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Effect of hydrogen on the cracking mechanisms of cycloalkanes over zeolites

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ABSTRACT

Hydrocracking of secondary interest refinery streams (high aromatic content) can yield valuable products for transportation and petrochemical industry. In order to promote the hydrogenation and cracking steps, a bifunctional catalyst (metal + acid function) is required. We have studied the effect of the operating conditions on cycloalkane (product of aromatic hydrogenation) ring opening over a monofunctional HZSM-5 zeolite, by focusing on the effect of hydrogen in the cracking mechanisms. Methylcyclohexane has been selected as the test reactant and the conditions used corresponds to temperature, 250–450 °C; space velocity, 0.7–1.1 h^{-1}; pressure, 2–80 bar; hydrogen/methylcyclohexane molar ratio, 1–79; conversion, 0–100% (integral reactor). At these conditions the zeolite catalyses hydrogenation as well as cracking (bifunctional capabilities), thus the cracking mechanisms are directly affected by hydrogen as products (alkenes) and intermediates (carbenium ions) are saturated. The overall effect of rising hydrogen partial pressure is an enhancement of (hydro)isomerization and monomolecular cracking, that is, an increase of the yield/selectivity of methane, ethane, penthane and isoalkanes.

1. Introduction

Petrochemical industry needs to adequate its production to the shifting demands of the market. Thus, the severe restrictions in aromatic content of fuels can cause a surplus generation of these compounds [1]. In particular, light aromatics (C_{9-}) can saturate the market since they are by-products of processes that are being increasingly used for obtaining light olefins (steam cracking), coke (coking) and novel routes of waste and biomass valorization (pyrolysis and FCC) which generate streams of high aromatic content [2]. Furthermore, the processes that use light aromatics as raw materials are currently insufficient to absorb the surplus production [1].

Hydroprocessing is an increasingly used technology by refiners in order to convert heavy-refractory feedstock, aromatics and heteroatoms (sulphur, oxygen and so on) into raw materials for petrochemical processes or valuable blending for transportation [3]. For example, light aromatics from steam cracking (so called pyrolysis gasoline) can be hydroconverted to C_{2+} *n*-alkanes and, when recirculated, these products boost the yield of light olefins of the unit [4]. Alternatively, the hydroconversion of pyrolysis gasoline can be selectively tuned to produce highly branched isoalkanes (with high octane number) for the gasoline pool [5].

In severe hydrocracking conditions (simplifying the reactions), the aromatics are first hydrogenated over the metallic function and then the cycloalkanes (products of the first step) are cracked on the acidic function. In these conditions the acidic function plays a determining factor since its shape selectivity [6] and its acidity [7,8] control the catalytic performance more than the metallic function [9]. We previously studied the effect of shape selectivity by means of using different zeolitic (Hβ and HY) and amorphous structures, from this work we concluded that HZSM-5 zeolite have a good compromise between activity–selectivity–stability [6].

The macroscopic mechanisms of cyclohexanes ring opening over acid zeolites have been previously reported and modeled [10,11]. This scheme of reaction facilitates the interpretation of the data and predicts faithfully the product distribution under a specific set of experimental conditions. On the other hand, a more fundamental approach is needed to understand the impact of hydrogen on the cracking mechanism [12]. Raichle et al. [13] studied this system and pointed out the importance of oligomeric cracking. However the same authors concluded that bimolecular mechanisms (oligomeric cracking needs also two molecules) are hindered in HZSM-5 zeolite [1]. Thus, the hydrogenation capacity of the zeolite [14,15] can possibly explain better the observations as some authors have reported [16–18].

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The aim of this work is to understand the mechanisms of cycloalkane ring opening over acid zeolites (metal free) in the presence of hydrogen. In a previous paper [10] we pointed the effects of hydrogen on the kinetic model and selectivity of the same reaction, the main contribution of the present work is to propose fundamental interpretation of the cracking mechanisms and how they change by the presence of hydrogen. The acid sites of the zeolite are able to perform both cracking and hydrogenation simultaneously, leading to a modification of the classical cracking mechanisms.

2. Experimental

The catalyst has been prepared from: (i) 25 wt.% HZSM-5 zeolite, Zeolyst International, Si:Al = 15, Na_2O = 0.05 wt.%, (ii) 30 wt.% bentonite as binder and (iii) 45 wt.% of inert α-Al_2O_3, Merck. The solids are wetted and mixed, then extruded, dried (24 h, 120 °C), crushed, pelletized (0.15–0.30 mm) and calcined (3 h, 550 °C). The final step assures an optimal number and distribution (Brönsted-to-Lewis) of acid sites for the ring opening of cycloalkanes [8].

The physical properties of the catalyst (N_2 adsorption–desorption in a Micromeritics ASAP 2010 apparatus) are: BET surface area, 220 m^2 $(g_{cat})^{-1}$; pore volume, 0.092 cm^3 $(g_{cat})^{-1}$; micropore volume, 0.040 cm^3 $(g_{cat})^{-1}$. Total acidity (NH_3–TPD in a Setaram TG-DSC 111 equipped on-line with a Balzers Quastard 422 mass spectrometer) at 150 °C is 175 mol_{NH_3} $(g_{cat})^{-1}$, with a uniform distribution of acid sites, having an average acid strength of 152 J$(mmol_{NH_3})^{-1}$. The Brönsted-to-Lewis acid site molar ratio, obtained in a FTIR spectrophotometer (Nicolet 740 SX), from the vibrational bands of adsorbed pyridine at 1547 and 1453 cm^{-1} at 150 °C, is 2.62.

The reaction system consists of a tubular fixed bed rector where the gas-phase (hydrogen and hydrocarbons) down-flow. The bed is made up of a mixture of catalyst and diluent (SiC) in a weight ratio of 1:1. This system has already been described elsewhere [10]. The sampling was undertaking by a 6-way-valve actuated by the analysis setup; GC Hewlett Packard 5890 Series II equipped with a flame ionization detector (FID) and a capillary column, Tracer TRB-1. The conditions employed are the following: temperature, 250–450 °C; WHSV, 0.7 h^{-1}; pressure, 2–80 bar; N_{H_2}, $1-79\,mol_{H_2}/mol_{MCH}$; conversion, 0–100% (integral reactor); time on stream, 0–7 h.

3. Reaction mechanisms

In the conditions employed, the hydrocarbons suffer cycles of cracking-hydrogenation to form lighter products. In our previous work [10] we named these cracking steps as primary, secondary and so on. Nevertheless, we must consider that each of the mentioned steps could represent one or more mechanism.

The mechanisms of catalytic cracking involve carbocations, in particular carbenium and carbonium ions. As we previously demonstrated, the presence of hydrogen affects the conversion and selectivity of the methylcyclohexane hydroconversion [10]. In this work we will focus on how the mechanisms of cracking are affected from a more fundamental viewpoint. Under the conditions employed, the methylcyclohexane on the surface of the HZSM-5 zeolite can donate a pair of electrons to form a carbenium ion which undergoes β-scission, isomerization or hydrogen transfer with another molecule, hence, this mechanism is known as bimolecular or classical cracking. Additionally, the methylcyclohexane can accept a proton to form a carbonium ion which undergoes protolytic scission through the monomolecular or non-classical cracking (Haag–Dessau cracking). It is worthwhile to mention that the catalyst without zeolite (binder + α-Al_2O_3) have negligible activity: The conversion of methylcyclohexane (MCH) is lower than 1% under the most severe conditions, due to the low concentration and strength of the binder acid sites, measured by NH_3–DSC [7,19].

Considering all the possible reactions pathways make interpretation complex, however several approaches can be done in order to simplify the problem [20,21]. In our case, the presence of hydrogen increase the complexity of the reaction even further, as hydrogen can possibly incorporate into two different hydrocarbons; double-bond-molecules (alkenes and aromatics) and carbenium ion (to form carbonium ion). Additionally, the latter reaction could also inhibit the formation of alkenes, as carbonium ion does not necessarily produce alkenes. Due to the resonance energy, alkenes hydrogenate faster than aromatics. There is controversy in regard to how carbeniun ion is hydrogenated, and the most convincing explanation is that carbenium ions adsorbed on the catalysts react via hydrogen transfer with molecular hydrogen.

Let us take for example the first ring-opening in a simplified scheme; the most stable carbenium formed from methylcyclohexane is the most substituted one (ternary), β-scission followed by hydrogenation of the produced alkene would yield 2-methylhexane (2MH), whereas 3-methylhexane (3MH) would be produced from isomerization of 2MH or one of its intermediates previously described. Cycloalkanes, and their carbenium counterparts in particular, can suffer ring-contraction and ring-extension. As these reactions do not imply the decrease in molecular weight but a rearrangement of the hydrocarbon molecule, we will designate them ring-isomerization to discriminate them from chain-isomerization. Thus, the formation of 2-methylhexane can be also ascribed to ring-contraction and subsequent β-scission followed by hydrogenation, without regard, involving an isomerization reaction. On the other hand, the protolytic cracking of the carbonium ion (of MCH, in C_1) would yield heptane or methane and cyclohexane, other carbonium ions could yield other seven-carbon-molecules: in C_2, heptanes or 2MH; in C_3, 2MH or 3MH; and in C_4, 3MH. All of these mechanisms involving methylcyclohexene are summarized in Fig. 1 but represent only the minimal pathways, too much oversimplified.

In synthesis (excluding monomolecular cracking which is non-selective), 2MH is mainly formed trough ring-isomerization/scission/hydrogenation or scission/hydrogenation while 3MH can be formed through scission/chain-isomerization/hydrogenation. In order to quantify the importance of chain-isomerization over β-scission and ring-isomerization, the index associated with the yields (Y) of C_7 isomers has been defined as follows:

$$R_7 = \frac{Y_{2MH}}{Y_{3MH}} \tag{1}$$

Increasing the severity of the reaction by means of rising temperature and/or pressure will reduce the average molecular weight of the products so that R_7 is no longer useful. Then, another index is needed for quantifying the impact of isomerization over

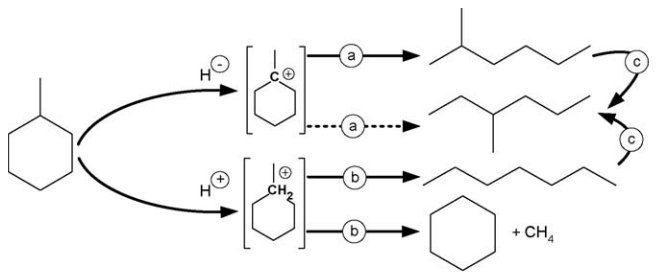

Fig. 1. Simplified scheme of the ring opening of methylcyclohexane trough carbenium and carbonium ions. This scheme does not consider other reactions involved as ring contraction, but is useful to recognize the reactions involved. (a) β-scissions, (b) protolytic scission and (c) isomerization.

cracking at these conditions:

$$R_4 = \frac{Y_{C_4}}{Y_{C_4} + Y_{iC_4}} \qquad (2)$$

The narrower pore network of HZSM-5 as compared to HY or Hβ zeolites (more severe shape selectivity) leads to a hindrance of bimolecular reactions on the benefit of monomolecular ones [22], and β-scission (one molecule) over hydrogen transfer (two molecules). The cracking mechanism ratio (CMR) quantifies the relative contribution of the Haag–Dessau mechanism on the global cracking mechanisms [23,24] and is calculated as follows:

$$\mathrm{CMR} = \frac{Y_{C_1} + Y_{C_2}}{Y_{iC_4}} \qquad (3)$$

In the condition employed we assumed that all the methane and ethane are produced through monomolecular cracking (of methyl and ethylcycloalkanes as well as long-chain alkanes and isoalkanes). In a FCC unit, methane is considered to be produced via radicals (thermal cracking) [25]. Nevertheless, the lower temperatures and the high concentration of hydrogen used in hydrocracking limit the influence of these mechanisms [26]. Enhancing the monomolecular cracking would induce an increase in the yield of methane, which is virtually inert for any other type of reaction. However, ethane is an interesting feedstock for steam-cracking accounting for the increase in the production of ethene when ethane is co-fed into the unit [4].

4. Results

Fig. 2 shows the hydrogen incorporation in the hydrocarbon stream (in wt.% of the initial flow-rate) at different temperatures and hydrogen partial pressures. This parameter has been calculated by applying the carbon–mass balance over the reactor assuming no accumulation or conversion of the mass introduced. As observed in the figure, the higher the hydrogen partial pressure and temperature the more hydrogen is incorporated into the hydrocarbon feed; that is, the hydrogen effect on the mechanisms is more pronounced when the conditions are more severe. Assuming no hydrogenolysis reactions (no metallic sites), hydrogen can only be incorporated into the feed by hydrogenating the alkenes generated in the β-scission or the carbenium ion [14,15].

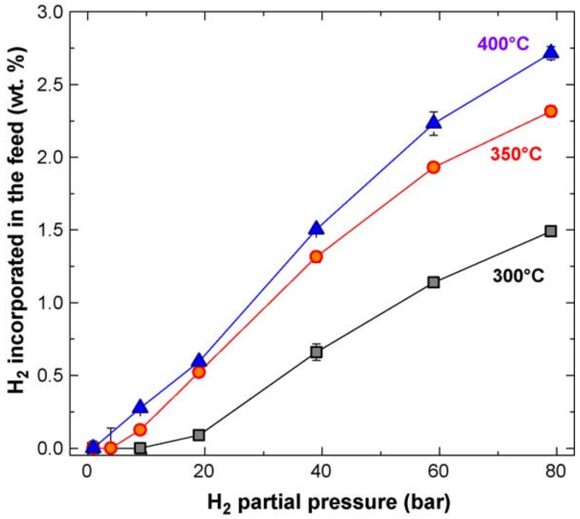

Fig. 2. Fraction of H_2 (in wt.%) incorporated in the hydrocarbon stream of methylcyclohexane. *Conditions*: WHSV = 0.7 h^{-1}.

Table 1
Conversion and product yields of methylcyclohexane on a HZSM-5 zeolite and different partial pressures of hydrogen. Conditions: WHSV = 0.7 h^{-1} and 350 °C.

H_2 pressure (bar)	4	19	79
Conversion (%)	81.56	94.66	99.87
Methane	**0.10**	**0.42**	**1.08**
C_{2+} n-alkanes	**46.42**	**62.06**	**68.72**
Ethane	0.49	1.15	3.03
Propane	30.50	44.81	45.63
Butane	13.98	14.45	17.67
Pentane	1.34	1.54	2.28
Hexane	0.10	0.11	0.11
Isoalkanes	**11.01**	**17.96**	**28.23**
Isobutane	5.93	10.50	16.48
Isopentane	3.18	5.41	8.95
Dimethylbutane	0.41	0.55	0.78
Methylbutane	1.12	1.26	1.91
2 Methylhexane	0.09	0.03	0.01
3 Methylhexane	0.14	0.07	0.03
Dimethylpentane	0.14	0.13	0.07
Cycloalkanes	**3.59**	**1.21**	**0.53**
Cyclopentane	0.00	0.09	0.16
Methylcyclopentane	0.89	0.12	0.01
Cyclohexane	0.09	0.03	0.01
Dimethylcyclopentane	1.28	0.35	0.14
Ethylcyclopentane	0.32	0.02	0.00
Trimethylcyclopentane	0.26	0.09	0.01
Dimethylcyclohexane	0.45	0.34	0.14
Cycloalkanes C_{8+}	0.30	0.18	0.05
Aromatics	**20.45**	**13.02**	**1.31**
Benzene	3.23	1.69	0.15
Toluene	12.93	8.74	0.50
Aromatics C_{8+}	4.26	2.54	0.64

Table 1 summarizes the product distribution of methylcyclohexane hydroconversion on a HZSM-5 zeolite at 350 °C and three different hydrogen partial pressures (4, 19 and 79 bar). As it can be seen, the yield of methane, alkanes and isoalkanes increased with hydrogen pressure in detriment of cycloalkanes and aromatics. However, these tendencies are not applicable to the compounds of each lump; the yield of all the hydrocarbons C_{7+} decreases as the hydrogen pressure increases. These results indicate that hydrogen favors the hydroconversion of methylcyclohecane by enhancing isomerization, bimolecular and monomolecular routes and limiting all the oligomerization (chain or ring extension) and dehydrogenation reactions. Now we will try to disguise which is the specific influence of hydrogen on each of the mechanisms of reaction.

Fig. 3 illustrates the effect of hydrogen partial pressure on the conversion (of methylcyclohexane) and selectivity of the products, corresponding to 300 °C (less sever conditions that Table 1). As observed, the conversion has a minimum at 10–20 bar. At lower pressures, cycloalkanes mainly are transformed into aromatics (as demonstrated by its higher selectivity). Furthermore, C_{2+} *n*-alkane selectivity is the highest. These two simultaneous observations can be explained if we consider that certain amount of methylcyclohexane is converting to alkenes through the typical cracking mechanisms, according to which both alkenes and cycloalkanes transfer hydrogen between each other to form aromatics (more stable than alkenes) and alkanes, as depicted in Fig. 4. When hydrogen partial pressure is increased, conversion decreases because selectivity of aromatics is reduced; the faster hydrogenation of alkenes accounts for these observations, in which hydrogen transfer is inhibited. As we increase hydrogen partial pressure above 20 bar, the amount of H_2 incorporated into the hydrocarbon increases drastically (Fig. 2) and so it does the hydrogenation of alkenes and carbenium ions. As a result, isoalkane and methane selectivity increases (see also the yields in Table 1), indicating a shift in the dominant mechanisms when hydrogen is present in an

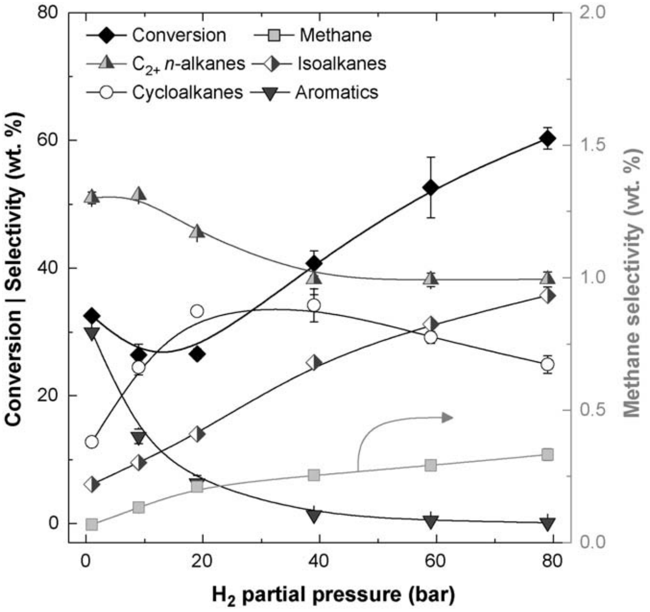

Fig. 3. Effect of the hydrogen partial pressure on the conversion and selectivity during methylcyclohexane ring opening. *Conditions*: 300 °C, WHSV = 0.7 h^{-1}.

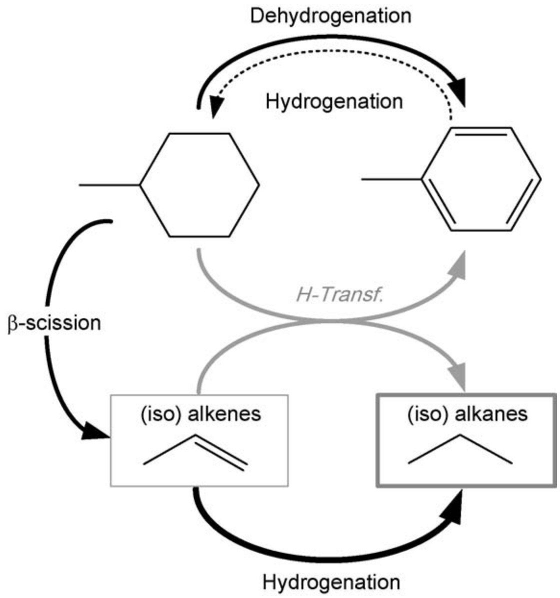

Fig. 4. Simplified scheme of individual reaction steps based on hydrogenation, hydrogen transfer and β-scission (monomolecular cracking and isomerization are not considered). The mechanisms represented with gray lines are enhanced at lower partial pressures of hydrogen.

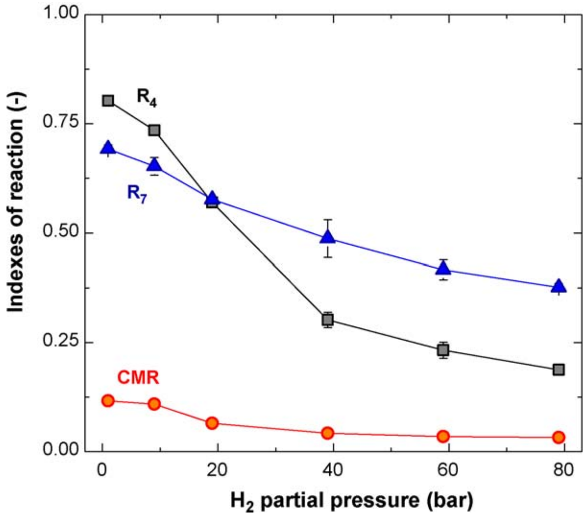

Fig. 5. Effect of the hydrogen partial pressure on the reaction indexes during methylcyclohexane ring opening. *Conditions*: 300 °C, WHSV = 0.7 h^{-1}.

significant amount, that is, more isomerization and monomolecular cracking. Interestingly, hydrogen does not block the active sites of the catalyst, since pressures of 79 bar of hydrogen are not able to reduce the conversion of methylcyclohexane (Fig. 3). Two facts can explain this result; (i) the high mobility of chemisorbed species of hydrogen on the catalytic surface or (ii) the hydrogenation of reaction intermediates (alkenes and carbenium ions) occurs through an Eley–Rideal type mechanism, meaning that hydrogen is not adsorbed on the acid sites but directly reacts with hydrocarbon-adsorbed-species. Considering that no metallic site is present and the acid sites are able to make hydrogen highly movable and, at the same time, they are presumably responsibly for its adsorption, we tentatively explain our observation according to fact (ii).

By working at pressures lower than 20 bar the selectivity of aromatics and alkanes is increased, but the deactivation is much higher so that coke precursors are easily formed over the zeolite surface. In fact, the results presented in Fig. 3 correspond to the initial activity observed in the first 2 h of reaction. For pressures of 1 bar of hydrogen, the catalyst deactivates severely within 3 h, approaching the behavior of standard catalytic cracking [11].

Coke does not have a single effect of deactivation, but some carbonaceous deposits could act as catalysts, or enhance shape selectivity [27]. In terms of deactivation both cracking and hydrogenation reactions decay, nevertheless such decay is negligible by using pressures higher of 20 bar. The TPO of spent catalyst showed very low content of coke [8] so its contribution to the catalysis and therefore to the mechanisms is, in this case, insignificant.

Fig. 5 represents the impact of hydrogen pressures on the indices of reaction described in section 3, at the same conditions as in Fig. 3. As observed, R_7 decreases as does the hydrogen partial pressure, indicating that more 3MH is formed than 2MH. In correspondence with this result, R_4 index also decreases; more and more isobutane is formed. Together with the results of Fig. 3, we conclude that carbenium ions react faster in the presence of hydrogen, allowing more recombinations of these ions and particularly isomerization. The CMR index decreases with hydrogen partial pressure indicating that monomolecular cracking is less important at these conditions. On the contrary, methane selectivity increases, as shown in Fig. 3. Considering the enhancement of isomerization reactions, particularly the formation of isobutene (denominator of CMR) as demonstrated with R_4 index, the monomolecular cracking is indeed favored at higher pressures of hydrogen trough the hydrogenation of the carbenium ion (to form carbonium ion). The CMR decreases as a result of the higher yield of isobutene as compared to methane (coming from the exocyclic–protolytic scission of methycyclohexil–carbonium ion as illustrated in Fig. 1).

This discrepancy between methane selectivity and CMR is better understood when this index is plotted versus the complete spectrum of hydrogen pressures and temperatures, see Fig. 6. The figure has been divided into two sections in order to see better the differences in scales. At temperatures higher than 350 °C, CMR increases exponentially with temperature, which means a more

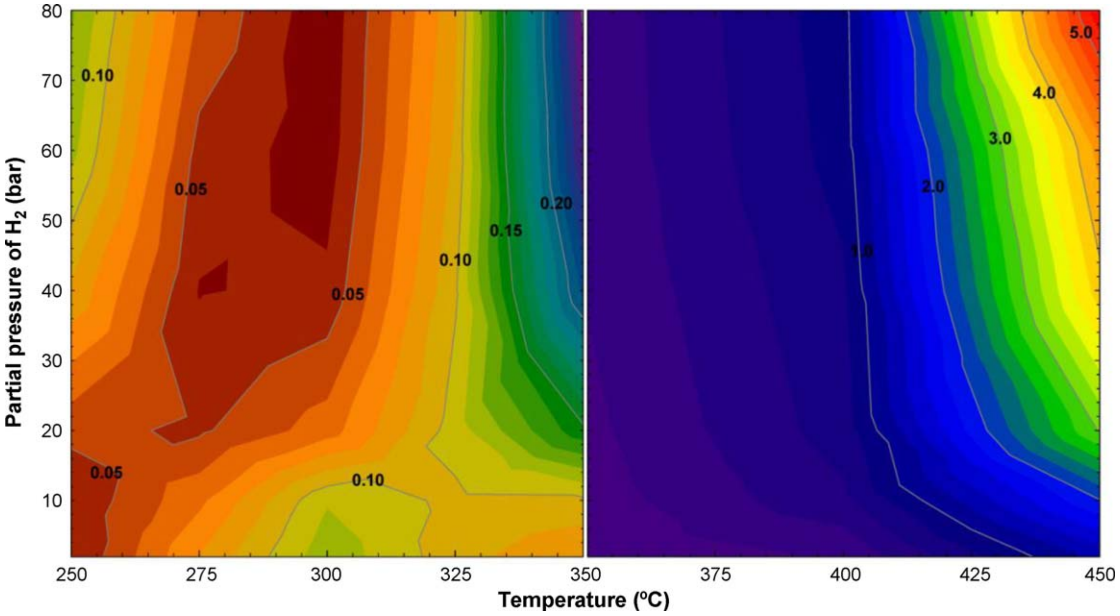

Fig. 6. Effect of hydrogen partial pressure on the CMR index (Eq. (3)) during methylcyclohexane ring opening. *Conditions*: WHSV = 0.7 h^{-1}.

significant monomolecular cracking. At lower hydrogen pressures, CMR decreases as the hydrogenation of carbenium ion is less favored, so that bimolecular cracking is more important; more alkenes can be formed which quickly react with cycloalkanes through hydrogen transfer to form aromatics and alkanes (see Fig. 4). The isomerization reactions can hinder the result interpretation for a correct evaluation of the significant of monomolecular cracking. The minimum of CMR observed at 80 bar and 300 °C is due to a maximum of isobutene formation; that is, bimolecular cracking and isomerization reactions under these conditions are faster than monomolecular cracking.

5. Conclusions

The cracking mechanisms of ring opening of cycloalkenes over zeolites in the presence of hydrogen are fundamentally different from the classical cracking mechanisms due to the fact that the zeolite hydrogenates reaction intermediates and products. As a result, the metal-free zeolite behaves as a bifunctional catalyst when the pressure of hydrogen is sufficiently high, promoting (hydro-) isomerization and decreasing instaurations caused by double bounds and cycles.

By introducing hydrogen, the non-classical monomolecular cracking is enhanced by an extra production of carbonium ions, coming from the hydrogenation of carbenium ions. On the other hand, at high hydrogen pressures the isomerization reaction is favored over the cracking so that the selectivity of isoalkanes increases dramatically.

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