

Nanocrystalline cobalt oxide: a catalyst for selective alkane oxidation under ambient conditions†

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Nanocrystalline cobalt oxide activates propane, yielding propene at room temperature and pressure.

Nanomaterials currently receive a high degree of interest from many fields of science, such as medicine, optics, energy and computing...¹ In catalysis too. Nanomaterials have opened a new era for many catalytic reactions due to their particular characteristics.² In fact when materials approach molecular dimensions their properties usually change when compared with a bulk material. For example, nanocrystalline materials present different adsorption capacities, high surface area and increased accessibility of the active sites. Unfortunately, many of them have a limited stability and usually cannot tolerate severe reaction conditions. In the present work a nanocrystalline cobalt oxide has been prepared and it exhibits exceptional properties for the oxidation of some short chain alkanes. These types of reactions are important and they are a major research area, as there is a strong driving force to develop efficient processes for utilization of alkanes under mild conditions.

The cobalt oxide was synthesized by solid state reaction and the surface area of the sample is 159 m² g⁻¹.[‡] The nanocrystalline nature of the catalyst is consistent with the relatively high surface area. Powder XRD of this material only shows the presence of a cobalt oxide phase with the stoichiometry of Co₃O₄ (Fig. S1). The nanocrystalline catalyst shows very broad diffraction peaks. The average particle size, calculated by X-ray line broadening through the Scherrer equation, is 12 nm. The XRD data were unchanged for the used catalyst. TPR of this sample shows two main reduction bands around 260 and 340 °C, that can be attributed to the reduction of Co₃O₄ to CoO and from CoO to Co.³ Comparison of the reduction behaviour has been made with a commercial sample of Co₃O₄ and there is little difference between the high temperature features of the two samples (Fig. 1). A surprising low intensity reduction feature was also observed at 90–100 °C for the nanocrystalline cobalt oxide catalyst, and this was not present for the commercial cobalt oxide (Fig. 1 insert).

The most remarkable characteristic of the nanocrystalline material is that at ambient temperature and pressure it activates propane, yielding propene with 100% selectivity of the gas phase products. Unfortunately, deactivation of the catalyst takes place and after a period depending on the contact time employed no further propane activity was observed. One of the most positive

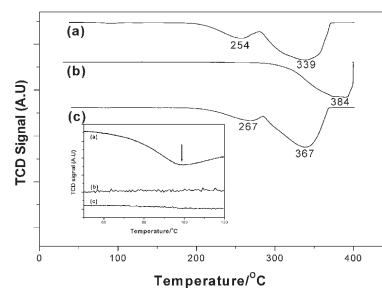


Fig. 1 Temperature programmed reduction profiles for (a) fresh nanocrystalline Co₃O₄, (b) fresh commercial Co₃O₄ (Avocado) and (c) used at 40 °C nanocrystalline Co₃O₄. Insert shows an expanded view of the low temperature reduction features.

aspects of this catalyst is that it can be reactivated relatively easily by heating in air at a temperature as low as 180 °C (below this temperature the catalytic activity is only partially restored). Investigation of the catalyst deactivation and regeneration cycle is presented in Fig. 2 (1% propane in air, reaction temperature = 40 °C and contact time = 250 g_{cat} h mol⁻¹ C₃). After the first few deactivation and regeneration cycles the catalyst profile with time on stream was extremely reproducible. These data indicate that the catalyst was regenerated fully even after several deactivation and regeneration cycles. The ability to operate the catalyst in a reproducible cycle means that propane selective oxidation can be performed at low temperature followed by regeneration at elevated temperature.

It is important to indicate that although propane conversion decreases with time on line for reaction temperatures below 120 °C, above this temperature the propane conversion remained constant

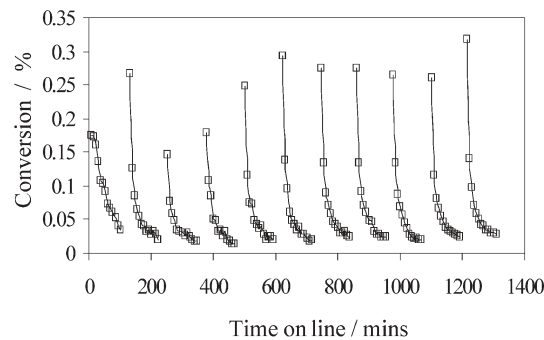


Fig. 2 Deactivation profile at 40 °C of the Co₃O₄ catalyst prepared by solid state reaction. After reactivation the catalyst was regenerated at 180 °C and the cycle repeated 9 times.

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† Electronic supplementary information (ESI) available: Fig. S1. Powder X-ray diffraction patterns of the nanocrystalline cobalt oxide catalyst and the commercially supplied cobalt oxide catalyst. See DOI: 10.1039/b606973h

with prolonged time on line. However, above 120 °C at steady state propane selectivity was lower than 100%. At this stage the mechanism of deactivation is unclear; it may be due to a reactive surface site that is unable to be regenerated at low temperatures. Alternatively, deactivation may be due to species adsorbed on the surface and these are unable to desorb at the low temperatures employed. Temperature programmed desorption studies of the deactivated catalyst showed that heating to 180 °C resulted in the evolution of CO₂. These data indicate that the latter explanation is more likely, however, the adsorbed species may be CO₂ or they may be propene which is oxidised on the catalyst surface during the experiment.

Decreasing the gas hourly space velocity, and consequently increasing the catalyst contact time, resulted in the expected increase of propane conversion and *vice versa*. The influence of gas hourly space velocity on propene selectivity was negligible at low temperatures, as propene selectivity remained unaltered in the range of contact times studied at temperatures below 100 °C. Thus, hugely increasing the contact time, higher propane conversions were achieved. In this way, using 10 000 g_{cat} h mol⁻¹C₃ initial propane conversions of 1.25% were achieved at only 25 °C. After 10 h on line the conversion was still 0.15%, and 100% propene selectivity was maintained throughout the time on line.

The nanocrystalline cobalt oxide was compared with a commercial cobalt oxide (Avocado, 4 m²/g, particle size 103 nm). Fig. 3 shows the evolution of the propane conversion with the reaction temperature using a contact time of 250 g_{cat} h mol⁻¹C₃. The selectivity towards propene for the Co₃O₄ catalyst prepared by solid state reaction, compared with the commercial Co₃O₄ catalyst is also shown in Fig. 3. The nanocrystalline Co₃O₄ catalyst prepared by solid state reaction was 100% selective towards propene from 25 to 80 °C; no other products were detected in this temperature range. Above 80 °C propene selectivity decreased as the reaction temperature was increased, however, propene selectivity still remained high and was *ca.* 70% at 100 °C. The commercial Co₃O₄ catalyst was considerably less active and selective than the nanocrystalline catalyst. No activity was observed below 100 °C for the commercial catalyst, indicating that conversion was not a simple function of catalyst surface area.

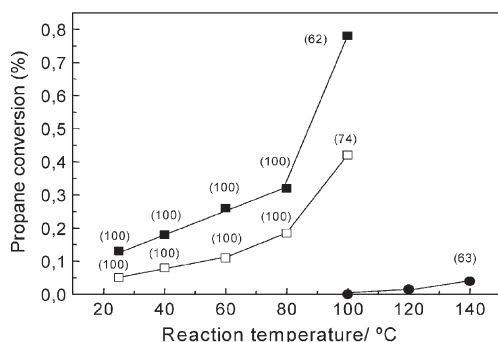


Fig. 3 Comparison of propane conversion over Co₃O₄ catalysts: (■) Initial conversion on Co₃O₄ prepared by the solid state method, (□) conversion after 60 min on line over Co₃O₄ prepared by the solid state method, (●) conversion on commercial Co₃O₄ (time on line either 0 or 60 min). Reaction conditions: propane/oxygen/helium = 1/19/80. Contact time = 250 g_{cat} h mol⁻¹C₃. Note: In brackets, selectivity to propene.

Using the nanocrystalline cobalt oxide, similar experiments to those made with propane were carried out using other alkanes as substrates. In the case of ethane, activation at low temperatures and deactivation were observed as for propane. However, important differences were apparent. To achieve the same conversion to that observed for propane *ca.* 40–50 °C higher temperature was required. In addition, the selectivity to ethylene did not exceed 70%. In the case of methane no activity was demonstrated even at a reaction temperature of 100 °C.

At this stage the origin of this catalytic behaviour is uncertain. However, it is probable that it is related to the presence of a very active species, that reduces in the TPR experiments at 90 °C (Fig. 1). As-synthesised nanocrystalline cobalt oxide exhibits this feature but the deactivated catalyst after reaction at 25 or 40 °C does not. If the deactivated catalyst is calcined in air at 180 °C, which are the conditions used to regenerate catalyst activity, the low temperature reduction feature reappears. Therefore, we assign the low temperature catalytic behaviour to the presence of this very active species, which could be cobalt in a high oxidation state or a very reactive oxygen species. Thus, as discussed previously, the deactivation of the catalyst could be due to the exhaustion of this very active species or blocking of the site where it is generated. Therefore, we think that this low temperature reduction feature is associated with a surface oxygen species that affects the low temperature selective oxidation. This postulation is enforced by experiments in which the fresh catalyst was treated with hydrogen *in situ* at 80 °C prior to being tested for propane oxidation. The pre-treated catalyst showed no activity for propane oxidation, either selective or non-selective. Regeneration of the hydrogen pretreated catalyst at 180 °C in air resulted in the propane conversion and selectivity to propene being fully restored to those of the fresh catalyst. In addition, the commercial Co₃O₄ catalyst did not present the low temperature reduction at *ca.* 90 °C (Fig. 1) and propane oxidation results confirmed that the catalyst was inactive at low temperatures.

To date the precise nature of the active site is not known. It is clear that the nanocrystalline nature of the Co₃O₄ is important and the origin of the activity is more complex than a consequence of the increase of surface area. It is likely that the nanocrystalline catalyst has more open surfaces than the more highly crystalline commercial Co₃O₄ and the number of defect sites will also be greater. Identification of this low temperature selective oxidation site will aid in the scientific design of more effective catalysts for alkane oxidation as catalysts that are capable of activating alkanes at low temperatures. Thus, these facts are of fundamental importance.

At this moment most of the catalysts reported in the literature for oxidative dehydrogenation of short chain alkanes (ethane, propane, n-butane) operate at temperatures over 300 °C and are based on vanadium and molybdenum oxides.⁴⁻⁶ In the case of catalytic dehydrogenation in the absence of molecular oxygen the temperatures employed are even higher (> 550 °C) since this reaction is thermodynamically limited.^{7,8} In contrast, for the present work very low reaction temperatures have been employed. It is true that the conversions obtained are low but if the nature of the extremely reactive species could be identified and materials could be synthesised with higher concentration of this species, very interesting catalytic results should be obtained at ambient temperature. Another problem that arises is the deactivation of

the catalyst. It has been reported that the main problem of redox catalytic reactions at low temperature is the reoxidation step of the reduced catalyst.⁹ It appears that a similar effect may be operating with the nanocrystalline Co_3O_4 ; strategies such as using a different oxidant or increasing reaction pressure may help to overcome this limitation. Nevertheless, the ability to operate the catalyst with high selectivity and then fully regenerate the original activity is important. This mode of operation has already been successfully commercialised by DuPont using the Riser reactor for the selective oxidation of butane to maleic anhydride at elevated temperature.¹⁰

The production of chemicals by energy efficient and environmentally friendly routes is an important aim for the modern pharmaceutical and chemical industries. In particular, the facile utilisation of cheap and relatively abundant feedstocks such as short chain alkanes (C1–C4) remains a challenging target.^{11,12} The activation of these hydrocarbons under benign conditions has not yet been reported. The efficient utilisation of short chain alkane feedstocks is highly desirable as their production volumes are set to increase significantly, due to large scale international investment in new gas to liquids technology. Experimental evidence has been found for the selective oxidation of methane to methanol at room temperature on Fe-ZSM-5 catalysts.¹³ However, the methanol product is bound strongly to the catalyst surface and upon heating it is not released into the gas phase, but decomposes to evolve carbon monoxide. On the other hand, Busca and coworkers¹⁴ studied the oxidation of propane on a cobalt oxide catalyst, obtaining similar catalytic results to those obtained with our commercial Co_3O_4 sample.

In the present work we demonstrate a catalyst that achieves selectivity to propene of 100% at low reaction temperatures. The per pass yields to the olefin obtained are relatively low, but the results are highly significant as no other catalyst has shown any activity for this reaction under the same conditions. The low yield means that considerable improvement is required before the catalyst could be considered for industrial use. However, these are still very significant fundamental results for alkane activation, since we show for the first time a catalyst capable of selectively activating propane and ethane using ideal reaction conditions:

atmospheric pressure, ambient temperature and using air as an oxidant.

Notes and references

‡ Nanocrystalline Co_3O_4 was prepared by solid state reaction following a method similar to that described previously.¹⁵ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) and NH_4HCO_3 (2 : 5 molar ratio) were ground with a pestle and mortar for 0.5 h, and then thoroughly washed with distilled water and dried for 16 h at 100 °C. The precursor was calcined at 300 °C for 2 h in static air. The commercial Co_3O_4 (ex Avocado) was used as supplied. Reactor studies were mainly performed in a fixed bed quartz tube microreactor using 0.25 g of catalyst. The total flow rate was between 20–40 ml min⁻¹. The temperature of the reaction was between 25–200 °C and was monitored with a thermocouple placed directly in the outlet of the catalyst bed. Experiments employing high contact time (10 000 g_{cat} h/mol C₃) at 25 °C were performed in a reactor placed in a thermostatic bath. The feed composition was 1% C₃H₈, 19% O₂ with a balance of helium. The effluent from the reactor was analysed using a Varian 3800 GC equipped with a TCD and FID. We must emphasize that the selectivity to propene obtained at low temperatures is 100% or very close to this since in our analysis conditions CO₂ can be clearly detected and quantified for propane conversions of 0.05% and selectivity lower than 3%.

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