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On the conversion of 1-butene over Pt-ZSM5

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The conversion of 1-butene over Pt-ZSM5 was studied in the presence and absence of hydrogen. In the absence of hydrogen, the catalytic activity of the metal was rapidly poisoned and in the steady state the catalyst showed identical properties as the parent ZSM5. In the presence of hydrogen, the skeletal isomerization of butene was not affected, but the rate of oligomerization/cracking was enhanced. From the by-products butadiene, propane, ethane and methane, ethane and propane originated mainly from oligomerization/cracking on the acid sites and not from hydrogenolysis on Pt. The contribution of the metal to the overall by-product formation was small. Thus, an adaptation of the acid rather than of the metal sites is necessary to improve the performance of the bifunctional catalyst.

Keywords: bifunctional catalysis, Pt-ZSM5, butene isomerization

1. Introduction

Pt-ZSM5 with a high Si/Al ratio is a promising catalyst for the one-step dehydroisomerization of n-butane to isobutene [1]. However, at high conversions side reactions of the primarily formed butenes increase significantly, thereby reducing the selectivity of the catalyst and limiting the yields of isobutene. In order to improve the performance of Pt-ZSM5 as a dehydroisomerization catalyst it is crucial to understand the nature of these side reactions. Previous work showed that the most important side reaction of butenes is acid-catalyzed oligomerization/cracking, leading primarily to the formation of ethene, propene and pentene [2]. Propane and ethane, which are the most abundant by-products at high conversions, were proposed to be formed by hydrogenation of the corresponding alkenes on the metal sites rather than by hydrogenolysis. If this holds true all major by-products originate from oligomerization/cracking reactions of butenes, whereas the contribution of the metal to the overall by-product formation is very small. It is, however, possible that a synergy between metal and acid sites affects the nature and extent of side reactions of the butenes.

In order to address these questions the conversion of 1-butene was studied over a series of Pt-ZSM5 catalysts with different metal loadings and acid site concentrations under the conditions used for dehydroisomerization of butane. The aim of the paper is to identify the reaction pathways of the conversion of butene over Pt-ZSM5 and to describe the parameters that influence the extent and nature of the side reactions.

2. Experimental

2.1. Catalyst preparation and characterization

The parent ZSM5 materials were supplied by ZEOLYST. Pt was incorporated by competitive ion exchange with a diluted solution of $Pt(NH_3)_4(OH)_2$ and ammonia [1]. After drying, the sample was slowly heated (0.5 K/min) in a flow of air to 723 K and kept there for 2 h. The calcination reactor was cooled down and flushed with nitrogen. Then the sample was reduced in a flow of hydrogen for 2 h at 773 K (temperature increment 5 K/min) [3].

The elemental composition of the samples was determined by X-ray fluorescence. Hydrogen chemisorption for determining the Pt dispersion was carried out in a volumetric system [4]. About 1 g of the sample was reduced for 1 h at 823 K in H_2. After reduction, the sample was degassed at 823 K (which was also the reaction temperature) for 1 h in vacuum (10^{-5} mbar). After degassing, the sample was cooled to room temperature and the hydrogen adsorption isotherm was measured by dosing decreasing amounts of H_2 (in the range of 500–50 mbar) to the sample. The hydrogen chemisorption capacity was calculated by extrapolation of the hydrogen uptake to zero pressure. The relative concentration of Brønsted acid sites was determined from the intensity of the band at 3610 cm^{-1} in the IR spectrum of the sample, attributed to the stretching vibration of the Brønsted OH groups. Details of the experimental procedures are given in [1]. The results of the characterization are summarized in table 1.

2.2. Catalyst testing

For the catalytic tests the samples were pressed, crushed and sieved to obtain a particle size in the range of 300–500 μm. 10–50 mg of the catalyst were mixed with 50–100 mg quartz and filled into a quartz tube with an inner

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Table 1
Physico-chemical characterization of the Pt-ZSM5 samples.

Sample code	SiO_2/Al_2O_3	H^+ (mmol/g)	Pt loading (wt%)	H/Pt
0.1% Pt ZSM5(480)	480	0.07	0.09	>2.0
0.5% Pt-ZSM5(480)	480	0.07	0.46	1.2
0.1% Pt-ZSM5(80)	80	0.40	0.10	n.d.[a]

[a] n.d. = not determined.

diameter of 4 mm. The catalyst bed had a typical length of 5–15 mm and was supported on both sides by quartz wool.

The samples were reduced *in situ* at 830 K for at least 1 h in a mixture of H_2/Ar (18/82). 830 K was also the temperature of the reaction. The reaction was started by switching from H_2/Ar to the feed, which was under standard conditions a mixture of 7.5% 1-butene, 0 or 20% H_2, balance Ar. The outlet pressure of the reactor was regulated by a back-pressure regulator to 1.8 bar. The pressure drop over the reactor was not higher than 0.1 bar.

In order to follow the performance of the catalyst at very short time on stream the reactor effluent was stored in sampling loops for later GC analysis. After 10 min time on stream online GC analysis was employed. The details of the analysis are described in [1].

Conversions and yields were calculated on a carbon basis, using the FID areas and corresponding response factors. Since the double-bond isomerization is a very facile reaction and usually reaches equilibrium [5], *cis*- and *trans*-butene were counted as reactants and not as products.

3. Results

Figure 1 (a) and (c) shows the major products in the conversion of 1-butene over 0.1% Pt-ZSM5(480) in the absence of hydrogen. At steady state Pt-ZSM5 showed identical catalytic properties as the parent zeolite. A stable yield of 17% isobutene was obtained. The major by-products were propene and pentene. Traces of ethene, n-butane, isobutane (not shown in figure 1) and butadiene were also found. In contrast to the parent ZSM5 (which was stable already after 1 min when the first data point was taken), the formation of propene and butadiene decreased at short time on stream with Pt-ZSM5 (see figure 1(c)).

The comparison of figure 1 (a), (b) and (c), (d) demonstrates how the product pattern changed, when hydrogen was added to the feed. The formation of isobutene was almost unaffected (it decreased from 17 to 16%). The by-product formation, on the other hand, was drastically changed. Not only propene and pentene, but also the saturated by-products n-butane, propane, isobutane, ethane and methane (in this order) were formed. n-butane was the most abundant by-product, followed by propene and buta-

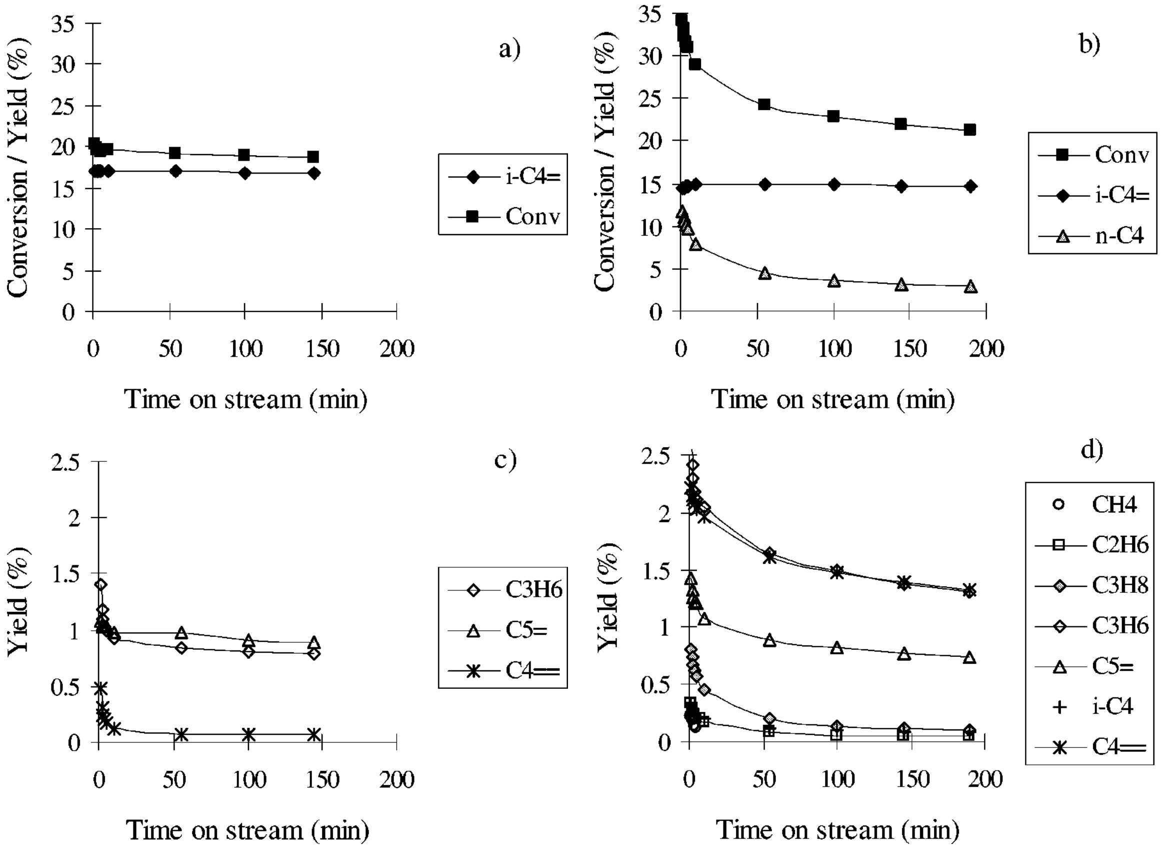

Figure 1. Butene isomerization over 0.1% Pt-ZSM5(480) in the presence (b, d) and absence (a, c) of H_2. WHSV = 82 h^{-1}, 830 K, 1.8 bar, 7.5% 1-butene, 0 or 20% H_2. Conversion of 1-butene and yield of the major products.

Table 2
Reaction of 1-butene over (Pt-)ZSM5(480).[a]

	Pt content (%)				
	0.0	0.1	0.1	0.5	0.5
H_2 (%)	0	0	20	0	20
Yield i-$C_4^=$ (%)	16.5	16.9	14.9	16.6	11.8
i-$C_4^= / \sum C_4^=$ (%)	16.9	17.2	16.2	16.9	15.1
Conversion (%)	18.2	18.9	22.7	18.5	33.8
Yield by-products (%)					
CH_4	0.01	0.00	0.07	0.00	0.34
C_2H_6	0.00	0.00	0.06	0.00	0.39
C_3H_8	0.00	0.00	0.14	0.00	0.69
n-C_4	0.14	0.11	3.6	0.11	15.8
i-C_4	0.03	0.05	0.10	0.04	0.24
C_2H_4	0.12	0.08	0.10	0.08	0.12
C_3H_6	0.65	0.81	1.5	0.76	1.4
$C_5^=$	0.42	0.91	0.82	0.85	0.74
$C_4^{==}$	0.07	0.07	1.5	0.09	2.3

[a] Reaction conditions: WHSV = 82 h^{-1}, 1.8 bar, 830 K, 7.5% 1-butene, 0 or 20% H_2, 100 min on stream.

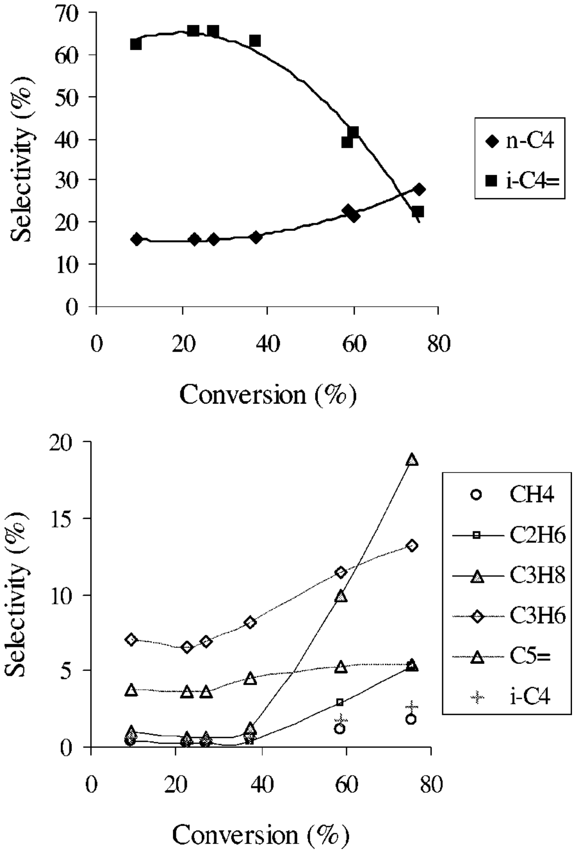

Figure 2. Selectivity to the major products as a function of 1-butene conversion. 0.1% Pt-ZSM5(480), 830 K, 1.8 bar, 7.5% 1-butene, 20% H_2, 100 min on stream.

diene. The by-product formation decreased with time on stream for all components.

Increasing the metal loading from 0.1 to 0.5 wt% Pt led to a further increase in the formation of n-butane, butadiene, propane, isobutane, ethane and methane (see table 2). The typical products of butene isomerization, i.e., isobutene, propene and pentene, were less affected. The rate of isobutene formation decreased slightly, that of propene slightly increased. As observed for 0.1% Pt-ZSM5, the by-product formation decreased with time on stream, whereas the rate of isobutene formation was constant.

Figure 2 shows the selectivity over 0.1% Pt-ZSM5(480) as a function of conversion. Isobutene and n-butane were the major primary products with an initial selectivity of 65 and 16%, respectively. Also propene and pentene were primary products (4 and 7% initial selectivity). At conversions above 40%, the selectivity to isobutene decreased sharply, while the formation of especially propane, and to a smaller extent also of propene and pentene increased.

Figure 3 shows the influence of the acid site concentration on the conversion of butene in the presence of hydrogen. The conversion increased by more than a factor of two and the yield of isobutene rose from 15 to 26%, when the SiO_2/Al_2O_3 ratio decreased from 480 to 80. The formation of n-butane remained unchanged. The yield of by-products, however, was drastically increased, especially the yield of propene which went up by a factor of six. Initially, also large amounts of propane, ethane and isobutane were observed, but as in the other experiments the formation of the saturated products decreased rather quickly with time on stream.

4. Discussion

4.1. The formation of (saturated) by-products

In the presence of hydrogen methane, ethane and propane were found as products in the conversion of 1-butene over Pt-ZSM5. Table 3 shows how the yield of methane, ethane and propane depended on the metal loading and the SiO_2/Al_2O_3 ratio. Methane formation increased with the metal content rather than with the concentration of acid sites, the yield of ethane and propane formation, on the other hand, depended mainly on the concentration of acid sites. The products also showed a different dependence on conversion (see figure 4). The selectivity to propane and ethane increased drastically above 40% conversion, in parallel with a decrease in selectivity to isobutene (see figure 2).

The decrease in selectivity to isobutene is connected to the approach to thermodynamic equilibrium. As the ratio i-$C_4^=/C_4^=$ approaches its thermodynamic limit, the net rate of isomerization becomes very low. The by-product formation, on the other hand, is unlimited. As a result, the selectivity to by-products increases. In the absence of hydrogen and Pt, these by-products are propene and pentene [2]. Here, the selectivity to propene and pentene increased only moderately compared to propane and ethane. Also the selectivity to methane remained rather low. Both, the strong dependence on the concentration of acid sites and the strong increase in selectivity with conversion, indicate that ethane and propane originate from the oligomer-

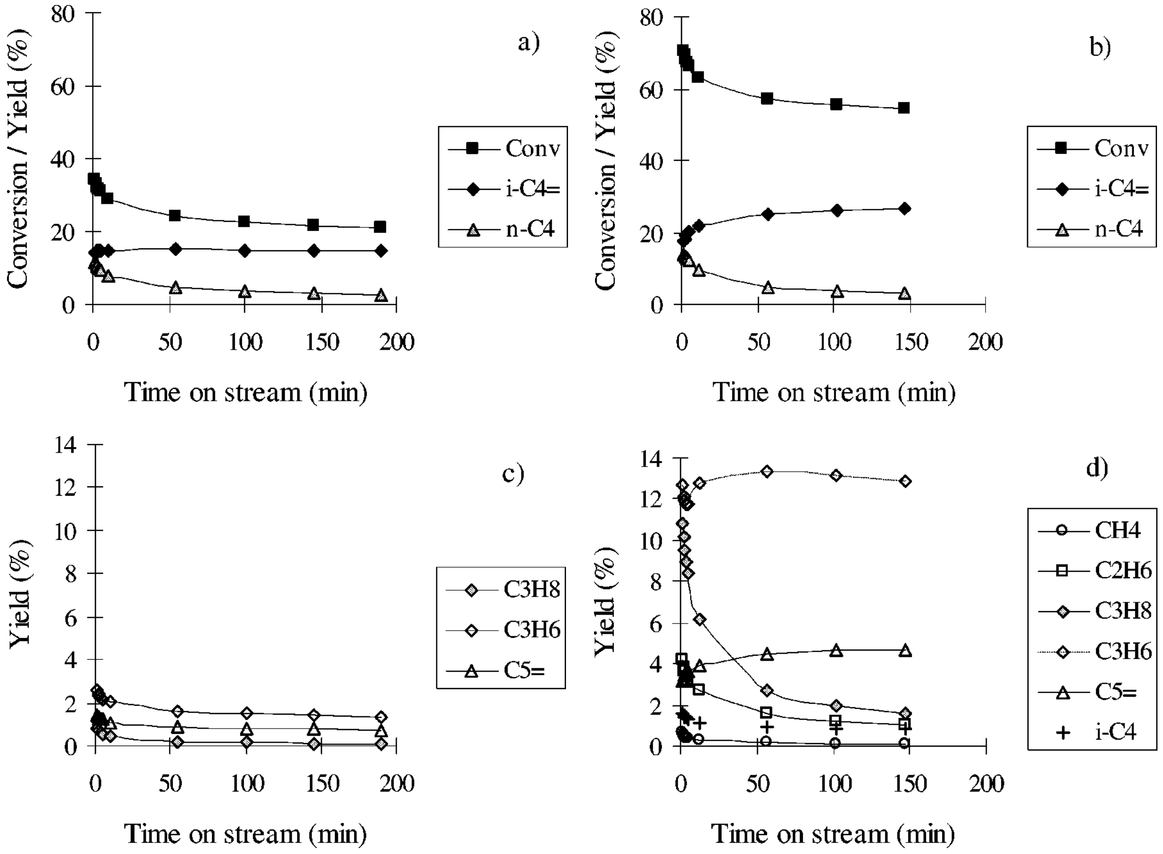

Figure 3. Butene isomerization over 0.1% Pt-ZSM5 with $SiO_2/Al_2O_3 = 480$ (a, c) and 80 (b, d). WHSV = 82 h^{-1}, 830 K, 1.8 bar, 7.5% 1-butene, 20% H_2. Conversion of 1-butene and yield of the major products.

Table 3
Yield of saturated by-products in the reaction of 1-butene over (Pt-)ZSM5.[a]

	SiO_2/Al_2O_3			
	480	480	80	480
Pt content (wt%)	0	0.1	0.1	0.5
Conversion (%)	11.7	22.7	55.3	33.8
Yield (%)				
CH_4	0.04	0.07	0.13	0.34
C_2H_6	0.01	0.06	1.22	0.39
C_3H_8	0.00	0.14	1.93	0.69
i-C_4	0.04	0.10	0.84	0.24

[a] Reaction conditions: WHSV = 82 h^{-1}, 1.8 bar, 830 K, 7.5% 1-butene, 20% H_2, 100 min on stream.

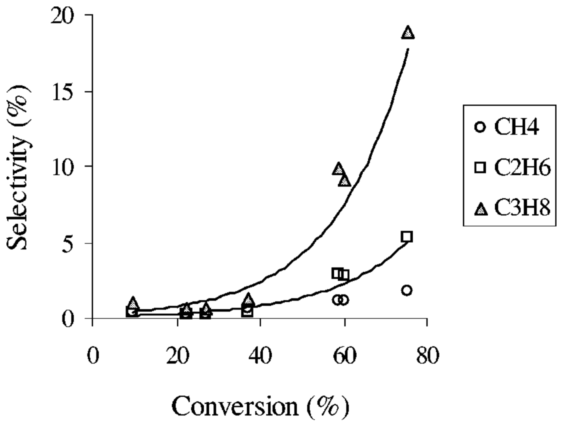

Figure 4. Selectivity to methane, ethane and propane as a function of conversion. 0.1% Pt-ZSM5(480), 830 K, 1.8 bar, 7.5% 1-butene, 20% H_2, 100 min time on stream.

ization/cracking route. Methane, on the other hand, is produced by metal-catalyzed hydrogenolysis (note the increase of the yield with metal content) as well as by cracking over the acid sites (note the small increase of the yield with acid site concentration).

There are two mechanisms by which the formation of ethane and propane via the oligomerization/cracking route can happen. The classical explanation is that the alkenes formed by oligomerization/cracking on the acid sites are hydrogenated on the metal to the corresponding alkanes. It has been suggested, however, that desorption of the alkene from the acid site and diffusion to the metal site may not be necessary [6]. Hydrogen can be spilt over from the metal to the zeolite and assist the desorption of cracking products as saturated species, for example, according to the reaction

$$Z\text{–O–CH}(CH_3)_2 + 2H_{\text{spill}} \rightarrow Z\text{–OH} + CH_3\text{–}CH_2\text{–}CH_3 \quad (1)$$

It is difficult to distinguish between the two routes because a similar dependence on metal loading and hydrogen partial pressure is expected for both.

Not only the formation of saturated by-products increased in the presence of Pt and hydrogen, but also the rate of propene formation (see table 2 and figure 1). Figure 1 (c) and (d) shows that the time on stream behavior of propene is closely related to the one of butadiene. When reacting butadiene with ZSM5 at 775 K it oligomerizes and cracks into propene, pentene, ethene and higher hydrocarbons (C_{5+}) [7]. Thus, the higher propene formation is attributed to cracking of butadiene oligomers. Since the cracking products are richer in hydrogen than butadiene also some carbonaceous deposits have to be formed in order to maintain the hydrogen balance. These deposits deactivate the metal. In the absence of hydrogen the deactivation is fast and after a few minutes on stream Pt-ZSM5 gives the same product pattern as ZSM5. In the presence of hydrogen, however, the deactivation of the metal is slow. Thus, a significant amount of butadiene is observed even after 100 min on stream, leading to the higher yield of propene by cracking of its oligomers. Note that from a thermodynamic point of view the formation of butadiene should be inhibited in the presence of hydrogen.

4.2. *The competition between butene isomerization and hydrogenation*

Butene isomerization over the acid sites and butene hydrogenation over the metal sites are parallel, competing reactions. As the metal loading increased, the relative importance of hydrogenation increased, while as the acid site concentration increased, the relative importance of butene isomerization and butene cracking increased (see figure 2). Like in dehydroisomerization [1], the ratio of metal to acid sites changed the way the reaction mixture approached the thermodynamic equilibrium between n-butene, isobutene and n-butane. This is depicted in figure 5. In the absence of hydrogen n-butane did not form and the composition of the reaction mixture moved along the line from n-butene to the equilibrium point between n- and isobutene (point F). Over 0.1% Pt-ZSM5(480) the reaction mixture approached the overall equilibrium point G along a curve following first the line of butene isomerization, only then turning into the direction of hydrogenated products (line FG). Over 0.5% Pt-ZSM5(480), the reaction mixture approached the overall equilibrium point G more directly, i.e., hydrogenation dominated, while over 0.1% Pt-ZSM5(80) isomerization dominated.

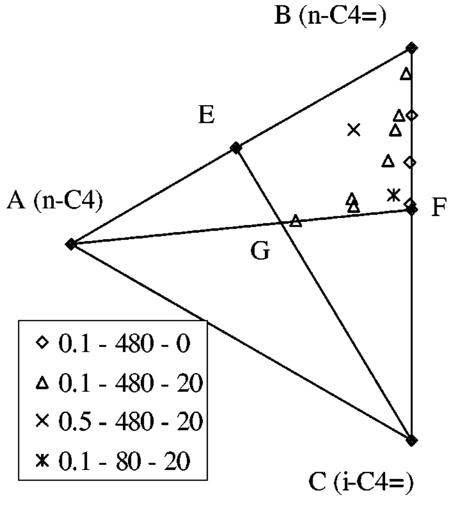

Figure 5. The three corners of the triangle represent the compounds n-butane (A), n-butene (B) and isobutene (C). Every mixture of the three compounds is represented by a point in the triangle. Points E and F represent the thermodynamic equilibria between n-butane/n-butene and n-butene/isobutene, respectively, G the equilibrium between all three components. The reaction data (830 K, 1.8 bar, 7.5% 1-butene, 100 min on stream) are illustrated in the graph using the mol fractions of n-butane, n-butene and isobutene in the reaction mixture after normalization to 1 ($\sum x_i = 1$). Legend: metal loading – SiO_2/Al_2O_3 – % H_2 in feed.

5. Conclusions

From the results discussed above we can propose a reaction network for the conversion of 1-butene over Pt-ZSM5 as shown in figure 6. Four parallel reactions take

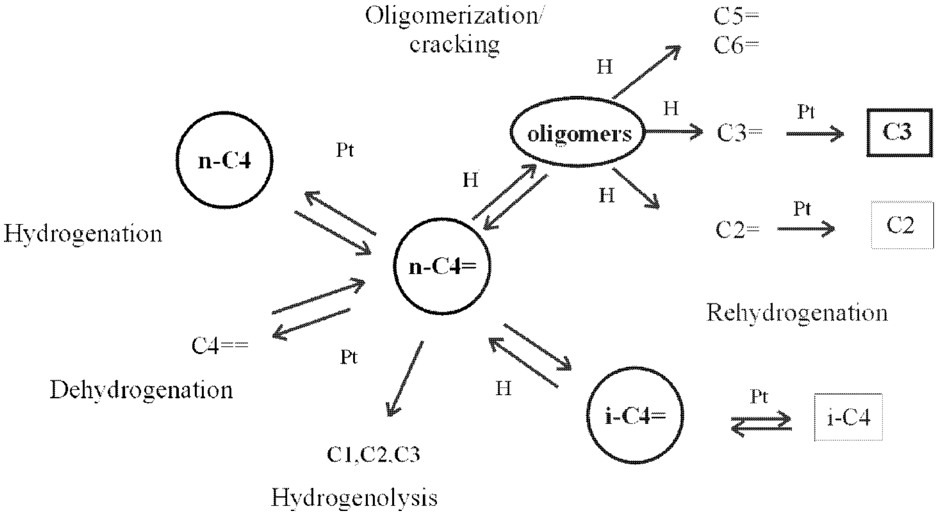

Figure 6. Scheme of the reaction network of the conversion of 1-butene over Pt-ZSM5.

place: (i) isomerization to isobutene (the desired reaction), (ii) oligomerization/cracking of butenes leading to the formation of propene and pentene, (iii) hydrogenation of 1-butene to n-butane as well as dehydrogenation to butadiene, (iv) hydrogenolysis. Ethane and propane are not mainly formed by hydrogenolysis, but via the oligomerization/cracking route. Propane, propene and pentene are the major by-products at high conversions. Thus, even in the presence of Pt and hydrogen, the acid sites are the main source of by-product formation. Note that these conclusions are in line with the results of dehydroisomerization of n-butane to isobutene [1].

The formation of butadiene (by dehydrogenation of 1-butene on the metal) leads to an enhanced rate of oligomer formation, and as a consequence also to an enhanced rate of propene formation, which is the cracking product of the oligomers. In the oligomerization process also coke deposits are formed which lead to a deactivation of the metal, but not of the acid sites. The isomerization activity is not significantly affected.

With respect to catalyst design the results confirm that the high cracking activity of ZSM5 is the bottleneck for the application of ZSM5 in dehydrogenation reactions. Synergetic effects between metal and acid sites in the by-product formation exist only indirectly, via hydrogenation of cracking products and enhanced oligomer formation from butadiene.

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