Propane conversion over a H-ZSM5 acid catalyst
Part 1. Observed kinetics

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Abstract

This is the first of a series of papers concerning the transformation of propane over a H-ZSM5 catalyst comprising experimental data, a kinetic model, and molecular dynamics calculations. The aim of this work is to provide a more fundamental insight on the catalytic processes involving light alkanes activation over solid acid catalysts. Experimental data for propane cracking was collected in the temperature range 623–773 K and low propane feed partial pressures varying from 3.0 to 9.1 kPa. The results show the existence of two parallel reaction pathways: (1) two monomolecular initiation steps (protolytic cracking or dehydrogenation), characterized by a relatively high activation energy, which becomes predominant at low conversions and high temperatures. Bond rupture may occur on either a C–C or C–H position leading to stoichiometric amounts of methane and ethene, or hydrogen and propene, respectively, when extrapolated at zero conversion; (2) a bimolecular route (classical cracking mechanism) with lower activation energy which involves carbenium ions chain carriers, and whose relative importance grows with increasing conversion and decreasing temperature, as secondary products, mainly olefins, become important. It is also clear that dehydrogenation reactions are favored at low temperatures, while at higher temperatures cracking is the dominant reaction pathway.
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Keywords: Propane; Kinetics; Zeolite H-ZSM5; Catalytic cracking

1. Introduction

The study of the transformation of small alkanes is important from several points of view: on one hand small alkanes are potentially valuable feedstocks for the production of several chemical species but are hard to activate and transform, except for the reaction where they are most used, i.e. combustion; on the other hand, their intrinsically difficult transformation over acid sites makes them very interesting species for the probing of the fundamentals on acid-catalyzed transformation of hydrocarbons over solid acids (namely zeolites), which is a very important reaction at the industrial level, both in the petroleum and the petrochemical domains. H-ZSM5 is a strong acidic catalyst, an important feature for the activation of small alkanes, and

possesses a very narrow range of acid strengths which is an important factor to simplify kinetic analysis.

Despite the fact that the transformation of propane is, predictably, a simple transformation, with only propene, ethene, methane, and hydrogen as expected products, its kinetics shows a variety of features that will enable us to probe into the chemistry of the adsorbed hydrocarbons, namely carbenium and carbonium ions, and into the interactions of the adsorbed species and gas-phase species. In fact, the existence of a significant number of secondary products can provide insight into these interactions, which occur even at relatively low conversion levels. The information that can be gathered from the studies of small alkane conversion can bear light into the reactivity of heavier alkanes and into processes that are as important as catalytic cracking.

The catalytic cracking of short-chain alkanes has been subject of several papers in the literature. A comprehensive review on the mechanism of catalytic cracking of light alkanes (C_3–C_6) is given by Jentoft and Gates [1]. Bandiera

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and Ben Taarit [2] have studied the cracking reaction of propane over H-ZSM5 (Si/Al = 13) and de-aluminated H-mordenite, and found that the relative rates for dehydrogenation and cracking did not depend on temperature nor on catalyst acid strength or acid sites topology. In fact, similar activation energies ($142 \, kJ \, mol^{-1}$) were observed for both cracking and dehydrogenation in the absence of secondary reactions for both catalysts. Therefore the active sites responsible for dehydrogenation and cracking were proposed to be of the same nature and acid strength regardless the zeolite structure or composition. Based on these findings, the authors suggest that the rate limiting step is the formation and subsequent decomposition of a common pentacoordinated carbonium ion to yield both dehydrogenation and cracking products over the same type of active sites at a fixed relative rate, governed by the energetics and statistical considerations on the carbonium ions involved.

Based on the results from Kwak and Sachtler [3] Jentoft and Gates [1] explain the relative cracking to dehydrogenation ratio of propane on a pure statistical basis, i.e., assuming similar carbonium ion energetics either for C–C or C–H bond rupture. Krannila et al. [4] reached the same conclusions from the results of n-butane reaction over H-ZSM5. Upon extrapolation to the limit of zero conversion their results indicate a statistical decomposition of the carbonium ion into equimolar amounts of hydrogen + butenes, methane + propene, and ethane + ethene with the corresponding rates being nearly the same and having the same activation energy of ca. $140 \, kJ \, mol^{-1}$. In addition to the stated monomolecular conversion of n-butane, a significant contribution of bimolecular hydride transfer steps becomes more important with increasing conversion and decreasing temperature. Narbeshuber et al. [5,6] analyzed the conversion of light alkanes and also found a higher cracking rate relative to dehydrogenation for propane. However, they observed that the cracking to dehydrogenation ratio increased with temperature. Apparent activation energies for cracking and dehydrogenation of 155 and $95 \, kJ \, mol^{-1}$, respectively, were obtained. This contradicts the original proposal from Bandiera and Ben Taarit [2] who found at low conversion that the dehydrogenation to cracking ratio was temperature independent. Accordingly, Bandiera and Ben Taarit [7] later reported that actually the relative selectivities to primary protolytic dehydrogenation and cracking, depending on the catalyst acid strength by using catalysts with varying Si/Al ratios. They concluded that a stronger acidity favored selectivity towards cracking while the dehydrogenation selectivity was lowered.

Furthermore Rudham and Winstaley [8], in opposition to Bandiera and Ben Taarit [2], proposed that dehydrogenation could be partially decoupled from cracking by introducing Lewis acid sites, leading to a temperature dependent dehydrogenation to cracking ratio. Narbeshuber et al. [6] have put in evidence using ^{13}C isotopic labeling studies that the rate determining steps of cracking and dehydrogenation are different. They conclude that protolytic cracking is rate lim-

iting whereas dehydrogenation is controlled by olefin desorption. Evidence was also pointed to the existence of two pathways for dehydrogenation of alkanes, one of them presumably occurring on extra framework aluminium moities, in contrast with cracking which is known to occur exclusively on Brönsted acid sites.

By using an in situ ^{13}C MAS NMR technique Ivanova et al. [9] confirmed the monofunctional mechanism involving protonation of propane over strong Brönsted sites on H-ZSM5, which can evolve to ^{13}C scrambling in propane, cracking, dehydrogenation, and disproportionation products. Depending on the propane partial pressure, two distinct regimes were found. At low pressures, monomolecular dehydrogenation of propane occurred, which produced an increase of the oligomerization of propene and subsequent cracking to yield mainly i-butane. At high propane pressure, a bimolecular disproportionation route prevails, yielding ethane, n-butane, and i-butane.

It appears that some controversy still subsists regarding the detailed mechanism of light alkanes cracking. In the present study, propane transformation over H-ZSM5 was carried under conditions so that primary monomolecular pathways were privileged although secondary reactions were also present to a limited extent. Since secondary reactions result from the interaction of adsorbed carbenium intermediates and feed molecules, the underlying kinetics constitutes a useful probe to provide insight into the bimolecular mechanism.

2. Experimental

The kinetic measurements were performed in an interrupted-flow quartz reactor having 10 mm ID. Propane (analyzed 99.90% C_3, 0.0065% $C_2^=$, 0.0922% cis-2-$C_4^=$) was previously dried through a zeolite X bed and subsequently diluted in dry nitrogen, whose flow rate was set (Brooks mass-flow controller) to give 3.0, 5.1, 7.1, and 9.1 kPa propane partial pressure in the feed. The H-ZSM5 zeolite was used as provided (ca. Si/Al = 30) after pre-treatment in a purified nitrogen flow at 773 K for 4 h prior to reaction. The reaction was carried at 623, 673, 723, and 773 K under atmospheric pressure. Propane molar flow rate and catalyst mass were kept constant at $0.0085 \, mol \, h^{-1}$ and 100 mg (WHSV = $3.74 \, h^{-1}$) respectively. The reactant was fed in 6 min. pulses, and then, interrupted for the duration of the analysis, while nitrogen kept flowing through the reactor. Product analysis was carried-out in a Perkin-Elmer (Perkin-Elmer 8420) gas chromatograph equipped with a 50 m KCl/Al_2O_3 PLOT column and a flame ionization detector. Products selectivities were normalized on a molar basis to assess the reaction stoichiometry using:

molar selectivity product i

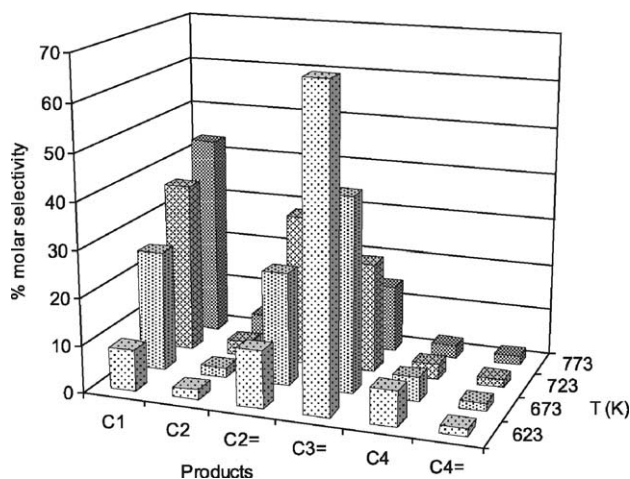$$= \frac{\text{product } i \text{ weight fraction}}{MM_i} \times MM_{C_3}$$

Fig. 1. Products molar selectivities from a 9.1 kPa propane feed as a function of reaction temperature. Traces of aromatics as well as pentenes and heptenes were hardly detected. Conversions were 0.28% at 623 K, 0.75% at 673 K, 2.63% at 723 K, and 10.61% at 773 K.

3. Results and discussion

Preliminary test runs carried out on an empty reactor did not show any products resulting from thermal reaction in the temperature range covered by these studies. Neither the conversion nor the product distribution changed with time-on-stream, indicating that no visible deactivation was observed under reaction conditions. For each set of experimental conditions, two independent measurements were made. Conversions were kept under ca. 11%, thus ensuring a differential mode operation in order to limit the extent of secondary reactions.

Whatever the experimental conditions used, three main products were identified, namely methane, ethene, and propene. Other reaction products such as ethane, butanes, and butenes were also detected in substantially lower amounts.

Propene was found to be the main product at low temperature while methane and ethene prevailed at higher temperatures. From Fig. 1 two main trends were observed as temperature increased from 623 to 773 K. While the dehydrogenation product (propene) selectivity decreases with increasing temperature, cracking products methane and ethene both increase at nearly the same rate, therefore suggesting a common precursor. Trace amounts of heavier products including aromatics were only observed at higher temperatures and propane partial pressure.

In order to clarify primary and secondary products contributions, plots of molar yields against conversion were drawn for each reaction temperature as shown in Fig. 2.

Initial product molar selectivities were obtained from curve slopes extrapolated to zero conversion.

At 623 K propene appears as the main primary product as it can be seen in Fig. 2a. A secondary contribution accounts for its non-linearity, especially at higher conversions. As the conversion increases, more propene is adsorbed on the cat-

alyst surface to yield adsorbed propyl carbenium ions. Consequently, bimolecular steps between carbenium ions and gas-phase species will be enhanced. The other two primary products, methane and ethene, show initial equimolar selectivity in agreement with the stoichiometry of the protolytic C–C bond rupture of the alkanium ion, as originally proposed by Haag and Dessau [10]. At higher conversion, the selectivity for ethylene increases above that of methane, as secondary reactions become more important. At low temperatures, ethene is formed both as a primary and secondary product, the latter resulting from propene oligomerization followed by classical β-scission (Eq. (1)).

$$2C_3H_6 \rightarrow C_2H_4 + C_4H_8 \tag{1}$$

Besides, also n-butane appears to have a non-negligible primary contribution as seen in Table 1. However, no reactions involving propane can account for the presence of n-butane among primary products. For n-butane to be formed as a primary product in the early stages of the reaction, propane disproportionation, as described in Eq. (2), would have to take place:

$$2C_3H_8 \rightarrow C_2H_6 + C_4H_{10} \tag{2}$$

Accordingly, also equimolar amounts of ethane would be formed from propane disproportionation, which is not consistent with our observations. Therefore, we propose instead that n-butane is formed from the butene impurity (0.09%) originally present in the propane feedstock that can immediately adsorb on the catalyst acid sites, forming butyl carbenium ions that can abstract hydride ions from propane to yield butanes and adsorbed propyl ions. This also explains why a smaller amount of butenes is present in the reaction products at low temperatures compared to those originally present in the propane feedstock as impurities. From ^{13}C MAS NMR in situ mechanistic studies by Derouane [9]

Table 1

Initial products molar selectivities as calculated from extrapolating molar yields against conversion curves in the limit of zero conversion

| Products (mol%)	Initial product molar selectivity (%)			
	623 K	673 K	723 K	773 K
C_1	10.34	34.49	56.60	70.68
C_2	0.00	0.00	0.00	0.00
$C_2^=$	9.51	36.44	55.99	72.60
$C_3^=$	93.58	64.24	45.39	29.12
i-C_4	0.33	0.00	0.00	0.00
n-C_4	1.26	2.75	1.71	1.37
$C_4^=$	0.28	0.66	0.24	0.00
$C_2^=/C_1$ ratio	0.92	1.06	0.99	1.03
Olefins/paraffins ratio	8.66	2.72	1.74	1.41
Percentage conversion at				
3.0 kPa	0.06	0.22	0.79	2.99
5.1 kPa	0.12	0.40	1.28	5.11
7.1 kPa	0.19	0.61	1.85	7.60
9.1 kPa	0.28	0.75	2.63	10.61
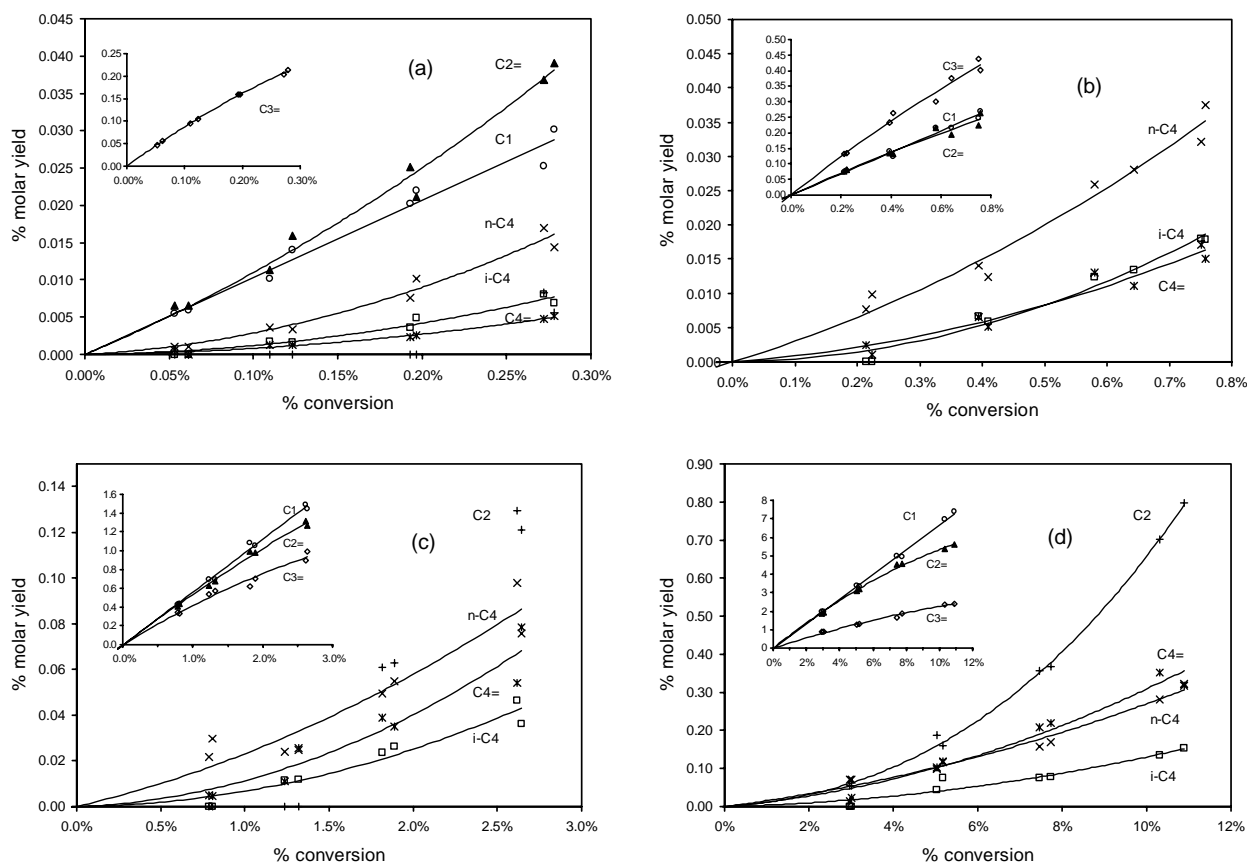
Fig. 2. Products molar yields against propane conversion over H-ZSM5 at: (a) 623 K, (b) 673 K, (c) 723 K, and (d) 773 K.
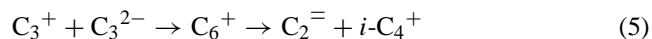
also observed the formation of butane in the early stages of propane transformation over H-MFI. Depending on the propane coverage, two regimes were identified: low propane pressure, where mainly i-butane was formed from propane dehydrogenation followed by oligomerization and cracking; and high propane pressure, where bimolecular disproportionation of propane occurred yielding both butane isomers and ethane. Under the experimental conditions used, the low propane pressure regime applies, and hence, i-butane was expected to predominate relative to n-butane, contrarily to the observations. This, however, gives additional support to the importance of the presence of an olefine impurity in the feedstock.

There is a different behavior between the n- and iso-butane isomers: n-C$_4$ is a primary product, while i-C$_4$ appears as a secondary product. According to our proposal stated above, n-C$_4$ comes from butene impurities adsorption followed by hydride transfer with a propane feed molecule (Eqs. (3) and (4)):

$$n\text{-C}_4^= + \text{H}^+ \rightarrow n\text{-C}_4^+ \tag{3}$$

$$n\text{-C}_4^+ + \text{C}_3 \rightarrow \text{C}_3^+ + n\text{-C}_4 \tag{4}$$

where H$^+$ represents an acid site. Secondary i-C$_4$ proceeds from a different reaction pathway involving oligomerization of adsorbed propyl ions and subsequent cracking to yield ethylene and isobutyl carbenium. The latter can further abstract an hydride ion from a propane molecule leaving an adsorbed propyl and producing i-C$_4$ (Eqs. (5) and (6)).

$$\text{C}_3^+ + \text{C}_3^{2-} \rightarrow \text{C}_6^+ \rightarrow \text{C}_2^= + i\text{-C}_4^+ \tag{5}$$

$$i\text{-C}_4^+ + \text{C}_3 \rightarrow \text{C}_3^+ + i\text{-C}_4 \tag{6}$$

At high temperature (773 K), the same primary products methane, ethylene, propene, and some n-butane were observed, as shown in Fig. 2d. However, as conversion increases the selectivity for ethene decreases below that of methane, contrarily to the observations at low temperatures. This may mean that ethene is now being consumed in secondary reactions.

The secondary products distribution is also affected at high temperature. As seen in Fig. 2, ethane becomes the predominant secondary product followed by butenes. Ethane can be formed through hydride transfer from a feed propane molecule to an adsorbed ethyl carbenium leaving an adsorbed propyl on the acid site (Eq. (7)).

$$\text{C}_2^{2-} + \text{C}_3 \rightarrow \text{C}_3^= + \text{C}_2^+ \tag{7}$$

Product initial selectivities extrapolated at zero conversion are given in Table 1, together with ethene to methane and olefin to paraffin ratios (Fig. 3). Ethene to methane initial ratio agrees with a protolytic pathway through a non-classical
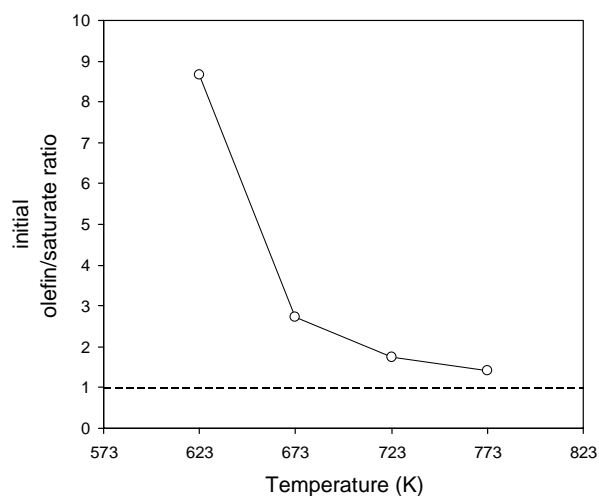
Fig. 3. Olefin to paraffin ratio extrapolated at zero conversion as a function of temperature.

Table 2
Reaction orders on propane for each of the primary products obtained from propane transformation over H-ZSM5

	Experimental reaction order			
	623 K	673 K	723 K	773 K
Propane	1.44	1.15	1.10	1.29
Methane	1.47	1.17	1.15	1.35
Ethene	1.58	1.07	1.06	1.15
Propene	1.29	1.05	0.91	1.06

pentacoordinated carbonium [10] that cracks to give methane and leaves an ethyl ion adsorbed on the catalyst surface, which may then desorb as ethylene or further react to yield other products.

In contrast to Bandiera and Ben Taarit observation [2], the selectivities for dehydrogenation and for cracking of propane over H-ZSM5 were found strongly dependent on the reaction temperature. As seen in Table 1 the ratio dehydrogenation/cracking is particularly high at low temperatures and approaches unity as temperature increases (Fig. 3).

For each temperature, the kinetic rate constants for the overall rate were calculated assuming first-order kinetics with respect to propane. As shown in Fig. 4, they strongly deviate from the presumed Arrhenius law.

At low temperatures, the slope appears to be less pronounced than at high temperatures, which indicates a strongly activated process at high temperatures. This is what we expect from a competitive mechanism where two parallel reactions are to occur. Whenever two parallel reactions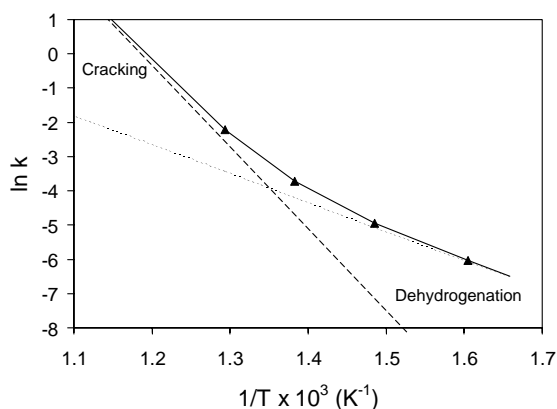 are possible, the faster pathway will prevail and determine the global reaction rate. Therefore, if we have two or more possible pathways having distinct activation energies, the overall reaction will proceed at a rate governed by the one having a lower activation energy at low temperatures and by the one possessing a higher activation energy at high temperatures.

By considering two first-order parallel reactions for propane consumption, we were able to describe the temperature dependency of the overall rate constant. This implies the existence of two parallel reaction pathways, having distinct activation energies.

Experimental reaction orders for propane and its primary products were investigated at each temperature. The values obtained are presented in Table 2.

All primary products experience a reduction of the experimental reaction order with increasing temperature. An exception, however, occurs at 500 °C, where an apparent increase may be related with a deviation from differential behavior at higher conversion (ca. 11%), since reaction orders were calculated based on outlet propane partial pressure assuming differential operation. However, the conversion at 500 °C is somewhat high, and the reactor deviates from differential mode, approaching a PFR regime. Since in a PFR, the reactant's outlet partial pressure is lower than in a CSTR, this leads to a false increase in the apparent reaction order. Nevertheless, the results indicate an evolution in the reaction order from low to higher temperatures that is consistent with the existence of two distinct reaction mechanisms:

- A bimolecular pathway with a relatively small activation energy prevailing at lower temperatures. Important second-order effects are visible in all primary products, including methane.
- A monomolecular route involving pentacoordinated carbonium ions which cracks via protolytic route in a C–C or C–H bond position to yield methane and ethyl, or propyl and hydrogen. This pathway has a lower reaction order as well as higher activation energy, and prevails mainly at high temperatures.

Narbeshuber et al. [5,6] reported first-order reaction rates on methane, ethylene, and propene primary products from propane cracking, based on kinetic data collected in the temperature range from 723 to 823 K. This is true, especially at high temperatures where monomolec-
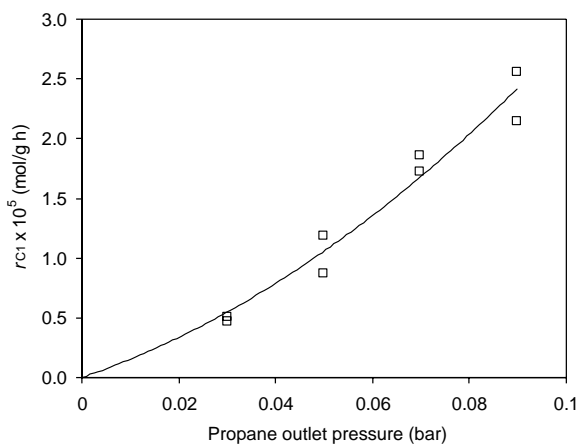

Fig. 4. Arrhenius plot for the overall propane consumption rate, assuming first-order reaction rate on propane.

Fig. 5. Rate of methane formation versus propane partial pressure over H-ZSM5 at 623 K.

Fig. 6. Second-order component of methane rate against butanes rate, at 623 K.

ular cracking prevails. At lower temperatures, however, we observe first-order plus second-order reaction rates on methane, ethane, and ethene. This is not surprising for olefins since they are highly reactive, and tend to favor classical bimolecular oligomerization/cracking routes. While this holds for ethene and propene, it cannot explain the observed second-order effect in methane rate, which is a rather inert molecule under the present conditions. Therefore, a different explanation for methane excess relative to first-order rate has to be sought. Let us consider the rate of methane formation r_{C_1} (Eq. (8)) as a primary plus secondary reaction order on propane, which fits well the experimental data as shown in Fig. 5 (as well as data at other temperatures).

$$r_{C_1} = k_1 P + k_2 P^2 \tag{8}$$

The first-order $k_1 P$ contribution to methane is well-established as coming from monomolecular propane C–C bond rupture (Eq. (9)).

$$C_3H_8 + H^+ \xrightarrow{k_1} CH_4 + C_2H_5^+ \tag{9}$$
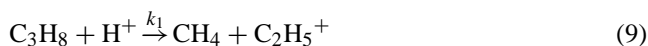
Products other than propane, namely butanes, can also undergo monomolecular cracking to give methane. Narbeshuber et al. [5] showed that *n*-butane monomolecular cracking is even faster than propane cracking. Bandiera and Ben Taarit [2] have also previously attributed excess methane formation to the monomolecular cracking of higher alkanes.

In view of this, we can propose that the second-order effects on methane formation is due to the rate of butanes formed, assuming that the monomolecular cracking reaction represented in Eq. (10) occurs:

$$C_4H_{10} + H^+ \xrightarrow{k_1} CH_4 + C_3H_7^+ \tag{10}$$
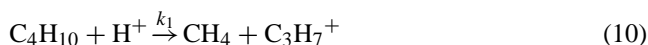
In fact, if we look at Fig. 6, we can see that it shows a linear relation between the butanes that are formed and the excess methane formation at 623 K. The same linear trends were
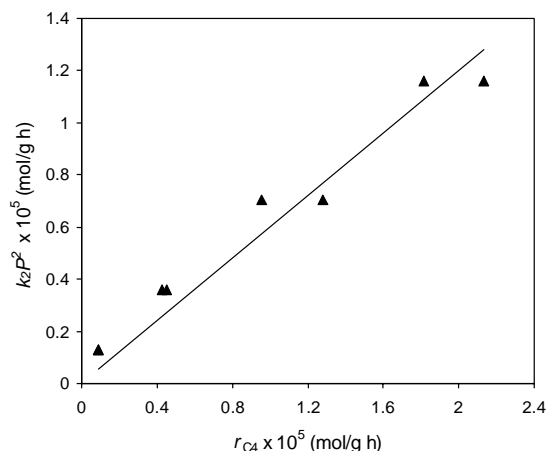
observed at all reaction temperatures studied (not shown), thereby reinforcing our assumption that the second-order behavior on methane rate comes from monomolecular cracking of product butanes.

Apparent activation energies were determined from first-order rate constants on propene, methane, and ethane (see Fig. 7) formation.

Methane and ethene formation showed comparable activation energies of 152 ± 13 and $142 \pm 10 \, \text{kJ mol}^{-1}$, respectively, while the dehydrogenation reaction revealed a lower value of $70 \pm 32 \, \text{kJ mol}^{-1}$ (uncertainties were estimated for a 95% confidence level). Furthermore, the Arrhenius fit quality increased as products' second-order contributions became less important, as expected. Apparent activation energies are in good agreement with previously published values from Narbeshuber et al. [5], who found 155 and 95 kJ mol^{-1} energy barriers for monomolecular cracking and dehydrogenation, respectively.
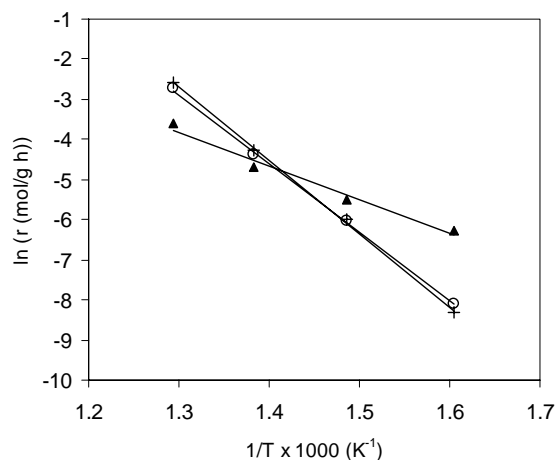

Fig. 7. Arrhenius plots for the formation of primary products resulting from propane transformation over H-ZSM5: (+) C_1, (○) $C_2^=$, and (▲) $C_3^=$.

4. Conclusions

Propane activation over H-ZSM5 was found to proceed through two parallel reaction pathways. A monomolecular mechanism involving non-classical pentacoordinated carbonium ions, resulting from the protolytic attack of a C–C or C–H bond over strong Brönsted acid sites; the former leading to cracking and the later to monomolecular dehydrogenation. These two processes have distinct apparent activation energies, and therefore, must involve different carbenium ions, depending on the type of bond cleaved. At low temperatures, however, experimental reaction orders as well as an excess ethene constitute evidence of the classical bimolecular mechanism that proceeds through carbenium ions acting as chain carriers. This process has a lower activation energy, and involves hydride transfer, oligomerization, and β-scission reactions.

The presence of butene impurities in the reactant feedstock is responsible for the appearence of *n*-butane as a primary product. The excess methane formed is explained from subsequent monomolecular cracking of higher alkanes, namely butanes.

Further work has been undertaken so as to probe the kinetic mechanism of the reaction in terms of elementary steps occurring on the catalyst surface as well as molecular dynamics theoretical studies to elucidate on the energetics of the transition states and intermediates involved. These studies will be presented in forthcoming papers.

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