Cobalt-zeolite catalysts for the synthesis of hydrocarbons from CO and H_2

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Catalysts prepared by mechanical mixing of high-silica zeolite ZSM-5 with cobalt oxide Co_3O_4, basic cobaltous carbonate, and cobaltous carbonate were studied. The nature of the cobalt compound introduced into the mixture affects the catalytic and physicochemical properties of the catalyst. The presence of Co_3O_4 in the sample (introduced as oxide or obtained by thermal decomposition of the carbonate) is favorable to the formation of aromatic compounds from CO and H_2. The use of cobaltous carbonates for the preparation of catalysts results in development of the porous structure of the catalyst. During preparation of samples, the mechanical treatment partially destroys the zeolite framework of the support.

Key words: synthesis of hydrocarbons, hydrogenation of CO, Co catalysts.

Cobalt catalysts prepared by mechanical (dry) mixing of components are used for the direct synthesis of aromatic hydrocarbons from CO and H_2.[1,2] These bifunctional systems normally contain Co_3O_4 (for obtaining hydrocarbons from synthesis gas) and the H-form of high-silica zeolite pentasil (for performing aromatization). The necessity of retaining the H-form of the catalysts determines the choice of the procedure for preparing a catalyst. In the presence of these systems, hydrocarbons containing up to 60—70 wt % of aromatic compounds are formed, the yield of which is yet no more than 15—20 g m^{-3}. It is also known[3,4] that analogous catalysts prepared by the coprecipitation or wet mixing method (*i.e.*, with the use of basic cobaltous carbonate) and promoted with magnesium oxide make it possible to synthesize aliphatic hydrocarbons from CO and H_2 in a yield of 150—170 g m^{-3}.

In this work, we compare the activity and physicochemical properties of Co catalysts prepared by dry mixing of the H-form of high-silica HZSM-5 zeolite with cobaltous carbonate or Co_3O_4.

Experimental

The H-form of ZSM-5 zeolite ($SiO_2 : Al_2O_3 = 38$) prepared by calcination of the NH_4-form of ZSM-5 in air at 500 °C for 8 h was used for preparing catalysts. To obtain the homogeneous mixture, the components of the catalyst were thoroughly ground in a mortar for 12—15 h, the mixture was tableted and then crushed, and a 3—4-mm fraction was taken.

Samples were first reduced in a hydrogen flow ($w = 100\ h^{-1}$) at 450 °C for 5 h. The catalytic reaction was performed in a flow-type apparatus at $p = 0.1$ MPa, $CO:H_2 = 1:2$ (vol.), and $w = 100\ h^{-1}$. The temperature was varied from 200 to 300 °C, increasing by 10 °C every 6 h.

Initial compounds and the products of the synthesis were analyzed by GLC using a procedure similar to that described previously.[2]

Thermogravimetric studies were performed in an argon atmosphere on a Netzsch STA-409 instrument. The temperature was increased from 20 to 1200 °C at the rate of 10 °C per min.

Adsorption isotherms of cyclopentane were recorded on an Accusorb 2100 instrument (Micromeritics, USA) at 20 °C. Samples were evacuated to 10^{-4} Pa at 200 and 400 °C.

Results and Discussion

From the data given in Table 1, it follows that the activity and selectivity of Co catalysts prepared by dry mixing of components depend on the nature of the cobalt compound introduced into the mixture. Catalysts based on Co_3O_4 are characterized by a low total yield of hydrocarbons and low selectivity of the formation of liquid products. However, these liquid products contain more than 60 wt % of aromatic compounds (mainly benzene, toluene, and xylenes). When basic cobaltous carbonate (BCC) and cobaltous carbonate (CC) were used for preparing the catalysts, an increase in the yield of liquid hydrocarbons (up to 42 g m^{-3}, when CC was used) and in the selectivity of their formation (44—56 %) was observed. However, in this case, the concen-

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Table 1. Effect of the initial cobalt compound and oxide aditives on the activity of zeolite-containing Co catalysts in the synthesis of aromatic hydrocarbons from CO and H_2

Initial Co compound	Additives	Concentration of the oxide additive in the catalysts (%)	Temperature /°C	Conversion of CO (%)	Yields of hydrocarbons/g m^{-3}				Concentration of aromatic compounds (%)
					C_1	C_2—C_4	C_{5+}	Total	
Co_3O_4	—	—	280	56	28.3	11.3	12.1	51.4	66.0
BCC	—	—	220	25	7.9	6.2	18.2	32.3	31.9
CC	—	—	240	42	32.0	20.9	41.8	94.7	41.8
CC	$MgCO_3$	3MgO	240	36	25.1	11.4	25.5	62.0	18.9
CC	$Zr(NO_3)_2$	$2ZrO_2$	220	32	11.1	10.1	34.1	60.3	15.5
CC	$La(NO_3)_2$	$2La_2O_3$	220	44	16.8	13.8	46.7	77.3	13.6

Note. [Co] = 30 wt %, $p = 0.1$ MPa, CO : H_2 = 1 : 2 (vol.), $w = 100\ h^{-1}$.

tration of aromatic compounds decreases substantially and becomes 32 and 42 % for BCC and CC, respectively.

The introduction of 2—3 wt % of magnesium, zirconium, and lanthanum oxides into the catalyst leads to enhancement of the selectivity of the formation of liquid hydrocarbons; however, the yield of these products and the concentration of aromatic compounds decrease.

The regularities obtained can be explained qualitatively by comparing the results of catalytic studies with the results of adsorption measurements and thermogravimetric analysis.

The isotherm of adsorption of cyclopentane on the catalyst prepared from CC and evacuated at 200 °C is similar in character to the isotherm obtained for the Co_3O_4/HZSM-5 catalyst (Fig. 1). For both samples, at the relative pressure $p/p_s < 0.05$ (where p and p_s are the equilibrium pressure and the pressure of saturated vapor of adsorbate, respectively), the isotherms obtained correlate with the curve of adsorption on pure zeolite and characterize the adsorption of cyclopentane in micropores of the zeolite carrier. In the range $0.05 < p/p_s < 0.35$, combined adsorption in zeolite micropores and on the mesopore surface of the catalyst occurs. When $p/p_s > 0.35$, hysteresis characterizing capillary condensation of cyclopentane vapor in mesopores was observed for the synthesized catalysts. The calcination of the cobaltous carbonate/HZSM-5 sample at 400 °C leads to an increase in the hysteresis loop, which is determined by the formation of a looser structure of the catalyst and an increase in the mesopore fraction. According to the results of thermogravimetric analysis, this results from decomposition of cobaltous carbonate. By contrast, the form of the adsorption isotherm for the Co_3O_4/HZSM-5 catalyst is almost independent of the temperature at which the sample is evacuated.

Therefore, the use of CC and BCC for preparing bifunctional catalysts by the dry mixing method makes it possible to substantially enhance the porosity of catalytic systems, which leads to an increase in the yield of liquid hydrocarbons. However, despite the extensive surface, the BCC/HZSM-5 catalyst exhibits lower activity than the CC/HZSM-5 catalyst. This fact suggests that the formation of the extended surface of Co catalysts for the synthesis of aromatic hydrocarbons from CO and H_2 is a necessary but insufficient condition for their efficient action. The nature of the carbonates used or, more precisely, the compounds formed from these

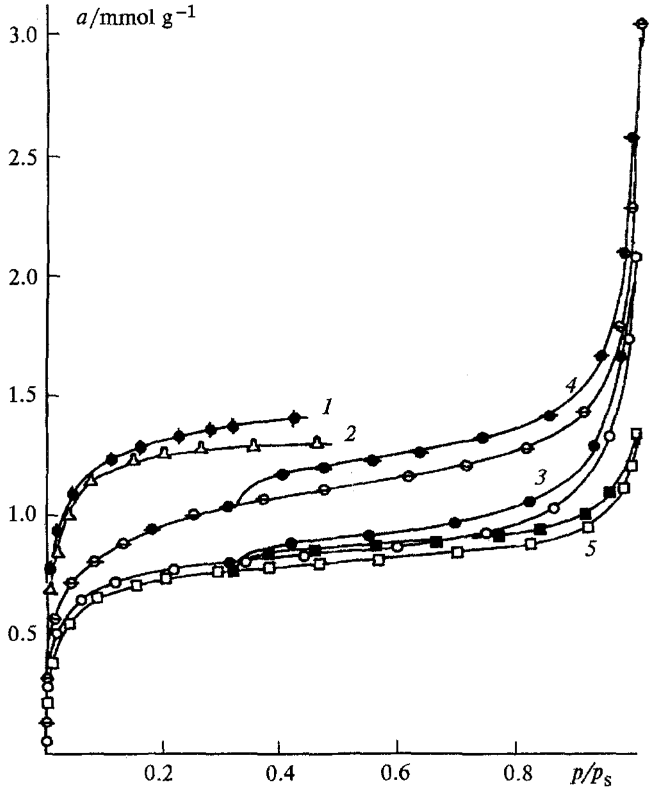

Fig. 1 Adsorption isotherms of cyclopentane in the samples: *1, 2,* initial HZSM-5 and HZSM-5 obtained after mechanical treatment for 3 h, respectively; *3, 4,* CC/HZSM-5 evacuated at 200 and 400 °C, respectively; *5,* Co_3O_4/HZSM-5 (solid circles and squares on isotherms *3-5* correspond to desorption).

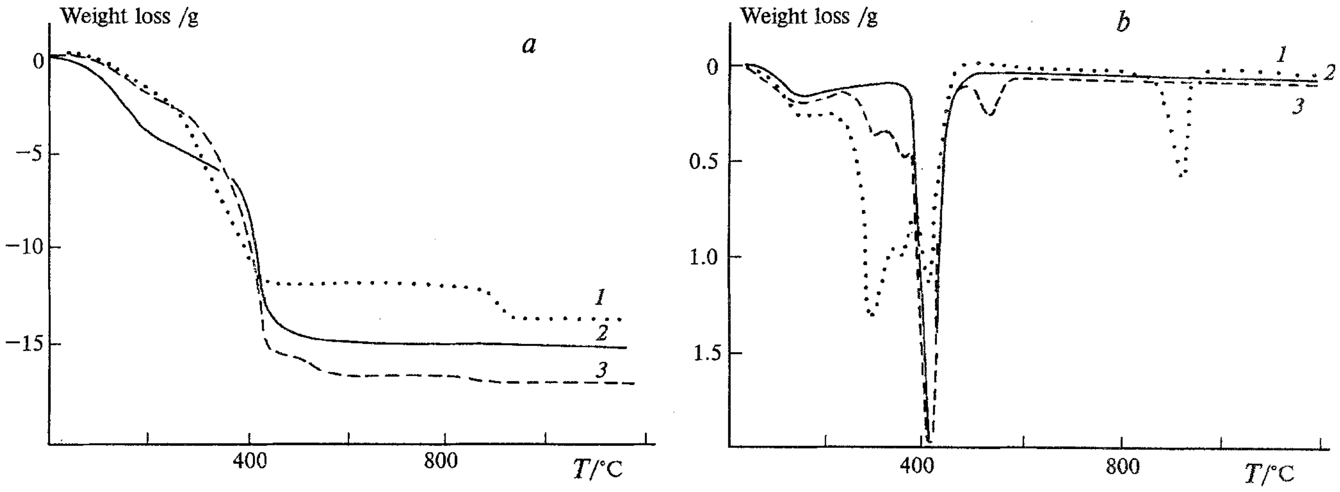

Fig. 2. TG (*a*) and DTG (*b*) curves for the samples: *1*, CC/HZSM-5; *2*, BCC/HZSM-5; *3*, CC + $MgCO_3$/HZSM-5.

carbonates by decomposition during pretreatment (reduction) are of great interest.

Figure 2 shows the results of derivatographic investigation of some catalysts under study. When temperature increases from 300 to 400 °C, a substantial weight loss indicative of the decomposition of the corresponding carbonates was observed for all samples, except for Co_3O_4/HZSM-5, in inert media. However, a substantial weight loss at ~400 °C in the decomposition of BCC corresponds to the formation of CoO, whereas the decomposition of CC/HZSM-5 is more complex and proceeds with a stepwise weight loss of cobaltous carbonate in the temperature range 300—400 °C (see Ref. 5) and the formation of Co_3O_4 at the last stage. In turn, at ~900 °C Co_3O_4 is converted to CoO, as evidenced by the appearance of signals in the TG—DTG curves for the Co_3O_4/HZSM-5 and CC/HZSM-5 catalysts. Therefore, the decomposition of basic cobaltous carbonate under conditions of pretreatment of the catalyst (450 °C) affords CoO, while the decomposition of cobaltous carbonate affords Co_3O_4. The comparison of these data with the results of catalytic studies given in Table 1 suggests that the presence of CoO is favorable to an increase in the total yield of liquid hydrocarbons, while the presence of Co_3O_4 favors the formation of aromatic compounds. This suggestion is confirmed by the results of derivatographic studies of the CC+$MgCO_3$/HZSM-5 catalyst (see Fig. 2). The DTG curve for this sample, while being slightly more complex, differs little in character from the curve for the decomposition of BCC/HZSM-5 and is indicative of the formation of CoO at the surface. When the CC+$MgCO_3$/HZSM-5 catalyst is used, the presence of basic magnesium oxide, which is formed from $MgCO_3$ during decomposition, in a catalyst sample substantially decreases the concentration of aromatic compounds in the products of synthesis.

The method of sample preparation in addition to the nature of the components used affects the properties of bifunctional Co catalysts prepared by the dry mixing method. Figure 3 shows the results of comparative analysis of the adsorption isotherms of cyclopentane performed according to the method described previously.[6] The curves were calculated from the adsorption isotherms for the corresponding samples and the standard (pure zeolite not subjected to mechanical treatment)

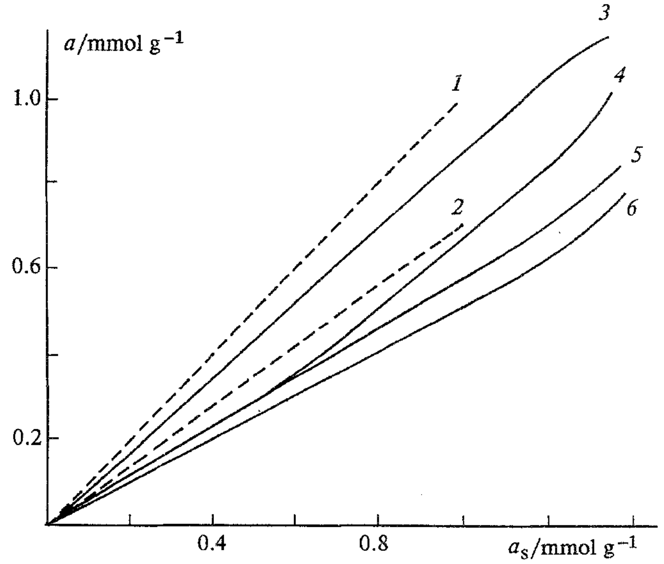

Fig. 3. Comparison of adsorption capacity of the samples studied relative to the HZSM-5 zeolite contained in the catalyst: *1*, *2*, theoretical curves for the initial zeolite (standard) and 30 % cobalt catalyst, respectively; *3*, HZSM-5 after mechanical treatment for 3 h ; *4*, *5*, CC/HZSM-5 evacuated at 200 and 400 °C, respectively; *6*, Co_3O_4/HZSM-5.

obtained under analogous conditions. When the sample under study and the standard are identical in the a—a_s coordinates (where a and a_s are adsorption of cyclopentane at equal values of p/p_s for the studied sample and the standard, respectively), we have a straight line (see Fig. 3, line *1*), for which $a = a_s$ and $f'(a_s) = 1$. The slope of this line may decrease with increasing concentration of a cobalt component in zeolite.

For HZSM-5 zeolite mechanically treated for 3 h, $f'(a_s)$ is 0.87 (see Fig. 3, line *3*), *i.e.*, 13 % of zeolite loses adsorption capacity because of destruction. For catalysts containing CC, the curves obtained in the a—a_s coordinates for a_s <0.3 mmol g^{-1} are identical and characterize adsorption in the channels of zeolite, which is a constituent of the catalyst (see Fig. 3, lines *4* and *5*), whereas for a_s >0.5 mmol g^{-1}, a departure from linearity because of capillary condensation of the adsorbate in mesopores of the catalytic system is observed. When a catalyst containing 30 % of Co is used, the slope of the linear regions of the obtained curves would be 0.7 (see Fig. 3, line *2*); however, in fact, $f'(a_s)$ in this region is 0.57, *i.e.*, ~18 % (0.7—0.57/0.7) of zeolite is destroyed. An even greater departure from the theoretical curve is observed for the Co_3O_4/HZSM-5 sample. In this case, $f'(a_s) = 0.5$, which corresponds to the destruction of ~28 % of the zeolite contained in the catalyst.

Therefore, when mechanical (dry) mixing of components is used for the preparation of bifunctional cobalt—zeolite catalysts, a substantial departure of the adsorption isotherms for the catalysts from the adsorption isotherm for the initial sample is observed, which points to the fact that, under the mechanical action, a portion of zeolite loses adsorption capacity because of destruction, the degree of which depends on the duration of this action on the sample.

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