

The effect of temperature and manganese on the crystallographic evolution of metallic cobalt thin films under reductive conditions

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Introduction

The conversion of CO and H₂ to liquid fuels through Fischer-Tropsch synthesis (FTS) is known to be sensitive to the structure of the active catalyst. In cobalt-based catalysts, the crystallographic structure of the active phase - metallic cobalt, influences the FTS performance since *hcp*-Co⁰ exhibits higher FTS intrinsic activity and lower methane selectivity than *fcc*-Co⁰.¹ However, in powder catalysts, this structure sensitivity of the catalyst performance under FTS is complicated by phase change from *hcp*-Co⁰ to *fcc*-Co⁰ with temperature and decreasing crystallite size.²⁻⁴ Typically, the reduction of *spinel*-Co₃O₄ at low temperatures yields an *hcp*-Co⁰ phase, which transforms into the *fcc*-Co⁰ phase structure above 420 °C.³⁻⁴

An insight into the relationship between structural-electronic properties and catalytic behavior is still lacking in the field since the study of the phenomena at the metal surface and metal-insulator interface of powder catalysts is challenging. Contrarily, a wide range of surface sensitive techniques can be used to examine the surface and buried interfaces of thin film catalysts. Additionally, thin film catalysts, grown over large areas with preferred crystallographic structure, mimic single crystal model catalysts. Various economical deposition techniques enable tailoring of physio-chemical properties crucial for technical catalysis. Thus, an understanding of the effect of crystallite size and the addition of promoter on the crystallographic transformation of *spinel*-Co₃O₄ with temperature during reduction would be important to fully exploit these advantages. This study reports on the effect of Mn structural promoter on the temperature-dependent phase transformation behavior of *spinel*-Co₃O₄ from *hcp*-Co⁰ to *fcc*-Co⁰ morphologies on Mn-Co thin-film catalyst stacks on SiO₂.

Materials and Methods

The samples were prepared by depositing a 25 nm thick cobalt layer fused silica wafer (12 mm × 12 mm), using magnetron sputtering. Thereafter, one sample was subsequently decorated with Mn using the successive ionic layer adsorption reaction (SILAR) method to produce a Mn-Co thin-film catalyst stacks on SiO₂. The second sample consisting of a Co thin-film on SiO₂ which was used as a basis for comparison. Both samples are calcined under flowing O₂ (30 mL/min) at 350 °C for 24 hours to obtain a *spinel*-Co₃O₄ layer.

The reduction monitoring studies were carried out at the KMC-2 beamline at the BESSY Synchrotron light source in Berlin.⁵ The KMC-2/Diffraction beamline station is fitted with an X-ray transparent furnace (Anton Paar DHS 1100) that enables high-temperature *in-situ* GI-XRD studies in controlled atmospheres. The reduction behavior of both samples was thus investigated under flowing forming gas (20 vol.-% H₂/N₂, 1 bar), under heating from 30 °C to 600 °C, at 2 °C/min. Grazing incidence X-ray diffraction was performed using a high-photon energy of 8 keV and a 2D Bruker Vantec 2000 detector was used to provide sufficient time and spectral resolution as well as surface sensitivity at a low incident angle of 2 °. The gas treated samples were quenched under flowing forming gas from 600 °C to 30 °C at a cooling rate of 50 °C/min.

Results and Discussion

Figure 1 shows diffractograms of Co/SiO₂ (left) and Mn-Co/SiO₂ (right) stacks as the annealing temperature and atmosphere were varied. The Co/SiO₂ stack was reduced from *spinel*-Co₃O₄ at 30 °C to *hcp*-Co⁰ at 350 °C. As the temperature further increased to 600 °C, *fcc*-Co⁰ emerged, thus giving a mixture of *hcp*- and *fcc*-Co⁰. Upon cooling from 600 °C to 30 °C under reducing atmosphere, the *hcp*-Co⁰ phase is more pronounced, as expected. In contrast, Mn-Co/SiO₂ yielded predominantly *fcc*-Co⁰ at 600 °C and maintained the *fcc*-Co⁰ structure even after cooling to room temperature under gas treatment. Thus, decorating the cobalt thin-film catalyst with Mn appears to retain the crystallographic structure of the cobalt moiety formed before quenching.

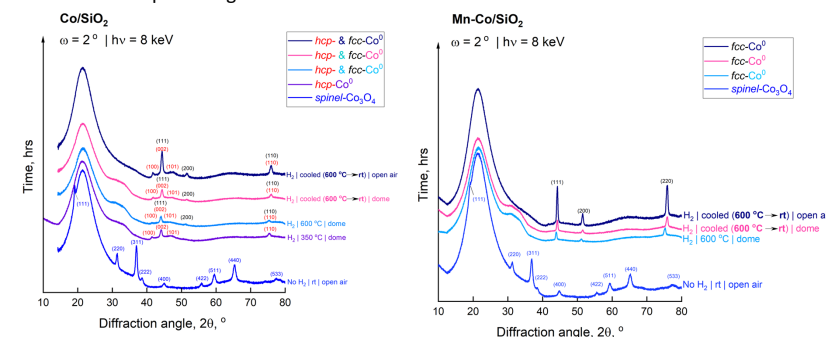


Figure 1. In-situ grazing incidence diffractograms of Co and Mn-Co thin film catalysts on fused SiO₂ acquired at an incidence angle of $\omega = 2^\circ$ with a photon energy of 8 keV.

Significance

Selection of the appropriate heat treatment sequence and addition of a structural promoter can be used to tune the crystalline phase of Co-based thin films as required for use as model or technical catalysts for FTS.

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