IRON/ZEOLITE CATALYSTS FOR SYNTHESIS OF HYDROCARBONS FROM CO AND H_2

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Catalysts obtained by deposition of $Fe_3(CO)_{12}$ on HY or NaY zeolite are active in the synthesis of C_1-C_5 alkanes from CO and H_2 at 250°C and 20 atm [1]. The catalyst based on NaY is more active than that based on HY. Catalysts obtained by deposition of Fe carbonyls on Al_2O_3 promoted with KOH give C_1-C_3 alkanes and C_2-C_3 alkenes in the synthesis reaction with CO and H_2 at 350-450° and atmospheric pressure [2]. An increase in the potassium content leads to an increase in the CO conversion and a decrease in the relative amount of olefins in the synthesis products. The influence of the zeolite structure on the properties of the Fe/zeolite catalysts has not been studied adequately.

The present work has been aimed at investigating the influence of the nature of a bivalent cation, introduced into Y zeolite by ion exchange, on the activity and selectivity of catalysts obtained by deposition of $Fe(CO)_5$ on zeolite, in the synthesis of hydrocarbons from CO and H_2 at 300-400°C and atmospheric pressure.

EXPERIMENTAL

In this work we used MY zeolites obtained by ion exchange from NaY zeolite, replacing the Na^+ by a cation M^{2+} (Be, Mg, Ca, Sr, Ba), following a procedure given in [3]. The Na^+ was 67-73% replaced by M^{2+}, as determined by flame photometry. In the preparation of the catalysts, 2-5 g of the zeolite was heated for 5 h at 400°C in a vacuum adsorption unit (10^{-3} mm Hg). After cooling, the sample was treated for 12 h with $Fe(CO)_5$ vapor at 20°C, after which the catalyst was pumped down at 20°C. The treatment was considered complete when the sample arrived at a constant weight (as checked by means of a McBain balance).

In the experiments on the synthesis of hydrocarbons from a mixture of CO and H_2 (1:2 volume ratio) at atmospheric pressure in a flow unit, the catalysts were first vacuum-conditioned at 20°C. A 1-2 g sample of the catalyst was placed in the quartz reactor, and the mixture of CO and H_2 was passed through at a space velocity of 100 h^{-1}. The reaction products were analyzed by GLC. The main reaction products were C_1-C_3 alkanes, with small amounts of C_4H_{10} and C_2-C_3 alkenes. The products also contained CO_2.

The IR spectra of the catalysts were taken in white mineral oil (KBr glasses) in a Specord 75-IR spectrophotometer.

DISCUSSION OF RESULTS

It was shown in [4] that when $Fe(CO)_5$ is chemisorbed on CaY zeolite, trinuclear and tetranuclear carbonylferrates are formed. According to [1, 5], when $Fe(CO)_5$ is chemisorbed on HY zeolite, chemisorbed $Fe_3(CO)_{12}$ is localized in the void spaces of the zeolite. The chemisorption of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ on more basic supports such as MgO leads to the formation of $[HFe_3(CO)_{11}]^-$ [6].

Since carbonylferrate cluster anions are formed from $Fe(CO)_5$ under the influence of alkaline agents [7], we can assume that the increase in basicity of Y zeolite when the change is made from HY to $M^{2+}Y$ will lead to conversion of the originally adsorbed $Fe(CO)_5$ to the carbonylferrate, by analogy with the behavior of iron carbonyl in alkaline solutions. On HY zeolite, $Fe_3(CO)_5$ is formed, but on $M^{2+}Y$ zeolites the anions $[HFe_3(CO)_{11}]^-$, $[Fe_3(CO)_{11}]^{2-}$, and $[Fe_4(CO)_{13}]^{2-}$.

The quantity of chemisorbed $Fe(CO)_5$ is practically independent of the nature of the alkaline-earth metal cation and is apparently determined by the structure of the matrix of the Y zeolite. The content of Fe after pumping down the catalysts at 20°C is 9-12%.

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TABLE 1. CO Conversion and Composition of Hydrocarbons Obtained from CO and H_2, in Relation to Temperature ($CO:H_2$ = 1:2, space velocity 100 h^{-1}, 1 atm)

Zeolite	T., °C	K_{CO}, %	Content of hydrocarbons, %				$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
			CH_4	$C_2H_4+C_2H_6$	$C_3H_6+C_3H_8$	C_4H_{10}		
BeY	350	2	79	14	5 *	2	10,1	–
	375	5	75	17	6 *	2	8,6	–
	400	11	80	15	4 *	1	5,9	–
MgY	350	2	80	14	6	Traces	8,3	30,0
	375	4	78	15	7	»	8,0	24,6
	400	18	81	13	6	»	4,3	15,2
CaY	350	3	77	17	5	1	5,3	4,8
	375	6	74	18	7	1	5,2	2,4
	400	22	77	16	6	1	3,0	1,4
SrY	350	7	73	20	7	Traces	5,1	11,4
	375	16	65	28	7	»	3,8	10,1
	400	31	71	20	9	»	3,3	5,2
BaY	350	13	58	25	17	»	2,5	7,5
	375	46	54	26	20	»	1,0	4,0
	400	78	74	16	10	»	0,2	1,0

*Content of C_3H_6.

It can be assumed that the chemisorbed carbonylferrate anions, which have diameters of 12-13 Å, are localized in the large void spaces of the zeolite. The diameter of the large void space in Y zeolite is 13 Å, and the aperture dimension is 7.4 Å. Therefore, no more than one anion can be placed in each void space.

Thermal decomposition of carbonyl complexes of Fe chemisorbed on HY zeolite leads to the formation of Fe^{2+} ions [5]. NaY zeolite stabilizes Fe in the zero-valent state [1]. It has been suggested [1, 5] that the oxidation of Fe(0), the form in which it exists in $Fe(CO)_5$ to Fe(II) is due to its interaction with protons of the OH groups of the zeolite. With respect to their concentration of OH groups, the Y zeolites containing bivalent cations are intermediate between HY and NaY zeolites. Thus, in the catalysts under investigation, upon thermal decomposition of the carbonylferrate anions, both Fe(0) and Fe(II) could be formed.

Our studies of the properties of Fe/MY catalysts, obtained on the basis of $Fe(CO)_5$, in the synthesis of hydrocarbons from CO and H_2 have shown that the activity and selectivity of the catalysts depend on the nature of the alkaline earth metal (Table 1). The catalysts can be ranked in the following order of increasing activity in hydrocarbon synthesis: BeY < MgY < CaY < SrY < BaY. This ranking is the same as that of the basis properties of the MY zeolites used as the supports. Thus, the increase in basicity of the Y zeolite as the change is made from Be^{2+} to Ba^{2+}, with an identical content of Fe in the catalyst, leads to an increase in the catalyst activity.

The nature of the zeolite also influences the composition of the synthesis products, the main products being C_1-C_4 hydrocarbons (Table 1). The highest selectivity in the formation of C_2-C_4 hydrocarbons is shown by the Fe/BaY catalyst. For all of the catalysts examined, an increase in the synthesis temperature from 350 to 400°C leads to an increase in CO conversion (K_{CO}). The content of methane in the synthesis products remains unchanged, and the olefin/paraffin ratio decreases.

At 300 and 325°C, the catalysts based on BeY, MgY, CaY, and SrY are essentially inactive, with K_{CO} < 2%. For the Fe/BaY catalyst, K_{CO} at 300 and 325°C is 4 and 8%, respectively. Along with the increase in catalyst activity in the series BeY < MgY < CaY < SrY < BaY, there is a considerable decrease in the olefin/paraffin ratio. For example, the C_2H_4/C_2H_6 ratio for the Fe/BeY catalyst is in the range from 10.1 down to 5.9, and for the Fe/BaY catalyst, from 2.5 to 0.2. The change in the C_3H_6/C_3H_8 ratio for all of the zeolites, with the exception of the CaY, is analogous to the change in the C_2H_4/C_2H_6 ratio. Thus, the highest values of the olefin/paraffin ratio are characteristic for the least active catalysts based on BeY and MgY. In contrast, the Fe catalysts containing CaY, SrY, or BaY are characterized by a higher content of olefins in the catalysate.

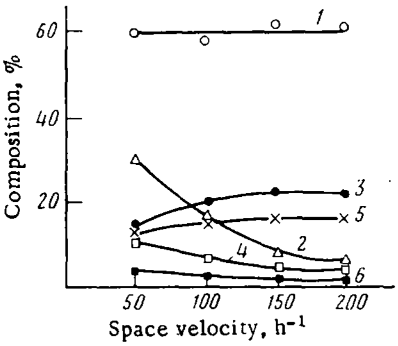

Fig. 1. Hydrocarbon composition and K_{CO} as functions of original gas space velocity: 1) CH_4; 2) K_{CO}; 3) C_2H_4; 4) C_2H_6; 5) C_3H_6; 6) C_3H_8. Fe/BaY catalyst, $CO:H_2 = 1:2$, 350°, 1 atm.

For the Fe/BaY catalyst, an increase in the space velocity from 50 to 200 h^{-1} at 350°C results in a decrease of K_{CO} from 30% to 6% (Fig. 1). Simultaneously, the contents of ethylene and propylene in the synthesis products increase, and the relative amounts of ethane and propane decrease. The content of methane remains practically unchanged. For the Fe/BeY and Fe/MgY, an increase in the space velocity in this same range has practically no effect on the composition of the synthesis products. We can assume that the increase in the relative amounts of ethane and propane in the synthesis products with the Fe/BaY catalyst is due to hydrogenation of the ethylene and propylene formed during the course of synthesis from CO and H_2. Therefore, an increase in the space velocity with an increase in the linear velocity in the case of the Fe/BaY catalyst leads to a decrease in K_{CO} and also to an increase in the olefin/paraffin ratio (Fig. 1). On the other hand, the catalysts that are less active in CO hydrogenation (Fe/Bay and Fe/MgY) probably manifest low activity in olefin hydrogenation as well, and this is apparently the explanation for the negligible influence of the space velocity on the olefin/paraffin ratio.

Thus, the basicity of Y zeolite has a decisive influence on the activity and selectivity of the catalysts that we have investigated. The BaY, which is the most basic of these zeolites, can be used to prepare a catalyst with high activity in synthesis from CO and H_2.

CONCLUSIONS

1. Catalysts obtained by deposition of $Fe(CO)_5$ on Y zeolites containing bivalent cations are active in the synthesis of C_1-C_4 hydrocarbons from CO and H_2 at 300-400°C and atmospheric pressure. The activity of the iron-containing catalysts increases in the same order as the increase in basicity of the cation: BeY < MgY < CaY < SrY < BaY.

2. The content of C_2-C_3 olefins in the products from synthesis at 350-375°C on the iron-containing zeolites increases in the series BeY < MgY < CaY < SrY < BaY.

LITERATURE CITED

1. D. Ballivet-Tkatchenko, G. Goudurier, H. Mozzanega, I. Tkatchenko, and A. Kiennemar, J. Mol. Catal., 6, No. 2, 293 (1979).
2. A. L. Lapidus, M. M. Savel'ev, and M. V. Tsapkina, Neftekhimiya, 24, 376 (1984).
3. D. W. Breck, Zeolite Molecular Sieves, Wiley, New York (1974).
4. A. L. Lapidus, M. M. Savel'ev, L. M. Muranova, S. D. Sominskii, L. T. Kondrat'ev, I. G. Borisovich,and V. É. Vasserberg, Izv. Akad. Nauk SSSR, Ser. Khim., p. 24 (1985).
5. D. Ballivet-Tkatchenko and G. Goudurier, Inorg. Chem., 18, 558 (1979).
6. F. Hugues, A. K. Smitk, J. Ben Taarit, and J. M. Basset, Chem. Commun., p. 68 (1980).
7. A. N. Nesmeyanov (ed.), Organic Syntheses Through Metal Carbonyls [in Russian], Mir, Moscow (1970).