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# Effect of water on the secondary transformations of hydrocarbons in the Fischer–Tropsch synthesis on Co-zeolite catalysts

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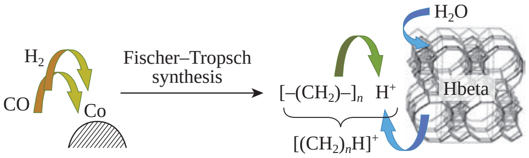
**Water is involved into the secondary reactions of the Co-catalyzed Fischer–Tropsch process in the presence of H-form zeolites due to water-induced generation of additional Brønsted acid sites. As a result, significant changes in the group and fractional compositions of formed hydrocarbons are observed.**



The Fischer–Tropsch (FT) synthesis is a catalytic process for hydrocarbon production from CO and $H_2$. It is a key stage of XTL (anything-to-liquid) process for producing alternative fuels from carbon-containing feedstock such as biomass, coal or natural gas.[1]

The main reactions for cobalt-based FT catalyst are

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O} + 140n\ \mathrm{kJ} \quad (1)$$

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} + 140n\ \mathrm{kJ} \quad (2)$$

Cobalt is an attractive active metal in the FT synthesis due to low activity in the formation of undesirable by-products (oxygenates and aromatic hydrocarbons). The cobalt catalyst provides the formation of linear long-chained hydrocarbons, including wax, which require an additional step of hydroprocessing to obtain liquid hydrocarbons.

The strong exothermal effects of reactions (1) and (2) can affect catalyst deactivation rate, selectivity to desired product and process productivity. Therefore, efficient heat removal from reaction sites can be performed by adding a heat conductive component to the catalyst.[2,3] For example, aluminum flakes may be added to form an efficient heat removal network in the catalyst pellet.[4,5] Another heat-conductive option is skeletal cobalt, which can be used in the FT synthesis due to its high intrinsic thermal conductivity.

Reactions (1) and (2) show that water is the main by-product in the Co-catalyzed FT synthesis. Since the process over a cobalt-based catalyst proceeds at relatively low temperatures (<250 °C), it has low activity in a water gas shift reaction and, as a consequence, water tends to accumulate in the reaction space. Water exerts a negative effect on the FT synthesis,[6] although one can find some indications that it could be neutral[7] or even positive.[8] It is believed that water influences through the sintering of active metal clusters or through the formation of inactive metal oxides.[9]

However, the mechanism of water impact over Co-based H-zeolite catalysts seems to be different. It was shown that the cobalt phase crystallites become larger (from 6–8 up to 20 nm) after 50 h FT runs and then stay intact for another 2000 h run.[10]

H-form zeolites are widely used as supports in bifunctional catalysts for high quality fuel production from CO and $H_2$.[11,12] Long-chain hydrocarbons produced over cobalt-containing sites may undergo cracking or hydrocracking over zeolite acid sites to obtain gasoline and diesel range hydrocarbons. In addition, isomerization and alkylation can proceed on H-zeolite acid sites to produce branched paraffins and olefins.[11,13] A carbocationic mechanism is one of the most commonly proposed ones for hydrocarbon transformations over H-zeolites.[11,14] In the presence of bifunctional catalysts, this mechanism can occur through the activation of hydrogen over metal sites with the subsequent spillover to Brønsted acid sites and proton transfer from an acid site to an olefin, which is obtained on a metal surface.[15]

Moreover, zeolites in H-forms can produce additional Brønsted acid sites by interacting with water.[16] The H-form zeolites are hydrophobic, while their hydrophobicity increases with the Si/Al ratio.[17] Thus, zeolites in a cation form are hydrophilic. Water molecules in such zeolites are held by electrostatic forces, and they can depart from a zeolite only at higher temperature treatment (above 350 °C).[18] Weitkamp *et al.*[19] proposed a hydrophobicity index as a ratio between the zeolite absorption capacity for a hydrocarbon (toluene or hexane) and water. Note that, unlike HZSM-5 and HY zeolites, 13 water molecules can be adsorbed over a Brønsted acid site of HBEA zeolite, and only 7 water molecules can be adsorbed on the other types of sites.[20]

It means that H-form zeolites can be used as catalyst components in the FT synthesis for obtaining liquid synthetic oil with a minimum amount of waxes. This kind of oil is actually comprised of light fuel fraction suitable for warm climates.

The aim of this work was to study the effect of water in secondary reactions of the FT synthesis of hydrocarbons over cobalt catalysts containing H-form zeolites. The zeolites BEA in H-form (Hbeta, Si/Al = 19) and NaX (Si/Al = 2) were used as the supports or catalyst components. The methods of cobalt introduction into catalysts were different, namely: the $\mathrm{Co_{im}}$, Co-$\mathrm{Hbeta_{im}}$ and Co-$\mathrm{NaX_{im}}$ samples were prepared by the impregnation of supports with an aqueous solution of cobalt nitrate. Skeletal cobalt (prepared in our laboratory) was added as an active metal in the samples $\mathrm{Co_{mix}}$, Co-$\mathrm{Hbeta_{mix}}$ and Co-$\mathrm{NaX_{mix}}$ (Table 1).[†] Aluminum

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[†] Catalysts were activated in hydrogen at 400 °C, 0.1 MPa and at a gas-hour space velocity (GHSV) of 3000 h$^{-1}$. The FT synthesis was carried out in a fixed bed tubular reactor. The temperature rise was programmed

**Table 1** Catalyst composition (wt%).[a]

| Catalyst | $T_{opt}$/°C | Al flakes | Zeolite |
|---|---|---|---|
| $Co_{im}$ | 244 | 27 | – |
| $Co\text{-}Hbeta_{im}$ | 234 | 25 | 24 |
| $Co\text{-}NaX_{im}$ | 239 | 29 | 24 |
| $Co_{mix}$ | 249 | 38 | – |
| $Co\text{-}Hbeta_{mix}$ | 234 | 42 | 10 |
| $Co\text{-}NaX_{mix}$ | 247 | 38 | 10 |

[a] Co content is 20 wt%. Binder (boehmite) content makes a material balance.

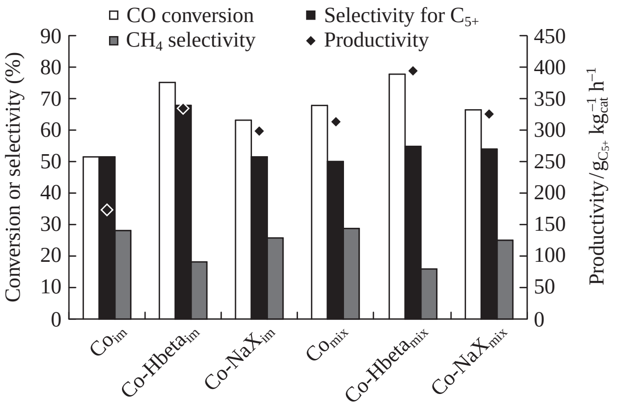

**Figure 1** Influence of zeolite support on CO conversion, selectivity for $C_{5+}$ and $CH_4$ and productivity (3000 $h^{-1}$ at an optimal temperature).

was used in the form of flakes to create a heat-conductive network.

All the test catalysts were active in the FT synthesis. The highest conversion (76–77%) was achieved for Hbeta based catalysts (Figure 1). The highest productivity was obtained for mixed catalysts with Hbeta zeolite, 384 $g_{C_{5+}}$ $kg_{cat}^{-1}$ $h^{-1}$. Hbeta addition in catalysts led to an increase in selectivity for liquid hydrocarbons. Thus, it was the highest over impregnated catalyst containing Hbeta (68%) and over mixed catalyst containing Hbeta (56%). The introduction of zeolites led to a decrease in methane selectivity by a factor of 1.7.

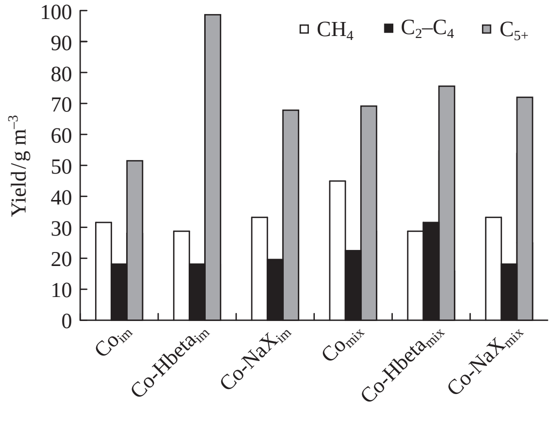

**Figure 2** Influence of zeolite support on yields of $CH_4$ and $C_{2+}$ hydrocarbons (3000 $h^{-1}$ at an optimal temperature).

As shown in Figure 2, the yield of $C_{5+}$ hydrocarbons was the highest (up to 100 g $m^{-3}$) in the presence of Hbeta containing catalysts regardless of cobalt introduction method. The addition of zeolite Hbeta in a mixed catalyst increased the yield of $C_2$–$C_4$ hydrocarbons, but there were no changes for the impregnated catalyst. The introduction of NaX zeolite also led to an increase in $C_{5+}$ hydrocarbon yield for both impregnated and mixed catalysts. At the same time, the $Co\text{-}NaX_{mix}$ showed a decrease in the yield of the main by-product, methane. However, the introduction of NaX into the impregnated catalyst did not affect the methane yield.

The introduction of Hbeta zeolite led to an increase in the content of $C_5$–$C_{10}$ fraction in $C_{5+}$ hydrocarbons by a factor of 1.4–1.5 for both catalysts [Figure 3(*a*)]. However, the addition of NaX zeolite did not increase the content of $C_5$–$C_{10}$ fraction for $Co\text{-}NaX_{mix}$ and rose slightly for impregnated NaX catalyst. The olefin and isoparaffin contents increased by the factor of 8 and 2.7, respectively, for impregnated or 3.5 and 2.3 for mixed catalysts Hbeta [Figure 3(*b*)]. The slight growth of olefins content and no change in isoparaffins content were observed for both $Co\text{-}NaX_{im}$ and $Co\text{-}NaX_{mix}$ catalysts. We suppose that secondary reactions of the FT synthesis hydrocarbons on Brønsted acid sites proceed by a carbocationic mechanism in the presence of H-form zeolite. It is interesting to mention the decrease of the $C_{19+}$ hydrocarbon content to 0 and the chain growth probability to 0.69 for impregnated $Co\text{-}Hbeta_{im}$, and to 1% and 0.73, respectively, for $Co\text{-}Hbeta_{mix}$. Meanwhile, the NaX addition resulted in less significant decrease of either $C_{19+}$ hydrocarbons or the chain growth probability for both catalysts. Thereby, in the presence of Hbeta zeolite in catalysts, the intense cracking of higher molecular hydrocarbons occurred.

Note that the introduction of H-form zeolite into the Co catalysts diminished the optimal synthesis temperature by 10–15 °C. We suggest that cracking and hydrocracking reactions lead to the lower viscosity of liquid products inside the pores of the

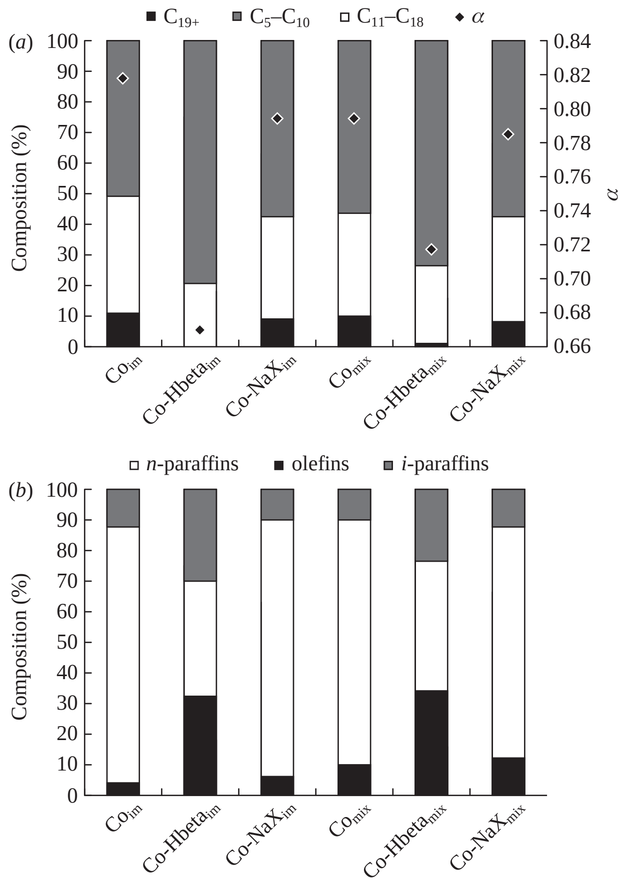

**Figure 3** Influence of zeolite support on (*a*) fractional and (*b*) group composition (3000 $h^{-1}$ at an optimal temperature).

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in 3–10 °C steps every 6 h starting from 170 °C. The optimal temperatures were 244 and 249 °C for the catalysts $Co_{im}$ and $Co_{mix}$ without zeolite, 234 °C for both of Hbeta based catalysts and 239 and 247 °C for $Co\text{-}NaX_{im}$ and $Co\text{-}NaX_{mix}$, respectively. Syngas with the molar ratio $H_2/CO = 2$ was fed at a space velocity of 1000 $h^{-1}$ in processing mode during increasing and optimizing the temperature and at 3000 $h^{-1}$ in the productivity optimization mode. The temperature was optimized for each GHSV to achieve the highest productivity.

catalyst particles and hence accelerate the product transport out of the catalyst. Such a facilitation of product removal leads to reaching the maximum productivity at the lower temperature.

It is important that both catalysts, which did not contain any zeolites, and both catalysts, which contained cation-form zeolites, were destroyed under the FT process conditions, presumably due to the oxidation of aluminum flakes by FT synthesis water. Thus, for the $Co_{im}$ catalyst, the aluminum metal content decreased from 27 to 11%, or from 38 to 16% for $Co_{mix}$. For $Co\text{-}NaX_{im}$ catalysts, its content decreased from 29 to 10%, whereas for $Co\text{-}NaX_{mix}$, from 38 to 21%. Meantime, in the catalysts containing zeolite Hbeta, which pellets remain intact, decrease in the content of aluminum metal in the FT synthesis did not exceed 3%.

Consequently, it can be assumed that the presence of H-form zeolite in the FT synthesis cobalt catalyst prevents oxidation of heat conductive additive due to involvement in secondary reactions with the FT synthesis water to produce an additional amount of Brønsted acid sites[16] regardless of an active metal introduction method. The oxidation of aluminum metal flakes in $Co\text{-}NaX_{im}$ and $Co\text{-}NaX_{mix}$ samples occurs presumably due to hydrophilicity of NaX zeolite,[17] *i.e.*, the FT synthesis water is held by electrostatic forces and not involved in the formation of Brønsted acid sites. Only one water molecule per aluminum atom is sufficient for the filling of NaX zeolite with water;[21] thus, the rest of water remains in the reaction space and tends to oxidize aluminum of a heat conductive lattice in the same way as it happens in non-zeolite catalysts.

Hence, the FT synthesis water may participate in the secondary transformations of hydrocarbons on Brønsted acid sites over Hbeta containing cobalt catalysts, which results in drastic changes in the group and fractional composition of the hydrocarbons formed.

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