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Effects of manganese and reduction promoters on carbon nanotube supported cobalt catalysts in Fischer–Tropsch synthesis

J. Thiessen [a,*], A. Rose [a], J. Meyer [a], A. Jess [a], D. Curulla-Ferré [b]

[a] Department of Chemical Engineering, University of Bayreuth, 95440 Bayreuth, Germany
[b] Total S.A., Gas & Power, Paris La Défense, France

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ABSTRACT

Carbon nanotube (CNT) supported Co catalysts were promoted with manganese and noble metals (Pt, Ru) and tested in Fischer–Tropsch synthesis at temperatures between 200 and 250 °C and pressures of 1 and 30 bar. A significant decrease in methane selectivity and with that an increase in C_{5+} selectivity was found due to promotion with manganese. In addition, the activity (syngas conversion) slightly increases and the olefin selectivity drastically increases. The promotion with noble metals (Pt, Ru) resulted in a higher degree of catalyst reduction, yet otherwise only had small effects. The double promotion of Co with Mn and Pt or Ru lead to a higher activity and activation energy in the case of Pt, and in both cases to a lower olefin selectivity compared to the catalyst promoted with manganese only.

For a Mn promoted and an unpromoted Co/CNT catalyst, an increase of total pressure from 1 to 30 bar leads to a lower methane selectivity and higher chain growth probability. The rate of syngas consumption was found to be very similar at 30 bar compared to 1 bar.

1. Introduction

Sustainable energy production is one of the key challenges the world faces in the near future. Energy demand is increasing steadily in the EU and in the United States of America, but it is increasing fast in emerging countries such as China and Brazil. Forecasts by the International Energy Agency (IEA WEO 2008) [1] show that the energy demand will increase by 40% with respect to current levels until 2030. Despite the increasing share of renewables, 75% of the energy demand will be supplied by fossil energies with the resulting increase in CO_2 emissions. Some countries, especially in the European Union, are already promoting the development of low CO_2-footprint or CO_2-neutral technologies for sustainable energy production. Biomass (residues from forestry, industry and agriculture) conversion into biofuels or synthetic fuels using Fischer–Tropsch (F–T) technology can become a key technology platform for the successful implementation of a sustainable energy production.

F–T technology is a mature technology that is currently being used for the production of ultraclean synthetic fuels in South Africa, Qatar, Malaysia and China from coal (CTL) or natural gas (GTL) [2]. Yet, there is a lot of work going on that aims at reducing both capital and operation costs. An important share of the operational costs, particularly for cobalt-based F–T, is the cost of the catalyst. Therefore research is being conducted to achieve better performing longer life catalysts.

Cobalt-based catalysts represent the optimal choice for synthesis of middle distillate fuels and the companies that commercialize F–T technology have chosen cobalt for all their projects aiming at the production of liquids fuels; Shell in Malaysia and Qatar, and Sasol in South Africa, Qatar and Nigeria. Cobalt-based catalysts have also been the choice of other F–T companies like BP, Exxon, Statoil, Velocys and CGTL. Compared to iron-based catalysts, cobalt-based catalysts exhibit higher stability, higher productivity, negligible effect of co-produced water and higher resistance to attrition in slurry bubble column reactors. A drawback of cobalt in conventional silica-supported or alumina-supported cobalt catalysts is its high reduction temperature [3–5] with the consequent possible sintering of the cobalt particles. Typically, the reduction temperature of cobalt is lowered by introducing a noble metal as reduction and activity promoter, such as platinum or ruthenium. [5–7]. The necessity of using (expensive) reduction promoters can be circumvented by the use of alternative catalyst supports such as carbon nanotubes (CNT), as presented in this paper. When using nanocarbon as catalyst support, the reduction temperature (hydrogen consumption maximum) of CoO to Co^0 is typically in the region of 350 °C. A value of about 530 °C reached with rhenium promoted cobalt on alumina is, for instance, given in [8]. The reduction temperature of Co on silica and Pt promoted Co on alumina was found to be around 450 °C and 600 °C for unpromoted cobalt on alumina by [9]. Easy reducibility and an inert support is also important

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* Corresponding author. Tel.: +49 0921 55 7439; fax: +49 0921 55 7435.
E-mail address: johannes.thiessen@uni-bayreuth.de (J. Thiessen).

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when studying promoter effects with promoters that do not reduce the reduction temperature (e.g. Mn), as every other component (e.g. the reduction promoter Pt) added to a catalyst can affect the catalytical behaviour.

Promoter(s) should enhance the activity of the catalyst, but even more important, the methane selectivity should be low and the selectivity to C_{5+} hydrocarbons should be high, respectively. With regard to the use of short chain C_2 to C_4 hydrocarbons as petrochemical feedstocks, the olefin-to-paraffin ratio should be high. A candidate known to increase the C_{5+} selectivity and decrease methane selectivity is manganese, which was therefore investigated in this work. The use of manganese as promoter in FTS has already been examined, but not with CNT as support. For example, Keyser et al. and Colley et al. [10,11] examined co-precipitated Co/MnO catalysts and found relatively high olefin and low methane selectivities. The same trend was observed by Morales et al. [12,13] for MnO promoted Co on titania, who measured a higher chain growth probability, lower methane selectivity and higher activity as result of manganese addition at 1 bar and 220 °C.

An approach to examine the promoter effect of manganese on a non oxidic and inert carrier was delivered by Bezemer et al. [14,15]. Different Mn contents, adjusted by re-infiltration of manganese nitrate on Co supported on carbon nanofibres (CNF) were studied. A recent study from the same group [16] tested Mn promoted Co on a classical carrier (SiO_2), yet here platinum was added as a reduction promoter.

In this study the catalytical behaviour of Mn/Co/CNT, for comparison of the CNF catalysts, and the influence of addition of noble metals (Pt, Ru) at ambient pressure and 30 bar is presented.

2. Experimental

2.1. Catalyst preparation

The CNT were produced via catalytical chemical vapour deposition as described elsewhere [17,18]. The nano materials (5–10 g) were oxidised in a Soxhlet extractor with 1 l of 65% nitric acid for 24 h. After oxidation the samples were filtrated and washed with copious amounts of demineralised water, until the filtrate was pH neutral. Then the samples were dried for 20 h at 120 °C.

Oxidized and dried nanotubes were added to a solution of cobalt nitrate hexahydrate (Carl Roth) with about 0.11 g Co per g of CNT and the respective amount of promoter salt in water (app. 100 ml water/$g_{(C)}$) and stirred for a day. Then the water was slowly removed by gradually decreasing the pressure in a rotary evaporator at 60 °C. The Promoter salts used were ($Pt(NH_3)_4(NO_3)_2$ (Aldrich), $Ru(NO)(NO_3)_3$ 1.5 wt% Ru in water (ABCR) and $Mn(NO_3)_2$ 51 wt% Mn in water (ABCR). The dried samples were pyrolysed and reduced in one step in flowing hydrogen (GHSV > 1000 h^{-1}), heating to 360 °C with 3 K/min and maintaining at that temperature for 2 h. After cooling the reduced samples to room temperature they were exposed to 2% oxygen in nitrogen for some time, before slowly exposing them to air. Spot tests to check the metal content were conducted via thermogravimetry (temperature programmed oxidation) using the self reduction of Co_3O_4 to CoO at about 830 °C. All the metal in the precursor solution was found in the resulting catalyst.

2.2. Analysis

Nitrogen physisorption measurements were conducted in a Micromeritics Gemini V analyser, the surface area was calculated from the adsorption isotherm in the partial pressure range of 5–30% of the saturation pressure via the BET-method [19]. The micro porosity was calculated via the t-method (Harkins and Jura) [20].

Temperature programmed reduction measurements were conducted with a Quantachrome ChemBET 3000, equipped with a thermal conductivity detector (TCD).

Particle size distributions were obtained by evaluating TEM-pictures (Zeiss 922 Omega) and measuring as many particles as possible.

2.3. Fischer–Tropsch synthesis

FTS at 1 bar: The FTS unit consists of an electrically heated vertical tubular steel reactor (inner diameter 9 mm). The reactor can be supplied with nitrogen, hydrogen, synthesis gas ($H_2/CO = 2$ mol/mol) or mixtures thereof. The gas flow is controlled by Brooks 5850 mass flow controllers (MFC). 0.3–0.5 g of the FTS catalyst were diluted with quartz sand (filling up to 3 ml) to prevent temperature runaway. The reduction of the catalyst was carried out by heating the bed to 360 °C with a heating rate of 10 K/min in flowing hydrogen and a 2 h hold. The reduced catalysts were cooled in flowing H_2 to temperatures below 100 °C and the system was then purged with syngas. The bed was then heated to 210 °C in a volume flow of 2.5–3 l/h (STP, GHSV (ratio of volume flow rate (STP) to volume of catalyst bed) = 833–1000 h^{-1}) syngas ($H_2/CO = 2$ mol/mol) and maintained there for 20 h to assure steady state prior to measurement. Between temperature changes the system was held at the new temperature for at least an hour prior to measurement. The reaction products pass a 0 °C cooling trap and a gas sampling tube before entering a flow meter. The gas phase (C_1 to C_5 hydrocarbons (HC)) was analysed by GC (Varian LHA analyser; Varian CP-Sil Pona CB 100 m × 0.25 mm ID × 0.5 μm column) for determination of the C_{5+}, methane and the olefin selectivity.

FTS at 30 bar: The FTS lab-scale unit consists of an electrically heated vertical tubular steel reactor (inner diameter 15 mm). The reactor tube is cladded with a 18 cm aluminium cylinder, to assure that the reactor wall around the fixed bed is isothermal. A carbonyl decomposer is mounted upstream of the synthesis unit.

The reactor can be supplied with nitrogen, hydrogen, syngas ($H_2/CO = 2$ mol/mol) or mixtures thereof. The gas flow was controlled by Brooks 5850 MFCs. The pressure was controlled via a back pressure regulator.

The FTS catalyst (3 g) was diluted with quartz sand (filling up to 30 ml) to prevent temperature runaway and to reduce the temperature gradient in the catalyst bed. Catalysts tested in FTS were reduced at 360 °C in 20% H_2 in N_2 (20 l/h STP). After a 3 h hold the feed gas was switched to 20 l/h pure H_2 and the temperature was held for further 2 h. The reduced catalyst was cooled to RT in hydrogen.

FTS was conducted by heating the reactor to 210 °C in 20 l/h (STP) syngas (GHSV 667 h^{-1}), and holding the reactor in those conditions for 70 h, to assure steady state. Products were collected and analysed during 8 h of synthesis time. Before changing the temperature the synthesis unit was run for 16 h with the new parameters prior to 8 h measuring.

The liquid reaction products were collected in cooling traps at 70 °C, room temperature, and 0 °C at ambient pressure and analysed with a Varian CP 3800 Gas Chromatograph (DB5 ht 15 m × 0.32 mm ID × 0.1 DF column). The remaining gas phase was analysed by GC (Varian LHA analyser) and by a gas analyser (Fisher–Rosemount) to measure the content of CO, CO_2, H_2, and CH_4 in the fresh syngas and in the product gas. 1% cyclopentane in N_2 as internal standard was introduced into the exhaust gas before entering GC and gas analyser.

The activity (rate) at both total pressures (1 and 30 bar) was checked after readjusting to the first measured temperature to assure a negligible deactivation.

Product selectivities were calculated by Eq. (1), where $\dot{m}_{C,i,out}$ denotes carbon related mass of the product species (e.g. the assigned