be noted that the variations in the index do not depend on the yields of particular compounds, like MCPE, which could have suggested diffusional limitations.

The variation of i_{HT} was also analysed as a function of various parameters. The amount of extraframework aluminum species does not affect hydrogen transfer, since, for example, catalysts with similar EFAl amounts show very different indexes (Fig. 3 and Table 3). It is to be noted that the amount of extraframework aluminum species can only be assessed in series A1, B1, C1 and A2, since the other series have Al_2O_3 in their matrices and, moreover, it cannot be assured that in series B2 and C2 the acid treatment does not alter the compositions. Also the type of coordination of the aluminum atoms in the catalyst is not influencing hydrogen transfer properties. As a matter of fact, the proportions of tetrahedral, octahedral and pentacoordinated aluminum atoms change widely, as it can be seen in Table 3, but the values of the index i_{HT} do not follow a given trend. As also expected, the index is not related to the amount of crystalline material remaining on the catalysts after steaming and/or acid treatment.

In order to study other important reactions occurring in FCC, it was decided to analyse the relationship

Table 3
Relative amount of tetrahedral (approximately 60 ppm), octahedral (approximately 0 ppm) and pentacoordinated (approximately 30 ppm) aluminum species in the catalysts

Zeolite	Matrix	Catalyst	Aluminum type (%)			EFAl (%)
			Tetrahedral	Octahedral	Pentacoordinated	
		B	69.0	31.0	–	–
		C	62.5	37.5	–	–
USY	SiO_2	A1	43.2	41.8	15.0	–
		A1-1	27.3	26.2	46.5	83.0
		A1-3	24.3	28.7	47.0	85.2
		A1-5	28.7	15.8	55.5	89.7
USY	12% Al_2O_3	B1	56.1	31.7	12.2	–
		B1-1	27.9	30.1	42.0	82.8
		B1-3	24.6	20.7	54.7	83.6
		B1-5	22.0	19.9	58.1	82.6
USY	25% Al_2O_3	C1	40.3	43.9	15.8	–
		C1-1	20.6	19.2	60.1	88.9
		C1-3	18.0	19.0	63.0	91.6
		C1-5	18.4	18.3	63.3	91.7
USY-A	SiO_2	A2	43.1	44.2	12.7	–
		A2-1	42.3	39.3	18.4	4.2
		A2-3	29.9	57.1	13.0	21.5
		A2-5	53.7	35.9	10.4	52.7
USY-A	12% Al_2O_3	B2	56.2	30.1	13.7	–
		B2-1	25.5	35.3	39.2	–
		B2-3	27.7	26.1	46.2	–
		B2-5	27.3	27.8	44.9	–
USY-A	25% Al_2O_3	C2	39.3	52.1	8.6	–
		C2-1	28.6	35.9	35.5	–
		C2-3	29.7	39.1	31.2	–
		C2-5	30.2	29.5	40.3	–
USY		USY	36.5	12.5	51.0	12.5
USY-A		USY-A	40.1	11.5	48.4	11.5

^{27}Al MAS-NMR spectroscopy.

between the two main branches of reaction occurring on cyclohexyl cation (refer to Fig. 2): hydride transfer and desorption of cyclohexane molecules, expressed by the constant k_1^*, or isomerization to methyl cyclopentyl cation, expressed by the constant k_B. Both reactions have the same adsorbed cation as the starting reactant and, in view of the relative stability of cations, it is expected that the branch of isomerization to methyl cyclopentyl cation be the favored pathway. It is possible in this way to define the selectivity of reaction pathways (S_{RP}) as the ratio between k_1^* and ($k_1^* + k_B$). This index would represent the relative importance of the processes of desorption via hydride transfer against retention of the cation via isomerization, which could be associated to catalyst properties that do not become evident through the index i_{HT}. A high value of S_{RP} would mean that a given catalyst has a lower ability to retain adsorbed species that can be subjected to additional reactions like, in this particular reaction, isomerization and further proton transfer to the catalyst surface, or cracking. The following are the mass balances of the species involved in the reaction branches described:

$$\frac{d[CHA]}{dt} = k_1^*[CHE^+] \qquad (2)$$

$$\frac{\mathrm{d}[\mathrm{MCPA}+\mathrm{MCPE}+\mathrm{Cr}]}{\mathrm{d}t} = (k_2^*+k_4^*+k_5^*)[\mathrm{MCPE}^+] \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{MCPE}^+]}{\mathrm{d}t} = k_B[\mathrm{CHE}^+] - (k_2^*+k_4^*+k_5^*)[\mathrm{MCPE}^+] \tag{4}$$

By assuming the steady state in the concentration of the surface methyl cyclopentyl cation,

$$\frac{\mathrm{d}[\mathrm{MCPE}^+]}{\mathrm{d}t} = 0 \tag{5}$$

it is possible to deduce from Eq. (4) that

$$[\mathrm{MCPE}^+] = \frac{k_B[\mathrm{CHE}^+]}{k_2^*+k_4^*+k_5^*} \tag{6}$$

This expression can be introduced into Eq. (3). Hence:

$$\frac{\mathrm{d}[\mathrm{MCPA}+\mathrm{MCPE}+\mathrm{Cr}]}{\mathrm{d}t} = (k_2^*+k_4^*+k_5^*)\frac{k_B[\mathrm{CHE}^+]}{k_2^*+k_4^*+k_5^*} = k_B[\mathrm{CHE}^+] \tag{7}$$

It is easy to see that the ratio between the constants k_1^* and $(k_1^*+k_B)$, defined as the index S_{RP}, selectivity of reaction pathways, can be expressed by the combination of Eqs. (2) and (7):

$$\frac{\mathrm{d}[\mathrm{CHA}]}{\mathrm{d}[\mathrm{CHA}+\mathrm{MCPE}+\mathrm{Cr}+\mathrm{MCPA}]} = \frac{k_1^*}{k_1^*+k_B} = S_{\mathrm{RP}} \tag{8}$$

It is possible then to assess the values of S_{RP} directly from the slopes of the curves of the yield of CHA against the total yield of CHA, MCPA, MCPE and Cr products. Some examples are presented in Fig. 4 for catalysts of series A1, where it can be appreciated that straight lines are obtained.

Following an approach similar to the one used for the hydrogen transfer index, the variation of the index S_{RP} was analyzed as a function of different catalyst parameters. The values of S_{RP} for all the samples are presented in Fig. 5 as a function of unit cell size, where it is possible to observe different evolutions according to the catalyst matrix and treatment. In effect, the values for series A1 (silica matrix) and B1 (low alumina silica/alumina matrix) increase as unit cell size decreases, while series C1 (high alumina silica/alumina matrix) and A2 (silica matrix, acid treated) show steady values in the whole range of unit cell sizes. On the contrary, series B2 (low alumina silica/alumina matrix, acid treated) and C2 (high alumina silica/alumina matrix, acid treated) follow a decreasing trend with decreasing unit cell size.

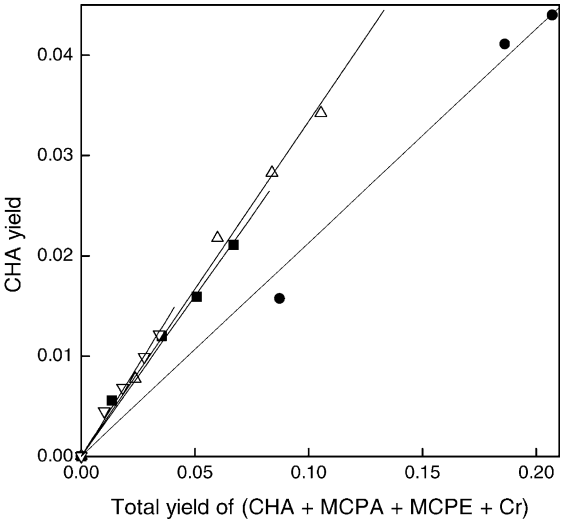

Fig. 4. Yield of CHA as a function of the total yield of CHA, MCPA, MCPE and Cr products. Samples of the series A1. Symbols: A1, (●); A1-1, (△); A1-3, (■); A1-5, (▽).

It can be seen in Fig. 5 that the acid extraction of EFAl species leads to lower values of S_{RP}, (this fact can be observed comparing homologous series A1 and A2, or B1 and B2, or C1 and C2, since they have the same matrix, and only differ in the acid treatment). However, the values of the index cannot be explained based only on the amount of EFAl species; it can be seen in Fig. 6 that catalysts with about the same amount of EFAl (series A1, B1 and C1) do have different values of S_{RP} or, on the contrary, catalysts with widely differing amounts of EFAl (e.g. catalysts from series C1 and A2) show similar index values. It is also evident that the removal of the first portion (or a particular type) of EFAl is sufficient to induce severe drops in the index. For example, it can be observed in the comparison between samples of the series A1 and A2 (silica matrix, without and with acid extraction) that the reduction of about 40% of EFAl produces a strong decrease in the index to values that then keep

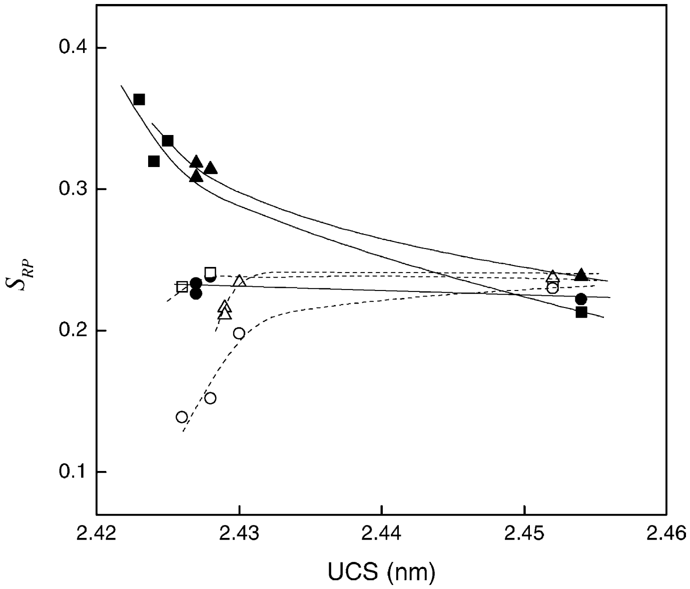

Fig. 5. Index S_{RP} as a function of zeolite unit cell size. Symbols as Fig. 3.

approximately constant in the other samples in series A2, that have significantly less EFAl species.

The values of S_{RP} were also analyzed considering the different degrees of coordination of the aluminum atoms in the catalysts (total pentacoordinated, total octahedral, total tetrahedral and zeolitic tetrahedral types). The index did not show a clear relationship with most of these types, but it is interesting to see that it does change as a function of EFAl octahedral species in series A1 (silica matrix) catalysts, decreasing as the

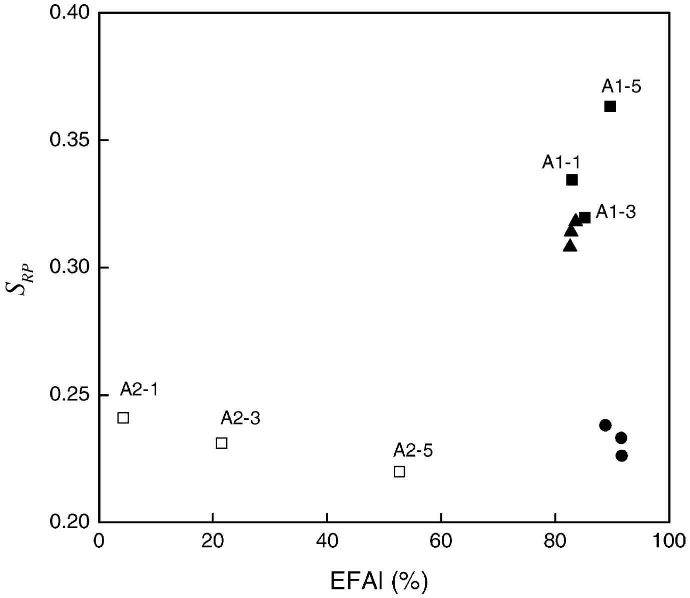

Fig. 6. Index S_{RP} as a function of extraframework aluminum. Symbols as Fig. 3.

relative amount of octahedral aluminum increases. In effect, the values of S_{RP} for steamed samples in series A1 are 0.319, 0.334 and 0.363, the percentages of octahedral aluminum atoms being 28.7, 26.2 and 15.8%, respectively. It can be stated that in the catalysts of series A1, since the matrix is silica, the octahedral aluminum atoms belong only to EFAl species. At least part of these atoms would be involved in the formation of a new silica/alumina phase from the reaction of EFAl species produced during steaming and silica from the matrix [11,26]. In the thermal treatments of catalyst samples devoted to the study of zeolite – silica interactions, Falabella et al. [13] observed a decrease in the amount of octahedral aluminum in the EFAl species and an increase in the amount of tetrahedral aluminum, that assigned to the formation of a new silica/alumina phase, which was more important when silica contents were higher. Following this idea, accepting that octahedral aluminum atoms are involved in the formation of this new phase, then, the lower the amount of octahedral atoms in the remaining EFAls, the higher the amount of new phase formed, which correlates with higher values of the index S_{RP}.

Catalysts in series B1 and C1 could also be associated to these modifications. In these cases, it is expected that the feasibility of forming a new silica/alumina phase is lower, due to the lower concentration of silica and the previous existence of octahedral atoms in the matrix [11]. In the case of series B1 catalysts, the index increases from 0.25 in the base catalyst to about 0.32 in the steamed samples, thus suggesting that the new phase is formed to some extent. However, series C1, where the concentration of silica is even lower, shows quite similar values for the index (about 0.23) that do not change with steaming, suggesting that the new phase even might not be formed. It is clear, however, that the changes in the index cannot be related exclusively to the sole existence of the new phase, but other factors are surely influencing it.

Indeed, homologous series A1 and A2 are the only pair that allows one to observe clearly the impact of EFAl species and their interactions with the matrix, since they do not have initially aluminum species in the matrix. As it can be seen in Table 3, the calculations from ^{27}Al MAS-NMR spectra show that pentacoordinated aluminum atoms increase with steaming (series A1) and that these species are removed by the acid extraction (series A2). It is to be noted that these aluminum atoms at 29–32 ppm shift have been considered indeed as tetrahedral coordinated aluminum species greatly affected by quadrupolar induced shift, corresponding to a extraframework silica/alumina phase, that can be easily removed by acid extraction [26], as confirmed by catalysts of series A2. In part, this extraction can justify the drop in the S_{RP} values in steamed samples in series A2 as compared to their homologous in series A1.

Essentially the same observations can be applied to homologous series B1 and B2: pentacoordinated aluminum increase with steaming and the acid extraction eliminates a fraction of them, but to a lower degree in comparison to series A2 (refer to Table 3). The shape of the trend followed by the values of S_{RP} for series B2 is consistent with a significant extraction of the newly formed silica/alumina phase, but also including some other extraframework species (they could be even from the matrix) that influence the index. While the reaction between extraframework aluminum and silica, if any, is expected to be minimum in series C1 steamed samples, it is apparent that the acid extraction in series C2 removes aluminum species that affect the index.

The formation of a new silica/alumina phase would influence selectivity through a decrease in catalysts' adsorption ability that would allow additional transformations on the adsorbed intermediate like, in this particular reaction, isomerization and further proton transfer to the catalyst surface, or cracking, as indicated by the index S_{RP}.

4. Conclusions

The conversion of cyclohexene on FCC catalysts was useful to study the influence that the type of matrix and its composition, and the interaction between zeolite and matrix, have on selectivity.

The different compositions of the matrices in the catalysts, on which steaming, and the acid extraction of extraframework species in some cases, were used, generated a large number of samples with widely changing properties (unit cell size, amount of extraframework aluminum, coordination of aluminum atoms). It was confirmed that hydrogen transfer does not depend directly on the coordination of the aluminum atoms in the catalyst, but rather on the density of paired sites in the zeolite component.

The selectivity of reaction pathways (S_{RP}) was defined to express the relative importance of the processes of desorption via hydride transfer to yield cyclohexane against retention of the cation cyclohexil via isomerization and further reaction. A catalyst with higher value of S_{RP} will have lower ability to retain adsorbed species on the surface that could be subjected to further reactions. Thus, less secondary products would be expected. The index increased as the relative amount of octahedral aluminum atoms decreased; this observation could be linked to the formation of a new silica/alumina phase. Such phase would be formed by the reaction of aluminum extracted from the zeolite upon steaming and silica present in the matrix; thus, the lower the aluminum content in the matrix, the more important the interaction.

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