ON THE POSSIBLE MECHANISMS OF HIGHER N-ALKANES ISOMERISATION

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Abstract

The influence of fluorine, sodium oxide, iron oxide and platinum on the activity of aluminium-platinum catalyst in *n*-hexadecane isomerisation has been assessed. The isomers composition was determined and the effect of fluorine and platinum amount on the yield of the corresponding isomers has been evaluated, Probable mechanisms of the isomerisation process of higher *n*-alkanes consistent with the obtained results have been proposed.

Key words: isomerisation*; n*-hexadecane*;* aluminium-platinum catalyst*;* mechanism*,*fluorine effect,

1. Introduction

The kinetics and mechanism of isomerisation depend on the type of the catalyst and the reaction conditions. The research carried out so far shows that the isomerisation occurring under conditions of heterogeneous catalysis takes place via a thermodynamically –controlled mechanism [1]. The reaction ability of alkanes to isomerise usually is evaluated by the rate of their transformation into the corresponding isomer or mixture of isomers. Studying the various steps of the process as well as the intermediate products, which are inevitably formed, can assess the mechanism of isomerisation of various hydrocarbons. It has been established that the mechanism of isomerisation in presence of bi-functional catalysts depends on the degree of acidity of the catalyst support. In the case of strongly acidic support, the process is concentrated on the catalyst acid centres. In this case, the metal of the catalyst limits the coke formation and prevents the deactivation of the corresponding acid centres [2]. For catalysts, which have a very low acidity of the support, the isomerisation takes place predominantly on the metal centres and the mechanism of the reaction depends on the size of the metal crystallites [3]. In the case of using a catalyst support of moderate acidity, the isomerisation proceeds via the so-called bi-functional mechanism. This mechanism is characteristic for catalysts of platinum type on amorphous alum silicate or fluorine-containing aluminium oxide. Under these conditions intermediate compounds are formed firstly on the catalyst metal sites followed by the isomerisation of the unsaturated compounds on the acid sites [4]. Unsaturated compounds can be formed, if, two hydrogen atoms are spitted off from two adjacent carbon atoms of the alkanes adsorbed on the metal site of the catalyst. The studies devoted to evaluate the isomerisation mechanism have demonstrated that a new carbon-carbon bond can be formed if the alkane adsorption on the catalyst metal surface does not take place through from two neighbouring carbon atoms from the paraffin chain. As a result, five or six member cyclic hydrocarbons can be obtained, which further undergo decomposition, and the hydrocarbon cycle is cleaved at another site [5].

Another possible mechanism of isomerisation is related to the formation of α,α,γ-triadsorbed compounds, which are bound to two adjacent metal atoms of the catalyst, In this case an intermediate cyclopentane structure is also formed. It has a very short lifetime and after the cleavage of the cycloalkane ring yields the corresponding isoalkanes, It has been established that the size of the metal crystallites in the catalyst has a decisive effect on the type of the isomerisation mechanism. At sizes of the crystallite smaller than 2 nm, usually the cyclic isomerisation and the non-selective hydrocarbon

hydrogenolysis prevail. At larger sizes of the metal crystallites the isomerisation occurs mainly via a mechanism of shifting the isomer bond along the hydrocarbon chain with occurrence of selective hydrogenolysis. Obviously, the activity of the metal and acid centres predetermines the rate-limiting steps of the reaction. In case the isomerisation is carried out in the presence of bi-functional catalysts, the rate-determining step of the total reaction rate is alkyl rearrangement of the carbon ion [6, 7].

There are also theories, which explain the carbon ion formation by hydrogen atom abstraction from the Louis acid. In this case gaseous hydrogen may be formed resulting from the recombination of proton and hydrogen ion.

The proceeding of isomerisation in strongly acidic medium can lead to protonisation of the alkane hydrocarbon along the σ-bonds. This leads to the formation of non-classical carbon ion with two-electron tri-centre bond, Its cleavage results in the formation of the classic tri-coordinate carbon ion and hydrogen.

The last stage, at which the alkyl rearrangement of the carbon ion takes place, determines the selectivity of various promoters and poisons of the metal and acidic sites of the catalyst system [2].

The main goal of the present study is to propose determine the probable mechanism of the isomerisation reaction of higher *n*-alkanes.

2. Experimental

The effect of fluorine, sodium, iron and platinum on the activity of aluminium-platinum catalyst in *n*-hexadecane isomerisation was studied in a series of experiments.

The process was carried out at temperature of 350°C, pressure - 3 MPa and volume rate of n-hexadecane feed of 0.5 – 4.5 h⁻1. The isomerisation process was carried out in two reactors, each containing an equal volume of catalyst. Valves and pumping are provided, which permit reversal of the process positions of the two reactors and isolation of either for catalyst replacement. Over time, the catalyst became deactivated by water. When the catalyst in the lead reactor was spent, the reactor was taken off-line for reloading. The effluent from the first reactor was cooled by heat exchange with cold incoming feed before entering the second reactor. The isomerisation process was accomplished at a high rate in the first reactor and under more favourable equilibrium conditions in the second reactor. The results given in fig, 1 demonstrate that the promoting of the catalysts by fluorine in amounts ranging from 0 to 20% leads to essential increase in its isomerisation activity. It is the highest in the presence of 3-7% fluorine without any visible changes of the catalyst' surface. Most probably, the increase in the isomerisation activity of the catalyst is due to change of its chemical activity closely related to increase in the acid properties on its surface.
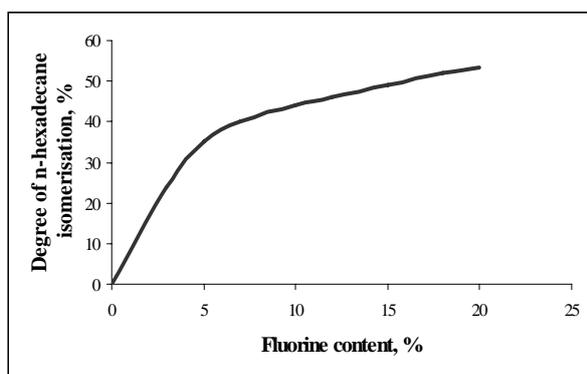

Fig. 1. Effect of fluorine content in the aluminium-platinum catalyst on the degree of *n*-hexadecane isomerisation
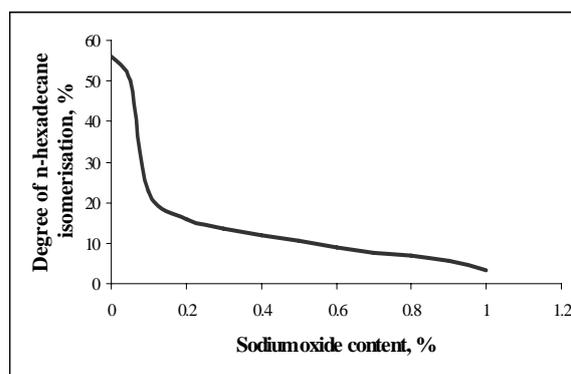

Fig. 2. Effect of sodium oxide content in the aluminium-platinum catalyst on the degree of *n*-hexadecane isomerisation,

3. Discussion

Some studies have been undertaken with the aim of establishing the change in the isomerisation activity of aluminium-platinum catalyst at its poisoning by sodium oxide added in amount of up to 1%, The results are given in fig. 2.

It has been established that the increase in sodium oxide content from 0,04 to 0,2% results in strong reduction in the degree of *n*-hexadecane isomerisation. The addition of 1,0% sodium oxide decreases the aluminium-platinum catalyst activity more than 10 fold.

The studies suggest that the efficiency of isomerisation of high-molecular normal alkanes (in this case – *n*-hexadecane) may be enhanced by increasing the acidity of the aluminium-platinum catalyst support.

Further research was undertaken with the purpose of revealing the effect of different admixtures, usually present in the support, and which do not change considerably its acidity, but have a negative impact on hydration and dehydration reactions. For this purpose, 1% iron was introduced into the aluminium-platinum catalyst in the form of Fe_2O_3. The effect of iron content on the catalyst activity in *n*-hexadecane isomerisation has been investigated, The results are demonstrated in fig. 3.

It has been found that the catalyst activity decreases, but to a lower extent, than the increase in the iron content. Irrespective of the twenty fold increase in the iron content in the aluminium-platinum catalyst, the degree of *n*-hexadecane isomerisation has remained comparatively high, i.e. it has dropped from 60 to 47%.

A similar phenomenon has been observed also changing the dehydrating activity of the catalyst at the addition of platinum (fig. 4). It has been established that irrespective of the sharp increase in the Pt content in the catalyst, the degree of *n*-hexadecane isomerisation increases from 20 to 39%. This observation suggests that the processes, which are of major significance for the proceeding of isomerisation, are those, which take place on the acid centres of the catalyst. This does not exclude, in extreme cases, i.e. at very low or very high partial pressure of hydrogen and reduced metal content, the significant role of reactions, occurring also on the metal centres of the catalyst.

Studying the composition of the end products from the *n*-hexadecane isomerisation some suggestions about the probable mechanisms have been advances. The gas chromatography data for the composition of the products obtained from *n*-hexadecane isomerisation are presented in table 1.

Table 1. Composition of the products from *n*-hexadecane isomerisation in the presence of aluminium-platinum catalyst containing fluorine and platinum,

Amount of additives to the catalyst (% wt.)							
fluorine	5	10	15	20	5	10	15	20
platinum	0,01	0,01	0,01	0,01	0,10	0,10	0,10	0,10
Composition of the isomerisation product, % wt.							
n-hexadecane	63,2	51,8	47,1	44,7	62,8	52,2	47,2	44,8
5-methylpentadecane	25,1	29,2	30,3	31,0	15,2	14,7	14,3	13,9
4-ethyltetradecane	2,8	6,4	7,1	8,2	8,7	14,3	17,0	19,2
3-propyltridecane	0,7	2,1	3,5	4,1	4,6	9,4	12,5	12,5
3-butyldodecane	5,7	9,2	10,7	11,4	7,2	8,3	8,1	8,9
alkyl-cycloalkane hydrocarbons (C_5+C_6)	0,6	0,5	0,4	0,3	1,2	0,8	0,6	0,5
Non-identified hydrocarbons and losses	1,9	0,8	0,9	0,3	0,3	0,3	0,3	0,2

Amount of additives to the catalyst (%)			
fluorine	5	10	15	20
platinum	0,01	0,01	0,01	0,01
Composition of the isomerisation product, % wt.			
fluorine	5	10	15	20
platinum	1,00	1,00	1,00	1,00
n-hexadecane	52,1	42,5	36,2	34,3
5-methylpentadecane	17,2	16,5	16,8	16,0
4-ethyltetradecane	10,3	16,9	19,9	21,8
3-propyltridecane	6,9	11,8	14,8	14,9
3-butyldodecane	11,1	10,7	10,4	11,5
alkyl-cycloalkane hydrocarbons (C_5+C_6)	2,1	1,5	1,1	0,9
Non-identified hydrocarbons and losses	0,3	0,6	0,8	0,6

It is seen that increasing the catalyst acidity by the addition of fluorine to the catalyst, the amount of the isomerised hydrocarbons rises. The same relationship, but to a lower extent, is observed at the

addition of platinum. The differences in the yield of the isomers obtained indicate that the processes at the studied cases occur through different mechanisms during the separate steps of the isomerisation reaction. It may be assumed that the isomerisation of *n*-hexadecane at higher catalyst acidity takes place mainly via the so-called mechanism of "skeleton isomerisation" (fig. 5). As a result, the end products are rich in 5-methylpentadecane. The increase in the metal content probably favours the formation of α,α,γ-triadsorbed intermediate compounds, which are bound to two adjacent platinum atoms. Under these conditions the reactions take place mainly via the mechanism of the so-called "cyclic isomerisation" with formation of the extremely stable cyclopentane ring. The cleavage of its ring at various sites, as shown in fig. 6. leads to the formation of the corresponding compounds. The increase in the amount of cyclic compounds in the isomerisation products supports this supposition.
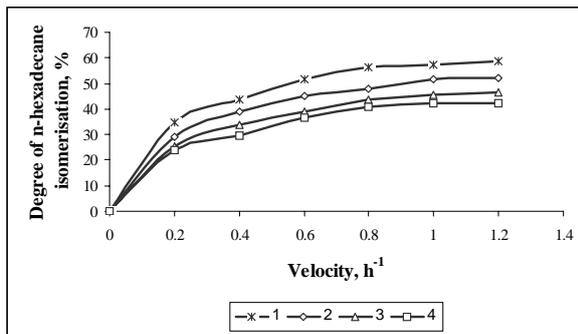

Fig. 3. Effect of iron content on the activity of the aluminium-platinum catalyst in *n*-hexadecane isomerisation: 1 – Fe_2O_3 – 0,05%; 2 – Fe_2O_3 – 0,10%; 3 – Fe_2O_3 – 0,20%; 4 – Fe_2O_3 – 1,00%
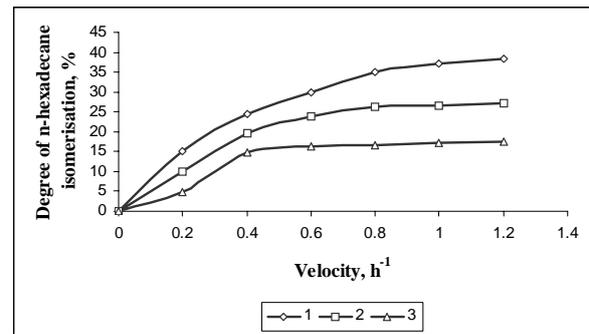
Fig. 4. Effect of platinum content on the activity of the aluminium-platinum catalyst in *n*-hexadecane isomerisation: 1 – Pt – 1,00%; 2 – Pt – 0,10%; 3 – Pt – 0,01%
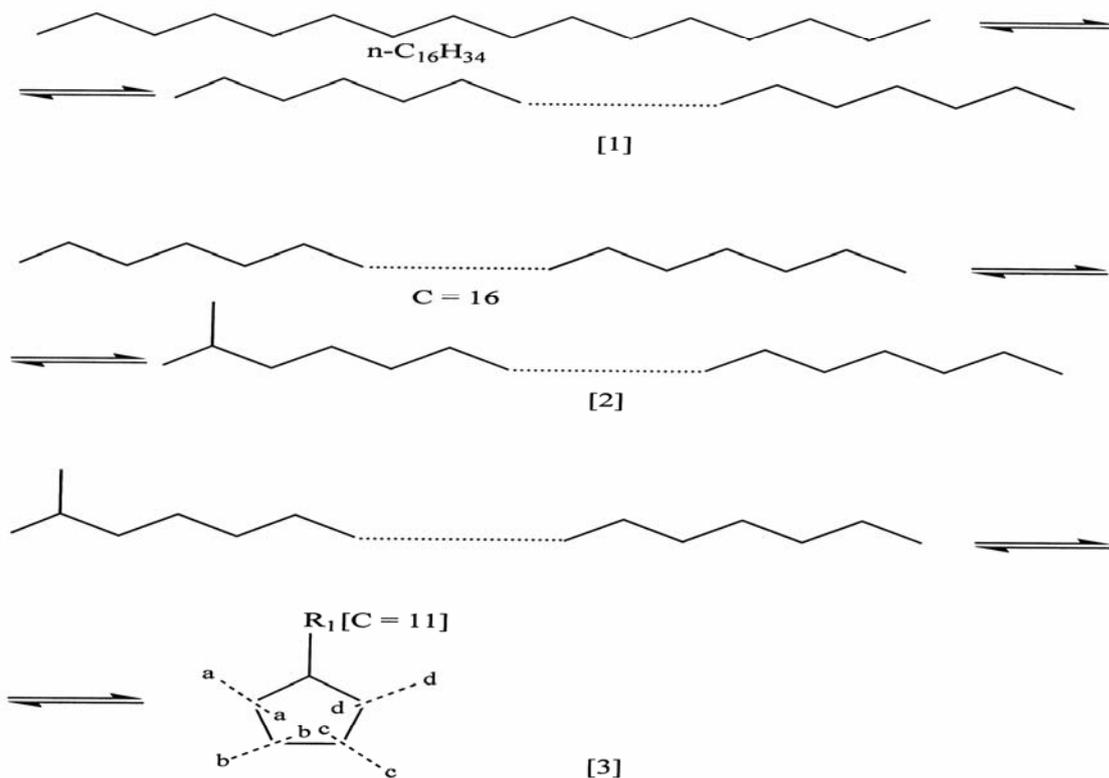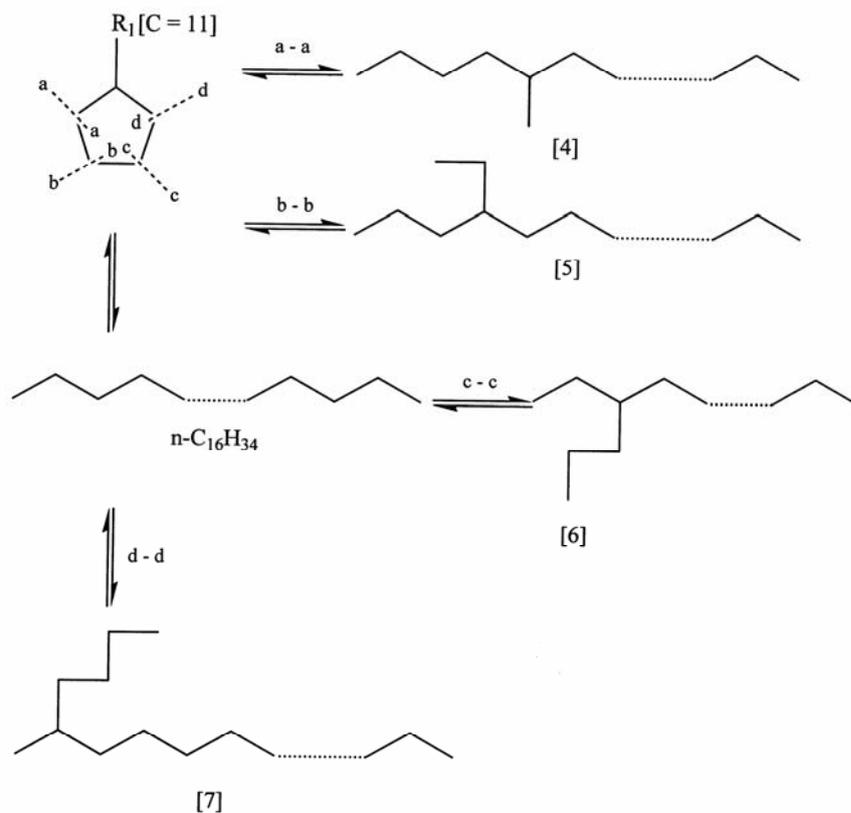

Fig. 5. Scheme of n-hexadecane isomerisation at increased acidity of the aluminium-platinum catalyst

Fig. 6. Scheme of the n-hexadecane isomerisation at higher platinum content in the aluminium-platinum catalyst

4. Conclusions

The present studies demonstrate that the isomerisation reaction of higher n-alkanes on aluminium-platinum catalyst yields products of definite composition. For this purpose, the preliminary optimisation of the platinum content in the catalyst and its acidity is regarded as a decisive factor for the selective occurrence of the isomerisation reaction yielding isomers of important practical application.

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