

# Characterizing the Processes of Calcination and Reduction in the Preparation of Supported Cobalt Catalysts.

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## 1. Introduction

Although it was initially thought that the support played no role in Fischer-Tropsch chemistry, it has been shown [1] that in fact it has a major role in influencing the overall hydrocarbon production rate. Indeed it is believed that variation of the support can have a much more significant impact on cobalt dispersion, and hence catalytic activity, than the overall cobalt loading [2]. A variety of supports are used to prepare cobalt catalysts depending on the properties required; however the bulk of the literature is concerned with high surface area oxide supports, in particular silica, alumina and titania supported cobalt catalysts. The use of supports such as zeolites [3] and carbon [4] have also been reported in the literature. There have been many studies into the interaction between the support and the cobalt species. This is due to the fact that the interaction between cobalt species and support can affect the response of cobalt to reduction as well as dispersion [5]. The choice of the oxide support largely determines the number of active cobalt metal sites stabilized after reduction as well as the percentage of cobalt oxides that can be reduced to cobalt metal. This is due to a difference in the Co-support oxide interaction. A strong Co-support oxide interaction, as occurs in the case of alumina and titania, stabilises small clusters therefore favouring high dispersion, but at the same time decreases their reducibility. In contrast, a much weaker interaction leading to higher reducibility occurs for the silica supported cobalt catalysts. In this case the cobalt particles tend to appear as large clusters on the support surface. This however, results in a relatively low cobalt dispersion [6-8]. It has also been shown that the pore structure of the supports has a significant effect on the cobalt particles produced. Storsæter *et al.* [7] using a variety of techniques, to investigate the effect the support had on the size, appearance and shape of the cobalt particles. They reported that the cobalt oxide crystallite size was found to increase with increasing pore diameter of support. Similar effects have been observed for cobalt catalysts supported on silicas with increasing mean pore diameters

[6]. Despite the previous research in this area, opportunities remain in gaining detailed physiochemical insights into the cobalt-support interfacial chemistry. This is of paramount importance in giving us a profound knowledge of the catalyst material which is necessary for improvement of current or design of totally new catalyst systems. In this study we have used a range of techniques to study the conversion of cobalt nitrate supported on silica and alumina into metal. We have examined both calcination and reduction stages.

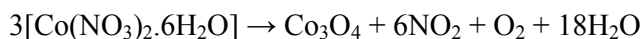
## 2. Experimental

Catalysts containing 20 wt% cobalt were prepared by impregnation of silica (Degussa Aerosil 200) and alumina (Engelhard Al-3992) with aqueous solutions of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . These are referred to as CoNS and CoNA respectively. Prior to impregnation, the supports were dried at 373 K overnight. To ensure uniform metal dispersion on the support, the precursor salt was dissolved in a volume of water equal to the support pore volume. After impregnation, water was slowly removed at 353 K by a rotary evaporator before the catalyst was dried further in an oven at 373 K overnight. The catalysts were characterised using *in situ* hot stage XRD with a controlled gas environment using a Siemens D5000 X-ray diffractometer (40kV, 40mA) using monochromatic  $\text{CuK}_\alpha$  x-ray source (1.5418Å). The scanning range used was  $15^\circ < 2\theta < 75^\circ$  with a step size of  $0.02^\circ$  and counting time of 2 secs per step. The samples were heated at  $12 \text{ deg.K min}^{-1}$  and scans taken at 303 K, 373 K and then at 100 K increments thereafter to 1173 K. At each stage the sample was held for 15 minutes at the desired temperature before the scan was taken, with each scan lasting 100 minutes. Each catalyst was subjected to heating in three gas environments, argon, oxygen and hydrogen.

Thermo-gravimetric analysis (TGA) was performed on all catalysts using a combined TGA/DSC SDT Q600 thermal analyser coupled to an ESS mass spectrometer for evolved gas analysis. Fresh sample was heated from 303 K to 1273 K using a heating ramp of  $10 \text{ deg.K min}^{-1}$ . Again for each sample this temperature profile was employed in three gas environments, argon, oxygen and hydrogen at a flow rate of  $100 \text{ ml min}^{-1}$ . For mass spectrometric analysis, mass fragments with  $m/z = 2, 14, 16, 17, 18, 28, 30, 32, 40, 44$  and 46 (amu) were followed. The sample loading was typically 10-15mg.

### 3. Results and discussion

The decomposition of cobalt nitrate in an inert gas flow is reported to occur as detailed below [9], with the release of nitrogen dioxide, water and oxygen:



In contrast however we observed the evolution of nitrogen monoxide as well as water, oxygen and nitrogen dioxide during the decomposition of cobalt nitrate in argon. Suggesting that the following equation may be a more accurate representation:  $3[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}] \rightarrow \text{Co}_3\text{O}_4 + 6\text{NO} + 18\text{H}_2\text{O} + 4\text{O}_2$ . However, given that a small amount of nitrogen dioxide is also produced, it is possible that decomposition is represented by both of these equations and may occur simultaneously. This decomposition was complete by 573 K. From the calculated weight loss, the decomposition was found to proceed to  $\text{Co}_3\text{O}_4$  by 673K. Decomposition of the spinel oxide to the thermodynamically more stable divalent cobalt oxide with the release of oxygen was also observed at 1107 K.

Decomposition studies in argon of cobalt nitrate impregnated onto silica and alumina were undertaken. The nitrate decomposition for the CoNS is similar to that of the bulk cobalt nitrate, in that the double event still occurs except that the maximum temperatures of the two nitrate decomposition events are reduced by around 50 deg.K. This indicates that the silica has a mild catalysing effect on the decomposition. However, the temperature at which the decomposition is completed was higher than that found with the unsupported compound. Like the cobalt nitrate decomposition, there is also a weight loss at the slightly lower temperature of 1098 K for the CoNS, and this is again accompanied by the evolution of water. There are two possibilities for this event. It may be due to the break down of the spinel oxide to  $\text{CoO}$ , as seen with the bulk nitrate around the same temperature. However it also may be attributed to the interaction of the Co surface species with the support. It should be stressed that these two options are not mutually exclusive and a combination of both cannot be discounted. Unfortunately due to insufficient material to allow measurements to be performed there is no XRD data to confirm species present above these temperatures. In contrast, the alumina support stabilised a portion of the cobalt nitrate, causing one of the decomposition events to occur 75 deg.K higher in temperature (Figure 1). From the XRD data, it can be seen that, after decomposition, the cobalt is present as the spinel oxide on the support. Therefore although the cobalt used to prepare the catalyst

was in the trivalent form, after decomposition it is present as both trivalent and divalent states in the form of  $\text{Co}_3\text{O}_4$ . At 873 K, both  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  as well as metallic cobalt are present on the catalyst surface. By 973 K only metallic cobalt and cobalt oxide spinel are detected. It is not clear what the redox process is that converts

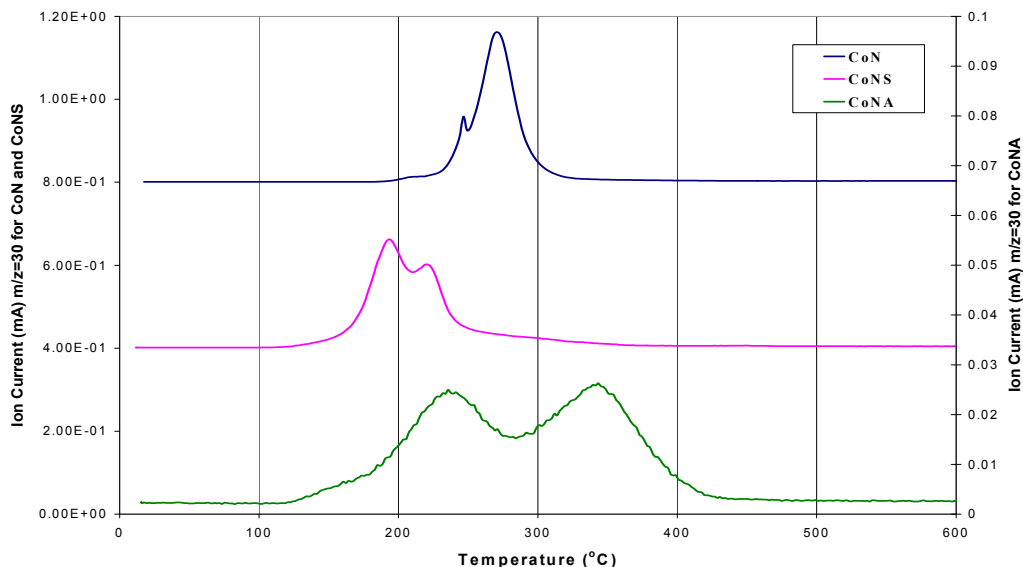


Figure 1. Mass spectrometric data for Nitrogen monoxide evolved for CoN, CoNS and CoNA

cobalt oxide to metallic cobalt given that it is run in an inert atmosphere. Similar effects were noticed when decomposition was followed under oxidative conditions, revealing that to generate a similar species on both silica and alumina the calcination temperature needs to change by 125 deg.K.

Insight into the reduction process was provided by characterisation studies of the supported cobalt catalysts in a hydrogen atmosphere. Similar to the effect observed with the decomposition in argon and oxygen, the silica support caused reduction to occur at a lower temperature. However, this was clearly a complex process, with multiple endothermic and exothermic events. Decomposition occurs as three overlapping events at temperatures much lower than those observed for the double decomposition event for the cobalt nitrate.  $\text{NO}_2$  was only detected for two of the three nitrate decomposition events. Several peaks ranging from 556 K to 1085 K accompanied by the uptake of hydrogen, corresponding to the evolution of water may be attributed to the reduction of the cobalt oxide species. These events are similar to that of the unsupported cobalt nitrate in that the reduction still occurs as three events, however, the maximum of these peaks is approximately 100 deg.K lower in

temperature. This suggests that similar to the effect seen with the nitrate decomposition in argon and oxygen, the silica support is causing the reduction to occur at a lower temperature. It is possible that this effect could be related to the dispersion of the cobalt species on the silica support compared with the bulk metal nitrate. This will increase the surface area of the cobalt complex, making more surface sites available and therefore causing reduction to occur more rapidly. Unfortunately, due to the poor separation of peaks and lack of XRD data, attribution of reduction events to specific reduction steps is not possible.

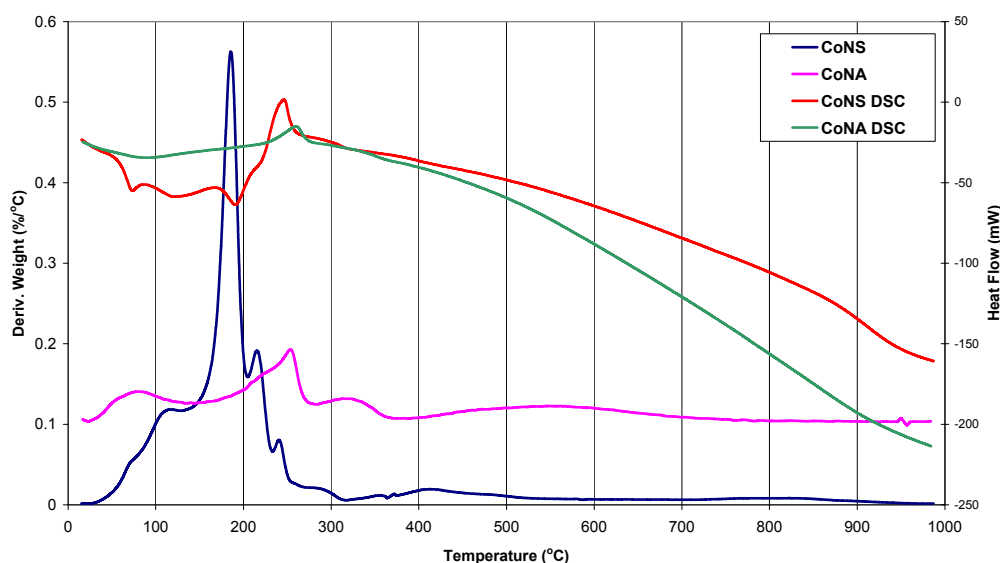
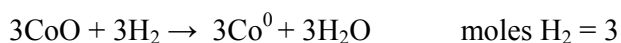


Figure 1. TGA/DSC of Cobalt Nitrate of silica and alumina.

For the alumina supported system the reduction was a far simpler process with only a single exothermic event below 573 K (Figure 2). Decomposition of the nitrate occurs as a single event at a temperature much lower than the two decomposition events of unsupported cobalt nitrate. Therefore, in contrast to the treatments in argon and oxygen, where the alumina stabilized the cobalt nitrate, the support decreases the temperature of decomposition. Two reduction peaks corresponding to the uptake of hydrogen and evolution of water are observed at 595 K and 829 K. From previous studies these two events are most likely to represent a two-step reduction of  $\text{Co}_3\text{O}_4$  to metallic cobalt. In quantifying these results, it is known that there is a direct relationship between the amount of hydrogen consumed and the amount of metal contained in the sample. Using this, it is possible to determine the oxidation state of

the metal in the reaction. Integration of the two peak areas for the uptake of hydrogen gave a ratio of ~1:3 which could then be interpreted by the following equations:



It can be seen that a two-step reduction fits in well with the hydrogen consumption ratio for the CoNA catalyst in this study. This confirms that the reduction of  $\text{Co}_3\text{O}_4$  proceeds in a stepwise manner possibly involving complete conversion to CoO prior to subsequent reduction to metallic cobalt. The first peak attributed to the reduction of the trivalent Co to the divalent Co, and the second larger peak being the reduction of CoO to metallic Co.

The XRD pattern of CoNA at 573 K, after the nitrate decomposition, shows the presence of  $\text{Co}_3\text{O}_4$  and CoO. It is thought that the  $\text{Co}_3\text{O}_4$  is the product of the nitrate decomposition and since the first reduction peak begins before 573 K, that the CoO present is a consequence of the reduction of the spinel oxide. From the XRD pattern at 673 K,  $\text{Co}_3\text{O}_4$  and CoO species are observed. At this temperature, the second reduction event has begun, suggesting that not all the  $\text{Co}_3\text{O}_4$  is reduced to CoO before the start of the second step of reduction. From 773-1173 K, the presence of metallic cobalt is detected, however, some  $\text{Co}_3\text{O}_4$  still remains.

It has been shown that by using a combination of TGA-DSC coupled to MS and hot-stage XRD in different gas environments, it is possible to characterise the thermal, electronic and structural changes occurring during calcination and reduction of supported cobalt catalysts. Using this methodology it is possible to optimise the preparation and subsequent processing to deliver a catalyst with optimal dispersion and reduction properties.

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