

^{13}C MAS NMR mechanistic study of propane conversion into butanes over H-MFI catalyst

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Abstract

The mechanism of propane conversion into butanes over H-MFI as catalyst has been investigated using controlled atmosphere ^{13}C MAS NMR spectroscopy. The labelled reactant was propane $2\text{-}^{13}\text{C}$ and the reactant loading was varied from 0.5 to 4 molecules per MFI unit cell. The nature of the primary labelled products was found to depend on the propane partial pressure. A high pressure of propane enhances its bimolecular disproportionation to ethane and both butane isomers. At low pressure, the formation of *i*-butane only is favoured. A detailed mechanistic pathway is proposed to account for both high pressure and low pressure observations. The proposed mechanisms were ascertained by studying the effect of several additional probe molecules (C_3H_6 , $2\text{-}^{13}\text{C}$, C_6H_6 , H_2 , H_2O and CO). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The activation and functionalisation of light ($\text{C}_1\text{--C}_3$) alkanes are current major challenges of catalytic chemistry. Innovation in this field would open commercially attractive routes for the replacement of olefinic reactants by more economical alkane feeds. From a fundamental point of view, the unveiling and understanding of novel selective routes to activate C–H bond and form new C–C bonds are problems which have received and continue to attract the greatest attention of both homogeneous and heterogeneous catalysis researchers.

We have recently demonstrated that activation of propane on zeolite H-MFI occurs via a monofunctional mechanism involving the protonation of propane on the strong Brønsted sites of H-MFI, to form carbonium-ion type transition states which can evolve further in four different ways resulting in ^{13}C scrambling in propane, cracking, dehydrogenation and disproportionation [1,2]. Our model is in line with the non-classical carbonium ion mechanism proposed for the activation of alkanes on acidic zeolites [3–9] which relies on the formation of pentacoordinated carbonium ions followed by their cracking and dehydrogenation.

By tracing the fate of the ^{13}C label in strategically labelled propane, two additional mechanistic pathways for the evolution of propanium

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heated to a selected temperature at which it is maintained for a given time. The NMR spectrum is recorded after quenching of the sample cell down to 293 K. After collecting the NMR data, the cell is returned to pre-determined reaction conditions and heated for progressively longer periods of time. Propane 2-¹³C was the labelled reactant. In some experiments, the reaction was performed in the presence of additional molecules (propylene 2-¹³C, benzene, H₂, H₂O and CO) to probe the nature and behaviour of reaction intermediates with a short life time. The experimental conditions are reported in Table 1.

2.3. Treatment of data

The conversion of propane at time t is defined as $X_{r,t} = (1 - I_{r,t}/I_{r,0})$, where $I_{r,t}$ is the sum of the integral intensities of the resonances corresponding to propane in the NMR spectrum after heating for t minutes, $I_{r,0}$ is the integral intensity of the propane resonance in the initial NMR spectrum ($t = 0$). Selectivity (%) to product p at time t is calculated as $S_{p,t} = (I_{p,t}/\sum I_{p,t}) * 100$ where $I_{p,t}$ is the integral intensity of the resonance lines of product p in the NMR spectrum after heating for t minutes. Initial selectivities were obtained from plots of selectivity vs. conversion by extrapolation to zero conversion.

3. Results and discussion

3.1. Effect of propane partial pressure on the formation of butanes

¹³C MAS NMR spectra observed after adsorption and reaction of various amounts of propane 2-¹³C (see Table 1) over zeolite H-MFI are shown in Figs. 1 and 2. The initial spectra show resonances at ca. 17–20 ppm, corresponding to the labelled methylene group of propane. The number of resonance lines, their chemical shifts and their linewidths depend strongly on propane coverages. At low surface coverage by

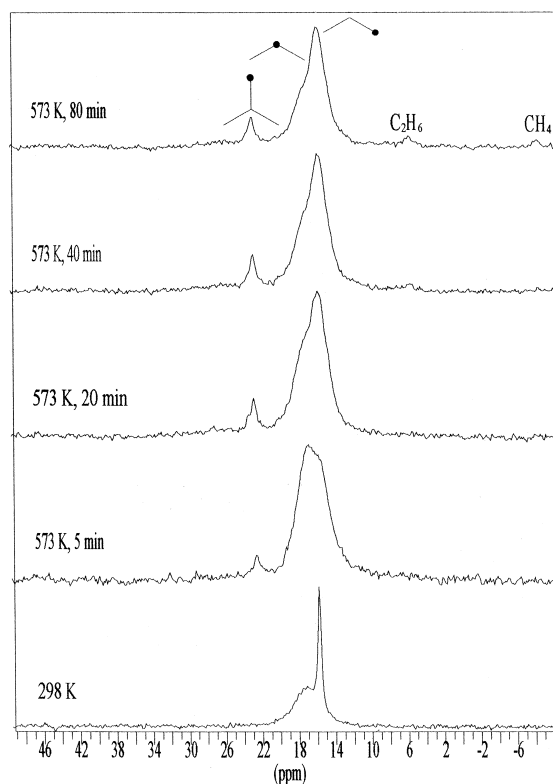


Fig. 1. ¹³C MAS NMR spectra for the propane 2-¹³C reaction at 573 K with low loading of propane (Sample 1, Table 1).

propane (Fig. 1), strong adsorption sites are preferentially populated, resulting in a broad resonance shifted relative to solution data and a narrow resonance corresponding to more mobile propane species. As the propane surface coverage increases (Fig. 2), adsorption sites of weaker energies also become populated and the resulting resonance is narrower and only slightly shifted.

Activation and reaction of propane begin at 573 K. The labelled products observed in the ¹³C NMR experiments are listed in Table 2. A comparison of the ¹³C MAS NMR spectra represented in Figs. 1 and 2 shows that propane coverage indeed influences the nature of the products which are formed and thus the reaction mechanism. The main NMR lines observed in experiments at high propane coverage correspond to propane 1-¹³C (16 ppm), *n*-butane (13 and 26 ppm), *i*-butane (24 ppm), ethane

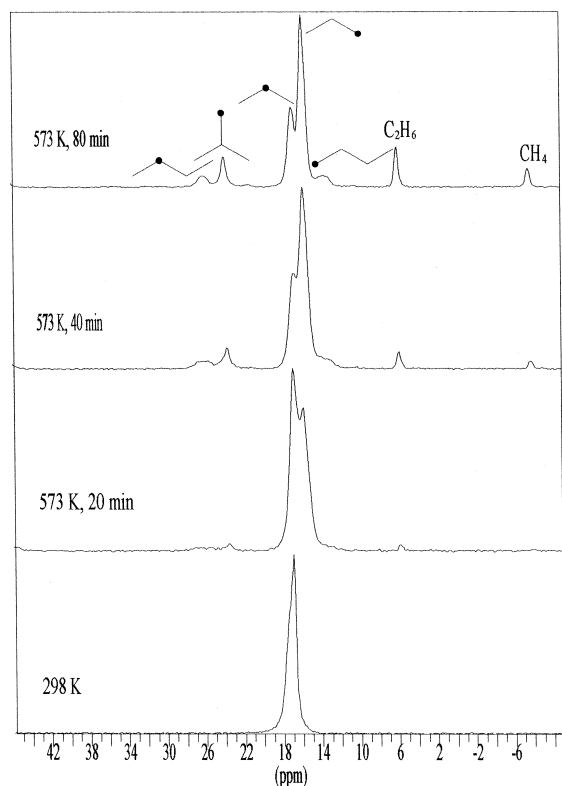


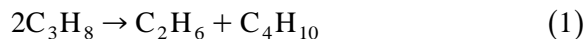
Fig. 2. ^{13}C MAS NMR spectra for the propane 2- ^{13}C reaction at 573 K with high loading of propane (Sample 2, Table 1).

(6 ppm), and methane (−7 and −11 ppm). A more detailed discussion of these line assignments is given elsewhere [10,13]. At low propane coverage, the major product is *i*-butane; small amounts of ethane and methane appear only at longer reaction times.

The stoichiometry of paraffin cracking requires the formation of 1 mol of olefin for each mole of lower paraffin or hydrogen produced. However, olefinic products are usually not observed in NMR experiments of the type described in the present work [12–16], probably because they undergo rapid secondary reactions leading to heavier products with low mobility and interacting strongly with the zeolite. These products are oligomers and carbonaceous residues. Indeed, ^{13}C carbon balances indicate that, in some experiments, up to 20% of ^{13}C labels are not detected. The resonances of oligomers and polymeric species appear to be

broadened beyond detection limit. Although the identification of such olefinic products would not give information on the reaction mechanism, paraffins are diagnostically useful at low conversion [3] since they undergo only few secondary reactions.

Initial selectivities to the labelled paraffinic products are listed in Table 1. At high propane loading, both butane isomers and ethane are found to be the major primary reaction products, suggesting that the main reaction pathway at high partial pressure of propane is the bimolecular disproportionation of propane:



The initial ratio of labelled products, $\text{C}_4\text{H}_{10}/\text{C}_2\text{H}_6$, is about 9 (Table 1), much higher than expected from Eq. (1). This may be due to the fact that non-labelled ethane and double-labelled butanes are preferentially formed at the initial stages of the reaction when ^{13}C scrambling in

Table 2

Assignments of the resonances observed during propane 2- ^{13}C reaction over H-ZSM-5

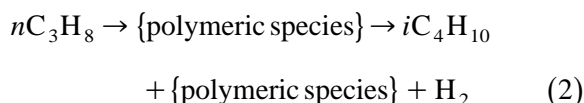
Assignment	Chemical shift (ppm)		
	Solution data [41]	Gaseous phase data [49]	Experimental
Reactant:			
	16,3	16,1	16,9
Products:			
	21,9		21,9
	29,7		30,0
	31,7		32,0
	11,4		11,0
	13,2		13,4
	24,9		26,0
	24,6		24,1
	23,3		-
	16,1	15,4	15,9
CH_3CH_3	6,5	3,2	6,2
CH_4^*	-2,3	-11	-11,0; -7,4
	34,1		36-37

• Indicates ^{13}C labelled carbon atoms.

* Assignments confirmed in separate experiments with corresponding model compounds adsorbed on the same zeolite.

propane is low. Another possible explanation is the competitive adsorption of products by the zeolite when the NMR cell is quenched to ambient temperature for spectra acquisition. Indeed, the adsorption energy of alkanes in zeolites increases in the following order: $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \text{C}_4\text{H}_{10}$ [17]. Hence, when initial surface coverages are high, butanes should be preferentially adsorbed while ethane may largely remain in the gas phase and only be partially detected in our experimental conditions.

At low surface coverage of propane, neither ethane nor *n*-butane are observed at the initial stages of the reaction; *i*-butane is the only primary product. The formation of *i*-butane only can hardly be explained by disproportionation (Eq. (1)). To account for the low pressure observations, we proposed earlier another mechanistic pathway [2] which is consistent with an oligomerization–cracking mechanism via carbenium ion-type intermediates [18–21]. It involves the formation of polymeric hydrocarbon chain intermediates by classical cationic polymerization of propylene formed upon decomposition of protonium ions. These polymeric intermediates are known to give mainly *i*-alkanes by cracking [18,19]. In our case, *i*-butane should preferentially be formed:



As discussed earlier, (polymeric) olefinic species cannot be observed under our experimental conditions and *i*-butane therefore appears as a pseudo-primary reaction product.

The latter mechanistic pathway was investigated further by carrying similar experiments in the presence of small amounts of propylene. In a first experiment (sample 3, Table 1), unlabelled propane (4 molecules/uc.) was reacted in the presence of propylene 2- ^{13}C (0.5 molecules/uc.). In the second experiment (sample 4, Table 1), the reactants were propane

2- ^{13}C and unlabelled propylene (same loadings as for sample 3).

The ^{13}C MAS NMR spectrum of sample 3 (Fig. 3) taken immediately after adsorption shows two narrow NMR lines at 17 and 16 ppm, corresponding to the methyl and methylene groups of unlabelled propane (^{13}C in natural abundance), and a broad line at about 32 ppm corresponding to CH_x groups in polymeric species formed as a result of the rapid oligomerization and polymerization of propylene on H-MFI [14]. Heating of this sample at 523 K leads to isomerisation and ^{13}C label scrambling in these long chain hydrocarbon species, followed by their cracking and formation of isobutane (line at 24.1 ppm), *n*-butane (13.4, 26.0 ppm) and isopentane (21.9 ppm). *i*-Butane is the major primary product (Table 1) as predicted by classical carbenium ion chemistry [18,19].

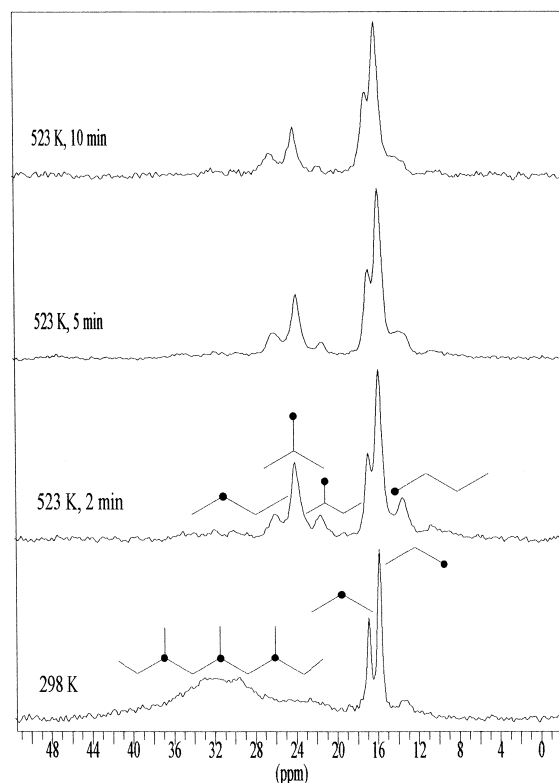


Fig. 3. ^{13}C MAS NMR spectra for the propane 2- ^{13}C reaction at 523 K in the presence of propylene (Sample 3, Table 1).

For sample 4 (Fig. 4), the initial spectrum shows only a resonance at 17 ppm, corresponding to the methylene group of propane 2-¹³C; non-labelled propylene-derived species are beyond the detection limit due to their small abundance (only 0.5 molecules/uc.) and line broadening. Heating at 523 K leads to the formation of *i*-butane as the main initial product (Table 1), confirming thereby that the observation of *i*-butane as a pseudo-primary product at low loading in propane is due to the formation and oligomerisation of propylene followed by the cracking of the oligomers.

In conclusion, controlled atmosphere NMR results suggest that high partial pressures of propane favour the bimolecular disproportionation of propane to ethane and both butanes, whereas monomolecular propane dehydrogenation is preferred at low partial pressures of propane; the latter is followed by propylene

oligomerization and cracking of the oligomers to yield *i*-butane as the main reaction product.

Proponium ions are the most probable transient species in the former pathway while for the latter, propenium ions as transient state and propylene as the first product are key intermediates. Hence, confirming further the nature and the behaviour of these intermediates and transient species in the initial steps of the reaction becomes of key importance for a more detailed understanding of propane activation and butanes formation.

3.2. Trapping of highly reactive intermediates by various probe molecules

It has been demonstrated that highly reactive carbenium ions formed on zeolite catalysts can be trapped in the presence of various additives such as CO, H₂O [22,23] or benzene [24,25]. When carbenium ion chemistry is suspected to operate, such experiments provide additional information on the nature and mechanistic role of these ions.

3.2.1. Effect of CO and H₂O

The reaction of CO and H₂O with olefins (Koch reaction) is known to proceed easily at ambient temperature over acidic zeolites [23]. The first step of this reaction is the protonation of the olefin on a Brønsted site leading to a carbenium ion. The latter reacts with CO and H₂O to yield the corresponding carboxylic acid. If propenium ions or propylene are indeed intermediate species for the low pressure mechanistic pathway (Eq. (2)), one expects the formation of some isobutyric acid when the reaction is carried out in the presence of CO and H₂O.

To confirm this hypothesis, sample 5 with low loadings of propane 2-¹³C, CO and H₂O was prepared as described in Table 1. Since isobutyric acid decomposes on H-MFI at 573 K, the reaction was carried out at a lower temperature (473 K) and longer contact times. ¹³C CP MAS NMR spectra obtained immediately after adsorption and in the beginning of the reaction are presented in Fig. 5. The only resonance (36

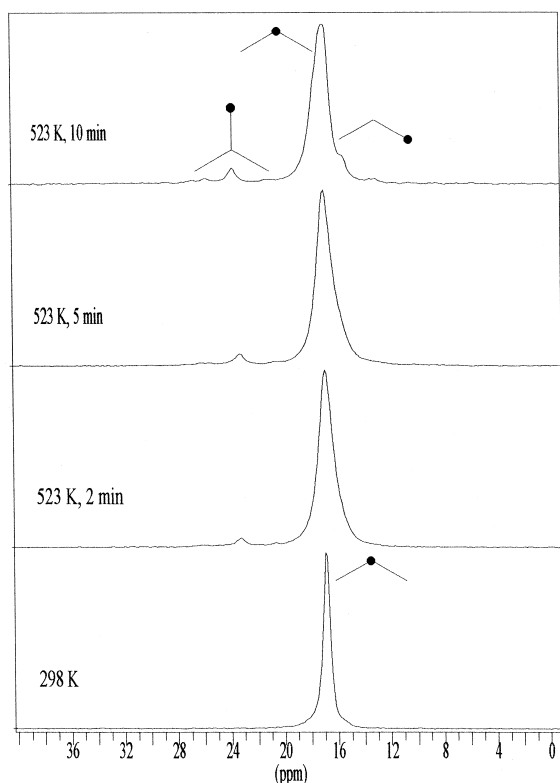


Fig. 4. ¹³C MAS NMR spectra for the propane reaction at 523 K in the presence propylene 2-¹³C (Sample 4, Table 1).

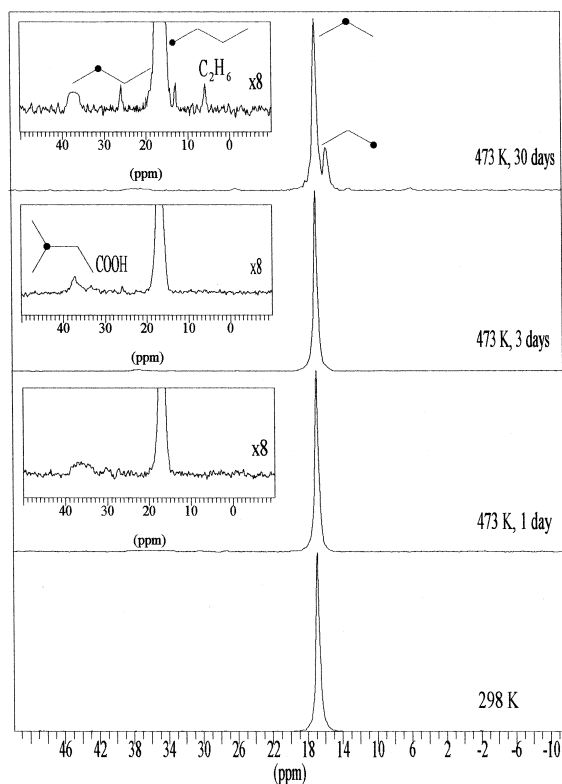


Fig. 5. ^{13}C CP MAS NMR spectra for the propane $2\text{-}^{13}\text{C}$ reaction at 473 K in the presence of equimolar amounts of CO and H_2O (Sample 5, Table 1).

ppm) detected in the beginning of the reaction corresponds to the methyne group of isobutyric acid $2\text{-}^{13}\text{C}$ (Table 2). It is very broad and slightly shifted with respect to solution data (34.1 ppm), and is only observed in CP conditions. It corresponds therefore to strongly bound species with low mobility. At longer reaction times, the NMR resonances of the butanes and ethane are also detected. The observation of isobutyric acid, labelled at its methyne group as the only primary product confirms our proposal of a mechanistic pathway involving the preferential dehydrogenation of propane and the formation of 2-propenium species at low partial pressures of propane.

At high partial pressures of propane $2\text{-}^{13}\text{C}$, CO and H_2O , a quite different picture was obtained (Table 1, experiment 6). No isobutyric acid was detected at 473 K and the reaction

carried out at 573 K gave butanes and ethane as in the case of propane alone. These experiments confirm our proposals about the nature of the intermediate species and reaction pathways.

3.2.2. Effect of benzene

The formation of transient carbenium ion species at low propane partial pressures was confirmed previously by reacting propane with benzene on H-MFI catalysts [24,25]. The observation of cumene and *n*-propylbenzene as primary reaction products (Table 1, propylbenzenes in experiment 7) evidenced the role of propenium ions. It should be noted however that propylbenzenes are not stable under our experimental conditions [24]. Therefore the initial selectivity towards propylbenzenes was low (10%) and thermodynamically favoured species, toluene and ethylbenzene, were preferentially observed. The formation of butanes was inhibited in the presence of benzene due to the trapping of highly reactive propene carbenium ions by benzene and the subsequent formation of alkylbenzenes.

3.2.3. Effect of H_2

As dehydrogenation was proposed to be the major reaction pathway at low propane coverage, one may expect that addition of hydrogen will inhibit dehydrogenation and enhance the contribution of parallel reactions.

Sample 8 (Table 1), comprising co-adsorbed propane $2\text{-}^{13}\text{C}$ and H_2 , was prepared to verify this proposal. The only primary products observed after reaction at 573 K are ethane and methane, confirming that in the presence of hydrogen cracking is favoured at the expense of dehydrogenation.

3.3. Mechanism proposal

Two routes are proposed for the formation of butanes from propane: (1) monomolecular dehydrogenation followed by oligomerization and cracking, at low partial pressure of propane, (2)

bimolecular disproportionation to butanes and ethane at high partial pressure of propane.

The identification of the primary labelled products observed in experiments carried out at either high or low loading of propane, the mechanistic analysis of possible reaction intermediates, and the confirmation of the nature of these intermediates through the effects of various probe molecules substantiate these proposals.

The scheme shown in Fig. 6 rationalizes and integrates further these mechanisms. Propane interacts with strong Brønsted sites of H-MFI via direct protolytic attack of C–H or C–C bonds, leading to isomeric $C_3H_9^+$ carbonium ions previously proposed to explain the activation of propane by H-MFI catalysts [1,2]. These $C_3H_9^+$ carbonium ions evolve to yield butanes via two different pathways depending on propane partial pressure. It is expected that a bimolecular pathway should be favoured at higher propane pressure (coverage).

The monomolecular dehydrogenation of $C_3H_9^+$ carbonium ions leading to dihydrogen and 2-propenium ions is preferred at low propane coverage (pressure). 2-Propenium ions can further rearrange to propylene, restoring the Brønsted acid sites. Propylene then undergoes rapid cationic polymerization on H-MFI [14] followed by isomerization and cracking of intermediate carbenium ions, yielding preferentially *i*-butane [21]. The reaction intermediates leading

to *i*-butane cannot be observed under our experimental conditions, which explains why *i*-butane is observed as a pseudo-primary product at low propane loading.

At high propane pressure, $C_3H_9^+$ carbonium ions react with other propane molecules to give ethane and butonium ions. The latter ions evolve to yield *n*-butane or *i*-butane via deprotonation and regeneration of the zeolite Brønsted acid sites. Consecutive or concerted mechanistic pathways can be proposed to explain the formation of butanes as shown in Fig. 7. The consecutive route is initiated by the attack of a zeolite proton on the C–C bond of propane. The transient propenium ion is stabilized by two basic oxygens in the vicinity of the framework Al site (Fig. 7a). Cleavage of the three-center and O–H bonds results in the formation of ethane and of a CH_3^+ carbenium ion bound to the zeolite framework (methoxy group). In the second reaction step, this CH_3^+ carbenium ion attacks the C–C bond of another propane molecule similarly to the attack of a zeolite proton. The butonium ion which is formed and stabilized by zeolite framework can rearrange further to butanes and restore the Brønsted acid site. Both *n*-butane and *i*-butane can be formed depending on the structure of transition state (Fig. 7a).

In contrast, only one reaction step is involved in the concerted reaction pathway: the direct attack of the C-propenium ion on the C–C bond of propane (Fig. 7b). The possible transition

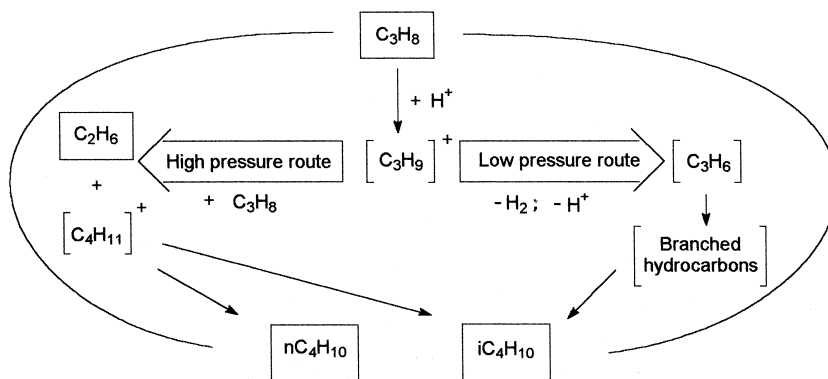


Fig. 6. Effect of the partial pressure of propane on the mechanism of butanes formation over H-MFI catalysts.

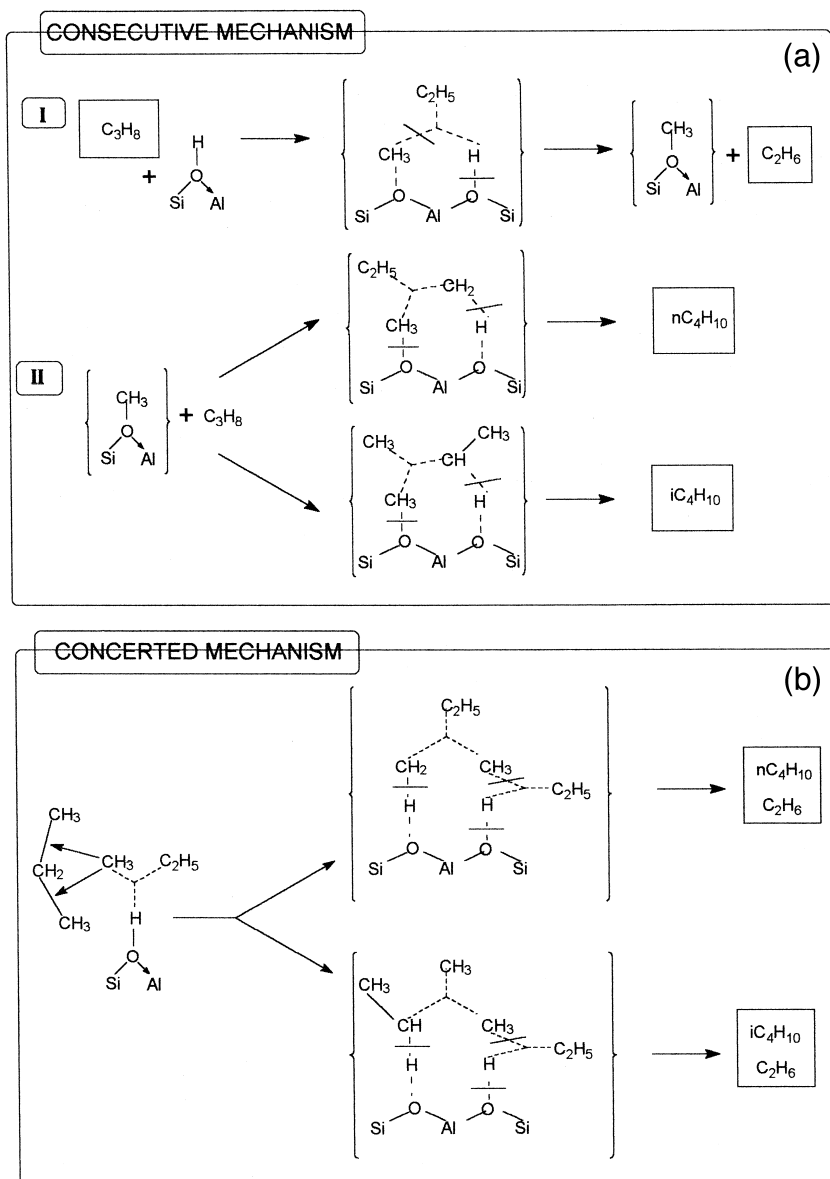


Fig. 7. Consecutive (a) and concerted (b) mechanisms for the disproportionation of propane on H-MFI catalysts.

state includes two basic oxygen anions of the zeolite framework. As for the consecutive mechanism, both isomers of butanes can be formed depending on the structure and evolution of the transition state.

The mechanisms proposed in Figs. 6 and 7 account for our experimental observations. Quantum mechanical calculations are however required to confirm the possibility of achieving

such transition states, establishing their role, and to support our proposals.

4. Conclusions

It is proposed that the propane conversion, yielding *n*-butane and *i*-butane on H-MFI catalysts, occurs via two reaction pathways of which

the relative importance depends on the propane partial pressure. Low propane pressure (coverage) favours the monomolecular dehydrogenation of propane followed by the oligomerisation of propylene, the formation of polymeric hydrocarbons, and their cracking. This pathway leads preferentially to *i*-butane. High propane pressure (high coverage) leads to bimolecular disproportionation which yields ethane and the two butane isomers.

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