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# The catalytic activity of Fe-containing SiBEA zeolites in Fischer–Tropsch synthesis

Karolina A. Chalupka<sup>a,\*</sup>, Waldemar Maniukiewicz<sup>a</sup>, Pawel Mierczynski<sup>a</sup>, Tomasz Maniecki<sup>a</sup>, Jacek Rynkowski<sup>a</sup>, Stanislaw Dzwigaj<sup>b,c,\*\*</sup>

<sup>a</sup> Lodz University of Technology, Institute of General and Ecological Chemistry, Zeromskiego 116, 90-924 Lodz, Poland <sup>b</sup> Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France

<sup>c</sup> CNRS, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France

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#### ABSTRACT

This work is focused on catalytic activity of Red-C-Fe<sub>x</sub>SiBEA zeolites in Fischer–Tropsch synthesis. The Fe-containing zeolites were obtained by two-step post-synthesis method, which allowed incorporating the metal ions into zeolite framework and in this way to obtain materials with new physicochemical and catalytic properties. The TPR-H<sub>2</sub> studies allowed to determine the reducibility of different kinds of iron species present in C-Fe<sub>x</sub>SiBEA zeolites. The catalytic investigations indicated that the most active catalyst in FTS is Red-C-Fe<sub>20</sub>SiBEA, which achieved the CO conversion of 70% and selectivity towards liquid products of 71%. The isoalkanes, *n*-alkanes, olefins and oxidative products (alcohols, ketones and aldehydes) were identified among of liquid products. The most probably reason of catalysts deactivation is coke formation, which amount, calculated on the base of DTG-DTA data, was 7% for Red-Fe<sub>4.0</sub>SiBEA, 20% for Red-C-Fe<sub>10</sub>SiBEA and 35% for Red-C-Fe<sub>20</sub>SiBEA.

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#### 1. Introduction

During Fischer–Tropsch synthesis (FTS), syngas (mixture of CO and  $H_2$ ) is catalytically converted into wide spectrum of hydrocarbons chain [1,2]. This process is heterogenous reaction, where substrates are gaseous, products are present in gas and liquid phase and catalyst is solid [3]. As industrial catalysts of FTS, mainly cobalt and iron supported on  $Al_2O_3$  or  $SiO_2$  are used. Depending on the process conditions and the kind of catalysts used, the reaction products spectrum can be shifted to alkenes or alcohols [3,4].

The low costs of iron, its wide availability and its high activity to Water–Gas-Shift reaction (WGS) are mentioned among the advantages of the application of iron catalysts in Fischer–Tropsch process. In the case of WGS process, the iron catalyzes the reaction between water and carbon monoxide and during this process the carbon dioxide and hydrogen are produced. Moreover, during FTS over iron catalysts the wider spectrum of liquid products, including *n*-hydrocarbons, alcohols and alkenes can be formed, in

\* Corresponding author. Tel.: +48 42 631 31 34.

\*\* Corresponding author at: Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France. Tel.: +33 1 44 27 21 13. *E-mail addresses:* karolina.chalupka@p.lodz.pl (K.A. Chalupka),

stanislaw.dzwigaj@upmc.fr (S. Dzwigaj).

http://dx.doi.org/10.1016/j.cattod.2015.02.017 0920-5861/© 2015 Published by Elsevier B.V. contrast to cobalt catalysts. The huge favour of iron catalysts using in FTS is their high activity even when the syngas is derived from coal and biomass sources which have a very low CO/H<sub>2</sub> ratio ( $\leq$ 1) [3,5].

However, despite of many advantages, the iron-based catalysts possess few unfavourable properties such as rapid deactivation by coke deposition and sintering and high costs of their regeneration [3,5]. These disadvantages are still challenge in catalysts design.

It seems that choice of proper support with high specific surface area could prevent partially the high deactivation rate. The very good support for iron catalysts can be zeolites. They have high specific surface area, which ensures small size of metal nanoparticles and their good dispersion [6,7], what makes them very useful in catalysis [7]. These properties of zeolites can lead to limit chain growth and form of lighter products. Moreover, the acidity of these materials may catalyze the secondary cracking, isomerization and aromatization of primary FT products which contribute to improvement of the products distribution. The many zeolites were tested as supports of iron, among them can be mentioned: NaY, NaX, Na-ß, Na-MOR and Na-ZSM-5 [8]. It is shown that the acidity of zeolites has influence on the product selectivity in FTS. Bessel [9] has found that cobalt supported on ZSM-5, Y and MOR zeolites, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and bentonite showed similar selectivity to methane and carbon dioxide, however the distribution of higher hydrocarbons is strongly depended on the support acidity. The highest

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selectivity towards gasoline-range hydrocarbons showed ZSM-5, the most acidic type of zeolite [9].

The aim of this work was the investigation of catalytic activity in Fischer–Tropsch synthesis of iron catalysts based on BEA zeolite, prepared by two-step postsynthesis method. This method allows incorporating of transition metal ions into zeolite framework [10] and in this way modelling of new catalytic centres. This method allows also modelling acidic sites in BEA zeolite.

### 2. Experimental part

#### 2.1. Samples preparation

The Fe<sub>x</sub>SiBEA samples were obtained by two-step postsynthesis method (where x = 4, 10 and 20 wt% of Fe) described earlier by Dzwigaj et al. [11].

To prepare these samples, firstly, the TEABEA zeolite was treated in a 13 mol L<sup>-1</sup> HNO<sub>3</sub> aqueous solution (4 h, 80 °C) to obtain a dealuminated and organic-free SiBEA support (Si/Al = 1300) with vacant T-atom sites (where T = Al). SiBEA was then separated by centrifugation, washed with distilled water and dried overnight at 80 °C. To incorporate iron into vacant T-atom sites, 2 g of SiBEA was stirred under aerobic conditions at 25 °C for 24 h in 200 mL of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O aqueous solution (pH = 2.4–2.6) with different concentrations to obtain the solids with various Fe content [10]. Then, the suspensions were stirred for 2 h at 80 °C until water was evaporated and the resulting solids were dried in air at 80 °C for 24 h and labelled as Fe<sub>x</sub>SiBEA. Then, the solids were calcined in air at 500 °C for 3 h and labelled C-Fe<sub>x</sub>SiBEA.

Before FT reaction tests, C-Fe<sub>x</sub>SiBEA were reduced *in situ* under atmospheric pressure in flow of 95%  $H_2$ -5% Ar stream at 370 °C for 1 h and such obtained catalysts were labelled as Red-C-Fe<sub>x</sub>SiBEA.

#### 2.2. Methods of characterization

Powder X-ray diffractograms were recorded on a PAN analytical X'Pert Pro MPD using Cu K $\alpha$  radiation ( $\lambda$  = 154.05 pm) in 2 $\theta$  range of 5–90°.

The TPR-H<sub>2</sub> measurements were carried out in an automatic TPR system (AMI-1) in the temperature range of 25–900 °C, using H<sub>2</sub> stream (5% H<sub>2</sub>–95% Ar, flow 40 mL min<sup>-1</sup>). H<sub>2</sub> consumption was monitored by a thermal conductivity detector (TCD).

Thermal analysis data (SETSYS 16/18, Setaram (France) and mass spectrometer ThermoStar, Balzers (Germany)) were used to define the formation of carbon deposit.

The measurements were made in the range of 25–1000  $^\circ\text{C}$  in flowing air.

#### 2.3. Catalytic tests

The FTS catalytic tests were carried out in a fixed bed reactor using a gas mixture of H<sub>2</sub> and CO with molar ratio of 2/1 and total flow of reagents of 60 mL min<sup>-1</sup>. Reaction was carried out under 30 atm at 340 °C and gaseous reagents were analyzed by gas chromatograph (Shimadzu GC-14) equipped with TCD detector and two columns: measuring – Carbosphere 7A and comparative – molecular sieves 7B. Parameters of GC measurements: column's temperature – 45 °C, detector's temperature – 120 °C, detector's current – 100 mA; carried gas – He. Before FT reaction, catalysts were reduced *in situ* under atmospheric pressure in a flow of 95% H<sub>2</sub>–5% Ar gas mixture at 370 °C for 1 h.

The liquid products were analyzed by GC–MS coupled technique. Gas chromatograph was equipped with capillary column Zebron Phase ZB-1MS order No: 7HG G011-11 and coupled with quadrupole mass spectrometer. The liquid products in the aim of water removal, which could be formed during reaction, were concentrated by SPE method on octadecyl columns C18. Before extraction each of column was preconditioned with 2 mL of *n*-hexane. After this process 1 mL of liquid products samples were injected on column and then it was washed with 2 mL of *n*-hexane. GC–MS analysis were carried out in helium flow  $(1.0 \text{ mL min}^{-1})$  in temperature range 70–250 °C with linear temperature increase of 8 °C min<sup>-1</sup>. The volume of analyzed sample was 1 mm<sup>3</sup>.

The quantitative analysis of CO conversion ( $K_{CO}$ ) and selectivity towards CO<sub>2</sub> ( $S_{CO_2}$ ), CH<sub>4</sub> ( $S_{CH_4}$ ) and liquid products ( $S_{LP}$ ) were calculated in the following way:

$$K_{\rm CO} = \frac{S_{\rm CO \, in} - S_{\rm CO \, ari}}{S_{\rm CO \, in}} \times 100\%$$
$$S_{\rm CH_4} = \frac{X_{\rm CH_4 \, i} \times 100\%}{X_{\rm CH_4 \, out}} / F$$

$$X_{\rm CH_4\,out} = \frac{X_{\rm CH_4\,s} \times K_{\rm CO}}{100\%}$$

$$S_{\text{CO}_2} = \frac{X_{\text{CO}_2 \text{ i}} \times 100\%}{X_{\text{CO}_2 \text{ out}}} / F$$
$$X_{\text{CO}_2 \text{ s}} \times K_{\text{CO}_2 \text{ s}}$$

$$X_{\rm CO_2\,out} = \frac{X_{\rm CO_2\,s} \times X_{\rm C}}{100\%}$$

where  $K_{\rm CO}$  – CO conversion;  $S_{\rm CO in}$  – the peak's surface of CO on inlet before reaction (standard);  $S_{\rm CO ari}$  – the peak's surface of CO after reaction; ( $S_{\rm CH_4}$ ) – selectivity towards CH<sub>4</sub>; ( $S_{\rm CO_2}$ ) – selectivity towards CO<sub>2</sub>;  $X_{\rm CH_4 i}$  – the peak's surface of CH<sub>4</sub> formed during reaction;  $X_{\rm CO_2 i}$  – the peak's surface of CO<sub>2</sub> formed during reaction;  $X_{\rm CH_4 out}$  – the theoretical peak's surface of CH<sub>4</sub> which could be formed during reaction in the case when all CO is converted to CH<sub>4</sub>;  $X_{\rm CO_2 out}$  – the theoretical peak's surface of CO<sub>2</sub> which could be formed during reaction in the case when all CO converted to CO<sub>2</sub>;  $X_{\rm CH_4 s}$  – the peak's surface of CH<sub>4</sub> standard when only methane is analyzed;  $X_{\rm CO_2 s}$  – the peak's surface of CO<sub>2</sub> standard when only carbon dioxide is analyzed; F – contraction coefficient taken into account the changes of flow and differences between gaseous substrates and liquid products:

$$F = \frac{S_{\text{Ar} i}}{S_{\text{Ar} s}}$$

 $S_{\text{Ar i}}$ -peak's surface of Ar (inert gas) during reaction;  $S_{\text{Ar s}}$ -peak's surface of Ar on inlet before reaction (standard).

The  $C_2$ - $C_6$  hydrocarbons were not identified during GC analysis. The selectivity towards liquid products (all formed liquid products) was calculated from following equation:

$$S_{\rm LP} = 100 - (S_{\rm CH_4} + S_{\rm CO_2})$$

#### 3. Results and discussion

#### 3.1. The phase composition of C-Fe<sub>x</sub>SiBEA samples – XRD analysis

The phase composition of prepared samples was studied by using of XRD method. In Fig. 1 the diffractograms of Fe<sub>x</sub>SiBEA zeolites calcined at 500 °C for 3 h (x=4.0, 10 and 20 wt% of Fe) are shown. The phase analysis was done on the base of JCPD data.

For all studied samples reflexes characteristic of BEA zeolite  $(2\theta = 22.52 - 22.59^{\circ})$  are identified. This indicates that structure of BEA zeolite after iron incorporation and samples calcination is preserved. Moreover, this proves that dealumination does not destroy the BEA zeolite structure and leads to obtain good dispersion of iron ions in BEA zeolite. The decrease of  $2\theta$  value is related to expansion of BEA matrix and incorporation of part of iron ions into zeolite

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Fig. 1. XRD of C-Fe $_{4.0}$ SiBEA, C-Fe $_{10}$ SiBEA and C-Fe $_{20}$ SiBEA zeolites recorded at room temperature and ambient atmosphere.



Fig. 2. TPR-H<sub>2</sub> profiles of C-Fe<sub>4.0</sub>SiBEA, C-Fe<sub>10</sub>SiBEA and C-Fe<sub>20</sub>SiBEA zeolites.

framework as pseudo-tetrahedral Fe(III) species, as evidenced by DR UV–vis data in our earlier report [10].

The reflexes assigned to presence of hematite phase were also observed for all samples. This suggests that iron is present in Fe<sub>x</sub>SiBEA zeolites not only as framework pseudo-tetrahedral Fe(III) but also as extra-framework octahedral Fe(III) and/or iron oxides, what is in line with earlier work [10].

#### 3.2. The reducibility of C-Fe<sub>x</sub>SiBEA samples – TPR-H<sub>2</sub> studies

The temperature programmed reduction was used to determine reducibility of iron present in C-Fe<sub>x</sub>SiBEA zeolites. The TPR-H<sub>2</sub> profiles are shown in Fig. 2.

The TPR-H<sub>2</sub> patterns indicate different reducibility of various kinds of iron species present in C-Fe<sub>x</sub>SiBEA zeolites and suggest that reduction of iron is involved in several stages. For C-Fe<sub>4.0</sub>SiBEA, C-Fe<sub>10</sub>SiBEA and C-Fe<sub>20</sub>SiBEA zeolites the reduction peaks in four temperature ranges are identified. In the first temperature range a peak at 350–360 °C is observed for all C-Fe<sub>x</sub>SiBEA zeolite samples and could be attributed to reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>, in line with our earlier report concerning very similar Fe-containing SiBEA zeolites [10] and literature data [12,13]. In the second temperature range, the TPR peaks at 430–480 °C are likely related to reduction of framework pseudo-tetrahedral Fe(III) to pseudo-tetrahedral Fe(II) identified by DR UV–vis spectroscopy in Fe-containing SiBEA zeolites in our earlier work [10] (not shown here). As shown in [10], in the Fe-containing SiBEA zeolites with lower than 2 wt% of Fe



Fig. 3. XRD of Red-C-Fe $_{4.0}$ SiBEA and Red-C-Fe $_{10}$ SiBEA zeolites recorded at room temperature and ambient atmosphere.

only one TPR peak at 420 °C was observed related to reduction of framework pseudo-tetrahedral Fe(III) to framework pseudotetrahedral Fe(II). The TPR peaks in the third temperature range between 520 and 650 °C observed for all C-Fe<sub>4.0</sub>SiBEA, C-Fe<sub>10</sub>SiBEA and C-Fe<sub>20</sub>SiBEA zeolite samples may be related to reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO, in line with literature data [12,13]. The different positions of the peaks in TPR-H<sub>2</sub> for investigated C-Fe<sub>x</sub>SiBEA zeolite samples are related to different amount of Fe<sub>3</sub>O<sub>4</sub> in each sample and the presence of others iron phase what involve some shift of the TPR peaks in compared TPR profils of C-Fe<sub>x</sub>SiBEA samples.

The two mechanism for  $Fe_2O_3$  reduction are postulated (threestep or two-step reduction) in the literature [12,13]:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe^0$$
 (1)

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe^0 \text{ or } Fe_2O_3 \rightarrow FeO \rightarrow Fe^0$$
 (2)

The TPR peaks, appeared in the fourth temperature range between 680 and 730 °C for all studied Fe-containing zeolite samples with maximum at 730, 680 and 710 °C for C-Fe<sub>4.0</sub>SiBEA, C-Fe<sub>10</sub>SiBEA and C-Fe<sub>20</sub>SiBEA zeolite samples, respectively, are probably related to reduction of FeO to Fe(0).

### 3.3. Catalytic activity of Red-C-Fe<sub>x</sub>SiBEA zeolite samples in Fischer–Tropsch synthesis

The catalytic activity of Red-C-Fe<sub>x</sub>SiBEA catalysts were studied at 340 °C under pressure of 30 atm of synthesis gas (CO:H<sub>2</sub> = 1:2) and total flow of 60 cm<sup>3</sup> min<sup>-1</sup>). Before catalytic tests the each of C-Fe<sub>x</sub>SiBEA zeolite sample was reduced in situ at 370 °C for 1 h in hydrogen flow of 40 cm<sup>3</sup> min<sup>-1</sup>. The reduction temperature was chosen on the base of TPR results and the literature reports. Many scientists suggest that active centre in Fischer-Tropsch synthesis over Fe catalysts is iron carbide [3], however the functions of these phases is still considered and ambiguous. Moreover, the iron carbide is more active than metallic iron [8]. In Fig. 3 the XRD patterns are presented for Fe<sub>x</sub>SiBEA samples after reduction at 370 °C for 1 h in hydrogen flow. These results suggest that the reduction of Fe<sub>2</sub>O<sub>3</sub> is partial. The XRD patterns recorded for samples after reduction at 370 °C show presence of the peaks with low intensity, characteristic for Fe<sub>2</sub>O<sub>3</sub> phase. The main phase observed on diffractograms is  $Fe_3O_4$ , what is in line with TPR-H<sub>2</sub> results (point 3.2.).

In Fig. 4 the CO conversion and selectivity towards  $CH_4$ ,  $CO_2$  and liquid products during FTS carried out on Red-C-Fe<sub>x</sub>SiBEA zeolite catalysts are shown. The most active and selective towards liquid products catalyst is Red-C-Fe<sub>20</sub>SiBEA, which achieves CO conversion of 62% and selectivity towards liquid products near of 70% (selectivity towards  $CH_4$  and  $CO_2$  is of 15 and 16%, respectively). In the case of Red-C-Fe<sub>4.0</sub>SiBEA and Red-C-Fe<sub>10</sub>SiBEA, the CO

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Table 1

The quantitative analysis of identified liquid products formed on Red-C-Fe<sub>40</sub>SiBEA, Red-C-Fe<sub>10</sub>SiBEA and Red-C-Fe<sub>20</sub>SiBEA zeolite catalysts (calculation done on the basis of GC-MS data).

Catalyst	Iso-/n-alkanes ratio	(Olefins + iso-olef.) $/n-C_xH_{2x+2}$ ratio	(Alcohols, aldehydes and ketones)/n-C <sub>x</sub> H <sub>2x+2</sub> ratio	
Red-C-Fe <sub>4.0</sub> SiBEA Red-C-Fe <sub>10</sub> SiBEA	1.44 0.30	– 0.15 (isoolef./olefins: 0.49)	0.029 (ketones only) 0.148 (alc. 0.019; ket. 0.129)	
Red-C-Fe <sub>20</sub> SiBEA	0.87	0.034 (isoolef./olefins:1.33)	0.099 (alc. 0.024; ald. 0.055: ket. 0.020)	



Fig. 4. CO conversion and selectivity towards CH<sub>4</sub>, CO<sub>2</sub> and liquid products formed during FTS carried out at 340°C for 20h under pressure of 30 atm on Red-C-Fe4.0SiBEA, Red-C-Fe10SiBEA and Red-C-Fe20SiBEA zeolite catalysts.

#### Table 2

The amount of carbon deposition on Spend-Red-C-Fe<sub>4.0</sub>SiBEA, Spend-Red-C-Fe10SiBEA and Spend-Red-C-Fe20SiBEA zeolite catalysts (data from TG-DTA analysis).

Catalysts	Amount of carbon deposition (%)
Red-C-Fe <sub>4.0</sub> SiBEA	6.7
Red-C-Fe <sub>10</sub> SiBEA	20.4
Red-C-Fe <sub>20</sub> SiBEA	35.4

conversion is of 10 and 26% and liquid products selectivity is of 44 and 60%, respectively.

The changes of CO conversion and selectivity towards CH<sub>4</sub>, CO<sub>2</sub> and liquid products versus time for Red-C-Fe10SiBEA and Red-C-Fe<sub>20</sub>SiBEA are presented in Fig. 5. These results indicate that CO conversion of both catalysts slightly decreased with increasing of reaction time. In the case of Red-C-Fe<sub>10</sub>SiBEA, the CO conversion changes from 33 to 21% and selectivity towards liquid products increases from 45 to 60%. In the case of Red-C-Fe<sub>20</sub>SiBEA, the CO conversion decreases from 73 to 56% and selectivity towards liquid products changes from 59 to 71%. Among of the identified by GC-MS analysis liquid products are *n*-hydrocarbons, isoalkanes, olefins and oxidative products. The ratios of isoalkanes to n-alkanes, olefins and isoolefins to n-alkanes and oxidative products to n-alkanes are shown in Table 1. For Red-C-Fe<sub>4.0</sub>SiBEA, mainly isoalkanes is identified and very small amount of ketones is noted. In the case of Red-C-Fe<sub>10</sub>SiBEA, *n*-alkanes are mainly observed with very small amount of alcohols and ketones. Similarly, in the case of Red-C-Fe<sub>20</sub>SiBEA, the isoalkanes and *n*-alkanes are identified mainly and very small amounts of isoolefins, olefins and oxidative products (alcohols, aldehydes, ketones) are observed (Table 1).

The main reason of deactivation of iron catalysts in Fischer-Tropsch synthesis is coke formation. The amounts of carbon deposition on Spent-Red-Fe<sub>x</sub>SiBEA catalysts, calculated from TG-DTA-MS analysis data, are collected in Table 2. The TG-DTA-MS analysis, which results are also shown in Fig. 6, indicates that this kind of carbon deposition on Spent-Red-C-Fe<sub>x</sub>SiBEA catalysts is easily oxidized and its total oxidation occurs below

#### Red-C-Fe<sub>10</sub>SiBEA (340 °C, 30 atm)



Red-C-Fe20SiBEA (340 °C, 30 atm)



Fig. 5. CO conversion and selectivity towards CH<sub>4</sub>, CO<sub>2</sub> and liquid products versus time during FTS carried out at 340 °C under pressure of 30 atm on Red-C-Fe<sub>4.0</sub>SiBEA, Red-C-Fe10SiBEA and Red-C-Fe20SiBEA zeolite catalysts.

temperature of 600 °C. The amount of carbon deposition changes from 7% for Spent-Red-C-Fe<sub>4.0</sub>SiBEA to 35% for the most active Spent-Red-C-Fe<sub>20</sub>SiBEA catalyst.

In the Table 3 the comparison of catalytic activity in Fischer-Tropsch synthesis of iron catalysts supported on different zeolite samples are collected. The tested iron catalysts containing 10 wt% of Fe was carried out at 270 °C under pressure of 2 MPa (19.6 atm). The highest CO conversion and selectivity towards liquid products was found for iron catalysts supported on NaX (48% of CO conversion and 47.1% of LP selectivity) and NaY (49% of CO conversion and 48.9% of LP selectivity). Both catalysts showed also very small selectivity towards CH<sub>4</sub> (5.6 and 7.8% for Fe/NaX and Fe/NaY respectively) [8].

The usually used iron supported catalysts are promoted by potassium, zinc or cooper and also noble metals in the aim to improve their catalytic activity in Fischer-Tropsch synthesis (mainly for increasing of the selectivity towards C<sub>5+</sub> hydrocarbons). Li and collaborators proved, that doped by potassium iron catalysts achieved very high selectivity towards liquid products hydrocarbons of 85-88%, selectivity towards CO<sub>2</sub> of 11.5-20.2% and

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Catalysts	CO conv. (%)	Selectivity (%)			Reaction conditions ( $T$ , $p$ , CO:H <sub>2</sub> ratio)	
		CH <sub>4</sub>	CO <sub>2</sub>	$C_2-C_4$	LP	
Fe/SiO <sub>2</sub>	22	15	12	40	33.2	<i>T</i> = 270 ° C
Fe/Na-ZSM-5	3.0	14	19	48	19	<i>p</i> = 2 Mpa
Fe/Na-MOR	29	12	20	35	33.2	$CO:H_2 = 1:2$
Fe/Na-ß	5.8	16	24	46	15	Fe loading 10 wt%
Fe/NaX	48	5.6	30	18	47.1	-
Fe/NaY	49	7.8	21	23	48.9	
Fe <sub>10</sub> SiBEA	26	22	18	-	60	$T = 340 \circ C p = 30 \text{ atm } t = 20 \text{ h}; \text{ CO:H}_2 = 1:2$
e20SiBEA	62	15	16	-	70	$T = 340 \circ \text{C}; p = 30 \text{ atm}; t = 20 \text{ h}; \text{CO}; \text{H}_2 = 1; 20 \text{ h}; \text{CO}; \text{CO}; \text{H}_2 = 1; 20 \text{ h}; \text{CO}; \text{CO}; \text{H}_2 = 1; 20 \text{ h}; \text{CO}; \text{CO}$



Fig. 6. TG-DTA analysis of Spend-Red-C-Fe $_{\rm 10}SiBEA$  and Spend-Red-C-Fe $_{\rm 20}SiBEA$  zeolite catalysts after FTS.

selectivity towards CH<sub>4</sub> of 2.0–2.8%, while the CO conversion was kept at 13–16%. Reaction was carried out under 2.14 MPa (21 atm) and CO/H<sub>2</sub> ratio was 2.508 [14]. Those catalysts appeared as higher selective towards liquid products that these investigated in our work presented here, however, it was measured at CO conversion 13–16%, while our Red-C-Fe<sub>x</sub>SiBEA zeolite catalysts are characterized by slightly smaller liquid products selectivity of about 70% but with much higher CO conversion of 70%. Moreover, iron supported BEA (10 wt% Fe/Na- $\beta$ , Table 3) obtained by traditional method showed very low CO conversion of 5.8%) and selectivity towards C<sub>5</sub>–C<sub>9</sub> hydrocarbons of 14%. During FT reaction carried out on these catalysts the C<sub>1</sub>–C<sub>4</sub> was of 62%). Our Fe-containing zeolites catalysts

obtained by two-step postsynthesis method are more active than Fe/Na-ß catalyst what suggests that dealumination of BEA zeolite and incorporation of iron into framework of BEA zeolite can lead to improve the activity of BEA zeolite modified by iron in FT reaction. This allows to consider the Red-C-Fe<sub>x</sub>SiBEA zeolites as active and useful catalysts of Fischer–Tropsch synthesis.

#### 4. Conclusions

The Fe<sub>x</sub>SiBEA zeolites with different iron content (4.0, 10 and 20 wt% of Fe) were prepared by two-step postsynthesis method.

The XRD studies showed that in C-Fe<sub>x</sub>SiBEA zeolites, the hematite phase reflections have been distinguished beside of reflections coming from BEA zeolite.

Moreover, these investigations indicated that dealumination process and incorporation of iron ions into zeolite framework did not destroy BEA structure.

The TPR-H<sub>2</sub> patterns suggest presence of different kinds of iron species in Fe<sub>x</sub>SiBEA zeolites. These TPR-H<sub>2</sub> investigations together with our earlier DR UV–vis studies on similar Fe-containing SiBEA zeolite allow us to suggest that in C-Fe<sub>x</sub>SiBEA zeolites iron is present as framework pseudo-tetrahedral Fe(III) and extra-framework octahedral Fe (III) and/or iron oxides.

Catalytic activity tests showed that the Red-C-Fe<sub>x</sub>SiBEA zeolite catalysts can be considered as efficient catalysts of Fischer–Tropsch synthesis. The most active catalyst was Red-C-Fe<sub>20</sub>SiBEA. Some deactivation of Red-C-Fe<sub>x</sub>SiBEA zeolite catalysts during Fischer–Tropsch reaction is probably related to coke formation.

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