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Synthesis of iso-hydrocarbons mixture from CO_2 and H_2 on hybrid catalysts†

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The activity and selectivity of hybrid catalysts of the content $\alpha(Zn_aCr_bCu_cK_d\text{–}O_x)/\beta[Fe^{3+}/\text{ZSM-11}]$ have been studied in the reaction of hydrogenation of CO_2 to hydrocarbons, where α, β, a, b, c, d, and x are variables. The process was carried out in a flowing-type reactor with the fixed layer of the catalyst at 3 MPa within the temperature interval 613–653 K and the volumetric rate of the gaseous mixture was 1325–5000 h^{-1}. For the most selective catalyst the degree of CO_2 into hydrocarbons conversion was 64.2% (653 K, 3.0 MPa, 1500 h^{-1}) at the ratio of the hydrocarbons (C_5–C_{11}) of iso-structure to the hydrocarbons of normal structure equal to 3.91. As the temperature of the process increased, the content of the products changed: in hydrocarbons with the same carbon numbers the iso-structure products content rises. As the volumetric rate increases, the selectivity for hydrocarbons of petrol fraction C_5–C_{11} decreases, and for the diesel fraction C_{12}–C_{18} and cerezines C_{19}–C_{24} it increases. The maximum selectivity for hydrocarbons of the petrol fraction is up to 57.3%. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: hydrogenation; carbon dioxide; catalyst; petrol and diesel hydrocarbons; activity; selectivity; degree conversion; yield

INTRODUCTION

The selectivity of direct higher hydrocarbons (C_{2+}) synthesis from CO_2 and H_2 on the catalysts normally used in HO Fischer–Tropsch reaction (consisting primarily of transitional metals) is very low. There is some evidence in to literature concerning catalysts for hydrocarbons mixtures direct synthesis from CO_2 and H_2, the content of which is different from that of the catalysts for Fischer–Tropsch synthesis. However, on those catalysts the yield of C_{4+} is very low, so the problem of iso-structure hydrocarbons production was not considered. The so-called hybrid or composite catalysts belong to those contacts. The known hybrid catalytic compositions of hydrocarbons synthesis from CO_2 and H_2 usually consist of a mixture of low-temperature catalyst of methanol synthesis (Cu–Zn–Al, Cu–Zn–Cr) with zeolite (HY, NaY, HM, ZSM-5, SAPO-5, SAPO-44).[1–6] On one such catalyst (Cu–Zn–Cr/HY) the degree of CO_2 conversion is 36% at selectivity (mol%) for: $CO = 56.5$; $CH_4 = 2.1$; $C_2H_6 = 8.5$; $C_3H_8 = 12.9$; $C_4H_{10} = 10.8$; $(CH_3)_2O = 9.2$.[1]

The promotion of hybrid catalysts with alkaline metals raises the selectivity for C_{2+}-hydrocarbons. The best promoter is cesium.[3] Iron addition to the composite catalysts results in an increase of selectivity for light olefines.[7]

Fujimoto *et al.*[8] think that the reaction of alkenes hydrogenation with the catalyst for methanol synthesis (one of the constituents of the composite catalysts) during CO_2 hydrogenation is the crucial factor for selectivity of the composite catalyst of C_{2+}-hydrocarbons synthesis. This becomes clear by considering the scheme for CO_2 hydrogenation presented in Ref. 3.

The processes depicted within the box take place in the zeolite part of the composite catalyst.

The alkenes hydrogenation occurring on the methanol-producing constituent of the composite further inhibits the growth of the carbon chain. So to reach a higher selectivity for higher hydro-

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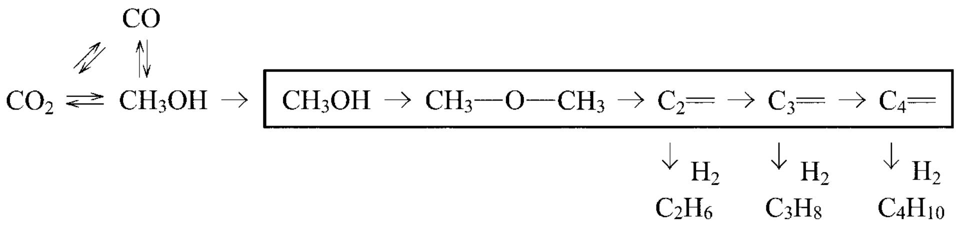


carbons (at higher probability of the carbon chain growth) the following conditions are required for the methanol constituent of the hybrid catalyst:

- high efficiency in methanol synthesis at high temperatures (higher than 570 K) at which the dehydration can take place a sufficiently high rate;
- low hydration ability of olefines being produced on the zeolite constituent.

The methods for hybrid catalysts preparation described in the literature did not presume some special techniques promoting the mutual enhancement of each part of the hybrid catalyst, but only allowed a combination of the two processes flowing at the same temperature with the comparable velocities (that is methanol synthesis and dehydration into hydrocarbons through dimethyl ether production).

EXPERIMENTAL

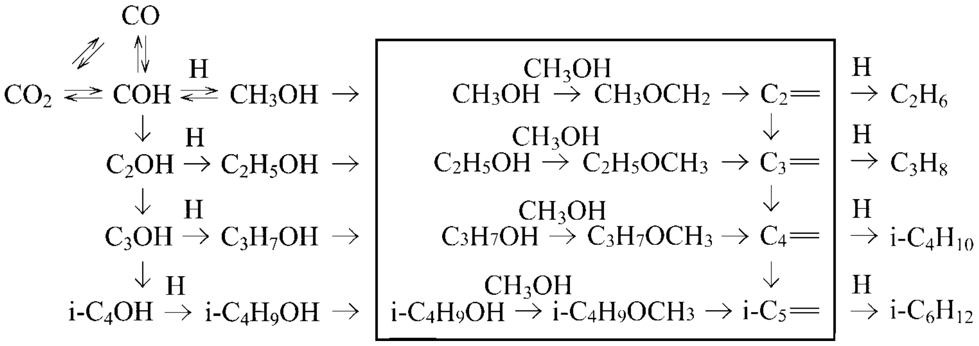
New ways of increasing the activity and selectivity for higher hydrocarbons (especially C_{5+}) that promote the mutual enhancement of the effectiveness of each part of the hybrid catalyst are considered in this work. As the first constituent of the composite system the catalyst meant for the alcohol's mixture synthesis (particularly methanol and *iso*-butanol mixture) was chosen. The zeolite chosen was the highly siliceous ZSM-11 modified by iron ions to increase the probability of hydrocarbons production and be efficient in the reaction of hydrocarbons isomerization.

By changing the alcohol to zeolite hybrid catalyst ratio by increasing the latter; this allowed us to avoid the equilibrium values of alcohols' concentrations as they were completely converted into hydrocarbons. The equilibrium concentration values of the hydrocarbons were considerably higher than those for methanol and other higher alcohols under the same conditions.

In the case of using this hybrid catalyst for the reactions occurring according to the scheme mentioned in Ref. 3 and presented above, it is possible that the reactions will take place according to the following scheme.

Within the box the reactions flowing on the zeolite constituent of the hybrid catalyst are shown.

Alcohol production is also possible at the expense of cross-reactions ($C_2 + C_2$), ($C_2 + C_3$), ($C_3 + C_3$), ($C_3 + C_4$), ($C_4 + C_4$) through the production of the corresponding ethers. In this case the probability of higher molecular weight hydrocarbons formation clearly rises. The selectivity for iso-structure hydrocarbons production also must essen-



tially increase. Moreover, conducting the process at high temperatures on the highly siliceous zeolite part of the composite catalyst allows is to obtain hydrocarbons of normal structure isomerization (at a considerable excess of the zeolite part of the catalyst over the alcoholic one).

THE TECHNIQUE OF CATALYST PREPARATION

As the hydrogenating oxide constituent of the hybrid catalyst we used the zinc–chromium–copper oxide contact promoted with potassium carbonate, with the components content (wt%) calculated as: ZnO = 39–65; Cr_2O_3 = 26–45; CuO = 9–12; K_2CO_3 = 1.5–3.0.

Potassium introduction as a promoter into the hydrating part of the catalyst is caused by reduction of its hydrating ability, resulting in an increase of the probability of the alcohol's carbon chain growth, and also of the hydrocarbons on the zeolite constituent. The efficiency for higher alcohols through their dehydration must, in turn, raise the summary activity and selectivity of the composite catalyst for higher hydrocarbons (primarily for iso-structure hydrocarbons).

As a dehydrating constituent of the hybrid catalyst the highly siliceous zeolite ZSM-11 with the module Si/Al = 20, modified by Fe^{3+} cations, which were introduced into the zeolite both by ionic exchange (1.5 wt%), and by the impregnation technique (up to 10 wt%). The summary number of iron-ions in zeolite reached 11.5 wt% (by recalculating for atomic iron). It was presumed that the iron introduction into the zeolite constituent would result in an increase of carbon chain probability during hydrocarbons production.

Table 1 Composition of the hybrid catalyst samples in HC synthesis from CO_2 and H_2

Sample no.	Composition of the components (wt%)				
	ZnO	Cr_2O_3	CuO	K_2CO_3	Fe^{3+}/ ZSM-11
1	12.1	6.0	1.6	0.3	80.0
2	9.7	4.7	2.0	0.3	83.3
3	9.5	4.7	2.0	0.5	83.3
4	7.3	6.9	2.0	0.5	83.3
5	8.8	8.2	2.4	0.6	80.0

The samples of hybrid catalysts were prepared by mechanical mixing of modified oxide and zeolite constituents with their further tabletting. The composition of these catalysts can be represented by the following summary formula: $\alpha(Zn_aCr_b Cu_cK_dO_x)/\beta[Fe^{3+}/ZSM\text{-}11]$, where α, β, a, b, c, and d, are defined from Table 1, and x by stoichiometry. The no. 3 samples were prepared by mixing of the ZnO aqueous paste with a solution of chromic acid. Then the dried contact mass was impregnated by a solution of potassium carbonate. After repeated drying it was impregnated by a solution of copper nitrate, dried and crushed.

The ratio of zinc oxide to chromium anhydride was selected in such a way that in the formed (reduced) state it would correspond to the formula $3ZnO{\cdot}ZnCr_2O_4$, and the contents of potassium carbonate (wt %) for the samples before mixing were: no. 1, 1.5; no. 2, 1.8; no. 3, 3.0.

The samples of catalyst nos 4 and 5 were prepared by the method of combined precipitation from the concentrated solutions of nitrate salts of zinc, chromium and copper. After precipitation, washing and drying the Zn–Cr–Cu contact mass was impregnated by the potassium carbonate solution. The ratio of zinc and chromium salts was selected by taking into account that the catalyst in the ready form would correspond to the formula $ZnO{\cdot}ZnCr_2O_4$. For sample no. 4 the potassium carbonate content was 1.8 mol%, and for no. 5 it was 3.0 wt%.

The zeolite constituent of the hybrid catalyst was prepared by ionic exchange of zeolite ZSM-11 of the sodium form by Fe^{3+} ions. The amount of Fe^{3+} introduced was 1.5 wt% (calculated for atomic iron). Iron was additionally introduced into the modified zeolite after calcination, so that its general content in the zeolite was 11.5 wt%.

Powders of the hydrogenation component Zn–Cr–Cu–K–O constituent were carefully mixed with that of the zeolite. The ratios of α/β components in the hybrid catalyst were 1/4 for samples nos 1 and 5 and 1/5 for sample nos 2–4. The mixtures of constituents obtained were tabletted after careful mixing, crushed and then the size fraction of 2–3 mm was selected.

The samples of hybrid catalysts prepared were formed (reduced) in the flowing-type reactor with a fixed layer of the catalyst. The conditions of the samples formation–reduction were: temperature T = 673–683 K, pressure P = 0.4–0.5 MPa, volumentric rate W = 9000–11,000 h^{-1}; the gas-reducer content (vol.%) was H_2 = 2.5–3.0, CO_2 = 1.0, and

Table 2 Activity and selectivity of products in the reaction of CO_2 hydrogenation on hybrid catalysts

Sample no.	Reaction products	Degree of CO_2 conversion (%)	Yield ($g/g_{ct}\cdot h\cdot 10^2$)		Selectivity (%)		i-HC/n-HC ratio
			n-HC	i-HC	*n*-HC	i-HC	
1	CO		4.98				
	CH_3OH		0.92				
	HC-C_1–C_3		3.39				
	HC-C_4	53.9	0.45	1.88	2.4	10.0	4.18
	HC-C_5–C_{11}		1.37	5.15	7.3	27.4	3.76
	HC-C_{12}–C_{18}		0.27	0.29	1.4	1.55	1.08
	HC-C_{19}–C_{24}		0.07	0.02	0.3	0.1	0.29
2	CO		4.76				
	CH_3OH		0.29				
	HC-C_1–C_3		4.15				
	HC-C_4	60.0	0.54	2.31	2.57	11.1	4.30
	HC-C_5–C_{11}		1.68	6.31	7.97	30.2	3.79
	HC-C_{12}–C_{18}		0.29	0.42	1.38	2.03	1.44
	HC-C_{19}–C_{24}		0.12	0.03	0.60	0.11	0.19
3	CO		4.11				
	CH_3OH		0.22				
	HC-C_1–C_3		3.60				
	HC-C_4	55.5	0.47	2.15	2.40	11.1	4.63
	HC-C_5–C_{11}		1.57	6.24	8.12	32.2	3.97
	HC-C_{12}–C_{18}		0.33	0.48	1.71	2.45	1.43
	HC-C_{19}–C_{24}		0.17	0.03	0.89	0.16	0.18
4	CO		5.06				
	CH_3OH		0.33				
	HC-C_1–C_3		4.25				
	HC-C_4	64.2	0.52	2.36	2.33	10.5	4.53
	HC-C_5–C_{11}		1.77	6.97	7.96	31.2	3.91
	HC-C_{12}–C_{18}		0.36	0.51	1.64	2.26	1.38
	HC-C_{19}–C_{24}		0.19	0.05	0.82	0.16	0.20
5	CO		5.13				
	CH_3OH		1.09				
	HC-C_1–C_3		3.60				
	HC-C_4	57.1	0.41	1.81	2.06	9.04	4.39
	HC-C_5–C_{11}		1.50	5.71	7.53	28.6	3.80
	HC-C_{12}–C_{18}		0.23	0.26	1.23	1.84	1.50
	HC-C_{19}–C_{24}		0.12	0.02	0.60	0.10	0.17

Process conditions: $T = 653$ K, $P = 3.0$ MPa, $W = 1500\ h^{-1}$, $H_2/CO_2 = 3{:}1$.

helium made up the rest; the reduction time was 12–14 h.

EXPERIMENTAL METHOD

The reaction of CO_2 hydrogenation was conducted in a three-channel reactor with a fixed layer of the catalyst at $T = 613$–653 K, $P = 3$ MPa, $W = 1325$–$5000\ h^{-1}$ while using synthesis gas of the following composition (vol.%): $H_2 = 74.5$–75.5; $CO_2 = 24.5$–25.5. The reaction products were hydrocarbons C_1–C_{24}, carbon monoxide, methanol, and water.

The initial gaseous mixture was prepared in the balloon by mixing of the pure components—hydrogen and carbon dioxide. The reaction mixture first entered the buffer part of the experimental device, and then through the pressure regulator it entered the three in-parallel-located channels of the reactor. Moreover, the preliminary heating of the working mixture up to the reaction temperature occurred in the beginning of each channel, then gas entered the area of the catalyst location. The reaction products were cooled in the condenser

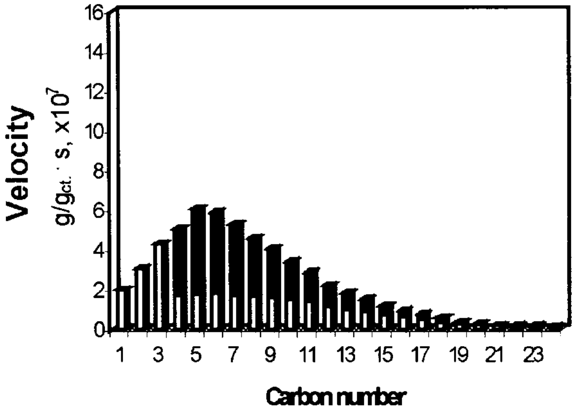


Figure 1 Velocity vs carbon number ($T = 613$ K, $P = 3.0$ MPa, $W = 5000$ h^{-1}, black column—i-HC, white column—n-HC).

with aqueous cooling and were separated from the aqueous products (condensate) being produced. The condensates were collected in the samples selection areas separately for each channel, and the gaseous products and the mixture that did not take place in the reaction was throttled to the atmosphere pressure. The gas expenditure was established by means of rheometers separately for each of the reactor channels, also the gaseous products volume, and CO_2 and H_2 that did not take part in the reaction were determined according to the gas meters (watches) readings. After throttling, some share of gas was taken for the chromatographic analysis conducted on three devices (two LXM-8 and Biochrom, Russia).

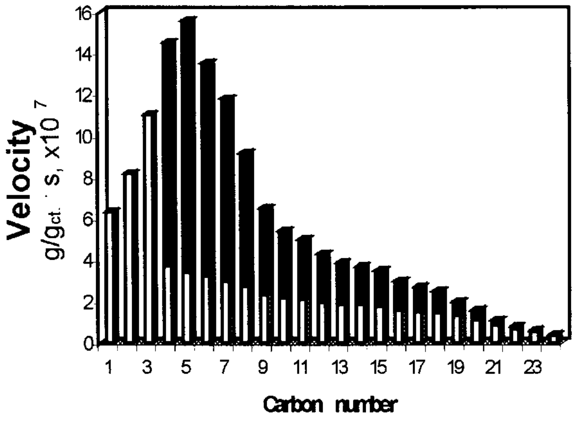


Figure 2 Velocity vs carbon number ($T = 653$ K, $P = 3.0$ MPa, $W = 5000$ h^{-1}, black column—i-HC, white column—n-HC).

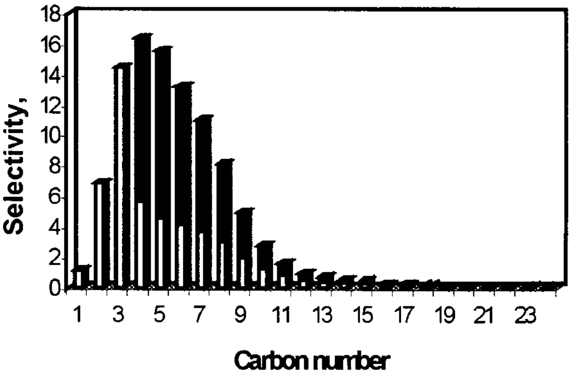


Figure 3 Selectivity vs carbon number ($W = 1325$ h^{-1}, $T = 613$ K, $P = 3.0$ MPa, black column—i-HC, white column—n-HC).

TECHNIQUE OF CHROMATOGRAPHIC ANALYSIS

The inorganic share of the gaseous mixture (H_2, CO, CO_2 and CH_4) was analyzed on the catalysis meters (LXM-8, gas-carriers were argon and helium) using the packed metallic columns with different absorbents (molecular sieves CaA, CaX, Polysorb, Carbosieve B). The organic share of the gaseous mixture (hydrocarbons C_1–C_6, ethers and alcohols) were analyzed on the flame-ionization detector (Biochrom, metallic column with the absorbent Separon BD-22).

The reaction liquid products obtained were periodically poured away from the sample selection areas. Their volumes were measured and analyzed on two 'Hewlett & Packard' chromatographs equipped with glass capillary columns and flame-ionization detectors in a regime of programmed rise

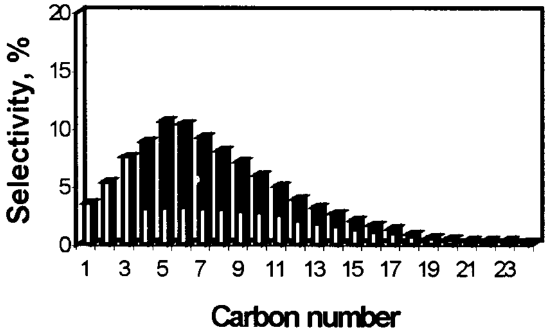


Figure 4 Selectivity vs carbon number ($W = 4340$ h^{-1}, $T = 613$ K, $P = 3.0$ MPa, black column—i-HC, white column—n-HC).

in temperature (80–200, 250 °C). To separate the non-polar organic components of the condensates (hydrocarbons and simple ethers) the column ($l = 60$ mm, $d = 0.25$ mm) with the film corpulence of the immobile liquid phase Superwax 10–25 mcm (helium is the gas-carrier) was used. To determine the content of the liquid polar condensates components (primarily alcohols) the column with the immobile liquid phase Carbowax-20M was used. The identification of the synthesis products was carried out mainly by comparison of the time retention data with those for individual pure compounds, and also taking into account the references.

RESULTS

In Table 2 the data for the samples of hybrid catalysts activity and selectivity are presented, the contents of which are shown in Table 1.

The degree of CO_2 conversion in the samples under study was 54–64%. The best indices in relation to C_{4+} hydrocarbons synthesis were the samples with increased chromium content that had on atomic ratio Zn/Cr equal to 1:1. In sample no. 4 the degree of CO_2 conversion was 64.2%. The overall yield of hydrocarbons was 16.98×10^{-2} g h^{-1} per gram of catalyst (including hydrocarbons C_5–C_{11} 8.74×10^{-2} g h^{-1} per gram of catalyst), and the ratio i-C_4/n-$C_4 = 4.5$; i-C_5–C_{11}/n-C_5–$C_{11} = 3.91$. Heavy hydrocarbons C_{19}–C_{24} were produced of primarily normal structure, and hydrocarbons of diesel fractions C_{12}–C_{18} contained the normal and iso-hydrocarbons in approximately equal quantities.

The influence of temperature (Figs 1 and 2) and volumetric rate (Figs 3 and 4) on the velocity of hydrocarbons production and their distribution along the length of carbon chain, and also the ratio between hydrocarbons of normal and iso-structure, were studied on the sample of the catalyst no. 4.

While the temperature increased from 613 K to 653 K (Figs 1 and 2), the summary rate of hydrocarbons production increased, and the selectivity for the hydrocarbons C_1–C_4 and C_{19}–C_{24} increased; that for the hydrocarbons C_5–C_{11} decreased, and for C_{12}–C_{18} it remained practically invariable. While the temperature was increasing, the relative content of hydrocarbons of iso-structure increased. The maximum relative content of liquid hydrocarbons of iso-structure corresponds to the hydrocarbons C_5–C_{11}, first of all to C_5. The amount of iso-pentanes was three times as much as that of *n*-pentane. The resulting C_{14+} hydrocarbons had mainly normal structure.

While the volumetric rate increased from 1325 to 5000 h^{-1} (Figs 3 and 4), the summary yield of hydrocarbons was unexpectedly reduced. The selectivity for hydrocarbons somewhat reduced, and the selectivity for hydrocarbons of petrol fraction C_5–C_{11} reduced; Had for the diesel fraction C_{12}–C_{18} and cerezines C_{19}–C_{24} increased. The volumetric rate of i-HC/*n*-HC had practically no influence on the hydrocarbons content.

Thus, on the synthesized hybrid catalysts that are a mixture of Zn–Cr–Cu–K–O catalysts for the synthesis of aliphatic alcohols using iron-modified highly siliceous zeolite ZSM-11, during CO_2 hydrogenation the hydrocarbons of petrol fraction C_5–C_{11} were prevelent and consisted mainly of the iso-structure hydrocarbons.

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