N. I. Ershov and Ya. T. Eidus

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Abstract

Full Text

N. I. Ershov and Ya. T. Eidus

EXPERIMENTAL SUBSTANTIATION OF THE CHAIN MECHANISM OF THE HETEROGENEOUS-CATALYTIC REACTION OF OLEFIN HYDROPOLYMERIZATION OCCURRING UNDER THE INFLUENCE OF CARBON MONOXIDE AND HYDROGEN

(Presented by Academician B. A. Kazanskii, 19 IV 1957)

Chain reactions proceeding in the bulk and initiated by free atoms or radicals are widely known and have been studied in detail. However, until now there has been no direct and unambiguous experimental proof of the possibility of a chain process occurring on the surface of a solid catalyst, although it has been shown that some reactions proceed on a solid catalyst by a radical mechanism, and theoretical works have also been published ((^1)) allowing for the possibility of chain heterogeneous-catalytic reactions. We have previously shown ((^2)) that the radicals formed in the heterogeneous-catalytic reduction of carbon monoxide by hydrogen are initiators of olefin hydropolymerization. It was of interest to determine whether this reaction has a chain character, since in the homogeneous polymerization of olefins under the action of free atoms and radicals the process proceeds, as a rule, by a chain mechanism. This applies to polymerization reactions of olefins (ethylene, propylene, butylenes) initiated both by the simplest alkyl radicals (methyl and ethyl) and by methylene radicals obtained by decomposition of ketene. In carrying out the hydropolymerization reaction with olefins (C_2–C_4) and (C_6) ((^{3–8})), it was established that at low concentrations of carbon monoxide (1-2%), contained in approximately equimolecular mixtures of olefin with hydrogen, at (190^{ }) and atmospheric pressure, one molecule of carbon monoxide that has entered into reaction involves up to 45 molecules of olefin (ethylene) in the hydropolymerization process (Fig. 1, curve (b)). It is evident from this that, in view of the very small amounts of carbon monoxide that have entered into reaction, carbon monoxide cannot be regarded as a reagent in the ordinary sense. In its influence on the reaction, which proceeds only with its participation, carbon monoxide may act as an initiator of the chain polymerization process or else as a catalyst. However, the role of a catalyst in the present case is excluded, since carbon monoxide enters into the final reaction products without regeneration. In this reaction carbon monoxide is the initiator of a process that clearly possesses some of the principal features determining the chain character

Fig. 1

of olefin polymerization reactions in bulk, initiated by free alkyl radicals—the

Fig. 1

Figure 1: Fig. 1

chain length, or yield per initiator (the number of polymerized olefin molecules per initiator particle), considerably exceeding unity, and the regular decrease in chain length or yield per initiator with an increase in its concentration.

One of the characteristic features of homogeneous chain reactions of olefin polymerization under the influence of free alkyl radicals is the dependence of the chain length, or yield per initiator, on the concentration of these radicals. This dependence is due to the difference in the rates of reaction of radicals with olefin molecules and of radical recombination. At substantial radical concentrations their recombination predominates, while addition to olefins (initiation) proceeds slowly or even does not occur at all; at low concentrations of free radicals, on the contrary, conditions are unfavorable for their recombination, as a result of which their mass addition to the olefin takes place, leading to an increase in the polymerization rate. Thus, it was observed that the yield per initiator increases as the concentration of the initiator (free radicals) decreases. All this is clearly seen from the following examples: when introducing[^9] 117, 34, 4, and 0.1 ml of tetraethyllead per each 15.3 l of ethylene, the decomposition of which formed ethyl radicals, 0.15, 0.83, 6.4, and 225 molecules of ethylene, respectively, were polymerized per ethyl radical; in the polymerization of ethylene[^{10}] under the action of methyl radicals formed by the decomposition of tetramethyllead, when 0.5 and 7.3% of the latter was used relative to the weight of ethylene, the yields per initiator were 5 and 0.59, respectively. An analogous dependence of the yield per initiator on the concentration of carbon monoxide is also observed in the olefin hydropolymerization reaction: lower concentrations of carbon monoxide correspond to higher yields per initiator, as is seen from curve in Fig. 1, relating to the reaction with ethylene, and from Table 1, where data are given for the hydropolymerization of ethylene, propylene, and butene-1.

Table 1

Initial olefin*	CO concentration in the initial gas, %	Yield per initiator, %
Ethylene	0.1	44.0
Ethylene	0.5	22.0
Ethylene	4.6	8.0
Ethylene	15–20	4.0
Propylene	5.7	3.7
Propylene	6.2	3.7
Propylene	11.6	0.7
Propylene	13.6	0.4
Propylene	15.4	0.2
Propylene	18.4	0.1

Initial olefin*	CO concentration in the initial gas, %	Yield per initiator, %
Propylene	22.0	0.0
Butene-1	4.0	2.2
Butene-1	5.5	2.4
Butene-1	6.0	1.7
Butene-1	12.2	0.4
Butene-1	14.8	0.16

At the maximum reaction rate, which is observed for all olefins at 5–6% CO in the initial gas and hydrogen-to-carbon monoxide ratios of 6–8, the yield per initiator for ethylene is approximately 8, for propylene ~4, butylene ~3, and hexene 1–2. The reaction rate has a complex dependence on the concentration of carbon monoxide: in the range up to 5–6% carbon monoxide in olefin-hydrogen mixtures, a continuous increase in the reaction rate is observed, which slows with further increase in CO concentration, up to complete cessation of the reaction for olefins C_3–C_4. The dependence of the rate of formation of reaction products on the concentration of carbon monoxide in the hydropolymerization of ethylene is shown in Fig. 1 (curve). The heterogeneous-catalytic character of the hydropolymerization reaction is expressed in the influence exerted on the reaction by adsorption of the olefin: the reaction proceeds only when adsorbed olefin is present on the catalyst. When working with a gas containing 50% C_3H_6, 25% H_2, and 25% CO, propylene does not participate in the reaction and also is not hydrogenated by hydrogen to propane, although the usual reaction of hydrocarbon formation from carbon monoxide and hydrogen is observed. Carbon monoxide,

possessing a greater tendency toward adsorption than propylene, blocks the catalyst surface; and in the absence of propylene on the surface there is no hydropolymerization reaction. The heterogeneous-catalytic character of the reaction is also proved by the obtaining of constant yields of hydrocarbons, referred to unit volume of the initial active gas, upon dilution of the latter with nitrogen ([1]).

It follows from this that the reaction of olefin hydropolymerization under the influence of carbon monoxide and hydrogen is a heterogeneous-catalytic reaction with a radical-chain mechanism.

Thus, using this reaction as an example, the possibility of the occurrence of heterogeneous-catalytic reactions by a radical-chain mechanism has for the first time been experimentally substantiated in heterogeneous catalysis.

It is quite probable that, in the process related to the hydropolymerization reaction—the formation of hydrocarbons from CO and H_2—there is likewise, at a certain stage, a radical-chain mechanism. The initial stage of this process proceeds by a radical mechanism (hydrocondensation), with formation of olefins.

As the latter accumulate on the catalyst surface, their hydropolymerization begins, proceeding by a chain mechanism and complicated by a number of other reactions, for example hydrocracking, hydrogenation, etc. The formation of hydrocarbons takes place through a complex combination of a radical mechanism with a radical-chain one. In this light, the hydropolymerization reaction of olefins, beginning with the stage of olefin introduction, is regarded as the final part of the complex reaction of hydrocarbon formation from CO and H_2.

The identity of their dependence on temperature and the great similarity in the character of the reaction products convince us of the common nature of the reactions of hydropolymerization and hydrocarbon formation from CO and H_2.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.