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Temperature dependence of the USHY + HZSM-5 mixing effect on the *n*-heptane transformation

I.P. Dzikh[a,b], J.M. Lopes[a,*], F. Lemos[a], F. Ramôa Ribeiro[a]

[a] *Centro de Engenharia Biológica e Química, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[b] *Petroleum Refinery Engineering Department, State University "Lvivska Polytechnica", Bandera St. 12, Lviv-13, 290646, Ukraine*

Abstract

The temperature dependence of the USHY + HZSM-5 zeolites mixing effect on the catalytic properties for the *n*-heptane transformation is analysed; several mixture compositions were tested at 350, 400 and 450°C. The observed activities and product selectivities for the mixtures were compared to the predicted ones based on the pure zeolite tests assuming its relative contributions to the product yields and conversion with no mechanistic interactions. The most important detected synergism in the product selectivities, which is the increased C_4 products ramification, is reduced with the temperature rising.

Keywords: Zeolites; USHY; HZSM-5; Catalytic cracking; *n*-Heptane

1. Introduction

Several studies have been performed concerning the additive effect of HZSM-5 in FCC catalysts for the transformation of industrial gas/oil charges [1–9] or hydrocarbon mixtures simulating these charges [10]: in general, there is a change in selectivities leading to an improvement of gasoline quality, but the mixing effect on the reaction mechanisms is under debate.

Few studies have been performed with model reactions [11–14]. Namely the observed selectivity features resulting from these simpler studies can sometimes be extrapolated to the industrial charge transformations and more important, they allow some insights in the study of the reaction mechanistic interactions due to the simultaneous presence of different catalysts by comparing the observed and predicted product distribution parameters. Buchanan [11] concluded that the cracking of olefins over HZSM-5 can reduce paraffin formation by hydrogen transfer in Y zeolite based catalysts, from a study on *n*-hexene transformation over sequential beds of Y and HZSM-5 zeolite; in a more recent work [12] this author concluded that an HZSM-5 sample with higher silica content induced a reduction in cracking versus isomerization in a model olefin feeds transformation, which will contribute to the explanation of the higher gasoline selectivity observed with silica rich HZSM-5 FCC additives. Zainuddin et al. [13] reported a study on *n*-octane transformation over sequential combinations and random mixtures of HY ($Si/Al = 2.4$) and HZSM-5 ($Si/Al = 105$) zeolites at 400°C; they found important differences in the product distributions relative to the predicted ones.

Considering the model reaction of *n*-heptane transformation, the corresponding product distribution

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[*] Corresponding author. Tel.: +351-21-841-9286; fax: +351-21-841-9062.
E-mail address: jmlopes@alfa.ist.utl.pt (J.M. Lopes).

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parameters such as olefin/paraffin ratio, ramified/linear ratio, of C_4 and C_5 products, light products selectivities, can express the relative catalytic ability to promote hydrogen transfer processes and the relative effectiveness of the β-scission cracking and protolytic mechanisms [15]. In a previous work, the effect of mixing of an ultrastabilised acid form of Y zeolite, USHY, with HZSM-5 samples presenting different acidic properties was studied for this model reaction at 350°C [16]. Some synergisms were observed in the product selectivities whose extension was dependent on the HZSM-5 acidity and relative amount in the mixture. In the present study, the temperature dependence of this mixing effect is analysed.

2. Experimental

2.1. Catalyst preparation and characterisation

The acidic forms of the zeolites, USHY and HZSM-5, were prepared by calcination of the corresponding ammonium forms, NH_4USY (LZY-82) from Union Carbide and NH_4ZSM-5 from AO (Angarsknefteorgsyntez, Russia), at 500°C, under a flow of dry air, for 8 h. Both samples were characterised by X-ray, presenting a good level of crystallinity. Scanning electron microscopy (SEM) was used to evaluate crystallite sizes and morphology; USHY presented spherical particles with $\approx 1\,\mu$m diameter and HZSM-5 showed cubic particles with 0.5–1 μm. The samples global composition was obtained from the elemental chemical analysis, and their framework composition was determined by ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) in an MSL-400 Brucker instrument; USHY presented a framework Si/Al of 4.5 and a global Si/Al of 2.7, with a residual sodium content of 2% of the total cationic positions; HZSM-5 presented a framework Si/Al of 26 with practically no extra framework aluminium and a residual sodium content lower than 5%.

The acidity was evaluated by temperature-programmed desorption (TPD) of ammonia. Details of the procedure and the corresponding thermograms can be found in Ref. [16]; a remarkable stronger acidity was detected in the HZSM-5 sample relative to USHY.

2.2. *n*-Heptane transformation

The catalysts were pre-treated at 450°C, for 12 h, under a flow of dry nitrogen. The transformation of *n*-heptane was performed in a fixed bed flow reactor, at 350, 400 and 450°C, total pressure of 1 bar, nitrogen/hydrocarbon ratio of 9 and *n*-heptane fed at a rate of 3 ml/h. Several masses of catalyst were used for each catalyst, from 50 up to 200 mg. For the mixtures tests, simple mechanical mixtures of USHY + HZSM-5 were prepared with mass compositions of 90%:10% (A), 75%:25% (B) and 50%:50% (C), with a total mass of 200 mg. The reaction products were separated and identified by gas chromatography on a 50 m KCl/Al_2O_3 PLOT capillary column (from Chrompack), with an FID detector. Blank tests showed that the thermal transformation of *n*-heptane under the operating conditions that were used is negligible.

3. Results and discussion

According to the classical β-scission cracking mechanism [15,17], the first step in a steady-state situation will be the formation of an *n*-heptyl carbenium ion on an acid site, usually by hydrogen transfer between the *n*-heptane and another adsorbed carbenium. This ion can isomerise in order to form the most stable carbenium ion and the scission will occur in the β position relative to the carbon bearing the positive charge, resulting in a smaller olefin and an adsorded carbenium that can originate a paraffin by hydrogen transfer namely with the reactant. The stability of the intermediate carbenium ions will determine the selectivity of the process, imposing almost exclusively the formation of $C_3 + C_4$ cracking products, with important ramification of C_4 products if the previous isomerization of the reactant is allowed by the porous structure of the zeolite. The olefinic products are involved in several secondary reaction processes leading to the formation of coke, such as olefin oligomerization and polimerization, cyclization and dehydrocyclization, enabled by the hydrogen transfer ability of the catalyst [15]. These secondary processes are responsible for the observed low value of the olefin/paraffin ratio in the cracking products.

The other possible catalytic process, the protolytic mechanism, which is most effective for the cracking of small chain paraffins, is assumed to be initiated by the formation of a pentacoordinated carbonium ion on a Brönsted acid site [15,18,19]; after that, the scission path over a C–C bond or C–H bond will generate an adsorbed carbenium ion and smaller paraffin or hydrogen, respectively. The adsorbed ion can then be desorbed producing an olefin and regenerating the acid site, or participate in a chain propagation process via hydrogen transfer, namely that leading to coke formation, as in the classical mechanism. High temperature, stronger acidity and smaller zeolite pores favour the protolytic initiation followed by termination [18,20]. A very important feature associated with the protolytic mechanism is that the formation of the lighter products (C_1+C_2) is not restricted, since there are no primary carbenium ions involved as intermediates, contrarily to what occurs in the classical process.

The observation made from the TPD characterisation that HZSM-5 presented a stronger acidity than USHY, with a significantly higher amount of ammonia desorbed for the highest temperature, is in good agreement with the relative initial catalytic activities presented by the isolated samples in the demanding reaction of *n*-heptane cracking (Table 1). The large preponderance of C_4 and C_3 products shows that the most effective mechanism corresponds to the classical β-scission cracking process. As expected, the contribution of the protolytic mechanism increases with the temperature rising and is always higher in the case of HZSM-5, due to its higher acid strength; this is clearly expressed in the relative amount of $C_1 + C_2$ species in the reaction products. The olefin/paraffin ratio shows that hydrogen transfer processes proceed to a larger extent in USHY, this parameter being much more close to unity in this case than in HZSM-5; the relative importance of these processes, which are less activated than the cracking transformation, decreases for higher temperatures in both catalysts. Another important parameter is the observed ramification in the cracking products (*i*/*n* ratio expresses the ramified/linear relation in the products); this is higher for USHY due to its larger pore dimensions, allowing a more easier isomerisation of the adsorbed *n*-heptane prior to the scission path; a temperature increase reduces the observed ramification.

The general features of this product distributions comparison between the catalysts for all the reaction temperatures tested, are not changed significantly by changing the contact time.

Concerning the study of the mixing effect, a total catalyst mass of 200 mg was used, and three catalyst ratios USHY:HZSM-5 were studied: A (90:10), B (75:25) and C (50:50), expressed as wt.%.

The measured cracking conversions, for all the mixtures and temperatures, were quite close to the corresponding predictions based on the pure zeolite tests and assuming no interaction; these predicted conversions were computed by summing the conversions obtained for each pure catalyst, taking into account the relative amount of each one present in the mixture.

In opposition to what was observed with the mixture conversions, the selectivities for the cracking products were not additive. In fact, the predicted product distributions for the mixtures, obtained by calculating the predicted yield of each product considering an additive linear combination of the corresponding yields for the pure zeolites, deviates significantly from the real ones.

Fig. 1 reports the observed mixing effect in the parameter olefin/paraffin ratio, for 2 min time-on-stream,

Table 1
Initial conversions (2 min time-on-stream) for the pure zeolites (200 mg) and initial product distribution parameters

	HZSM-5			USHY		
Reaction Temperature (°C)	350	400	450	350	400	450
Initial conversions (%)	31	33	38	17	21	31
C_4+C_3 (%)	78	80	78	86	89	89
C_1+C_2 (%)	2.8	5.4	13	0.41	1.0	3.0
Olefins/paraffins	0.45	0.68	0.86	0.14	0.27	0.34
iC_4 (%) total	17	14	10	39	36	31
iC_4 (%) paraffins	12	7.3	4.6	38	33	29
iC_4/nC_4 total	0.83	0.72	0.57	5.7	3.7	2.5

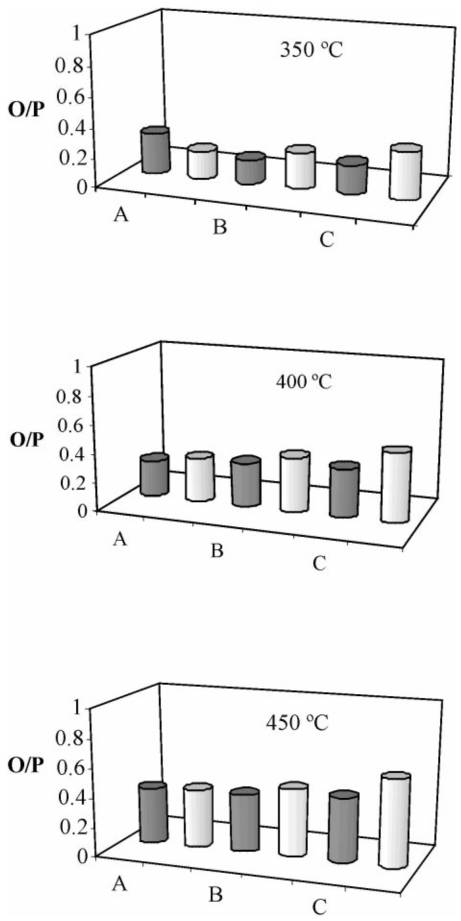

Fig. 1. Initial olefin/paraffin ratio (2 min time-on-stream) in the cracking products for the mixtures of USHY + HZSM-5 A(90:10), B(75:25) and C(50:50); experimental (■) and predicted (☐) values.

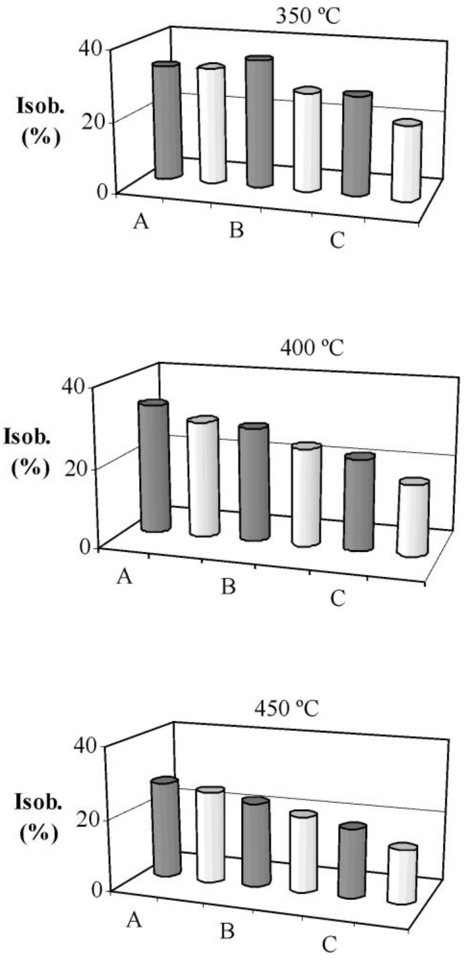

Fig. 2. Initial isobutane molar compositions (%) (2 min time-on-stream) in the cracking product distributions for the mixtures of USHY + HZSM-5 A(90:10), B(75:25) and C(50:50) at different temperatures; experimental (■) and predicted (☐) values.

and its dependency on the reaction temperature. As observed in the isolated zeolite tests, changing the reaction temperature from 350 to 450°C, results in a reduction of the relative participation of the secondary processes leading to coke deposition and olefin consumption, so that the olefin/paraffin ratio approaches unity.

With mixture A, the olefin/paraffin ratio is higher than the prediction (+50%) at 350°C but this effect is inverted for the higher temperatures (−16% at 400°C and −5% at 450°C). With mixtures B and C, the observed ratio is always lower than the predicted one, the magnitude of the effect being reduced with temperature increase, −33%, −18% and −15% in case B and −37%, −29% and −27% in case C, for 350, 400 and 450°C, respectively. Therefore, only in the case of mixture A, at 350°C, a decrease in the hydrogen transfer relative participation in the global reaction network is observed. In all the other cases the hydrogen transfer processes are enhanced in relation to the predictions; the same effect was observed by Zainuddin et al. [13] in the study of *n*-octane transformation at 400°C. The reduction of the relative participation of the secondary processes with increasing temper-

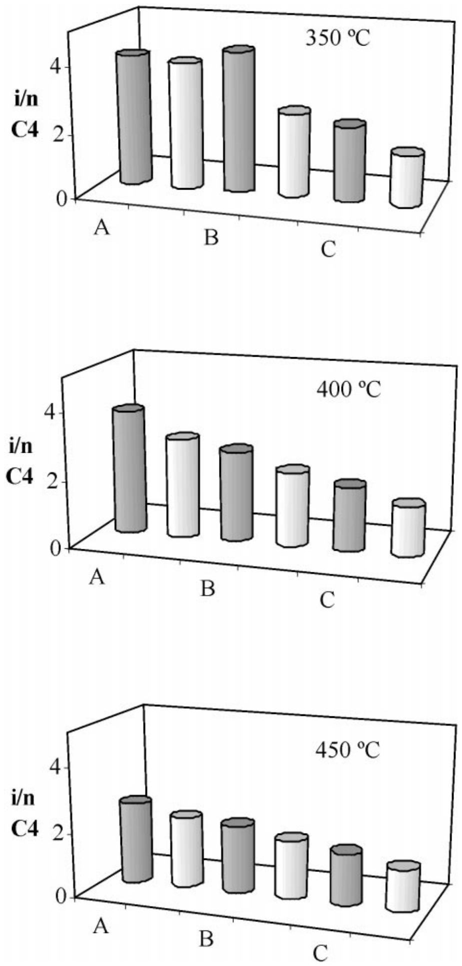

Fig. 3. Initial ramified/normal (*i*/*n*) ratio (2 min time-on-stream) of total C_4 products for the mixtures of USHY + HZSM-5 A(90:10), B(75:25) and C(50:50); experimental (■) and predicted (☐) values.

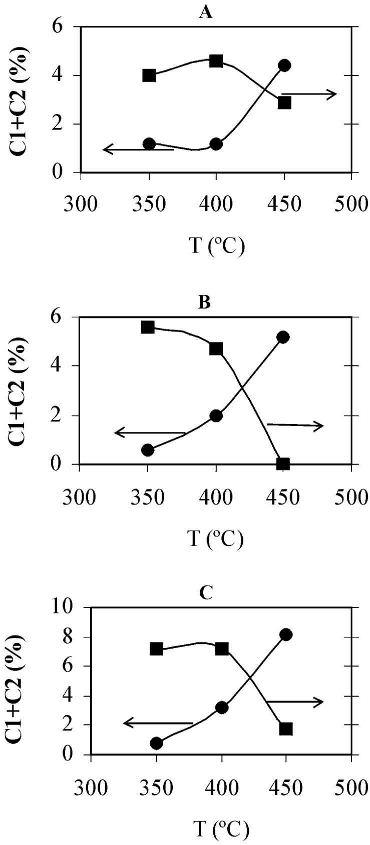

Fig. 4. Initial $C_1 + C_2$ (●) and $C_3 + C_4$ (■) relative amounts (%) (2 min time-on-stream) in the cracking products for the mixtures of USHY + HZSM-5 A(90:10), B(75:25) and C(50:50), at different temperatures.

ature will induce a reduced extension in the mixing effect for the olefin/paraffin ratio.

A very important feature concerning the product distributions is the ramification presented by these products. The relative amount of isobutane obtained with the mixtures and the corresponding predictions are presented in Fig. 2, for 2 min time-on-stream. Isobutane is formed in higher amounts than predicted, especially for the cases B and C; this mixing effect is reduced for the highest temperatures. The observed ramified/normal ratio (*i*/*n*) of total C_4 products is also always higher than the predictions. From Fig. 3, it is clear that for mixtures B and C, where the effect is observed in higher amplitude, there is a remarkable reduction in this important mixing effect for the higher temperatures: +68%, +23% and +17% in case B and +45%, +27% and +23% in case C, for 350, 400 and 450°C, respectively.

Since the formation of branched products over the HZSM-5 component of the mixture is highly inhibited by shape selectivity factors, the ramified species that generates the ramified C_4 products by cracking, such as the heptane isomer 2,4-dimethylpentane, will be essentially produced in the USHY zeolite. The higher than predicted ramification should result from a selective isomerization, over the USHY, of the linear C_4 species produced in large amounts over the

HZSM-5, probably occurring through a bimolecular dimerization followed by C_8 isomerization and cracking.

The described reduction in the mixing effect occurs with a simultaneous increase in the relative participation of the protolytic mechanism in the *n*-heptane transformation, for higher temperatures the relative amount of light products $(C_1 + C_2)$ increases, and the relative amount of $(C_3 + C_4)$ products decreases, as shown in Fig. 4. This increase in the participation of the protolytic mechanism, compared to the β-scission process, which is always the most effective one, will probably contribute to the reduction in the mixing effect, since the amount of C_4 products in the reaction gaseous mixture is reduced. Another important factor is that higher temperatures are relatively less favourable to the C_4 dimerization-isomerization-cracking process occurring over USHY.

4. Conclusions

The measured conversions for the USHY+HZSM-5 mechanical mixtures were quite close to the corresponding predictions based on the pure zeolites results, assuming no interaction. Nevertheless, the observed selectivities for the reaction products were clearly not additive, and this mixing effect is strongly dependent on the reaction temperature.

The observed ramification of C_4 products is always higher than the predictions. For mixtures B (75:25) and C (50:50), where the effect is observed with higher amplitude, there is a remarkable reduction in this important mixing effect with increasing temperature. The increase in the relative contribution of the protolytic mechanism with temperature rising, compared to the β-scission process, which is always the most effective one, will probably contribute to this result. The values of the ramified/normal C_4 ratio are in fact decreased with increasing temperature, simultaneously with an enhancement of $C_1 + C_2$ products and a decrease of C_3+C_4 products. Another important factor is that higher temperatures are relatively less favourable to the linear C_4 dimerization-isomerization-cracking process occurring over USHY.

The hydrogen transfer processes are reduced relative to the predictions only in mixture A at 350°C. In all the other cases they are enhanced. The extension of the synergetic mixing effect in the hydrogen transfer processes is also reduced with temperature rising.

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