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The Activity and Selectivity of FeCo/SiO₂ Catalysts in Carbon Monoxide Hydrogenation

Aktywność i selektywność bimetalicznych katalizatorów żelazowo-kobaltowych
w reakcji uwodorniania tlenku węgla

The reaction of carbon monoxide hydrogenation may be a source of many hydrocarbons, mainly those with straight carbon chains. One of the directions of this process which seems to attract particular interest is the synthesis of short-chain olefins.

Iron and cobalt are the basic components of the traditional catalysts of hydrocarbon production from the synthesis gas [1-4]. However, their main disadvantage is very low selectivity. Depending on the catalyst and the conditions of the process, the length the hydrocarbons formed may be between that of methane and those of solid paraffins of high molecular mass. The application of such unselective catalysts greatly hinders the direction of the reaction towards the production of a desired hydrocarbon or even a narrow spectrum of hydrocarbons. For this reason catalytic systems of better selectivity are highly desirable and are sought in many laboratories [5-7].

One of the promising possibilities to control the selectivity of Fischer-Tropsch reaction seems to be the application of alloy catalysts, among others, iron-cobalt systems [8-12]. In paper [8] the authors report that unsupported iron-cobalt catalysts show an improved selectivity towards hydrocarbons C₂-C₃ formation. Further research [9-11] on alloy FeCo systems (atomic ratio Fe:Co = 80:20) shows that under the employed conditions of the reaction (1 atm, 250°C, CO:H₂ = 2.68-3.67), the ratios of C₂/C₂ and C₃/C₃ are higher for this catalyst than in the case of either single component of the alloy. These data motivate the studies presented below which concern the activity and selectivity of bimetallic iron-cobalt catalysts of varying Fe:Co ratio in the reaction of carbon monoxide hydrogenation. Special attention has been paid to

the formation of light olefins. One of the ways of increasing olefin content in synthesized hydrocarbons is the application of a reaction mixture with a small hydrogen excess or even hydrogen insufficiency [6, 7, 12]. For this reason the presented studies were carried out under conditions which, though more advantageous for olefin synthesis, differed from those employed in papers quoted above.

EXPERIMENTAL

MATERIALS

Experiments were carried out on silica supported iron-cobalt catalysts with a variable Fe:Co ratio. The whole amount of both metals was 15 wt %.

All the catalysts were prepared by the impregnation of the support SiO₂ (Kieselgel 100-Merck) whose surface area was 250 m²/g and mean pore diameter — 10 nm. Bimetallic catalysts were obtained by coimpregnation. Impregnation was applied to SiO₂ of the sieve fraction of 0.2–0.5 nm, dried at 110°C, and while constantly stirring the support, by slowly dropping in a water solution of iron and cobalt nitrates of analytic purity grade. The amounts of the solutions were adjusted in such a way as to fill up the support pores (2 ml/g SiO₂) until the occurrence of incipient wetness. In order to achieve uniform impregnation of the whole support the procedure was carried out twice. After each impregnation the support was dried at 110°C. It was then calcined at 400°C. The catalysts were reduced with dry hydrogen at 450°C for 5 hours directly before the experiments. The characteristics of the catalysts after reduction are set up in Table 1.

METHODS

Experiments in carbon monoxide hydrogenation were carried out in a continuous flow fixed-bed glass reactor. The catalyst loading was 5 ml and the flow of the CO and H₂ mixture at the volumetric ratio H₂/CO=1.1 was 50 ml/min (the space velocity was 600 hours⁻¹). Hydrogen was purified on silica gel and Cu/SiO₂, (200°C), while carbon monoxide (BOC Ltd.) on a molecular sieve 5 A. In addition, the CO and H₂ mixture was dried in two liquid nitrogen traps coupled in tandem. The reaction was carried out at a constant temperature of 275°C for 50 hours.

The analysis of the reaction products was performed with two gas chromatographs. One of them, with a thermal conductivity detector and a column packed with activated carbon, was used to determine the amounts of CO, N₂, CH₄ and CO₂. The other chromatograph, with a flame ionization

Table 1. The properties of the catalysts studied

Catalyst	Fe:Co [wt]	Reduction degree [%] ^a	Phase composition ^b	^d Me [nm]	Uptake ^d [$\mu\text{mol/g}_{\text{cat}}$]	
					H ₂	CO
Fe		92.9	α -Fe Fe ₃ O ₄ trace	17	10.566	12.500
75Fe25Co	75:25	97.6	FeCo alloy	15	13.552	12.188
50Fe50Co	50:50	99.0	FeCo alloy β -Co trace	12	11.904	13.661
Co		98.0	β -Co	12	31.565	12.946

^a Determined by a gravimetric method;

^b Determined by X-ray diffraction;

^c Mean size of metal crystallites determined by X-ray line broadening;

^d The chemisorptive properties of catalysts were based on the value of total H₂ chemisorption at 100 mm Hg and of irreversible CO chemisorption at 200 mm Hg.

Details of above experimental methods have been described elsewhere [16].

detector and a Porapak Q column, served for the determination of hydrocarbons C₁—C₄. The calibration of the chromatographs employed a standard mixture containing amounts of hydrocarbons and carbon monoxide comparable with those analysed.

In order to determine volume contraction a small stream of nitrogen (about 8 ml/min) was injected into effluent gas. By comparing the size of N₂ peak in the effluent mixture ($S_{N_2}^{\text{exit}}$) and the size of this peak ($S_{N_2}^{\text{inlet}}$) in the input mixture of CO + H₂ (determined in a separate analysis) contraction f was calculated as

$$f = \frac{S_{N_2}^{\text{inlet}}}{S_{N_2}^{\text{exit}}}$$

The total degree of carbon monoxide conversion ($X_{\text{CO}}^{\text{total}}$) and the degree of CO converted to particular products (product yield) were calculated on the basis of mole concentration values [] of CO and of the products from the following equations

$$X_{\text{CO}}^{\text{total}} = \frac{[\text{CO}]^{\text{inlet}} - [\text{CO}]^{\text{exit}}}{[\text{CO}]^{\text{inlet}}} \cdot f \cdot 100\%,$$

$$X_{\text{CO}}^{\text{CO}_2} = \frac{[\text{CO}_2]}{[\text{CO}]^{\text{inlet}}} \cdot f \cdot 100\%,$$

$$X_{\text{CO}}^{\text{C}_n\text{H}_m} = \frac{n \cdot [\text{C}_n\text{H}_m]}{[\text{CO}]^{\text{inlet}}} \cdot f \cdot 100\%.$$

Product yield is defined as a ratio between the number of moles of CO converted to a given product and the number of moles of CO introduced into the reaction.

RESULTS AND DISCUSSION

The picture of the reaction of carbon monoxide hydrogenation, illustrated by changes in the degree of its conversion, both total and to particular products, is shown in Fig. 1.

On the initial stage of the reaction the total degree of converted CO is higher than its conversion to the sum of all the analysed gas products. In this period apart from hydrocarbon synthesis two processes are also taking place on the catalyst, namely, the formation of bulk metal carbides and/or the setting of carbonaceous deposit on metal surface [13–16]. Both processes take up some carbon monoxide and this mainly accounts for the difference in the conversion of CO, both total and that to the sum of the gas products. After the reaction we found the presence of $\chi\text{-Fe}_5\text{C}_2$ in iron catalyst, $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ in alloy catalysts, and Co_2C in cobalt catalyst.

Surface carbonaceous deposit causes the blocking of the metal surface (or metal carbide) and, in consequence, a decrease in its area. It may simultaneously decrease the hydrogenating properties of the metal or metal carbide [16]. On the other hand, metal recrystallization and the formation of bulk carbide cause an increase in the activity and a higher degree of carbon monoxide conversion [13–15].

The carbonaceous deposit remaining on the surface and the formation of bulk carbide, producing opposed catalytic effects, create a complicated picture of the reaction.

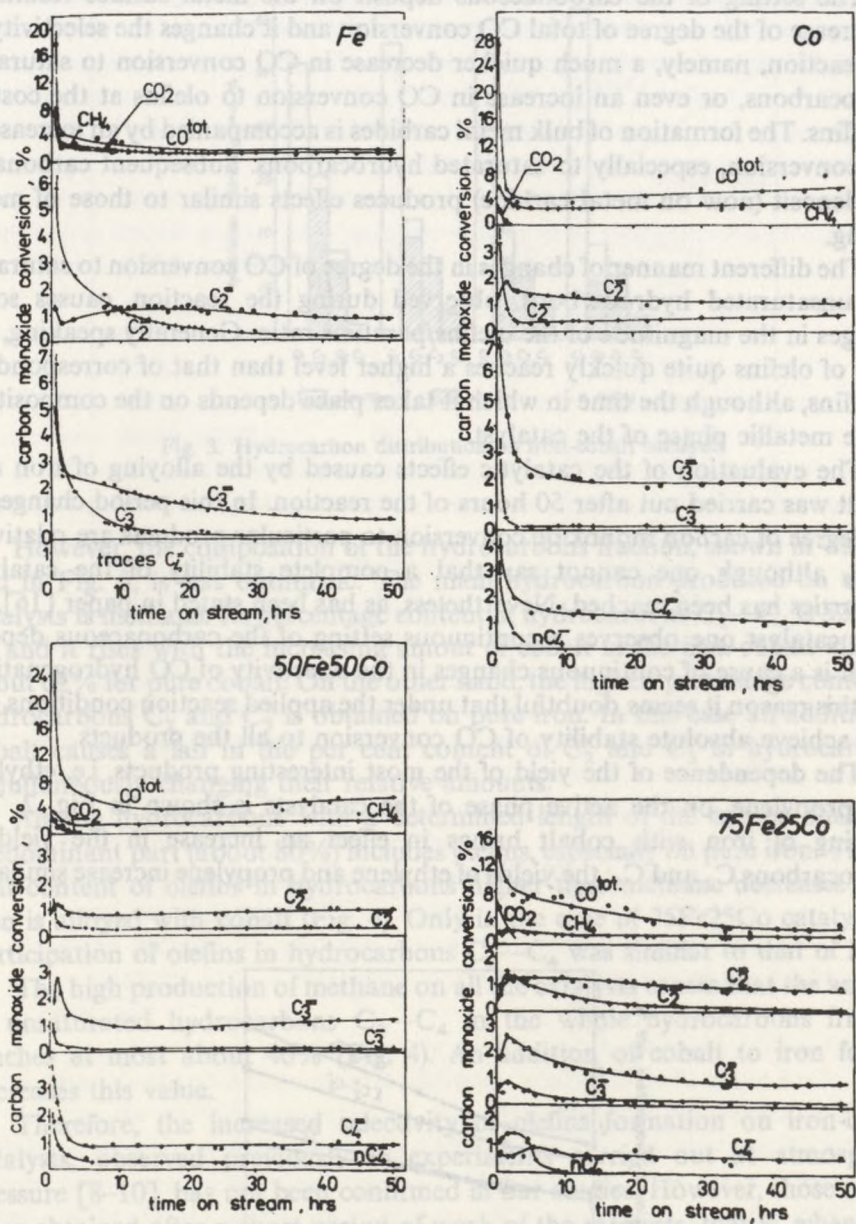


Fig. 1. Carbon monoxide conversion towards reaction products v. time on steam on different catalysts

The setting of the carbonaceous deposit on the metal surface results in a decrease of the degree of total CO conversion and it changes the selectivity of the reaction, namely, a much quicker decrease in CO conversion to saturated hydrocarbons, or even an increase in CO conversion to olefins at the cost of paraffins. The formation of bulk metal carbides is accompanied by an increase in CO conversion, especially to saturated hydrocarbons. Subsequent carbonaceous deposit (now on metal carbide) produces effects similar to those of metal coking.

The different manner of changes in the degree of CO conversion to saturated and unsaturated hydrocarbons, observed during the reaction, causes some changes in the magnitude of the olefins/paraffins ratio. Generally speaking, the yield of olefins quite quickly reaches a higher level than that of corresponding paraffins, although the time in which it takes place depends on the composition of the metallic phase of the catalyst.

The evaluation of the catalytic effects caused by the alloying of iron and cobalt was carried out after 50 hours of the reaction. In this period changes in the degree of carbon monoxide conversion to particular products are relatively small, although one cannot say that a complete stability of the catalytic properties has been reached. Nevertheless, as has been stated in paper [16], on these catalyst one observes a continuous setting of the carbonaceous deposit which is a cause of continuous changes in the selectivity of CO hydrogenation. For this reason it seems doubtful that under the applied reaction conditions one may achieve absolute stability of CO conversion to all the products.

The dependence of the yield of the most interesting products, i.e. ethylene and propylene, on the active phase of the catalysts is shown in Fig. 2. The alloying of iron with cobalt brings in effect an increase in the yield of hydrocarbons C_2 and C_3 ; the yields of ethylene and propylene increase similarly.

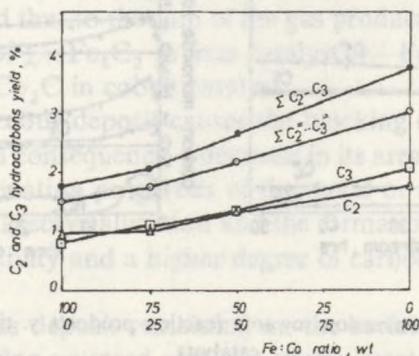


Fig. 2. Yield of C_2 and C_3 hydrocarbons on iron-cobalt catalysts

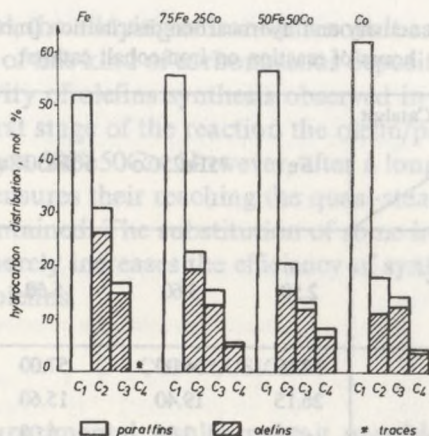


Fig. 3. Hydrocarbon distribution on iron-cobalt catalysts

However, the composition of the hydrocarbons fraction, shown in Table 2 and in Fig. 3, is less optimistic. The main hydrocarbon produced on all the catalysts is methane. Its percentage content in hydrocarbons C₁—C₄ is 52% for Fe and it rises with the increasing amount of cobalt in the iron-cobalt alloy to about 62% for pure cobalt. On the other hand, the highest percentage content of hydrocarbons C₂ and C₃ is obtained on pure iron. In this case an addition of cobalt causes a fall in the per cent content of C₂ and C₃ in hydrocarbons, simultaneously changing their relative amounts.

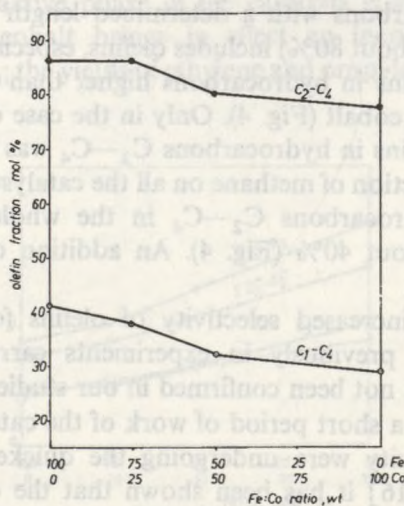
Among hydrocarbons with a determined length of the carbon chain the predominant part (about 80%) includes olefins, especially on pure iron. The per cent content of olefins in hydrocarbons higher than methane decreases when iron is alloyed with cobalt (Fig. 4). Only in the case of 75Fe25Co catalyst the participation of olefins in hydrocarbons C₂—C₄ was similar to that of Fe.

The high production of methane on all the catalysts causes that the amount of unsaturated hydrocarbons C₂—C₄ in the whole hydrocarbons fraction reaches at most about 40% (Fig. 4). An addition of cobalt to iron further decreases this value.

Therefore, the increased selectivity of olefins formation on iron-cobalt catalysts, observed previously in experiments carried out at atmospheric pressure [8–10], has not been confirmed in our studies. However, those results were obtained after a short period of work of the catalysts, that is, when their activity and selectivity were undergoing the quickest and greatest changes (Fig. 1). In study [16] it has been shown that the olefin/paraffin ratio rises quicker in the course of the reaction, when the strongly chemisorbed carbonaceous deposit is quicker settled on the catalyst surface. When compared

Table 2. The activity and hydrocarbon distribution [mol %] after 50 hours of reaction on iron-cobalt catalyst

Hydrocarbon	Catalyst			
	Fe	75Fe25Co	50Fe50Co	Co
$X_{CO}^{C_nH_m}$	2.50	3.60	5.60	6.70
C_1	52.10	56.00	57.00	62.50
C_2^-	26.15	19.40	15.60	11.50
C_2^+	4.75	3.20	5.00	6.50
C_3^-	15.10	12.90	12.10	12.80
C_3^+	1.80	2.70	1.40	1.80
C_4^-	tr	5.60	7.00	4.80
C_4^+	tr	tr	1.80	tr
C_2-C_3/C_1-C_4	47.80	38.20	34.10	32.60
$C_2^-/\Sigma C_2$	84.60	85.80	75.50	63.80
$C_3^-/\Sigma C_3$	89.30	82.70	89.70	87.70

Fig. 4. Olefin fraction in C_1-C_4 and C_2-C_4 hydrocarbons on iron-cobalysts

with either pure metal, the alloying of iron with cobalt causes an increase in the rate of the formation of this kind of carbonaceous deposit. This fact may explain the increased selectivity of olefins synthesis observed in studies [8–10]. In our experiments in the first stage of the reaction the olefin/paraffin ratio is also the greatest for the catalyst 50Fe50Co. However, after a long period of the work of the catalysts, which ensures their reaching the quasi-steady state, this increased selectivity is not maintained. The substitution of some iron in the catalyst with more active cobalt merely increases the efficiency of synthesized hydrocarbons, also including light olefins.

CONCLUSIONS

The presented experimental results make it possible to offer some observations and conclusion:

1. The stabilization of the properties of iron-cobalt catalysts in the reaction of carbon monoxide hydrogenation is very slow. The causes of the instability of the activity and selectivity are: the formation of bulk metal carbides characterized by properties different than those of initial metals, and catalyst coking.

2. The main hydrocarbon produced on all the catalyst is methane. Its percentage content in hydrocarbons C₁—C₄ exceeds 50 mole %. The olefins constitute predominant part (about 80%) of hydrocarbons higher than methane.

3. The yield of hydrocarbons synthesized from carbon monoxide and hydrogen may be controlled by adjusting the Fe : Co ratio. The alloying of iron with cobalt causes an increase in the yields of ethylene and propylene, although in the composition of the whole hydrocarbons fraction their amounts are smaller than those obtained on pure iron.

4. An addition of cobalt to iron also causes:

- an increase in catalyst activity
- an increase in methane content in hydrocarbons obtained
- changes in the relative proportions of hydrocarbons higher than methane
- a decrease in the percentage olefin content in hydrocarbons higher than methane when a cobalt addition exceeds 25 wt% in the FeCo alloy.

5. Because of various rates of the carbonaceous deposition and carbidization of both metals only on the initial stage of the reaction can the alloying of iron with cobalt cause an increase in the olefin/paraffin ratio in respect to either single metal. In the quasi-steady state iron-cobalt catalyst cannot be regarded as “catalyst of an improved selectivity towards light olefins”; they merely increase their yield in comparison with iron catalysts.

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STRESZCZENIE

Zbadano aktywność i selektywność bimetalicznych katalizatorów żelazowo-kobaltowych w reakcji uwodornienia tlenku węgla. Głównym węglowodorem produkowanym na wszystkich katalizatorach był metan. Przeważającą część (około 80%) węglowodorów wyższych od metanu stanowiły węglowodory nienasycone. Dodatek kobaltu do żelaza powoduje wzrost aktywności katalizatorów, zwiększenie zawartości metanu w węglowodorach, zmienia wzajemny stosunek węglowodorów wyższych od metanu, zmniejsza procentową zawartość olefin w węglowodorach. W stanie pseudostacjonarnym katalizatory żelazowo-kobaltowe nie mogą być uznane za „katalizatory o zwiększonej selektywności do lekkich olefin”; zwiększają jedynie ich wydajność w stosunku do katalizatora żelazowego.