Cooperative effect of cobalt and zeolite in controlling activity and stability of a catalytic Fischer–Tropsch process

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Abstract

The use of zeolites in Co-catalysts of Fischer–Tropsch synthesis (FTS) results in cooperative effect in the form of sudden increase of the zeolite activity in catalysing secondary transformations of FTS-generated hydrocarbons at unusually low temperatures in the range of 170–260 °C. In addition, hydrophobic zeolites in H-form allow changing the hydrophobicity of the pore walls and influence capillary condensation phenomena for intermediate species. The most unexpected effect of Co and hydrophobic zeolites is the improvement of degradation behaviour of the catalysts due to involvement of FTS-generated water into formation of additional Bronsted centres thus preventing undesirable oxidation of heat-conductive metal additives and other water-induced degradation processes. In addition, the stability of catalyst behaviour and its lifetime increase.

Keywords Heterogeneous catalysis · Cobalt · Zeolite · Fischer–Tropsch synthesis · Cooperative effect

Introduction

Liquid hydrocarbons synthesized from CO and H₂ by Fischer–Tropsch synthesis (FTS) remain one of promising sources of high-quality sulfur-free motor fuels [1, 2]. The composition of the liquid hydrocarbon mixtures (syn-crudes) depends on both the catalyst properties and the process parameters [1–3]. In particular, the common Co-based catalysts on alumina or silica support provide formation of predominantly linear hydrocarbons including high molecular weight compounds aka waxes. To receive drop-in fuels it is necessary to subject such mixture to additional chemical transformations including costly hydrocracking of waxes.

It is very attractive to skip the hydrocracking step in producing syncrude by Fischer–Tropsch method [4–6]. The use of hybrid catalysts where cobalt Fischer–Tropsch active centres are complemented by zeolite acidic cracking centres may help reaching the desirable target. The activity of zeolites in cracking, hydrocracking and other reactions of interest is revealed at the temperatures of 300 °C and higher, which is too different from the FTS typical temperature

range. This difference in temperature ranges implies that a cobalt–zeolite catalyst should not perform as hybrid one. Despite this argumentation, the works [4–8] report experimental results, which can be interpreted as manifestation of cooperative catalysis effect, i.e. the activity of zeolite centres in secondary transformations of FTS-generated hydrocarbons is much higher than it could be expected.

Such multifunctional catalyst granule should be theoretically capable of generating more product due to lower viscosity of light syncrude as compared with wax-laden classical FTS product. It would require the solution of the main problems of FTS proper, namely high exothermicity and low productivity of a packed catalyst bed. The hybrid catalytic system is to provide heat removal and product transport from the core of the catalyst granules [9, 10]. One of the ways providing such effect is the introduction of heat-conducting additives such as aluminium metal [9, 11]. This method is well developed and even used in industrial practice [12].

The understanding of the possible cooperative effect requires revealing that H₂O is a main FTS by-product, which forms the environment of all the reactions proceeding in a bed as illustrated by main reaction equations shown below:

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There are few ways for the water to get out of the reaction zone; the only H_2O -consuming reaction is the reaction with CO with formation of CO_2 and hydrogen. It is well known that Co has catalytic effect in this reaction although it is limited and conversion dependent [13, 14]. Therefore, the FTS-generated water is accumulated in the reaction bed inspiring oxidation and sintering of active Co particles as well as formation of catalytically inactive cobalt-support compounds. As a result, it often leads to quick degradation determined mostly by the properties of a support and by partial pressure of water vapor (the ratio $p\text{H}_2\text{O}/p\text{H}_2 < 1.5$ as a criterion of slower degradation) [3, 15, 16]. The removal of water from the reaction zone can help improving catalyst service life. The negative effect of water is enhanced in case of pelletized catalysts with thermally conductive additives, where the additive (metal flakes or micro-particles) is quickly oxidized by the water [8, 11].

The problem of negative effect of water in FTS can be solved by controlling hydrophilicity/hydrophobicity of a catalyst/product interface. Zeolites are known as capable of revealing hydrophilic or hydrophobic properties depending on their form and composition [17–19]. Conventional classification is based on competitive absorption of water from water–hydrocarbon mixtures. Zeolites with high concentration of alkali or alkaline earth cations are hydrophilic as they have high affinity towards polar molecules, which are small enough to enter the zeolite micropores [20]. High silica zeolites absorb preferably hydrocarbons from water–hydrocarbon mixtures, so they are hydrophobic [21–23]. Hydrophobicity can be varied as stipulated in [17, 19, 23]—so the introduction of a zeolite into FTS catalyst granule can allow controlling catalyst/product interface properties and hence controlling water impact on a catalyst. This suggestion was earlier confirmed for a simpler case of a catalyst based on support-free skeleton Co [24].

The purpose of this work is to reveal a cooperative catalytic effect of Co and zeolites in impregnation catalysts for Fischer–Tropsch synthesis.

Experimental

Supports were prepared by extrusion of the paste consisting of aluminium metal powder (RUSAL), zeolite HBeta with Si/Al = 19, HY with Si/Al = 30 (both Zeolyst), CaX with Si/Al = 2, NaX with Si/Al = 2 and CaA with Si/Al = 1 (all ZAO “Nizhegodskie sorbenty” binder (Disperal P2, Sasol) and a liquid phase (the distilled water, nitric acid and triethylene glycol). One type of support was prepared zeolite-free for reference. Diameter of the extruder die was 2.5 mm. Ready extrudates were dried, calcined and cut to

Table 1 Composition of catalysts in % wt. Co-Ref catalyst was prepared as a reference

Catalyst	Cobalt ^a	Zeolite	Al_2O_3	Al metal ^b	
				As prepared	After catalytic run
Co-Ref	20	—	53	27	11
Co-HBeta	20	24	30	26	24
Co-HY	20	24	29	27	24
Co-CaX	20	24	28	28	12
Co-NaX	20	24	27	29	10
Co-CaA	20	24	32	24	14

^aCobalt content was confirmed by chemical analysis

^bAl metal content was determined by volumetric method (measurement of the volume of hydrogen released in the reaction between a sample and NaOH aqueous solution). The composition adds up to 100% accounting the “as-prepared Al metal” column only; while the “after catalytic run” column is shown for comparison

Fig. 1 SEM of the Co-HBeta catalyst fracture. Al metal can be seen in the form of chips or flakes, while zeolite particle are visualized as polyhedrons in between the flakes

2.2–2.5 × 2.5–3.0 mm pellets. All catalysts were prepared by two-step incipient wetness impregnation of supports with water solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, every step was followed by calcination in air flow at 250 °C for 1 h. Cobalt content was 20% wt. for each catalyst. The composition of catalysts is given in Table 1. SEM picture of a catalyst fracture shows that the zeolite particles are evenly distributed between aluminium metal flakes thus providing a heat-conductive network across the catalyst pellet—see Fig. 1. Catalyst Co-Ref did not contain any zeolite and served as a reference.

Table 2 summarizes data on surface area and pores of the catalysts under investigation. The macropore volume was measured by water pycnometry method, all the other parameters were determined using nitrogen adsorption method. The mesopores were measured in the pore size range 30–1000 Å. The influence of a zeolite type on a catalyst structural properties can be understood by the analysis of

Table 2 Surface area and pores in the catalysts under investigation

Catalysts	Macropore volume, cm ³ /g	Mesopore volume, cm ³ /g	BET, m ² /g
Ref	0.228	0.138	109
Co-HBeta	0.427	0.100	155
Co-HY	0.592	0.197	192
Co-CaX	0.638	0.128	134
Co-NaX	0.632	0.087	75
Co-CaA	0.631	0.098	93

Fig. 2 Flowsheet of a laboratory rig for testing highly productive Fischer–Tropsch catalysts: 1–3—gas cylinders; 4—mass flow controller; 5—reactor; 6—liquid product separator; 7—GC; 8—receiver; 9—water supply tank; 10—water pump; 11—water heater; 12—thermocouples

Table 2. Indeed, the introduction of H-form zeolites resulted in macropore volume increase by 1.9–2.5 times, while the cationic forms led to 2.8-fold increase. Mesopore volume decreased as a result of introduction of all the zeolites with single exception of HY. The distinction of CaA and NaX was revealed by decrease in the specific surface of a catalyst from 106 m²/g down to 93 and 75 m²/g, respectively.

Fischer–Tropsch catalysts testing was done at 2 MPa in a laboratory test rig (Fig. 2). The temperature of the catalyst bed was maintained by circulation of pressurized pre-heated water through the reactor jacket. The pressure of the circulating water was kept constant, which was 0.5–0.7 MPa higher than the boiling pressure at the reaction temperature. This technical solution provides efficient heat removal at stationary conditions and quenches undesirable effects of hot spot

development. In the latter case, the circulating water undergoes phase transition due to hot spot overhear, thus removes an excess heat and returns the bed into the stationary condition. The amount of a sample in this rig was approximately 2.5 cm³, the reactor inner diameter—11 mm. Syngas with molar ratio of H₂/CO = 2 was fed at space velocities of 1000 h^{−1} and 3000 h^{−1}. Catalysts were activated in hydrogen at 400 °C, 0.1 MPa and at gas-hour space velocity (GHSV) of 3000 h^{−1}.

Composition of gaseous and liquid products was determined chromatographically. The analysis of feed mixture and gaseous products (CH₄, CO₂, C₂–C₄ hydrocarbons) was done by gas adsorption chromatography (thermal conductivity detector, carrier gas—helium, gas flow rate 20 ml/min). The column with CaA molecular sieves (3 m × 3 mm) was used to separate CO and CH₄. The HayeSep column (3 m × 3 mm) was used to separate CO₂ and C₂–C₄ hydrocarbons. The temperature-programmed mode was used (60–200 °C, heating rate 10 °C/min).

Composition of liquid syncrude was determined by gas–liquid chromatography (flame ionization detector, carrier gas—helium, gas flow rate 30 ml/min). The 50 m length capillary column with DP-Petro plate was used. The temperature-programmed mode was used (50–270 °C, heating rate 4 °C/min). The water–liquid phase was accounted for in calculation of material balance. The water phase contained only negligible amounts of acids/alcohols, which never exceeded 400 ppm.

The material balance closure was achieved in the experiments with accuracy 1% or better.

Results and discussion

Experimental results on CO conversion and C₅₊ selectivity are shown in Fig. 3 as a function of reaction temperature for GHSV 1000 h^{−1}. It is obvious that temperature influence is drastically different for zeolites in H-form and in cationic form. CO conversion is higher in the presence of H-zeolites at the temperature below 200 °C. The C₅₊ selectivity decreases with temperature for H-zeolites while for cationic zeolites it does not depend on temperature. CO conversion jumps in the temperature range 200–220 °C for cationic zeolites while C₅₊ selectivity is still constant. H-zeolites show almost opposite behaviour in that same temperature range. As soon as reaction temperature exceeds 220 °C the CO conversion increases for all the catalysts although much slower for cationic zeolites. The C₅₊ selectivity in the temperature range 220–240 °C drops down for H-zeolites and stays almost constant for cationic ones. In case of the Ref catalyst, CO conversion rises with temperature at the temperatures exceeding 200 °C, while C₅₊ selectivity keeps constant in a wide temperature range.

Fig. 3 Influence of reaction temperature on CO conversion (a) and C_{5+} selectivity at GHSV 1000 h^{-1}

Methane yield and selectivity are shown in Fig. 4 as a function of the reaction temperature. The methane formation selectivity manifests the most distinctive dependencies with maximum for H-zeolites and monotonous rise for cationic zeolites. The latter also show steeper rise at the temperatures beyond $210\text{ }^{\circ}\text{C}$. The yield of methane increases through all the temperature range for all the catalysts, however distinctions between zeolite forms are still clear. In particular, the H-zeolites provide linear rise of the CH_4 yield at the temperatures below $220\text{ }^{\circ}\text{C}$ with almost no change at higher temperatures. Unlike that, the cationic form demonstrates the steepest increase at the temperatures beyond $220\text{ }^{\circ}\text{C}$. In case of Ref catalyst, the temperature dependence of methane selectivity is similar to that for the catalysts with H-form zeolites and very different from the catalysts with cationic form zeolites.

We believe that these results can be explained on the basis of competitive water/hydrocarbon adsorption, which influences capillary condensation of both water and hydrocarbons. The suggestion is that $210\text{ }^{\circ}\text{C}$ is the temperature of water release from the pores of the catalyst. It means that this release of the capillary-condensed liquid results in intensification of mass transport in the catalysts containing

Fig. 4 Influence of reaction temperature on methane selectivity (a) and methane yield at GHSV 1000 h^{-1}

H-zeolites. Unlike that, the cationic zeolites keep water in the pores at higher temperatures due to adsorptive and Coulomb forces. This explains difference in catalysis in the temperature range of $200\text{--}220\text{ }^{\circ}\text{C}$ between catalysts with H-zeolites and with cationic zeolites. Above $220\text{ }^{\circ}\text{C}$ in the presence of H-zeolites a mass exchange is further intensified. Thanks to involvement of Bronsted centers into secondary transformations of hydrocarbons thus promoting promotes higher activities and productivities. At the same time water serves as a source of additional Bronsted centers [25–27], also promoting an intensification of a mass exchange and increase in activity and productivity.

Figure 5a allows comparing Fischer–Tropsch synthesis parameters at 1000 h^{-1} for different catalysts. It is obvious that the catalysts with cationic forms of zeolites are characterized by lower CO conversion and productivity. The catalysts with H-form zeolites performed better. Apparently, the reference catalyst was not much different at this particular GHSV.

The distinction of the catalysts with zeolites became evident at higher GHSV as can be seen from Fig. 5. In particular, the CO conversion over reference catalyst dropped

Fig. 5 FTS parameters of the catalysts with different zeolite forms at GHSV 1000 h⁻¹ and 3000 h⁻¹

by 30% after GHSV increase up to 3000 h⁻¹; while Hbeta demonstrated unchanged CO conversion and threefold jump in productivity.

The experiments at higher GHSV of 3000 h⁻¹ showed that the most active and productive catalysts are those based on zeolites in H-form—see Fig. 5b. The comparison of the productivity values with turn over frequency (TOF) suggests that the Co activity does not depend on a bed productivity, which is explained by contribution of diffusion limitations, which is typical for a trickle-bed Fischer–Tropsch process. One can also observe that the methane selectivity is determined primarily by a catalyst composition not CO conversion.

The composition of FTS-generated syncrude C₅₊ depended first on the form of a zeolite, namely the presence of H-zeolites resulted in higher content of olefins, isoparaffins and C₅–C₁₀ fraction—see Fig. 6. It is necessary to note that the content of the heaviest fraction C₁₉₊ was almost negligible in case of H-zeolites, which witnesses strong contribution of cracking. These observations are in

Fig. 6 Group and fractional composition of liquid syncrude synthesized in presence of different forms of zeolite

line with the effect of carbocation mechanism of secondary transformations of FTS-generated hydrocarbons in presence of H-zeolites and water as explained elsewhere [5–8].

Molecular-weight distribution of *n*-alkanes for Co-Ref, Co-HBeta and Co-CaA catalysts is shown in Fig. 7. The impact of zeolites is apparent especially in case of H-form. It can be seen from Fig. 7 that the introduction of HBeta zeolite leads to sharp drop in the content of heavier alkanes and to general decrease in the content of normal alkanes in the syncrude.

The comparative stability (deactivation behaviour) of the catalysts under investigation was estimated by carrying out experiments with longer time on stream—see Table 3. The Co-HBeta catalyst manifested the best stability among the others, i.e. its activity remained as high as 98% of initial one after 100 h on stream. Meanwhile, both Co-Ref and Co-CaX catalysts dropped their activity down to 87% level. The Co-NaX manifested the lowest stability with 62% activity after 100 h on stream.

Besides, we observed that only in the presence of zeolites in H-form the heat-conducting component (aluminium metal flakes) was not exposed to oxidizing effect of water under conditions of Fischer–Tropsch synthesis (Table 1) whereas

Fig. 7 Molecular weight distribution of *n*-alkanes in the syncrudes received over Co-Ref, Co-HBeta and Co-CaA catalysts

Table 3 Deactivation behavior of the catalysts under investigation after 100 h on stream

Catalyst	Initial activity, mmol/(s g _{Co})	Activity after 100 h on stream, mmol/(s g _{Co})
Co-Ref	33	29
Co-HBeta	48	47
Co-CaX	65	57
Co-NaX	63	39

the catalysts with zeolites in cationic form as well as the reference catalyst showed sharp drop in the aluminium metal content after relatively short time on stream. It is possible to assume that degradation of heat-conducting additives affects the stability of work and service life of the catalyst. It is possible that zeolite in H-form in a Co catalyst prevents oxidation of a heat-conducting component (oxidation of aluminium metal into alumina) because it involves water into secondary reactions, forming additional Bronsted acid centres and also providing protection for water-vulnerable surfaces by forming an intermediate hydrocarbon film. It is possible that H-form zeolites help protecting Co particles from oxidation and sintering. In this respect it is interesting to compare TEM images of catalysts with different forms of zeolites after certain time-on-stream. Figure 8 shows TEM results for Co-HBeta with hydrophobic zeolite vs Co-CaA with hydrophilic zeolite after 100 h on stream. As discussed

in the “[Introduction](#)”, hydrophobicity/hydrophilicity classification is based on competitive absorption of water from water–hydrocarbon mixtures [17–19]. The comparison of Co particle sizes suggests that H-form zeolite hinders Co particle sintering under hydrothermal conditions of a Fischer–Tropsch bed. Indeed, while the as-synthesized catalysts are characterized by CO particle size of 10–15 nm, the 100-h run leads to approximately 20 nm in case of Co-HBeta vs 40–50 nm in case of Co-CaA.

The difference in hydrocarbon behaviour on the surface between hydrophobic and hydrophilic catalysts can be clearly seen in Fig. 9. Figure 6 shows SEM images of Co-HBeta and Co-CaX catalysts after catalytic run. Residual hydrocarbon on the surface of Co-HBeta forms rather dense protective coating while Co-CaX is characterized by scarce hydrocarbon spheres on the surface. EDX was used for identification of the hydrocarbon-covered surfaces. In addition, prolonged exposition to the impact of SEM electron beam resulted in melting of hydrocarbons, which was easily detected by eye. The after-melting hydrocarbon spheres on the surface of Co-CaX were seen as quick liquid drops.

Thus, the use of zeolites in Co catalysts of Fischer–Tropsch synthesis results in cooperative effect in the form of sudden increase of the zeolite activity in catalysing secondary transformations of FTS-generated hydrocarbons (cracking, isomerization, etc.) at untypically low temperatures. In addition, hydrophobic zeolites in H-form allow changing hydrophobicity of the pore walls and influence

Fig. 8 TEM images of the Co particles on the catalyst surfaces after 100 h on stream: **a** Co-HBeta with hydrophobic zeolite, **b** Co-CaA with hydrophilic zeolite

Fig. 9 SEM of the surface of the catalysts after Fischer–Tropsch synthesis run: **a** Co-HBeta with hydrophobic zeolite, **b** Co-CaX with hydrophilic zeolite

capillary condensation phenomena [19]. The most unexpected cooperative effect of Co and hydrophobic zeolites is the improvement of degradation behaviour of the catalysts due to involvement of FTS-generated water into formation of additional Bronsted centres [25–27] thus preventing undesirable oxidation of heat-conductive metal additives and other water-induced degradation processes.

Conclusion

The use of zeolites in Co catalysts of Fischer–Tropsch synthesis (FTS) results in cooperative effect in the form of sudden increase of the zeolite activity in catalyzing secondary transformations of FTS-generated hydrocarbons at unusually low temperatures. In addition, hydrophobic zeolites in H-form

allow changing hydrophobicity of the pore walls and influence capillary condensation phenomena for intermediate species. The most unexpected effect of Co and hydrophobic zeolites is the improvement of Al metal degradation behavior due to involvement of FTS-generated water into formation of additional Bronsted centers thus preventing undesirable oxidation and decreasing negative effect of water.

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