EFFECT OF PRELIMINARY HEATING ON THE PHYSICOCHEMICAL PROPERTIES
OF 10% Co/A12O3 CATALYST AND ITS BEHAVIOR
IN HYDROCARBON SYNTHESIS FROM CO AND H2

A. L. Lapidus, A. Yu. Krylova, V. V. Kazanskii, V. Yu. Borovkov, A. V. Zaitsev, G. V. Kozlova,
A. Zukal, I. Ratkhouski, and M. Yanchalkova

The effect of preliminary heating of 10% Co/A12O3 in air at 20-600°C on its surface composition, reducibility, and adsorption properties has been studied by programmed thermal reduction (PTR), IR spectroscopy, and DTA. It has been shown that increasing the pretreatment temperature strengthens the interaction between cobalt and the carrier, resulting in an increase in the fraction of weakly bound adsorbed CO on the surface of the reduced catalyst. The activity of Co/A12O3 has been studied in the Fischer-Tropsch synthesis and it has been proposed that the centers of weakly bound linear forms of CO adsorption are involved in the formation of C2+ hydrocarbons from CO and H2.

The activity and selectivity of Co catalysts in the synthesis of hydrocarbons from CO and H2 is mainly determined by their method of preparation [1]. However, the conditions of the preliminary treatment of the sample—temperature and medium—exert a significant influence on the behavior of catalytic systems. Thus it has been established [2] that increasing the temperature of preliminary treatment (Ttr e) of 10% Co/A12O3·SiO2 in air from 20 to 400°C significantly decreases the yield of liquid hydrocarbons formed from CO and H2.

In this present study we have looked at the effect of Ttr e on the physicochemical properties of 10% Co/A12O3 and its behavior in the synthesis of hydrocarbons from CO and H2.

EXPERIMENTAL

The catalysts were prepared by impregnating γ-A12O3 grade A-64-K with aqueous cobalt nitrate solution with subsequent removal of the solvent in a stream of air at -20°C; then the samples were heated in air at 100-400°C.

All the catalysts were reduced in H2 (450°C, V = 100 h⁻¹, 5 h) and tested in an integral type catalytic flow reactor. The synthesis conditions were as follows: 0.1 MPa, 180-240°C, CO:H2 = 1:2 (by volume), V = 100 h⁻¹. Each isothermal run lasted 5 h. The total synthesis time for one sample was 35 h.

The PTR curves were obtained with an apparatus analogous to that in [3] under the following conditions: Ar + 6.5% H2 (3 ml/sec), 20-700°C (24 deg/min), weighed catalyst sample ~90 mg. Thermogravimetric measurements were made using a Netzch STA-409 (GDR) instrument in the temperature range 20-1000°C (10 deg/min). IR diffuse scattering spectra were recorded on a Perkin-Elmer 580B spectrometer.

RESULTS AND DISCUSSION

The value of Ttr e in air for the 10% Co/A12O3 catalyst had a significant effect on its properties in the synthesis of hydrocarbons from CO and H2 (Table 1). On increasing Ttr e from 20 to 400°C there was a marked increase in CO conversion accompanied by an increase in the yield of all synthesis products. The overall hydrocarbon yield increased by ~1.5 times. The selectivity toward formation of liquid products (C5+) remained constant at ~60%. However, the composition of the liquid products produced in the presence of samples...
that had been treated in air at different temperatures varied. Increasing $T_{\text{tre}}$ had virtually no effect on the olefin content but altered the ratio of branched chain to n-paraffins increasing the isoalkane content. At the same time there was a marked decrease (by a factor of 3.5) in the heavy fraction of products with more than 19 atoms per molecule ($C_{19}^+$) and an increase in the catalyzate of the light paraffin fraction, i.e., there was a decrease in the number of carbon atoms per molecule in the synthesis products.

These observations are probably linked with a variation in the surface catalytic properties of the 10% Co/Al$_2$O$_3$ samples that had been heated in air at different temperatures. At least three forms of cobalt are known to exist on a Co/Al$_2$O$_3$ surface [4, 5]: Co$_T$ formed as a result of diffusion of Co ions into the tetrahedral units of the Al$_2$O$_3$ lattice, Co$_O$ as a result of penetration into octahedral units, and Co$_3$O$_4$ not bonded to the carrier, having properties similar to those of the bulk oxide. The ratio of these forms is determined to a significant extent by the conditions under which the sample has been heated and the amount of active component deposited. These surface forms of cobalt differ in their susceptibility to reduction. In particular, Co$_T$ can be regarded as a surface spinel CoAl$_2$O$_4$ difficult to reduce even at $T > 500^\circ\text{C}$ [5]. The presence of these compounds could explain the decrease in the degree of reduction of cobalt ($R$) observed when the temperature $T_{\text{tre}}$ is raised (Table 1). This is also likely to be the reason for the lower value of $R$ (<55%) for a 10% Co/Al$_2$O$_3$ sample compared to values (up to 65%) for analogous samples based on silica gel.

In order to determine the capacity of 10% Co/Al$_2$O$_3$ for reduction the corresponding PTR curves were measured (Fig. 1). Their character changes significantly with $T_{\text{tre}}$. For the sample dried at $\sim 20^\circ\text{C}$(Co/Al$_2$O$_3$-$20^\circ\text{C}$) the PTR curve has two peaks: a very strong well-defined signal at $T_{\text{max}} = 248^\circ\text{C}$ and a diffuse one at $T > 400^\circ\text{C}$. The intensity and shape of the first signal would indicate that it characterizes the reduction of deposited cobalt nitrate on the catalyst surface probably accompanied by decomposition. Thermogravimetric analysis and DTA established that during decomposition in air Co(NO$_3$)$_2$·6H$_2$O lost 25% mass