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Selective deep catalytic cracking process of hydrocarbon feedstocks for the production of light olefins: II. Cooperative effect of thermal cracking and catalytic reactions observed in a 1-zone reactor

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Hybrid catalysts comprising a chromium-based cocatalyst and a silica-rich ZSM-5 zeolite, when doped with lithium, showed quite a high on-stream stability even at a relatively high reaction temperature (735 °C). The cooperative effect of the thermal cracking and the catalytic reactions, and the interactions between the two catalyst components of the hybrid catalyst, resulted in maximum production of light olefins when the hybrid catalyst contained ~40 wt% of zeolite. The main chemical links between the thermal cracking (TC) and the catalytic reactions were the conversions of diolefins and large olefins, the latter being produced by the TC and the active sites of the chromium-bearing cocatalyst, respectively.

KEY WORDS: selective deep catalytic cracking of n-hexane and n-octane; Catlever effect; 1-zone reactor.

1. Introduction

Steam cracking is a thermal cracking process performed in the presence of steam, a diluant which is cofed with the hydrocarbon mixture [1]. Adding a small reactor, which contained a hybrid catalyst comprising a ZSM-5 zeolite, to the steam cracker might significantly increase the production of light olefins and aromatics [2,3]. Recently, enhanced production of light olefins and a variable ethylene-to-propylene ratio were obtained by using a two-zone reaction system [4]. In fact, by varying the temperature of zone 1, where only thermal cracking occurred, it was possible to significantly change the final product spectrum obtained after conversion over the hybrid catalyst packed in zone 2. The catalytic lever (Catlever) concept was therefore hypothesized [4].

In this paper, a 1-zone reactor which contained a hybrid catalyst was used. The objective of this work was to show that the reaction essentially initiated with thermal cracking whose product spectrum was then refined by the catalyst. Among the many products of the thermal cracking there were some compounds, such as diolefins, which acted as intermediates undergoing conversion on the catalytic active sites [4]. Moreover, the hybrid nature of the catalyst allowed the desired final products to be obtained. Therefore, indications of the cooperative action of the thermal cracking and the catalytic conversion, and the interactions between the zeolite component and the cocatalyst of the hybrid catalyst, are reported herein. It is obvious that firm evidence of such interactions will come in the future with more systematic studies of so complex a reaction system.

2. Experimental

2.1. Preparation of the hybrid catalysts

2.1.1. H-ZSM-5 zeolite

The H-ZSM-5 zeolite used was the Zeocat PZ-2/50, H-form, powder, purchased from Chemie Uetikon AG (Switzerland). It was activated in air overnight at 700 °C. Its main physical properties are: surface area $= 483\,m^2/g$, microporosity $= 277\,m^2/g$, and Si/Al $\simeq 50$. This material is referred to as HZ. The extrudates of this reference zeolite catalyst were obtained by extrusion with bentonite clay (Spectrum Products, 15 wt%). They were dried in air overnight at 120 °C, then activated at 500 °C for 3 h and finally at 750 °C for 2 h.

2.1.2. Chromium-based cocatalyst

A solution of 34.0 g of chromium trioxide (Fisher) in 300 ml distilled water was homogeneously impregnated onto 210 g silica–alumina (Aldrich, support grade 135, $SiO_2 = 86$ wt%; $Al_2O_3 = 13$ wt%; surface area $= 455\,m^2/g$). The solid, first left at room temperature for 30 min, was dried overnight at 120 °C and then activated at 500 °C for 3 h. The resulting solid had the following physicochemical properties: $SiO_2 = 77$ wt%,

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$Al_2O_3 = 12$ wt%, $Cr_2O_3 = 11$ wt%, surface area = 273 m^2/g, microporosity = 0 m^2/g, median pore size = 4.9 nm. This material is referred to as Cocat.

2.1.3. Hybrid catalysts

A series of hybrid catalysts was prepared by admixing the Cocat with the HZ zeolite in well-defined proportions, so that the final catalysts had the following formula: Cocat (X) HZ, X being the weight percent of zeolite in the solid mixture. The extrudates of these hybrid catalysts were obtained by extrusion with bentonite clay (Spectrum Products, 15 wt% of the previous solid mixture). These hybrid catalysts were dried in air overnight at 120 °C, then activated at 500 °C for 3 h and finally at 750 °C for 2 h. They are referred to as Cc(X)HZ. In particular, samples Cc and HZ mean catalysts of pure Cocat and of pure HZ zeolite, respectively.

2.1.4. Doping with Li

10.0 g of Cc(X)HZ extrudates were homogeneously soaked (dropwise, using a pipet) with a solution of 0.72 g $LiNO_3$ (Aldrich) in 8.5 ml of distilled water. The wet extrudates were left at room temperature for 30 min, then dried in air overnight at 120 °C and finally activated at 750 °C for 3 h. The final catalyst had a Li content of 1.5 wt% and is referred to as Cc (X) HZ/Li.

2.2. Characterization

1. The HZ zeolite (powder) and the Cocat (powder) were analyzed by atomic absorption spectroscopy for their chemical composition.
2. X-ray powder diffraction was used for determining the relative crystallinity (RC) value of the zeolite component of the hybrid catalysts, assuming, only for convenience, that the commercial H-ZSM-5 is 100% crystalline. The determination of RC was based on the area of the characteristic peaks in the 2θ range of 22.5–25.0° in accordance with the method of Kulkarni *et al.* [5]. X-ray diffraction was carried out on a Philips PW 1050/25 diffractometer, which has been automatized with the SIE Ray 112 system from Sietronics, using zero background holders.
3. BET total and micropore surface areas were determined by nitrogen adsorption/desorption, using a Micromeretics ASAP 2000 apparatus.
4. Ammonia adsorption and temperature-programmed desorption (TPD) were used to study the surface acidity. To prevent physisorption phenomena, ammonia was adsorbed at 100 °C. In particular, the measurement of the acid density was carried out, using a 0.02 N HCl solution which was then back-titrated with a 0.05 N NaOH solution in accordance with the method reported elsewhere [6].

The ammonia TPD profile was obtained for the parent zeolite (HZ) and the Li-doped HZ (HZ/Li) by first chemisorbing ammonia at 100 °C and then desorbing it from 100 °C to 550 °C at 25 °C/min ramping in a flow of helium of 20 ml/min.

2.3. Experimental set-up

Experiments were performed using a quartz reactor set in a Lindberg tubular furnace, similar to that described in reference [4]. However, only the reaction zone, where the catalyst bed was located, was heated.

2.4. Testing procedure and data reporting

n-Hexane and n-octane were used as model molecules for the conversion of petroleum naphthas. Liquids, namely n-paraffin (hexane or n-octane) and water, were injected into a vaporizer using two infusion pumps. In the vaporizer, nitrogen (used as the carrier gas) was mixed with the n-paraffin vapor and steam. The gaseous stream was then sent into the tubular reactor.

The testing conditions were as follows: Weight of catalyst = 7.5 g, weight hourly space velocity (WHSV) = g of reactant, *i.e.* n-paraffin, injected per hour per g of catalyst = 0.57–0.61 h^{-1}, water/n-paraffin wt ratio = 0.71, reaction temperature = 735 °C, nitrogen flow rate $\simeq$ 11.5 ml/min, duration of a run = 4 h.

Gaseous and liquid products were collected separately using a system of condensers. The gas-phase components were analyzed using a Shimadzu Mini-3 FID gas chromatograph equipped with a 30-m-long GS-alumina micropacked column (J & W Scientific) while the liquid phase analysis was carried out using a Hewlett-Packard 8790 FID gas chromatograph equipped with an EC-Wax 30-m-long capillary column (Alltech).

The total n-paraffin conversion (mol% or wt%) is expressed as $C_t = 100 \times$ (moles of converted n-paraffin/moles of n-paraffin fed).

The selectivity (to product i) is expressed in C atom% as $S_i = 100 \times$ (number of carbon atoms of product i/number of carbon atoms of converted products).

The yield in product I is expressed (in C atom%) as $Y_i = 1/100 \times C_t \times S_i$.

The conversion into yields expressed in wt% is calculated by using appropiate conversion factors which correspond to the ratio of molecular weight to the total weight of the carbon atoms in the molecule, *i.e.* 1.33. 1.21, 1.17 and 1.08 for methane, other paraffins, olefins and aromatics, respectively.

R is the ratio of the product ethylene to the product propylene in wt%.

3. Results and discussion

In our previous work [4], the Catlever concept was proposed to explain the following phenomena: in a two-reaction-zone system, if the products of thermal cracking of n-hexane (occurring in zone 1) underwent

Table 1
Data of reference runs

Sample	C_t	Product yields (wt%)								R	Y_0
		Ethene	Propene	Butadiene	Isobutene	Butenes	C_5^+	Ar	CH_4		
Feed: n-hexane											
NO	79.55	29.63	20.64	3.07	0.19	4.52	4.69	2.07	9.44	1.44	50.27
Bentonite	77.69	29.30	21.23	3.13	0.17	5.42	3.72	0.82	8.73	1.38	50.53
Feed: n-octane											
Bentonite	92.36	35.36	22.00	3.61	0.23	5.54	7.77	3.73	7.00	1.61	57.36

further conversion over a catalyst (zone 2), the final product spectrum was very different from that of the thermal cracking alone. In addition, by changing the temperature of zone 1, the products of the overall reaction significantly changed. This temperature dependence of the final product spectrum was assimilated to the effect on a lever [4]. The main intermediary products, which acted as chemical modifiers for the catalytic steps, included diolefins (butadienes) and large olefins, and were produced by the thermal cracking in zone 1. Therefore, just by varying a reaction parameter (the temperature of zone 1), a great production flexibility, mostly in terms of light olefins (ethylene, propylene, butenes), was obtained and the resulting technology might be of great commercial importance.

The next challenge was to reduce the two-reaction-zone system into a one-zone reaction system, so that the technology became much simpler. Since now the two reactions (thermal cracking and catalytic (refining) conversion) were carried out in the same reactor (thus at the same temperature), to effect the thermal cracking meant to modify the residence time, provided that the thermal cracking and the catalytic refining reactions had different responses to that change.

By combining the two reaction zones in one, the catalyst has to work in conditions which provide the thermal cracking with some significant conversion, *i.e.* at quite high reaction temperatures. However, these conditions can be very detrimental to the catalyst, mostly when the latter contains a ZSM-5 zeolite. In addition, since steam is used as a diluant and coke retardant, the zeolite component of the hybrid catalyst is submitted to strong structure-collapsing effects if there is no suitable pretreatment to prevent them.

4. On-stream stability of the zeolite catalysts

The choice of the reaction temperature used in this work was dictated by the need to have an already significant conversion of n-hexane or n-octane due to steam (thermal) cracking, in order to induce the refining catalytic reactions over the hybrid catalyst (table 1). Table 1 also shows that the presence of the catalyst mass reduced markedly the residence time: in fact, tests with bentonite clay which was catalytically inert but having almost the same texture as the hybrid catalysts, resulted in some decrease of the conversion. Essentially, there was little change except for the aromatics the production of which was significantly reduced because of the smaller residence time. Thus, the reaction data obtained with bentonite extrudates are used herein as reference data for all the catalytic tests.

Two criteria are used to assess the catalyst stability:

1. on-stream stability: during the normal run which lasts 5 hours, the catalyst performance should be stable, *i.e.* the conversion after an unsteady state of 20 min should show a total conversion being measured periodically, not different by 3%.
2. stability after several reaction cycles.

Since our hybrid catalysts contained a ZSM-5 zeolite in various proportions, partial collapses of the zeolite structure—and thus significant activity decay—were unavoidable although the ZSM-5 had a quite high Si/Al ratio (~50). In our laboratory, it was seen that pure ZSM-5 catalyst underwent rapid coking so that its conversion (of n-hexane) was reduced to more than 50% after 2 h of reaction. In addition, the presence of steam in the feed resulted in a very significant structural

Table 2
On-stream stability of the Cc(40)HZ/Li hybrid catalyst ($T = 735\,^{\circ}C$, n-hexane)

Time on-stream (min)	C_t	Product yields (wt%)								R	Y_0
		Ethene	Propene	Butadiene	Isobutene	Butenes	C_5^+	Ar	CH_4		
40	90.50	30.20	29.04	0.96	2.86	3.67	2.22	3.91	6.10	1.04	59.24
118	91.59	29.61	28.92	0.86	2.75	3.56	1.99	4.54	6.77	1.02	58.53
180	90.80	28.48	28.65	0.88	2.68	3.47	1.87	4.69	7.28	1.00	57.13
255	90.54	28.69	28.34	0.91	2.58	3.35	1.89	4.81	7.32	1.01	57.03
Average	90.73	28.93	28.43	0.91	2.69	3.48	2.01	5.22	6.79	1.02	57.36

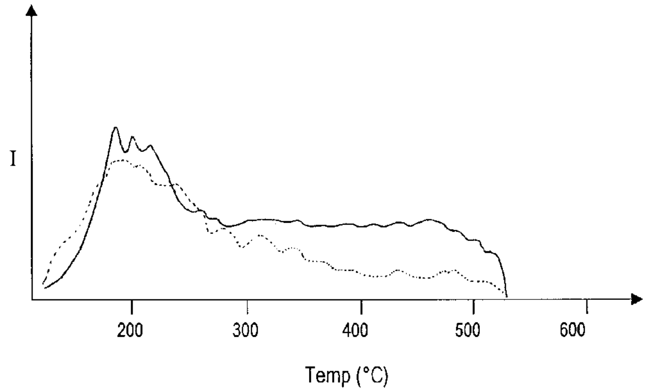

Figure 1. Ammonia TPD profile of HZ (—) and HZ/Li (····). (I = intensity of desorption peak in arbitrary units *versus* temperature.)

collapse [7]. Therefore, a treament of the zeolite with alkaline ions was carried out in order to slow down such detrimental effects. It was seen that among the alkaline ions of Li, Na, K and Cs investigated, Li^+ ions at a loading of 1.5 wt% were the best for the "on-stream" stabilization of the zeolite activity and selectivity for a several-hour run, as reported in table 2. In fact, upon doping with Li^+, most of the strong acid sites of the zeolite were eliminated (figure 1) while the density of the acid sites was significantly reduced (table 3). As a result, the loss in terms of zeolite crystallinity value of the hybrid catalyst, the Cc(40)HZ/Li sample, during a catalytic run was not significant despite the presence of steam and the use of a relatively high temperature.

Table 3
Density of the acid sites of the catalyst components used for the preparation of the hybrid catalysts of this work

Catalyst component	Hybrid catalyst	Density of acid sites (mmol/g)
HZ	–	1.02
HZ/Li	–	0.58
Cc	–	1.08
Cc/Li	–	0.41
	Cc(40)HZ/Li (containing 20 wt% of non-acidic bentonite)	0.38

5. Activity of the Li-doped zeolite catalysts

In terms of conversion of n-hexane or n-octane, there was actually some significant increase when the monocomponent catalysts, Cc/Li and HZ/Li, were used in lieu of bentonite extrudates (tables 1, 4 and 5). Some change in product selectivity was also observed. For the zeolite catalyst tested with both feeds, the ethylene/propylene

Table 4
Data obtained with reference (monocomponent) catalysts and hybrid catalysts (feed = n-hexane)

Sample	C_t	Product yields (wt%)								R	Y_0
		Ethene	Propene	Butadiene	Isobutadiene	n-Butenes	C_5^+	Ar	CH_4		
Cc/Li	84.68	28.26	20.58	2.96	1.82	4.29	4.45	2.83	10.82	1.37	48.84
Cc(10)HZ/Li	80.63	27.77	23.87	1.72	2.90	3.47	1.29	2.15	8.92	1.16	51.64
Cc(25)HZ/Li	89.31	28.75	28.02	0.84	2.71	3.54	1.72	4.23	8.18	1.03	56.77
Cc(40)HZ/Li	90.73	28.93	28.43	0.91	2.69	3.48	2.01	5.22	6.79	1.02	57.36
Cc(55)HZ/Li	87.77	28.70	26.89	0.63	3.13	3.99	2.02	4.01	8.25	1.07	55.59
Cc(70)HZ/Li	89.67	27.97	28.20	0.86	2.80	3.61	2.16	3.72	7.98	0.99	56.17
Cc(90)HZ/Li	83.11	29.61	22.71	2.06	2.88	3.95	3.25	2.29	7.35	1.30	52.32
HZ/Li	83.49	28.99	23.41	1.54	2.74	3.65	2.79	4.08	8.14	1.24	52.40

Table 5
Data obtained with reference (monocomponent) catalysts and hybrid catalysts (feed = n-octane)

Sample	C_t	Product yields (wt%)								R	Y_0
		Ethene	Propene	Butadiene	Isobutadiene	n-Butenes	C_5^+	Ar	CH_4		
Cc/Li	91.19	32.04	18.84	3.36	2.18	4.65	6.60	3.98	10.05	1.70	50.88
Cc(10)HZ/Li	92.47	29.80	28.60	1.30	3.08	3.89	2.52	2.10	9.06	1.04	58.40
Cc(25)HZ/Li	97.57	32.45	29.79	1.21	3.33	4.26	2.36	5.33	8.39	1.09	62.24
Cc(40)HZ/Li	98.62	34.00	28.55	0.89	2.85	3.85	2.10	6.24	8.88	1.19	62.55
Cc(55)HZ/Li	97.09	35.33	26.61	0.69	2.82	3.55	2.39	7.81	8.51	1.33	61.94
Cc(70)HZ/Li	96.71	32.19	27.32	0.94	3.22	4.11	4.07	7.66	6.65	1.18	59.51
Cc(90)HZ/Li	94.70	34.31	24.42	2.87	3.35	4.22	5.16	3.42	8.64	1.40	58.73
HZ/Li	93.05	32.95	22.68	3.37	2.92	4.50	5.35	4.68	8.35	1.45	55.63

ratio is slightly lower than the reference bentonite extrudates, indicating a higher tendency for the ZSM-5 zeolite to produce more propylene. Both monocomponent catalysts produced more aromatics and less butadiene. One of the most surprising features was the high amount of isobutene produced suggesting that, over these catalysts, isobutene is a secondary product of the oligomerization of olefins followed by cracking.

6. Activity of the Li-doped hybrid catalysts

Incorporating the ZSM-5 zeolite into the hybrid catalyst resulted in (broad) bell-shaped curves when the conversion of n-hexane (figure 2, table 5) and that of n-octane (figure 3, table 5) were plotted against the wt% zeolite loading. The same shape was obtained for the curves of the (ethylene + propylene) yield *versus* zeolite loading (figures 2 and 3, tables 4 and 5). The maxima of the total conversion and the (ethylene + propylene) yield (Y_0) were all observed at 40–50 wt% of zeolite for both paraffinic feeds. The yield in aromatics had almost the same trend (tables 4 and 5).

This surprising "synergistic" effect can be explained by the cooperation of the two catalyst components, the chromium-based cocatalyst and the ZSM-5 zeolite, in the "refining" conversion of the following two products of the thermal cracking, butadiene and large olefins (table 1), in accordance with the following sequence of reaction steps, using n-hexane feed [4]:

$$\text{butadiene} + \text{hexane} \rightarrow \text{butene} + \text{hexene} \qquad \text{(I)}$$

$$\text{hexene} \rightarrow \text{propylene} + \text{propylene} \qquad \text{(II)}$$

In fact, the Cc(40)HZ/Li hybrid catalyst produced much smaller amounts of butadiene and large olefins than other hybrid catalysts, as well as the reference monocomponent catalysts (tables 4 and 5). As a result of this "secondary" conversion, the total conversion and the yield in (ethylene + propylene, or Y_0) of this catalyst showed the highest values (figures 2 and 3). It was not actually surprising that the ratio R (ethylene/propylene) showed the opposite trend, *i.e.* going through a minimum with the increasing proportion of the ZSM-5 zeolite in the hybrid catalyst (tables 4 and 5). This was due to reaction (II), which produces more propylene. However, if the content of ZSM-5 zeolite was relatively high, the normal tendency of the zeolite component (β-scission and hydrogen transfer) prevailed, mostly in the case of n-octane feed (table 5), resulting in more butadiene and paraffins such as ethane and propane.

On the other hand, the use of the cocatalyst support, the pure silica-alumina, did not result in such a high cooperative effect as with the supported chromium (table 6 *versus* tables 4 and 5).

It is also worth noting that, for now, there is no indication of any transfer of surface species between the cocatalyst and the zeolite component during the preparation of the hybrid catalyst, which might significantly change the surface properties of the final catalyst. In fact, as an example, the Cc(40)HZ/Li hybrid catalyst,

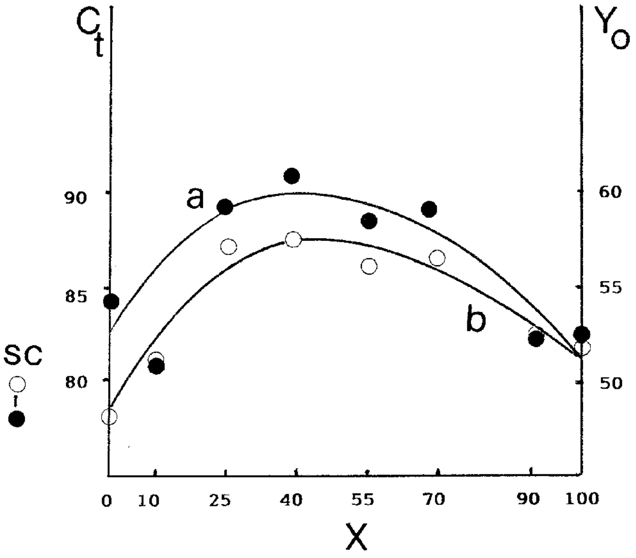

Figure 2. Curves of the total conversion (C_t, wt%) of n-hexane (a) and the yield in (ethylene + propylene) (Y_0, wt%) (b) as functions of the ZSM-5 zeolite content (X, wt%) of the hybrid catalyst. The corresponding values obtained with the thermal cracking alone (bentonite extrudates) are also reported (sc).

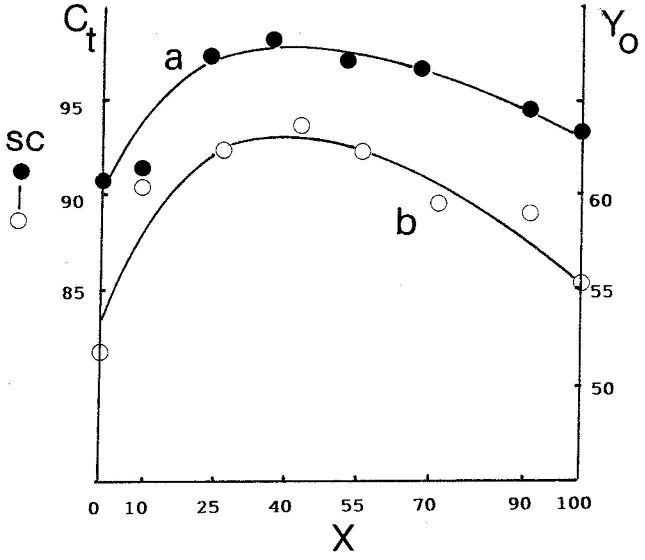

Figure 3. Curves of the total conversion (C_t, wt%) (a) of n-octane and the yield in (ethylene + propylene) (Y_0, wt%) (b) as functions of the ZSM-5 zeolite content (X, wt%) of the hybrid catalyst. The corresponding values obtained with the thermal cracking alone (bentonite extrudates) are also reported (sc).

Table 6
Data obtained with the hybrid catalyst SA(40)HZ/Li

Feed	C_t	Product yields (wt%)								R	Y_0
		Ethene	Propene	Butadiene	Isobutadiene	n-Butenes	C_5^+	Ar	CH_4		
n-Hexane	89.08	28.46	26.94	1.16	2.63	3.43	2.06	5.03	7.61	1.06	55.40
n-Octane	95.23	30.63	27.66	1.25	1.70	3.97	4.84	6.64	7.18	1.11	58.29

Table 7
Structural stability of the zeolite component in the Cc(40)HZ/Li hybrid catalyst (extrudates, catalytic reaction carried out at 735 °C, using n-hexane as feed)

State	RC (%)	BET surface area (m^2/g)		C_t (wt%)	Product yields (wt%)		
		Total	microporosity		Y_0	CH_4	Ar
1st cycle	100	261	82	90.7	57.4	6.8	5.2
2nd cycle	n.a.	n.a.	n.a.	88.3	57.0	7.4	4.6
3rd cycle	84.7	146	57	89.7	56.0	8.5	2.8

n.a. = not available

containing 20 wt% of non-acidic bentonite clay used as binder, showed a density of acid sites which fit well with its weight composition in cocatalyst (Cc/Li) and in zeolite (HZ/Li) (table 3).

7. Catalyst stability after several reaction cycles

Although this study was quite premature, some tests were carried out in order to see the stability of the hybrid catalyst which was submitted to several reaction cycles, each cycle comprising a reaction step and a regeneration or decoking step. With the current conditions of reaction (high temperature and presence of steam) and decoking (3 h of heating in sustained air flow at ~580–600 °C), the Cc(40)HZ/Li hybrid catalyst underwent some significant deactivation which could be associated to a loss of crystallinity and surface area of the zeolite component.

In fact, the crystallinity value (RC) of the catalyst and its pore characteristics, measured after three full reaction cycles, show some marked difference from those of the fresh catalyst (table 7). Table 7 also reports the catalyst activity which did not show any significant decay in terms of total conversion and combined yield "ethylene + propylene". However, the yield of aromatics markedly decreased while methane experienced some significant increase, suggesting that some partial collapse might occur within the zeolite structure. Our current investigation attempts to define the reaction conditions and the regeneration procedure which are not damaging to the structure, thus maintaining catalyst integrity for a much longer period of time.

8. Conclusions

This work showed that by using a hybrid catalyst in the conditions of (mild) thermal cracking of n-hexane and n-octane, it was possible to achieve high total conversion and high selectivity to (ethylene + propylene). Significant interactions between the two catalyst components were also observed. Current investigations are being carried out to elucidate the respective roles of these components, and mostly on that of the chromium species of the cocatalyst surface, as normally identified [8,9].

It is also planned to identify the reaction parameters whose concerted variations can allow us to reproduce the effect of the catalytic lever, as in the case of a two-zone reaction system [4], in order to provide the so-appreciated product flexibility in any commercial application. Finally, the catalyst stability over a great number of "reaction–decoking" cycles has to be systematically studied since the reaction temperature used in this work was quite high with respect to that reported elsewhere for the same ZSM-5 zeolite structure [10,11].

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