

Linear Butenes Isomerization on Mono and Poly-Components Solid Catalysts

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Abstract

n-butenes isomerization on solid acid catalysts carries on in order to promote test reactions for catalysts selection. Catalysts tested were oxides (zirconia, sulphated zirconia, niobia), mix oxides – supported on alumina (Ni-Mo/alumina, Mo-W/alumina) and zeolites (Ultrapet, Sulphated Ultrapet, HZSM-5* and modified HZSM-5*) as well as ion-exchange resin. The majority proved good activity in position and geometric isomerization. Only HZSM-5* showed a good activity for skeletal isomerization due to its crystalline structure and pores shape and size.

Key words: linear butenes, solid acid catalysts, isomerization, crystalline structure

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.

Isobutene is a reaction product in pyrolysis and catalytic cracking, but is much higher, because of international regulations concerning gas composition. So, isobutene can be obtained from *n*-butane isomerization followed by dehydrogenation, but direct *n*-butene isomerization is desired. A great catalysts variety (alumina or zeolites) have been studied and they proved good activity in *n*-butenes skeletal isomerization. Zeolitic catalyst is active at lower temperatures than catalysts with alumina [17].

10-membered ring zeolite catalysts have been proven to be efficient catalysts for this reaction. On H-ZSM-5, reactions of *n*-butene takes place in the cavities and oligomerization reactions take place 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 behavior of linear butenes concerning isomerization on solid acid catalysts (skeletal, geometric and position isomerization), conversions and reaction products distribution.

Experimental

Catalysts characteristics

- Ni-Mo/alumina and Mo-W/alumina – usually used for hydrofining process in petroleum processing.
- ZrO_2 of 99% purity, as well as H_2SO_4 95-97%, are Riedel de Haën AG, Seelze Hannover reactives.
- Ion-exchange resin B-23 from Technische Institut Clausthal, having a surface area of 38 m²/g, pores diameter 20 nm and porosity 0,24 mval/g.
- Niobia HY-340 ($Nb_2O_5 \cdot nH_2O$) from Companhia Brasileira de Metalurgia e Mineração.
- Zeolit Na-Y
- Catalyst Ultrazet produces by Institut Chemii Przemystlowej, Warszawa (1984), Si/Al de 195.
- HZSM-5* (Z_1) and Si-HZSM-5* (Z_2) prepared to INCERP S.A. Ploiești.

Experimental Program

0,3 to 1g catalyst were introduced in a quartz reactor U shape. Catalysts have been calcinated 1 h to 400°C. After activation temperature was adjust to chosen reaction temperature, according to experimental program.

Raw material (butane-butenes) admission carries on opening the valve from gas cylinder. Reaction temperatures studied were between 300-500°C

Reaction products and unreacted n-butenes were analyzed with gas-chromatograph Carlo Erba HRGC-5300 MEGA SERIES, FID detector and column length 13 m - 8m with stationary phase 25% β - β' -oxidipropionitril Chromosorb P/NAW (60-80 mesh) supported and 5 m with diizobutil malonat). Carrier was He 99,99% puriss. from Lynde Gas (320kPa) and hydrogen flow (for FID ionization flame) of 37,2 cm³/min.

It has been studies mainly isobutene formation during reaction, but also double-bond isomerization over selected catalysts. Experiments carried on at constant flow (100 cm³/min) and atmospheric pressure. Conversion, isomerization activity, selectivity and cis/trans have been calculated.

Raw Material

Standards for raw material and reaction products components has been established from a gaseous mixture of known components ($iC_4-1C_4^- - iC_4^- - 2C_4^-$) (table 1).

Raw material is an industrial C_4 cut rich in 1-butene, used for MTBE plant.

Isobutene could be formed by different reactions in the processes, so all indicators are conventional and related to 1-butene.

Table 1. Standard isobutan-butene fraction

Component	% gr	Retention time, s
Iso-butane	54,9334	16,05
Butane	1,3027	19,41
1-butena	19,0102	26,41
i-butene	23,4319	27,81
Trans-butene	0,4529	31,27
Cis-butene	0,1031	35,93

Table 2. Raw material composition

Component	% gr	Retention time, s
propane	1,2490	13,44
Iso-butane	9,3370	16,24
Butane	28,2381	19,41
1-butene	46,8142	26,41
Trans-butene	10,1903	31,27
Cis-butene	4,1713	35,84

Results and Discussions

Ni-Mo/alumina

On catalyst Ni-Mo/alumina at 345-430°C conversions were 50-60 % and showed activity for double-bond isomerization and geometric isomerization [9]. Small values of cis/trans show an acid catalyst but its acidity is weak. [2, 3, 4-8].

Mo-W/alumina

For Mo-W/alumina catalyst results were different. At 370°C and conversion 70,53 % a small percent of isobutene was obtain, isomerization activity was 5,71% and selectivity 8,62 %.

ZrO₂+H₂SO₄

Catalyst ZrO₂ was pretreated with H₂SO₄. At 350°C conversion increased to 36,88% and at 450°C conversion practically doubled. Skeletal isomerization had place, isomerization activity was 12,14% and selectivity 18,81% (figure 1). Over 450°C cracking increased and coke deposit led to lower values for conversion and selectivity, of 57,62% respectively 9,80%.

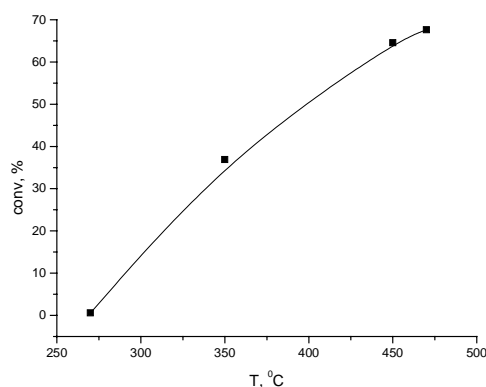


Fig.1. Variation of 1-butene conversion/temperature on ZrO₂+H₂SO₄

Ion-exchange resin

This catalyst proved no activity for olefin isomerization, although it was recommended to have strong acidity in temperature range 80-120°C. extremely low conversions don't recommend it to have isomerization activity.

Nb₂O₅

In literature, Nb₂O₅nH₂O is presented to have good double-bond isomerization activity [9].

Niobia (Nb₂O₅) proved activity over 300°C, conversion was 43.57% at 300°C.

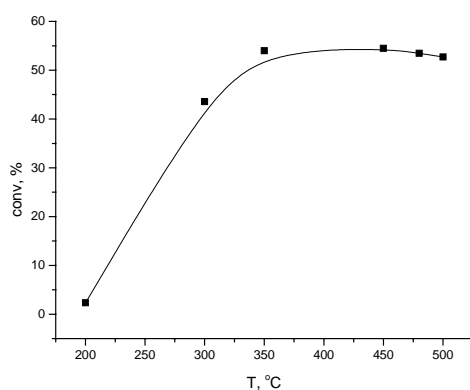


Fig.2. Variation of 1-butene conversion/temperature on Nb₂O₅

At 350°C conversion increased to 53,99 (figure 2) and maximum conversion value (54,50%) attended at 450°C. Over this temperature conversion decreased, probably due to catalyst deactivation because of coke deposits.

Zeolite Na-Y

Y zeolites Na forms are less active. Test reaction proved no activity, even in cracking, less than 470°C. At 470°C it showed activity, conversion was 54,56% and cis/trans 0,9.

ULTRAZET

This catalyst having Si/Al 195 has been tested to but conversions were very low (max. 26,49% at 400°C) and double-bond isomerization activity very low too.

HZSM-5* (Z₁)

HZSM-5* is a hybrid catalyst between H-ZSM-5 (85%) and bentonite (15%). Pure ZSM-5 is an extensively studied catalyst [11, 12, 13-15].

In temperature range 260-320°C experiments showed an increasing conversion (64,50%), with activity only for double-bond isomerization.

Over 340 °C showed skeletal isomerization activity. Conversion increased from 76,78% to 96,96% (340-450°C), and cis-trans isomerization decreased (cis/trans is 3,20 at 450°C).

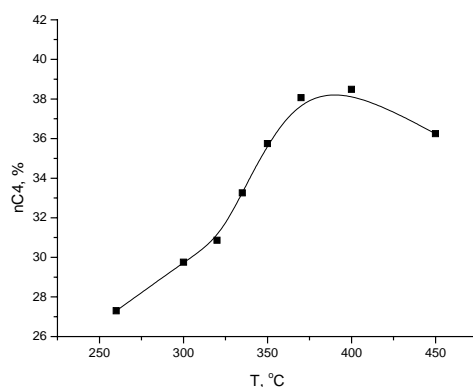


Fig.3. Variation of nC₄ concentration/ temperature on HZSM-5*

Significant amounts of isobutane and n-butane, as well as cracking products (12%wt), have been obtained. Isobutane and n-butane amounts increases with temperature variation, with a maximum at 370°C (figure 3). These products are the effect of hydrogen transfer reactions.

Over 370°C although n-butane decrease, isobutene increase (figure 4), due to different reaction mechanisms: n-butane is formed directly by n-butene hydrogenation (conversion increases and so n-butene is no longer available for direct hydrogenation) and isobutene could be formed by n-butene conversion to isobutene followed by hydrogenation (isobutene concentration increases with temperature).

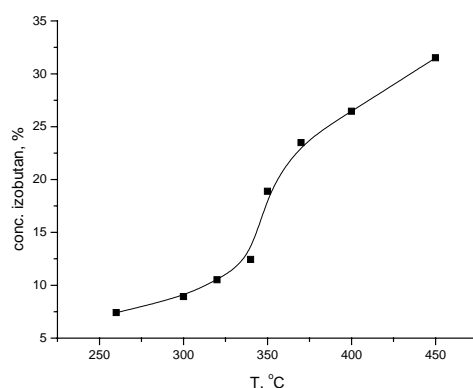


Fig.4. Variation of iC₄ concentration/ temperature on HZSM-5*

Selectivity increase confirms the possibility of pseudo monomolecular mechanism occurrence [17]. Activity of skeletal isomerization increases continuously on temperature range 340-400°C, and slightly decreases at 450°C.

Continuously conversion increasing to 96,96%gr at 450°C (figure 5) indicates that this catalyst is steel active and coke depositions doesn't affect it .

HZSM-5* appears to be a very active catalyst (high conversions).

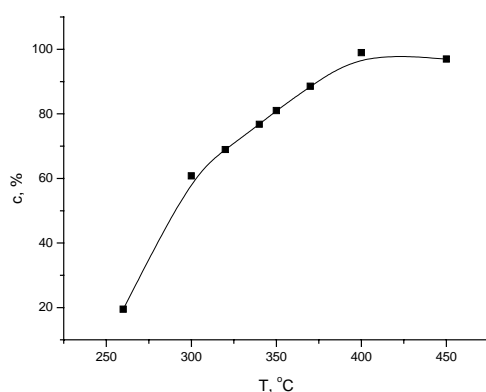


Fig.5. Variation of 1-butene conversion/temperature on HZSM-5*

HZSM-5*+1% SiO₂ (Z₂)

HZSM-5* was modified by adding 1% SiO₂ to Z₁. On temperature range 300-450°C catalyst show comparable results as Z₁.

Acidity determinations proved that Z₂ acidity is slightly reduced relative to Z₁, and acid sites distribution indicate an increase in medium acid sites strength on the decreasing of weak and strong acid sites. This is in correlation with catalytical tests that revealed higher selectivities for Z₂ relative to Z₁.

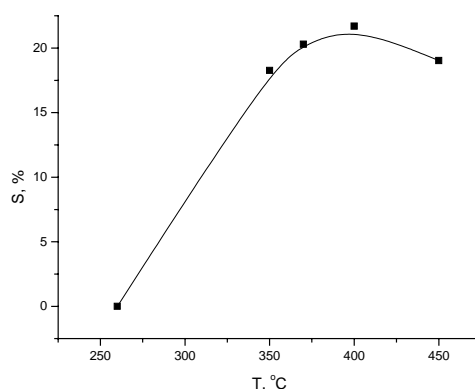


Fig.6. Variation iC₄= selectivity/temperature on HZSM-5* + 1% SiO₂ (Z₂)

Conclusions

Accepting Mo-W/Alumina and Z1, Z2 zeolites, all tested bulk catalysts promoted only double-bond and cis-trans isomerization. The above mentioned catalysts proved skeletal isomerization activity.

Conversions values for tested catalysts were from 20%gr (Clausthal) and 60-70%gr (Mo-W/alumina) to 97%gr HZSM-5*.

Selectivity and isomerization activity of HZSM-5* were about 20%gr. Conversions are very high and increases with temperature.

Significant amounts of n-butane and isobutene as well as propane-propylene amounts over 400°C seems to be a consequence of bi-molecular mechanism oligomerization-cracking.

Isobutene can be formed by monomolecular mechanism or bi-molecular from dimerization product octene scission that could be split up disproportionate in propene-pentene or n-butene-isobutene [12].

Extra frame aluminum that occupies cationic positions in MFI zeolites pores and channels, affects diffusion, with consequences on shape selectivity and coke precursors formation rate.

HZSM-5* is able to permit interconversion reactions of olefins and hydrogen transfer reactions in its cavities.

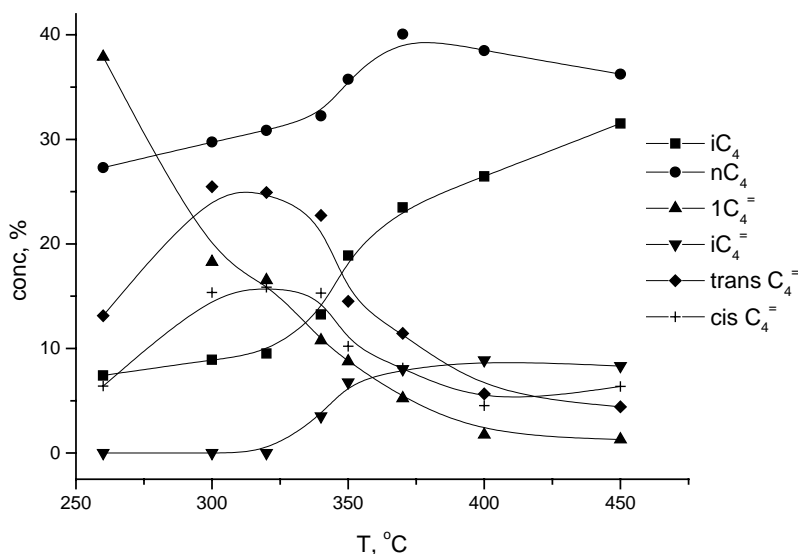


Fig.7. Concentration/temperature variation for main reaction products for 1-butene isomerization on HZSM-5*

From figure 7 we could observe at 260-350°C 1-butene concentration decreasing due to cis-trans butane increase (double-bond and cis/trans isomerization). Over 350°C isobutene, isobutane and n-butane amounts increase (skeletal isomerization and hydrogen transfer).

Optimal temperatures for C₄ cut quality improvement (isobutene and isobutane increasing) are in 350-380°C range.

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Izomerizarea butenelor liniare pe catalizatori solizi mono și policomponent

Rezumat

Izomerizarea *n*-butenelor pe catalizatori acizi solizi a fost efectuată pentru a stabili reacțiile test în vederea selectării catalizatorilor cu performanțe în această reacție. Catalizatorii testați au fost oxizi (zirconie, zirconie sulfatată, niobie), oxizi de Ni-Mo și Mo-W/alumină și zeoliți (Ultrazet, Ultrazet sulfat, HZSM-5* și HZSM-5* modificat) ca și o rășină sulfonică. Majoritatea au demonstrat o bună activitate de izomerizare de poziție și geometrică. Pe catalizatorii de tip HZSM-5* au avut loc reacții de izomerizare de catenă, datorată structurii cristaline și mărimii și formei porilor.

Cuvinte cheie: *n*-butene, catalizatori acizi solizi, izomerizare, structură cristalină