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Influence of the Porous Structure of the Support on the Properties of Cobalt Catalysts for Hydrocarbon Synthesis from CO and H_2

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Abstract—The dependence of the properties of supported cobalt catalysts for hydrocarbon synthesis from CO and H_2 on the porous structure of the supports (aluminas and aluminosilicates) is reported. A correlation between the mean Co^0 crystallite size and the pore diameter of the support is established. The specific CO conversion rate falls sharply as the size of Co^0 particles decreases to 6 nm and below. The methane and C_{5+} hydrocarbon selectivities as a function of the Co^0 crystallite size pass through an extremum.

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Hydrocarbon synthesis from CO and H_2 (Fischer–Tropsch synthesis) is presently considered a promising method of obtaining motor fuel components, lubricants, and feedstocks for basic organic synthesis from nonpetroleum sources of carbon, such as natural gas, coal, slates, peat, and agrowaste [1–3]. The value of Fischer–Tropsch fuel fractions is largely due to their environmental friendliness. Because synthetic diesel fuel contains no unsaturated compounds and nitrogen- or sulfur-containing admixtures, its combustion emits much smaller amounts of NO_x, CO, formaldehyde, benzopyrene, and other incomplete combustion products than the combustion of the conventional fuel [4].

The Fischer–Tropsch synthesis is catalyzed by Group VIIIB metals, among which ruthenium, iron, and cobalt are the most active. Ruthenium has never been considered as a commercial catalyst because it is expensive and rare [2]. Industrial Fischer–Tropsch catalysts are based on iron or cobalt. The cobalt catalysts are viewed as being preferable for the lower temperature variant of this process (200–240°C), which is mainly intended for producing fuel and oil fractions of paraffins. As compared to the iron catalysts, they are more active, afford a higher CO conversion per pass, are not poisoned by water resulting from the synthesis, are more selective toward paraffins, and show much lower catalytic activity in the undesired water gas shift reaction [2–5].

The activity and selectivity of supported cobalt catalysts depend considerably on the nature of the support [1, 2]. The state of the active phase (cobalt) is governed both by the interaction between the precursor and the support and by the porous structure of the latter. The porous structure of the support determines the size of Co crystallites [6–12]. The extent of reduction of cobalt increases with an increasing pore size of the support. This leads to a higher specific activity of the catalyst and to a higher C_{5+} hydrocarbon selectivity [8, 9, 11, 13]. However, it was demonstrated for a number of impregnating solutions of various natures that the highest hydrocarbon yield is attained when the mean pore size of the support is 4.6–8 nm [6, 7]. Recent works of other authors [10, 12, 14] have corroborated this finding: the highest activity and the maximum higher hydrocarbon selectivity was observed for catalyst with a mean pore size of 6–10 nm. It was reported that, as the pore size of the Al_2O_3 support is increased, the reducibility of Co, CO conversion, and C_{5+} hydrocarbon selectivity decrease and the methane selectivity increases [15].

Thus, there is some uncertainty about the influence of the texture of the catalyst surface on the state of the active Co phase and on the activity of the catalyst in hydrocarbon synthesis from CO and H_2. In this study, we examined a series of Co catalysts prepared in the same way using supports with different mean pore sizes of 6 to 100 nm. The supports were aluminosilicates (SIRAL, Condea) and wide-pore Al_2O_3 (PURALOX, Sasol). Their composition and texture parameters are listed in Table 1.

EXPERIMENTAL

Catalysts were prepared by incipient-wetness impregnation of a support with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$. The resulting materials were dried in a water bath at 60–80°C and were pressed into pellets. The pellets were crushed, and the 1–3 mm size fraction was collected, which was then calcined at 400°C in flowing air for 1 h. The calculated cobalt content of the catalysts was 10 wt %. The actual cobalt content was 8.5–9 wt %, according to atomic absorption spectroscopic data. Hereafter, the samples based

Table 1. Properties of the supports used in the preparation of supported cobalt catalysts

Composition	Specific surface area, m^2/g	Specific pore volume, cm^3/g	Pore diameter, nm*	Catalyst designation
Al_2O_3	219	0.74	12	$CoAl_2O_3(12)$
Al_2O_3	172	1.19	20	$CoAl_2O_3(20)$
Al_2O_3	135	1.25	40	$CoAl_2O_3(40)$
Al_2O_3	100	1.41	100	$CoAl_2O_3(100)$
SiO_2 1.3%, Al_2O_3	304	0.60	7.9	CoAS(7.9)
SiO_2 9.5%, Al_2O_3	402	0.76	7.6	CoAS(7.6)
SiO_2 19.8%, Al_2O_3	433	0.78	7.2	CoAS(7.2)
SiO_2 30.2%, Al_2O_3	472	0.83	7.0	CoAS(7.0)
SiO_2 40.1%, Al_2O_3	498	0.74	5.9	CoAS(5.9)

* For the aluminosilicates, the pore diameter was calculated in the cylindrical pore approximation.

on Al_2O_3 and aluminosilicates are designated $CoAl_2O_3$(xx) and CoAS(xx), respectively. The number in parentheses will indicate the mean pore diameter of the support in nanometers (Table 1).

The specific surface area of cobalt metal in the reduced catalysts was determined using a GC-type setup by measuring the oxygen uptake from a pulsed 10% O_2 + He mixture at −78 and 400°C. It was assumed that oxygen is sorbed by Co^0 in a 1 : 1 ratio at −78°C and that the entire cobalt is oxidized into Co_3O_4 at 400°C. From the oxygen uptake data, we derived the extent of reduction of cobalt (R_{Co}) and the degree of dispersion of cobalt metal (D_{Co}). The mean diameter of Co^0 crystallites was calculated under the assumption that the particles are spherical [16].

Catalytic tests were performed in a fixed-bed quartz reactor. A 20-cm^3 catalyst sample was activated in the reactor with flowing H_2 at 450°C for 1 h. After the reduction of cobalt, synthesis gas ($CO : H_2 = 1 : 2$) was fed into the reactor while raising the temperature from 160 to 190°C in 10-K steps, operating for 5 h at each temperature point. The catalysts were compared in terms of their performance at 190°C. The condensable products of the synthesis were collected in a flowing water–cooled receiver and in a liquid-nitrogen trap placed in series downstream of the reactor.

The gaseous products of the synthesis—CH_4, C_2, C_3, C_4, and CO_2—were analyzed by gas chromatography (LKhM-80 chromatograph, 1 m × 3 mm columns packed with molecular sieve 5A (for CH_4 and CO) and Porapak Q (for C_2, C_3, C_4, and CO_2), 1 m × 3 mm column packed with activated carbon SK-4, helium as the carrier gas, thermal-conductivity detector).

Table 2. Oxygen titration data for catalysts reduced with H_2 at 450°C

Catalyst	O_2 uptake, μmol/g		R_{Co}, %	D_{Co}, %
	−78°C	400°C		
$CoAl_2O_3(12)$	93	591	54	10.5
$CoAl_2O_3(20)$	104	790	72	8.8
$CoAl_2O_3(40)$	106	984	90	7.2
$CoAl_2O_3(100)$	101	997	91	6.8
CoAS(7.9)	180	610	56	19.7
CoAS(7.6)	210	783	72	17.9
CoAS(7.2)	289	928	85	20.8
CoAS(7.0)	317	606	56	34.9
CoAS(5.9)	341	735	67	30.9

RESULTS AND DISCUSSION

The active phase in hydrocarbon synthesis is cobalt metal that forms from Co_3O_4 on the surface as a result of catalyst activation with hydrogen [1–3]. Measurements of oxygen chemisorption by reduced samples demonstrated that, for catalysts supported on wide-pore Al_2O_3, the extent of reduction of Co increases with an increasing pore size and reaches 90–91% for $CoAl_2O_3(40)$ and $CoAl_2O_3(100)$. Conversely, the degree of dispersion of Co^0 crystallites decreases. For aluminosilicate-supported catalysts with different SiO_2 contents, the pore diameter varies in a narrower range and there seems to be no simple correlation between the extent of reduction of Co and the pore diameter (Table 2). The Al_2O_3, SiO_2, and aluminosilicate phases are present on the surface of these supports in different proportions, which are determined by the total SiO_2 content [17]. Obviously, the reducibility of Co depends not only on the porous structure of the support, but also on the chemical composition of the support surface.

The mean size of Co^0 crystallites increases with an increasing pore diameter of the support. For all samples, the mean crystallite size does not exceed 75% of the mean pore diameter, indicating that the metal is localized inside the porous structure of the support

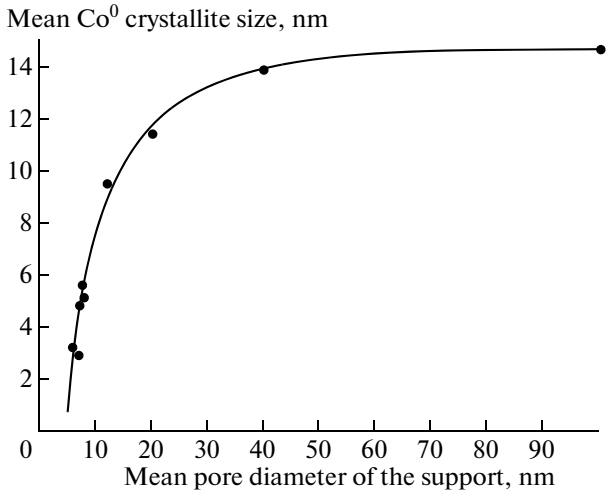

Fig. 1. Mean Co^0 crystallite size as a function of the mean pore diameter of the support.

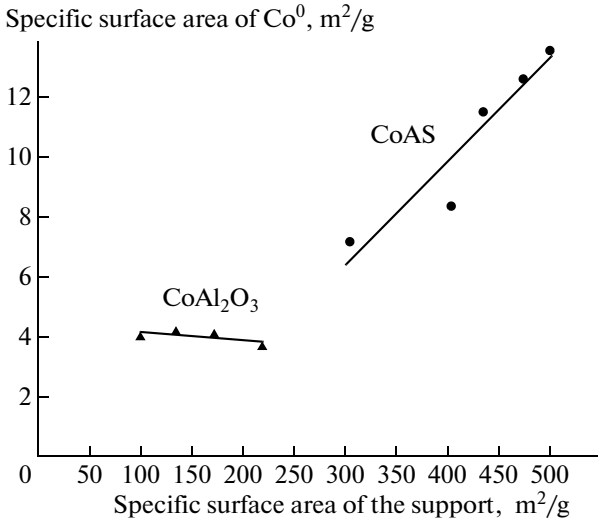

Fig. 2. Correlation between the specific surface area of Co^0 and the specific surface area of the support.

even in the case of the narrow-pore aluminosilicates. The observed dependence of the crystallite size on the pore size is nearly linear in the 6–20 nm pore size range, which is in agreement with data reported by other authors [10, 11]. For the wide-pore Al_2O_3 supports, the Co^0 crystallite size grows less rapidly than the pore diameter and plateaus at a pore diameter of 5 nm (Fig. 1). It is likely that the determining factor in the formation of an active surface on wide-pore supports is the catalyst preparation thermal conditions rather than the pore size. As a consequence, the surface area of cobalt metal in the $CoAl_2O_3$ catalysts is practically independent of the specific surface area of the support and is ~4 m^2/g, while that of cobalt metal in the catalysts supported on the narrow-pore aluminosilicates increases markedly with an increasing specific surface area of the support and with an increasing SiO_2 content of the support (Fig. 2).

The results of the catalytic tests are presented in Table 3. The CO conversion at 190°C varies between 16 and 67%. The catalysts supported on wide-pore Al_2O_3 are more active than the catalysts supported on the narrow-pore aluminosilicates. The maximum conversion is attained with the $CoAl_2O_3$(40) catalyst, whose support has a pore-diameter distribution mode at 40 nm.

The specific CO conversion rate (turnover frequency, TOF) was calculated as the CO conversion rate normalized to the number of CO metal atoms on the surface of the reduced catalyst. For the Al_2O_3-supported catalysts, TOF at 190°C varies in the $(2.6–3.7) \times 10^{-3}$ s^{-1} range. The aluminosilicate-supported catalysts are much less active, with TOF = $(0.4–0.8) \times 10^{-3}$ s^{-1} (Table 3).

Iglesia [18] demonstrated by extensive experimental data that CO hydrogenation on SiO_2-, Al_2O_3-, and TiO_2-supported cobalt catalysts is a structure-insensi-

Table 3. Results of catalytic tests in the Fischer–Tropsch synthesis at $T = 190$°C

Catalyst	CO conversion, %	Selectivity, %				Specific CO conversion rate $\times 10^3$, s^{-1}
		CH_4	$C_2–C_4$	C_{5+}	CO_2	
$CoAl_2O_3$(12)	47	5	4	90	1	2.60
$CoAl_2O_3$(20)	58	11	8	80	1	2.92
$CoAl_2O_3$(40)	67	12	12	75	1	3.74
$CoAl_2O_3$(100)	51	14	13	72	1	2.58
CoAS(7.9)	16	5	5	88	2	0.42
CoAS(7.6)	23	4	3	91	2	0.61
CoAS(7.2)	22	6	5	88	1	0.44
CoAS(7.0)	30	7	8	84	1	0.67
CoAS(5.9)	34	8	9	83	0	0.77

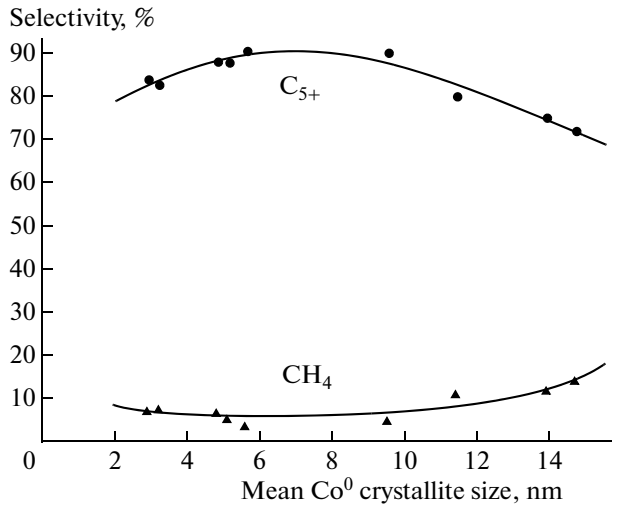

Fig. 3. Molar CH_4 and C_{5+} selectivities as a function of the Co^0 crystallite size.

tive reaction and that its rate is independent of the degree of dispersion of Co in the 0.5–12% range. However, the rate of this reaction on finely dispersed catalysts is lower [19, 20]. This observation was confirmed by recent studies [21, 22]. The rate of CO conversion on Co particles smaller than 7 nm is lower than is observed for larger crystallites [22]. In our study, the mean Co crystallite size in the CoAS catalysts was determined to be below 6 nm. It is likely due to this fact that the CO conversion rate on these catalysts is lower than that on the $CoAl_2O_3$ catalysts. Another plausible explanation is that the nature of the metal–support interaction changes on passing from alumina to the mixed oxide $SiO_2 \cdot Al_2O_3$. This issue needs further investigation.

The low specific activity of the finely dispersed catalysts can be due to the oxidation of small Co crystallites by water present in the reaction mixture. It was demonstrated that the addition of water vapor to synthesis gas rapidly deactivates the cobalt catalyst and that smaller crystallites are oxidized more rapidly than larger crystallites [23, 24]. Thermodynamic calculations confirmed that spherical Co particles smaller than 4.4 nm would be oxidized quickly by water vapor under Fischer–Tropsch conditions and larger particles would be more resistant to oxidation [25]. Along with the oxidation of the small Co particles, their interaction with oxides on the surface, which shifts electron density from Co^0 to the oxide phase, can also affect their reactivity [6].

Catalytic tests demonstrated that the highest molar selectivity with respect to the target hydrocarbons C_{5+} is 88–90% and is observed for catalysts whose support has a mean pore diameter of 7–12 nm. The same samples show the lowest methane selectivity, 5–7% (Table 3). Catalysts with smaller or larger pore sizes are less selective toward C_{5+} and more active in methane formation. The C_{5+} selectivity as a function of the Co crystallite size passes through a maximum at 6–10 nm (Fig. 3).

The effect of the pore size on selectivity can partly be explained in terms of diffusion limitations. The transport of CO molecules in the narrow-pore catalysts is hindered to a greater extent than the transport of more mobile H_2 molecules. As a consequence, the effective H_2 : CO ratio at the active sites is larger. This is favorable for the reactions consuming larger amounts of hydrogen—methanation and the formation of lower hydrocarbons. However, the presence of an extremum in the plot of selectivity versus the particle size of the metal (Fig. 3) can hardly be accounted for by the above considerations. It is possible that the polymerizing function of the catalyst declines with an increasing crystallite size because of the weakening interaction between Co^0 and the surface oxides, according to the views presented in our earlier work [6]. This inference is corroborated in part by the results of Khasin et al. [26], who demonstrated that the Anderson–Schulz–Flory distribution parameter α for the resulting hydrocarbons decreases monotonically as the mean particle size of the active metal increases from 5 to 150 nm.

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