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Complete List of Authors:	Tsakoumis, Nikolaos; Norwegian University of Science and Technology (NTNU), Chemical engineering Johnsen, Rune E.; Technical University of Denmark, DTU Energy Conversion and Storage van Beek, Wouter; SNBL, Ronning, Magnus; Norwegian University of Science and Technology, Department of Chemical Engineering Rytter, Erling; Norwegian University of Science and Technology (NTNU), Chemical engineering Holmen, Anders; Norwegian university of science and technology, chemical engineering



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## Capturing metal-support interactions *in situ* during the reduction of a Re promoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

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N. E. Tsakoumis,<sup>\*a</sup> R. E. Johnsen,<sup>b</sup> W. van Beek,<sup>c</sup> M. Rønning,<sup>a</sup> E. Rytter,<sup>a,d</sup> and A. Holmen<sup>a</sup>

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**Reduction of a Re promoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was monitored *in situ* by synchrotron X-ray powder diffraction (XRPD) under H<sub>2</sub> environment. Whole powder pattern analysis revealed a non-linear expansion of the unit cell of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the reduction process, suggesting diffusion of Co cations into the structure of the support. The non-linear cell expansion coincided with the formation of CoO phase. In addition, space resolved diffraction at the inlet and outlet of the reactor evidenced a negative effect of the partial pressure of indigenous H<sub>2</sub>O<sub>(g)</sub> on the reduction process.**

Catalyst activation is a critical step in the start-up procedure for most industrial catalytic processes. Commonly a solid precursor is subjected to conditions that allow its transformation to the catalytically active component. In many catalytic applications, the metallic surface of nanoparticles (NPs) is the active phase and therefore reduction of supported metal oxide precursors precedes. The reduction process is affected by various parameters such as the nature of precursor, the size of the nanoparticles, the reactivity of the support and the reducing atmosphere. The execution of catalyst activation may have an impact on catalyst structure and consequently performance, involving risks of sintering or a low degree of reduction<sup>1</sup>. In the last decades, *in situ* investigations have boosted catalysis research and allowed the deconvolution of complex phenomena like catalyst activation<sup>2</sup>.

Cobalt NPs supported on high surface area porous materials such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, are used in various industrial processes like Fischer–Tropsch synthesis (FTS)<sup>3</sup> and hydrodesulfurization reaction<sup>4</sup>. FTS is the heart of Gas-to-Liquid (GTL) technologies and a tool for the utilization of synthesis gas derived from different feedstocks i.e. natural gas, coal and

biomass. In Co-based FTS carbon monoxide and hydrogen are converted into a mixture of linear long-chain hydrocarbons, while significant amounts of steam are co-produced. The active metallic Co phase is commonly formed by H<sub>2</sub> reduction of the Co<sub>3</sub>O<sub>4</sub> spinel precursor produced after drying and calcination of the impregnated source. The activation procedure is important for the optimization of catalyst performance<sup>5,6</sup>, since catalysts activity and selectivity are related to the reduction extend and Co particle size and thus reduction conditions have to be carefully optimized. Reduction of promoted and un-promoted  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Co<sub>3</sub>O<sub>4</sub> NPs has been studied in detail either by conventional temperature programmed reduction (TPR)<sup>7–9</sup> or by advanced *in situ* techniques including X-ray powder diffraction (XRPD)<sup>10,11</sup>, X-ray absorption spectroscopy (XAS)<sup>12–15</sup> and transmission electron microscopy (TEM)<sup>16</sup>. From the majority of the reports, it is evident that the reduction is a two-step process that reaches polycrystalline metallic Co through a CoO intermediate. Use of dopants like Re promotes the reduction process most likely through H<sub>2</sub> spillover effects<sup>7</sup>.

Although most of the reports agree on the steps of the reduction procedure, formation of mixed compounds of Co with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support during reduction has been debated. The mixed phase, due to its amorphous nature, low concentrations and possible chemical similarities with divalent Co species present in other Co oxides, is difficult to be probed. Commonly H<sub>2</sub> consumption in the high temperature (> 600 °C) region of TPR profiles is commonly related to Co species that are difficult to be reduced as a result of strong interaction with the support<sup>17</sup>. The Co-support interaction has been indirectly detected for catalysts calcined at high temperatures (> 500 °C) by the lattice expansion of Al<sub>2</sub>O<sub>3</sub> as observed by *ex situ* XRPD performed after calcination<sup>17</sup>. Rutherford backscattering spectrometry (RBS) and X-ray Absorption Near Edge Structure (XANES) studies also suggested that the formation of such compounds is size sensitive and takes place during catalyst calcination<sup>17,18</sup>. Furthermore detailed TPR and XANES studies pointed at the formation of such compounds during catalyst reduction<sup>7,8,19,20</sup>.

<sup>a</sup> Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway.

<sup>b</sup> Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark.

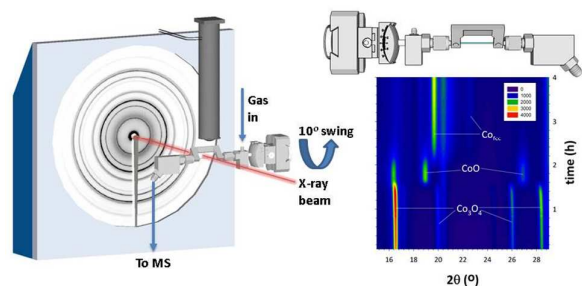
<sup>c</sup> Swiss–Norwegian Beamlines at ESRF, BP 220, Grenoble 38043, France.

<sup>d</sup> SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

† Footnotes relating to the title and/or authors should appear here.

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**Fig. 1** Representation of the used set-up (BM01A) configuration together with a 3D representation of the *in situ* cell and a contour plot of the obtained data set showing the main crystalline phases evolving during the course of reduction.

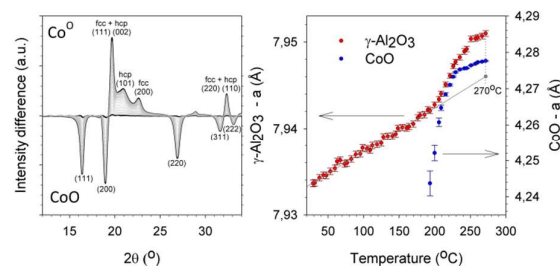
XANES has been regularly applied for the detection of Co-support mixed compounds that are formed during reduction and FT reaction<sup>14,20–22</sup>, due to its sensitivity towards oxidation state and local geometry, however direct observation of this interaction in a time-resolved manner has not been reported.

In the present study a Re/Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has been reduced and monitored *in situ*. Synchrotron XRPD was applied in order to shed light on the structural changes that occur during the reduction process. Apart from the crystalline phases that are evolving, indirect information on the development of cobalt-support mixed compounds was also obtained by an irregularity in the lattice expansion of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

The catalyst used in this study consists of 20 wt% Co, 1 wt% Re supported on a high surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (170 m<sup>2</sup>/g, Puralox SCCa Sasol GmbH), with pore volume of 0.73 ml/g and average pore diameter of 12 nm. The catalyst was prepared by co-impregnation of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and HReO<sub>4</sub>. More details on the catalyst preparation and properties can be found elsewhere<sup>14</sup>. *In situ* XRPD measurements were performed at stations BM01A and BM01B of the Swiss-Norwegian Beamlines (SNBL) located at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A quartz capillary based *in situ* cell has been used<sup>14</sup>. The sample was heated by a vertical hot air blower. A swing movement of a few degrees was applied for increased diffraction signal statistics (BM01A). A scheme of the experimental configuration together with the design of the cell and acquired diffraction patterns can be seen in Fig. 1.

The Co<sub>3</sub>O<sub>4</sub> NPs were reduced by exposing the catalyst to a pure hydrogen flow of 2.5 ml/min at ambient pressure, while the temperature was increased from 25 °C to 400 °C at a heating rate of 3 °C/min. The temperature was held at 400 °C for 4 hours before returning to ambient conditions. For the second TPR-XRPD experiment a temperature range from 100 to 700 °C was applied.

The diffraction patterns obtained during the course of reduction, clearly demonstrate that phase transformations occur during the process. Initially, Co<sub>3</sub>O<sub>4</sub> NPs of spinel structure, consisting of a mixture of Co<sup>3+</sup> in octahedral environment (O<sub>h</sub>) and Co<sup>2+</sup> in tetrahedrally coordinated positions (T<sub>d</sub>), are transformed to CoO. CoO has octahedrally coordinated Co<sup>2+</sup> cations packed in a face-centred cubic (rock salt type) crystal structure. During reduction oxygen is removed from the lattice by generating H<sub>2</sub>O<sub>(g)</sub>.



**Fig. 2** Normalised X-ray diffraction patterns from 250 °C to the reductions end, obtained by the subtraction of the diffractogram with CoO at maximum intensity (at 250 °C), showing the formation of metallic Co (top half) and disappearance of CoO (bottom half), (left). Variation in the lattice constant for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoO as a function of reduction temperature (right),  $\lambda = 0.7042$  Å.

Ultimately, metallic Co forms in a convoluted nature containing contributions from both hexagonal closed packed (hcp) and face-centred cubic (fcc) Co, with the second being more pronounced (Fig. 1). By subtracting the pattern with maximum intensity of the intermediate CoO phase (obtained at 250 °C) from the following patterns the formation of metallic Co can be clearly visualised (Fig. 2). With exception of the (100) reflection of hcp Co, that cannot be seen due to overlap with the (200) reflection of CoO, the peaks demonstrate existence of both cubic and hexagonal phases of metallic Co. It also becomes apparent that the phases are growing simultaneously, similarly to the reduction of carbon supported Co NPs<sup>23</sup>.

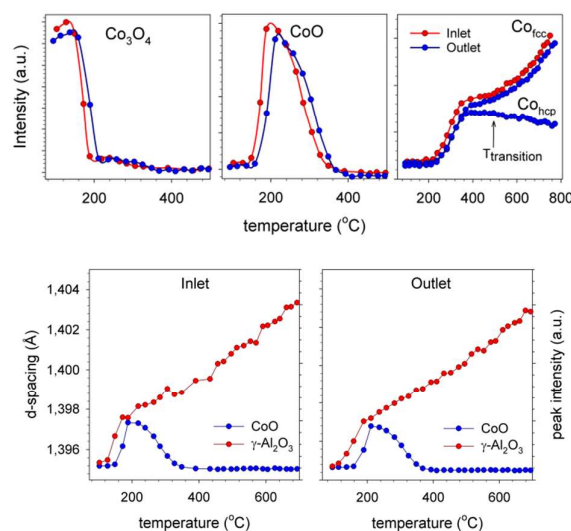
At the examined temperature range and with a linear temperature ramp of 3 °C/min, a linear thermal expansion of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support is expected<sup>24</sup>. Nevertheless, a sudden increase in the unit cell dimensions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is observed at temperatures exceeding 190 °C. This deviation from linearity coincides with the formation of CoO (Fig. 2). The non-linear behaviour suggests that partial incorporation of Co<sup>2+</sup> ions into the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> lattice occurs. Extrapolation of the linear part at 270 °C and its comparison with the observed value at the same temperature reveals a 0.064 % increase in the lattice constant and an expansion of the unit cell volume equal to 0.19 % (Fig. 2). Line broadening analysis on the (440) reflection of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (not shown here) supports the above observation. Peak broadening occurs simultaneously with the formation of the CoO phase, suggesting that microstrain is induced by Co diffusion and leads to cell expansion or the formation of a new phase. The transition from the amorphous to the crystalline CoO has an initial unit cell with a lattice constant of 4.243 Å. As the CoO crystallites grow, a significant expansion of the cell can be seen that cannot be merely explained by thermal effects. At about 225 °C the lattice parameter is stabilizing and further characterized primarily by the thermal expansion of CoO (Fig. 2).

The magnitude of the lattice expansion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> cannot be explained by the simplified approach of cobalt NPs dispersed on the surface of the support. By taking into account the concentration of Co (20 wt%), the diameter of CoO crystallites (8.6 nm, from scherrer equation) and with the assumption of hemispherical particles, the interface of the CoO NPs and support is estimated to be less than 2.5 % of the

total available surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Considering the small number of lattice entry points of Co<sup>2+</sup> due to the minor interfacial area between CoO and the support it seems unlikely that the significant expansion detected here originates only from the Co-support interphase. In addition, the phenomenon is initiated at low temperatures early in the reduction process, a fact that further disputes the simplified model of scattered NPs. Reduction kinetics are governed by the diffusion of H and O through the particle from the outer surface. Therefore, transformations at the Co-support interphase are expected to happen later in the course of reduction process.

A more appropriate hypothesis involves, in addition to the dispersed Co NPs on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, the existence of a Co containing amorphous layer covering a major part of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. It has been reported that the amorphous layer is created during catalyst preparation and Co loading, calcination temperature, and preparation method may play a role on its chemical nature<sup>25</sup>. Furthermore, It is well established that catalysts with low loading are inactive in CO hydrogenation reaction, suggesting a strong interaction of the Co clusters with the support<sup>26</sup>. It has also been reported that during aqueous impregnation  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may partially dissolve and assist in co-precipitation with Co forming hydrotalcite-like structures<sup>27,28</sup>. Recent theoretical calculations support the creation of strong epitaxial interactions that lead to a Co(OH)<sub>2</sub> precipitate at high Co coverages<sup>29</sup> during catalyst preparation. Depending on the conditions of preparation procedure the amorphous precipitate may form CoAl<sub>2</sub>O<sub>4</sub>-like layered structures or other oxides, with Co at O<sub>h</sub> or T<sub>d</sub> configurations covering a major part of the support surface area<sup>25,30</sup>. In the context of the present findings the amorphous layer that contains positively charged Co ions after calcination, appears to interact with the bulk of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under H<sub>2</sub> environment at moderate temperatures. This interaction occurs at temperatures near the transition of Co<sup>3+</sup> to Co<sup>2+</sup> resulting in a significant expansion of the unit cell of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Presumably one would suggest that the Co containing layer after calcination has a high concentration of cations in trivalent state (Co<sup>3+</sup>). However, this contradicts with previous X-ray photoelectron spectroscopy<sup>30</sup> and Mössbauer emission<sup>25</sup> studies at similar calcination temperatures showed that the amorphous layer is rich in Co<sup>2+</sup>. Therefore, the exact chemical nature of the layer and the H<sub>2</sub> induced transformation that leads to the interaction of Co and the support still remains unclear. Furthermore, no bulk CoAl<sub>2</sub>O<sub>4</sub> was detected suggesting that the formed domains lack long-range order.

It is therefore suggested that diffusion of Co<sup>2+</sup> cations takes place at sub-surface layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and grain boundaries of the 10 nm crystallites that are binned together, forming the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous structure. Apparently, deeper diffusion of individual Co atoms into the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bulk also occurs. The interfacial area between Co NPs and the support may also provide a minor contribution to the observed expansion. Solid-state reactions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with transition metal cations of low valence have previously been identified to proceed through counter-diffusion of metal in divalent state and Al<sup>3+</sup> ions, yet at much higher temperatures and O<sub>2</sub> rich environments<sup>31</sup>.



**Fig. 3** Peak intensities of selected reflections for Co<sub>3</sub>O<sub>4</sub> (220), CoO (220), hcp-Co (101) and fcc-Co (200) in the inlet and the outlet of the reactor (top). The d-spacing of (440) reflection of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> plotted together with the intensity of CoO (bottom),  $\lambda = 0.5052$  Å.

Here, under H<sub>2</sub> environment and although the examined temperatures are moderate, penetration of Co<sup>2+</sup> cations is observed and detected as expansion in the unit cell of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. One could also speculate that entry points are Al<sup>3+</sup> O<sub>h</sub> vacancies explaining the fact that XANES cannot probe and distinguish the structure from the Co<sup>2+</sup> O<sub>h</sub> cations in the CoO phase.

For the TPR-XRPD experiment (BM01B) the reactor profile was analysed during catalyst reduction. For this reason the inlet and outlet were probed sequentially. The results are presented in Fig. 3. It becomes apparent from the steep increase at ca. 160 °C in the d-spacing for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that diffusion of Co<sup>2+</sup> cations occurs in the entire length of the reactor during the reduction process. It is also observed that the phenomenon is irreversible, even at temperatures as high as 700 °C. Besides, the reactor outlet exhibits a delay of the reduction process. The delay concerns both reduction steps. The CoO intermediate at the outlet reaches its highest intensity approximately 20 °C higher than the observed maximum for the inlet. The evolution of both fcc and hcp Co phases are equally delayed. Furthermore, the phase transition of metallic Co from the hcp to the fcc structure, although not well resolved in the current dataset, appears to occur at temperatures higher than 450 °C, a temperature higher than the transition of bulk Co or Co NPs supported on the less interacting carbon structures<sup>23</sup>. This delay in transition temperature could be linked to the developed metal-support interactions.

Here it should be noted that in contrast to the former experiment, where a thermocouple was nearly touching the outer surface of the quartz capillary reactor, in the particular experiment the temperature is extracted from the probed area with an internal standard; this explains the observed temperature difference of the two experiments. More specifically the (400) reflection of the hexagonal boron nitride

(h-BN) was followed in the diffraction patterns and temperature was calculated by using the thermal expansion coefficient of the c-axis<sup>14</sup>.

$$c = 6.6515 (\text{\AA}) + 2.74 \cdot 10^{-4} T (\text{\AA} / \text{K}) \quad (3)$$

Since the process is temperature normalized the only difference between the reactor ends is their chemical environment. In particular, the ratio of partial pressures of H<sub>2</sub> (pH<sub>2</sub>) and the *in situ* generated water (pH<sub>2</sub>O) is changing throughout the length of the reactor. Although the applied gas hourly space velocities are high and consequently the pH<sub>2</sub>:pH<sub>2</sub>O ratio is not expected to change dramatically, it is evident that even minor changes have an effect on the reduction process. The results are in agreement with previous model TPR studies on Ru/Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts demonstrating that even with an inlet pH<sub>2</sub>:pH<sub>2</sub>O ratio of 8, an approximate delay of 5 °C and 65 °C in the temperatures of the maximum H<sub>2</sub> consumption rates was observed<sup>8</sup>.

The loss of active metal due to strong interaction with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has been a topic of scientific interest for many years. It has been proposed that formation of mixed cobalt-support oxide phases take place during calcination, reduction and at reaction condition. Although the high temperature chemistry of this solid-state reaction resulting in a rich in Co<sup>2+</sup> T<sub>d</sub> crystalline CoAl<sub>2</sub>O<sub>4</sub> spinel is reasonably known, the formation of the non-stoichiometric compounds that lack long range order under H<sub>2</sub> conditions is difficult to detect. Here we take advantage of the global information that is obtained from synchrotron X-ray diffraction patterns and contains both the changes in the state of the catalytically active compound as well as in the support. The expansion of the unit cell of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support is an indirect evidence of partial diffusion of Co<sup>2+</sup> that takes place during the first step of the reduction process coinciding with the formation of Co<sup>2+</sup> O<sub>h</sub>. The Co-support interaction has been captured *in situ*. The observation supports the hypothesis of the existence of an amorphous Co containing layer covering major surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It has also been demonstrated that the overall reduction process is inhibited by H<sub>2</sub>O<sub>(g)</sub> generated *in situ* during the process.

The present findings provide a better understanding of the nature and possible influence of the Co-support mixed compounds that are formed during H<sub>2</sub> activation of a Re/Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined catalyst. Such synchrotron experiments can also aid investigations on catalyst preparation procedures that are aiming at minimizing Co losses. Ultimately, optimization of reduction kinetics for the formation of a catalyst with balance between performance (high degree of reduction) and better stability (sintering prevention, due to increased metal-support interactions) can be investigated further in light of the assessed onset of Co-support interactions.

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