

Cis-trans Isomerism at o-xylene and p-xylene Hydrogenation on the Ni/Al₂O₃-SiO₂ Catalyst

TRAIAN JUGANARU¹, DORIN BOMBOS^{1*}, GABRIEL VASILIEVICI²

¹Petroleum-Gas University Ploiești, 39 Calea București, 100520, Ploiești, Romania

²National Institute for Research Development for Chemistry and Petrochemistry, ICECHIM-Bucuresti, 202 Splaiul Independetei, 060021, Bucharest, Romania

Hydrogenation of o-xylene and p-xylene to 1,2-dimethylcyclohexan, and 1,4-dimethylcyclohexan was performed using an industrial type catalyst Ni/Al₂O₃-SiO₂. Experiments were performed on a laboratory installation at a pressure of 10 bar, with a weight hourly space velocities of aromatic component (WHSV) of 0.2 h⁻¹ and a molar ratio hydrogen / aromatic component aromatic of 10; as raw materials were used the synthetic mixtures of o-xylene, p-xylene and toluene diluted in n-hexane. Temperature varied in the range 60-150°C. Experimental results show a change of cis-trans isomers, with a maximum around the temperature of 100 °C. This report is subunitary for p-xylene hydrogenation and above par for o-xylene hydrogenation. This is probably due to the position of methyl groups in aromatic compound molecules, respectively of steric effect of these groups and hydrogenation mechanism type, "roll over".

Keywords : catalyst, hydrogenation, support acidity, xylene, isomerism

Recent studies have led to concern catalytic hydrogenation of monocyclic aromatic hydrocarbons like benzene, toluene, o-xylene and p-xylene [1-4]. This interest is mainly due to restrictions imposed by UE rules regarding the content of aromatic hydrocarbons in various industrial solvents or motor fuels. Hydrogenation of benzene and o-xylene conversion close to 100% were achieved on Ru/ZnH-ZSM-5/Al₂O₃ type catalytic systems [5]. In the same paper and other systems were studied using as catalytic active component Pd, Pt or Ni, but with lower performance. Experiments were carried out in a continuous reactor with fixed bed catalyst at a pressure of 10 bar, a temperature of 20 - 180°C and aromatic H₂/component molar ratio of 10/1.

In another work it was studied the hydrogenation of benzene, toluene and o-xylene on catalytic systems differentiated by the nature of the active component (Pd and Ru) and by catalytic support, ZnH-ZSM-5/Al₂O₃, H-ZSM-5/Al₂O₃ or MOR-Cu [6]. In other studies was approached the hydrogenation of complex mixtures, such as gasoline or n-hexane containing different proportions of benzene, toluene, ethylbenzene, o-xylene and p-xylene [7]. Catalytic system used in this case was Ni/Al₂O₃-SiO₂. Conversion of p-xylene was higher than of o-xylene.

The same catalyst type Ni/Al₂O₃-SiO₂ was used in a study of hydrogenation of aromatic hydrocarbon from a petroleum solvent with boiling range of 60-200°C [8]. Stereoselectivity hydrogenation kinetics of aromatic hydrocarbons was studied using a catalyst Pd/Al₂O₃ type and o-xylene as aromatic hydrocarbon [9].

The experimental program aimed at studying the ratio of cis-trans isomers resulting from the catalytic hydrogenation of o-xylene and p-xylene on a Ni/Al₂O₃-SiO₂ catalyst type.

Experimental part

The raw materials used in experiments were toluene, o-xylene, p-xylene and n-hexane of analytical grade (Merck) and electrolytic hydrogen purity from Linde company.

The experimental program was performed in a continuous fixed bed catalytic reactor. A mobile metallic jacket for thermocouple was also placed in the axis of the bed, in order to measure the reaction temperature. The process was carried out in isothermal conditions, the temperature being measured with a mobile thermocouple, the sheath of which was axially placed in the central zone of the catalyst layer.

Reaction conditions for catalysts were:

-pressure: 10 bar;

-temperature: 60 -150 °C;

-weight hourly space velocities of aromatic component: 0.2 h⁻¹;

-molar ratio hydrogen/aromatic component: 10/1.

The total content of aromatic hydrocarbons in the reaction mixture was 10% by volume. The catalyst used was a Ni/Al₂O₃-SiO₂. Textural characteristics of the catalyst are shown in table 1. Chemical composition of the catalyst used in the experimental program was determined by atomic absorption (table 2). Acid strength distribution catalyst type Ni/Al₂O₃-SiO₂ was determined by termodesorption of ammonia (table 3) and electron microscopy image (fig. 1).

Catalyst activation was performed „in situ” in the presence of hydrogen at a temperature of 450 °C during 6 h.

The composition of the reaction mixture was determined through gas chromatography on a Varian CP-3800 chromatograph equipped with an CP-Sil 5 CB capillary column of 50 m in length and 0.32 mm in diameter.

Results and discussions

Selectivity in cis / trans isomers with temperature, at p-xylene hydrogenation is shown in figure 2 (solution 10 vol% p-xylene in hexane). Note that the process occurs with a change to cis / trans ratio with a reaction temperature. So if at low temperature (60 °C) the cis / trans ratio is 0.82, it passes through a maximum at a certain value of the temperature (100 °C), where it reaches the value of 0.86,

* Tel.: 004 0740001304

Table 1
TEXTURAL CHARACTERISTICS OF CATALYST TYPE Ni/Al₂O₃ - SiO₂

No crt.	Characteristics	Value
1	Density, g/cm ³	1,1
2	Mechanical strength, kgf/cm ²	150,6
3	Specific surface area, m ² /g	157,13
4	Pore volume, cm ³ /g	0,207

No. crt.	Characteristics	Value
1	Total acidity, m equiv. NH ₃ / g catalyst	0,2
2	Total acid centers /g_catalyst	1,20 x 10 ²⁰
3	Distribution centers acids – weak acid centers, %	12
	– medium acid centers, %	75
	– strong acids centers, %	13

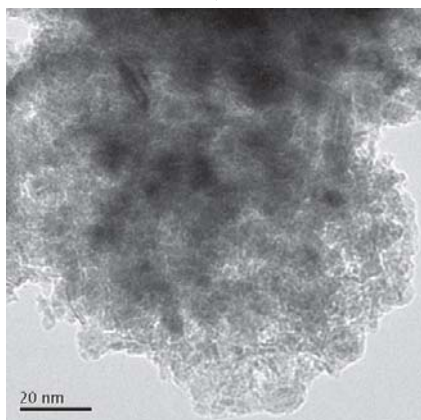


Fig. 1. Electron microscopy image for catalyst type Ni/ Al₂O₃ - SiO₂

then decrease, and at 150 °C, to reach a value of 0.78. The downward trend in the share of cis isomer compared to trans isomer with increasing reaction temperature, respects thermodynamic equilibrium, which gives greater stability of the trans isomer; the temperature of 100 °C is temperature inversion of isomers stability.

Selectivity in cis / trans isomers with temperature at hydrogenation of o-xylene solution in hexane (10% volume o-xylene) is shown in figure 3. It is shown that the same thing happens as in the case of hydrogenation of o-xylene,

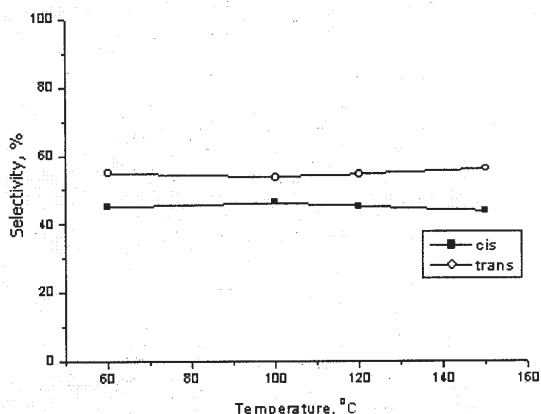


Fig. 2. Effect of temperature on selectivity in the hydrogenation of cis and trans isomers of p-xylene on the catalyst Ni/ Al₂O₃ - SiO₂

Table 2
CHEMICAL COMPOSITION OF Ni/Al₂O₃ - SiO₂ CATALYST TYPE

No. crt.	Characteristics	Valoare
1	NiO, %	59,02
2	Al ₂ O ₃	24,12
3	SiO ₂ , %	16,05
4	Na ₂ O, %	0,1
5	Fe ₂ O ₃ , %	0,9

Table 3
ACID STRENGTH DISTRIBUTION OF Ni/Al₂O₃ - SiO₂ CATALYST TYPE

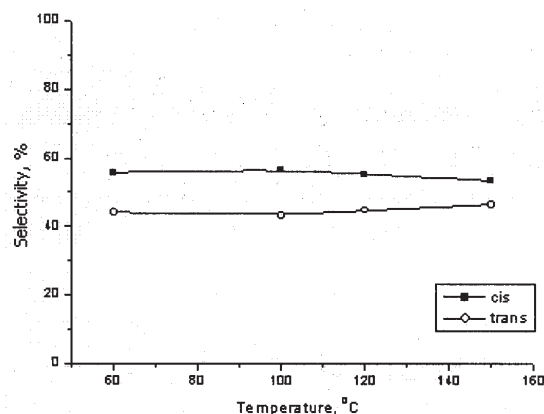


Fig. 3. Effect of temperature on selectivity in cis and trans isomers at the hydrogenation of o-xylene on the catalyst Ni/ Al₂O₃ - SiO₂

but the ratio of cis / trans subunitary one for p-xylene hydrogenation is higher than one in case of o-xylene hydrogenation, the proportion of the two isomers is reversing. So at 60 °C, the report cis / trans for hydrogenation of o-xylene is 1.26, then reaches a maximum at the temperature of 100 °C when it reaches the value of 1.31, then decrease to 1.15 at 150 °C, when the conversion is 100%.

Selectivity in isomers cis / trans with temperature at hydrogenation of mixture echimolecular o-xylene - p-xylene (o-xylene solution 5% and p-xylene 5% in hexane) is presented in figure 4. It is shown that in case of hydrogenation of mixture p-xylene and o-xylene, selectivity in cis and trans isomers dimethylcyclohexane does not change much, showing the trend of maximum and minimum temperature near 100°C, which is more pronounced in the case of isomers obtained from hydrogenation of p-xylene, respectively 1.4 dimethylcyclohexanes.

Presence of toluene at hydrogenation of mixture p-xylene and o-xylene (concentrations of the three reactants being 3.33% in solution of hexane) does not change the behaviour of the two xylenes, as shown in figure 5.

Reversing the ratio between isomers cis / trans at hydrogenation of o-xylene compared to p-xylene

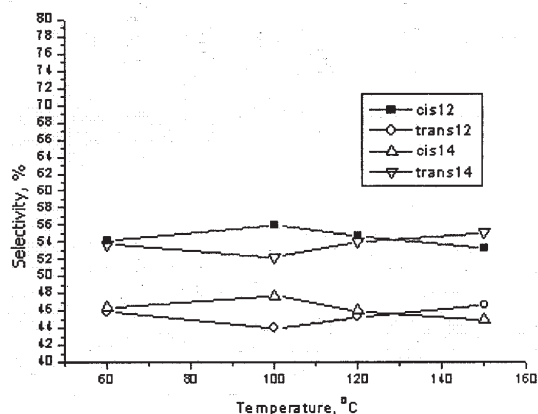


Fig. 4. Effect of temperature on selectivity in cis and trans isomers at hydrogenation of p-xylene and o-xylene mixture on the catalyst Ni/ Al₂O₃ - SiO₂

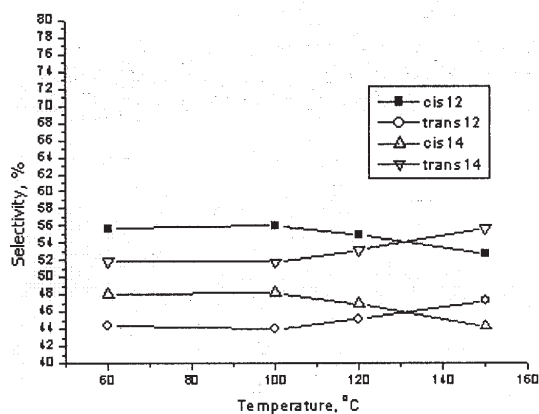


Fig. 5. Effect of temperature on selectivity in cis and trans isomers at hydrogenation of mixture reactant p-xylene, o-xylene and toluene on the catalyst Ni/ Al₂O₃ - SiO₂

hydrogenation is probably due to the steric effect of the methyl groups located in 1.4 position for p-xylene and 1.2 position for o-xylene, as well as hydrogenation mechanism of "roll over" type [9]. Trend to formation of a maximum and a minimum selectivity of cis and trans isomers is probably due to the difference between the adsorption energy of aromatic components and activation energy of the overall process, which manifests strong difference around the temperature of 100 °C.

Conclusions

Hydrogenation of o-xylene and p-xylene from synthetic mixtures in n-hexane was performed on a industrial catalyst of Ni/Al₂O₃-SiO₂ type using a fixed bed catalytic reactor in continuous systems.

The reaction mixture was analyzed chromatographically, and the results showed the presence of two isomers, cis and trans, for each corresponding hydrogenated cis and trans 1.2 dimethylcyclohexane respectively cis and trans 1.4 dimethylcyclohexane.

Variation in cis and trans isomers selectivity with temperature at o-xylene hydrogenation confirms the greater stability of trans to cis isomer, increasing the temperature favors decrease of selectivity for cis isomer.

Selectivity in cis and trans isomers resulting from hydrogenation of o-xylene and p-xylene passes through a maximum and minimum around 100°C temperature.

The ratio cis / trans is subunitary for p-xylene hydrogenation and higher than one for o-xylene hydrogenation. Changing this ratio at the hydrogenation of p-xylene compared to o-xylene hydrogenation is probably due to steric effect of the methyl groups. An important role is

probably determined by the mechanism type „roll over” according to which the hydrogenation process of xylenes is carried.

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