INITIATED HETEROGENEOUS-CATALYTIC REACTIONS

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

INITIATED HETEROGENEOUS-CATALYTIC REACTIONS

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If ethylene or its nearest homolog is passed, in a mixture with hydrogen at 190-200°, over a cobalt catalyst deposited on clay, the olefin is hydrogenated to the paraffin hydrocarbon with the same number of carbon atoms. In the presence in the reaction zone of small amounts of carbon monoxide ($> 0.01\%$), along with this reaction, hydropolymerization of the olefin to higher hydrocarbons also takes place. When 5% carbon monoxide is added to the mixture of olefin and hydrogen, hydropolymerization becomes the main reaction, and hydrogenation becomes secondary. Thus, small amounts of carbon monoxide at 190-200° initiate the reaction of hydropolymerization (CO-hydropolymerization) of olefins. In the absence of hydrogen this reaction does not proceed, which indicates that the true initiator of the reaction is not carbon monoxide itself, but the products of its incomplete reduction, having the character of surface intermediate species (methylene, oxymethylene radicals) (^{1}).

Fig. 1. Dependence of the yield of products of O_2-hydropolymerization of olefins on the oxygen concentration in the initial mixture:
1—$C_2H_4 : H_2 = 1 : 1$,
2—$C_2H_4 : H_2 = 2 : 1$,
3—$C_2H_4 : H_2 = 3 : 1$,
4—$C_2H_4 : H_2 = 4 : 1$,
5—$C_3H_6 : H_2 = 1.7 : 1$,
6—$n\text{-}C_4H_8 : H_2 = 1.5 : 1$.

Recently, a new heterogeneous-catalytic reaction requiring the presence of an initiator was discovered: the reaction of olefin hydropolymerization under the action of small amounts of oxygen (O_2-hydropolymerization of olefins), proceeding on the same catalyst, but at 100-120°. Under optimal conditions, hydropolymerization proceeds to 35-45%, and hydrogenation to the corresponding paraffin hydrocarbon to 17-30% (calculated with respect to the initial olefin C_2—C_4). The optimal oxygen content in the initial mixture is 1.7-2% (Fig. 1).

One of the conditions for the course of the O_2-hydropolymerization reaction is the simultaneous hydrogenation of the olefin. A catalyst inactive in this reaction is also inactive in the hydropolymerization reaction. The optimal reaction temperature is 100-120° (Fig. 2). At 50° the reaction already proceeds, but only by 5-8%, and at 200° by 3%. At temperatures above 120°, with increasing temperature, the hydrogenation process intensifies (Fig. 3), and the average molecular weight of the reaction products also decreases.

The reactions of CO- and O_2-hydropolymerization of olefins are distinguished by the feature that the quantitative ratio of the molecules of olefin and CO or, respectively, O_2, entering into the reaction (yield per initiator), is usually greater than unity, may reach values of tens, and increases with decreasing initiator concentration. Such ratios are usual for radical-chain reactions, and this gives grounds for considering these reactions radical-chain reactions ([3]). Here, apparently, are rare examples of such reactions in heterogeneous catalysis. The heterogeneous-catalytic character of CO-hydropolymerization was shown in studying the influence of adsorption displacement of the olefin by carbon monoxide and dilution of the initial mixture.

by an inert gas on the course of reaction (4). The yield with respect to initiator in O_2-hydropolymerization reaches a maximum at the optimum temperature (Fig. 4).

A very interesting feature of the reactions of CO- and O_2-hydropolymerization of olefins is the distinctive character of the final products.

After initiation of the reaction, new intermediate active forms are produced on the catalyst surface; these arise chiefly as a result of special "soft" destruction processes ([5]), which have a very strong effect on the composition and character of the final products and on their distribution by molecular weight. Along with true polymeric forms, hydrocarbons are formed with a number of carbon atoms in the molecule not multiple with respect to the starting olefin. Their yield, greatly exceeding the possible yield of products of direct hydrocondensation of the olefin with carbon monoxide (alkylation) ([1,6]), increases with increasing molecular weight of the olefin, while the average degree of multiplicity of the hydropolymerization product decreases (the fraction of catalyst containing hydrocarbons with a number of carbon atoms greater than in the starting olefin ([7])). The sum of nonmultiple forms in the products of the reaction is, in CO-hydropolymerization, 34 for ethylene, 48 for propylene, 73 for butylene, and 85% for 1-octene. The formation of nonmultiple forms is due mainly to rupture of C–C bonds with the formation of surface radicals that enter into interaction with the starting olefins and the products of their transformation. A large role in this is apparently played by partially hydrogenated forms of olefins—surface alkyl radicals ([7]). Data on the high probability of participation of such radicals in chain processes on the catalyst have also been obtained in the study of CO-hydropolymerization and the synthesis of hydrocarbons from CO and H_2 by the tracer-atom method ([8]).

Fig. 2. Dependence of the yield of products of O_2-hydropolymerization reactions on reaction temperature: 1—ethylene, 2—propylene, 3—*n*-butylene, 4—

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

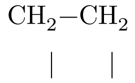
isobutylene, 5—CO-hydropolymerization of ethylene

Fig. 3. Dependence of the yield of the hydrogenation product (paraffinic hydrocarbon) on reaction temperature in experiments with the starting mixture: 1–C_2H_4—H_2—O_2, 2–n-C_4H_8—H_2—O_2, 3–C_2H_4—H_2—O_2—CO

Fig. 4. Dependence of the yield with respect to initiator (oxygen) on the reaction temperature in O_2-hydropolymerization: 1–C_2H_4, 2–C_3H_6, 3–iso-C_4H_8

The similarity of the mechanism of CO- and O_2-hydropolymerization also accounts for the similarity in the composition of the final products, which are n-hydrocarbons of the aliphatic series with an admixture of iso-structure hydrocarbons, predominantly with one lateral methyl group (Table 1).

Hydropolymerization of olefins initiated by oxygen shows a certain analogy to the reaction of thermal polymerization of ethylene and propylene activated by small amounts of oxygen, in which unsaturated forms are also formed; moreover, the formation of intermediate active forms is assumed, close in character to the surface forms arising in initiated catalytic reactions, for example methylene radicals and biradicals ([9]). The latter find their surface analogs in the π-complexes formed by an olefin with the surface:



$$\begin{array}{c} CH_2-CH_2 \\ |\qquad| \end{array}$$

Such surface biradicals are postulated by some theories ([10]) and have been confirmed by IR spectra ([11]). It may be assumed that in O_2-hydropolymerization, at the initiation stage, peroxide radicals play an important role, as in thermal polymerization ([9]), and then they are converted into hydrocarbon radicals. CO- and O_2-hydropolymerization of olefins in the presence of hydrogen probably proceed according to similar schemes. The difference in reaction temperature of 100° is caused by the different temperature of conversion of the added initiator (CO or O_2) into surface active forms—the true initiators of the reactions.

Figure 4

Figure 4: Figure 4

From the results presented, it may be concluded that at present one can speak of initiated heterogeneous-catalytic reactions as a special group of complex multistage processes proceeding entirely on the surface of a solid catalyst.

Table 1

Comparison of the composition of products of CO- and O_2-hydropolymerization

Initial olefin $C_{nH_{2n}}$	CO-hydropolymerization* C_5	CO-hydropolymerization* C_6	CO-hydropolymerization* C_7	CO-hydropolymerization* C_8	CO-hydropolymerization* C_9	O_2-hydropolymerization** C_5	O_2-hydropolymerization** C_6	O_2-hydropolymerization** C_7	O_2-hydropolymerization** C_8	O_2-hydropolymerization** C_9
C_2H_4	11	18	17	13	9	24	27	11	9	11
C_3H_6	12	19	13	12	12	14	29	13	10	8
-C_4H_8	22	15	8	8	9	9	12	14	15	10

* In the initial gas mixture $C_{nH_{2n}} : H_2 = 1 : 1;\ 5\% CO$.

** In the initial gas mixture $C_{nH_{2n}} : H_2 = 1 : 1;\ 2\% O_2$.

The distinctive feature of these reactions is that, for their occurrence, along with a specific catalyst, the presence in the reaction zone of a compound different from the immediate starting reactants is required. Such a compound may be designated by the term "reaction initiator." The chief and determining characteristic of an initiator is its ability to cause a reaction which, in its absence, despite the presence of a heterogeneous catalyst, does not proceed. It is conceivable that the role of the initiator is sometimes performed by one of the starting reactants, but in these cases it is very difficult to reveal the initiated character of the reaction.

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