

## Carbon monoxide hydrogenation on bifunctional iron-HZSM5 zeolite catalysts

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The HZSM5 zeolite with the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio lower than 200, used as a support of the iron phase or in a physical mixture with the silica supported iron catalyst, increases few times the conversion of carbon monoxide and decreases the rate of the catalyst coking in comparison with those achieved on the zeolite-free Fe/SiO<sub>2</sub> catalyst. The reasons of these phenomena have been explained on the basis of disturbance of an adsorption-desorption equilibrium of olefins on the iron phase, resulting from immediate, subsequent conversion of olefins on the zeolite. Their presence in hydrocarbons formed is strongly suppressed. The synthesis of C<sub>5+</sub> hydrocarbons is changed in the opposite way to that of olefin amounts. The hydrocarbons derived from carbon monoxide hydrogenation on the HZSM5 zeolite supported iron catalysts contain the aromatic fraction and branched hydrocarbons.

The HZSM5 zeolite with the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio below 200 present in the bifunctional catalyst composition may be sufficient when C<sub>5+</sub> hydrocarbons production is targeted, but for high contents of branched and aromatics hydrocarbons in the liquid product, the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio equal to 30-40 should be preferred.

### 1. INTRODUCTION

The high price of crude oil has attracted increasing attention to the possibility of synthetic hydrocarbons production from carbon monoxide and hydrogen derived from the gasification of coal or biomass, or from the natural gas conversion. The Fischer-Tropsch catalysts used in carbon monoxide hydrogenation exhibit a low selectivity for any specific hydrocarbon product or

even for any group of products [1-5]. Bifunctional catalysts which can convert the part of primary straight chained hydrocarbon synthesis product into diesel fuel and gasoline-range liquid hydrocarbons, abounding with aromatics and branched hydrocarbons, give the possibility to improve the process selectivity [2-4]. Such catalysts consist of conventional FT catalyst, e.g. cobalt [4, 6-24] or iron [3-6, 25-36], and a zeolite. The FT active metal is responsible for carbon monoxide hydrogenation, while acidic sites of the zeolite lead to the second function of the catalyst, i.e. to the secondary conversion of hydrocarbons formed on FT catalyst. The ZSM class of zeolites have been preferred for bifunctional catalyst compositions, as they were successfully used in the conversion of methanol and other oxygenates to gasoline in the Mobil process [37-39]. However, in carbon monoxide hydrogenation there was no evidence reported for the ZSM functioning shape selectively and restricting the growth of hydrocarbon chains, in contrary to the methanol conversion, where the zeolite limits the growth of hydrocarbon molecules to gasoline range hydrocarbons [3, 38, 39].

The medium pore ZSM5 zeolites can be made within a wide range of values of the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio. The present paper reports experimental results concerning the influence of the HZSM5 zeolite composition, i.e. of the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio, on the activity and selectivity of bifunctional iron catalysts in the reaction of carbon monoxide hydrogenation. The aim of the paper was also to propose an elucidation of the role of these zeolites in the catalyst activity variation.

## 2. EXPERIMENTAL

NaZSM5 zeolites of the molar  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio from 35 to 550 were provided by the Institute of Industrial Chemistry in Warsaw. The acidic form (HZSM5) was obtained by the threefold ion exchange at 355 K using 0.5 M hydrochloric acid. After washing with distilled water and drying, zeolites were calcined at 820 K for 2 hours, pressed and crushed to the grains of 0.2-0.5 mm.

The supported iron catalysts were prepared by HZSM5 zeolites or  $\text{SiO}_2$  (Merck, Kieselgel 100, 0.2-0.5 mm) impregnation with an aqueous solution of iron(III) nitrate to obtain the incipient wetness of the carrier. The procedure was repeated three times. After each impregnation the solids were dried at 380 K and finally the catalyst precursors were calcined (670 K, 2 h). Prior to the use all catalysts were reduced ( $\text{H}_2$ , 720 K, 2 h). The data regarding characterization of catalysts are presented in Table 1.

A physical mixture of  $\text{Fe/SiO}_2$  and HZSM5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 43$ ) in a volume ratio of 1:1 was also used as the bifunctional catalyst.

The weight content of iron in catalysts was determined by X-ray fluorescence spectroscopy technique. Pellets for the XRF analysis were prepared by pressing

catalyst powders. The measurements were performed by the energy-dispersive XRF spectrometer (Canberra 1510) equipped with the liquid nitrogen-cooled Si(Li) detector. The AXIL software package was used for spectral deconvolution and for the calculation of iron content.

Tab. 1. Catalyst characterization results.

Catalyst	Support composition (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio)	Iron content (wt.%)	Iron oxide reduction degree (%)	Average diameter of iron crystallites (nm)
Fe/HZSM5(35)	35	9.0	87.8	24.6
Fe/HZSM5(43)	43	9.1	81.3	21.6
Fe/HZSM5(71)	71	10.4	81.5	20.1
Fe/HZSM5(183)	183	8.0	97.2	22.3
Fe/HZSM5(330)	330	8.8	98.7	26.7
Fe/HZSM5(550)	550	9.0	93.6	25.6
Fe/SiO <sub>2</sub>	-	14.2	92.9	17.7

The reduction degree of iron phase was determined by the continuous-flow gravimetric method, using a home-made thermobalance.

The average sizes of iron crystallites were determined from X-ray line broadening, after Warren, employing MgO crystallites larger than 100 nm as a reference. X-ray powder diffraction patterns of reduced catalysts were collected with an upgraded Zeiss HZG-4 diffractometer using Ni-filtered CuK<sub>α</sub> radiation. The samples were scanned by a step-by-step technique, at 2θ intervals of 0.05° and recording time of 10 s for each step.

Catalytic reaction measurements were carried out in a continuous flow reactor with a fixed bed of the catalyst, reduced just before reaction. The reaction was carried out under the pressure of 0.1 MPa at 548 K, using a reaction mixture of hydrogen and carbon monoxide at a ratio of 1.1 and gas hourly space velocity of 300 hour<sup>-1</sup>. The reaction mixture was purified over silica gel, ascarite and soda lime, and finally, it was dried on a molecular sieve 5A and at two liquid-nitrogen traps. The analysis of the reaction products was performed with three 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, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>. The second chromatograph, with a flame ionization detector and a Porapak Q column, served for the determination of C<sub>1</sub>-C<sub>5</sub> hydrocarbons. The third chromatograph, also equipped with a flame ionization detector and a Carbowax 20M/Chromosorb column, was used to determine of

C<sub>6</sub>-C<sub>10</sub> aromatic hydrocarbons. The calibration of chromatographs employed standard mixtures containing hydrocarbons and other gases, concentrations of which were comparable with those analysed.

In determination of degree of carbon monoxide conversions, volume contraction evaluated from the comparison of the peak area of nitrogen added to a stream of post-reaction gases,  $S_N^{out}$ , and to the CO+H<sub>2</sub> feedstock,  $S_N^{in}$  (determined in the preliminary analysis), was taken into account. The total conversion of carbon monoxide,  $X_{CO}$ , conversions into particular hydrocarbons,  $X_{HC}$ , and into carbon dioxide,  $X_{CO_2}$ , were calculated from equations:

$$X_{CO} = \frac{c_{CO}^{in} - c_{CO}^{out} \cdot K}{c_{CO}^{in}} \cdot 100 \quad X_{HC} = \frac{n \cdot c_{HC} \cdot K}{c_{CO}^{in}} \cdot 100 \quad X_{CO_2} = \frac{c_{CO_2} \cdot K}{c_{CO}^{in}} \cdot 100 \quad (\%)$$

where:

$c_{CO}^{in}$  is the molar concentration of carbon monoxide in the reaction mixture,

$c_{CO}^{out}$  is the molar concentration of carbon monoxide in the post-reaction mixture,

$c_{HC}$  is the molar concentration of hydrocarbon in the post-reaction mixture,

$c_{CO_2}$  is the molar concentration of carbon dioxide in the post-reaction mixture,

$n$  is the number of carbon atoms in the hydrocarbon molecule,

$K$  is the volume contraction factor ( $K = S_N^{in} / S_N^{out}$ ).

The selectivity of carbon monoxide conversion into individual products was expressed as the  $(X_{HC} \text{ or } X_{CO_2}) / X_{CO}$  ratio. The total selectivity to all hydrocarbons formed was the result of the subtraction of CO<sub>2</sub> selectivity from 100 percent.

The studies of carbonaceous deposit formation (the rate of catalyst coking) during the reaction of carbon monoxide hydrogenation were carried out by the gravimetric method in a continuous-flow reactor, under the same conditions as those described above.

The carbon monoxide conversion, the reaction selectivity and the rate of catalyst coking underwent continuous changes during the reaction. The changes were the quickest in the initial stage of the reaction. Therefore, the evaluation of the catalytic effects caused by various zeolites used as the catalyst supports was carried out after 30 hours of the reaction, when its pseudo-stationary state was achieved.

## 3. RESULTS AND DISCUSSION

Figure 1 shows that the use of the HZSM5 zeolite with the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio lower than 200, as a support for the iron catalysts, resulted in 8-9 times increase in carbon monoxide conversion degree in comparison with that achieved on the  $\text{SiO}_2$  supported catalyst. Simultaneously, the selectivity of carbon monoxide conversion to all hydrocarbons is also increased (Fig. 2). When the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio is below 200, the total selectivity of hydrocarbons formation exceeds the level of 90 %. It means that the presence of HZSM5 zeolite in the catalyst composition reduces the carbon dioxide formation – it inhibits the reaction  $2\text{nCO} + \text{nH}_2 \rightleftharpoons (\text{CH}_2)_\text{n} + \text{nCO}_2$  and/or it inhibits the water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$ ).

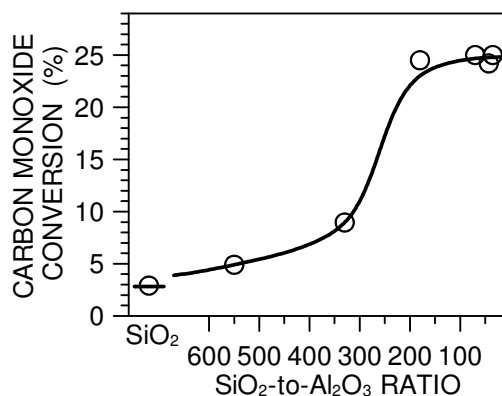


Fig. 1. Dependence of carbon monoxide conversion on the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio in Fe/HZSM5 catalysts.

The composition of the zeolite support influences also the distribution of hydrocarbons formed. The hydrocarbon product stream formed on Fe/ $\text{SiO}_2$  is rich in olefins. The content of light olefins in hydrocarbons synthesized on that catalyst is about 17 wt.%. The zeolite support decreases formation of olefins and they are almost absent in the hydrocarbon products in the case of catalysts containing zeolites with the lowest  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio (Fig. 3). The concentration of iso-butane among all  $\text{C}_4$  hydrocarbons is strongly increased when the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio is lower than 200, up to about 70% for the Fe/HZSM5(43) and Fe/HZSM5(35) catalysts (Fig. 4). When the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio in the zeolite support is higher than 330, branched linear hydrocarbons are not formed at all. The content of higher hydrocarbons,  $\text{C}_{5+}$  ( $\text{C}_5$  and higher hydrocarbons), in all hydrocarbons formed is changed in the opposite way to that of olefin amounts. It is increased parallel with the increase of the conversion

degree of carbon monoxide and with the increase of aluminum content in the zeolite (Fig. 5). In the case of the low content of silicon in the zeolite support, the  $C_{5+}$  fraction constitutes about 95% of all hydrocarbons synthesized. We believe that higher hydrocarbons, including liquid fractions in gasoline and diesel boiling temperature ranges, are also impoverished in linear olefins (alkenes-1) and enriched in branched hydrocarbons. Such changes in the composition of liquid hydrocarbons formed over bifunctional catalysts were reported in some cited papers [6, 17, 27-29].

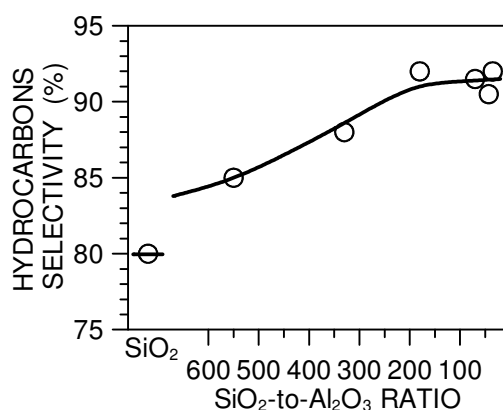


Fig. 2. Relation between selectivity of hydrocarbon product formation and the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio in Fe/HZSM5 catalysts.

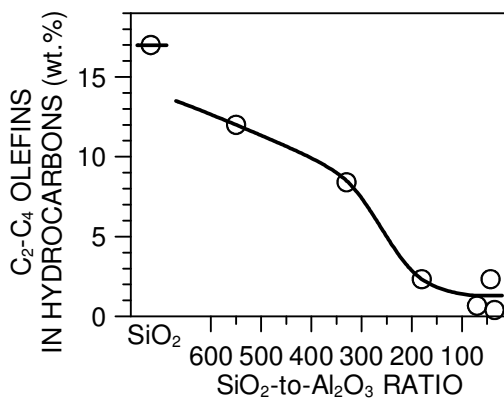


Fig. 3. The influence of the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio in Fe/HZSM5 catalysts on C<sub>2</sub>-C<sub>4</sub> olefins content in the hydrocarbon product.

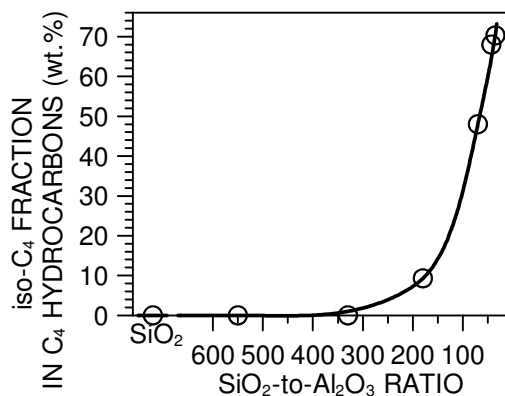


Fig. 4. Variation of percentage of iso-butane in the C<sub>4</sub> product fraction with the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio in Fe/HZSM5 catalysts.

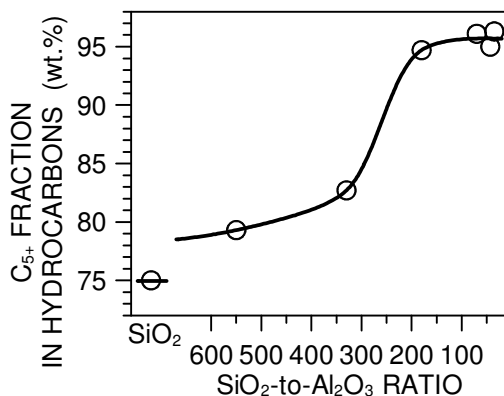


Fig. 5. C<sub>5+</sub> hydrocarbons in the hydrocarbon product versus the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio in Fe/HZSM5 catalysts.

The higher hydrocarbons derived from carbon monoxide hydrogenation on the HZSM5 zeolite supported iron catalysts contain aromatic fraction, which is absent at all in the case of the reaction product synthesized on the Fe/SiO<sub>2</sub> catalyst (Fig. 6). The zeolites with the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio higher than 200 enable formation of similar amounts of aromatic hydrocarbons. The increase of aluminum content in the zeolite to the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio of 30–40 causes the twofold rise of aromatics content in C<sub>6+</sub> hydrocarbons. The distribution of aromatic hydrocarbons also depends on the zeolite composition (Fig. 7). The high SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio, equal to 550, enables formation of benzene as main aromatic hydrocarbon. The higher amounts of aluminum in the zeolite support result in a very significant depression of benzene formation, from 60 to

3-4 mole%, and the main aromatic hydrocarbons become  $C_8$  aromatics, i.e. xylenes and ethylbenzene. Their contents in the aromatic fraction achieve about 35 mole%.

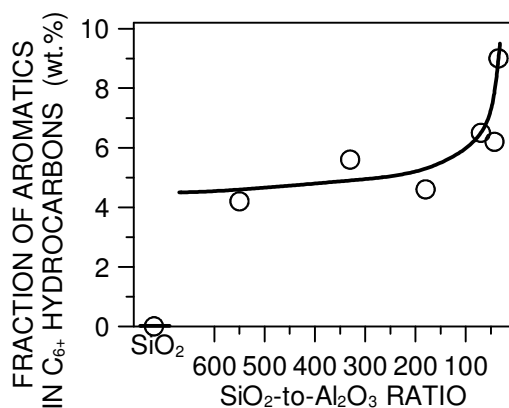


Fig. 6. Effect of the  $SiO_2$ -to- $Al_2O_3$  ratio in Fe/HZSM5 catalysts on aromatics content in the  $C_{5+}$  hydrocarbon product.

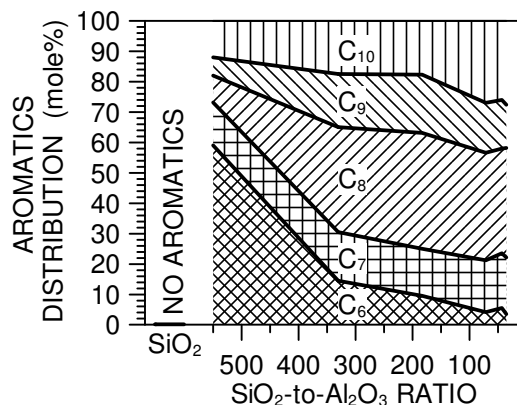


Fig. 7. Composition of the aromatic product fraction versus the  $SiO_2$ -to- $Al_2O_3$  ratio in Fe/HZSM5 catalysts.

It results from the Table 2 that the similar changes in the activity and selectivity occur also in the case of a physical mixture consisting of the Fe/ $SiO_2$  catalyst and the HZSM5 zeolite.



Tab. 2. Carbon monoxide conversion and hydrocarbon product distribution over iron bifunctional catalysts.

Catalyst	Fe/SiO <sub>2</sub>	Fe/HZSM5(43)	Fe/SiO <sub>2</sub> +HZSM5(43) physical mixture
Carbon monoxide conversion, %	2.9	25.0	22.5
Hydrocarbons selectivity, %	80.0	90.5	88.3
	Hydrocarbons distribution, wt.%		
CH <sub>4</sub>	7.5	1.8	2.5
C <sub>2</sub> -C <sub>4</sub> olefins	17.0	2.5	2.0
C <sub>2</sub> -C <sub>4</sub> paraffins	0.5	2.7	10.0
C <sub>5+</sub> hydrocarbons	75.0	95.0	85.3
iso-C <sub>4</sub> in C <sub>4</sub> hydrocarbons, wt.%	0	68.0	52.5
Aromatics in C <sub>6+</sub> hydrocarbons, wt.%	0	6.5	8.5
	Aromatics distribution, mole%		
C <sub>6</sub>	-	5.5	1.7
C <sub>7</sub>	-	18.0	19.0
C <sub>8</sub>	-	34.5	36.3
C <sub>9</sub>	-	16.0	16.0
C <sub>10</sub>	-	26.0	27.0

This experiment clearly demonstrates the synergistic interaction of both components of the bifunctional catalyst. However, the reaction effects over physically mixed FT catalyst and HZSM5 zeolite are quantitatively different from those obtained on the zeolite supported iron. In the former case the hydrocarbon product contains smaller amounts of higher and branched hydrocarbons, and a larger amount of olefins. There are also higher amounts of aromatics among C<sub>6+</sub> hydrocarbons than it was obtained in the case of the iron phase supported directly on the HZSM5 zeolite. The differences in the aromatic hydrocarbons formation on both bifunctional catalysts have only the quantitative aspect, the qualitative compositions of these fractions are very similar. These differences may be attributed to the decrease of the number of the surface Brønsted acid sites in the zeolite support in Fe/HZSM5 catalysts as compared with that on the zeolite in the catalyst obtained by physically admixing.

Preparation of the bifunctional catalysts by the impregnation of the zeolite with iron ions affects its acidity because some of iron ions are exchanged with protons from surface hydroxyls [7, 9]. It is known [4, 11, 19, 23, 37, 40] that Brønsted acid sites are necessary for restructuring of the primary hydrocarbons to aromatics. Only somewhat weaker acid sites are needed for isomerization of the linear FT hydrocarbons. The composition of higher hydrocarbons and particularly the aromatic hydrocarbon content, depending in the decisive manner on the acidic properties of the zeolite, changes with the decrease of this ratio. Therefore, as it was shown in Figures 4 and 6, these groups of hydrocarbons were formed more intensively and the aromatics fraction contains higher amounts of heavier hydrocarbons (Fig. 7) in the case of catalysts which contain the zeolite component having the relatively low  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio.

The reaction of carbon monoxide hydrogenation is accompanied by continuous setting of small amounts of a carbonaceous deposit on all catalysts. When HZSM5 zeolites were employed as supports of the iron phase, the rate of the catalyst coking was strongly suppressed (Fig. 8). The decrease in the coking rate is more evident when the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio in the zeolite support is lower than 200.

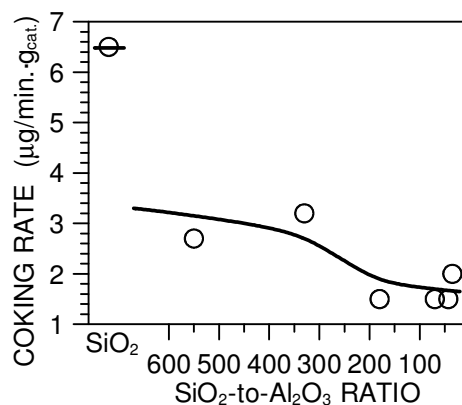


Fig. 8. Dependence of the rate of coke formation on the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio in Fe/HZSM5 catalysts.

The general direction of changes in the distribution of synthesized hydrocarbons, resulting from the introduction of HZSM5 zeolites into the bifunctional Fischer-Tropsch catalyst composition, was intended and expected. One of the aims of our work was to find the dependence of the scale of these changes on the zeolite composition. However, the most amazing is a very marked increase in the activity of zeolite-containing catalysts. It was also previously

notice [6, 13, 14, 17, 26, 27] that a side effect of the selectivity change is an increase in the catalyst activity, in comparison with that of a zeolite-free catalyst. The increase in the activity of the catalytic composition after introduction of the HZSM5 zeolite, which alone does not accelerate the reaction of carbon monoxide hydrogenation [3, 18, 19], can not be caused by any direct interaction between the zeolite support and the metal, e.g. by a strong metal-support interaction. The phenomenon of the activity increase was observed even in the case of the physical mixture of the Fe/SiO<sub>2</sub> catalyst and zeolite grains, not securing sufficiently close contact of iron and zeolite.

The changes in distribution of hydrocarbons formed and in the rate of catalysts coking suggest that the reason of the great improve of the activity is the adsorption and secondary conversion of olefins into aromatics, branched and normal aliphatic higher hydrocarbons on the zeolite. Simplified reaction network of carbon monoxide hydrogenation on zeolite-containing iron catalysts is shown in Figure 9.

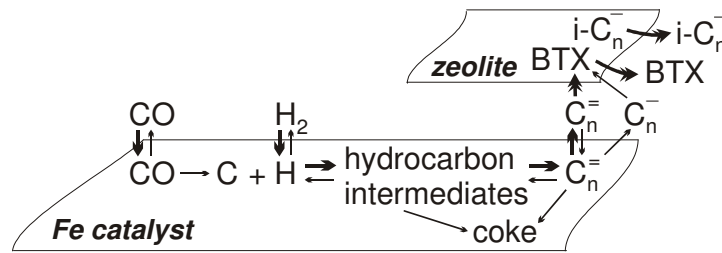


Fig. 9. Simplified reaction network of carbon monoxide hydrogenation on zeolite-containing iron catalysts.

In the case of lack of the zeolite in the catalytic composition olefins ( $\text{C}_n^-$ ) undergo readsorption on the iron catalyst, causing the formation of long-chain, poorly-hydrogenated, low-volatile hydrocarbons [41, 42] which coverage the surface of iron with a low-reactive carbonaceous deposit ("coke"). The fraction of the free iron surface which can be occupied by both reagents ( $Q_H$  and  $Q_C$ ) and by hydrocarbon intermediates ( $Q_{HC\_INTERMEDIATES}$ ), determining the catalyst activity, is equal to:

$$Q_H + Q_C + Q_{HC\_INTERMEDIATES} = 1 - Q_{C_n^-} - Q_{COKE} \quad (1)$$

where:  $Q_{C_n^-} \gg 0$  and  $Q_{COKE} \gg 0$ .

When the catalyst composition contains the zeolite, the majority of olefins undergoes conversion on zeolite and the amount of olefins in the gas phase is significantly decreased and brings near to zero ( $C_n^{\text{gas}} \rightarrow 0$ ). The adsorption-desorption equilibrium of olefins on the iron surface is disturbed. In order to maintenance of the adsorption-desorption equilibrium state equal (or close) to that resulted from the value of the equilibrium constant of this phenomena, the amounts of new formed and desorbed olefins must be increased [28]. It causes that the coverage of the surface of iron with these hydrocarbons decreases significantly ( $Q_{C_n} \rightarrow 0$ ). The smaller amount of olefins readsorbed on the surface of iron should also decrease significantly the amount of carbonaceous deposit ( $Q_{\text{COKE}} \rightarrow 0$ ). These effects mean that both component of the right side of equation (1), which decrease the coverage of the iron surface with the reagents and hydrocarbon intermediates, may be neglected and the equation assumes the following form:

$$Q_H + Q_C + Q_{\text{HC\_INTERMEDIATES}} \cong 1 \quad (2)$$

Thus, almost a whole surface of iron is accessible for adsorption of reagents and synthesis of hydrocarbons, which makes possible a significant increase in amounts of synthesized hydrocarbons and in carbon monoxide consumed.

The increase of the bifunctional catalysts activity and the significant lowering of their coking rate in the reaction of carbon monoxide hydrogenation take already place in the case of a relatively high value of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the zeolite. However, the composition of hydrocarbons formed, particularly the content of branched and aromatic hydrocarbons, is changed advantageously with the decrease of this ratio. Therefore, it may be stated that the presence of the HZSM5 zeolite with the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio lower than 200 in the bifunctional catalyst composition may be sufficient when the  $\text{C}_{5+}$  hydrocarbons production is targeted, but for high contents of branched and aromatics hydrocarbons in the liquid product, the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio equal to 30-40 should be preferred.

#### 4. CONCLUSIONS

The presence of the HZSM5 zeolite with the  $\text{SiO}_2$ -to- $\text{Al}_2\text{O}_3$  ratio lower than 200 in bifunctional composite catalysts results in 8-9 times increase in the conversion degree of carbon monoxide and in decrease of the rate of the catalyst coking in comparison with those achieved on the zeolite-free iron catalyst. The reasons of these phenomena may be explained on the basis of disturbance of the adsorption-desorption equilibrium of olefins on the iron phase. The zeolite acts

as a draw-lift pump, resulting from immediate, subsequent conversion of olefins on the zeolite. It makes possible to decrease of the amount of olefins readsorbed on the iron surface and to increase of the surface concentration of reagents and hydrocarbon precursors on the FT catalyst. The presence of olefins in hydrocarbons formed is strongly suppressed, the synthesis of C<sub>5+</sub> hydrocarbons is changed in the opposite way to that of olefin amounts. The hydrocarbons derived from carbon monoxide hydrogenation on the HZSM5 zeolite supported iron catalysts contain also the aromatic fraction and branched hydrocarbons.

The HZSM5 zeolite with the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio below 200 present in the bifunctional catalyst composition may be sufficient when C<sub>5+</sub> hydrocarbons production is targeted, but for high contents of branched and aromatics hydrocarbons in the liquid product, the SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio equal to 30-40 should be preferred.

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## CURRICULA VITAE



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