Cracking of neopentane over acidic zeolites: influence of isobutane and isobutene admission

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Abstract

Catalytic cracking of neopentane on acidic faujasites, mordenites and ZSM-5 zeolites was studied applying a batch reactor. The reaction proceeds with measurable rates above 523 K. Methane and isobutane are the primary products. The rate of methane formation is in good correlation with the Al contents of ZSM-5 zeolites. Isobutane is the result of an intermolecular hydride transfer. The amount of initially added isobutene gradually decreases, while isobutane slightly increases the rate of reaction.

Keywords: Acidic zeolites; Cracking; Neopentane; Zeolites

1. Introduction

Concerning the first reaction step of paraffin cracking, various opinions can be found in the relevant literature (see e.g. [1]). The role of Brønsted acidity was proposed to be important since Haag et al. [2] concluded the formation of a pentacoordinated transition complex generated upon interaction of Brønsted acid sites of zeolites with paraffin molecules. Corma et al. [3] showed that protolytic cracking is energetically favoured compared to β-cleavage of carbenium ions, supporting the outstanding role of Brønsted acidity in paraffin cracking over zeolite catalysts.

Beyer at al. proposed the adsorption of neopentane to take place on Brønsted base sites of zeolites, accompanied by C–C bond weakening, thus resulting in a bond rupture [4,5].

Gajrbekov et al. have suggested that the proton attacks a C–C bond, resulting in its protolytic scission, which is the first step of neopentane cracking over acidic zeolites [6–8].

Hall et al. have recently shown that cracking of neopentane over zeolites proceeds via an ionic mechanism, following a path similar to that stated previously [9,10]. Decomposition of the intermediate thus formed results in the primary products of cracking, namely CH_4 and the isobutyl carbenium ion. From these investigations with various zeolite catalysts it was concluded that the position of the equilibrium

$$Z^- H^+ + (CH_3)_2C{=}CH_2 \leftrightarrows (CH_3)_3C^+ Z^- \qquad (1)$$
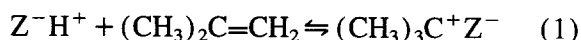
(where $Z^- H^+$ denotes a Brønsted acid site and Z^- the negatively charged zeolite skeleton binding the isobutyl carbenium ion by ionic forces) plays the most important role in further reactions. For a given carbenium ion, this equilibrium deter-

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mined by the acid strength of the zeolite, influences the lifetime of the carbenium ion and hence the extent of secondary reactions and the product distribution.

As the opinions about the mechanism of neopentane transformation are different and as equilibrium (1) can be shifted by adding isobutene or isobutane (which on Brønsted or Lewis acid sites form isobutyl carbenium ions) to the reacting mixture, further details are expected from investigation of neopentane cracking in presence or in absence of these products.

With this paper we aim to contribute to a better understanding of the role of products such as isobutane and isobutene on the transformation of neopentane over acidic zeolites of different structure.

2. Experimental

The samples used were faujasite, mordenite and ZSM-5 prepared from the parent sodium forms of zeolites by conventional NH_4^+ ion exchange. Their compositions are listed in Table 1.

The catalysts were checked by XRD, KBr-matrix IR spectroscopy and TG/DTA supplying data on the crystallinity of the samples and on the temperature of dehydration, deammoniation and dehydroxylation of the zeolites.

A recirculatory flow reactor of constant material content was applied for the catalytic experiments, the operation of which has been described by Beyer [11]. The zeolite catalysts were pressed into pellets, then crushed and sieved, and the 0.2–0.4 mm fraction was used. Generally, 0.1 g of the catalyst was activated in the reactor at 770 K in vacuo for 6 h (the final pressure was $2 \cdot 10^{-4}$ Pa).

During reaction samples were taken at predetermined reaction times and the products were analyzed with a Hewlett-Packard GC (type 5710 A, equipped with an FI detector, which excluded the determination of hydrogen) using a 4 m column filled with 20% BMEA on Chromosorb P (a.w.). A fresh sample of catalyst was used in each of the kinetic experiments.

3. Results

Fig. 1 shows the molar quantity of neopentane consumed and products formed vs. time under typical reaction conditions. Methane and isobutane are the primary products observed. Their initial rates of formation are not the same as might be naively assumed, as after cracking methane is immediately desorbed as a gaseous compound whereas isobutane is the result of a hydride transfer to the isobutyl carbenium ion (formed in the very first step) and only then subsequently released. The kinetic curve of isobutane (Fig. 2)
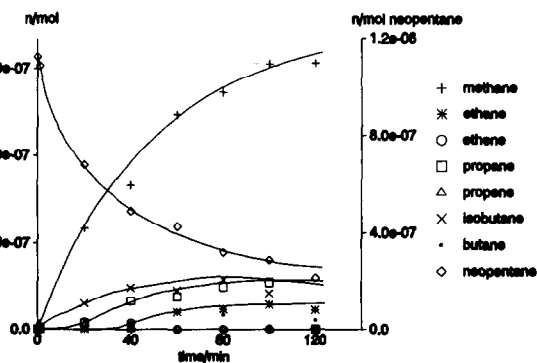
Table 1
Unit cell compositions of the samples

Type	ID	Unit cell composition	Degree of ion exchange or Si/Al ratio (ZSM-5) 45
HNaY-FAU	Y45	$(NH_4)_{26}Na_{32}Al_{58}Si_{134}O_{384}$	45
	Y65	$(NH_4)_{38}Na_{20}Al_{58}Si_{134}O_{384}$	65
	Y96	$(NH_4)_{56}Na_2Al_{58}Si_{134}O_{384}$	96
HNaM-MOR	M30	$(NH_4)_{2.2}Na_{5.2}Al_{7.4}Si_{40.6}O_{96}$	30
	M70	$(NH_4)_{5.2}Na_{2.2}Al_{7.4}Si_{40.6}O_{96}$	70
	M100	$(NH_4)_{7.4}Na_{0.04}Al_{7.44}Si_{40.6}O_{96}$	100
HZSM-5	Z50	$(NH_4)_{1.9}Na_{0.1}Al_{2.0}Si_{94.0}O_{192}$	50
	Z68	$(NH_4)_{1.3}Na_{0.1}Al_{1.4}Si_{94.6}O_{192}$	68
	Z100	$(NH_4)_{0.77}Na_{0.09}Al_{0.86}Si_{95.14}O_{192}$	100

Fig. 1. Molar quantity vs. time curves of nepopentane decay and product formation over Y96 ($T_{pretr} = 770$ K, $T_{react} = 760$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).

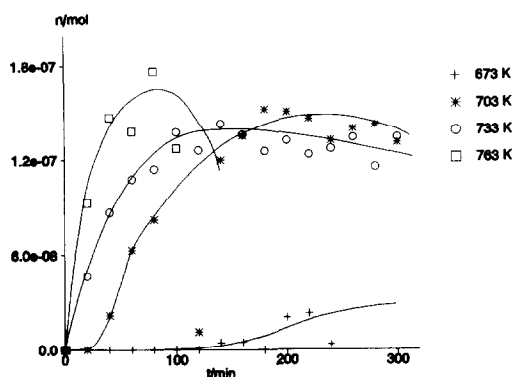Fig. 2. Kinetic curves of isobutane measured on Y96 at different temperatures ($T_{act} = 773$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).
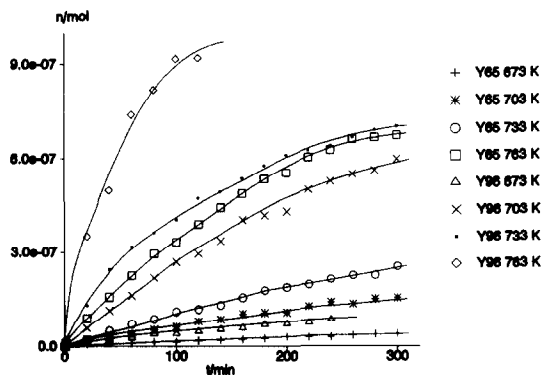

Fig. 3. Molar quantity of methane vs. time measured over zeolites HNaY with various Brønsted acidity, at different temperatures ($p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).
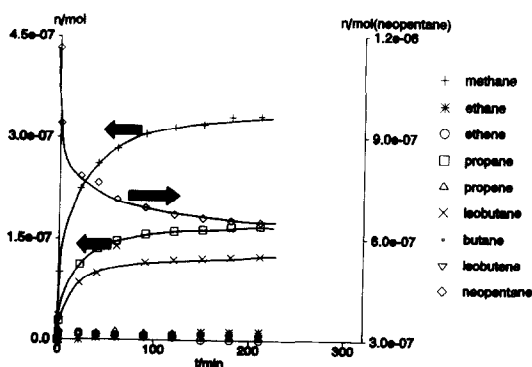

Fig. 4. Formation of products from neopentane over zeolite M100 ($T_{pretr} = 770$ K, $T_{react} = 760$ K. $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).

Fig. 5. Effect of temperature on isobutane and propane production during cracking of neopentane on zeolite M100 ($T_{pretr} = 770$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).

passes – especially at higher reaction temperatures – through a maximum, indicating its participation in secondary reactions. The formation of ethane, ethene, propane, propene, and n-butane have an induction period (Fig. 1) and they are therefore considered to be secondary products during neopentane cracking.

Olefins show a common characteristic: they are formed at the beginning of the reaction, but they are consumed after longer reaction times. The molar quantity of methane formed with reaction time over faujasite samples with two different degrees of ion exchange and the influence of temperature on the methane formation are depicted in Fig. 3. The correlation between the initial slope of the curves (representing the rate of methane formation) and the potential Brønsted site content of the catalysts is obvious.

Formation of cracking products over the mordenite catalyst can be seen in Fig. 4. It is remarkable that over mordenite M100 more propane than isobutane is formed (see Fig. 5).

The influence of the reaction temperature on the decay of neopentane and on the accumulation of methane on the M 100 sample can be seen in Fig. 6. The initial slopes of both types of curves are enhanced with increasing temperature.

The influence of the NH_4^+ ion exchange degree on the formation of methane, isobutane and propane showed a surprising behaviour. The rate of product formation followed the order
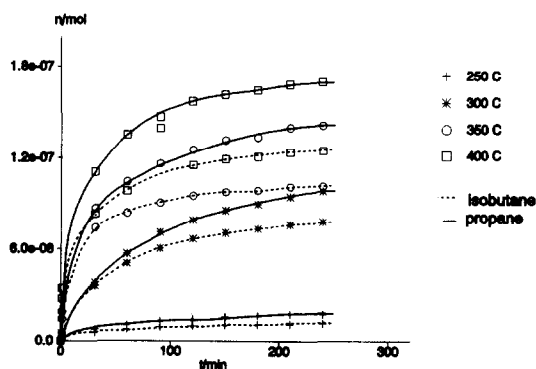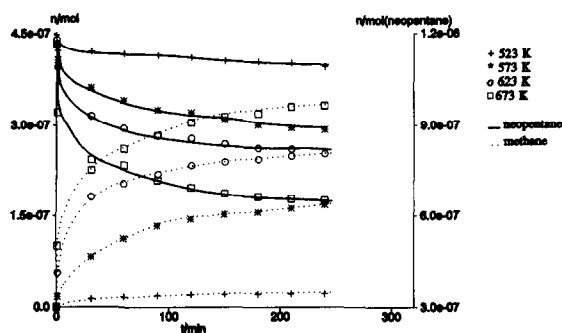
Fig. 6. Decay of neopentane and accumulation of methane vs. reaction time measured on zeolite M100 at different temperatures ($T_{pretr} = 770$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).
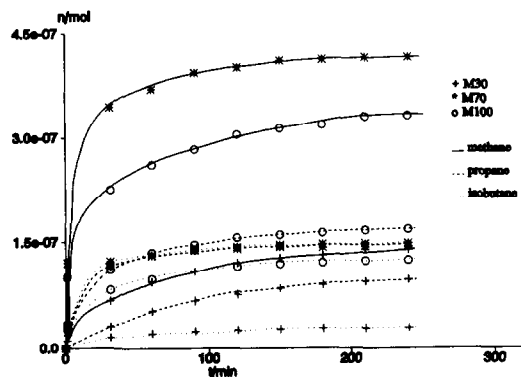

Fig. 7. Effect of ion exchange on isobutane and propane production during cracking of neopentane on mordenite type zeolites. ($T_{pretr} = 770$ K, $T_{react} = 760$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).
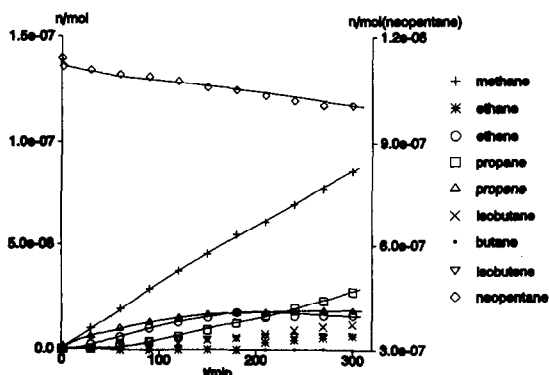

Fig. 8. Molar quantity vs. time curves of neopentane decay and product formation over the Z68 catalyst ($T_{pretr} = 770$ K, $T_{react} = 760$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).

Table 2
Initial rates r determined by extrapolation of the molar quantity vs. time curves to zero time of methane formation

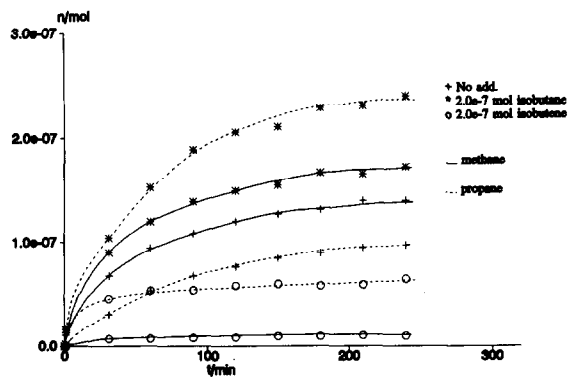| Sample	Y45	Y65	Y96
r/mol s^{-1} g$^{-1} \cdot 10^{-8}$	2.7	21.2	124.1
Sample	M30	M100	M70
r/mol s^{-1} g$^{-1} \cdot 10^{-10}$	7.5	122.5	136.4
Sample	Z100	Z68	Z50
r/mol s^{-1} g$^{-1} \cdot 10^{-5}$	1.4	2.8	3.2

Fig. 9. Influence of added isobutane on the formation of methane and propane in cracking of neopentane over zeolite M30 ($T_{pretr} = 770$ K, $T_{react} = 760$ K, $p_{neop} = 39.9$ kPa, $m_{cat} = 0.1$ g).

M70 > M100 > M30. This trend was found for methane, isobutane and propane as the main products of cracking (Fig. 7).

In Fig. 8 the kinetic curves measured during cracking of neopentane over zeolite HZSM-5 are displayed. Here again, methane is formed to a larger extent while the formation of isobutane is observed to be hindered. It was found that the rate of methane formation is in good linear correlation with the Al contents of the ZSM-5 samples (see Table 2).

In order to follow neopentane cracking, the rate of methane formation can be chosen, since methane was found to be the only primary product not undergoing further transformation, even at 770 K. The only interfering effect is that there are other secondary reactions like cracking, leading to methane formation, too. The initial pressure of neopentane exerts only a minor effect on the reaction rate.
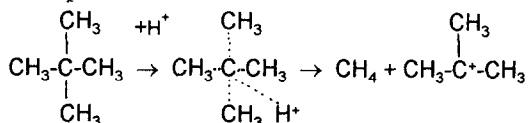
Experiments were carried out to clarify the influence of isobutane and isobutene on the rate of neopentane cracking. From both hydrocarbons the isobutyl carbenium ion may form in zeolites, therefore by their admission the coverage of this carbenium ion can be influenced. As can be taken from Fig. 9, addition of isobutane increases, while isobutene suppresses the formation of methane and propane.

4. Discussion

Carbocations generated during adsorption and reaction of hydrocarbons over acidic zeolites have been discussed in the literature. The formation of alkyl, alkenyl and cycloalkenyl carbenium ions as well as pentacoordinated carbonium ions has been proven experimentally [9,10,12–16].

Various suggestions have been made to explain the generation of the very first carbocations in catalytic cracking over zeolites and, as discussed by Hall at al., several contradictions exist between these ideas [9,10].

As far as adsorption and transformation of neopentane on acidic zeolites are concerned, it can be stated that methane is probably formed in the very first step:

$$CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 \;\overset{+H^+}{\rightarrow}\; CH_3\text{-}\underset{\underset{CH_3\ H^+}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 \;\rightarrow\; CH_4 + CH_3\text{-}\underset{}{\overset{\overset{CH_3}{|}}{C^+}}\text{-}CH_3$$
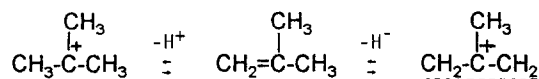
The isobutyl carbenium ion thus formed may take part in different processes: it may (i) desorb as isobutene with regeneration of a Brønsted acid site, (ii) leave the surface as isobutane, simultaneously generating a new carbenium ion as a result of intermolecular hydride ion abstraction, (iii) oligomerize with olefins formed (e.g. in reaction (i)), (iv) crack leading to formation of methane and allyl carbenium ion and (v) finally isomerize via intramolecular hydride and methyl shift forming some sec. butyl ions, too.

According to the classical cracking theory, intermolecular hydride ion abstraction should occur in order to propagate the cracking chain.

The fact that isobutane was formed at the beginning of the reaction but slowly disappeared from the gas-phase later, can be explained by supposing that isobutane itself might be one of the hydride ion donors due to its tertiary hydrogen. Assuming that only this process takes place should result in a steady-state coverage of the acid sites by isobutyl carbenium ions.

From inspection of the kinetic curves of isobutane measured at different temperatures on the Y96 sample (see Fig. 2), it can be concluded that the release of isobutane as a result of a hydride transfer reaction in which isobutyl carbenium ions and hydride ion donor reactants are involved, becomes enhanced only at higher temperatures. In our kinetic experiments isobutene never appeared as a product in the gas phase; which may be due to its very strong bonding to the acid sites as isobutyl carbenium ions. Therefore, the equilibrium represented by reaction (1) must lie on the right side in the temperature range of our kinetic studies. This finding supports the distinctive role of equilibrium (1), as suggested by Hall et al. [9]. Assuming that this equilibrium is not completely lying on the right hand side, i.e., when a small amount of isobutene is still available in the cavities, its adsorption on Lewis acid sites or reaction with the carbenium ions present, cannot be disregarded. In this way, the formation of alkenyl carbenium ions and oligomerized intermediates can be expected at elevated temperature, too.

Formation of alkenyl carbenium ions in the course of neopentane cracking may be realized in the following way: Isobutene which according to (1) is in equilibrium with isobutyl carbenium ions undergoes hydride ion abstraction on Lewis acid sites under generation of isobutenyl carbenium ion represented by

$$CH_3\text{-}\underset{}{\overset{\overset{CH_3}{|+}}{C}}\text{-}CH_3 \;\overset{-H^+}{\rightleftharpoons}\; CH_2\text{=}\underset{}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 \;\overset{-H^-}{\rightleftharpoons}\; CH_2\text{-}\underset{}{\overset{\overset{CH_3}{|+}}{C}}\text{-}CH_2$$

Alkenyl carbenium ions thus formed are the precursor of carbonaceous deposits, the generation of which leads to the deactivation of catalysts.

Their formation is in connection with free olefins present, the concentration of which is determined by equilibrium (1).

As far as deactivation is concerned, the types of behaviour observed on HNaY-FAU, HNaM-MOR and HZSM-5 was dissimilar. Fig. 10 shows the carbon and hydrogen balance curves calculated from GC analysis. It is clearly seen that the total carbon present as gaseous hydrocarbon product remains constant after an initial decrease probably due to adsorption at the beginning of the reaction. For longer contact times (>70 min) a second diminishing of the gas phase products was found for HNaY-FAU, while almost constant material balance was detected for the two other catalysts. From this follows that deactivation of faujasite type zeolites is fast compared to that of mordenite and ZSM-5. This finding is in agreement with the general feature of zeolite deactivation by coking reviewed by Guisnet and Magnoux [17].

Oligomer carbenium ions of longer chain are the second source for isobutane, propane and other small hydrocarbons in the product. This classical route of cracking should operate at lower temperatures where the formation of oligomers is more probable.

As far as the formation of isobutane as product is concerned, it may crack itself, in addition to its participation in intermolecular hydride ion transfer reactions. Similarly to the neopentane transformation, cracking of isobutane is also

Fig. 11. Yield vs. conversion curves (OPE) of (□) methane and (■) isobutane for discrimination of primary against secondary products over zeolites.

accelerated with increasing temperature. Therefore, the decrease of the isobutane kinetic curve may be due to its consumption by cracking, giving rise to the formation of methane and propane. Therefore the methane generation is not a selective measure for the transformation of neopentane, it is, however, rather characteristic of the overall cracking process.

Fig. 11 displays the so-called optimum performance envelopes (OPE) determined for typical runs on HNaY-FAU. According to the classification of Corma and Wojciechowski [18] isobutane is a 2U product in the course of neopentane cracking, forming and disappearing in secondary transformations, which is enhanced with increasing temperature. Methane is clearly a $(1 + 2)S$ product on faujasite, being generated in both primary and secondary reactions. On mordenite and ZSM-5, however, the assignment of the OPEs to a distinct type was equivocal.

Influencing equilibrium (1) by adding isobutene to neopentane results in the suppression of the cracking reactions. Blocking the acid sites took place by high molecular weight oligomers as shown by Fajula et al. [19]. This observation also supplements Hall's statement on the importance of equilibrium between free olefins and carbenium ions.

Upon adding isobutane the initial rate of methane formation increases, accompanied by the enhanced production of propane. The increased methane formation is due to cracking of isobutane.
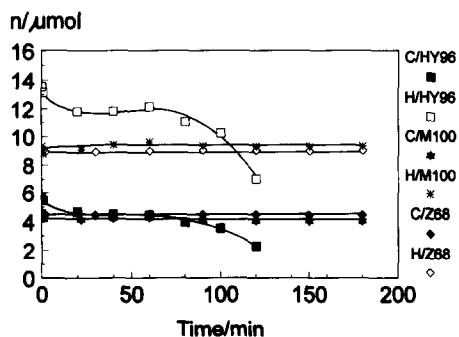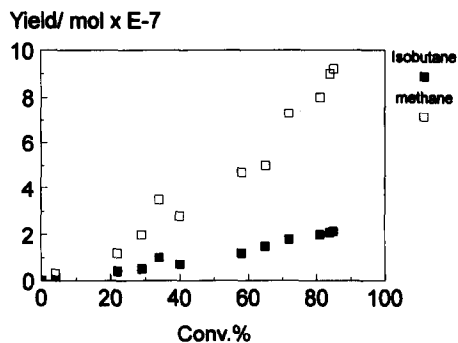

Fig. 10. Carbon (C) and hydrogen (H) balance curves vs. time on stream for neopentane cracking on zeolites Y96: (■) C; (□) H; M100: (★) C, (☆) H; and Z68: (◆) C, (◇) H, at 760 K.

Table 3
Atomic net charges on the neopentane molecule, calculated by MNDO semiempirical methods. c = central carbon atom, m = carbon atom of methyl group

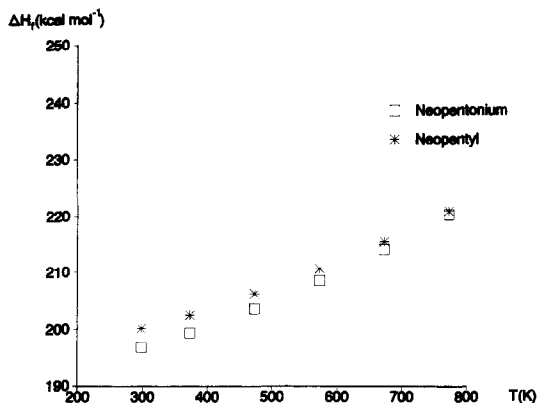| Method	c-carbon	m-carbon	hydrogen
ab initio [19]	+ 0.151	+ 0.214	− 0.084
MNDO-ZDO	− 0.126	+ 0.052	− 0.007
MNDO-EP	− 0.060	+ 0.075	− 0.020

Fig. 12. Calculated heats of formation ΔH_f/kcal mol^{-1} as a function of temperature for the generation of (□) neopentonium and (*) neopentyl carbenium ions.

Table 4
Standard heats of formation $\Delta H^{\circ}_{f\,298}$ (kcal/mol) of neopentane and some carbocations, obtained by different quantum-chemical methods

Species	MNDO	AM1	PM3
neopentane	− 24.6	− 32.8	− 35.8
$(CH_3)_4CH^+$ carbonium ion	238.3	196.8	200.4
$(CH_3)_3CCH_2^+$ carbenium ion	208.6	200.2	205.8
isobutyl carbenium ion	187.8	174.5	178.4
isopentyl carbenium ion	182.2	167.4	172.0
isobutenyl carbenium ion	213.7	217.3	221.8
isopentenyl carbenium ion	201.8	199.0	201.8

The large propane concentration originates from the hydrogenation of propyl carbenium ions generated during both isobutane and neopentane cracking. For the former this finding is in accordance with the assumption that isobutane represents the main hydride ion donor in the cracking reaction.

The question arises: Which carbon atom is the target of proton attachment? The results of sem-iempirical quantum-chemical calculations performed with the PcMol program system [20] indicated that the MNDO net charges on the central carbon (c-carbon) atom of the neopentane molecule, obtained from population analysis within the ZDO approximation (MNDO-ZDO) and from the electrostatic potential (MNDO-EP), were negative compared to the terminal carbon atoms of the methyl groups (m-carbon) (see Table 3). These results are in good agreement with those calculated by the more sophisticated ab initio method [21]. From this follows that, to a first approximation, the proton attack may occur on the c-carbon atom, while the methyl groups may lose a hydride ion upon interaction with Lewis acid sites.

In the preliminary step neopentane is transformed either into a neopentonium ion or a neopentyl carbenium ion. In order to check which way is more favoured, the heats of formation for both ions were calculated for a number of temperatures in the range of interest, using the AM1 method. As shown in Fig. 12 the former is more stable at lower temperatures, while at higher temperatures the generation of both becomes probable, at least theoretically.

The standard heats of formation of the carbocations, assumed to be formed from neopentane, have been recently calculated with the MNDO method [22]. Their sequence has now been confirmed applying the two additional semiempirical methods AM1 and PM3 and the results are listed in Table 4 showing a distinct preference for formation of isopentyl and isobutyl ions.

5. Conclusions

The adsorption and reaction of neopentane or zeolites with different structures and acidities were studied in kinetic experiments, the results obtained show that:

(i) Cracking of neopentane occurs with measurable rate on HNaY-FAU only at 623 K, but at 523 K on HNaM-MOR and HZSM-5.

(ii) In this reaction, the role of the Brønsted acid sites predominates.

(iii) The methane production can be regarded as a measure of the overall reaction.

(iv) Good linear correlation was established between the methane formation and the Al-contents of ZSM-5 zeolite.

(v) While admission of isobutene decreases, admission of isobutane slightly increases the rate of cracking.

(vi) Our results support the statement of Hall, according to which the cracking reaction is mainly regulated by the equilibrium between free olefins and corresponding carbenium ions.

Acknowledgements

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