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Abstract

Full Text

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Zirconium Dioxide and Titanium Dioxide—Promoters of a Cobalt Catalyst for the Reaction of Synthesis of Higher Hydrocarbons from Carbon Monoxide and Hydrogen

(Presented by Academician B. A. Kazanskii, 3 VIII 1962)

The process of formation of higher hydrocarbons from carbon monoxide and hydrogen, in contrast to the reactions of synthesis of methanol and methane from these same gases, proceeds with the formation of carbon-carbon bonds. In addition, as in these reactions, carbon-hydrogen bonds are formed and carbon-oxygen bonds disappear. Catalysts for hydrocarbon synthesis must therefore possess both reducing-hydrogenating and polymerization-condensation action. The former is usually effected by a metal of Group VIII of the periodic system: Co, Ni, Fe, Ru, which constitutes the main part of the catalyst; the latter, by oxides that are difficult to reduce and are added as promoters (⁀1). At elevated temperatures and pressures, however, the synthesis reaction can also be carried out in the presence of catalysts that do not contain a Group VIII metal (⁀2). This is apparently explained by the fact that under these conditions semicontact hydrogenation occurs, in which, of the two starting components of the reaction—hydrogen and carbon monoxide—only the latter is activated by the catalyst (⁀3).

Among the Group VIII metals, cobalt has acquired special importance as the basis of a catalyst for the synthesis of higher hydrocarbons from CO and H_2, and among the promoters of the cobalt catalyst—thorium dioxide. The catalyst 100 Co—18 ThO_2—100 kieselguhr, proposed by Fischer and Koch (⁀4), is the classical catalyst for the synthesis reaction and has been used in theoretical and practical studies in this field. Subsequently, Roelen replaced part of the thorium oxide in the catalyst with magnesium oxide (⁀5). The addition to cobalt of a number of other oxides (MnO, MgO, Al_2O_3, Cr_2O_3, ZnO, U_3O_8) led to poorer results in comparison with ThO_2 (⁀1).

It seemed most probable that oxides of metals close in chemical properties to thorium might exert a promoting action on a Co-kieselguhr catalyst comparable with that of thorium dioxide. From this standpoint, the most interesting to us appeared to be the oxides of metals of subgroup I of Group IV of the periodic system, to which thorium also belongs, and first of all zirconium and titanium

Fig. 1. Promotion of the Co-kieselguhr catalyst (1 : 1). 1 —catalyst without promoter; 2 —12% zirconium dioxide; 3 —18% zirconium dioxide; 4 —24% zirconium dioxide; 5 —18% titanium dioxide; 6 —18% thorium dioxide.

Figure 1: Fig. 1. Promotion of the Co-kieselguhr catalyst (1 : 1). 1 —catalyst without promoter; 2 —12% zirconium dioxide; 3 —18% zirconium dioxide; 4 —24% zirconium dioxide; 5 —18% titanium dioxide; 6 —18% thorium dioxide.

dioxides. Despite the proximity of thorium to zirconium and titanium in position in the periodic system, these metals differ somewhat in chemical properties. Thorium, as the heavier metal, gives a more basic oxide than zirconium, while titanium dioxide exhibits acidic properties. Differences are also observed in catalytic properties. Thus, ThO_2 has only a dehydrating action, whereas ZrO_2 directs the decomposition of alcohols almost equally toward dehydration and dehydrogenation, and TiO_2 toward dehydrogenation (⌢6). Recently Balandin and co-workers showed that ZrO_2 dehydrates cyclohexane and alcohols, and with respect to the latter the dehydrating action predominates considerably over the dehydrogenating action (⌢7). TiO_2, when covered with carbon, dehydrates alcohols, having lost its dehydrogenating properties (⌢8).

Zirconium and titanium dioxides have practically not been studied as···

promoters of a cobalt catalyst for the reaction of hydrocarbon synthesis from CO and H_2. Some attempts in this direction did not give positive results (9). At temperatures of 180-200° and atmospheric pressure over the catalyst $Co—Cu—ZrO_2$, liquid hydrocarbons were obtained with a yield of 27 ml/m^3 of a CO and H_2 mixture, while over the catalyst $Co—Cu—TiO_2$ even fewer liquid hydrocarbons were formed.

In the present work the promoting action of zirconium dioxide and titanium dioxide on a Co-kieselguhr catalyst in the reaction of synthesis of higher hydrocarbons from CO and H_2 at atmospheric pressure was investigated. The results obtained show that these oxides possess promoting properties which are not inferior to, and under certain conditions exceed, the promoting properties of thorium dioxide.

Fig. 1. Promotion of the Co-kieselguhr catalyst (1 : 1).
1 —catalyst without promoter; 2 —12% zirconium dioxide; 3 —18% zirconium dioxide; 4 —24% zirconium dioxide; 5 —18% titanium dioxide; 6 —18% thorium dioxide.

Experimental Part

The apparatus and procedure for carrying out the experiments on the synthesis of higher hydrocarbons from CO and H_2 did not differ from those described previously (10). The reactor was a glass tube with an internal diameter of 10 mm, placed in a catalytic furnace with an automatic temperature regulator, which made it possible to maintain the temperature within $±1.5°.Intothetubewerecharged30cm^{3}$ of catalyst, the length of whose bed was ~40 cm. The catalysts were prepared by precipitation from solutions of chemically pure metal nitrates with potash in the presence of kieselguhr. The apparent specific gravity of the catalyst was 0.40–0.42 g/cm^3; grain size, 4 × 4 mm. With each sample, after preliminary reduction with hydrogen at 375° for 8-10 hr, the synthesis reaction was carried out for 100–200 hr while increasing the reaction temperature. Experiments at one and the same temperature lasted 20–30 hr. All experiments were carried out in a flow system at a space velocity of the initial gas mixture of 90-100 hr^{-1} and atmospheric pressure, with interruptions overnight. The initial gas mixture contained CO and H_2 in a ratio of 1 : 2 and not more than 5% ballast impurities (nitrogen). Hydrogen was obtained electrolytically, and carbon monoxide by decomposition of formic acid under the action of concentrated sulfuric acid on heating. The liquid reaction products were trapped in two receivers graduated to 0.05 ml at room temperature and at −80°, respectively; in the first, reaction water and oil condensed, and in the second, gasoline and gas oil (C_2-C_4).

Table 1

Promotion of the Co-kieselguhr catalyst (1 : 1)

Promoter content, % of Co	Optimum reaction temperature, °C	Average contraction, % of initial gas	Average yield of liquid hydrocarbons (from C_5 and higher), ml/m^3	Average yield of liquid hydrocarbons (from C_5 and higher), ml/l • hr	Volume ratio benzine/oil	Average water yield, ml/m^3
Without promoter	210	55.1	56.1	5.4	18.0 : 1	143.7
12% ZrO_2	200	61.0	97.4	8.8	2.8 : 1	165.2
18% ZrO_2	210	63.7	120.9	11.2	1.2 : 1	172.0
24% ZrO_2	210	62.1	113.7	9.7	1.2 : 1	143.2
18% TiO_2	195	63.2	156.0	14.4	0.6 : 1	200.3
18% ThO_2	200	63.8	117.2	10.1	0.9 : 1	174.9

The principal results obtained in the work are given in Table 1 and in Fig. 1.

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The Co-kieselguhr catalyst (1 : 1) was promoted with 24, 18, and 12% (by weight of Co) ZrO_2, 18% TiO_2, and, for comparison, 18% ThO_2. In addition, this catalyst without a promoter was also investigated. The cobalt-thorium and cobalt-titanium catalysts were deposited on Kyshtym kieselguhr, while the others were deposited on Hanover kieselguhr. From the data presented it is evident that the unpromoted catalyst, in agreement with the literature data (11), is of low activity. At the optimum temperature of 210°, the yield of liquid hydrocarbons (C_5 and higher) is 56 ml/m^3, or 5.4 ml/l $\cdot$ h, and a light reaction product is obtained: the volume ratio of gasoline to oil is 18 : 1. The most active of the catalysts tested proved to be the catalyst promoted with TiO_2; in its presence the highest yield of hydrocarbons was obtained: 156 ml/m^3, or 14.4 ml/l $\cdot$ h, and the heaviest product: gasoline/oil 0.6 : 1 at the optimum temperature of 195°.

The most active of the cobalt-zirconium catalysts was found to be the sample containing 18% ZrO_2. Earlier (4) it was found that the same content of ThO_2 is optimal. The results obtained show that catalysts containing 18% ZrO_2 and especially TiO_2 are more active than the Co—ThO_2 catalyst.

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