MECHANISM OF CARBON FORMATION
IN THE DECOMPOSITION OF ETHANOL
OVER A COPPER-SILICA GEL CATALYST

G. Stegner, A. A. Balandin, and A. P. Rudenko
M. V. Lomonosov Moscow State University

Problems related to the formation of a carbonaceous substance on a catalyst are attracting ever increasing attention at the present time. The study of the kinetics and mechanism of carbon formation is of practical importance in the search for ways of improving some chemical production processes which are complicated by the separation of carbon and is of theoretical importance for understanding carbon formation processes themselves. Most work in this connection has been devoted to hydrocarbon cracking [1-10]. Only a few papers touching on problems of carbon formation have been concerned with other processes and, in particular, catalytic dehydrogenation of alcohols [11-14]. In a number of papers [10, 15] it was shown that in general the kinetics of carbon formation during hydrocarbon cracking may be described by equations analogous to the known kinetic equation [16, 17]; sometimes, however, they are best described by empirical equations.

There are two contradictory opinions on the treatment of the mechanisms of carbon formation on catalysts. According to one of these, the carbonaceous material is free carbon and is formed from separate carbon atoms or carbon atoms joined to each other, on which the carbonizable substance is first decomposed. The foundation of these ideas was laid by Berthelot, who regarded the carbonaceous material as free carbon [18]. Subsequently these ideas were repeatedly supported and developed, especially in work in which the reactions were explained on the basis of free radicals [11, 19-22]. The second, more modern idea regards the carbonaceous material as polycondensation products of the starting materials or some of their conversion products. Thus, Sakhanov, Tilicheev, and Brooks [2, 3, 23] represent carbon formation as the thermal condensation of complex aromatic hydrocarbons and Nemtsov [24], as the thermal condensation of complex aromatic hydrocarbons with unsaturated bonds; Frost [25] and Balandin [5] also assumed the possibility of such a carbon formation mechanism. Other authors demonstrated the accuracy of this mechanism of carbon formation, representing it as a multistage process consisting of similar reactions: polymerizations in the case of carbon formation from butadiene [26], dehydrocondensation in the case of carbon formation during benzene pyrolysis [8], and polymerization of the reaction products in the case of the dehydrogenation of n-butane [10].

It seemed interesting to study carbon formation accompanying the catalytic decomposition of ethanol, since carbon formation proceeds readily in this case, even at low temperatures, and the decomposition products of ethanol have been studied thoroughly.

EXPERIMENTAL

For a quantitative and direct determination of the carbonaceous material obtained under various conditions of ethanol decomposition we used a special apparatus with a detachable reactor for heterogeneous catalytic investigations in the vapor phase in a flow system, described previously [8, 27]. The temperature was kept constant to within less than 1° automatically by a method of indirect furnace temperature regulation developed in the laboratory [28].

In the reactor, which was a casing, ground to fit the catalyst tube, 16 mm in diameter and 120 mm long,
was placed 10 ml (7.6 g) of catalyst with a grain size of 1 - 2 mm. The catalyst, copper on silica gel, was prepared by impregnating purified silica gel (KSM grade from the Voskresensk Chemical Combine) with a copper nitrate solution and then decomposing the salt at 600°. Each gram of catalyst contained 0.0002 mole of copper. The adsorption characteristics of the catalyst, determined from the adsorption of benzene at 0° by a gravimetric method, had the following values: specific surface 515 m², total pore volume 3.2 millimoles of benzene per g, and the maximum on the pore volume distribution corresponded to a radius of 13 Å.