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ON SPECIFIC TRANSFORMATIONS OF OLEFINS IN THE PRESENCE OF SOME SOLID CATALYSTS

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In the course of investigation on hydrogenation of olefins, particularly of ethylene, in the presence of such metals as nickel, the process of self-hydrogenation of olefin has been observed(1-6). The authors reported that ethane was formed from ethylene even when no hydrogen was admitted into the reaction vessel. Their experiments were carried out exclusively in a static system at low temperatures (in no case exceeding 200°C) and low pressures.

The object of our investigation was to examine the eventual transformations of propylene and other olefins in the presence of some metals and metal oxides supported on alumina at high temperatures in the range of 200 - 500°C at atmospheric pressure in a flow system. The catalysts were prepared by impregnation of γ- Al_2O_3 (surface area 137 m^2/g ; particle size 0,3 - 0,5mm) with the solution of metal salts, subsequent drying for 5 hours at 110°C and heating in the stream of air for about 6 hours at 530°C. The catalysts were then reduced with hydrogen at 530°C for 6 hours. The samples of catalyst of the weight 2 g containing 3 - 10 % of the metal were usually used. The experiments were carried out in a silica tubular reactor.

It has been shown that under experimental conditions in the presence of molybdenum - alumina catalyst prepared as described above, propylene undergoes some chemical transformation. The major reaction products determined by a gas chromatographic analysis were found to be hydrogen, propane and butenes (mainly isobutylene). Similar reaction was observed when transformations of other olefins, such as ethylene, butene-1 and isobutylene were studied. In each case, the main components of the complex reaction products were hydrogen, paraffin hydrocarbon with the same number of carbon atoms as in the initial olefin and higher olefins. It was established that on the surface of catalyst the complexes of some highly unsaturated products were deposited. The transformation of olefins proceeds in a similar way when catalyst not reduced in the last stage of its preparation is used. In that case, however, somewhat smaller proportion of hydrogen is obtained, perhaps due to its participation in the reduction of metal oxides.

Studying the effect of temperature on the relative amounts of reaction products formed from propylene, it was found that the ratios of hydrogen to propane and propane to butenes increased with the rise of temperature. With the rise of temperature the marked increase in the total yields of propane and hydrogen formed from converted propylene has been also observed.

Transformation of propylene, as described above, proceeds not only in the presence of molybdenum - alumina catalyst. Many other catalysts, such as the oxides of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ag, Cd, Pb, W and some others reduced in the hydrogen stream, supported on alumina have been used and shown to be active in this process, though to a very different extent. For illustration, the results of some experiments carried out in the presence of a few among the catalysts used are collected in table 1. The samples of the reaction products were withdrawn after 40 minutes of the reaction carried out at 350°C and contact time 18 seconds.

Table 1.

Yields of products of the transformation of propylene (350°C , 18 sec.)

Catalyst		V	Ni	Cd	Mo	Mo*	W
Conversion,%		5·8	6·6	6·8	22·8	28·5	46·5
Yield, mol.%	H_2	16·3	63·1	85·1	19·9	29·6	3·2
on converted	CH_4	2·4	3·6	2·5	1·7	3·3	0·4
propylene	C_2H_6	0·5	1·7	0·0	0·5	0·6	0·4
	C_2H_4	0·3	6·8	0·0	0·9	1·0	1·5
	C_3H_8	42·4	22·8	0·4	32·8	39·4	7·7
	C_4H_8	7·8	6·5	17·1	8·0	6·8	14·2
Ratio $H_2 : C_3H_8$		0·38	2·77	200	0·61	0·75	0·42
Ratio $C_4H_8:(H_2+C_3H_8)$		0·11	0·07	0·20	0·15	0·10	1·36

* - reaction temperature 380°C

Hydrogen, propane and butenes were in each case among the major reaction products; in some cases relatively high proportions of ethylene and butane were also formed. The conversion of propylene and the proportions of the reaction products varied very much from one catalyst used to another.

The results of present work clearly indicate that the chemical transformation of propylene and other olefins into hydrogen, paraffin hydrocarbon with the same number of carbon atoms and olefins is a general reaction which occurs in the presence of many different metals and their oxides.

While the formation of paraffin hydrocarbon has already been observed by other authors, though under quite different reactionconditions and could be explained in terms of selfhydrogenation, the generation of hydrogen and higher olefins is more obscure.

Taking propylene as an example, the following reaction scheme which accounts satisfactorily for the major products, could be suggested:

$$C_3H_6 \longrightarrow (C_3H_6)_{ads} \longrightarrow (C_3H_{6-a})_{ads} + a(H)_{ads} \qquad (1)$$

$$\longrightarrow (C_2H_{3-b})_{ads} + (CH_3)_{ads} + b(H)_{ads} \qquad (2)$$

$$2(H)_{ads} + (C_3H_6)_{ads} \longrightarrow C_3H_8 \qquad (3)$$

$$2(H)_{ads} \longrightarrow H_2 \qquad (4)$$

$$(CH_3)_{ads} + (C_3H_{6-a})_{ads} + (a-1)\ (H)_{ads} \longrightarrow C_4H_8 \qquad (5)$$

$$(C_3H_{6-a})_{ads} \text{ and } (C_2H_{3-b})_{ads} \longrightarrow \text{the complexes or polymerization products deposited on the surface of catalyst} \qquad (6)$$

According to the proposed mechanism olefins are adsorbed with the dissociation to an acetylenic or still more highly dissociated residue and hydrogen atoms (reaction (1)) or hydrogen atoms and methyl radicals (reaction (2)) able to react with adsorbed olefins (reactions (3) and (5)) or with other adsorbed atoms or radicals (reaction (4) and other not included steps leading to the minor products, such as methane and ethane).

The proposed mechanism is undoubtedly an oversimplification and some individual reactions may proceed in more than one step.

The dependence of the relative yields of reaction products on the catalyst used could be attributed to the change in the relative rates of certain individual reactions.

In view of an increase in the total yields of propane and hydrogen formed from converted propylene with the rise of temperature it can be postulated that the number of hydrogen atoms abstracted from the adsorbed molecule (a and b) increases with the rise of temperature and thus more highly dissociated C_3 species are formed. The increase in the amounts of molecular hydrogen produced in the reaction at higher temperatures may derive from the growing desorption of hydrogen from the surface of catalyst, from the falling concentration of adsorbed propylene able to undergo the process of hydrogenation and from the increase in the number of hydrogen atoms removed from the adsorbed molecule. On this basis a lack of hydrogen in the reaction products obtained by some other authors studying selfhydrogenation process at low temperatures could be explained.

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