Support effects on the catalytic behaviour of cobalt-nickel alloy catalysts for the Fischer-Tropsch synthesis

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The ever increasing demand for fuels has stimulated the development of alternative processes for fuel production. The catalytic transformation of carbon monoxide and hydrogen to hydrocarbons, also known as the Fischer-Tropsch (FT) synthesis, is key for the production of ultra-clean fuels. The FT process commonly employs cobalt-based catalysts due to their high selectivity towards long-chain hydrocarbons (C_{5+}), low water-gas shift activity and stable catalytic performance.[1] A drawback however is that cobalt is a relatively expensive metal which in the last year has tripled in price,[2] harming the competitiveness of FT.

In this research, we investigated the effect of gradual cobalt substitution by nickel, a more abundant and affordable metal, on supported FT catalysts and the influence of the support’s nature on the catalytic behaviour of the metals. For this, nanoparticles with different cobalt to nickel molar ratios (x = Ni/(Ni+Co): 0, 0.25, 0.5, 0.75 or 1 mol/mol) supported on reducible (TiO_2 and Nb_2O_5) or non-reducible (a-Al_2O_3) oxides were studied.

The FT performance of the samples was evaluated at various reaction pressures and temperatures with an H_2 to CO ratio of 2 v/v. At 1 bar and 220 °C, the samples with high nickel content supported on reducible oxides displayed increased activities and C_{5+} selectivities, doubling the catalytic activity compared to the monometallic catalysts (Figure A and B, purple squares). Contrasting, Al_2O_3-supported catalysts did not display this effect, resulting in similar activities and selectivities independently of the Co-Ni composition. Increasing total pressure (Figure A and B, red circles and green triangles) benefited the activity and selectivity of the TiO_2- and Nb_2O_5-supported samples with low nickel content (x = 0.0, 0.25 and 0.5). Likewise, higher pressures improved their C_{5+} selectivity whereas only a slight increase was observed upon increasing nickel content. In contrast, the activity of the samples with a high nickel content (x = 0.75) diminished by increasing the total pressure. STEM-EDX revealed that the Co-Ni nanoparticles exhibited an alloyed structure after reduction, whereas after catalysis (20 bar, 220 °C and TOS = 100 h) some of the particles show a cobalt-enriched surface (Figure C).

In summary, we showed that the combination of cobalt and nickel supported on reducible oxides allow for substantial cobalt substitution for nickel with increased FT activity and without sacrificing much C_{5+} selectivity. Reducible oxides used as support material strongly modified the reactivity of Co-Ni alloys, opening new possibilities for more efficient and affordable FT catalysts.


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