Study of temperature-programmed calcination of cobalt-based catalysts under NO-containing atmosphere

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ABSTRACT

Temperature-programmed calcination (TPC) experiments were performed under NO containing atmosphere for alumina supported cobalt catalyst. During these experiments the NO and NO_2 concentration of the effluent was measured continuously. It was observed that NO concentrations below 1 vol% significantly influence the TPC profile. With increasing NO content in the gas phase from 0 to 1 vol% an increasing amount of NO_2 evolves at temperatures below $100\,^{\circ}C$, which is correlated with consumption of NO. These results indicate decomposition of cobalt nitrate forming cobalt hydroxynitrates at low temperatures in the presence of NO. In agreement with literature, increased cobalt dispersion was obtained for materials calcined in NO containing atmosphere. Thus, the present method seems to be interesting for preparation of highly active Fischer–Tropsch catalysts.

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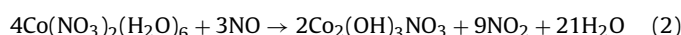
1. Introduction

Cobalt-based catalysts are known to be active in Fischer–Tropsch-Synthesis (FTS) and are thus widely used in producing fuels via that process. In order to maximize the productivity the activity of the catalyst needs to be optimized. This can be achieved by increasing the cobalt surface area. However, depending on the support material the turn-over-frequency (TOF) drops for cobalt particle sizes below 5–10 nm [1]. Consequently, the maximum activity can be achieved in the cobalt particle size range between 5 and 10 nm [2]. Even though these results were obtained with carbon nanofiber supported cobalt catalyst, it also seems to hold for other support materials, since the support effect appears to be marginal [3].

Consequently, a highly controllable catalyst synthesis procedure is required in order to adjust and maintain the desired cobalt particle size throughout the synthesis process. One of the most important preparation steps is the calcination to form Co_3O_4 species from cobalt nitrate. The transformation is achieved by calcining the catalyst precursor, obtained by impregnating a porous support with cobalt nitrate, at elevated temperature.

During calcination the nitrate is decomposed to the oxide under formation of gaseous NO_2 (Eq. (1)).

$$3Co(NO_3)_2(H_2O)_6 \rightarrow Co_3O_4 + 6NO_2 + O_2 + 18H_2O \qquad (1)$$

It is well-known that pretreatment conditions, such as atmosphere, heating rate, calcination temperature and gas flow rate, significantly influence the dispersion of the final catalyst [4]. Under these conditions sintering of the nitrate, oxide and intermediate species might occur, leading to a decreased active surface area. Two strategies appear to be promising in order to reduce sintering during calcination: the reduction of calcination temperature or the formation of sinter-stable intermediates. The group of de Jong presented a strategy to reduce the calcination temperature for formation of Co_3O_4 from cobalt nitrate by addition of NO to the calcination atmosphere [5–7]. It was shown by XRD, XANES and EXAFS measurements that the decomposition of cobalt nitrate into cobalt oxide proceeds under formation of an intermediate species, namely cobalt hydroxynitrate (Eqs. (2) and (3) [8,9]). The formation of the hydroxynitrate species was found to occur already at temperatures below $120\,^{\circ}C$ [9]. Even though several hydroxynitrate species could be formed, the stoichiometric ratio between NO consumption and NO_2 formation appears to be 3 (Eq. (2) [8]).

$$4Co(NO_3)_2(H_2O)_6 + 3NO \rightarrow 2Co_2(OH)_3NO_3 + 9NO_2 + 21H_2O \qquad (2)$$

$$6Co_2(OH)_3(NO_3) \rightarrow 4Co_3O_4 + 5NO_2 + NO + 9H_2O \qquad (3)$$

It was shown that the cobalt dispersion could be increased by NO addition compared to calcination under air [6,7,10]. Wolters

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et al. explain this effect by a moderated decomposition rate of the cobalt nitrate, the suppression of oxygen radicals and the reduced mobility of the intermediate hydroxynitrate species [9]. However, these results were obtained with silica supported cobalt catalysts and the transferability to other support materials remains unclear.

The effect of NO during calcination of alumina supported cobalt catalysts was studied by Jacobs et al. and Sietsma et al. [7,11]. Both authors report a reduced crystallite size in the final catalyst when NO was present during calcination. However, a detailed study of the evolution of alumina supported cobalt species during calcination has not yet been reported in literature.

Furthermore, the majority of studies was performed with NO concentrations of 1 vol% or more. However, Sietsma et al. reported for nickel based catalysts that NO concentrations of about 0.1 vol% already reduce NiO crystallite size significantly [12].

Hence, in this contribution the focus is on the effect of NO in the concentration range of 0–1 vol% in N_2 during calcination of alumina supported cobalt catalysts. The method of temperature-programmed calcination (TPC) with in situ analysis of the gas phase composition will be presented as a tool to study the transformation of cobalt nitrate into cobalt oxide quantitatively. The measured rates of NO consumption and NO_2 formation are used to conclude on the nature and amount of intermediate species.

2. Experimental

2.1. Chemicals and gases

For catalyst preparation cobalt (cobalt nitrate hexahydrate, $Co(NO_3)_2(H_2O)_6$, puriss. ≥98%, Riedel-de Haën) and rhenium (perrhenic acid, $HReO_4$, 53.74% in water, H.C. Starck) precursors were impregnated on alumina support material (γ-Al_2O_3, Puralox SCCa 150/200, Sasol). All chemicals were used as received. Gases used are of 5.0 purity. NO was used as gas mixture (2 vol% NO in nitrogen).

2.2. Catalyst preparation, pretreatment and characterization

The catalyst was prepared by impregnating a melt of cobalt nitrate and perrhenic acid into the pores of γ-alumina support to obtain ca. 20 wt% Co and 1 wt% Re on alumina catalyst. The novel melt infiltration method [13], used in the present study, requires no additional water to prepare a solution, since the melt of precursor species infiltrates the pore system. Thus, less water needs to be removed in the drying step. For catalyst preparation the metal precursors were mixed with the support material in a welted glass, heated to 75 °C in an oven and mixed again until it cooled down. This procedure was repeated three times and followed by drying at 85 °C in a convection oven for 16 h under air. All experiments were conducted using subsamples of one single batch of impregnated material.

The cobalt dispersion was measured by adsorption of H_2 on the Co surface using the volumetric adsorption method (ASAP 2020, Micromeritics). For that purpose ca. 70 mg of the calcined sample was reduced under pure H_2 for 16 h at 350 °C, followed by chemisorption of pure H_2 at 50 °C. Thermogravimetric analysis (TGA, Mettler TGA 860) was conducted heating ca. 15 mg of sample with a heating rate of 20 K/min to 950 °C under air flow (50 mL/min).

2.3. Temperature-programmed calcination

The dried catalyst was used for the temperature-programmed calcination experiments. Therefor 400 mg of the material was transferred into an electrically heated glass tube with an internal diameter of 7 mm and flushed by nitrogen at 30 °C. The powder

was fixed within the reactor by a quartz wool plug. The temperature of the sample was measured by means of a thermo couple inside the packed bed. The NO concentration in the process gas was adjusted by diluting NO into N_2 by means of mass flow controllers (Bronkhorst). The total gas flow rate of process gas was maintained at 400 mL_{STP}/min for all experiments. The effluent was analyzed using a Rosemount Analytical gas analyzer (NGA 2000) equipped with a UV detector for NO_2 and an IR detector for NO. The nitrogen oxides (NO and NO_2) can be quantified up to a concentration of 2000 ppm. The linear range is 500–2000 ppm and 250–2000 ppm for NO and NO_2, respectively.

Prior to each experiment the inlet concentration of NO was determined via by-pass measurements. The experiment was started by contacting the process gas flow with the sample. After reaching a stable concentration signal the sample was heated from 30 to 250 °C with a heating rate of 1 K/min and maintained at this temperature for 60 min. Subsequently, the sample was cooled down under process gas, which was switched to pure nitrogen after reaching temperatures below 50 °C. Additionally, some samples were partially calcined only. Therefor, the sample was heated to the desired temperature as described above. Subsequently the heater was shut off and the sample was allowed to cool down under process gas as described above. Data for sample temperature and NO and NO_2 concentration were collected during the whole experiment with a resolution of 5 s. After completion of the experiment the material was removed and stored in a sample glass.

2.4. Nitrogen balance

For quantitative statements the presented method of temperature-programmed calcination needs to be verified. For that purpose a nitrogen balance was used comprising NO, NO_2 and nitrate species. The total initial amount of nitrate was determined from the weight of the cobalt nitrate used for impregnation. The amounts of NO and NO_2 were estimated from the measured concentration and the total gas flow rate, which was assumed to be constant. Consequently, the rate of formation or consumption of a gaseous nitrogen oxide species $\Delta \dot{n}_i$ can be calculated by Eq. (4) using the difference in mole fraction between inlet $x_{i,in}$ and outlet $x_{i,out}$. The total volumetric gas flow rate $\dot{V}$ is given at STP (standard temperature T_{STP} and pressure p_{STP}).

$$\Delta \dot{n}_i = \dot{V}_{STP} \frac{p_{STP}}{RT_{STP}} (x_{i,in} - x_{i,out}) \tag{4}$$

The integration of the rates $\Delta \dot{n}_i$ over time gives molar amounts n_i of consumed NO and formed NO_2. The difference between the formed NO_2 amount and the consumed NO amount corresponds to the emitted amount of nitrogen originating from the cobalt nitrate. Thus, the nitrate conversion can be formulated according to Eq. (5). In this equation $n_{Co(NO_3)_2,0}$ represents the initial molar amount of cobalt nitrate in the sample.

$$X_{NO_3} = \frac{|n_{NO_2}| - |n_{NO}|}{2n_{Co(NO_3)_2,0}} \tag{5}$$

3. Results and discussion

3.1. Nitrogen balance

The conversion of cobalt nitrate was estimated based on an elemental balance of nitrogen oxide species. To obtain the conversion at different temperatures during TPC samples were partially calcined at 100, 250 and 350 °C, respectively. Table 1 shows the results of these experiments indicating an increasing conversion with temperature, as expected. At high temperatures a conversion