Interaction Between Propylene and H₂O over Rh-Ir/C-Catalysts of Clusters Type. Communication 1

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Abstract

The catalytic process of interaction between the propylene and H_2O over bimetallic Rh-Ir/C-catalysts of clusters type, has been studied. The possibility of the process interaction between C_3H_6 and H_2O according to and against Markovnikov rule are showed. The structure and state of Ru-Ir/C-catalysts surfaces were investigated by using electron microscopy.

Introduction

The reaction of electrophilic addition to isolated C-C bonds were studied in details by A.M.Butlerov and V.V. Markovnikov. In 1810 Markovnikov [1] formulated the rule concerning the direction of addition to multiple C-C bonds noted at the same time the conditions limiting it: «If the unsaturated particle CnHmX attaches to saturated YZ then at the comparative low temperature the negative element or a group attaches to the least hydrogenated carbon or to carbon connected with negative element (group)». The Markovnikov's rule expressed in common form by taking into consideration the charge of separate atoms or group of attaching molecule has found the numerous confirmations [2].

The water addition to olefin molecule permits to obtain the alcohols immediately. The interaction of olefin + H_2O usually takes place in liquid phase at pH<<7 with the Markovnikov's rule observance. At the same time the iso-alcohols are formed:

$$CH_3 \cdot CH = CH_2 + HOH \longrightarrow CH_3 \cdot \underset{\underset{OH}{|}}{C}H \cdot CH_3$$
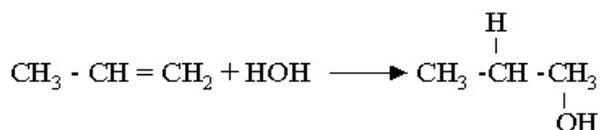
The use of heterogeneous catalysts in this reaction opens more wide possibilities, permitting at special conditions to carry it out against the Markovnikov's rule with the normal alcohols producing.

In this work the process of interaction between propylene and water vapors in flowing installation under high pressure on 5% Rh-Ir/C catalysts was investigated. The ratio Rh : Ir - 9:1, 1:1 and 1:9.

Experimental

The catalysts Rh-Ir/C were prepared by support impregnation with mixture of $RhCl_3$ and H_2IrCl_6 water solution. After impregnation the catalysts were reduced in hydrogen flow during 3 hours at 673K. Before the reaction $C_3H_6 + H_2O$ the catalyst was reduced additionally in the reactor during 1 hour at atmospheric pressure and experiment temperature.

As the supports were used: Activated carbon, $S_{sp} = 568$ m²/g, pores volume by $H_2O = 0,56$, particles size = 2-3 mm, pores size = 800 Å.

The mixture of propylene and argon in a 1:1 ratio was used as a reagent. The space velocity of reagents was varied within the 100-150 h⁻¹. The process was carried out at T = 473-723 K and P = 0,5-1,6 MPa in the installation of flowing type.

The structure and state of Ru-Ir/C-catalysts were studied by electron microscopy [3,4].

Results and discussion

The direction of interaction between propylene and conversion degree of C_3H_6 depends on conditions of

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Table 1

The products of reaction H$_2$O + C$_3$H$_6$ over Rh-Ir/C catalysts

Reaction conditions		Degree of conversion of C$_3$H$_6$, %	The products, mass.%			
P, MPa	T, K		acetone	propiohaldehyde	iso-propil alcohol	propil alcohol
1	2	3	4	5	6	7
Rh-Ir (9:1)/C						
0,9	523	5,6	16,6	-	81,4	-
0,9	573	13,4	35,4	trace	65,5	-
0,9	673	35,5	35,5	1,4	59,3	3,8
0,9	723	10,2	23,0	trace	41,8	28,9
1	2	3	4	5	6	7
0,7	573	-	-	-	-	-
1,2	573	9?3	33,0	trace	66,4	-
1,4	573	16,0	23,8	trace	76,4	-
1,4	673	14,2	39,3	1,2	56,7	2,4
1,6	723	7,5	14,7	18,5	66,8	-
Rh-Ir (1:1)/C						
0,9	473	28,7	30,3	-	69,7	-
0,9	523	25,2	15,9	-	84,1	-
0,9	573	26,0	25,3	trace	74,7	-
0,9	623	23,1	37,1	1,7	61,2	trace
0,5	573	7,4	30,7	2,0	67,3	-
0,7	573	9,1	33,6	2,9	63,5	-
1,2	573	21,8	24,2	trace	75,8	-
1,4	573	25,4	22,2	1,5	76,8	-
1,6	573	39,1	25,4	1,8	72,8	-
1,6	673	8,4	3,7	-	96,3	-
Rh-Ir (1:9)/C						
0,9	573	4,0	40,0	-	60,0	-
0,9	673	6,2	26,8	-	75,2	-
1,1	673	5,0	72,3	-	29,7	-
1,2	573	2,5	23,1	-	72,9	-

process holding. In the Table 1 the investigation results of interaction between propylene and water on Rh-Ir/C catalysts are represented.

The conversion degree of propylene at its interaction with H$_2$O on Rh-Ir(9:1)/C catalyst at T = 523 K and P = 0,9 MPa accounts for 5,6%. The temperature rise of the process to 673 K increases the propylene quantity taking part in the reaction to 35,5%. During

following rise of temperature (>723K) the conversion degree of C_3H_6 begins to drop: at P = 0,9 MPa and T = 723 K this magnitude is 10,2%. It is necessary to note, that at T<523 K (P=0,9 MPa) the integration between propylene and water doesn't occur. In the products of interaction between propylene and water on Rh-Ir(9:1)/C catalyst at temperature interval 523-573K (P=0,9 MPa) acetone and isopropyl alcohol were mainly found. The output of acetone in these conditions increases from 18,6 to 34,5 mass.% and isopropyl alcohol - decreases from 81,4 to 65,5 mass.%.

At experiment temperature > 573 K (P = 0,9 MPa) the direction of water addition to propylene molecule is changed significantly, in catalysate (T = 623K) the propyl alcohol (3,8 mass.%) appears, its quantity increase to 28,9 mass.% at 723K. Besides in the catalyst the insignificant quantity of propiohaldehyde (1,4 mass.%) is present.

So at relatively soft conditions (523-573K, P = 0,9 MPa) on Rh-Ir/C the interaction between propylene and water is carried out according to Markovnikov's rule with iso-structure alcohol formation. At temperature increase (>673K) the water addition direction is changed, the process is carried out according to and against Markovnikov's rule the i-propyl and the n-propyl alcohol is formed.

The analysis numerous investigations of olefins reactions with HX compounds (X = Cl, Br', J', OH' and oth.) with acids made in [2], showed that addition process is an electrophilic and begins with the attack of unsaturated compound by positive charged atom of molecule of the second component of the reaction. The reality of this assumption is confirmed by vast experimental material about the mechanism of various addition reactions [2]. The atoms or radicals existing in olefin molecule near the double bond because of their influence promote or complicate the transition of electron cloud at the adsorption on the catalyst. The addition process runs in that direction in what there is the most accordance between atoms interinfluence in olefin molecule and caused by the second component electron transition. The process runs the most fast at the addition of the positive charged atom of H-X molecule to b - position of substituents in olefin molecule:

$$\begin{array}{ccc} H & \sigma^+\sigma & H \\ | & & | \\ H\text{-}C\text{-}CH= CH_2 \longrightarrow HX \rightarrow H\text{-}C\text{-}CHX\text{-}CH_3 \\ | & & | \\ H & & H \end{array}$$
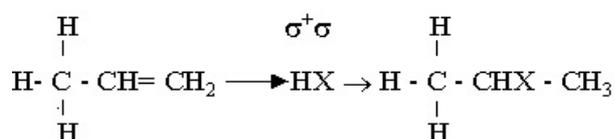
Probably it is concerned with change of formation mechanism of surface adsorption complexes olefin - water - active center of catalysts, where the heterogeneous catalysts are presented.

The temperature increase during the interaction between propylene and water on heterogeneous bimetallic Rh-Ir/C catalyst may promote the reconstruction of the catalyst surface centers in such a way that electron density in adsorbed olefin molecule will redistribute more favorable for HOH addition against the Marcovnikov's rule.

The influence of reaction mixture pressure (0,5-1,6 MPa) on interaction C_3H_8 was studied. It was established that temperature interval 523-623K and pressure < 7 MPa Rh-Ir(9:1)/C catalysts is low-active. During pressure rise from 0,9 MPa to 1,4 MPa (T=573K) the conversion degree of propylene increases from 13,4 to 16,0% (Table 1). At these conditions the output of acetone decreases from 34,5 to 23,8 mass.% and the amount of isopropyl alcohol increases from 65,6 to 76,4 mass.%, the n-propyl alcohol doesn't form.

The temperature rise from 573 to 673 K at P = 1,4 MPa decreases the propylene conversion from 16,0 to 14,2%. In the reaction products 2,4 mass.% n-propyl alcohol, 39,3 mass.% acetone, 1,2 mass.% propiohaldehyde and 56,7 mass.% isopropyl alcohol were found. At P = 1,6 MPa, T > 673 K the amount of converted propylene decreases to 7,5%, the products of interaction between propylene and water are acetone, propiohaldehyde and i-propanol (Table 1).

In comparable condition together with the rise of iridium concentration in the composition of Rh-Ir/C catalyst active phase the propylene conversion degree increases (Table 1) For example, at P = 0,9 MPa and T = 523 K the propylene conversion is 5,6% on Rh-Ir(9:1)/C and 25,2% on Rh-Ir(1:1)/C. The investigations have shown that at the interval of 0,5-1,6 MPa and 473-673 K on Rh-Ir(1:1)/C catalyst the interaction between propylene and water is carried out with the formation mainly acetone, isopropyl alcohol and small amount of propiohaldehyde (1,5-2,9 mass.%). The conversion degree of propylene on Rh-Ir(1:1)/C catalyst increase from 7,4 to 39,1 (Table 1). The tendency of isopropanol output increase from 67,3 mass.% (0,5 MPa) to 76,8 mass.% (1,4 MPa) is observed. The dependence of isopropyl alcohol output on process temperature in the interval 473-673K (P = 0,9 MPa) has an extreme character: the maximum output of isopropanol is observed at 523K - 84,1 mass.%. The conversion degree of C_3H_6 is 25,2%. It

is necessary to note that at specified conditions the amount of propylene converted practically changes a little (23,1-28,7%) (Table 1).

a
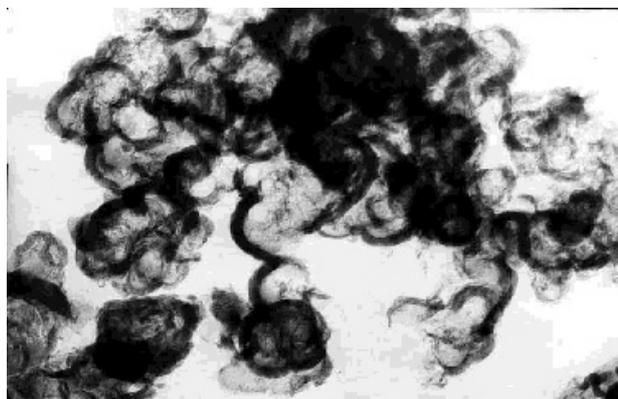
b
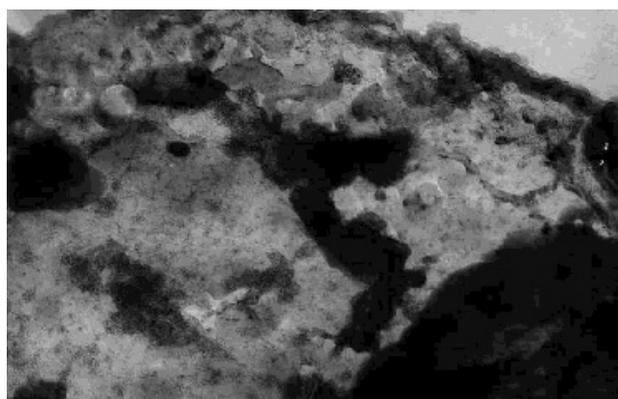
c

Fig.1. Electron-microscopic pictures of Rh-Ir/C-catalysts (x 120000). Ratio Rh:Ir:
a – 1:9, b – 1:1 and c – 9:1

During the interaction between propylene and water on Rh-Ir/C catalyst with a ratio Rh:Ir = 9:1 and 1:1 in gas phase together with non-reacted propylene the

small amounts of propane, C_1-C_2 - hydrocarbons and CO_2 were found. The running of side reaction were detected at all the conditions of the process.

On the bimetallic Rh-Ir(1:9)/C catalyst with high content of Ir the interactions between propylene and water practically doesn't occur.

So the increase of iridium concentration in the catalyst composition from 10 till 90% significantly influence not only on the direction of water addition to propylene molecule, but changes the catalyst activity too.

The optimal catalyst for the reaction $C_3H_6 + H_2O$ is the bimetallic Rh-Ir/C catalyst with the metal ratio 1:1.

Microscopy investigation is connected with the change of the catalyst surface state. It has been established that Rh-Ir(1:9)/Al₂O₃-catalyst particles size varies from 20 till 40 Å, more over high dispersed particles sufficiently uniformly and closely settle the support surface (Fig.1a). At the increase of rhodium concentration in the catalyst composition till 50% in Rh-Ir(1:1)/C-catalyst - the dispersity some what increase: the particles of d = 20-25 Å predominate (Fig.1b). At the same time with them the enough largest agglomerate of 60-75 Å consisting of small structures (d<<20 Å) appear. For the Rh-Ir (9:1)/C catalysts containing 90% of rhodium the non-uniform particle distribution of d - 60-75 Å on the surface (Fig.1c). Also the fine dispersed particles have been observed, its amount was increased with the rise of Ir concentration and got maximum when content of iridium was 50%. These particles were X-Ray amorphous.

Similar structure were discovered on the surfaces bimetallic catalysts contained the noble metal. They were identified as the bimetallic clusters [5,6,7].

Conclusions

The investigation of the process of $C_3H_6 + H_2O$ interaction over Rh-Ir/C with different ratio Rh:Ir have shown that on the surfaces of catalysts simultaneously exit two type of active centers (clusters) able to activate propylene and H_2O [8] molecules in a different way. The centers responsible for holding the reaction $C_3H_6 + H_2O$ against the Markovnikov's rule are the Rh-Ir clusters enriched with the rhodium.

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