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Catalytic cracking of decalin isomers over REHY-zeolites with different crystallite sizes

E. Falabella Sousa-Aguiar^{a,b,*}, Cláudio J.A. Mota^a, M.L. Murta Valle^a, M. Pinhel da Silva^b, D. Forte da Silva^c

^a Centro de Pesquisas e Desenvolvimento Leopoldo A.M. Mello (CENPES)/Petrobrás-Ilha do Fundão/Q.7-Cidade Universitária, CEP 21949-900, Rio de Janeiro, Brazil

^b Escola de Química/UF RJ-Ilha do Fundão, Centro de Tecnologia, Bloco E-Cidade Universitária, Rio de Janeiro, Brazil

^c COPPE/UF RJ-Ilha do Fundão, Centro de Tecnologia, Bloco G, Cidade Universitária, Rio de Janeiro, Brazil

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Abstract

Cracking of a mixture of *cis/trans*-decalin was carried out over small crystallite rare-earth containing Y zeolites (REHY). Results showed that, although the reactivity of *cis*-decalin is much higher than that of *trans*-decalin, no influence of crystallite size was detected, as an indication that differences in reactivity should be attributed to differences in the structure of the reacting molecules, and not to the characteristics of the zeolite. In fact, deuterium exchange between deuterated HY zeolite and decalin revealed that *cis*-decalin is much more reactive than its *trans*-isomer. *Trans*-decalin, according to its structure minimized by molecular mechanic force field MM2, presents a more hindered tertiary C–H bond, therefore making protonation and the formation of adsorbed carbocations difficult.

Keywords: Cracking; Naphthenes; Zeolites

Table 1
Main characteristics of the REHY-zeolites

Zeolite	SAR	CS (nm)	% Na ₂ O	% RE ₂ O ₃ ^a	ESA (m ² g ⁻¹)
A	5.9	193	3.0	9.8	11
B	5.8	63	3.1	10.5	35

CS = crystallite size, ESA = external surface area, SAR = molar silica-to-alumina ratio.

^a The weight compositions were 0.74% Ce₂O₃, 5.51% La₂O₃, 3.43% Nd₂O₃ and 0.93% Pr₂O₃ for case A and 0.75% Ce₂O₃, 5.83% La₂O₃, 3.67% Nd₂O₃ and 0.99% Pr₂O₃ for case B.

1. Introduction

* Corresponding author.

Several types of hydrocarbons such as alkenes, alkanes and alkyl aromatics have been used as model compounds for cracking reactions. However, very little work concerning the cracking of naphthenes has been reported. Previous studies [1] of the cracking of decalin derivatives over silica–alumina and REHX-zeolites showed that, albeit the cracking rate increased with the increasing molecular weight of naphthene when silica–alumina was used, for REHX a maximum was attained with 1,3,5-trimethyldecalin, as an indication of diffusional limitations for larger reactants. More recently, the reaction of decalin over several zeolites was reported [2]. The exclusion of decalin from HZSM-5 was observed, offretite

being the only zeolite which gave considerable cracking of this naphthene. Mostad et al. in very recent papers [3,4] studying the cracking of decalin isomers, suggested the existence of shape selectivity in Y-zeolite, since the reactivity of *cis*-decalin is much higher than that of the *trans*-isomer. This was explained by assuming that *cis*-decalin is smaller and more flexible than *trans*-decalin, in this way being able to penetrate the pores more easily.

In the present work, the cracking of a mixture of *cis*- and *trans*-decalin was carried out over small crystallite rare-earth containing Y zeolites, aiming at the determination of the influence of the crystallite size (and consequently of the external surface area) on the rate of reaction.

2. Experimental

NaY zeolites were synthesized using the method proposed by Toyo Soda patent [5]. In order to obtain different crystallite sizes, increasing amounts of seeds, prepared according to a Degussa patent [6], have been dosed to crystallization mixture. First, ion-exchange with a 5% ammonium sulfate solution and then with a freshly prepared rare-earth chloride solution (7% Ce₂O₃, 52% La₂O₃, 32% Nd₂O₃, 9% Pr₂O₃) in a stirred vessel was carried out. The method of ion-exchanging was described elsewhere [7]. Afterwards, zeolites were steam-calcined, with 100% steam, at 873 K, for 1 hour, in a fixed-bed reactor.

Zeolite composition was determined by using X-ray fluorescence in a XRF Philips PW1404. Crystallite sizes were estimated with the help of the Hall method [8] and an X-ray diffractometer Philips PW 1710. External surface areas were evaluated by employing the *t*-plot method [9] in a Micromeritics ASAP2400 equipment.

A purified mixture of *cis/trans*-decalin (47/52 wt%) is passed through a fixed-bed glass micro-reactor (0.8 cm internal diameter). The catalyst is composed by a mixture zeolite/kaolin (5/95 wt%), 80–100 mesh previously dried at 373 K, for 14 h under vacuum. Both temperature and

decalin flow-rate are varied and samples are automatically collected and analysed by means of GC-MS (HP 5890 and HP 5970-B), column HP-PONA (50 m, 0.2 mm, 0.5 μm) for liquid phase and a Al₂O₃/KCl column (50 m, 0.3 mm, 0.5 μm) for the gas phase.

The H–D exchange took place using a deuterated ultrastable Y zeolite (USY) according to previous published procedure [10,11]. About 550 mg of the zeolite was firstly pre-treated at 500°C for 30 min under 38 ml/min flow of dry nitrogen and the deuteration was carried out at 200°C directing the nitrogen flow to a saturator containing D₂O kept at room temperature. After 60 min, the deuteration was judged complete and the D₂O flow was interrupted. An additional purge with nitrogen at 200°C was done during 15 min to eliminate any residual D₂O. The deuterated zeolite was rapidly transferred under nitrogen atmosphere to a round bottom flask and a solution of 1.0 g of an equimolar mixture of *cis* and *trans* decalin in 10 ml of n-hexane was added. The system was closed and stirred overnight at room temperature. Then, the solution was filtered and the remained zeolite stirred with 20 ml of n-hexane, followed by filtration. The filtrated solutions were mixed and the n-hexane evaporated. The decalin obtained was then analysed by capillary GC (HP 5890-A) coupled with a quadrupole mass spectrometer (HP 5888-A). The deuteration of each isomer was measured, taking into account the correction for the natural abundance ¹³C.

3. Results and discussion

The main characteristics of the zeolites used are presented in Table 1. It is clear, from Table 1, that both zeolites present approximately the same chemical composition, differing, however, in the crystallite size and the external surface area. Therefore, differences in reactivity should be related to such textural properties.

Fig. 1 presents the results of the rate of consumption of decalin (*cis* + *trans*) against the time-on-stream for both crystallite sizes at different

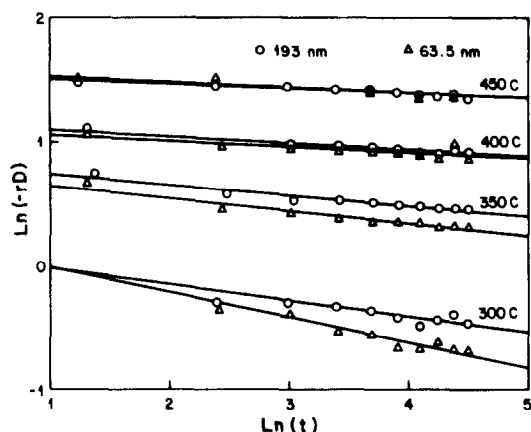


Fig. 1. Rate of reaction of decalin ($-rD$) against the time-on-stream in minutes (t), at various temperatures, for two crystallite sizes (zeolite deactivation).

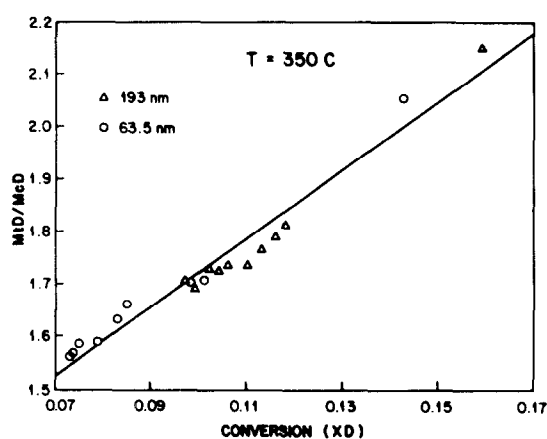


Fig. 2. *Trans/cis* ratio (MtD/McD) in the unreacted decalin as a function of the total decalin conversion (XD), for two crystallite sizes at 350°C.

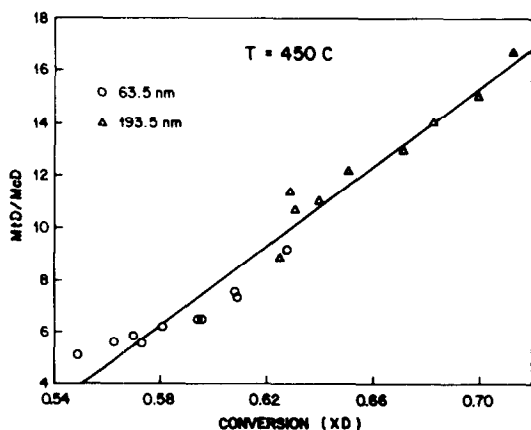


Fig. 3. *Trans/cis* ratio (MtD/McD) in the unreacted decalin as a function of the total decalin conversion (XD), for two crystallite sizes at 450°C.

temperatures. As clearly seen, the influence of the crystallite size either on the reactivity or on the deactivation is not significant, becoming negligible as temperature increases. Interestingly, the ratio *trans/cis* in the unreacted decalin increases with increasing conversion (Fig. 2 and Fig. 3), being always higher than 1.0, as an indication that *cis*-decalin reacts much faster than the *trans*-isomer. However, no influence of the crystallite size was observed. Smaller crystallite zeolites present much higher external surface areas, and should give higher reaction rates for large molecules, as confirmed by previous results with bulky molecules such as 1,3,5-triisopropylbenzene [12]. Shape selectivity in HY for cracking of decalin isomers has been recently proposed in the literature [3,4]. The results of Fig. 2 and Fig. 3 indicate, however, that differences in reactivity seem to be related to differences in the structure of the isomers.

To highlight this point, H–D exchange using a deuterated ultrastable Y zeolite was performed, and results are presented in Table 2.

The results of H–D exchange showed that *cis*-decalin was much more reactive, in accordance with the cracking reactivity data. Considering a kinetic of first-order on the hydrocarbon, we can estimate a relative rate k_{cis}/k_{trans} of about 300 for the H–D exchange at room temperature. Previous H–D exchange experiments with linear and branched alkanes, showed that only tertiary alkanes exchange at comparable temperatures [13–15]. Cyclohexane did not exchange either, indicating that protonation occurs at the tertiary C–H bond, probably involving a pentacoordinated carbonium ion [13,14]. The results of H–D

Table 2
Percentage of deuteration of *cis*- and *trans*-decalin over USY zeolite at room temperature

Reactant	% Deuteration	k_d^a	k_c^b
<i>Cis</i> -decalin	45.5	300	7×10^4
<i>Trans</i> -decalin	0.2	1	1

^a k_d stands for the relative first-order rate constant for deuteration.

^b k_c stands for the relative first-order rate constant for the cracking of decalin isomers, according to Mostad et al. [3].

exchange with *cis*- and *trans*-decalin, point out that the *trans*-isomer has a more hindered tertiary C–H bond, making the protonation and the formation of adsorbed carbocations difficult. Fig. 4 shows the structure of *cis*- and *trans*-decalin minimized by molecular mechanic force field MM2 [16]. One can see that in *trans*-decalin, the tertiary C–H is more hindered than in the *cis*-isomer. It should also be stressed that the structure of *cis*-decalin is more flexible, thus allowing less steric hindrance on the course of the electrophilic attack at the tertiary C–H bond. The steric hindrance near the tertiary C–H bond seems to have a general effect on the reactivity of the alkane molecules toward H–D exchange with zeolites and will be discussed on a separate report.

The most reasonable explanation for different reactivities of *cis*- and *trans*-decalin is the steric hindrance at the tertiary C–H bond. If one considers that the initial step of cracking involves the electrophilic attack of either a proton or a carbenium ion on the tertiary C–H bond, it is clear that the structure of *trans*-decalin makes this molecule more hindered and therefore less reactive.

Fig. 5 presents the results of selectivities for three main classes obtained in the cracking process: light hydrocarbons ($<C_{10}$), C_{10} isomers and aromatics. C_{10} isomers in this figure grow fast even at low conversions, indicating that the initial mechanism of cracking involves either the isomerization of decalin or the rupture of one ring, since previous studies [4] suggested that the rupture of both rings is less likely to occur. The proposed mechanism for the whole cracking pathway [17] considers the isomerization of decalin to hexahydromethylindanes, which undergo hydrogen transfer afterwards, forming methylindanes.

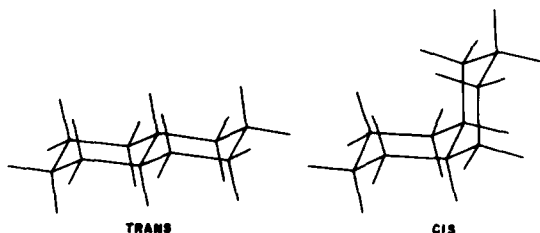


Fig. 4. Structure of *trans*- and *cis*-decalin minimized by molecular mechanic force field MM2.

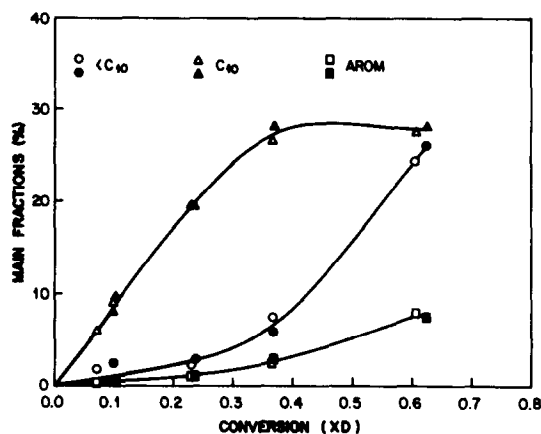


Fig. 5. Comparison of the main fractions found in the reaction products (light ($<C_{10}$), C_{10} isomers and aromatics) (●, ▲, ■ 193 nm, ○, △, □ 63.5 nm). Unreacted decalin is not presented.

Decalin isomers such as cyclohexylbutenes can also be formed via rupture of one ring. However, olefins generation takes place in very little amount, probably confirming that such compounds are being rapidly consumed via hydrogen transfer reactions. Aromatization and over-cracking are carried out afterwards, since aromatics and light hydrocarbons concentrations increase very slowly at low conversions. These results confirm previous data [18]. Nevertheless, as already observed for activity, no influence of crystallite size on selectivity can be depicted. This indicates that both isomers penetrate the cavities and undergo cracking in a very similar way, providing, in that manner, a very similar products distribution.

4. Conclusions

Results of the cracking of decalin (*cis*- and *trans*-)isomers over zeolites with different crystallite size clearly demonstrate that differences in reactivities observed for the isomers are not related to textural characteristics of the zeolites. In fact, despite the much higher reactivity of the *cis*-isomer with relation to *trans*, the ratio unreacted *cis*/unreacted *trans* for a given conversion was the same for both crystallite sizes. Hydrogen–deuterium exchange performed with deuterated USY zeolite and a mixture *cis*/*trans*-

decalin revealed that *cis*-decalin was again much more reactive, *trans*-decalin undergoing almost no deuteration. The analysis of the structure of both isomers minimized by molecular mechanic force field showed that, in *trans*-decalin, the tertiary C–H is more hindered than in *cis*-decalin. Considering that the mechanism of cracking involves electrophilic attack of a proton or a carbenium ion on the tertiary carbon, it is clear that the configuration of *trans*-decalin makes this molecule less reactive, since the attack on the tertiary C–H bond would be less likely to occur. Selectivity results, on the other hand, also indicate no influence of the textural characteristics of the zeolites on the products distribution. Regardless of the crystallite size (or external surface area), reaction products can be grouped in three main classes: light hydrocarbons, originated from the rupture of two rings, C₁₀ isomers as primary products and aromatics, resulting from secondary reactions of hydrogen transfer.

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