

Study of side products formation during n-butenes isomerization on modified zeolite catalysts

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Abstract

n-butenes conversion on zeolite catalysts lead to various reaction products. The main product is isobutene (skeletal isomerization), but very precious are cis-trans butene (position and geometric isomerization) and n-butane (hydrogenation). Besides isomerization reactions, oligomerization-cracking reactions are an important step. Side reactions involve a significant butanes amount and it is very important to identify them and understand the reaction mechanism in order to optimize catalysts and in the same time the process. Theoretical, there are many ways for side products formation. Their impact over n-butenes isomerization will be discussed in the present paper.

Keywords: *n*-Butenes; isomerization; oligomerization; cracking; catalysts.

Introduction

In the last decade, the demand for isobutene overtook the rate of production because of its increasing importance as raw material for the production of MTBE.

Because of the limited capacity of the traditional cracking processes, it is very important to develop new catalyst systems for skeletal isomerization of n-butenes to isobutene.

10-membered ring catalysts have been proven to be efficient catalysts for this reaction. Especially, ferrierite has been described as a very selective catalyst for skeletal isomerization. To explain the high selectivity, an intramolecular isomerization, the so-called monomolecular mechanism, and a pseudomolecular mechanism with carbenium ions as active sites have been proposed [1, 2, 3, 4, 5, 6, 7, 8, 9 and 14].

On HZSM-5, dimerization [3, 5, 7, 16, 17 and 18] or even trimerization [8 and 20] of n-butene takes place in the cavities at the intersections of the channels. This oligomerization is followed by non-selective cracking into short-chained olefins, among them isobutene. Because of its feature, this mechanism is called bimolecular or oligomerization–cracking mechanism.

The aim of the present paper is to elucidate the reaction behavior of olefins concerning oligomerization over modified HZSM-5 and over Pt/ferrierite catalysts.

Experimental

HZSM-5 with a Si/Al ratio of 104 was modified with 1% Ti(OC₃H₇iso)₄ named as Ti-HZSM-5* (K₁), 1% P(C₄H₉)₃ named as Porg-HZSM-5* (K₂), 1% P-(H₃PO₄) named as Pac-HZSM-5* (K₃)

and Ferrierit impregnated with H_2PtCl_6 0,01M (25ml acid to 10g ferrierit) named as Pt/HFER (K_4) were selected for n-butenes isomerization.

The zeolitic material was calcinated for 4 h at 673 K. The obtained catalysts were characterized by XRD, TEM and specific surface, porosimetry and acidity has been determinate.

Catalytic experiments were performed at temperatures from 553 to 723 K in a continuous reactor (fig.1.) at atmospheric pressure. A FCC cut mixture having 47% 1-butene in nitrogen was introduces with a gaseous hourly space velocity of 5500 h^{-1} . Prior to the experiments the catalyst (0,1-0,4 g) was heated in situ for 1 hour to 673 K.

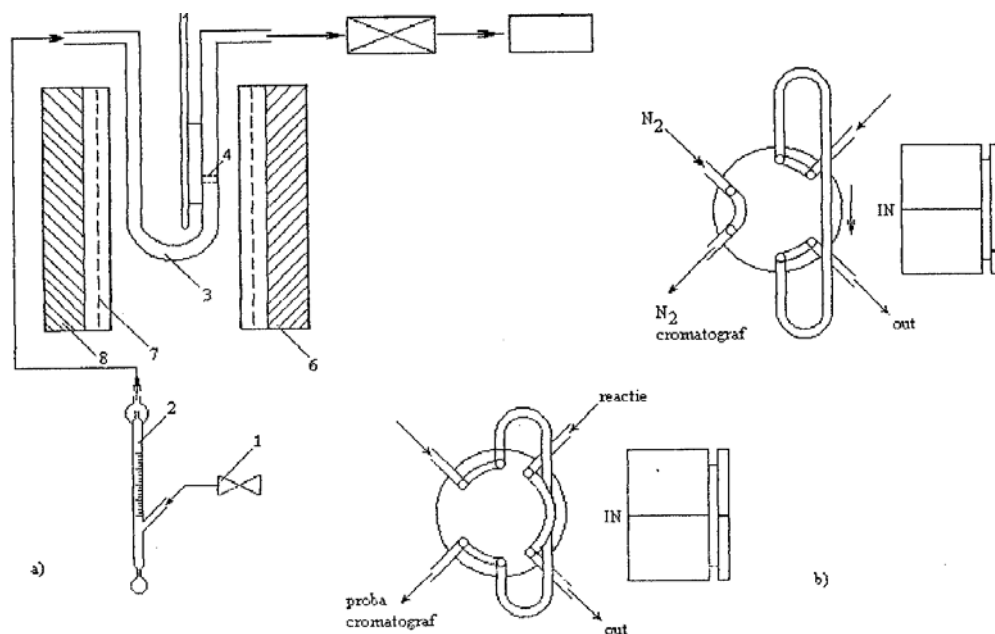


Fig. 1. a) 1 - valve; 2 - flow meter; 3 - reactor; 4 - catalyst; 5 - thermocouple; 6 - heater; 7 - electric resistance; 8 - shell

A Carlo Erba HRGC-5300 MEGA SERIES, FID detector and 13 m length column (8m with 25% β - β' -oxidipropionitril on Chromosorb P/NAW - 60-80 mesh and 5 m di-izobutil malonat) was used for products analysis.

For calculation purposes, it has been established the conventional indicators:

- Conversion is defined as the mass percentage of the linear butenes which are consumed
- Isomerization activity is defined as the mass percentage of the isobutene which is formed.
- Selectivity is defined as the mass percentage of the isobutene which is formed from linear butenes which are consumed.

Results and Discussions

Table 1 shows the light products (C_1 - C_3) distribution for 1-butene conversion on modified MFI (ZSM-5) type catalysts and on Pt/HFER catalyst for very short reaction time.

In all cases, the main products were C₃, C₃ (propane-propylene), C₄ (butane-izobutane) and C₄ cis-trans butene and isobutene. Heavier products were observed in the gaseous mixture only in traces. The total conversion of *n*-butenes was between 70 and 95%.

Table 1. Cracking light products concentrations on studied catalysts

Catalyst	T, °C	conv, %	C ₃ , %gr	C ₃ , %gr	Total
PT/HFER (K ₄)	350	71,32	0,13	1,05	1,18
	380	75,41	0,22	1,17	1,39
	400	76,29	0,78	1,09	1,88
	420	77,08	1,13	1,16	2,29
	440	71,87	2,06	1,35	3,41
	470	66,82	1,12	0,94	2,06
Ti-HZSM-5* (K ₁)	360	87,20	0,98	2,67	3,65
	380	94,00	4,78	4,40	9,18
	430	95,19	2,16	6,05	8,21
	450	96,11	6,76	6,33	13,09
Pac-HZSM-5* (K ₃)	350	85,21	0,48	1,92	2,40
	370	91,93	4,72	2,85	7,57
	390	95,47	5,85	3,23	9,08
	400	94,58	3,37	4,03	7,40
	430	90,73	2,15	3,88	6,03
	450	88,52	3,93	3,9	7,83
	480	84,47	3,38	3,64	7,02
Porg-HZSM-5* (K ₂)	380	81,86	1,87	3,79	5,66
	400	86,47	1,24	3,20	4,44
	450	88,24	3,09	5,04	8,13

To compare the fourth catalysts tested for *n*-butenes isomerization reactions, variation conversion with temperature have been plotted (fig.2.).

We can notice (fig.2.) that the lowest conversions are obtained on K₄ catalyst (77,08%) and the higher conversions on K₁ catalyst (96,81%) and K₃ catalyst (95,47%). Catalyst K₂ is placed between with a conversion of 88,62%. We can find out that for K₁ and K₂ conversion increases continuously with temperature increasing.

Different mechanisms for the isomerization of *n*-butenes to isobutene have been proposed in the literature, the monomolecular, the pseudomolecular and the oligomerization–cracking mechanism [22 and 23]. The monomolecular and the pseudomolecular mechanism are described as selective to isobutene. On the other side, the oligomerization–cracking mechanism is not selective to isobutene because it includes at least a dimerization to octenes, followed by cracking in not identical products (Eq. (2), (3)).

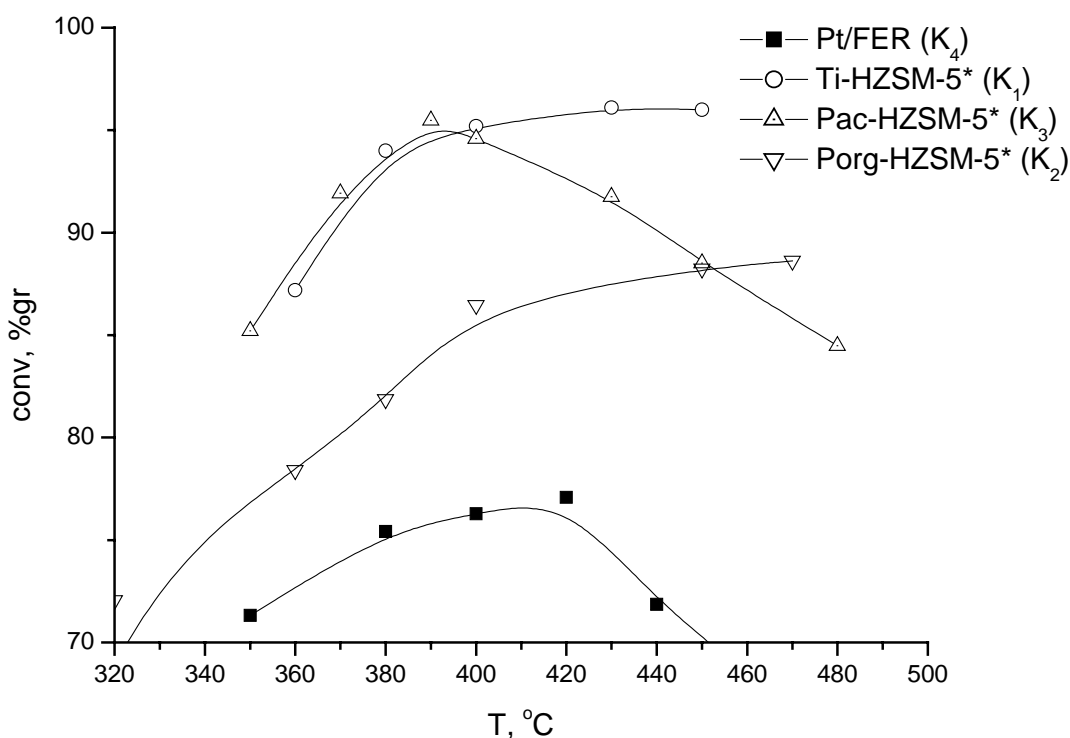
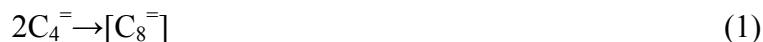


Fig.2. 1-butene conversion with temperature over Pt/FER (K₄), Ti-HZSM-5* (K₁), Pac-HZSM-5*(K₃) and Porg-HZSM-5* (K₂) (GHSV=5500h⁻¹; 47% 1-butene)

However, the increase of the isobutene production with increasing reaction temperature points to a partial contribution of a selective isomerization mechanism at higher temperatures, because the oligomerization of butenes is reduced at higher temperatures. This is in accordance to Rutenbeck et al. [13] who showed that for HZSM-5 with higher Si/Al ratios the mechanism depended on the reaction temperature.

The product distribution of the n-butene conversion from our experiments points to the dominance of the oligomerization-cracking mechanism. However, at all reaction temperatures, the concentrations of cracking products were not identical as would be expected for the bimolecular mechanism (Eq. (2)).



One reason for that unusual behavior could be the dimerization of propylene to hexene:



Other possible reactions are trimerizations:

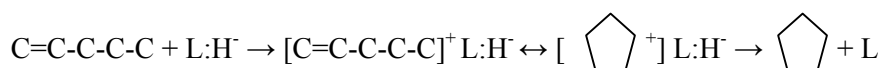


In this case, the sum of the concentrations of propylene and twice C_6^{\equiv} (includes two C_3^{\equiv} units) should be equal to the concentration of the pentenes. It can be concluded that around 673 K the reaction behavior is dominated by a dimerization-cracking mechanism according to reactions (1)–(3) accompanied by a slight dimerization of propylene to hexenes as shown by Eq. (4).

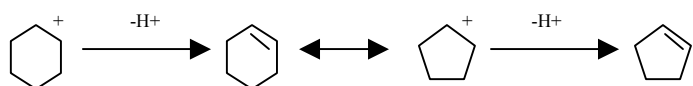
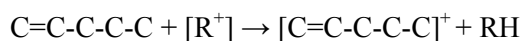
Indeed, in reaction products there are butane, propane, propylene and light hydrocarbons (methane, ethane and ethylene) that confirm the oligomerization-cracking step.

The program established for gas-chromatography did not emphasize pentenes and aromatics but they have to be present and an explanation could be that they reacted even in their adsorbed state on acid sites and further lead to polycyclic hydrocarbons, and finally to coke.

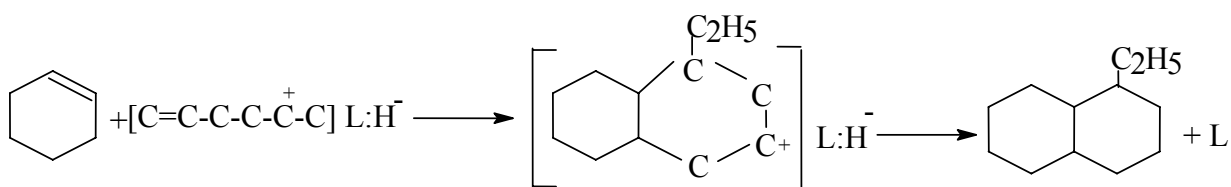
Thermodynamically was proved that olefins cycling in 5 or 6 carbon atoms cycles take place with high conversions on solid acids at 673-773K. On Lewis acid sites the possible mechanism is:

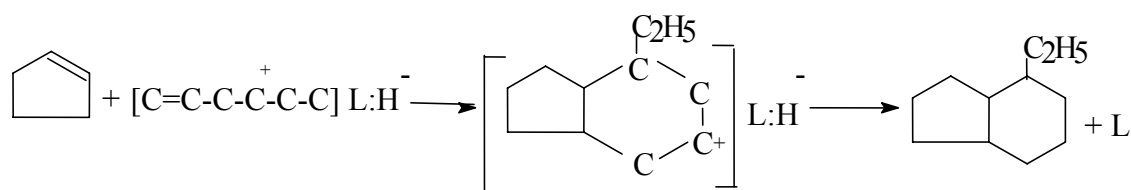


Cyclopentil and cyclohexil formation could also result from hydride ion transfer from a ion carbenium:



Cycloalkenes with 5 and 6 carbon atoms could easily isomerizes in between and interact with an adsorbed ion alkenyl forming hydrocarbons with two cycles.





Such reaction could carry on to condensed polycyclic hydrocarbons. 6 carbon atoms cycles dehydrogenation to aromatics occur with high conversions and finally lead to polycondensed aromatic hydrocarbons

Experimental data from table 1 show that C_3 concentrations increases with temperature increasing. For high conversions propane amount is much higher than propylene. For Pt/HFER (K_4) it could be explained by propylene hydrogenation on noble metal.

From kinetic and thermodynamic data we assume that on solid acid catalysts isobutane is formed by isobutene hydrogenation. Hydrogenations are promoted on hydrocarbons with reduce number of carbon atoms.

Cracking activity of Pt/HFER (K_4) catalyst, due to pores size and noble metal presence is low - from 0,13% C_3^- and 1,05% C_3 (propane-propylene) for 350°C, to 1,12% C_3^- and 0,94% C_3 for 470°C. This could be assigned to the perfect equilibrium between medium and strong acid sites for this catalyst (37%-37%).

On Ti-HZSM-5* (K_1) catalyst the reaction carry on different, and we can ascertain significant cracking. Thus, to 360°C it has been measured 0,68% C_3^- and 2,67% C_3 while for 450°C 6,76% C_3^- and 6,33% C_3 were found, total 13,09% cracking products, that represent an important percentage toward Pt/FER. These are in perfect agreement with acidity measurement that indicate for catalyst K_1 the highest percent of strong acid sites, so cracking reactions are favored.

HZSM-5* modified with phosphorus compounds (K_2 and K_3) presents a lower cracking activity that Ti-HZSM-5* (K_1) but higher that Pt/FER (K_4). These data are correlated with catalysts characterization. For K_2 strong acid sites percent is lightly higher that for K_3 (30% respectively 26%) and $C_3^-+C_3$ percent on these catalysts for 450°C are 8,13 respectively 7,83. Zeolite impregnation with phosphorus compounds modify the total density of acid sites, their strength and also affect the catalyst texture due to chemical interactions.

Between 380-400°C conversion is very high and from all the modified catalysts the lowest cracking activity presents Pt/FER (K_4) and Pac-HZSM-5* (K_3). It is possible that Ti-HZSM-5* (K_1) because the presence of Ti (one of the metals whose complexes combinations are catalysts used for olefins dimerization) promote oligomerizations and hydride ion transfer reactions. Modified MFI catalyst, due to its acidity and pores size and shape could promote the bimolecular mechanism of oligomerization-cracking. Phosphorus compounds impregnated on modified MFI catalyst reduces cracking activity so will reduce coke content. A smaller quantity of phosphorus makes inefficient the “anticoke” action. On the other side, too much phosphorus can block pores and can cover acid sites.

Dispersion of phosphorus species only on the external surface of crystallites is not enough for a better behavior in isomerization toward oligomerization-cracking. Modified MFI catalysts impregnation with powder, carry on with chemical interaction between modifying agent and acid sites of zeolite. Impregnation has no effects on unit cell of orthorhombic HZSM-5* zeolite.

These modifications effects are lower acidity, essential for a good selectivity (balance between isomerization and cracking) due to modifying agent coating especially on the external surface of crystallites.

It is possible that phosphorus compounds enter into pores and interact with Brønsted acid sites and thus P-OH became surface groups, replacing –OH groups (–OH groups with phosphorus are weaker and the zeolite total acidity is lower. Experimental results confirm these suppositions.

1-Butene isomerization on zeolite takes place on Brønsted acid sites and acid sites density determine isomerization activity. Oligomerization-cracking bimolecular mechanism is the main pathway for side products, followed by hydride ion transfer. Oligomers cracking leaden to propylene and propane (obtained by hydrogenation from propylene) – significant concentration – determined in reaction products at temperatures over 400°C at high conversions.

Catalytic tests results show that isobutene selectivity range on a medium level for studied catalysts in back-coupling conditions.

Conclusions

On modified zeolite catalysts cracking activity is higher than for zeolites.

The overall reaction behavior of n-butenes isomerization on modified zeolites catalysts is dominated by oligomerization–cracking steps. At the very beginning of the reaction, the formation of C₈ surface species should be the first step. These species decompose into propylene and pentenes. One part of the just formed and still adsorbed C₃ species dimerizes immediately to hexenes. In the further course of reaction, an oligomerization to C₁₂ surface species (trimerization) and following decomposition could occur. Furthermore, the tendency to oligomerization decreases with increasing temperature.

Pt/HFER (K₄) catalyst is a bifunctional catalyst and have structures and pores size different than MFI catalysts. Its cracking activity is reduced. Pt on ferrierit means that cracking products selectivity decreases due to the noble metal that promotes hydrogenation-dehydrogenation reactions. In this case, parts of unsaturated compounds hydrogenate (propane, butane, izobutane) and they are not allowing for subsequent oligomerization.

Concerning the reaction mechanism for n-butenes reactions on modified zeolite catalysts, we could appreciate that none of the presented mechanisms seems to be prevalent.

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Studiul formării produșilor secundari în reacțiile de izomerizare a n-butenelor pe catalizatori zeolitici modificați

Rezumat

În transformarea n-butenelor pe catalizatori zeolitici se obține o mare varietate de produși de reacție. Produsul principal este izobutena (izomerizare de catenă), dar importante sunt și obținerea cis-trans butenei (izomerizare de poziție și geometrică) și de asemenea obținerea n-butanului (hidrogenare). În afara reacțiilor de izomerizare, reacțiile de oligomerizare-cracare se desfășoară cu o pondere însemnată. Reacțiile secundare consumă o fracție semnificativă de butene și este imperios necesar să le identificăm, să înțelegem posibilul mecanism de reacție care să le explice, în scopul optimizării catalizatorilor și implicit a procesului. Teoretic sunt posibile mai multe căi de formare a produșilor secundari. Impactul lor asupra izomerizării n-butenelor face obiectul actualului studiu.