Catalytic Activity of Large-Pore High Si/Al Zeolites: Cracking of Heptane on H-Beta and Dealuminated HY Zeolites

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The catalytic activity, selectivity, catalyst decay, thermal and hydrothermal stability, and acidity of H-Beta and HY zeolites with Si/Al ratios of 7.5 and 10, respectively, have been studied during cracking of n-heptane at 450°C and atmospheric pressure. It has been found that the H-Beta zeolite is more active and decays more slowly than HY. H-Beta presents a higher steric hindrance for dibranched molecules and therefore its open structure should be smaller than that of HY. A lower hydrogen transfer activity and hydrothermal stability is observed for H-Beta in comparison with the corresponding HY. © 1987 Academic Press, Inc.

INTRODUCTION

It has recently been proposed (1–3) that the framework Si/Al ratio of zeolites is the controlling factor in the catalytic and hydrothermal behavior of zeolite-cracking catalysts. For good stability, and for formation of gasoline of high octane number and low coke production, HY and REHY ultrastable zeolites with a framework Si/Al ratio in the range 5–20 are desirable. The high Si/Al ratio in these samples can be achieved by deep-bed calcination of exchanged samples and steaming (4), by acid leaching of already partially dealuminated Y zeolites (5), and by $SiCl_4$ (6) or $(NH_4)_2SiF_6$ treatment (7). However, it would be useful to avoid the dealumination process by obtaining directly large-pore high Si/Al zeolites by synthesis. Some zeolites such as Beta and ZSM-20 which accomplish such properties are already available. In this way, the Beta zeolite can be synthesized with silica to alumina ratios in the range 5 to 200 (8, 9). Moreover, this zeolite has a void structure similar to that of zeolite L consisting of pores with 12-membered rings and lobes (10). An open structure such as this is able to take branched

alkylaromatics, and even molecules involving two benzene rings (11). This zeolite can be used for hydrocracking long-chain n-alkanes (8) and hydrocracking–dewaxing heavy oils (12).

All these properties indicate that Beta zeolite could be interesting as a cracking catalyst, and it is the aim of this work to study the behavior of a Beta zeolite during the cracking of the model molecule n-heptane, and to compare the results with those obtained with a dealuminated HY zeolite with the same Si/Al ratio.

EXPERIMENTAL

The tetraethylammonium-Beta zeolite (TEA-Beta) used in this work was given to us by Professor P. A. Jacobs, and was synthesized following the procedure described in Ref. (9). The sample with a crystallite size of 0.2 μm has the following chemical composition in weight percent: 84.8 (SiO_2), 9.5 (Al_2O_3), 1.7 (Na_2O), 4.0 (K_2O). The H form of this zeolite was obtained in the following way. The TEA-Beta sample was heated at 550°C for 3 h, by slowly increasing the calcination temperature (5°C/min), with 1-h intermediate steps at 350 and 450°C. After this treatment all TEA had been removed from the zeolite, as indicated

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by the IR spectra of the zeolite, while the crystallinity of the sample was 80% of the original. In a second step, the zeolite was exchanged in an ammonium acetate solution and then heated at 550°C for 3 h, following the same procedure as above. The exchange calcination was repeated up to six times, and the crystallinity of the final H-Beta zeolite was the same as that of the calcined sample.

A dealuminated HY zeolite (Si/Al = 10) (HYD) was obtained by treating NaY (SK-40, Si/Al = 2.4) with $SiCl_4$ following the procedure described by Beyer et al. (6). The dealuminated sample was thoroughly and repeatedly washed until no Cl^- was detected in the wash water ($AgNO_3$ test). Then it was exchanged at 80°C for 3 h with NH_4^+ acetate solution of density 190 kg/m^3 and calcined at 550°C. The exchange-calcination procedure was repeated three times. The final composition of the sample in weight percent was 88.3 (SiO_2), 11.4 (Al_2O_3), 0.14 (Fe_2O_3), 0.15 (Na_2O). The unit cell size of the sample (24.39 Å) was determined by X-ray diffraction using Cu$K\alpha$ radiation and following ASTM procedure D-3942-8. The estimated standard deviation was ±0.01. The crystallinity of the zeolite (70%) was calculated by comparing the peak heights of the (5,3,3) peak, and considering the NaY SK-40 as having 100% crystallinity.

Catalytic experiments were carried out in a fixed-bed glass tubular reactor at atmospheric pressure and at a reaction temperature of 450°C. The experiments were performed by feeding pure n-heptane (Merck, high purity) at different times on stream (TOS) and at the following range of catalyst-to-oil ratios (cat./oil): 0.0119–0.0171 g g^{-1} for the HYD and 0.0035–0.0250 g g^{-1} for the H-Beta sample. The cat./oil ratios were different for the two catalysts in order to keep the same range of conversion (up to 20%) in all cases. "Cat./oil" is defined here as the amount of catalyst in the reactor divided by the total amount of n-heptane fed in a given time on stream. The catalyst-to-

oil ratio is related with time on stream and contact time by the expression

$$\tau = bPt_f, \qquad (1)$$

where τ is the contact time, t_f is the final time on stream, P is the cat./oil ratio, and b is a proportionality constant (13). The experimental apparatus and procedure were similar to those described in previous studies (13, 14).

Infrared spectroscopic measurements have been carried out in a conventional greaseless IR cell. The samples were pretreated overnight at 450°C and 1.33 × 10^{-3} Pa of dynamic vacuum; then 6.6 × 10^2 Pa of pyridine was introduced into the cell at room temperature and after equilibrium was achieved, the samples were outgassed at 250 and 350°C under vacuum, and the spectra were recorded at room temperature using a Perkin–Elmer 580B spectrophotometer equipped with a data station.

RESULTS

Following the methodology previously described (2), the kinetic and decay parameters were calculated by computer fitting the experimental data to the equations

$$-\ln(1 - X) = k_1[S_0][(1 + (m - 1)k_{md}t)^{-1/(m-1)}] Pbt_f$$

$$\overline{X} = \frac{1}{t_f} \int_0^{t_f} X dt, \qquad (2)$$

where X and $\overline{X}$ are the instantaneous and cumulative average conversion, respec-

TABLE 1

Initial Rate Constants and Decay Parameters for the Cracking of n-Heptane over HYD and H-Beta Zeolites at 450°C

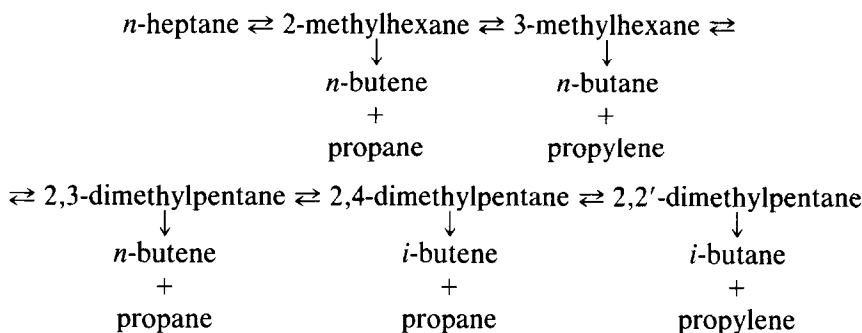|	Catalyst	
	HYD	H-Beta
$k_1 [S_0]$ (m^{3}s^{-1} kg cat.$^{-1}$)	0.547	1.019
k_{md} (s^{-1})	2.27	1.50
m	2.3	2.2

tively, t is the time on stream, $k_1[S_0]$ is the rate constant at zero time on stream, m is the apparent decay order, and k_{md} is a decay constant (15).

The calculated values of $k_1[S_0]$, m, and k_{md} are given in Table 1 for the two catalysts, while in Fig. 1 the experimental and the predicted conversions are shown. The selectivity curves for $C_1–C_7$ products are given in Fig. 2.

DISCUSSION

A general scheme for the monomolecular cracking of n-heptane on acid zeolites has been recently presented (16):

$$n\text{-heptane} \rightleftarrows 2\text{-methylhexane} \rightleftarrows 3\text{-methylhexane} \rightleftarrows$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$n\text{-butene} \qquad\qquad\quad n\text{-butane}$$
$$+ \qquad\qquad\qquad\quad +$$
$$\text{propane} \qquad\qquad\quad \text{propylene}$$

$$\rightleftarrows 2,3\text{-dimethylpentane} \rightleftarrows 2,4\text{-dimethylpentane} \rightleftarrows 2,2'\text{-dimethylpentane}$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$n\text{-butene} \qquad\qquad\quad i\text{-butene} \qquad\qquad\quad i\text{-butane}$$
$$+ \qquad\qquad\qquad\quad + \qquad\qquad\qquad\quad +$$
$$\text{propane} \qquad\qquad\quad \text{propane} \qquad\qquad\quad \text{propylene}$$

It was shown there that by considering the products in the C_3 and C_4 fractions it is possible to obtain some insight into the structure of the zeolite and the nature of the acid sites involved in cracking.
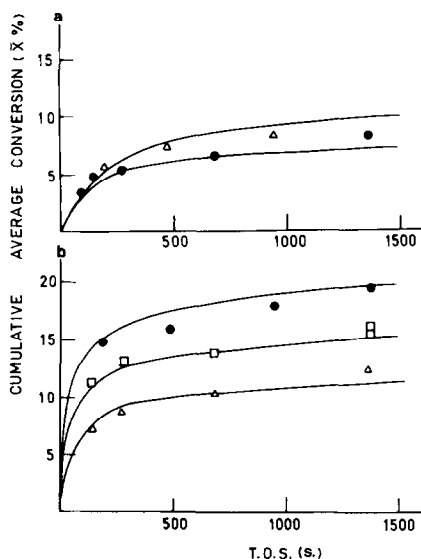

FIG. 1. Cumulative average conversion versus time on stream for HYD and H-Beta zeolites. (a) HYD: (●) 0.0119, (△) 0.0171 catalyst-to-oil ratio. (b) H-Beta: (△) 0.0120, (□) 0.0174, (●) 0.0250 catalyst-to-oil ratio. Continuous lines are the fitted curves.

In this way it can easily be seen in the above scheme that i-butane, which is the majority component observed in the C_4 fraction, is formed from the bulkiest isomer, i.e., 2,2'-dimethylpentane and to a minor extent, since we are using initial selectivities, from the 2,4-dimethylpentane via hydrogenation (hydrogen transfer) of the i-butene formed by cracking. Therefore the smaller the cavity of the channel of the zeolite is, the smaller are the amount of 2,2'-dimethylpentane and hydrogen transfer, and therefore the lower the selectivity to i-butane. This effect has been clearly shown by comparing the cracking (17) and hydrocracking (18) results of n-heptane on a large-pore and a medium-pore-size zeolite such as HY and HZSM-5, respectively.

The structure and therefore the dimensions of the cavities of the Beta zeolite are not known but it seems that its void structure is similar to that of zeolite L (9). From the initial selectivity values for i-butane on the HYD and H-Beta zeolites presented in Table 2, it can be seen that the i-butane/C_4 fraction ratio is higher for HYD than for H-Beta. This result indicates that the structure of H-Beta should present a higher steric hindrance than HYD zeolite for the
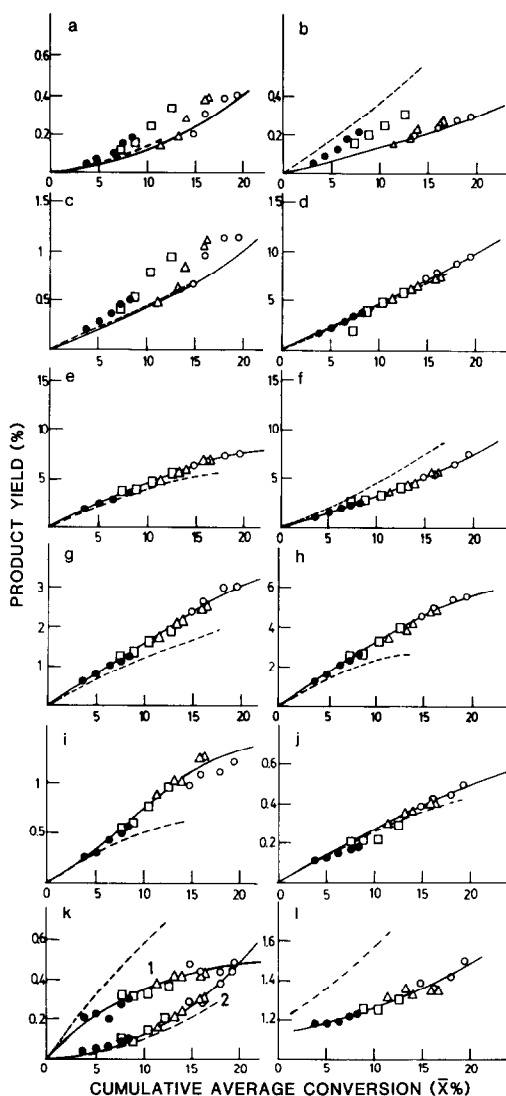
FIG. 2. Selectivity plots for the reaction products during cracking of n-heptane over HYD and H-Beta zeolite catalysts. (a) Methane, (b) ethane, (c) ethylene, (d) propane, (e) propylene, (f) i-butane, (g) n-butane, (h) butenes, (i) C_5 fraction, (j) C_6 fraction, (k) C_7 fraction (1) and aromatics (2), (l) paraffin-to-olefin ratio. (●) 0.0035, (□) 0.0120, (△) 0.0174, (○) 0.0250 catalyst-to-oil ratio. (—) H-Beta; (---) HYD.

TABLE 2

Initial Selectivities to Primary Products in the Cracking of n-Heptane on HYD and H-Beta Zeolites at 450°C

Product	Catalyst	
	HYD	H-Beta
Ethane	0.035	0.012
Ethylene	0.044	0.038
C_2 fraction	0.079	0.050
Propane	0.390	0.469
Propylene	0.444	0.459
C_3 fraction	0.834	0.920
i-Butane	0.400	0.300
n-Butane	0.130	0.161
Butenes	0.300	0.333
C_4 fraction	0.830	0.794
C_5 fraction	0.060	0.072
C_6 fraction	0.033	0.029
C_7 fraction	0.066	0.053
Paraffin-to-olefin ratio	1.30	1.17

formation of dibranched isomers, and therefore its cavities should be smaller than those of a faujasite-type zeolite, in agreement with the constraint index of the two zeolites (19). However, if the above ratio is calculated for a HZSM-5 zeolite (i-butane/ C_4 fraction = 0.17) (17), the comparison

with the results from Table 2 indicates that the pore dimensions of a Beta zeolite should be closer to those of a large-pore than to those of a medium-pore zeolite. This fact, together with the possibility of synthesizing Beta zeolite within a large range of Si/Al ratios, makes this zeolite a promising cracking catalyst. This is especially true if one considers that now refineries are asking for cracking catalysts which produce gasoline with an octane number as high as possible. This is achieved by catalyst manufacturers by preparing active zeolites with low Na content and low activity for hydrogen transfer reactions. Moreover, and since, in many fluid catalytic cracking (FCC) units, residues are incorporated in the feed, the new catalysts should also be low coke producers, something which is again related to their activity for catalyzing hydrogen transfer reactions. It is possible to analyze the importance of the hydrogen transfer reactions on the two catalysts under study by looking at the alkane/alkene ratio in the products. In this way, from Fig. 2 it is possible to see that the selectivity for olfeins is higher for H-Beta

than for HYD zeolite at all levels of conversion studied. Therefore, one would expect that during gas–oil cracking H-Beta zeolites could produce gasoline with a higher octane number than HYD.

The initial values of the alkane/alkene ratio, i.e., the values when conversion and time on stream tend to zero, given in Table 2, as well as the results at different levels of conversion given in Fig. 2, show that the ratio is higher for the HYD than for the H-Beta zeolite. In other words H-Beta produces a higher amount of olefins than HYD, indicating that one should expect H-Beta to be a superior catalyst to HYD zeolite from the point of view of the research octane number of the gasoline obtained when cracking gas–oil. Furthermore, a higher amount of olefins in the products has been related to a lower hydrogen transfer ability of the catalyst (1), which on the other hand depends on the density of Brønsted acid sites. The IR spectra of pyridine adsorbed and desorbed on these samples show that the amount of Brønsted sites (1545-cm^{-1} band) of medium (250°C of desorption temperature) and strong acidity (350°C of desorption temperature) is lower for the H-Beta than for the HYD sample, in agreement with the above hypothesis (see Table 3).

If we now look at the rest of the cracking products, by analyzing the selectivity curves given in Fig. 2 we can see that the same products with the same selectivity behavior are obtained regardless of the zeolite used as catalyst. Thus, in the range of conversions studied, ethane, ethylene, propane, and i-butane are primary plus secondary products. Propylene, n-butane, butenes, C_5, C_6, and C_7 (branched isomers) fractions are primary and unstable products, while methane, toluene, and xylenes are secondary and stable products or, if primary, their initial selectivities must be very low. This similarity in the product distribution indicates that catalytic cracking of n-heptane takes place by the same basic mechanisms on both zeolites. However,

the selectivities of the different products are not the same for these two zeolites, suggesting that even if the same reactions occur on both catalysts the extension of those reactions is a function of the type of zeolite. Indeed, if one calculates the fraction ratios C_i/C_{7-i} from the initial selectivities given in Table 2, one can see that $C_i/C_{7-i \neq 1}$ are different for the two catalysts. This result indicates that the products are formed not only by a direct cracking of n-heptane in the two complementary fragments ($C_i + C_{7-i}$), but also by other reactions such as recracking and disproportionation (20). If this is so, then the activity of these two zeolites for the different types of cracking reactions is not the same. In the case of the HYD zeolite the C_4/C_3 ratio is only slightly lower than unity and therefore most of these fractions should be obtained by direct cracking. The C_2/C_5 ratio in this zeolite is greater than unity indicating that the excess of the C_2 fraction is produced by recracking of the C_5 and C_6 fractions. However, in the case of the H-Beta zeolite those ratios are clearly lower than one. It is obvious that in this case the excess of C_3 can hardly be explained by recracking of the C_6 and C_5 hydrocarbons formed in a primary cracking event, as has been suggested (21), since then not only would methane have to appear as a primary product, which does not seem likely, but also its initial selectivity would have to be higher than that of C_6, which does not occur either. Moreover, the C_2 fraction could never be lower than the C_5 fraction if recracking of C_5 and C_6 took place to an important extent.

Another possible explanation for the selectivity results observed here is the existence, together with the direct cracking of n-heptane, of disproportionation reactions. At low levels of conversion, these reactions imply one alkylation process between two reactant molecules and/or a reactant and a product molecule, followed by a fast cracking of the longer chain formed (20). Reactions of this kind can account not only for the small amount of products with a num-

ber of carbons higher than seven, but also for the primary character shown by the C_6 fraction while methane appears as a secondary product, and also for the C_i/C_{7-i} ratios observed (20). Thus, if we accept the above explanation we should conclude that the H-Beta zeolite gives a higher disproportionation/direct-cracking ratio than the HYD zeolite. This, in turn, is a consequence of a higher capacity for alkylation of the former zeolite, probably due to the higher concentration of olefins caused by its lower hydrogen transfer activity. An alkylating capacity of a cracking catalyst is a very desirable property, since it increases the yield in liquid products while increasing the motor octane number. Therefore, also from this point of view zeolite Beta appears as a promising cracking catalyst.

Cracking Activity and Catalyst Decay

The conversions at different times on stream and cat./oil ratios given in Fig. 1 show that the behavior of the two catalysts is very similar. The kinetic and decay parameters given in Table 1 show again that there are no large differences in the values of the parameters for the two catalysts. Nevertheless, the activity of the H-Beta is higher than that of the HYD zeolite, while the former decays more slowly. The higher activity of the H-Beta zeolite should be a consequence of a higher number of strong acid sites, which are believed to be those active in n-heptane cracking (3, 22). From the area of the IR bands at 1545 and 1450 cm^{-1} and taking into account the extinction coefficients for these bands given by Hughes and White (23) the moles of pyridine remaining adsorbed on Brønsted and Lewis acid sites can be calculated; the values are given in Table 3. It is apparent that the H-Beta zeolite presents stronger Brønsted plus Lewis acid sites (pyridine remaining adsorbed after 350°C desorption treatment) than the HYD zeolite. The high density of Lewis acid sites in both catalysts should be pointed out. In the case of the HYD sample, the comparison of the total

TABLE 3

Amount of Pyridine Remaining Adsorbed on Brønsted and Lewis Acid Sites after 250 and 350°C Heat Treatment, and 1.33×10^{-3} Pa Outgassing Conditions, as Deduced from Infrared Absorption Spectra

Sample	μmol of pyridine adsorbed $\cdot$ g^{-1}			
	Brønsted (1545 cm^{-1})		Lewis (1450 cm^{-1})	
	250°C	350°C	250°C	350°C
H-Beta	93	55	68	60
HYD	126	66	60	42
H-Beta-steamed	11	5	8	5
HYD-steamed	16	5	10	5

Si/Al ratio obtained by chemical analysis, and the framework Si/Al ratio of 9.8 calculated from the unit cell size and expression of Fichtner-Schmittler et al. (24), clearly shows that extra framework aluminium is present in the zeolite, and this can make a contribution to the total Lewis acidity observed by pyridine. In the case of the H-Beta zeolite the Lewis acidity observed after calcination to eliminate the tetraethylammonium present is practically the same as the Lewis acidity observed after the six NH_4^+ exchange-calcination cycles. Therefore the Lewis acidity in the H-Beta zeolite must be related to the species formed during the decomposition of the alkylammonium cation, which on the other hand provokes a certain decrease in the crystallinity of the sample. Moreover, the deactivation of these catalysts during the reaction is due to self-poisoning by coke formation. Coke is formed mainly by hydrogen transfer from cycloalkanes and polyaromatics to olefins, and therefore it is not surprising that H-Beta decays more slowly since it is a worse hydrogen transfer catalyst than HYD.

From the point of view of activity and catalyst decay H-Beta seems to be a good cracking catalyst. However, it should be taken into account that since H-Beta shows

a higher steric hindrance for large molecules than HYD, the order of activities observed with *n*-heptane may change when gas–oil molecules must be cracked.

Hydrothermal Stability

In order to check their hydrothermal stability, both zeolites have been steamed for 3 h at 750°C and 1 atm of steam. In Fig. 3 X-ray diffractometer results for samples before and after steaming are given. It is apparent that HYD is more stable than H-Beta, and therefore the lost activity in a steam regeneration should be higher for the H-Beta than for the HYD sample. This assumption is supported by the cracking results obtained with the steamed zeolites which are given in Table 4, which, on the other hand, are in agreement with the acidity measurements in Table 3. Nevertheless, a modern engineering adaptation of the regeneration process involves two steps (25). The first stage of the regeneration takes place at 600°C in an insufficient amount of O_2, and the CO-rich flue gas is then separated from the catalyst before the second regeneration stage, in which the combustion occurs at 750°–900°C in excess oxygen. Following this process the catalyst is protected against hydrothermal deactivation, since steam is not pre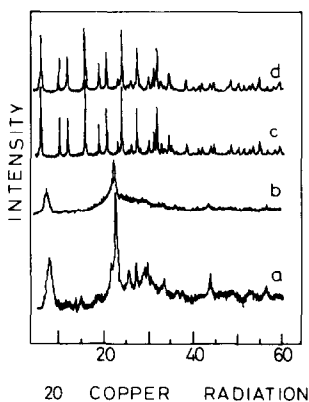sent and CO after burning is avoided. Therefore, in this process, thermal stability becomes even more important than hydrothermal stability, this being the reason why we have checked the thermal stability of H-Beta. The X-ray analysis of a sample heated at 750°C under a small partial pressure of steam, 2587.5 Pa, for 3 h showed that its crystallinity does not change significantly, indicating a good thermal stability of the sample.

In conclusion, the H-Beta zeolite shows a slightly higher activity for cracking *n*-heptane, a lower hydrogen transfer capacity, and a lower catalyst decay by self-poisoning than a HY zeolite with a closely similar Si/Al ratio. The former zeolite presents a higher steric hindrance for dibranched molecules, and finally, the hydrothermal stability of the H-Beta is lower than that of the HY dealuminated zeolite, while the thermal stability of the former is acceptable.

TABLE 4

Cumulative Average Conversion ($\overline{X}$) at 450°C,[a] for HYD and H-Beta Zeolites before and after Steaming (750°C and 1 atm of Steam)

Catalyst	$\overline{X}$ (%)	
	Fresh	Steamed
HYD	5.02	0.63
H-Beta	11.35	0.65

[a] Experimental conditions: HYD, cat./oil = 1.71×10^{-2} (g g^{-1}), TOS = 95 s.; H-Beta, cat./oil = 1.74×10^{-2} (g g^{-1}), TOS = 136 s.

FIG. 3. X-ray diffractograms for the fresh and steamed catalysts. Before steaming: (a) H-Beta, (c) HYD. After steaming: (b) H-Beta, (d) HYD.

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