

Bifunctional CoSiBEA zeolite catalyst for ecological fuel production in Fischer – Tropsch synthesis

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Introduction

Cobalt catalysts have been widely employed for Fischer–Tropsch synthesis of long chain hydrocarbons mixture from synthesis gas of carbon monoxide and hydrogen, which can be finally used for the manufacture of diesel fuel [1]. Because of increasing demands for the high-quality diesel fuel, many studies on both fundamental and technological aspects of Co-based Fischer–Tropsch synthesis catalysts have been made in order to improve their physico-chemical properties, activities and selectivities. Supported cobalt catalysts are preferred for the Fischer – Tropsch synthesis. Most previous studies have focused on physico-chemical properties of surface cobalt species, such as dispersion, distribution, and morphology and their effects on catalytic activity [2]. In recent years a considerable interest was focused on FT metal/zeolites catalysts because acidic sites present in zeolites can have influence on the catalyst's activity and selectivity in CO hydrogenation [3].

In this work the physico-chemical properties of CoBEA zeolite catalysts (CoSiBEA and CoAlBEA) and their catalytic activity in the Fischer-Tropsch reaction were investigated.

Materials and Methods

The cobalt zeolite catalysts were prepared by two different procedures: I) two steps postsynthesis (Co_xSiBEA) and II) classical wet impregnation (Co_xAlBEA). The first method of preparation allowed controlling the introduction of Ni ions in the zeolite framework [4]. The physico-chemical properties of cobalt zeolite catalysts were investigated by DR UV-vis, XRD, H₂-TPR, TOF-SIMS, TPD – NH₃, FTIR, TEM and TG – DTA – MS. The catalytic activity test of Fischer – Tropsch synthesis was carried out in a pressure reactor using a gas mixture of H₂ and CO with a molar ratio of 2:1 (total gas flow of 60 cm³ · min⁻¹) and catalyst sample of 0.5 g. Process was carried out under pressure of 30 atm at the temperature of 260 °C. The reagents were analyzed by gas chromatograph. Before the catalytic test the catalysts were pretreated in static air at 500 °C for 3 h and reduced in situ in H₂ flow at 500 °C for 1 h. The catalytic test was carried out for 12 – 20 h.

Results and Discussion

XRD studies have shown that crystallinity of BEA zeolite after dealumination and incorporation of cobalt ions into zeolite framework has been preserved (results not shown). The TPR patterns of Co_xSiBEA with low Co content (0,5 – 5 Co wt.%) exhibited one peak at high temperature (750 – 800 °C). This fact indicated the presence of isolated mononuclear Co

species. For Co_xSiBEA, with higher Co content (10 – 20 Co wt.%) mononuclear and polynuclear Co species were present as evidenced by TPR and DR UV-vis. For Co_xAlBEA both mononuclear and polynuclear Co species were observed. The reduction occurred at high temperature (at about 700 – 800 °C) can be related to the presence of cobalt aluminosilicate (CoAlO₂H⁺) or cobalt silicate (CoSiO₂H⁺) evidenced by TOF – SIMS analysis. IR studies proved presence of Lewis acidic sites and absence of Brønsted acidic sites for all Co_xSiBEA samples. In contrast, for Co_xAlBEA both Lewis and Brønsted acidic sites were present.

The investigation of catalytic activity showed that the most active catalysts were Co₁₀SiBEA and Co₂₀SiBEA, with CO conversion of about 90 – 95 % and selectivity towards liquid products (saturated and unsaturated hydrocarbons C₆ – C₁₈) of about 60 %. The most active catalyst from Co_xAlBEA was Co₂₀AlBEA with CO conversion of about 60 %, selectivity towards CH₄ of about 37 % and selectivity towards liquid products (saturated hydrocarbons C₆ – C₁₇) of 37 % (Fig. 1). The amount of carbon deposition on Co_xSiBEA catalysts (4 – 13 %) was 2 times lower than that on Co_xAlBEA catalysts (11 – 18 %). The higher activity of Co_xSiBEA catalysts than that of Co_xAlBEA one in Fischer-Tropsch synthesis and the difference between identified liquid products for Co_xAlBEA and Co_xSiBEA catalysts could be related to the various acidic sites present in both type of catalysts. It is very likely that Co_xSiBEA catalysts is bifunctional catalysts, for which the hydrocarbons chain propagation occurs on metallic Co nanoparticles, located in extra-framework position, and then formed hydrocarbons are transformed into lighter products, containing less n-alkanes, on Lewis acidic sites located in zeolite framework.

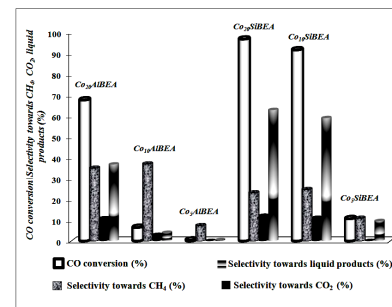


Figure 1. CO conversion and selectivity towards CH₄, CO₂ and liquid products in Fischer – Tropsch reaction for Co_xAlBEA and Co_xSiBEA catalysts.

Significance

The preparation of CoSiBEA catalysts by two-step postsynthesis method allows obtaining active and selective catalysts of Fischer – Tropsch synthesis and ecological fuel production.

References

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