

Thermodynamic and Kinetic Reaction Regimes in the Isomerization of 1-Pentene over ZSM-5 Catalysts

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Two interesting observations have been made during isomerization of 1-pentene over H-ZSM-5 catalyst. (a) It is possible to switch between two thermodynamically controlled regimes by changing the reaction temperature. At low temperature, only double bond isomerization is occurring whereas the total isomerization equilibrium involving both *n*- and isopentenes is attained at high temperature. The temperature range of the kinetically controlled regime between these two equilibrium states is narrow. The transition is accompanied by a sharp increase in the 1-pentene conversion from 90% to almost 100%. The skeletal isomerization reactions are sufficiently fast to maintain an equilibrium distribution although pentenes are continuously withdrawn for the formation of dimerization and cracking products. Changing the space velocity or the feed partial pressure did not result in a stretching or squeezing but rather in a temperature shift of the kinetic regime. (b) Increasing 1-pentene partial pressures favor skeletal isomerization over dimerization and cracking reactions. This result, unexpected at first sight, suggests that reactions yielding isopentenes exhibit a higher reaction order in *n*-pentenes than the competing reactions. We have also investigated the dehydroisomerization of *n*-pentane over a single fixed bed of bifunctional Pt/H-ZSM-5 and over stacked beds of Pt/ γ -Al₂O₃ and H-ZSM-5. The results confirm that very low partial pressures of *n*-pentenes, here generated *in situ*, have a negative effect on the yields of isopentenes. © 1999 Academic Press

Key Words: isomerization; dehydroisomerization; pentene; isopentene; TAME; MFI.

INTRODUCTION

At the beginning of this decade, triggered by the growing demand for MTBE (methyl tertiary butyl ether), several companies developed novel catalysts and processes for the manufacturing of isobutene by means of skeletal isomerization of *n*-butenes. Among the catalysts involved in these novel processes, high-silica ferrierite (1, 2) or related materials based on FER structure type (3), zeolites of structure type TON (4, 5, 10), and SAPO- or MeAPO-based mate-

rials of structure type AEL (6–10) showed the best performance.

In most of the patents mentioned above, the claims are stretched such that the skeletal isomerization of higher olefins is also covered although the accompanying examples only refer to the conversion of *n*-butenes. Among the higher olefins, *n*-pentenes are representing the most interesting feedstock. Isopentenes are used to manufacture the octane booster TAME (tertiary amyl methyl ether) which exhibits a much better biodegradability than MTBE. However, the availability of pentenes as a feedstock is much lower than in the case of *n*-butenes. Therefore, industrial research and development has been focused on the isomerization of *n*-butenes rather than on *n*-pentenes.

Among the six isomers of pentene, which are the linear pentenes 1-pentene (1P), *cis*-2-pentene and *trans*-2-pentene (*c*- and *t*-2P), and the isopentenes 2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B), and 3-methyl-1-butene (3M1B), only species with a tertiary double bond (2M1B and 2M2B) are selectively etherified with methanol to yield TAME. The other isomers are not reactive. As shown in Fig. 1, the formation of the two desired isopentenes is thermodynamically favored over a broad temperature regime, and their equilibrium mole fraction increases with decreasing temperature. The thermodynamic calculations are based on data in (11). Here, we report on our investigation of the isomerization of 1-pentene over H-ZSM-5 as a catalyst, which was aimed at establishing the effects of temperature, 1-pentene partial pressure, and space velocity on the yield of isopentenes. We will also report on our attempts to process *n*-pentane in a combination of dehydrogenation and isomerization both over stacked beds of Pt/ γ -Al₂O₃ and H-ZSM-5 and over a single bed of bifunctional Pt/H-ZSM-5.

METHODS

Catalyst Preparation

Zeolite H-ZSM-5 provided by Degussa AG was used as a base material. Pt/H-ZSM-5 was prepared by ion exchange of H-ZSM-5 with an aqueous solution (0.01 mol/liter) of

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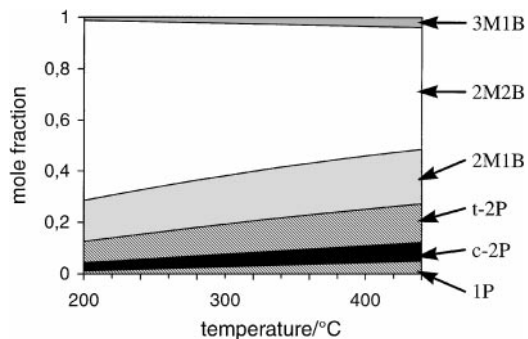


FIG. 1. Calculated thermodynamic equilibrium distribution of pentenes at different temperatures.

[Pt(NH₃)₄]Cl₂. The suspension containing 10 g of zeolite in 100 ml solution was stirred for 1 h at 50°C, filtered, washed with distilled water, and dried at 120°C overnight. Shallow bed (1–2 mm) calcination of the product was carried out in a ventilated oven for 0.5 h at 300°C (heating rate of 1°C/min). Reduction of both the platinum-containing zeolite and Pt/γ-Al₂O₃ was performed *in situ* after drying in a N₂ flow at 250°C and cooling down to room temperature again. Then, a H₂ flow of 25 ml/min was adjusted, and the temperature was raised to 400°C at a rate of 1.5°C/min. After 2 h, the sample was cooled down at reaction temperature. In all conversion experiments, catalyst particles of 315–500 μm size were used which were obtained by pressing, crushing, and sieving of the powder samples.

Characterization

The samples under study exhibited the X-ray diffraction pattern typical of a highly crystalline material of MFI structure type. Scanning electron micrographs revealed that the zeolite consisted of single crystals of 3–10 μm diameter. Amorphous material could not be detected. Elemental analyses were carried out at an external commercial laboratory. The Si/Al ratio was found to be 59 in accordance with the information given by Degussa AG, and the Al/Na ratio was 140. The platinum content of Pt/H-ZSM-5 was 0.5% (m/m).

The amount of coke on spent catalysts (after 10 h on stream) was determined after stripping in the reactor in a flow of nitrogen at 300°C in order to remove volatile deposits. Thermal analyses of the stripped catalysts were performed on a DTA/TGA analyzer. The samples were heated at a rate of 2°C/min up to a temperature of 800°C in a flow of air.

Catalytic Measurements

All experiments were carried out in an integral fixed bed plug flow reactor made of quartz operating in downflow mode. The reactor had an internal diameter of 15 mm and

was equipped with a central thermowell with an outer diameter of 2 mm. Generally, the fixed bed (8 cm length) consisted of 4 g of catalyst particles diluted with an equal volume of inert material (SiC, 200 μm). For the combined dehydrogenation and isomerization, either 4 g of Pt/H-ZSM-5 were loaded in a single bed or 1 g of Pt/γ-Al₂O₃ and 4 g of H-ZSM-5 were loaded in stacked beds with the Pt-catalyst upflow to the zeolite. Ongoing checks of the axial temperature profile in the bed during reaction ensured that the maximum gradient never exceeded 2°C. 1-Pentene (Merck, 95%, rest: isopentane) or *n*-pentane (Fluka, 99%) was used as a feedstock for the skeletal isomerization or the dehydroisomerization studies, respectively. The composition of the feed gas was adjusted in a saturator using nitrogen as carrier gas. All pipes of the unit were taped and heated at 200°C in order to prevent condensation. Off-gas compositions were determined by means of online GLC (Hewlett Packard GC 6890) equipped with a capillary column (Chrompack 7515, plot-fused silica, Al₂O₃/KCl coating, 50 m × 0.32 mm i.d.) and a flame ionization detector. Helium was used as a carrier gas. By-passing of the reactor enabled analysis of the feed gas composition. Blank runs with a fixed bed of SiC ensured that both reactor and diluent exhibited no catalytic activity.

Prior to every measurement the fixed bed was dried *in situ* in a flow of nitrogen at 250°C for 20 min. The regeneration of selected samples was performed in a gas stream of nitrogen and 5% (v/v) oxygen passing through the catalyst bed at a temperature of 500°C for 4 h.

Definition of Operational Parameters

- Fraction of carbon in species *i*

$$y_i = \frac{\dot{n}_i \cdot \varepsilon_i}{\dot{n}_{1\text{-pentene},0} \cdot \varepsilon_{1\text{-pentene}}}$$

- Molar yield of the pentene species *j*

$$Y_j = \frac{\dot{n}_j}{\dot{n}_{1\text{-pentene},0}} = y_j$$

- Conversion of 1-pentene

$$X = 1 - y_{1\text{-pentene}}$$

- Molar yield ratio of the iso-pentenes to all pentene isomers in the off-gas

$$\tilde{Y}_{\text{iso/total}} = \frac{Y_{\text{isopentene}}}{Y_{\text{isopentene}} + Y_{n\text{-pentene}}} = \frac{\sum \dot{n}_{\text{isopentene}}}{\sum \dot{n}_{n\text{-pentene}} + \sum \dot{n}_{\text{isopentene}}},$$

with \dot{n}_i = molar flow of species *i* [mol/s], ε_i = carbon number of species *i*, and subscript ₀ indicates “at reactor inlet.”

RESULTS AND DISCUSSION

Catalyst Coking and Regeneration

In the case of *n*-butene isomerization, H-ZSM-5 as well as many other catalysts shows a pronounced decrease in conversion after start of run which is accompanied by an increase in isobutene selectivity (2). In contrast, the conversion level in the isomerization of 1-pentene remains constant as illustrated in Fig. 2 for one representative set of reaction conditions. Breakthrough experiments have revealed that the test unit used operates at steady state after about 20 min. However, the product distribution—at constant conversion—still changes significantly within the first 1–2 h on stream during which the selectivities of light C₂–C₄ and heavy C₆₊ by-products decrease in favor of those of branched pentenes.

After 10 h on stream, the percentage of coke on the samples was found to be typically about 7% (m/m). This amount appears to be high but it represents only a small percentage of the pentene feed supplied (e.g., less than 0.5% m/m at weight hourly space velocity WHSV = 2 kg/(kg · h) and could, therefore, not be detected in the mass balance of the unit. The accuracy of the mass balance in all experiments reported amounts to ±2%.

Our catalysts could be repeatedly regenerated without any significant change in performance.

Only those data acquired in the period between 2 and 6 h on stream were evaluated in order to assess the effects of temperature, residence time, and pentene partial pressure as described below. In this time range, the product distributions were almost unaffected by catalyst aging. This was also confirmed by back-check experiments at initial reaction conditions, which were carried out at the end of the data acquisition period.

Effect of the Reaction Temperature

The results of a set of experiments carried out at varying temperatures and fixed space velocity and partial pressure

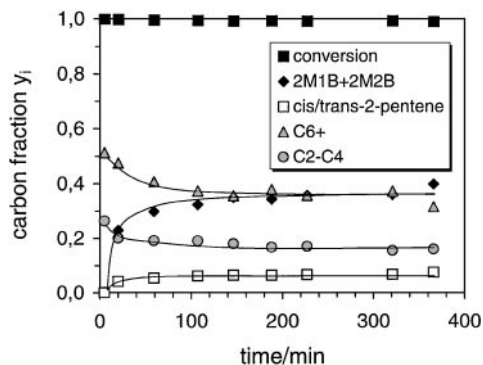


FIG. 2. Catalytic performance of H-ZSM-5 in the conversion of 1-pentene versus run time. $T = 290^\circ\text{C}$, $\text{WHSV} = 2 \text{ kg}/(\text{kg} \cdot \text{h})$, and $p_{1\text{-pentene},0} = 0.5 \text{ bar}$.

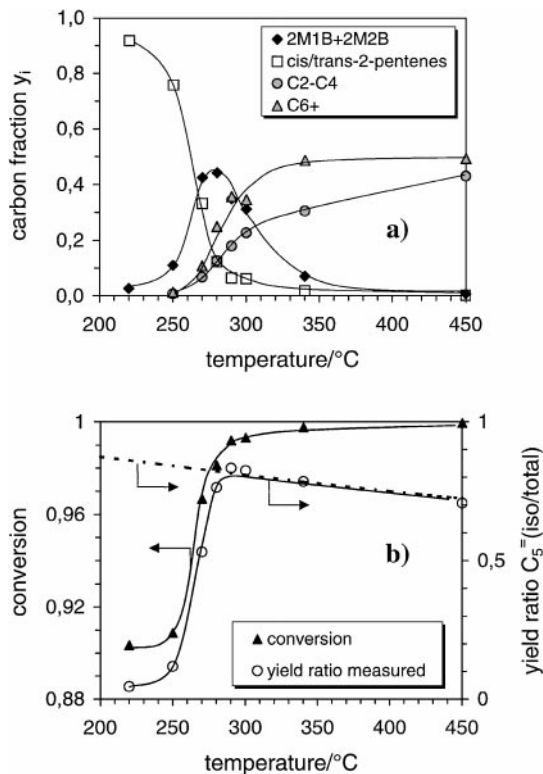


FIG. 3. Effect of reaction temperature on the isomerization of 1-pentene over H-ZSM-5 at $\text{WHSV} = 2 \text{ kg}/(\text{kg} \cdot \text{h})$ and $p_{1\text{-pentene},0} = 0.5 \text{ bar}$. (a) Carbon fractions y_i of the products. (b) Conversion of 1-pentene and molar yield ratio $\tilde{Y}_{\text{iso}/\text{total}}$ of all branched pentenes. The dotted line indicates the calculated molar yield ratio at thermodynamic equilibrium.

are shown in Figs. 3a and 3b. At temperatures between 220 and 250°C , the conversion of 1-pentene amounts to 90%. Double bond migration is the predominant reaction occurring, and only traces of other products except for *n*-pentenes are detected. A close inspection of the data as shown in Table 1 reveals that a “partial” thermodynamic equilibrium is attained; i.e., the three *n*-pentenes are present in an equilibrium distribution.

Raising the temperatures above 250°C results in a sharp increase in the conversion to 99% (at 290°C) with a concomitant shift in the product distribution. The yield of linear pentenes sharply decreases in favor of branched pentenes. At 280°C , the maximum overall yield of 2M1B and 2M2B

TABLE 1

Calculated and Measured ($\text{WHSV} = 2 \text{ kg}/(\text{kg} \cdot \text{h})$; $p_{1\text{-pentene},0} = 0.5 \text{ bar}$) Distribution of *n*-Pentenes at 250°C Normalized to a Yield of 1-Pentene (Value = 1.00)

Species	Equilibrium	Experiment
1-Pentene	1.00	1.00
<i>cis</i> -2-Pentene	2.47	2.50
<i>trans</i> -2-Pentene	5.84	5.80

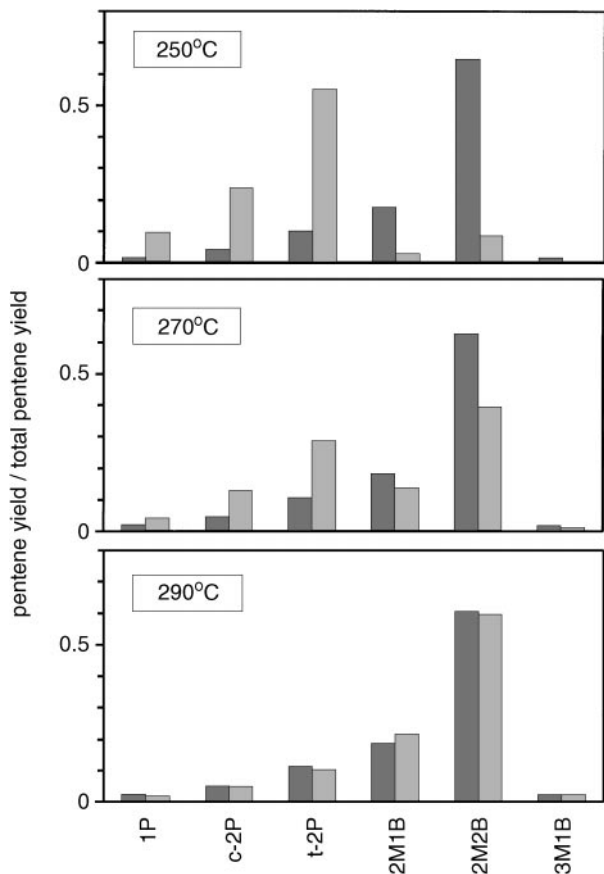


FIG. 4. Relative yield of pentene species at different temperatures. The dark bars represent calculated yield ratios at thermodynamic equilibrium, and the light bars indicate yields measured at $WHSV = 2 \text{ kg}/(\text{kg} \cdot \text{h})$ and $p_{1\text{-pentene},0} = 0.5 \text{ bar}$ (1P, 1-pentene; c-2P, *cis*-2-pentene; t-2P, *trans*-2-pentene; 2M1B, 2-methyl-1-butene; 2M2B, 2-methyl-2-butene; 3M1B, 3-methyl-1-butene).

of 44% is obtained which is considerably less than the equilibrium yield at this temperature. However, the plot of the molar yield ratio $\tilde{Y}_{\text{iso}/\text{total}}$ in Fig. 3b indicates that the reaction is nevertheless in thermodynamic equilibrium, now involving both *n*-pentenes and isopentenes. This is shown more clearly in Fig. 4, where the measured pentene distributions and calculated equilibrium distributions have been compared. At temperatures above 290°C , the catalyst produces an equilibrium “pentene pool” from which, however, pentenes are continuously withdrawn to form by-products in dimerization and cracking reactions. These reactions consume more of the pentenes at increasing reaction temperature. Above 400°C , the yields of pentene species are negligible (Fig. 3a); however, the molar ratios still indicating an equilibrium distribution. This result is interesting because H-ZSM-5 shows a different behavior in butene isomerization: equilibrium isomer distributions could not be realized with this catalyst. In the present case, the yields of both the light and the heavy by-products increase with increasing temperature. Also, their composition is changing. At lower

temperatures, the light fraction ($\text{C}_2\text{--C}_4$) has a more olefinic nature (propene, butenes, ethene) than at higher temperatures. The fraction (C_{6+}) could not be completely separated but a shift from heavier species to heptenes and hexenes at increasing temperatures was observable.

The fact that dimerization and cracking products are only detected when the skeletal isomerization takes place, i.e., above 250°C , seems to suggest that by-products are formed from isopentenes while the skeletal isomerization is a monomolecular, primary reaction. However, we are extremely cautious about a mechanistic interpretation because in this case the product distribution was changed with temperature rather than with residence time. Depending on the activation energies of the numerous reactions involved, a change in temperature may cause a shift from one prevailing reaction path to another.

In summary, three temperature regimes can be distinguished:

(1) Below 250°C , only double bond isomerization is observed, and the linear pentenes are in a “partial” thermodynamic equilibrium.

(2) Above about 250°C , the conversion of 1-pentene sharply increases from 90 to 99%. Branched pentene isomers together with dimerization and cracking products are released. The skeletal isomerization is kinetically controlled between 250 and 280°C , and the maximum yield of the desired isopentenes is obtained at 280°C .

(3) At 280°C and higher temperatures, the skeletal isomerization is no longer kinetically controlled. All pentene isomers form an “equilibrium pentene pool.” The total yield of pentenes decreases with increasing temperature since the pentene pool is tapped in favor of light and heavy by-products.

Effect of the Residence Time

At a fixed partial pressure of 1-pentene of 0.5 bar, the space velocity has been varied between $0.5 \text{ kg}/(\text{kg} \cdot \text{h})$ and $2 \text{ kg}/(\text{kg} \cdot \text{h})$. The maximum yield of 2M1B and 2M2B seems to increase slightly with decreasing space velocity, the overall effect, however, not being very pronounced (Fig. 5a). In contrast, the effect of space velocity on the peak temperature is significant. Higher space velocities tend to shift the transient regime between the two equilibrium states and the position of maximum isopentene yield to higher temperatures (Figs. 5a and 5b). Likewise, the S-shaped curve of the 1-pentene conversion (versus temperature) is shifted without a change in slope.

It is important to note that this narrow (in terms of temperature) kinetic regime is not stretched or squeezed but rather shifted. The same trend is observed at higher space velocities up to $20 \text{ kg}/(\text{kg} \cdot \text{h})$. These results are not depicted because the unit could not be run at steady state under these conditions.

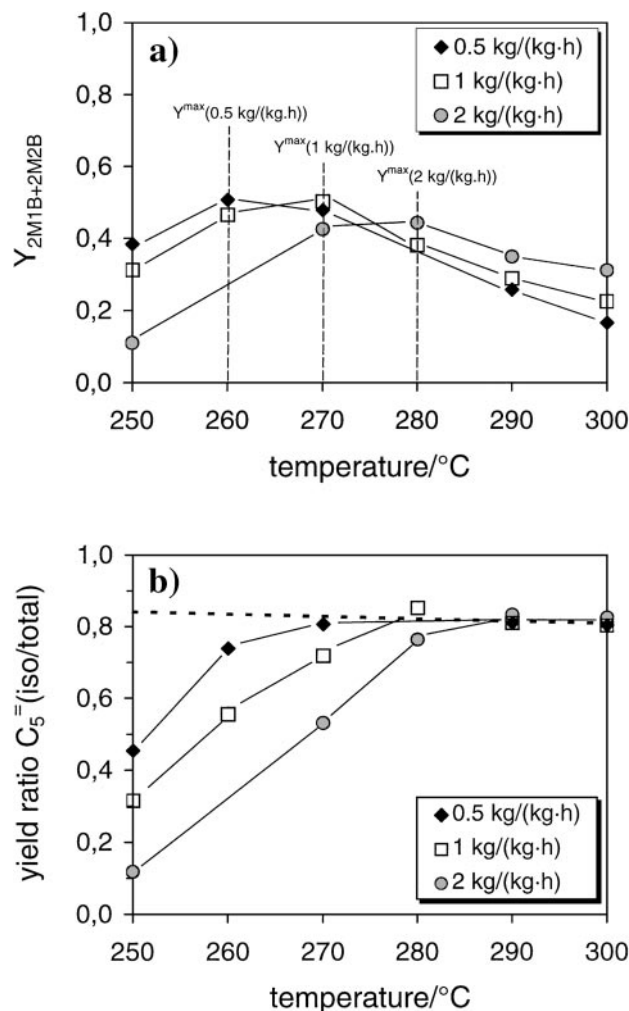


FIG. 5. Effect of the space velocity on the isomerization of 1-pentene over H-ZSM-5 at different temperatures and $p_{1\text{-pentene},0} = 0.5$ bar. (a) Yield of 2-methyl-1-butene and 2-methyl-2-butene. (b) Molar yield ratio $\tilde{Y}_{\text{iso}/\text{total}}$ of all branched pentenes. The dotted line indicates the calculated molar yield ratio at thermodynamic equilibrium.

Effect of the 1-Pentene Partial Pressure

Thermodynamic considerations would suggest that high olefin partial pressures could favor undesired dimerization reactions, i.e., the formation of heavy products, over isomerization reactions. Our results, however, obtained at 1-pentene partial pressures of 0.3, 0.5, and 0.8 bar indicate the opposite trend. The experimental data depicted in Fig. 6a show that the formation of heavy C_{6+} by-products increases with decreasing $p_{1\text{-pentene},0}$. The same holds for the light fraction ($C_2\text{--}C_4$) as shown in Fig. 6b, but the yield is always lower than in the case of heavy products.

In Fig. 7, the yields of the two desired isopentenes are shown for the same set of experiments. The yield maxima shift from 36% at $p_{1\text{-pentene},0} = 0.3$ bar to 56% at 0.8 bar. Again, we could observe three reaction regimes, i.e., a “par-

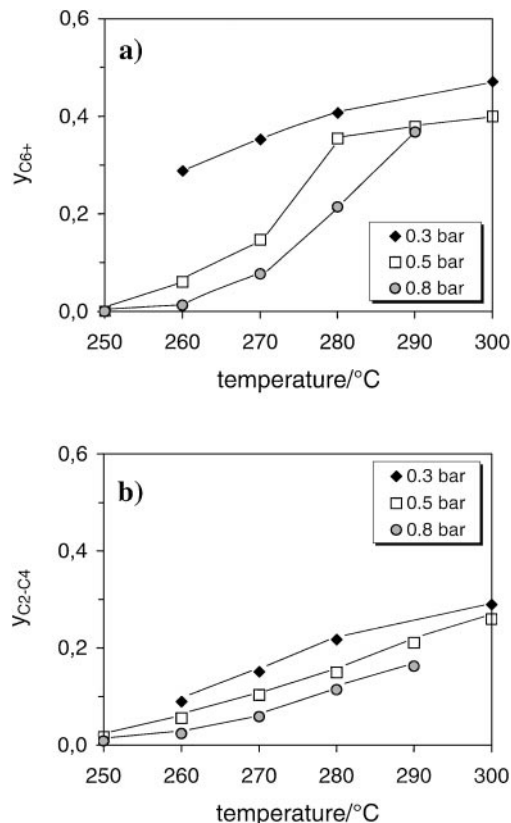


FIG. 6. Effect of the 1-pentene partial pressure on the isomerization of 1-pentene over H-ZSM-5 at different temperatures and WHSV = 1 kg/(kg·h). Carbon fractions of (a) heavy C_{6+} products and (b) light $C_2\text{--}C_4$ products.

“total” equilibrium between n -pentenes at low temperature, a kinetically controlled transition regime and a regime of “total” equilibrium among all pentenes. The locus of maximum isopentene yield in Fig. 7 indicates the temperature above which all pentenes are present in a perfect equilibrium distribution.

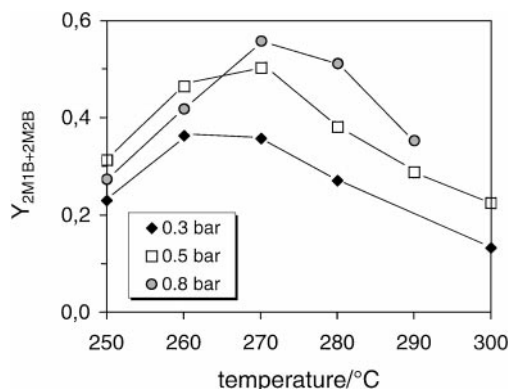


FIG. 7. Effect of the 1-pentene partial pressure on the yield of 2-methyl-1-butene and 2-methyl-2-butene at different temperatures and WHSV = 1 kg/(kg·h).

In view of the ongoing discussions about butene isomerization mechanisms, it seems necessary to emphasize that the beneficial effect of higher partial pressure on the isomerization of *n*-pentenes cannot be explained by simple mechanistic considerations combined with the application of Le Châtelier's principle. The number of molecular species does not change in isomerization reactions, irrespective of the reaction pathway involved. If such a pathway would, for instance, consist of dimerization and subsequent cracking, the first step would be thermodynamically favored at higher pressure, but the second would be disfavored to the same extent. While pressure has no effect on the equilibrium yields in isomerization reactions, it can, of course, affect the rates of isomerization reactions in relation to competing reactions. It is reasonable to assume that the rate laws of those reactions yielding isopentenes exhibit a higher reaction order in 1-pentene than those reactions yielding by-products. Unfortunately, the assessment of kinetic parameters was not possible with our equipment because the operational window between the regimes of partial and total isomerization equilibria is narrow. Nonstationary measurements involving rapid product analyses will be required to elucidate the kinetics of the reaction network.

Dehydroisomerization of *n*-Pentane

The effect of much lower *n*-pentene partial pressure has been further investigated in a combination of dehydrogenation and isomerization of *n*-pentane. Two process variants have been evaluated, i.e., with a bifunctional catalyst and with stacked beds of dehydrogenation and acid function. The experiments were carried out at 300 and 350°C, at a pentane partial pressure of 0.8 bar, and with a total gas flow of 93 ml/min (NTP). Under these reaction conditions, thermodynamic calculations show that the maximum partial pressure of *n*-pentene produced *in situ* would amount to approximately 0.01 (300°C) and 0.04 bar (350°C), respectively, if the dehydrogenation would attain the equilibrium state.

The yields of 2-methyl-1-butene and 2-methyl-2-butene obtained at these low olefin partial pressures are depicted in Fig. 8. Although produced in very low amounts, all pentene isomers were, again, found to be present in an equilibrium distribution. For comparison, we have plotted the yields of the desired isopentenes obtained with 1-pentene feed over H-ZSM-5 at higher partial pressures in the same graph. The dehydroisomerization experiments confirm the trend discussed in the previous section, i.e., that a low *n*-pentene partial pressure favors the formation of by-products at cost of the isomerization products.

In the case of the bifunctional Pt/H-ZSM-5 catalyst, high *n*-pentane conversions of 66% (at 300°C) and of almost 100% (at 350°C) were measured. The major products were C₃ and C₄ hydrocarbons. Only traces were found of C₂ and C₁ (and C₆₊) species, indicating that dimers rather than monomeric pentenes are rapidly cracked. Similar product

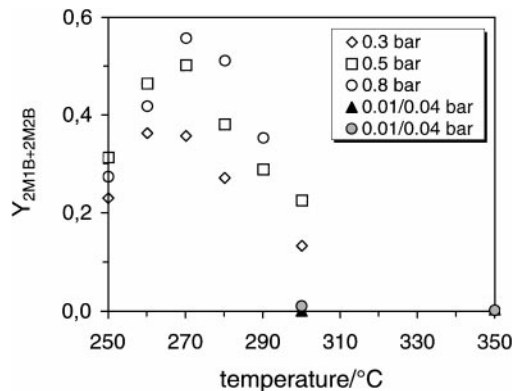


FIG. 8. Yield of 2-methyl-1-butene and 2-methyl-2-butene obtained in the dehydroisomerization of pentane over a single bed of Pt/H-ZSM-5 (▲) and over stacked beds of Pt/ γ -Al₂O₃ and H-ZSM-5 (●). The yields are less than 2%. For comparison, the data from Fig. 7 obtained with H-ZSM-5 and different partial pressures of 1-pentene are also depicted.

spectra were obtained using the stacked beds of Pt/ γ -Al₂O₃ and H-ZSM-5. In this arrangement, however, *n*-pentane could only be converted to 6.4 and 15.6%, respectively. Nevertheless, these conversions are higher than the equilibrium dehydrogenation conversions at the respective temperatures. The relatively high *n*-pentane conversion level and the product spectrum, i.e., the formation of C₃ and C₄ (C₄ iso: *n* ≅ 1:1) cracking products and the absence of C₂/C₁ species, are suggesting that part of the pentane is alkylated by pentene and subsequently cracked.

Our experiments clearly demonstrate that a combination of dehydrogenation and isomerization over ZSM-5 at one reaction temperature is no feasible option. In the previous section and in this section we have shown that the maximum yield of isopentenes increases with increasing pentene partial pressure. On the other hand, high local partial pressures of *n*-pentenes can only be realized at high dehydrogenation temperatures which, in turn, promote the formation of cracking products.

CONCLUSIONS

The present study was aimed at the quantitative description of the effect of process parameters on the yield of branched pentenes and, if possible, at an assessment of the kinetic parameters in the stationary isomerization of 1-pentene over a fixed bed of H-ZSM-5. We have found that increasing partial pressure of *n*-pentenes favors skeletal isomerization over competing dimerization and cracking reactions. This pressure effect, which must be kinetic in nature, deserves further investigation. However, the isomerization is kinetically controlled only in a narrow temperature regime which could not be stretched at higher space velocities. A kinetic analysis will require dedicated equipment, for instance, for nonstationary measurements.

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