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Effectiveness of catalyst passivation techniques studied *in situ* with a magnetometer

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ABSTRACT

Using an in house developed *in situ* magnetometer the passivation in diluted oxygen or pure carbon dioxide of a platinum promoted and silica supported cobalt catalyst was studied. No passivation of cobalt was observed after treatment in CO₂, neither at 30 °C nor at 150 °C. The magnetic cobalt metal phase content remained constant during these treatments and decreased in the subsequent exposure to air. The catalyst exposed to 1% O₂ in N₂ was stable in air at 30 °C. However, no long-term stability was observed. The magnetic measurements during passivation in 1% O₂ indicate partial oxidation of the nanoparticles in form of a CoO layer. The degree of reduction decreased from 89% to 51%, which corresponds to a theoretical oxide layer thickness of 1.3 nm surrounding the metallic core with a diameter of 9.8 nm. Upon re-reduction full recovery of the metal phase was obtained. The re-reduction occurred at significantly lower temperatures than the reduction of the freshly prepared catalyst or the re-reduction of a reduced catalyst after exposure to air without any passivation.

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1. Introduction

Passivation of highly air sensitive transition metal catalysts is often used to preserve reduced or spent catalysts to allow transfer of samples from the reactor vessel to conventional characterisation instruments [1–5]. This process allows the characterisation of the catalyst in a state which resembles the activated state. Furthermore, passivated samples can be stored under ambient conditions. Passivation is reported to avoid or at least suppress rapid and violent oxidation by air, which results in phase changes and local temperature hot spots. The latter can become a safety hazard in the case of pyrophoric materials and industrial catalysts are typically removed from the reactor under inert gas or after passivation.

The most common approach to passivate air sensitive metals is the controlled exposure to low concentrations of O₂ (typically in the range of 0.1–1%) in an inert [6,7], as applied in several catalytic studies [8–12]. This treatment is reported to lead to surface passivation by formation of a thin oxide layer protecting the metallic core from further oxidation in air [13–19]. Besides O₂, other mildly oxidising atmospheres including gaseous CO₂ [17,20–25], dry ice originated CO₂ [26,27], H₂O [14,17,28], or N₂O [29–31] were applied for the passivation of transition metal nanoparticles. Other approaches, avoiding the formation of an oxide phase, are the air-

tight encapsulation of the nanoparticles by a carbon layer [31–35], an organic [17,36–41], or a polymer phase [38,42]. However, in some instances these protective layers did not result in adequately passivated metal cores [14,17,20,28] and/or are reported to not provide long-term stability, as further diffusion limited oxidation was observed [31,38,41].

Though oxidising methods are widely applied, very little is reported about the effectiveness of these passivation processes. Only a few characterisation studies on passivation methods are published, which are mostly based on *ex situ* characterisation techniques [13,15,35,38] or on the measurement of an exotherm upon exposure of the ‘passivated’ sample to air [20,28,32]. In this study, an in house developed *in situ* magnetometer [43], which directly monitors the formation or loss of magnetic species, here metallic cobalt to CoO or Co₃O₄, was utilised to illustrate the passivation of a reduced Pt promoted Co/SiO₂ Fischer-Tropsch catalyst by low concentrations of O₂ in N₂ or pure CO₂.

2. Material and methods

2.1. Catalyst preparation

The cobalt catalyst (20 wt.% Co/SiO₂, promoted with 0.1 wt.% Pt) for this study was prepared by incipient wetness impregnation similar to the procedure published by Munnik et al. [44]. In short, silica gel (particle size: 75–150 μm, average pore diameter: 25 Å, Davisil Grade 923, Sigma Aldrich) was impregnated with aqueous solu-

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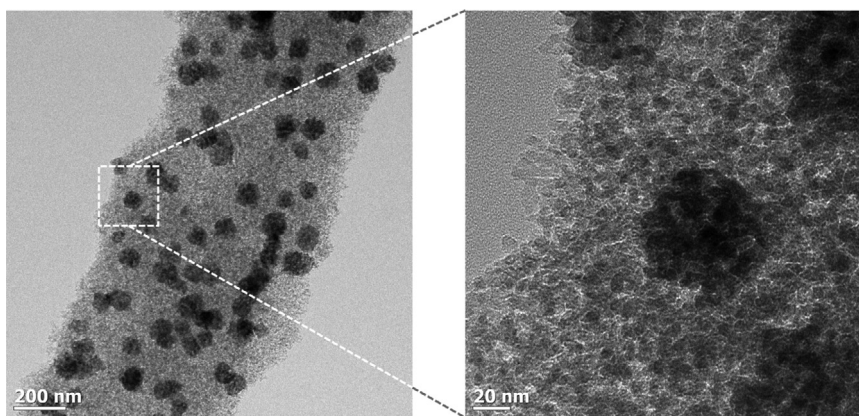


Fig. 1. TEM micrographs of the parent catalyst (left) and a detail of magnified particle agglomerations (right).

tions of $\text{Co}(\text{NO}_3)_2$ (4.2 M, Kimix, RSA) and $(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$ (0.007 M, Sigma Aldrich) equivalent to 80 vol.% of the SiO_2 pore volume. The catalyst was dried in a fluidised bed reactor under nitrogen at 100°C and calcined at 350°C (1°C min^{-1} , 1 h).

2.2. Catalyst characterisation

The size distribution of the cobalt oxide crystallites in the prepared catalyst was determined by measuring the diameters of more than 300 crystallites as obtained via transmission electron microscopy (TEM, F20 – FEI Tecnai). The phases present in the prepared and the treated catalysts were identified with an X-ray diffractometer (Bruker D8 Advance), equipped with a cobalt source ($\lambda_{\text{CoK}\alpha 1} = 0.178897 \text{ nm}$) and a position sensitive detector (VANTEC-2000, Bruker AXS). An *in situ* setup of the X-ray diffractometer [45] was utilised to study the temperature controlled reduction of 10 mg of the parent catalyst. For this, the sample was placed in a borosilicate capillary (Capillary Tube Supplies, UK) with a 1 mm outer diameter and 0.02 mm wall thickness and reduced for 10 h at 400°C (2°C min^{-1}) in H_2 at a space velocity of $400 \text{ mL g}^{-1} \text{ min}^{-1}$ (STP). The average crystallite size was determined by Rietveld refinement of the X-ray diffraction (XRD) patterns (TOPAS 4.1, Bruker AXS).

2.3. Magnetic measurements

Passivation experiments were conducted in an in house developed *in situ* magnetometer [21,43,46], based on the Weiss extraction method. The field-controlled electromagnet of this setup provides field strengths of up to 20 kOe (2.0 T). The installed $\frac{1}{2}$ " stainless steel fixed bed reactor can operate at temperatures up to 700°C and pressures in excess of 50 bar. A K-type thermocouple placed inside the catalyst bed measures and controls the temperature of the reactor which is heated through infra-red heaters. An amount of 500 mg of the oxidic parent catalyst was placed in the reactor and reduced for 10 h at 400°C in H_2 at a heating rate of 2°C min^{-1} . Three different passivation treatments were applied to the reduced catalyst: 1% O_2/N_2 at 30°C , 90% CO_2/Ar at 30°C and 90% CO_2/Ar at 150°C . At an external field strength of 20 kOe, the measured magnetisation (M_{sat}) is directly proportional to the amount of metallic cobalt, being the only magnetic compound at reaction conditions [47]. With a known cobalt loading in the parent catalyst, the degree of reduction (DOR) can be calculated by calibrating the magnetometer with defined amounts of metallic cobalt. The mass fraction of ferromagnetic material (γ) can be calculated with the measured magnetisation (M_{sat}) and the remnant magnetisation obtained after external magnetisation (M_{rem}) according to Dalmon [48] as $\gamma = 2 \times M_{\text{rem}}/M_{\text{sat}} \times 100\%$. This fraction describes the relative mass of ferromagnetic cobalt domains larger than a critical

diameter, which is reported to be approximately 15–20 nm at room temperature [48–50]. Below this critical diameter, metallic cobalt behaves superparamagnetic, while above it is ferromagnetic. An increase in γ semi-quantitatively describes an increased average cobalt crystallite size and/or a decreased overall fraction of smaller cobalt crystallites in the metallic phase.

After a stable magnetisation was reached in the passivation processes, the samples were exposed to a controlled air stream at 30°C . A freshly reduced catalyst without passivation was also exposed to air in a reference experiment. In a last step, the catalysts were re-reduced for 30 min at 400°C in H_2 using a heating rate of 2°C min^{-1} . Samples for crystallographic analyses via XRD were obtained in repetitions of the experiments without re-reduction.

The space velocity in all steps was $200 \text{ mL g}^{-1} \text{ min}^{-1}$ (STP) based on the initial mass of parent catalyst and the reactor outlet gases were analysed for Ar, CH_4 , CO, CO_2 , N_2 and O_2 via gas chromatography with TCD detection (Varian CP-4900 Micro GC). In addition, the temperature in the catalyst bed was monitored via the thermocouple which was placed directly inside the catalyst bed in order to assess as to whether exotherms occurred during the exposure to air.

3. Results and discussion

The volume based average cobalt oxide (Co_3O_4) crystallite size of the prepared catalyst was measured to be 16.5 nm (standard deviation 7 nm) as obtained from TEM analysis (Fig. 1s in the Supplementary material) and was confirmed by XRD (14.6 nm). The crystallites are mostly arranged in clusters of 40–100 nm (Fig. 1). After reduction, the dominating fraction of the metallic phase is the fcc allotrope having an average crystallite size of 11.8 nm and a smaller fraction of hcp cobalt is present (Fig. 2).

The phase change from non-magnetic cobalt oxide to magnetic metallic cobalt during the reduction of the parent catalyst is detected by the magnetometer as the saturation magnetisation increases with the amount of metallic cobalt formed (Fig. 3). The onset of the reduction is 210°C (as determined via extrapolation as described in Ref. [51]) and the final DOR at 400°C is 89%. It has to be noted that the sample magnetisation is a function of temperature and decreases with increasing temperature [52].

The high magnetisation level of the reduced catalyst rapidly decreases in the first 15 min of the exposure to 1% O_2/N_2 flow due to the reaction of metallic cobalt with O_2 to non-magnetic cobalt oxide (Fig. 4, left). The magnetisation continues to decrease slightly before a constant value is reached after about 30 h. It can be noted that this duration is significantly longer than the duration of similar passivation processes for cobalt nanoparticles applied in the literature, i.e. 10 min to 12 h [2,4,10,11,19]. The temperature remains constant

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