Brief Communications

Potassium as a promoter in the Co-based Fischer—Tropsch catalysis

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A doping effect of a Co catalyst with potassium in the Fischer—Tropsch synthesis was found to sharply decrease formation of methane, increase selectivity on the C_{5+} hydrocarbons, and increase the chain growth index.

Key words: carbon monoxide, the Fischer—Tropsch synthesis, cobalt catalysts, paraffins.

The synthesis of hydrocarbons from CO and H_2 is an important alternative process for the production of motor fuels and hydrocarbon raw materials from the non petroleum sources. Cobalt and iron catalysts are the most widely used industrially. Industrial iron catalysts contain alkaline additives, whose function is to intensify the reaction of the catalyst surface with carbon monoxide. As a result, an average molecular weight of the products increases, the yield of methane decreases, the yield of alkenes and oxygen-containing compounds increases.[1] At the same time, there is little information on the promotion of cobalt catalysts with alkali metals. It was shown that addition of potassium inhibits reduction of Co with hydrogen in the Co/SiO_2 catalyst, whereas introduction of K into the composition of Co/Al_2O_3 catalyst promotes reoxidation of Co in the atmosphere of synthesis-gas.[2] A degree of reduction of Co deposited on oxide supports on doping with potassium decreases,[3] though these data[2,3] were not compared with the results of catalytic tests. When potassium is added to a Co—Re catalyst as a promoter, the chain growth index value increases from 0.75 to 0.90, however, in this case activity of the catalyst decreases five-fold.[4]

We found that potassium as a promoter in the Co/Al_2O_3 catalyst significantly increases the average molecular weight of the products, decreases the methane selectivity without considerable decrease in activity of the catalyst.

The catalysts were prepared by impregnation of γ-Al_2O_3 (Sasol, S_{sp} = 204 $m^2\,g^{-1}$, d = 0.41 g cm^{-3}). The support fraction with the pellet sizes of 1—3 mm was impregnated with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ and KNO_3 with subsequent calcination in air at 400 °C. The active components were deposited either simultaneously, or by two successive impregnations in the following order: K, then Co. In the latter case, material was also calcined in air between the impregnation steps. Catalytic experiments were performed in a fixed-bed reactor at atmospheric pres-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1785—1786, September, 2010.
1066-5285/10/5909-1834

Table 1. The working indices of the catalysts 20%Co—K/Al_2O_3, CO/H_2 = 1/2, *P* 0.1 MPa

Entry	K/Co (mol/mol)	Depositing order of components	*T*/°C*	Conversion of CO (%)	Yield of C_{5+} /g m^{-3}	Selectivity (mol.%)		α**
						CH_4	C_{5+}	
1	0.00	Co	190	72	112	12	75	0.85
2	0.00	Co	200	94	80	29	42	0.68
3	0.01	K + Co	200	41	77	5	92	0.85
4	0.05	K + Co	200	51	93	6	86	0.86
5	0.01	(1) K, (2) Co	200	67	127	4	93	0.91
6	0.05	(1) K, (2) Co	200	75	119	9	77	0.89

*The reaction temperature.

**The chain growth index of the Anderson—Schultz—Flory distribution was determined in the range of hydrocarbons C_5—C_{20}.

sure. Before the tests, catalysts were activated directly in the reactor by passing hydrogen for 1 h at the volume rate of 2000 h^{-1} at 450 °C.

The results of catalytic tests are given in Table 1. The working indices of the unpromoted sample of 20%Co/Al_2O_3 are given for the comparison (entries *1*, *2*). Introduction of 1—5 mol.% of K calculated on Co into the catalyst composition leads to some decrease in the conversion of CO, but to a considerable increase in selectivity for the target C_{5+} hydrocarbons, and simultaneous strong suppression of the methane formation. The catalytic properties are affected by the depositing methods of the active components. Conversion of CO turned to be higher in the samples prepared by successive impregnations, respectively, increasing the yield of the C_{5+} fraction. The chain growth index α of the Anderson—Schultz—Flory distribution[5] is also considerably higher for the samples prepared by successive impregnation steps and reaches 0.91 for the 20%Co—1%K/Al_2O_3 catalyst (entry *5*). Earlier,[6] that high value of α could have been reached only at the pressure 2—4 MPa. At the same time, the selectivity on methane is little affected by the preparation method.

In conclusion, the promoter effect of K in the Co-based Fischer—Tropsch catalyst was discovered, which consists in suppression of the methane formation, increase in selectivity on the C_{5+} hydrocarbons, and increase in the average molecular weight of the products.

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Received March 29, 2010