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Mechanism of the skeletal isomerisation of linear butenes over ferrierite: analysis of side reactions

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Abstract

An investigation of the effect of reaction conditions on product distribution in the skeletal isomerisation reaction of linear butenes has been carried out. The main reaction routes over ferrierite have been identified. Beside the main product isobutene, major by-product formation occurs. The unwanted reactions include dimerisation of butene to form octenes, hydrogen transfer yielding small amounts of saturated C_3 and C_4 hydrocarbons and disproportionation producing propene and pentenes. The most abundant by-products were pentene and propene, though these were not formed in equimolar amounts as could be expected. Oligomerisation experiments of propene over ferrierite produced large amounts of butene and pentene, revealing the presence of adsorbed nonene. The cracking of this surface species to hexene and propene is the most likely reaction route for the excess propene formation. This additional path to propene formation operates mainly at temperatures above 623 K.

Keywords: *n*-Butene; Isomerisation; Ferrierite

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1. Introduction

Skeletal isomerisation of *n*-butenes is an attractive alternative for increasing the production of refinery-deficient isobutene. Isobutene is used in many important chemical processes today, and interest in new processes and technologies [1] based on isobutene is high. The reaction has been studied quite extensively previously, although the mechanism still remains controversial and has not yet been fully explained. Two main types of mechanisms have been proposed in the literature: the mono- and bimolecular reactions pathways, involving one and two butene molecules, respectively. Besides reaction mechanisms per se, the peculiar effect of catalyst deactivation by coking on isobutene selectivity is still debated. A systematic investigation of the influence of 1-butene partial pressure, weight hourly space velocity (WHSV) and temperature on the skeletal isomerisation over ferrierite has been carried out, the results of which will be presented in detail in a later paper. The present contribution aims at explaining the routes to by-product formation mainly through the use of alternative reactants.

2. Experimental

A fixed bed minireactor operating in the vicinity of atmospheric pressure connected to a GC with an on-line auto sampler for the gas phase was used in the study. The reactor was packed with catalyst particles (pelletised and sieved to 100–125 μm) and kept in place with quartz wool and sand. The reactor was heated in an oven and feedback for heating control was provided by a thermocouple inside the reactor bed. The effluent from the reactor was passed through a heated line to the gas chromatograph (Agilent 6890N), equipped with a flame-ionisation detector and a capillary column (HP-PLOT Al_2O_3 50 m × 530 μm × 15 μm). The catalyst was calcined in situ for 2 h at 773 K in air followed by drying for 2 h at 723 K in a nitrogen atmosphere. When

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the catalyst bed had reached reaction temperature, the reactant and nitrogen was introduced and the first sample was taken after 10 min on stream. Besides *n*-butene, ethene, propene and isobutene were also used as reactants. The experiments were carried out with reactant relative partial pressures varying from 0.1 to 1.0, temperatures ranging from 573 to 673 K and weight hourly space velocities between 6 and 44 h^{-1}, using a commercially available ferrierite type catalyst.

By adding an evaporator to the experimental setup, the cracking behaviour of the linear 1-octene and the heavily branched diisobutene isomers was also studied. The cracking experiments were performed at a temperature of 623 K with an octene-to-nitrogen molar ratio of approximately 1–5 and WHSV varying between 2.4 and 40 h^{-1}.

3. Results and discussion

3.1. Product distribution

Three reaction mechanisms of skeletal isomerisation of linear butenes have been proposed in the literature; the monomolecular [2], the pseudo-monomolecular [3] and the bimolecular [4,5] reaction routes. The various mechanisms will not be discussed in this paper. Thermodynamically the skeletal isomerisation of *n*-butene to isobutene is favoured at lower temperatures, although temperatures above 573 K were required for high catalytic activity over the tested catalyst. When feeding a 1:1 ratio of 1-butene and nitrogen at this temperature, conversion levels between 45 and 72 mol.% were obtained, depending on the WHSV used. The initial yield of isobutene was strongly influenced by the residence time and it also exhibited a maximum in the tested WHSV range at 573 K. This indicates that formed isobutene is consumed in a consecutive reaction producing mostly by-products as previously suggested in ref. [6]. The initial yield of by-products was, for all reaction temperatures tested, continuously increasing with increasing residence time. Based on the products formed the reaction scheme in Fig. 1 was proposed. Besides the main product isobutene, major by-product formation was present for all reaction conditions tested. The unwanted reactions include dimerisation of butene to form octenes, hydrogen transfer yielding mostly saturated C_3 and C_4 hydrocarbons and disproportionation producing propene and pentenes. Coking was also observed. However, coke exhibits a positive effect on product distribution as it seems to suppress by-product formation more than the skeletal isomerisation reaction. Propene and pentene were the most abundant by-products, in some cases accounting for more than one third of the yield. The formation of these products was most pronounced in experiments with low weight hourly space velocities and high reaction temperatures. If pentene and propene were mainly produced by cracking of octene, the molar ratio between them would be around unity. However, the propene to pentene ratio changes with reaction temperature in a way that cannot be explained only by considering dimerisation of propene to form hexene or cracking of pentene to propene and ethene. The yield of propene versus the yield of pentene for the *n*-butene experiments is shown in Fig. 2. Not only does the $C_3^=$ to $C_5^=$ ratio change with reaction temperature, but also during time-on-stream. The bending of the curves and the systematic grouping according to temperature can be seen as indications of one or more additional paths for the formation of propene at higher temperatures. The bending of the curves at low times-on-stream (TOS) can partially be explained by pentene cracking, especially for the cases where the yield to pentene goes through a maximum. However, the yields of hexenes and heptenes, which are

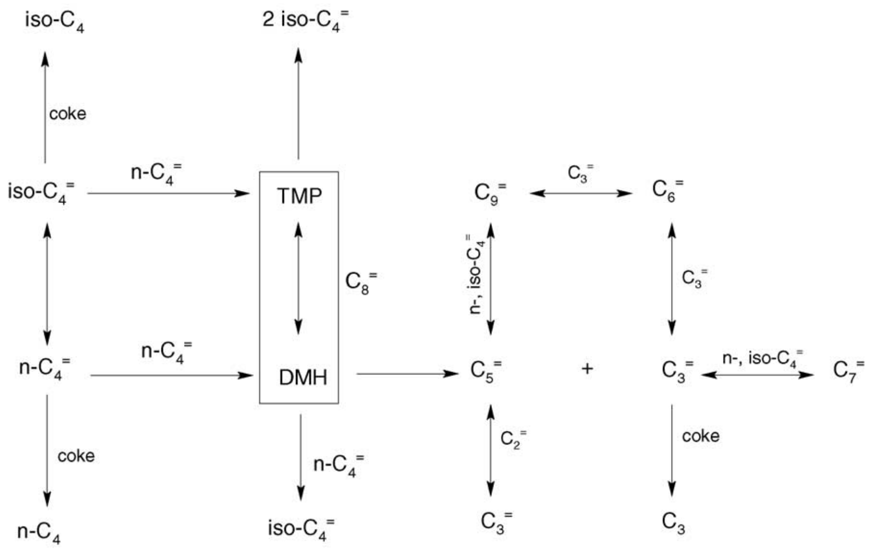

Fig. 1. Proposed reaction scheme to explain the obtained products. DMH = dimethylhexene, TMP = trimethylpentene.

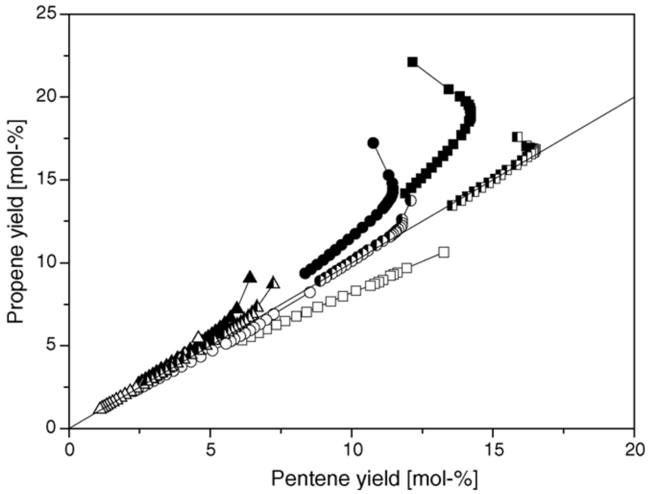

Fig. 2. Yield of propene vs. the yield of pentene. Conditions: butene-to-nitrogen molar ratio = 1:1. Experiments at 573 K (open symbols), 623 K (semi-filled symbols) and 673 K (closed symbols) using weight hourly space velocities of 6 h^{-1} (□), 12 h^{-1} (○) and 44 h^{-1} (△). The straight line represents equal amounts of propene and pentene.

dimers and codimers of propene, are typically around 1–5 mol.% each, whereas the ethene yield is almost always less than 1 mol.%.

Klepel et. al. [7] found that reacting ethene over H-ZSM-5 produced mainly propene and this reaction was therefore investigated over ferrierite in our reactor system in order to see if a part of propene is formed from ethene. With reaction temperatures ranging from 573 to 673 K, conversions of 5 mol.% or less were obtained and the selectivities to propene were less than 10 mol.% suggesting that formed ethene does not easily undergo further reactions over the tested ferrierite catalyst and that the excess propene is formed via another route. Feeding propene as a reactant confirmed that hexene was the main product, although pentene and butene, which are cracking products of nonene, were also obtained in relatively large amounts. With a 1:1 ratio of nitrogen and propene fed at a weight hourly space velocity of 12 h^{-1} conversions between 35 and 45 mol.% were achieved. The yield to hexene was more or less constant (20–25 mol.%) with temperature. The butene and pentene formation, however, exhibited a strong dependence on reaction temperature, with combined yields of 7 mol.% at 573 K and close to 20 mol.% at 673 K. The presence of butene and pentenes indicates that trimerisation of propene is indeed possible inside the pores of ferrierite. As no nonenes was observed in the gas phase, it probably only exists as a surface species that rapidly undergoes cracking and/or the amount was too small to be detected with the analytical setup. In light of this, the most likely route for excess propene formation at high temperatures is the codimerisation of butene and pentene followed by cracking to hexene and propene.

3.2. Deactivation and time-on-stream behaviour

The time-on-stream behaviour of ferrierite in *n*-butene isomerisation is very particular. High selectivity to isobutene is usually obtained only after a certain deactivation of the catalyst has occurred. Most researchers agree that the increase in selectivity and yield to isobutene are related to the formation of carbonaceous deposits (coke) on the zeolite, although the exact role of coke is still heavily debated [8]. The observed product distribution over a fresh catalyst is more or less what one would expect from a bimolecular mechanism involving successive steps of dimerisation, isomerisation and cracking, whereas the high selectivity to isobutene found over aged ferrierite is typical of a monomolecular mechanism. Experiments with ^{13}C labeled *n*-butene [9,10] support the idea about the change in prevailing mechanism. The selectivities to isobutene and the major by-products as well as conversion for fresh and aged ferrierite obtained in the present study are shown in Table 1. Not only the selectivity to isobutene, but also the selectivity to octene increases with time-on-stream. One possible explanation for this is that the higher isobutene concentration in the reactor increases the rate of isobutene and *n*-butene codimerisation and also the dimerisation rate of isobutene resulting in more branched octene isomers. In other words, both the amount and the nature of octene would change with time-on-stream. The simultaneous increase in octene selectivity and decrease in $C_3^=$ and $C_5^=$ selectivities is consistent with a change in octene nature, as cracking of diisobutene under similar conditions was very selective to isobutene (and to butenes overall) due to the fast A type cracking [11] whereas the linear 1-octene gave mostly propene and pentene.

Table 1
Selectivities (*S*) to isobutene and the main by-products and conversion (*X*) measured over fresh and aged ferrierite (low and high time-on-stream (TOS) values, respectively)

T (K)	TOS (min)	$S(C_3^=)$ (mol.%)	$S(i\text{-}C_4^=)$ (mol.%)	$S(C_5^=)$ (mol.%)	$S(C_6^=)$ (mol.%)	$S(C_7^=)$ (mol.%)	$S(C_8^=)$ (mol.%)	*X* (mol.%)
573	10	13.2	52.2	13.7	3.8	6.9	5.6	63.5
	2770	4.8	77.4	5.0	1.1	3.7	6.7	46.9
623	10	20.5	42.8	18.0	4.1	5.7	2.2	68.3
	2770	15.4	58.3	15.3	2.4	4.0	3.0	58.1
673	10	26.0	40.8	16.3	3.2	3.5	0.8	67.2
	2770	16.9	61.5	15.0	1.5	2.2	1.2	55.9

Butene-to-nitrogen ratio = 1:1, WHSV = 12 h^{-1}.

4. Conclusions

Ferrierite is a stable and selective catalyst for skeletal isomerisation of linear butenes. Beside the formation of isobutene, by-products like propene and pentene are formed. Small amounts of hexene, heptene and octene are also obtained. The main reaction mechanism for the by-product formation was most likely the dimerisation-cracking route. Furthermore, an additional route to propene formation is present at higher temperatures. Through the use of alternative reactants this path to excess propene has been identified as the codimerisation of pentene and butene to produce nonene followed by consecutive cracking to hexene and propene. Cracking of 1-octene and diisobutene showed that the branched isomer was more selective to isobutene, and to butenes overall, and its rate of cracking was higher than that of the linear 1-octene. This indicates that the active sites in ferrierite are accessible even to the heavily branched octenes.

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