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

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Procedures for the preparation of supports and catalysts

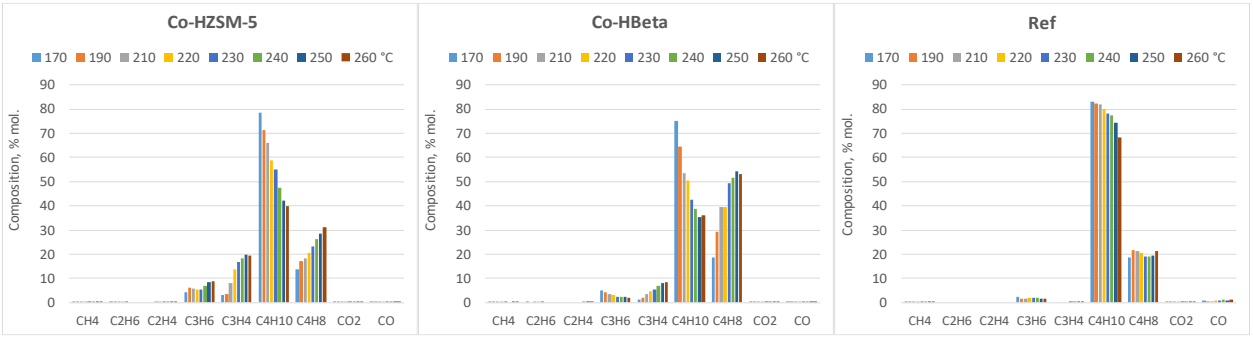
Supports were produced by extrusion of a mixture comprising boehmite (50% weight), heat-conductive carbon additive (20% weight), zeolite (20% weight) and water-based liquid phase. The extrudates were dried and calcined. The 20%-cobalt catalysts were obtained by double impregnation of supports with aqueous solution of cobalt nitrate with consequent annealing in the air flow at 250°C. A reference sample further referred to as 'Ref' was obtained in a similar way but without use of a zeolite (the zeolite in the recipe was substituted with boehmite).

Activation and testing of catalysts

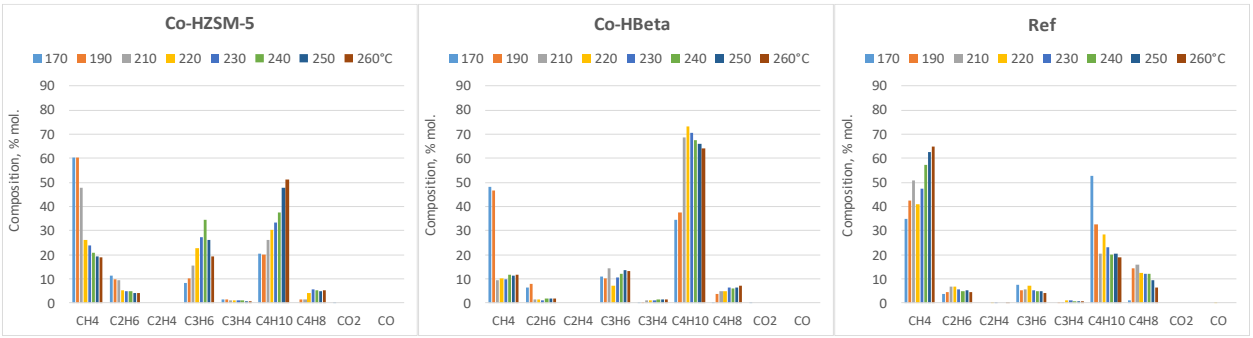
All the catalytic tests were preceded by 1 hour activation in a hydrogen flow at 400°C and 0.1 MPa. The testing was done in a stainless flow reactor at 0.1 MPa pressure and at temperature range of 170–260°C. Liquid hydrocarbons were fed by a syringe pump with rate of 0.02 ml·min^{-1} into a flow of inert gas (He + 5 % N_2) or hydrogen (H_2 + 5 % N_2). Inert gas provided a neutral environment, while hydrogen provided a reducing environment. A reducing-oxidative environment was provided by injection of water through an independent syringe pump at rate of 0.02 ml·min^{-1}. The composition of liquid and gaseous products was determined chromatographically.

A mixture of liquid hydrocarbons comprising C_nH_{2n} — 6.4–6.5; *n*-C_nH_{2n+2} — 82.1–82.6; *iso*-C_nH_{2n+2} — 11.0–11.5; C_5–C_{10} — 51.9–53.7; C_{11}–C_{18} — 36.7–37.3; C_{19+} — 9.6–10.8 % mol. — was used as a feedstock for catalytic tests. This mixture was produced by the Fischer–Tropsch synthesis from syngas over classical FTS catalyst 20%Co/Al_2O_3.

Neutral environment (He)



Reducing environment (H_2)



Reducing-oxidative environment (H_2 + H_2O)

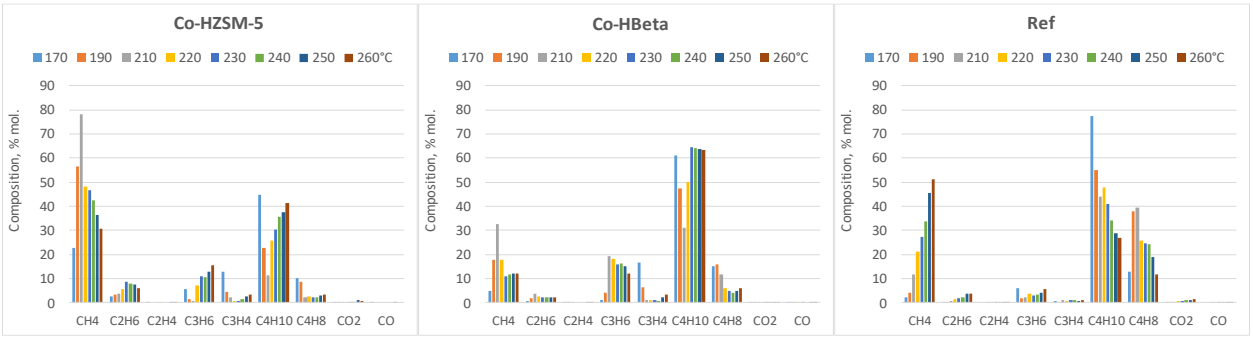
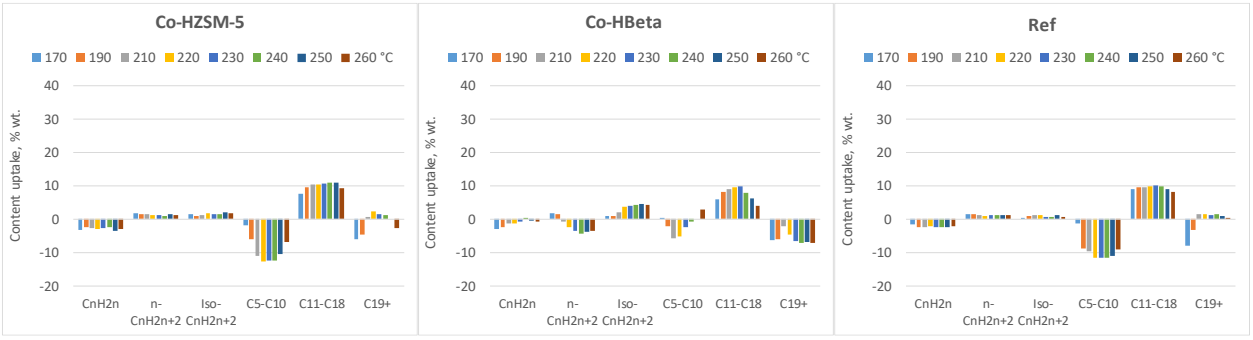
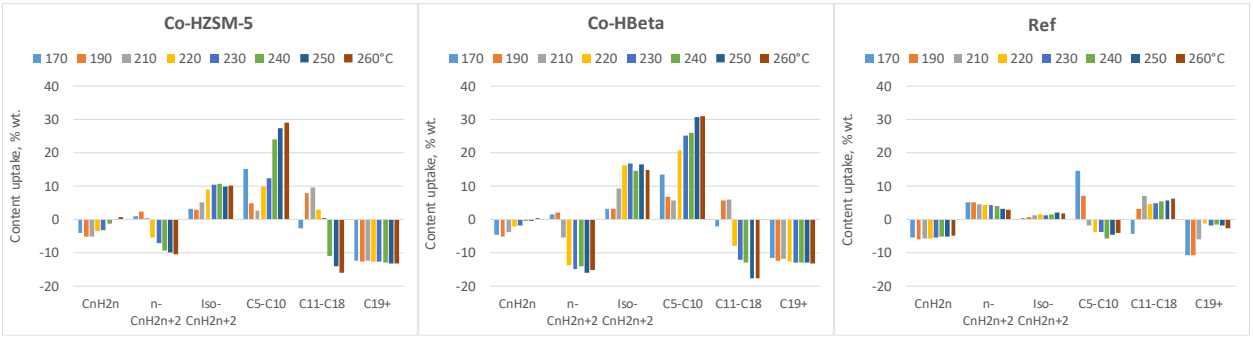


Figure S1 The temperature effect on the gaseous products composition, depending on the redox properties of environment and the type of catalyst system [Chromatograph Crystallux-5000M: thermal conductivity detector, helium as the carrier gas at flow rate 20 ml·min^{-1}; CaA molecular sieves (3 m × 3 mm) and HayeSep (3 m × 3 mm) columns; temperature-programmed mode (60–200°C, heating rate 10°C·min^{-1})].

Neutral environment (He)



Reducing environment (H_2)



Reducing-oxidative environment (H_2 + H_2O)

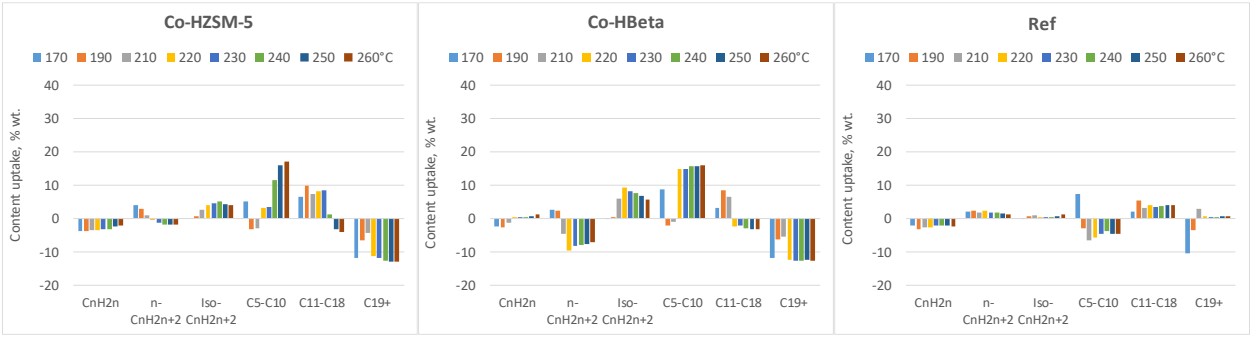


Figure S2 The temperature effect on the liquid hydrocarbons content uptake, depending on the redox properties of environment and the type of catalyst system [Chromatograph Crystallux-5000M: flame ionization detector; helium as the carrier gas at flow rate 30 ml·min^{-1}; DB-Petro capillary column (50 m); temperature-programmed mode (50–270°C, heating rate 4°C·min^{-1})].

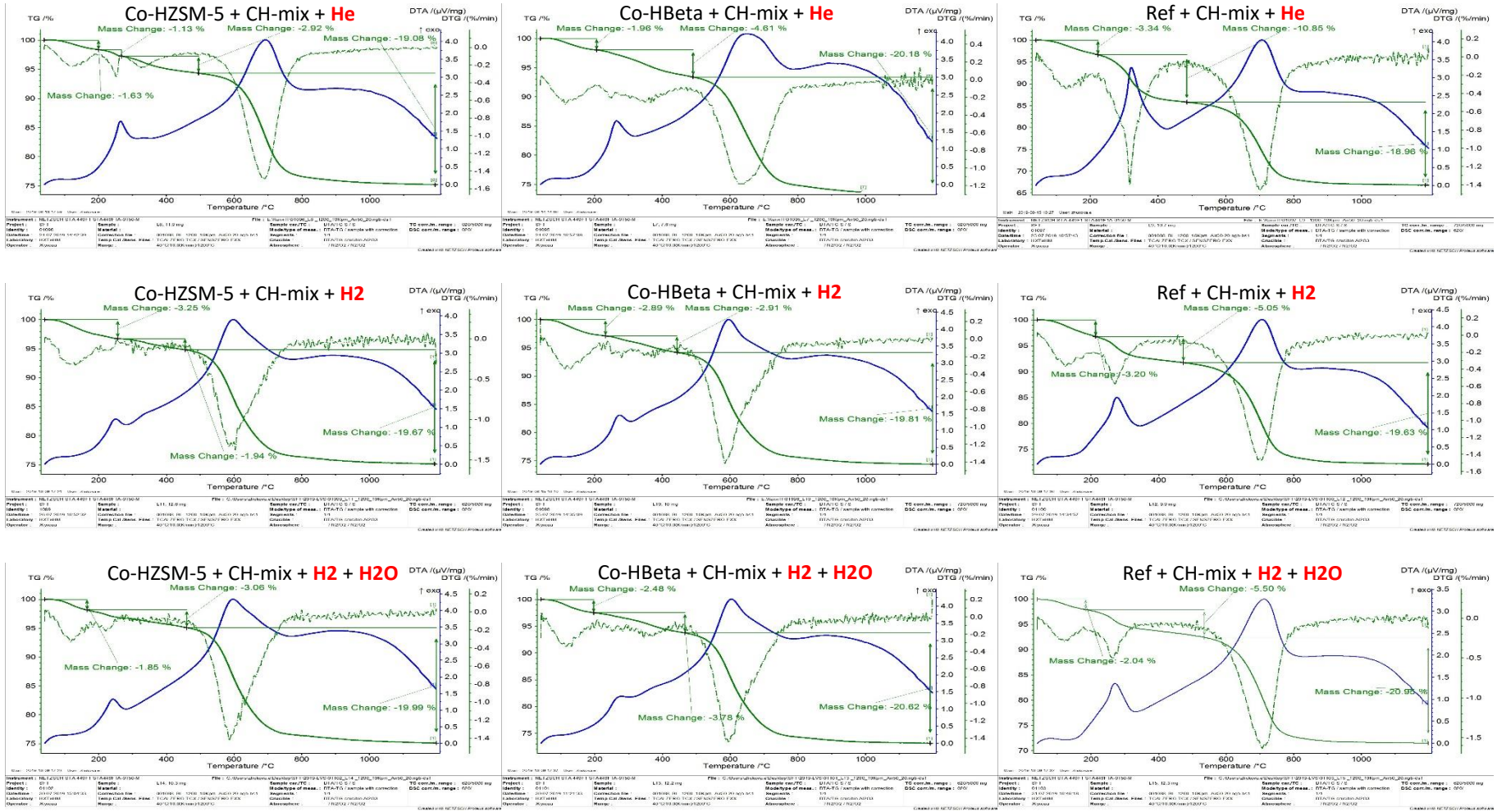


Figure S3 Data of complex thermal analysis: the effect of the redox properties of environment and the type of catalyst system (Thermal analizer STA 449 F1 Jupiter Netzsch: air atmosphere, 40–1200°C, heating rate 10°C·min^{-1}).

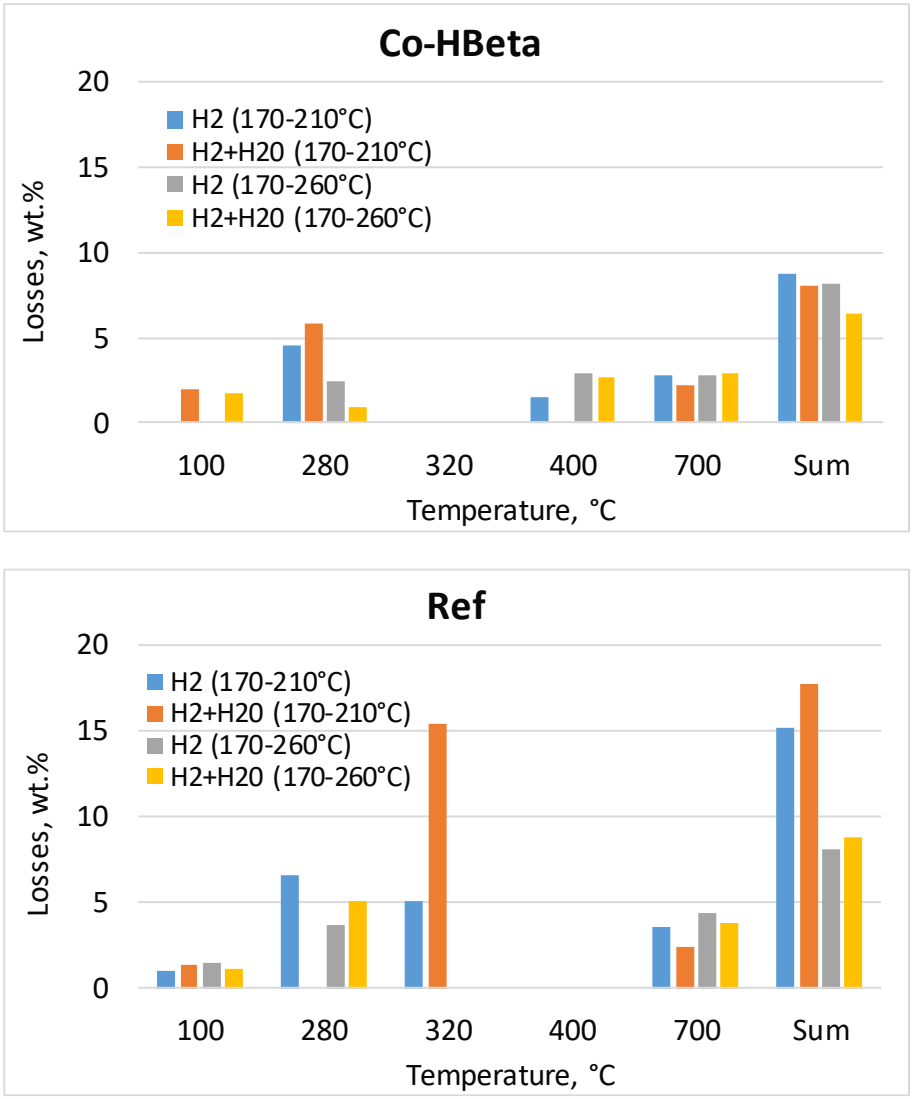


Figure S4 A comparison of TG data for the catalysts spent in reducing environment vs spent in reducing-oxidative environment (Thermal analizer STA 449 F1 Jupiter Netzsch: air atmosphere, 40–1200°C, heating rate 10°C·min^{-1}).