INFLUENCE OF Fe–Sb–O CATALYST COMPOSITION ON THE PRODUCTS ACCOMPANYING OXIDATIVE DEHYDROGENATION OF EtPh

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Sb₂O₄ in catalysts was found to accelerate oxidation processes, whereas Fe₂O₃ the formation of other hydrocarbons in the oxidative dehydrogenation of EtPh to styrene at 800 K over catalysts of the Fe-Sb-O system.

Recently we reported /1/ that some Fe-Sb-O catalysts are active in the oxidative dehydrogenation of EtPh to styrene. Although their selectivity may be relatively high, some amounts of by-products are nevertheless formed in the process. Beside decreasing the styrene yield, by-products affect the catalyst selectivity.

Lisovskii et al. /2/ report that CO poisons the active centers of styrene formation on Al₂O₃ catalysts, whereas some basic molecules cause selectivity-increasing poisoning of Al₂O₃ by elimination of strong acidic sites, on which the combustion of EtPh rather than its conversion to styrene occurs. Therefore examination of the by-product composition seems to be justified by the necessity for a better understanding of the role of individual oxide phases in Fe-Sb-O catalysts.
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EXPERIMENTAL

Oxidative (Ox, D.) and non-oxidative (D.) dehydrogenation of EtPh were re-investigated under the same conditions and over the same catalysts as described in a previous paper /1/, in order to determine the by-products by GC. The catalyst phase composition depends on the mole fraction of Sb (x) in the catalyst sample. FeSbO$_4$ and Fe$_2$O$_3$ (slightly contaminated with other iron oxides) were X-ray detected in Fe-Sb-O oxides in which $x < 0.5$, Sb$_2$O$_4$ accompanied FeSbO$_4$ in oxides where $x > 0.5$. On grounds of the results in Ref. /1/, an Sb$_2$O$_4$-FeSbO$_4$ solid solution is likely to exist in catalysts in which $0.6 < x < 0.8$.

RESULTS AND DISCUSSION

Conversions of EtPh at 800 K to (I) benzene and toluene, (II) benzaldehyde and benzoic acid, (III) CO$_2$ and CO, are plotted against $x$ in Fig. 1 to illustrate the tendency of catalyst phases to affect the direction of side reactions in both processes considered.

Curves (I) in Fig. 1 are similar to one another in both kinds of EtPh dehydrogenations. Generally, the formation of (I) depends rather weakly on the catalyst composition, but the assumption about a non-catalytic path of this side reaction could not be taken into account since no (I) was found when the mixture of EtPh and styrene was passed through the reactor in the absence of a catalyst under the same conditions. Were (I) obtained by catalytic cracking of EtPh or styrene, the process would be followed by cyclization of part of the cracking products – aliphatic hydrocarbons – since neither they, nor their oxidation products were detected during EtPh dehydrogenation. Brønsted acid sites existing due to water adsorption on the catalyst surface might be responsible for cracking. This assumption is in line with the observed correlation between the yield of (I) and $x$ values, in accord with the possibility of water sorption on individual catalyst phases. The slight decrease in the yield of