DIFFERENTIAL UTILIZATION OF THE SURFACE OF ALUMINUM OXIDE IN THE PRODUCTION OF COMPLEX AND MIXED CATALYSTS

COMMUNICATION 2. ZnO–Al₂O₃ CATALYSTS

F. É. Englina, V. É. Vasserberg, and A. A. Balandin

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In our previous article [1] it was shown that adsorption and catalytic inhomogeneity of the surface of aluminum oxide has a substantial influence upon the activity of complex catalysts prepared on the basis of Al₂O₃, namely, aluminosilicate catalysts. In this case, portions of the Al₂O₃ surface, differing in their adsorption and catalytic properties, prove to be differently suited to participate in the chemical process of interaction with the silicon oxide, in the course of which these active portions of the Al₂O₃ surface disappear, forming a surface aluminosilicate, in turn characterized by the presence of centers with different catalytic activity. It seemed interesting to verify the influence of inhomogeneity of the surface of the initial oxide not only in the case of formation of a complex catalyst, representing a new chemical compound, but also in the case of formation of a mixed catalyst, both components of which retain their chemical individuality. It could be assumed beforehand that in this case a similar influence should be manifested even more distinctly. As the object of investigation we selected the mixed catalyst ZnO–Al₂O₃, since this system was studied earlier with respect to the dehydration of isopropanol in the adsorption layer [2, 3], while the preparation of such catalysts according to the method of adsorption from the gas phase [1] presents no special difficulties.

EXPERIMENTAL

Two samples of Al₂O₃ of different methods of production – A1 and A5, the properties of which, as well as the apparatus and method of adsorption application, were described in [1], were used to prepare the ZnO–Al₂O₃ catalysts. The nature of the catalytic inhomogeneity of the surface of these samples was also studied beforehand [4]. Diethylzinc, possessing a rather high vapor pressure and readily decomposed by oxygen or air to zinc oxide, was used as the volatile organometallic compound. The adsorption of Zn(C₂H₅)₂ on Al₂O₃ was conducted at 20 °C; the value of the elementary area of the Zn(C₂H₅)₂ molecule, needed to calculate the degree of surface coverage, was calculated according to the formula cited in [5]. This value proved equal to 33.7 Å². An attempt to determine experimentally the value of the elementary area of Zn(C₂H₅)₂ from adsorption isotherms of this substance on Al₂O₃ ended in failure, since the experimental points plotted in the coordinates of the BET equation did not lie on a straight line.

After the completion of adsorption, before the required weight gain of the adsorbent had been reached, air was cautiously introduced into the apparatus, the catalyst was removed, and heated at 500 °C in a stream of air for 2 h.

Three series of samples were prepared on the basis of each preparation of the initial aluminum oxide:

1) Catalysts produced directly by the adsorption of Zn(C₂H₅)₂ and differing in amounts of it – from 0 to 90% of monolayer coverage (calculated on the basis of ZnO); moreover, high degrees of coverage were achieved with difficulty.

2) Catalysts prepared with preliminary blockage of part of the Al₂O₃ surface with pyridine, after which Zn(C₂H₅)₂ was adsorbed. Special experiments indicated that the preadsorbed pyridine was entirely

*Deceased.

removed during subsequent calcination at 500°. Certain samples of this series were also prepared by two applications of pyridine and Zn(C$_2$H$_5$)$_2$. The value of the elementary area of pyridine, equal to 43.0 Å$^2$, was found experimentally.

3) Catalysts produced by the usual method of impregnation of Al$_2$O$_3$ with an aqueous solution of zinc nitrate, followed by drying at 120° and calcination at 500° in a stream of air for 2 h. The amount of ZnO applied on these samples lay within the range from 15 to 350% of surface coverage.

To clarify the question of whether there is a change in the specific surface of the catalyst during the application of Zn(C$_2$H$_5$)$_2$, a comparative determination of $t_M$ quantity was made for certain samples of the ZnO--Al$_2$O$_3$ catalysts obtained. The specific surface of the initial Al$_2$O$_3$ was measured according to the isotherms of the low-temperature adsorption of nitrogen, using the usual gravimetric adsorption method. The constancy of this value was monitored after the adsorption of ZnO by a gas chromatographic method according to the adsorption of argon from a mixture of Ar + He. It was found that the values of the surfaces of the mixed catalysts obtained practically did not differ from those determined from the initial Al$_2$O$_3$.

Investigation of the Catalytic Activity of the Samples Obtained. The catalytic activity of the ZnO--Al$_2$O$_3$ catalysts was estimated according to the decomposition of isopropanol in an adsorption layer under vacuum conditions and according to the decomposition of the same alcohol in a pulsed chromatographic system. The method of investigation in the adsorption layer permitted a comparison of the activities of these catalysts with the activity of the initial Al$_2$O$_3$, measured under the same conditions, as well as a determination of the true activation energy. This method makes it possible to determine the activity of catalysts in the summary reaction (dehydration + dehydrogenation) according to the half-decomposition period, and to estimate the degree of selectivity of the action of the catalyst, namely its dehydrogenating ability, according to the amount of hydrogen in the reaction products, readily determined by freezing out the unsaturates in liquid nitrogen. In all the experiments the degree of surface coverage with respect to isopropanol was 0.06 mM/g. As a check on reproducibility, the experiments, as a rule, were repeated twice; good coincidence of the results was observed. In the case of a discrepancy, the corresponding experiment was repeated once more. The temperature of the experiment lay within the range from 130 to 145°.

Using a different method of investigation in a chromatographic pulsed system, data were obtained on the catalytic activity under conditions more approximating the actual conditions of the dehydrogenation reaction, namely, at atmospheric pressure and temperature 250°. The total degree of decomposition of the alcohol reached 100%. In all the experiments in a chromatographic pulsed system, the weight of the catalyst sample (0.2 g) and amount of alcohol admitted (0.02 g) were constant. The reaction products were analyzed chromatographically in a stream of nitrogen, freed of traces of oxygen.

Preliminary experiments indicated that the samples of Al$_2$O$_3$ used under the conditions of the experiments did not catalyze the dehydrogenation of the alcohol. Since there were indications in the literature of a change in the activity of the catalyst depending upon the number of the pulse [6], it was demonstrated experimentally that during 30 successive pulses the yields of the reaction products remained constant. Special experiments also indicated the absence of diffusion inhibition: variation of the dimensions of the catalyst grains within the interval from 0.5 to 2 mm had no effect upon the activity of the catalyst.

DISCUSSION OF RESULTS

Figure 1 (curves 1 and 2) shows the dependence of the period of half-decomposition of isopropanol in the adsorption layer upon the degree of surface coverage of the initial Al$_2$O$_3$, calculated on the basis of chemisorbed Zn(C$_2$H$_5$)$_2$ and on the basis of ZnO formed. From Fig. 1 it is evident that as the amount of ZnO is increased, there is an increase in the half-decomposition period. However, this decrease in the activity of the catalyst is only apparent. Actually, when the portion of the surface occupied by ZnO, where the comparatively slow reaction of hydrogenation can take place, is increased, the fraction of the surface of free Al$_2$O$_3$ on which the comparatively more rapid reaction of dehydration under these conditions takes place, is reduced. This leads to an increase in the period of half-decomposition of the summary reaction, with a simultaneous increase in the dehydrogenating activity of the catalyst, expressed in an increase in the amount of hydrogen contained in the reaction products. Actually, Fig. 2 shows a gradual increase in the dehydrogenating activity of the catalysts with increasing degree of coverage of the surface of the carrier with ZnO.