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Hydrocarbon transformations on Co–zeolite in catalytic environment of different redox properties at 170–260 °C

**Lilia V. Sineva,*[a] Ekaterina O. Gorokhova,[a] Ekaterina A. Pushina,[a]
Ekaterina V. Kulchakovskaya[a] and Vladimir Z. Mordkovich[a,b,c]**

[a] *Technological Institute for Superhard and Novel Carbon Materials, 108840 Troitsk, Moscow, Russian Federation. Fax: +7 499 400 6260; e-mail: sinevalv@tisnum.ru*
[b] *Moscow Institute of Physics and Technology, 141701 Dolgoprudny, Moscow Region, Russian Federation*
[c] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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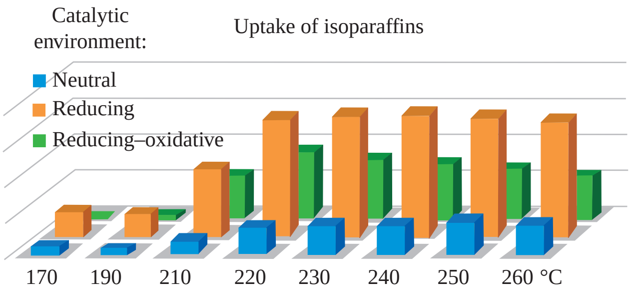
Redox properties of catalytic environment, namely He as neutral, H_2 as reducing and H_2–H_2O as reducing–oxidative one, determine the conversion of hydrocarbons on Co–zeolite catalysts at 170–260 °C as well as product distribution. The highest yield of isomerized products was achieved in reducing medium, while the methane formation was suppressed most efficiently in neutral and reducing–oxidative environments. Two distinct ranges can be identified for temperature dependencies of reaction parameters, namely 170–210 and 220–260 °C.



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Zeolites represent subject of intensive investigation as components of the Fischer–Tropsch catalysts.[1] The Fischer–Tropsch synthesis (FTS) is highly exothermal and requires a thorough bed temperature control, which can be achieved effectively at low conversion of feed gas, namely syngas or CO/H_2 mixture. In this respect, the industrial mainstream for production of higher hydrocarbons is in line with low conversions. Since the high molecular weight products fill the catalyst pores, thus clogging the active centres, the frequent rejuvenations of the catalyst becomes necessary by purging it with hot hydrogen gas. An alternative solution consists in introduction of zeolite into the catalyst to create additional acidic centers capable of catalyzing the cracking reaction. Molecular weight of the product synthesized over such hybrid catalyst is dependent on cobalt/acidic centers ratio,[2] thus allowing to escape the limitation of classical FTS. It seems promising to control fractional composition of the product by variation of zeolite nature.[3]

The majority of works on zeolite catalytic activity deals with the temperatures above 300 °C, which is far beyond the temperature range 170–260 °C typical for FTS.[4,5] The scarce data on zeolite activity in the 170–260 °C range allows one to put forward a hypothesis, that the liquid hydrocarbon composition synthesized from CO and H_2 over cobalt–zeolite hybrid catalysts depends mostly on the zeolite properties.[6] Note, that zeolite-induced hydrocracking can result in the extra formation of methane. However, at temperatures of 170–260 °C contribution of methane formation induced by acidic centers is low, *i.e.*, the cracking is more probable than hydrocracking. Therefore, it is important to optimize the amount of additional active centers introduced into a Co catalyst with a zeolite additive. This optimization requires additional investigations concerning the influence of an environment with gradually changing redox properties, namely from reducing hydrogen-rich, typical of a top layer of the catalyst bed, to reducing–oxidative steam-packed one, typical of a bottom of the catalytic bed.

In this work, we investigated hydrocarbon transformations on Co–zeolite catalysts in neutral (helium), reducing (hydrogen) or reducing–oxidative (hydrogen–H_2O mixture) environment in an FTS-typical temperature range of 170–260 °C.[†] Some features of the liquid hydrocarbon transformation over catalysts Co-HZSM-5, Co-HBeta and Ref in neutral atmosphere of He gas were discussed elsewhere (Ref is the reference zeolite-free catalyst).[7] In the neutral environment, the conversion into gaseous products decreased in the order Co-HZSM-5 > > Co-HBeta > Ref and constituted at 260 °C 13, 6 and 1%, respectively (Figure 1). The Ref catalyst demonstrated the lowest sensitivity to temperature. Hydrocarbons C_4 dominated in the gaseous product composition (see Online Supplementary Materials, Figure S1). All the catalysts revealed insignificant yields of CH_4, CO_2 and CO, which reached the highest values for catalyst Ref and were ~0.35, 0.3 and 0.9 mol%, respectively in all the temperature range (Figures 1 and S1).

The changes in the composition of liquid hydrocarbons after catalytic contact in the neutral environment are given in Figures 1 and S2. The role of both reaction temperature and zeolite type follows from the fact that catalyst Co-HBeta is more active in cracking and isomerization, while catalyst Co-HZSM-5 provides higher conversion of alkenes C_{5+}. This conversion value of 30–38% in all the temperature range over catalyst Ref can

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[†] The catalysts for hydrocarbon transformations were manufactured on a basis of zeolites HZSM-5 and HBeta with Si/Al ratio of 19 and 12.5, respectively, supplied by Zeolyst. For the procedures of their preparation and testing, see Online Supplementary Materials.

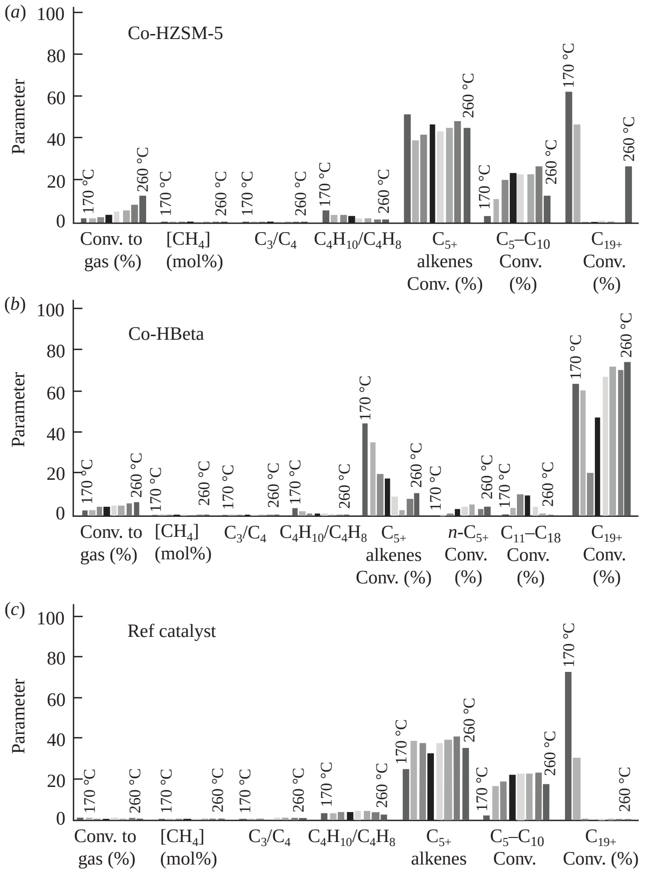

Figure 1 Parameters of the liquid hydrocarbon mixture transformation in neutral environment at temperatures of 170, 190, 210, 230, 240, 250 and 260 °C (only edge values of the interval are depicted numerically): (*a*) Co-HZSM-5, (*b*) Co-HBeta and (*c*) Ref catalysts.

originate only from the dismutation of alkenes into alkanes accompanied by carbonaceous deposit found on the surface of this catalyst in noticeable amount after catalytic run by thermal analysis (Figure S3). Heavy hydrocarbons C_{19+} demonstrated uneven temperature influence on conversion with very high values at lower temperatures of 170–190 °C, which was a result of surface adsorption of these heavy hydrocarbons, the control runs with inert contacts revealed similar effect at 170–190 °C.

Hydrocarbons C_{11}–C_{18} represent an interest as diesel fraction. Although they were formed over all the catalysts under investigation, their uptake depended on both temperature and zeolite type, which could be explained by superposition of several simultaneous reactions (see Figure S2). On catalyst Co-HZSM-5, hydrocarbons C_{11}–C_{18} were formed due to slight alkene alkylation and oligomerization, while the average molecular weight was limited by cracking of heavier hydrocarbons.[4,8–10] For the zeolite-free Ref catalyst, hydrocarbons C_{11}–C_{18} could be formed in the same way due to the presence of Lewis centers of cobalt oxides, although without cracking.[11]

Switching from neutral to reducing H_2 atmosphere led to higher conversion into gaseous products, however with preservation of the same trend, namely a decrease in the order Co-HZSM-5 > Co-HBeta > Ref, *e.g.*, at 260 °C 61, 46 and 6%, respectively (Figure 2). There are two distinct temperature ranges characterized by different dependence patterns. For the Ref catalyst, the conversion to gases increases from 2 to 7% in 170–210 °C range, while the range 220–260 °C reveals the increase from 4 to 6%.

The composition of gaseous products formed over Co–zeolite catalysts in hydrogen atmosphere changed dramatically with the temperature elevation. Below 210 °C, methane dominated in the gaseous product with yield up to 60 mol%, while above 210 °C hydrocarbons C_4 were predominatly formed with butane/butene ratio independent on temperature (see Figures 2 and S1). The Ref catalyst produced methane as practically single gaseous product in all the temperature range. Temperature dependences of the methane yield were different in the two distinct temperature ranges as well. However, the dependence pattern depended on the presence of zeolite. For the zeolite catalysts, the methane yield reached maximum below 210 °C and decreased with further temperature elevation. For the Ref catalyst, it increased both in the first (from 35 to 51%) and the second (from 41 to 65%) temperature ranges. The reaction in reducing environment provided a significant yield of C_2H_6 (see Figure S1), while the formation of CO and CO_2 was negligible.

The changes in composition of liquid hydrocarbons after the catalytic contact in the reducing environment are shown in Figures 2 and S2. The conversion of alkenes C_{5+} increased when helium was replaced by hydrogen, however for the zeolite catalysts it reached maximum below 230 °C, while for catalyst Ref the steady increase in all the temperature range occurred. Alkenes could be consumed in bimolecular reactions on the zeolite catalysts and in hydrogenation processes on catalyst Ref. The observed decrease in alkene conversion with temperature can be explained by greater contribution of alkene-generating cracking reaction. The conversion rate of hydrocarbons C_{19+} increased when helium was replaced by hydrogen. Note, that

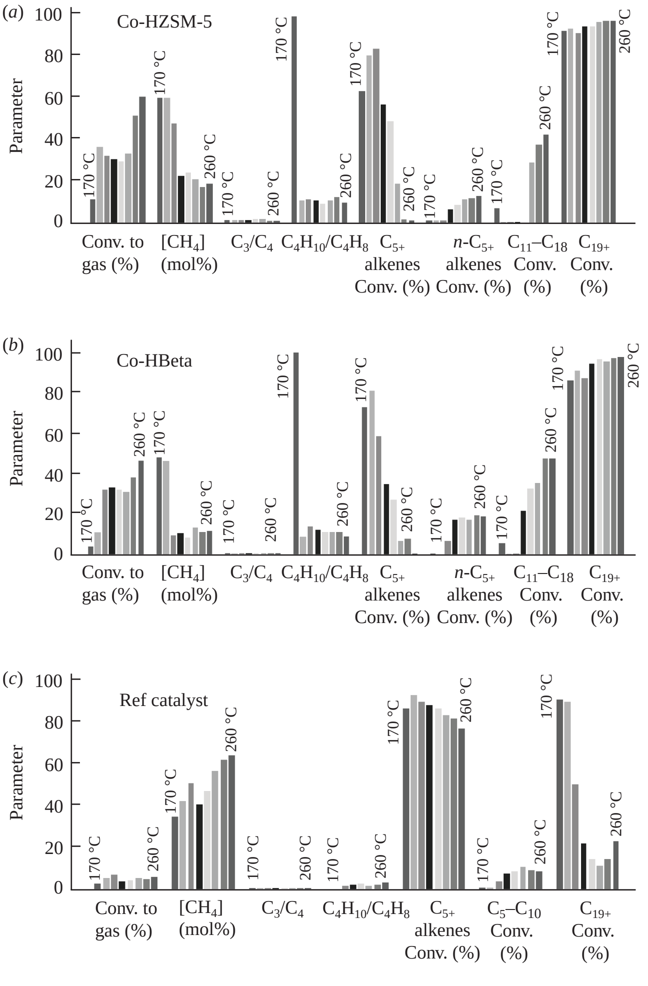

Figure 2 Parameters of the liquid hydrocarbon mixture transformation in reducing environment at temperatures of 170, 190, 210, 230, 240, 250 and 260 °C (only edge values of the interval are depicted numerically): (*a*) Co-HZSM-5, (*b*) Co-HBeta and (*c*) Ref catalysts.

consumption of C_{11}–C_{18} hydrocarbons and *n*-alkanes was observed only on the zeolite catalysts, while the hydrocarbons C_5–C_{10} consumption was observed on catalyst Ref only.

The change of environment from the neutral to reducing one led to multifold increase in the yield of isoparaffins over the zeolite-containing catalysts (see Figure S2). This effect was the most prominent on Co-HBeta. The yield of cracking products decreased with temperature in the range below 170–210 °C and then increased with a maximum at 260 °C. The liquid phase transformations on catalyst Ref in reducing atmosphere led mostly to appearance of *n*-alkanes. The fraction C_{11}–C_{18} grew substantially due to both oligomerization of alkenes C_5–C_{10} and hydrogenolysis of heavier hydrocarbons. The latter resulted in formation of additional methane.

Transfer to reducing–oxidative environment led to lower conversion into gaseous products as compared with the reducing environment and keeping the outcome of this transformation in the same order Co-HZSM-5 > Co-HBeta > Ref (Figure 3). Note, that for the zeolite-containing catalysts the temperature dependence of conversion changes dramatically, especially in the 170–210 °C range. However, one can still distinguish the areas in the temperature dependence of gaseous product yield in 170–210 and 220–260 °C ranges (see Figure S1). In particular, butanes dominated among the gaseous products in the reducing–oxidative environment over catalyst Co-HZSM-5 at 170 °C, while the minimum butane yield corresponded to the maximum methane yield at 210 °C. The temperature increase resulted in higher yield of butane with less methane. Catalyst Co-HBeta revealed similar pattern. For catalyst Ref, the temperature elevation led to the methane yield increase and butane yield decrease. Note, that water addition led to lowering of methane formation on catalysts Co-HBeta and Ref, while Co-HZSM-5 demonstrated the opposite trend. The temperature dependence of the yields of remaining gaseous products reveals distinct patterns in the two temperature ranges as well. A shift to reducing–oxidative environment led to increase in both butane/butane and C_3/C_4 ratios on catalyst Co-HZSM-5 only (Figure 3).

Addition of water to hydrogen brought changes to the pattern of the composition of liquid hydrocarbons (see Figure 3). Cracking of hydrocarbons C_{11}–C_{18} and C_{19+} was suppressed. For the latter, the difference between the ranges of 170–210 and 220–260 °C is clearly visible. This confirms the assumption that hydrocarbons C_{19+} are consumed by adsorption at 170–210 °C (water prevents the adsorption successfully), which changes to cracking at 210–260 °C. The alkene C_{5+} conversion is partially suppressed by water as well especially on catalyst Ref, which probably prevents hydrogenation at metal centers. In wet hydrogen, the activity of zeolite catalysts in the conversion of *n*-alkanes C_{5+} decreased, while for catalyst Ref the conversion of hydrocarbons C_5–C_{10} was water-independent.

The reducing–oxidative environment significantly suppressed the activity of zeolite catalysts in isomerization and cracking, although isoalkanes and hydrocarbons C_5–C_{10} were still the main products of liquid transformations (see Figure S2). The yield of both isoparaffins and hydrocarbons C_5–C_{10} was lower on catalyst Co-HZSM-5 compared with Co-HBeta, although catalyst Co-HZSM-5 generated additionally hydrocarbons C_{11}–C_{18} at the temperatures below 240 °C. Note, that *n*-alkanes C_{5+} were formed upon alkene hydrogenation in the temperature range 170–190 °C, while in the range of 220–260 °C they underwent isomerization.

Comparative analysis of thermogravimetric data for spent catalysts confirmed that the zeolite introduction into the catalyst composition reduces the amount of carbonaceous deposit on the catalyst surface by 1.5–2 times (Figure S3). Moreover, shift to the reducing environment also lowers their amount by 1.3–1.6 times, however in wet hydrogen it is supposed to grow. Also the TGA data revealed, that zeolite introduction led to decrease in the temperature of oxidation for a heat-conducting graphitic additive by 50–100 °C. This can be explained by zeolite influence on the size of cobalt crystallites and degree of their reduction.[12]

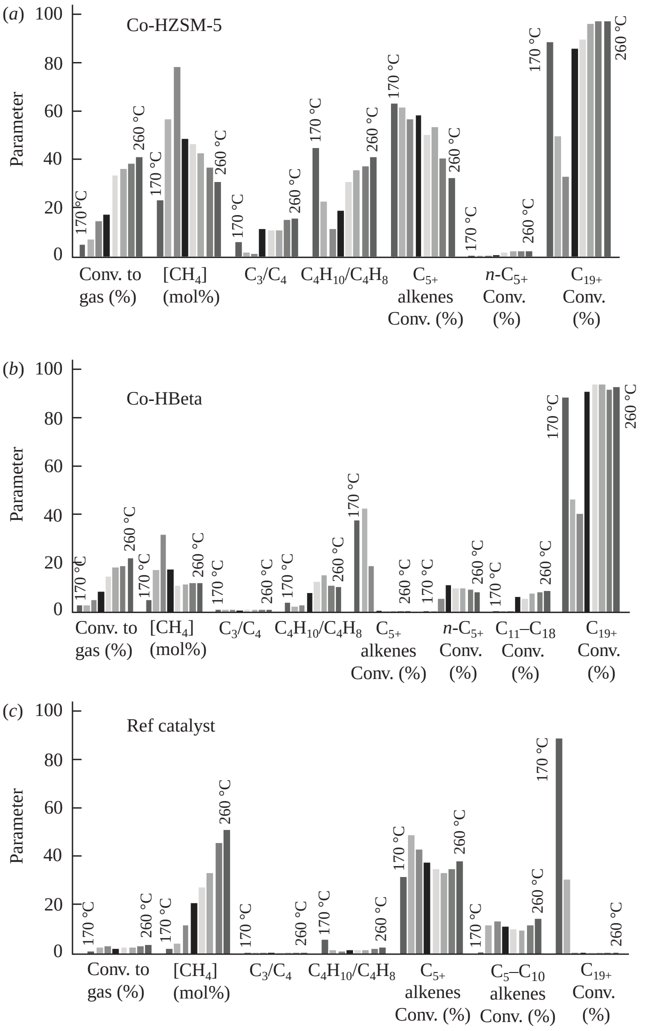

Figure 3 Parameters of the liquid hydrocarbon mixture transformation in reducing–oxidative environment at temperatures of 170, 190, 210, 230, 240, 250 and 260 °C (only edge values of the interval are depicted numerically): (*a*) Co-HZSM-5, (*b*) Co-HBeta and (*c*) Ref catalysts.

A comparison of TG data obtained for the spent catalysts after their use in the reducing environment demonstrates formation of the most of carbonaceous deposits in the range of 170–210 °C (Figure S4). The expansion of the temperature range leads to decrease in the deposit amount, especially in the presence of catalyst Ref. Note, that water addition leads to decrease in the carbonaceous deposit amount on the zeolite catalyst surface and to its increase for the Ref catalyst regardless of the temperature range. It may be related with possible catalytic activity caused by additional carbonium ions, which function as catalytic sites on silica-alumina surface due to formation of carbonaceous deposits aka polymeric residue as was interpreted earlier.[13]

In summary, this work revealed that redox properties of environment had a significant impact on the hydrocarbon transformations catalyzed by Co–zeolite catalysts at 170–260 °C. A shift from neutral atmosphere to reducing one leads to higher yield of gaseous products (primarily saturated hydrocarbons), higher yield of isoalkanes C_{5+} and lower average molecular weight of the liquid hydrocarbons mixture. Further shift to reducing–oxidative environment smooths these effects. Two distinct areas can be identified for temperature dependencies of reaction parameters, namely 170–210 °C and 220–260 °C. The former area is characterized by hydrogenolysis and hydrogenation at cobalt centers as main reactions, which are accompanied by carbonaceous deposits on the surface of the catalyst, while the latter area is characterized by strong contribution from acidic centers. The distribution of products in both gaseous and liquid phase is determined mostly by the zeolite properties. The introduction of zeolite into composition of a cobalt-based catalyst leads to lower methane formation, at least in neutral and reducing environments. The introduction of zeolite HBeta suppresses the methane formation even in the presence of water, *i.e.*, in reducing–oxidative atmosphere, which is determined by different properties of zeolite HBeta in competitive adsorption of water *vs*. hydrocarbons.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.034.

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