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Abstract

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Directed Catalytic Synthesis of Solid Paraffin from Carbon Monoxide and Hydrogen

(Presented by Academician B. A. Kazanskii, January 7, 1963)

It has been established (1) that zirconium dioxide and titanium dioxide, like thorium dioxide (2), exert a promoting effect on a cobalt-kieselguhr catalyst in the reaction for the synthesis of higher hydrocarbons from carbon monoxide and hydrogen at atmospheric pressure. It was of interest to investigate the promotion of a cobalt catalyst by means of ZrO_2 or TiO_2 simultaneously with MgO, since among all cobalt synthesis catalysts the catalyst jointly promoted with ThO_2 and MgO has so far acquired the greatest importance (3). This is to some extent connected with the fact that partial replacement of ThO_2 by MgO leads to greater mechanical strength of the catalyst, which prevents its pulverization, the latter being the cause of local overheating and, consequently, intensified carbon and methane formation during the reaction.

In the present work it is shown that the addition of magnesium oxide to a $Co-ZrO_2$–kieselguhr or $Co-TiO_2$–kieselguhr catalyst leads to an increase in catalytic activity and stability. When the reaction was carried out over these catalysts at atmospheric pressure, as usual, mainly liquid hydrocarbons were obtained, with an insignificant amount of solid high-molecular hydrocarbons.

In continuous operation at an elevated pressure of 10 atm, the character of the process changed sharply and the reaction products consisted predominantly of solid paraffin. This made it possible to carry out directed synthesis of solid paraffin from carbon monoxide and hydrogen under relatively mild conditions (4).

The greatest tendency toward the formation of solid paraffin, as is known, is exhibited by a ruthenium-based catalyst, which is active, however, at high pressures of 100-1000 atm. At 190° and 100 atm, about 100 g/m^3 of solid paraffin and 50 g/m^3 of oil are obtained on it (5). On an iron-copper catalyst at 10 atm and a temperature of about 200°, from a gas $0.7H_2 : 1CO$ one can obtain about 100 g/m^3 of hydrocarbons, including 30 g/m^3 of solid paraffin with a boiling point above 320°, containing 17.5% oxygen-containing compounds (6).

Table 1

Synthesis of hydrocarbons from CO and H_2 at atmospheric pressure

Fig. 1

Figure 1: Fig. 1

Promoter	Duration of catalyst operation, days	Average gas contraction, %	Average yield of hydrocarbons (from C_5 and higher), g/Nm^3
ZrO_2	34	67.6	108
TiO_2	30	70.7	110

Experimental Part

Experiments on the synthesis of hydrocarbons from CO and H_2 were carried out in a flow system with an initial gas mixture containing these components in a ratio of 1 : 2. The content of ballast gases, chiefly nitrogen, did not exceed 5%. The average space velocity of the gas was 100 h^{-1}. The apparatus and the procedure for carrying out the experiments at normal pressure, which were conducted with interruptions overnight, did not differ from those described earlier ([1,7]). The reactor was a glass tube with an internal diameter of 10 mm, placed in a catalytic furnace with an automatic temperature regulator—

temperatures (±1.5°). The volume of catalyst in the tube was 30 cm^3, and the bed length was 40 cm. Experiments at 10 atm were carried out with a tubular reactor made of stainless steel with an internal diameter of 18 mm, placed in a catalytic furnace with an automatic temperature regulator ([8]). The catalyst volume was 70 cm^3. The volume of the feed gas was measured with a rheometer, and that of the exit gas with gas meters. The reaction products were condensed in a receiver at room temperature (reaction water, oil, solid paraffin) and trapped in adsorbers with activated carbon (gasoline, gas oil), from which they were distilled off with superheated steam. The catalysts were prepared by precipitation from solutions of metal nitrates with "pure" grade soda in the presence of kieselguhr (kieselguhr). They contained, per 100 parts by weight of cobalt, 6 parts of zirconium dioxide or titanium dioxide, 10 parts of magnesium oxide, and 200 parts of kieselguhr. Before reduction, the catalyst grain size was 2 × 3—4 mm. The catalysts were reduced at 400° for 10—12 h with hydrogen at a space velocity of 100 h^{-1}.

Fig. 1

The principal results obtained in this work are given in Tables 1—3, which present average values of gas contraction and hydrocarbon yields expressed in g/Nm^3. Dividing the latter by 10 gives the hydrocarbon yields expressed in g/l • h, i.e., the catalyst productivity.

Table 1 gives the results of typical experiments lasting about 30 days at atmospheric pressure and an optimum temperature of 190°. The yield of higher hydrocarbons from C_5 and above averaged 108–110 g/Nm^3, or 11 g/l • h. The maximum yield reached 12.5 g/l • h at a space velocity of 100 h^{-1}. At a space velocity of 145 h^{-1}, the catalyst productivity reached 17 g/l • h. Despite paraffin deposition on the catalysts, after 30 days of operation the yield of higher hydrocarbons was still 95 g/Nm^3 at a space velocity of 100 h^{-1}.

Table 2

Synthesis of hydrocarbons from CO and H_2 at 10 atm over the catalyst Co–ZrO_2–MgO–kieselguhr
(during intermittent operation)

Duration of catalyst operation between regenerations, days	Average gas contraction, %	Average yield of hydrocarbons (from C_5 and above), g/Nm^3	Average yield of crude paraffin removed from the catalyst during regeneration, g/Nm^3
6.5	76	93	9
4	87	82	9
3	87	94	19
4.5	77	61	26
3	75	53	–

The liquid catalyzate obtained from a catalyst containing ZrO_2 and MgO, after washing with dilute alkali and water, drying, and complete hydrogenation ([9]), was fractionated in an amount of 128 g on a column with an efficiency of 40 theoretical plates to 127°, and the residue was fractionated from a Favorskii flask. The constants of the fractions (refractive index, specific gravity, aniline point), as well as qualitative determination by means of the reaction with ferric chloride ([10]), showed that all fractions consisted mainly of aliphatic hydrocarbons of normal structure. The gasoline fraction with b.p. up to 170° amounted to 45 wt.%, the oil with a boiling range of 170–303° to 41.5%, and the solid paraffin to 10.5%. Figure 1 gives the distillation curve on the column. Similar results were obtained in the study of the catalyzate obtained from a catalyst promoted with TiO_2 and MgO.

Table 2 gives the results of experiments carried out with interruptions for

at night at 10 atm and 190° with a Co–ZrO_2–MgO catalyst. During intermittent operation of the catalyst, liquid hydrocarbons were formed mainly, with a yield of 80-95 g/nm^3; moreover, within 3-6 days the catalyst became paraffined and lost activity. The latter, however, was restored by treating the catalyst with hydrogen at 400°. During such treatment, crude solid paraffin came off the catalyst; its yield over 20 days of operation increased from 9 to 26 g/nm^3, while the yield of liquid hydrocarbons simultaneously fell from 93 to 53 g/nm^3.

Table 3

Synthesis of hydrocarbons from CO and H_2 at 10 atm
(in continuous operation)

Promoter	Time from start of catalyst operation, days	Average gas conversion, %	Average yield of liquid hydrocarbons (from C_5 and above), g/nm^3	Average yield of solid paraffin, g/nm^3	Average yield of liquid hydrocarbons (from C_5 and above), g/nm^3
ZrO_2	1	73	4	0	4
ZrO_2	3	82	42	0	42
ZrO_2	4	81	22	32	54
ZrO_2	6	79	36	66	102
ZrO_2	20	78	39	71	110
ZrO_2	25	82	38	70	108
TiO_2	1.5	82	74	0	74
TiO_2	6	89	33	42	75
TiO_2	11	83	48	63	111
TiO_2	20	86	44	57	101
TiO_2	32	84	46	59	105

Table 3 gives the results of typical experiments carried out in continuous operation at a pressure of 10 atm and 190°. From the data in Table 3 it is evident that the catalyst is developed over the course of 1.5-3 days, giving exclusively liquid hydrocarbons and gas oil (C_2—C_4), after which crude solid paraffin begins to form; this is a mixture of solid paraffin and oil, the yield of which rises to a constant value. After the catalyst has been developed, the yield of liquid hydrocarbons, consisting mainly of oil that has impregnated the solid paraffin and a small amount of gasoline hydrocarbons, was 36-48 g/nm^3; the yield of solid paraffin with b.p. above 300° was 60-70 g/nm^3; the yield of gas oil was 12-15 g/nm^3. Thus, the yield of higher hydrocarbons from C_5 and above was approximately 110 g/nm^3, and together with gas oil about 125 g/nm^3. Distribution by weight: gas oil 10-14%, liquid hydrocarbons 32-39%, solid paraffin with b.p. above 300° 50-58%.

Co—MgO—kieselguhr contacts promoted with ZrO_2 and TiO_2 are in many respects similar to the contact promoted with ThO_2, which, also when operating under a pressure of 10 atm, gives, along with liquid hydrocarbons and gas oil, significant amounts of solid paraffin. However, all other conditions being equal, the yield of solid paraffin on this catalyst is several times lower, and the reaction is not so directed in character.

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Note: Figure translations are in progress. See original paper for figures.