

Solid-state NMR studies of *n*-butene isomerisation over H-ferrierite

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Abstract

The reaction of 1-butene over ferrierite has been studied by ¹³C MAS NMR. It is shown that extensive double bond isomerisation and the formation of dimers, mainly dimethyl-hexenes and trimethyl-pentenes, dominate the early catalytic events. Strong interactions between the butene double bond and the Brønsted acid sites shift and broaden the butene olefinic signal extensively. The olefinic carbon signals of isobutene and butene dimers are not observed in these experiments because of the interactions mentioned above and the effect of carbon scrambling. At higher reaction temperatures, the formation of isobutene dominates the spectra and this catalytic event parallels the consumption of 3,4,4-trimethyl-2-pentene. It is suggested that that 3,4,4-trimethyl-1-pentene isomerises to 2,4,4-trimethyl-1-pentene which in turn, rapidly cracks to form isobutene. At higher reaction temperatures, isobutene undergoes extensive secondary reaction leading to C₁–C₅ paraffins and aromatic coke. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Both, the academic and industrial interest in the isomerisation of *n*-butene to isobutene over ferrierite catalyst have been relentless in the last 10 years [1–7]. The vast commercial demand for isobutene is due to the synthesis of methyl *tert*-butyl ether (MTBE), a process based on isobutene. This reaction has been widely investigated and there is now a plethora of articles in the literature which debate the mechanistic pathways of this isomerisation process. When the reaction is carried out on fresh catalyst, a bimolecular

mechanism is proposed [4,5,7], which operates via the formation of octene dimers. These olefinic dimers undergo a sequence of isomerisation and cracking reactions to produce isobutene as a main product. This mechanism also leads to the formation of a number of side products, such as propene, pentenes and butane. When the reaction is performed on an aged catalyst, both the yield and selectivity are enhanced and a monomolecular mechanism is suggested [5,6] to operate in this case via the protonated cyclopropane intermediate. The enhanced selectivity over the aged catalyst has been a matter of debate and the role of coke in modifying pore structure and acidity has been seriously considered [7,20].

The potential of magic-angle-spinning NMR (MAS NMR) for monitoring hydrocarbon conversions

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proceeding inside the catalyst pores using sealed samples has been widely demonstrated [8–15]. In this contribution, the reaction of ^{13}C -labelled 1-butene over fresh ferrierite has been monitored by ^{13}C MAS NMR and these experimental findings provide an insight into the mechanism of this reaction. The spectra shown in this contribution provide spectroscopic evidence for the formation of dimers, whose consumption parallels the isobutene formation and thus, confirms the bimolecular nature of this reaction under the conditions used.

2. Experimental

The ammonium form of zeolite ferrierite ($\text{Si}/\text{Al} = 10$) was provided by British Petroleum and the proton form (H-FER) was prepared by heating the material at 450°C in a nitrogen flow for 24 h.

The reactant 1-butene-1- ^{13}C ($^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$) was obtained by Univar PLC-CDN isotopes. The catalyst H-FER (50 mg) was loaded into specially designed Pyrex capsules [8,9], which were in turn connected to a vacuum line. The catalyst was activated under vacuum at 400°C for 24 h and then loaded with a controlled quantity of the reactant (1 mol/acid site). The number of acid sites was determined by sorption and FTIR studies [21].

The sample capsules were sealed and heated at various reaction temperatures for a period of 3 min. Upon sealing, the temperature of the catalyst is raised to 80°C and thus, the lowest reaction temperature possible in these studies is 80°C .

All the ^{13}C MAS NMR spectra were recorded at room temperature on a Bruker MSL 400 spectrometer using a Chemagnetics APEX 400 pencil probe with spinning rates of 4.5 kHz. The ^{13}C MAS NMR spectra were recorded by means of single pulse direct excitation with high-power proton decoupling. Pulse delays of 5 s were found adequate to yield quantitatively reliable spectra. The cross polarisation experiments (^{13}C CP MAS NMR) were carried out with pulse delays of 5 s and contact times of 5 ms. Chemical shifts are referenced to external tetramethylsilane. In these spectra, asterisks denote spinning side bands and the background signal, only seen in the ^{13}C MAS NMR spectra, is clearly marked and results from the NMR probe. This background signal is not detected when the spectra are recorded with cross-polarisation.

3. Results and discussion

Figs. 1 and 2 illustrate the ^{13}C MAS NMR and ^{13}C CP MAS NMR spectra of *n*-butene isomerisation on H-FER, respectively, at a range of temperatures (80 – 400°C). The assignments of these spectra [19] at lower reaction temperatures (200°C) are summarised in Table 1.

3.1. Olefinic region

Although the butene used in these studies is ^{13}C enriched at the olefinic carbon ($^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$), no individual signal at ca. 114 ppm is observed at the early reaction stages (80 – 200°C).

As discussed later, double bond isomerisation and a random scrambling of the ^{13}C label, would

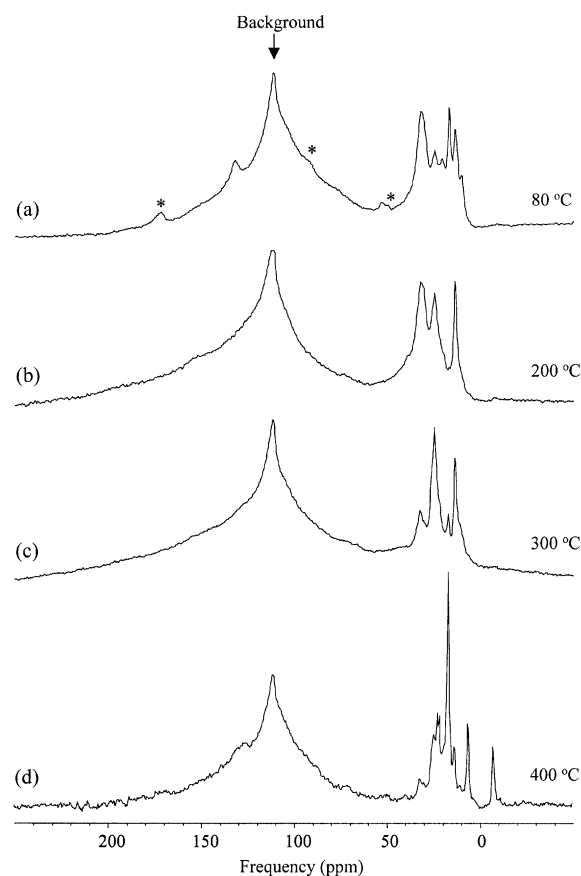


Fig. 1. The ^{13}C MAS NMR spectra of 1-butene-1- ^{13}C reaction on H-FER at a range of temperatures.

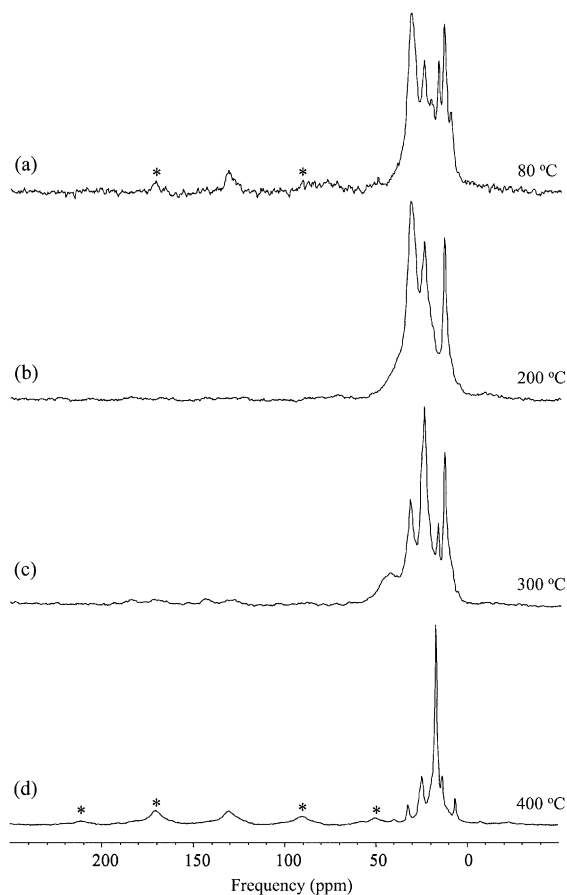


Fig. 2. The ^{13}C CP MAS NMR spectra of 1-butene-1- ^{13}C reaction on H-FER at a range of temperatures.

unavoidably shift the ^{13}C label towards the paraffinic range whereas one would also expect signals in the olefinic region (114–140 ppm). At the early reaction stages (Fig. 1(a)), a broad signal centered at ca. 133 ppm is seen which must result from the butene olefinic carbons.

The broadness and position of this signal signify a strong interaction between the Brønsted acid sites and the double bond [7]. Moreover, because this signal is not susceptible to cross polarisation as evidenced by its weak intensity in the cross-polarised spectrum (see Fig. 2(a)), this points to the mobility of the protons around the double bond and their possible exchange with the Brønsted protons as previously suggested [16]. It must be noted that the olefinic

signal completely disappears at later reaction stages (200°C), along with the paraffinic signals at 10.1 and 16.7 assigned to 2-butenes, signifying total consumption of butene at this reaction temperature. In the paraffinic range discussed below, the signal at 13.7 ppm, attributed to 1-butene at 80°C, is still observed at later reaction stages and must result from dimer methyl groups rather than 1-butene. Thus, one may conclude that *n*-butene is totally consumed at 200°C.


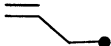
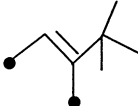
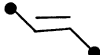
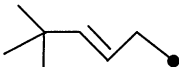
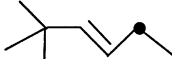
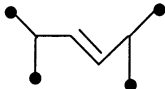

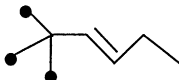
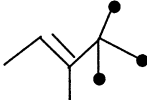

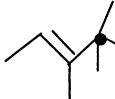

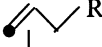
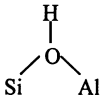
Evidently, the olefinic carbon signals of isobutene and butene dimers, formed at later reaction stages, are not observed in these experiments. The failure to detect the olefinic carbons of 1-octene adsorbed on H-ZSM-5 has already been discussed in the literature [16] and explained by a complete carbon scrambling through carbenium ion intermediates. In the same report [16], the carbons associated with the double bond are suggested to be in an ionic state, which cannot be clearly observed by NMR. In the present contribution, it is suggested that strong double bond–Brønsted acid sites interaction [7], as seen in butene, may be responsible for the failure to detect olefinic carbons of isobutene and dimers. Such an interaction would be more profound with the bulkier isobutene and dimers and would thus lead to an increase in the chemical shift anisotropy of these signals. Naturally, carbon scrambling also contributes to the failure to detect olefinic signals as it shifts the ^{13}C label to the statistically favoured paraffinic range. Therefore, the olefinic signal is weakened by carbon scrambling and is broadened by chemical shift anisotropy interactions to the extent that it becomes undetectable.

It should be noted that the signal, appearing in the final reaction ($T = 400^\circ\text{C}$) at 130 ppm, is assigned to aromatic coke. This signal is clearly observed in the cross-polarised spectrum corresponding to the reaction temperature of 400°C and the assignment is based on line shape, line width, catalyst colour and previous characterisation by FTIR [7].

3.2. Paraffinic region

A number of resonances appear initially in the spectrum at 80°C shown in Fig. 1(a), which depicts the very early stages of this reaction. The first three resonances (upfield) are assigned to butenes, which have undergone double-bond isomerisation. The lines at 10.1 and 16.7 ppm are assigned to *cis*- and *trans*-2-butene,

Table 1
Assignment of the resonances at the early reaction stages ($T \leq 200^\circ\text{C}$)

Chemical shift (ppm)	Assignment
10.1	
13.7	 
16.7	 
20.7	
24.3	 
31.6	  
37.6	
52.5	 
133	

respectively, and the signal at 13.7 ppm is attributed to 1-butene. As discussed later, a number of dimers are identified at this reaction stage and it is therefore possible that some of the terminal methyl groups may contribute to the signals at 13.7 and 16.7 ppm as shown in Table 1. The next two signals at 20.7 and 24.3 ppm are assigned to the 2,2-dimethyl-3-hexene methylene carbon and 2,5-dimethyl-3-hexene methyl groups, respectively. The strong broad signal at 31.6 ppm is attributed to methyl groups in 2,2-dimethyl-3-hexene, 3,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene. The broad resonance at 37.6 ppm is assigned to the quaternary carbon in 3,4,4-trimethyl-2-pentene and the weak signal at

52.5 ppm is attributed to the methylene group in 2,4,4-trimethyl-1-pentene. The cross-polarised spectrum at this reaction stage, shown in Fig. 2(a), exhibits all the features discussed above.

The spectra corresponding to 200°C , shown in Figs. 1(b) and 2(b), illustrate a relative increase of the signal at 24.3 ppm which must result from the formation of isobutene, which has already been reported [7] to form at this reaction temperature. The disappearance of the lines at 10.1 and 16.7 ppm points to the total consumption of 2-butene and this also agrees with the disappearance of the butene olefinic signal at 133 ppm discussed above. This spectroscopic evidence coupled with the high reactivity of butene and the long

residence time of these experiments, strongly suggest that butene is totally consumed at this reaction stage, and the line at 13.7 ppm must result from the methyl groups of 3,4,4-trimethyl-2-pentene. The notable formation of this dimer is also confirmed by a relative increase of the broad line at 37.6 ppm, assigned to the quarterly carbon in 3,4,4-trimethyl-2-pentene which must also be responsible for maintaining the strong intensity of the line at 31.6 ppm.

The spectra corresponding to 300°C, shown in Figs. 1(c) and 2(c), depict a number of additional catalytic events. While the resonance at 31.6 ppm assigned to a number of dimers decreases, the line at 24.3 ppm associated with isobutene increases noticeably. It is worth noting that the dramatic decrease of the line at 31.6 ppm parallels the decrease in the broad resonance at 37.6 ppm which is the fingerprint of 3,4,4-trimethyl-2-pentene and this, in turn, suggests that the majority of the signal at 31.6 ppm results from 3,4,4-trimethyl-2-pentene. The reappearance of the signal at 16.7 ppm must relate to the formation of propane resulting from extensive secondary reactions of isobutene. In the spectrum recorded with cross polarisation, shown in Fig. 2(c), an additional broad line is detected at ca. 42.0 ppm, which is very difficult to assign to any particular hydrocarbon species. Based on the position and shape of this signal, it is tentatively assigned to the formation of stable surface alkoxy species most probably with the *n*-butyl or *i*-butyl structure. In the cross-polarised spectrum, weak broad lines associated with coke formation are detected in the aromatic region.

The spectra corresponding to 400°C, shown in Figs. 1(d) and 2(d) exhibit a considerably different pattern to the spectra discussed above. Extensive secondary reactions of isobutene and remaining dimers lead to methane at -7.5 ppm, ethane at 6.1 ppm, *n*-butane and *n*-pentane at 13.4 ppm and predominantly propane at 16.7 ppm. The two signals at 21.2 and 22.2 ppm (not seen by cross polarisation) are assigned to methylene groups in *n*-pentane. The broad signal at 24.3 ppm is attributed to remaining isobutene while isobutane and the methylene groups of *n*-butane may also contribute to this signal. The signal at 31.6 ppm is assigned to remaining dimers while the extremely weak signal at 42.0 ppm, only seen in the cross-polarised spectrum, is assigned as above to remaining alkoxy species. The major reduction of

the signal at 42.0 ppm at these later reaction stages (300–400°C) suggests that such alkoxy species are relatively stable at 300°C but react further at 400°C, at the long residence times associated with the NMR experiments.

In the cross-polarised spectrum, a very broad signal centered at 130 ppm with a number of spinning sidebands is clearly seen and attributed to aromatic coke [7].

3.3. Summary of the NMR results

At 80°C, extensive double bond isomerisation takes place leading to a mixture of 2-butenes and 1-butene. At the same time, a number of dimers are identified largely dimethyl-hexenes and trimethyl-pentenes. Both scrambling and double bond isomerisation shift the ¹³C-label from its original position in the olefinic range to the paraffinic range. The broad olefinic signal observed at this stage indicates a strong interaction between the Brønsted acid sites and the butene double bond.

At later reaction stages (200–300°C), an extensive consumption of *n*-butenes and its dimers is seen while the isobutene signal gains intensity. The formation of isobutene parallels the consumption of 3,4,4-trimethyl-2-pentene. The olefinic signals of both isobutene and dimers are not detected because of carbon scrambling and large chemical shift anisotropy of the olefinic carbons.

Stable surface alkoxy species may also be formed at these conditions while coke is also detected in the aromatic region of the spectrum.

At 400°C, isobutene and remaining dimers undergo extensive secondary reactions, such as oligomerisation, isomerisation and cracking to produce a range of C₁–C₅ hydrocarbons [22] and aromatic coke. The final product distribution, seen in these spectra, differs from those reported earlier [1–7], because of the long residence times employed in the NMR experiments.

3.4. Mechanistic approaches

The mechanistic approaches discussed below are illustrated in Fig. 3. At lower reaction temperatures (*T* < 200°C), double bond isomerisation takes place extensively leading to 2-butenes and 1-butene and

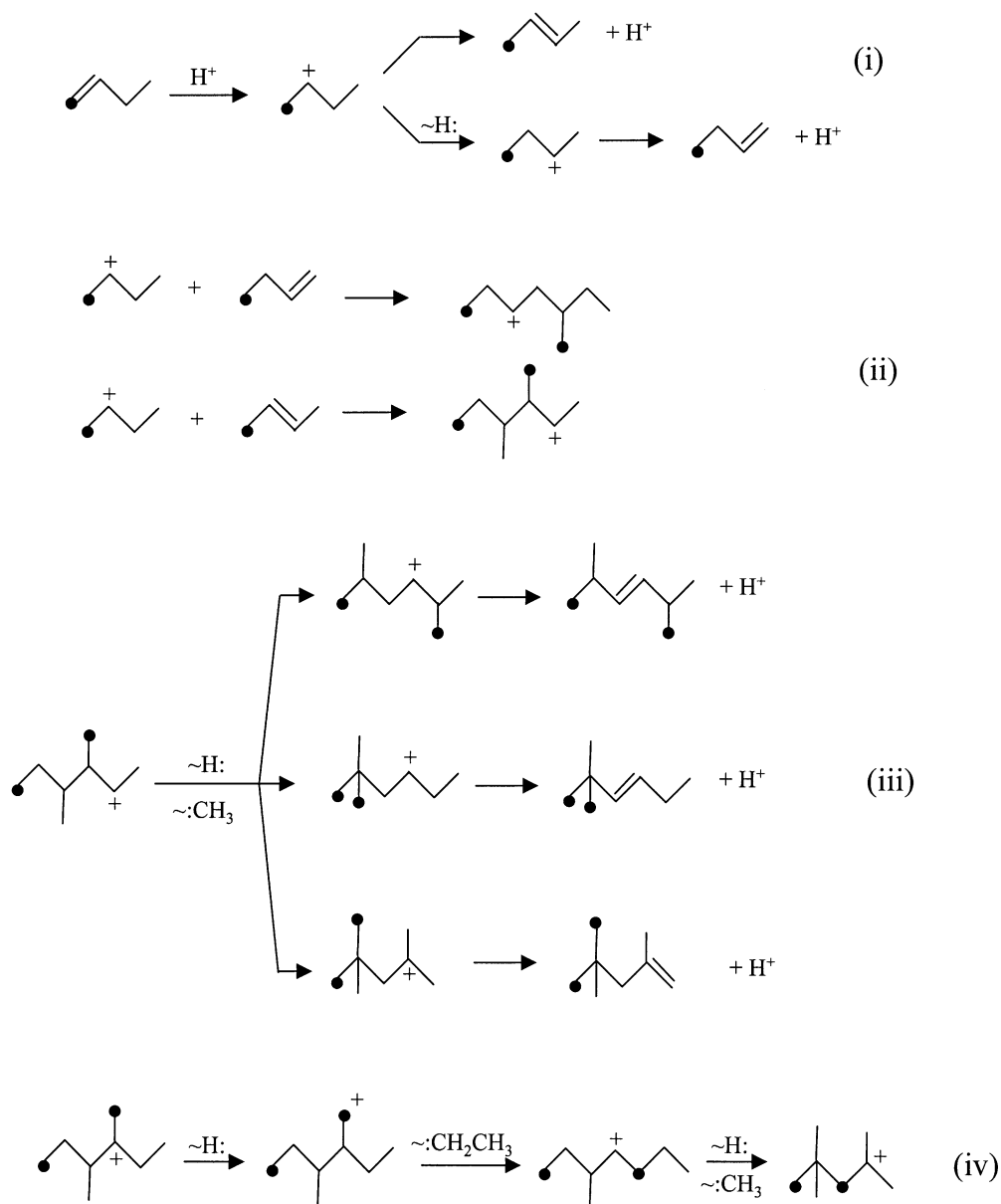


Fig. 3. Schematic mechanistic approaches for the isomerisation of *n*-butene.

scheme (i) pictures these early reaction stages. At the same time, dimers start to form and reaction schemes (ii) and (iii) describe the formation of dimers whereby oligomerisation, followed by skeletal isomerisation through hydride and methide shifts leads to a number of dimethyl-hexenes and trimethyl-pentenes. At these

reaction conditions, scrambling of the ^{13}C labelled is observed and scheme (iv) suggests a possible mechanistic pathway for scrambling.

The formation of dimers is a dominant feature in these spectra and it is therefore interesting to assess their contribution to isobutene synthesis. Reaction

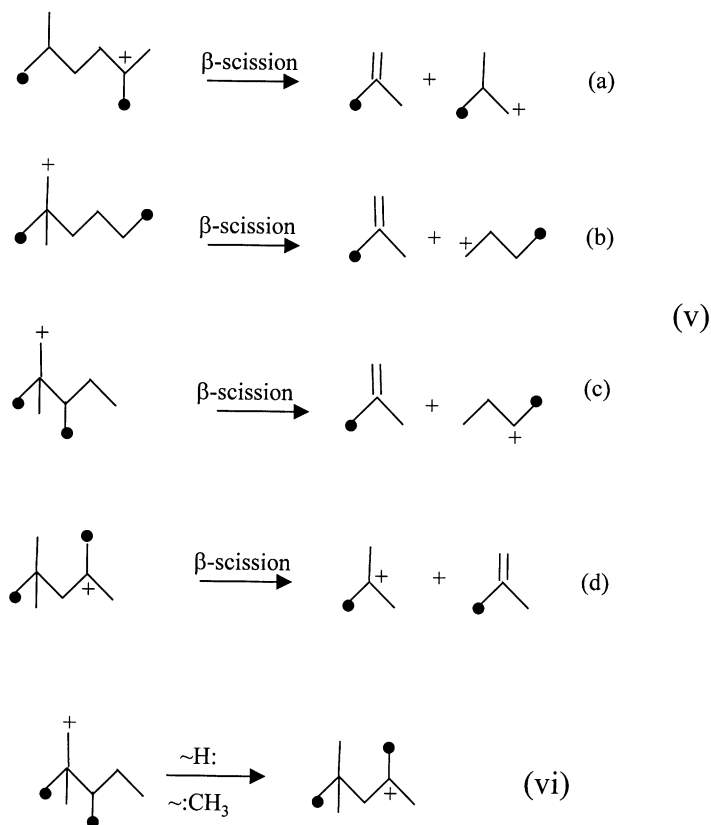


Fig. 3. (Continued).

scheme (v) illustrates the formation of isobutene by β -scission of the main dimers seen in these spectra. Ostensibly, the formation of isobutene by β -scission of the 2,4,4-trimethyl-2-pentyl carbenium ion (scheme (v) (d)) must be energetically favoured since it only involves tertiary carbenium ions. In the NMR spectra, 2,4,4-trimethyl-1-pentene is only observed in small amounts whereas 3,4,4-trimethyl-1-pentene appears to be the main dimer whose consumption parallels isobutene formation. As shown in scheme (v) (c), cracking of 3,4,4-trimethyl-1-pentene to produce isobutene is not energetically favoured as it involves primary carbenium ions. Therefore, it is reasonable to assume that 3,4,4-trimethyl-1-pentene isomerises to 2,4,4-trimethyl-1-pentene (scheme (vi)) which in turn, rapidly cracks to form isobutene as seen in scheme (v) (d). Since higher reaction temperatures favour cracking over isomerisation, 2,4,4-trimethyl-1-pentene is

not detected as a main isomer and thus, a parallel consumption of 3,4,4-trimethyl-1-pentene with isobutene formation is observed. Although, trimethylpentenes have been considered [17] to be too large to form in 10-membered ring zeolites, it has been recently demonstrated [18] that these bulky dimers can reach the acid sites and can therefore react to produce mostly isobutene. The experimental findings already reported [18], agree with the interpretation of the NMR spectra in the present contribution, and both reports highlight the significance of trimethylpentenes in isobutene synthesis.

At higher reaction temperatures, surface alkoxy species are detected while isobutene undergoes extensive secondary reaction leading to C_1 – C_5 paraffins and aromatic coke. The contribution of the alkoxy species to this reaction is unclear at this stage.

4. Conclusion

The reaction of ^{13}C -labelled 1-butene over ferrierite has been monitored by ^{13}C MAS NMR. In the early reaction stages (lower reaction temperatures), extensive double bond isomerisation is observed accompanied by the formation of dimers mainly dimethyl-hexenes and trimethyl-pentenes. Strong interactions between the butene double bond and the Brønsted acid sites shift and broaden the olefinic signal extensively. The olefinic carbon signals of isobutene and butene dimers are not observed in these experiments because of the interactions mentioned above and carbon scrambling. At later reaction stages, the formation of isobutene dominates the spectra and this catalytic event parallels the consumption of 3,4,4-trimethyl-2-pentene. It is suggested that that 3,4,4-trimethyl-1-pentene isomerises to 2,4,4-trimethyl-1-pentene which in turn, rapidly cracks to form isobutene.

At higher reaction temperatures, isobutene undergoes extensive secondary reaction leading to C_1 – C_5 paraffins and aromatic coke.

Acknowledgements

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