RESEARCH OF CATALYSTS PREPARED BY IMPREGNATION OF COBALT NITRATE

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https://doi.org/10.5281/zenodo.19381738

Abstract. The article describes the production stage of the catalyst – the step-by-step increase of the synthesis temperature in a syngas stream - is a necessary stage of the Fischer-Tropsch synthesis, as it has been established that during its development, under the influence of catalytically active centres, the formation of the product occurs. In the presence of cationic zeolites, such a plateau is absent due to the hydrophilicity of these zeolites, where it has been found that water is retained near the cations under the influence of electrostatic forces.

Keywords: oil, cationite, catalyst, conversion, condensation, zeolites, selectivity.

Introduction. The catalysts prepared by impregnation of the appropriate granular support with a cobalt nitrate aqueous solution, according to the method described in the article, contained cationites (NaX, KA and CaA) and H-form zeolites (HY6, HY30 and HB). A catalyst prepared by impregnation, but which did not contain zeolite, was selected as the reference catalyst.

Effect of the synthesis temperature

It is known that the production stage of the catalyst—the stepwise increase of the synthesis temperature in the synthesis gas stream—is an essential stage of the Fischer-Tropsch synthesis [1], as is formed under the influence of the catalytically active centres during the development process.

Studies by the authors [2] have shown that during the preparation of the cobalt catalyst a change in the cobalt state occurs: under the influence of the reaction medium, part of the Co0 is converted into Coδ+. This leads to a change in the nature of CO adsorption. Thus, during the production process, the catalyst's active surface is formed.

During the development process, the temperature dependence of the main synthesis parameters for each catalyst was determined. Figure 1 shows the dependence of CO conversion on the synthesis temperature in the presence of impregnated catalysts. With increasing temperature, the CO conversion increased for all catalysts. The highest CO conversion – 80% – was obtained with the catalyst containing HB zeolite. Interestingly, Co/HB, In the dependence obtained for the Co/HY6, Co/HY30 and zeolite-free catalysts, a 'step' was observed when the synthesis temperature was raised from 190 to 210°C, probably associated with the capillary condensation of the synthesis products [2]. It can be hypothesised that within this temperature range, water is desorbed from the capillaries of the binder – the microporosity of the aluminium oxide and H-type zeolites. In the presence of cationic zeolites, such a plateau is absent due to the hydrophilicity of these zeolites, where water is retained near the cations by electrostatic forces.

The lowest CO conversion was obtained in the presence of the KA zeolite-based adsorption catalyst – no more than 20% over the entire temperature range.

Figure 2 shows the dependence of the selectivity for C5+ hydrocarbon formation on the reaction temperature. In the presence of all catalysts, this indicator decreases with increasing temperature. In the presence of zeolite-free catalysts and catalysts containing HB and HY30 zeolites, the selectivity for the formation of C5+ hydrocarbons decreased 1.1-1.2 times in the temperature range of 190-210°C. In the presence of the Co/CaA and Co/NaX cationic zeolite-based catalysts, this indicator decreased by 1.5 and 1.3 times, respectively, upon raising the temperature from 210 to 220 °C. Furthermore, in the temperature range of 210–240 °C, the selectivity for the formation of C5+ hydrocarbons was almost independent of the synthesis temperature in the presence of all catalysts except Co/CaA and Co/NaX.

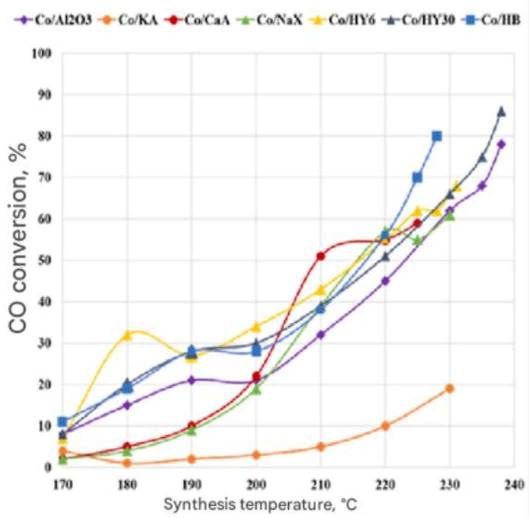

Figure 1. Dependence of CO conversion on FTS temperature

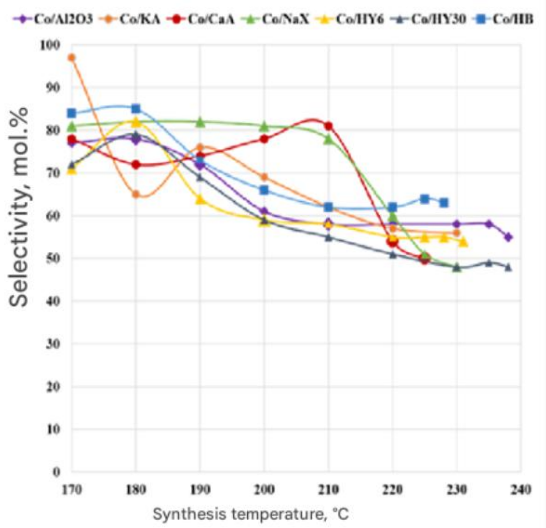

Figure 2. Dependence of the selectivity of the formation of C_{5+} hydrocarbons on the FTS temperature

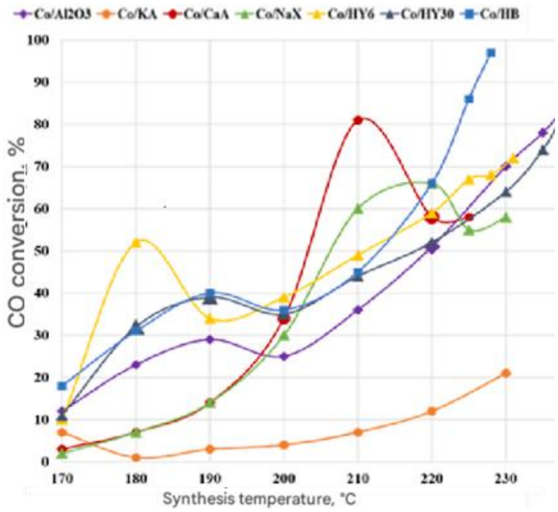

Figure 3. Dependence of the C5+ hydrocarbon yield on the FTS temperature

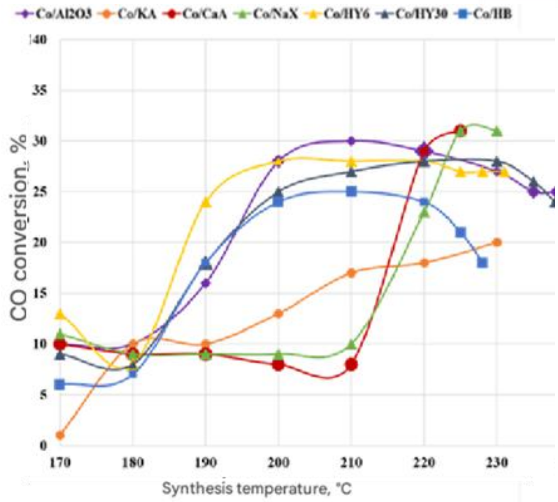

Figure 4. Dependence of CH4 formation selectivity on the FTS temperature

Figure 3 shows the dependence of the yield of C5+ hydrocarbons on the synthesis temperature. The yield of liquid hydrocarbons increased with rising synthesis temperature in all catalysts. A one-step process was observed at 180–200 °C in the presence of H-form zeolites and zeolite-based catalysts. The highest yield of C5+ hydrocarbons – over 97 g/m3 – was obtained with the HB zeolite-based catalyst. The yield of C5+ hydrocarbons was significantly lower in the presence of catalysts based on zeolites cation-exchanged with alkali and alkaline earth metals, amounting to 58 g/m3 for Co/NaX and Co/CaA, and 21 g/m^3 for Co/KA.

Conclusion. The selectivity for methane formation increases with rising synthesis temperature in the presence of all catalysts (Figure 4). However, the nature of this dependence is somewhat different. In the presence of the zeolite-free catalyst and the H-type zeolite-based catalysts, this dependence reached its maximum at 210–230 °C, corresponding to about 25–30 %. In the presence of catalysts based on cation-exchanged zeolites with Na and Ca, the selectivity for methane formation increased sharply—2.3- to 3.6-fold—as the temperature was raised from 210 to 220 °C. In the presence of Co/CA, this indicator increased uniformly from 1% to 20% with the rise in Fischer–Tropsch synthesis temperature. Thus, despite literature data on the sharp increase in methane formation when using zeolites as a support compared to a conventional Fischer-Tropsch synthesis catalyst, The selectivity of the catalyst containing HB zeolite is lower throughout the entire temperature range compared to the catalyst without zeolite.

References:

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