Choosing a suitable support for Co$_3$O$_4$ as an NH$_3$ oxidation catalyst†

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Co$_3$O$_4$ as an NH$_3$-oxidation catalyst may transform reversibly to CoO under reaction conditions, even in the presence of excess oxygen. The use of alumina may then result in the formation of cobalt aluminate rendering the catalyst inactive. The formation of cobalt aluminate can be avoided by using ZnAl$_2$O$_4$ as a support.

Introduction

Ammonia oxidation yielding NO/NO$_2$ forms the core of the nitric acid production plant. This process typically uses a platinum–rhodium gauze as a catalyst for ammonia oxidation, since it is active and highly selective. However, the lifetime of the platinum gauze is rather short (up to 12 months for operation at atmospheric pressure, and the lifetime decreases with increasing reaction pressure). Thus a variety of transition metal oxides for the oxidation of ammonia yielding nitrogen oxides have been studied. Co$_3$O$_4$ is utilized in some nitric acid plants and seems to have the added advantage of lower yield of the undesirable reaction pressure).2 Thus a variety of transition metal oxides for the oxidation of ammonia yielding nitrogen oxides have been studied.3 Co$_3$O$_4$ is utilized in some nitric acid plants and seems to have the added advantage of lower yield of the undesirable greenhouse gas N$_2$O and longer catalyst lifetime.

Ammonia oxidation is thought to proceed via a Mars–van Krevelen mechanism utilizing lattice oxygen.5,6 Hence, the catalytically active phase in Co$_3$O$_4$-catalyzed ammonia oxidation may be reduced to CoO, and this phase transformation may result in catalyst deactivation. The more stable perovskite LaCoO$_3$ has been investigated as an alternative. This may however result in a lower intrinsic catalytic activity, due to its resistance to the release of lattice oxygen. Another alternative would be to adapt the reaction conditions (oxygen partial pressure/temperature/crystallite size of Co$_3$O$_4$ – vide verde) to minimize the reduction of Co$_3$O$_4$ under the operating conditions.

The removal of lattice oxygen and re-oxidation are crucial steps in the Mars–van Krevelen mechanism.5,6 The completion of the catalytic cycle requires the oxidation of CoO, viz. 3CoO + $\frac{1}{2}$O$_2$ $\rightarrow$ Co$_3$O$_4$. The thermodynamic feasibility of this process is dependent on temperature, partial pressure of oxygen and the crystallite size of Co$_3$O$_4$ in the starting material (due to the difference in the surface energy contribution) and in the absence of sintering the thermodynamic feasibility of the re-oxidation process can be expressed as:

$$RT \ln \left( \frac{\rho_{CoO}}{\rho_{Co3O4}} \right) = \frac{\mu_{Co3O4}^0 - 3\mu_{CoO}^0 - \frac{1}{2}\mu_{O2}^0}{d_{Co3O4}^0} \left( 1 - \frac{\gamma_{CoO}}{\gamma_{Co3O4}} \left( \frac{3\rho_{Co3O4}}{\rho_{CoO}} \right) \right)$$

The surface energy for CoO is experimentally determined to be 1.96 J m$^{-2}$ (in reasonable agreement with the estimated surface energy using DFT+U$^{11}$). The reported experimental value for the surface energy of CoO$^{12}$ is 2.8 J m$^{-2}$. However, the theoretical values for the surface energy of CoO are lower than the surface energy of Co$_3$O$_4$, viz. 0.46 J m$^{-2}$ based on a classical model$^9$ and 0.79 J m$^{-2}$ using DFT+U for CoO calculated as the anti-ferromagnetic phase AFM$^{13}$. A higher surface energy of CoO than that of Co$_3$O$_4$ implies that the reduction of Co$_3$O$_4$ will be thermodynamically impeded for small crystallites, i.e. the transition temperature for the transformation of Co$_3$O$_4$ to CoO will increase with decreasing crystallite size of Co$_3$O$_4$. However, the auto-reduction of supported Co$_3$O$_4$ shows a lowering in the transition temperature in comparison to unsupported Co$_3$O$_4$ implying a lower surface energy of CoO in comparison to Co$_3$O$_4$. Fig. 1 shows the predicted dependency of the predicted transition of CoO to Co$_3$O$_4$ as a function of the reaction temperature and oxygen partial pressure. The re-oxidation of CoO is expected to be thermodynamically more feasible at low temperatures, high oxygen partial pressures and with large crystallites of Co$_3$O$_4$. However, high temperatures are required for ammonia oxidation to minimize N$_2$O formation.$^{15}$ Hence, an operating window for Co$_3$O$_4$ catalyzed NH$_3$ oxidation can be defined in terms of temperature, pressure and crystallite size of Co$_3$O$_4$. 

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In industrial operation, Co₃O₄ as an ammonia oxidation catalyst is typically used in the form of catalyst pellets resulting in severe mass transfer limitations.²⁵ The use of smaller pellets in conjunction with the high linear velocity typically employed in the ammonia oxidation would result in a high pressure drop. Hence, it is desirable to incorporate the catalytically active component in a structured reactor (e.g. monolith).⁸,¹⁶ The strong hydrothermal conditions prevalent during ammonia oxidation may result in the formation of the Co-support compound.¹⁷,¹⁸

The formation of such compounds would represent a thermodynamic sink. In this communication, we evaluate the activity of Co₃O₄ supported on alumina and zinc aluminate focusing on the possible formation of Co-support compounds. Alumina as a support may result in the formation of CoAl₂O₄ if Co₃O₄ is reduced to Co(II)O. However, the formation of CoAl₂O₄ is thermodynamically not feasible from Co(II)O and ZnAl₂O₄.

Experimental

γ-Al₂O₃ (Degussa; dₚellet = 3 mm; Sₐ BET = 225 m² g⁻¹; Vₚore = 0.63 cm³ g⁻¹; dₚore = 9 nm) and zinc aluminate were used as support materials. Zinc aluminate was prepared by co-precipitation.¹⁹

The resulting product was pressed into pellets with an average size of 3 mm. An industrial, unsupported Co₃O₄ catalyst (dₚellet = 3.54 g cm⁻³; Sₐ BET = 0.3 m² g⁻¹; Vₚore = 0.12 cm³ g⁻¹) containing an irregular distribution of Co₃O₄ crystallites ranging from 200 nm to 5 mm, with the smaller crystallites attached to the large crystallites, was used for comparison.

The support pellets were impregnated with a solution containing Co(NO₃)₂·6H₂O in deionised water.²⁰ The catalyst precursor was aged at room temperature for 20 minutes and dried at 120 °C for 2 hours. Subsequently, the dried precursor was calcined in air (180 ml (STP) min⁻¹) at 350 °C for 2 hours (heating rate: 5 °C min⁻¹). Catalyst pellets were crushed to a size between 125 and 212 μm for the activity test.

The Co₃O₄ loading was verified using AAS-ICP. The BET surface area and micro-pore volume was determined using N₂ adsorption–desorption at 77 K using a Micromeritics Tristar 3000. The phase composition on the catalyst and the average crystallite size of the various phases in the catalyst pellet were determined using X-ray diffraction (Bruker D8 Advance laboratory X-ray diffractometer; source Co-Kα,1; voltage: 35 kV; current: 40 mA) equipped with a position sensitive detector (VANTEC-2000, Bruker AXS). The obtained diffraction patterns were fitted using Rietveld refinement as employed in TOPAS 4.2 (Bruker AXS), such that the weight profile factor (Rwp) was <10 and the Bragg factor (Rbragg) was <5.

The catalytic activity of the catalysts in the ammonia oxidation was determined in a quartz, fixed bed reactor (d₁inner = 9 mm; douter = 12 mm, l = 410 mm) with an isothermal zone of 20 mm (AT < 5 °C). The catalyst (dₚ = 125–212 μm; m = 3 mg) was diluted with ca. 300 mg silicon carbide (dₚ < 75 μm) and loaded into the isothermal zone. The high degree of dilution (mₐlumina/mcatalyst = 100) may result in an inhomogeneous distribution of the catalyst and bypassing of the reactants,²¹ however the use of fines as a diluent mitigates this effect, due to extensive radial mixing. A bed of silicon carbide (dₚ = 425–600 μm; l = 125 mm) served as a pre-heating zone. A quartz thermo-well (douter = 4 mm) was inserted into the catalyst bed to monitor the reaction temperature. A pre-mixed gas containing 7.4% NH₃, 19.4% O₂ and the balance He was passed over the catalyst bed at a volumetric flow rate of 100 ml (NTP) min⁻¹. Ammonia oxidation was performed at atmospheric pressure in the temperature range 450–800 °C. The reactor temperature was raised to 450 °C and after 30 minutes the ammonia conversion was determined by bubbling the effluent gas for 20 minutes through deionised water ensuring complete absorption of ammonia. Subsequently, the reactor temperature was raised to investigate the activity at higher temperatures, viz. 580 and 740 °C. In order to test the reversibility of the observed deactivation the reactor temperature was subsequently decreased to 580 °C and 450 °C. The concentration of ammonia in the ammonia trap was determined at each reaction temperature spectro-photometrically using the Nessler method²² (Jenway 6405 UV/Vis spectrometer; λ = 450 nm). The repeatability of the experiments was good and deviations in the ammonia conversion on repeat runs were less than 2%.

The small amount of catalyst used to evaluate the activity does not allow for a post-mortem analysis of the spent catalyst. Hence, the catalyst was used in the form of pellets to enable the characterization of the ‘spent’ catalyst. The use of pellets introduces mass transfer limitations,²³ which should be kept in mind when interpreting the data. The catalyst pellets (300 mg) were loaded in the isothermal zone of the reactor. The void spaces were filled with ca. 300 mg silicon carbide (dₚ < 75 μm) to ensure sufficient radial mixing.

Results and discussion

The unsupported Co₃O₄ as a powder shows the normal increase in the ammonia conversion with increasing temperature (see Fig. 2). A further increase in the ammonia conversion is obtained upon the subsequent decrease in temperature. In order to explore this phenomenon better an unsupported Co₃O₄ pellet was loaded (which showed significant internal mass transfer limitations).²⁵ The ammonia conversion increases with increasing temperature up to 640 °C, after which a decrease in the activity is observed. XRD analysis on the catalyst pellet after exposure to a reaction
The impregnation of cobalt nitrate on alumina (a mixture of γ-Al₂O₃, ca. 80 wt% and θ-Al₂O₃) resulted in small Co₃O₄ crystallites with an average size of ca. 8.4 nm (see Table 2). The ammonia conversion decreases with increasing temperature even going from 450 to 580 °C. The NH₃ conversion at a reaction temperature of 740 °C was equal to the ammonia conversion in the absence of the catalyst. Lowering the reaction temperature did not restore the catalyst activity.

The spent catalyst, both in pellet and in powder form, was dark blue in colour indicating the presence of cobalt aluminate in the sample. The formation of cobalt aluminate cannot be confirmed beyond doubt from the XRD analysis of the spent catalyst due to strongly overlapping diffraction peaks. Tentatively, ca. 10% of cobalt is present as XRD-visible cobalt aluminate. Furthermore, ca. 20% of cobalt has been transformed into XRD-invisible cobalt (possibly amorphous cobalt aluminate).

The formation of cobalt aluminate requires the presence of CoO₁₇, which may react with alumina under hydrothermal conditions yielding cobalt aluminate. According to our thermodynamic analysis, neglecting the effect of crystallite size (which may become substantial in this size range²⁴), Co₃O₄ crystallites with a diameter less than 6.0 nm may be stable as CoO at temperatures as low as 560 °C at a partial pressure of O₂ of 0.1 bar. Crystallites with this diameter may be present in Co₃O₄/Al₂O₃, since the initial average crystallite diameter of Co₃O₄ was ca. 5.9 nm. The disappearance of small crystallites of Co₃O₄ from the crystallite size distribution is consistent with the slight increase in the average Co₃O₄ crystallite size observed.

After exposure to high temperature ammonia oxidation conditions, the average crystallite size of Co₃O₄ in Co₃O₄/Al₂O₃ is slightly larger than in the fresh catalyst consistent with the conversion of small Co₃O₄ crystallites to Co(II)O.

The rapid diffusion of divalent cobalt into the alumina phase as demonstrated for γ-Al₂O₃ may lead to a cobalt-poor aluminate, i.e. formation of XRD-amorphous cobalt aluminate with cobalt to aluminum ratio of less than 0.5. The location of the cobalt aluminate phase is currently unknown, but it may be associated with the cobalt oxide phase as suggested for the cobalt silicate formation, since the reaction will also take place at the interface between CoO and alumina. This is further substantiated
by the lack of catalytic activity of Co₃O₄/Al₂O₃ after being exposed to a high reaction temperature, since the mere reduction in the surface area of Co₃O₄ would only account for a decrease in the activity by 60%. Hence, it is plausible that cobalt aluminate type of structures are covering the surface of Co₃O₄.

The synthesized zinc aluminate has relatively large crystallites of ZnAl₂O₄ and thus a relatively small surface area. The average pore radius in this support is estimated to be ca. 26 nm. The synthesized Co₃O₄/ZnAl₂O₄ contains relatively large Co₃O₄ crystallites with an average size of ca. 29 nm. It should however be noted that ca. 35% of cobalt seems to be XRD-invisible, which may be present as a highly dispersed phase on the ZnAl₂O₄ surface.

The ammonia conversion obtained over the Co₃O₄/ZnAl₂O₄ catalyst increases with increasing reaction temperature. Upon lowering the reaction temperature back to 450 °C, a higher conversion is obtained than the one originally obtained. Using Co₃O₄/ZnAl₂O₄ as a pellet introduced mass transfer limitations, and thus a lower activity than observed when using the catalyst in powder form. Upon increasing the temperature from 570 °C to 740 °C a decrease in the conversion of ammonia is observed. It is plausible that the deactivation is due to reduction of small crystallites of Co₃O₄ in the catalyst to CoO. The thermodynamic calculations indicate that Co₃O₄ crystallites with a diameter less than 18 nm are susceptible to reduction under the conditions applied. Upon decreasing the reaction temperature a higher activity is obtained showing that the observed deactivation is taking place as well.

The amount of XRD-invisible cobalt in the catalyst pellet is drastically reduced with ca. 10% of the cobalt remaining XRD-invisible. This is accompanied by an increase in the average crystallite size of Co₃O₄. The increase in the crystallite size can partially be explained by the reduction in the amount of XRD-invisible cobalt. Well-dispersed cobalt may migrate resulting in crystal growth. However, the change in the average crystallite size cannot solely be explained by the reduction in the amount of XRD-invisible cobalt indicating that some sintering is taking place as well.

The use of large crystallites of Co₃O₄ on a support would allow operation at a higher reaction temperature without the formation of CoO. High temperature may lead to a reversible type of deactivation (as observed for unsupported Co₃O₄ and pellets of Co₃O₄/ZnAl₂O₄ – see Fig. 1), since the formation of cobalt aluminate from CoO and zinc aluminate is thermodynamically not allowed, even for nano-sized CoO crystallites if the surface energy of CoO is smaller than the surface energy of ZnO ($7_{ZnO}$ = 1.42 J m⁻²) assuming that the exchange reaction is not associated with simultaneous crystallite growth. The lack of incorporation of cobalt into the support makes zinc aluminate an ideal material as a washcoat to be applied in structured reactors or on foams, on which nano-crystallites of Co₃O₄ can be deposited.

The formation of cobalt aluminate is intrinsically linked to the ability to form CoO under reaction conditions. The thermodynamic driving force for the formation of this phase can be linked to the crystallite size of the catalytically active phase. At this stage it is not clear whether the reduction or the re-oxidation is the size dependent step. This can only be evaluated using catalysts with well-defined crystallite size distributions. Supporting these well-defined crystallites on the selected support materials would allow further insights into the deactivation behavior of this type of catalysts.

**Conclusions**

Co₃O₄-containing ammonia oxidation catalysts may undergo a reduction to CoO in the presence of oxygen at high temperature. Nano-sized Co₃O₄ crystallites are more susceptible to the reduction reaction in the presence of oxygen, if the surface energy of CoO is lower than the surface energy of Co₃O₄. The reduction of Co₃O₄ represents a reversible deactivation, since lowering the reaction temperature will result in the re-oxidation of CoO. However, CoO can further react under the hydrothermal conditions of ammonia oxidation with support materials, such as alumina, yielding cobalt aluminate, which may adhere to cobalt oxide reducing the catalytically active surface area accessible to the reactants. The reaction between CoO and ZnAl₂O₄ is thermodynamically not allowed, making zinc aluminate an ideal support material for Co₃O₄ as a catalyst for ammonia oxidation.

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