



# Green preparation of transition metal oxide catalysts using supercritical CO<sub>2</sub> anti-solvent precipitation for the total oxidation of propane

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## ABSTRACT

A series of metal oxide catalysts, including Fe<sub>3</sub>O<sub>4</sub>, NiO, CuO and Co<sub>3</sub>O<sub>4</sub>, have been prepared by supercritical anti-solvent precipitation and evaluated for the total oxidation of propane. Co<sub>3</sub>O<sub>4</sub> was found to be the most active catalyst and our studies have focussed on this oxide. The addition of water as co-solvent in the supercritical anti-solvent preparation was investigated. Powder X-ray diffraction and infrared spectroscopy indicated that the addition of water promoted the formation of carbonate species in the catalyst precursors. The formation of the catalysts from the precursor were optimised by investigating the thermal treatment conditions, by studying variables including time, temperature and atmosphere. The optimal conditions for catalyst preparation required precursor precipitation containing 10 vol% water co-solvent followed by a 2 h calcination at 250 °C. These conditions produced Co<sub>3</sub>O<sub>4</sub> with high surface areas (>100 m<sup>2</sup> g<sup>-1</sup>), which were very active catalysts producing 50% propane conversion at 175 °C.

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## 1. Introduction

The challenge to control atmospheric emissions from a wide range of sources is of great importance, with increasingly stringent legislation being introduced to limit their release in an attempt to abate their detrimental environmental properties. In particular, volatile organic compounds (VOCs) are recognised as major atmospheric pollutants. VOCs are involved in ground level ozone formation [1], ozone depletion [2] and the greenhouse effect [3]. Amongst compounds classified as VOCs, linear short chain alkanes are among the most difficult to eliminate [4]. Therefore, much research has been dedicated to their removal, with catalytic total oxidation being recognised as one of the most efficient methods, with supported platinum and palladium catalysts commonly used commercially.

Propane oxidation has been widely used as a model reaction to study the oxidation of short chain VOCs. A number of transition metal oxides have shown promising activity for propane deep oxidation, with Co<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> being particularly active [5–8]. Mixed metal oxide systems, such as NiMnO<sub>x</sub>, FeMnO<sub>x</sub> and CuMnO<sub>x</sub>, have also been investigated, with improvements in activity reported compared to the relevant single metal oxides

[8–10]. Solsona et al. observed that co-precipitated CuMnO<sub>x</sub> was more active than supported palladium catalysts, and activity was further improved by the incorporation of gold nanoparticles into the CuMnO<sub>x</sub> structure [11]. Moreover, the incorporation of gold enhanced catalyst stability over 24 h at 250 °C. Although some mixed metal oxides are very active and warrant further investigation, nanocrystalline Co<sub>3</sub>O<sub>4</sub> has shown higher activity, with total oxidation at 200 °C [6]. Therefore much interest remains focussed on this single metal oxide catalyst.

The preparation method of nanocrystalline Co<sub>3</sub>O<sub>4</sub> has been found to be highly influential for propane total oxidation activity. Several preparation techniques have been investigated, including mechano-chemical synthesis [5–7,12], sol gel synthesis [13], co-precipitation [13] and hard templating [14]. Mechano-chemical synthesis using cobalt nitrate and ammonium carbonate produced very active nanocrystalline Co<sub>3</sub>O<sub>4</sub> catalysts, with propane conversion reported at temperatures as low as 40 °C [5–7]. Solsona et al. [6,7] produced a very active nanocrystalline Co<sub>3</sub>O<sub>4</sub> catalyst using this technique with high surface area (160 m<sup>2</sup> g<sup>-1</sup>). It was observed that these high surface area cobalt oxides are more reducible, with low Co–O bond strengths, which suggests a high concentration of oxygen defect sites. Liu et al. also investigated mechano-chemical synthesis and proposed that lattice strain in nanocrystalline Co<sub>3</sub>O<sub>4</sub> was responsible for oxygen defect sites, and consequently the high activity [12]. The importance of a disordered structure was confirmed by Garcia et al. who prepared highly ordered and high

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surface area ( $177\text{ m}^2\text{ g}^{-1}$ )  $\text{Co}_3\text{O}_4$  by nanocasting using a mesoporous silica KIT-6 framework [14]. It was observed that partially ordered cobalt oxide was more active than the highly ordered oxides. The activity was attributed to the relatively high concentration of reactive oxygen defects which correlated with the measured concentration of  $\text{Co}^{2+}$  on the surface.

Amorphous or poorly crystalline high surface area metal oxides have been synthesised previously using supercritical  $\text{CO}_2$  anti-solvent (SAS) precipitation. There has been extensive research into SAS for the synthesis of semiconductors, polymers, pharmaceuticals and explosives [15–20]. With respect to use for heterogeneous catalyst synthesis, SAS produced materials have been investigated as supports for noble metals and as catalysts themselves. Medziak et al. [21] reported gold and palladium impregnated onto SAS precipitated  $\text{CeO}_2$  as catalysts for benzyl alcohol oxidation, while Tang et al. [22] supported gold on SAS precipitated  $\text{CeO}_2$  and  $\text{TiO}_2$  to show high catalytic activity for CO oxidation. Scanning transmission electron microscopy (STEM) analysis of these catalysts showed exceptionally high dispersion of the metals, which was attributed to the defective nature of the SAS prepared supports. Amorphous vanadium phosphate catalysts have also been successfully prepared for *n*-butane oxidation to maleic anhydride, demonstrating high intrinsic activity and no induction period, which is usually observed when conventionally prepared catalysts are used [23,24]. Similarly, hopcalite ( $\text{CuMnO}_x$ ) prepared by SAS had very high activity per unit area [25]. This high activity was attributed to the homogeneous distribution of metals and highly defective structure that was facilitated by the high nucleation rates provided by SAS precipitation. However, hopcalite surface areas from SAS precipitation using DMSO as solvent were found to be considerably lower, at *ca.*  $10\text{ m}^2\text{ g}^{-1}$ , when compared to surface areas of conventionally prepared Hopcalite ( $90\text{--}100\text{ m}^2\text{ g}^{-1}$ ) [26]. This resulted in the catalyst mass normalised CO conversion (which is a crucial factor for hopcalite catalysts) being lower for the SAS precipitated materials. However, the surface area of hopcalite was found to increase by adding water as a co-solvent during the SAS precipitation, which enabled materials with surface areas of up to  $175\text{ m}^2\text{ g}^{-1}$  to be obtained [27].

SAS precipitation, in addition to producing novel heterogeneous catalysts with advantageous properties, provides a preparation route which is in accordance with the principles of green chemistry [28,29]. The process avoids the use of metal nitrate salts, which result in environmentally damaging nitrate effluent streams, by preferentially using acetate salts [18,27]. The use of a supercritical fluid as an anti-solvent allows for easy separation of the solvents and recovery of the supercritical fluid [30]. In addition supercritical  $\text{CO}_2$  has a low cost, low toxicity, relatively mild operational conditions and can be easily recycled [30,31].

The current study investigates the preparation of a range of transition metal oxide catalysts, for propane total oxidation, using supercritical  $\text{CO}_2$  anti-solvent precipitation. This is the first time these catalysts have been prepared using a supercritical method, and their performance evaluated. After initial catalyst screening of the metal oxides,  $\text{Co}_3\text{O}_4$  was found to be the most promising material. The synthesis parameters for this catalyst were investigated in more detail, in order to evaluate the influence of addition of water as a co-solvent, calcination time and temperature on catalyst activity.

## 2. Experimental

### 2.1. Catalyst preparation

Various metal acetate salts (Sigma–Aldrich), shown in Table 1, were dissolved in methanol (reagent grade, Fischer Scientific) at a concentration of  $7\text{ mg ml}^{-1}$ . SAS experiments were performed

using apparatus manufactured by Separex, according to the methodology described previously [23].  $\text{CO}_2$  (BOC) was pumped through the system *via* the outer part of a coaxial nozzle at 120 bar,  $40^\circ\text{C}$  at a rate of  $9\text{ kg h}^{-1}$ . The metal salt solution was co-currently pumped through the inner nozzle, using a HPLC pump at a rate of  $3.75\text{ ml min}^{-1}$ . The resulting precipitate was recovered on a frit, while the  $\text{CO}_2$ -solvent mixture passed down stream, where the pressure was decreased to separate the two components. Precipitation was carried out for 90 min followed by a purge of the system with  $\text{CO}_2$  under the reaction conditions. The system was then de-pressurised and the dry powder collected and calcined in static air at  $250\text{--}400^\circ\text{C}$  for 2–5 h.

The effect of water addition during the precipitation of cobalt (II) acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ) was investigated by adding between 0 and 15 vol% water co-solvent to the methanol solution. SAS precipitation was performed under the same conditions as described above. The most active catalyst from the initial screening was then subjected to different calcination temperatures from  $250$  to  $400^\circ\text{C}$ . Several catalysts were used to benchmark the activity of the SAS catalysts. These included commercial  $\text{Co}_3\text{O}_4$  (Sigma–Aldrich) and  $\text{Co}_3\text{O}_4$  prepared from cobalt(II) acetate tetrahydrate (Sigma–Aldrich) by calcination at  $400^\circ\text{C}$  for 5 h with a ramp rate of  $5^\circ\text{C min}^{-1}$ . Finally the activity for propane total oxidation for the optimised SAS  $\text{Co}_3\text{O}_4$  catalyst was compared to a commercial 5 wt% Pt/ $\text{Al}_2\text{O}_3$  catalyst.

### 2.2. Catalyst characterisation

Surface areas were determined by multi-point  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  using a Micromeritics Gemini 2360 according to the Brunauer–Emmett–Teller method. Powder X-ray diffraction (XRD) was performed using a PANalytical X'Pert Pro diffractometer with a monochromatic  $\text{Cu K}\alpha$  source ( $\lambda = 0.154\text{ nm}$ ) operated at 40 kV and 40 mA. The scans were recorded over the range  $10\text{--}80^\circ 2\theta$  using a step size of  $0.016^\circ$  and a scan step time of 55 seconds. Fourier transform infra-red (FT-IR) analysis was carried out using a Jasco FT/IR 660 Plus spectrometer in transmission mode over a range of  $400\text{--}4000\text{ cm}^{-1}$ . Catalysts were supported in a pressed KBr disc. Scanning electron microscopy (SEM) was performed by dispersing the catalyst on an adhesive carbon disc, mounted on a 12.5 mm aluminium stub. Analysis was performed using a Carl Zeiss Evo 40 microscope, operated at 5–20 kV and 50–2000 pA. Thermal gravimetric analysis (TGA) was performed using a SETARAM Labsys thermogravimetric analyser. Temperature programmed reduction (TPR) was performed under 10%  $\text{H}_2/\text{Ar}$  to elucidate catalyst reducibility using a ChemBet 3000 instrument from  $50^\circ\text{C}$  to  $900^\circ\text{C}$ .

### 2.3. Catalyst testing

Catalysts were tested for propane total oxidation at ambient pressure under steady state conditions in a laboratory microreactor. 0.5 ml of catalyst were packed inside a stainless steel tube and placed inside a tubular furnace. The mass of SAS precipitated catalysts used was between 0.08 and 0.13 g, whilst the significantly denser standard catalysts used for comparison required *ca.* 0.2 g being used. A reaction gas mixture consisting of 0.5 vol% propane balanced with synthetic air (20 vol%  $\text{O}_2/\text{He}$ ) was flowed over the catalyst bed at  $50\text{ ml min}^{-1}$  (GHSV of  $6000\text{ h}^{-1}$ ) controlled by MKS mass flow controllers. The product stream was analysed using an on-line Varian 3800 gas chromatograph equipped with thermal conductivity and flame ionisation detectors. Activity was determined using incremental temperature steps. The catalyst was maintained at each temperature until steady state was achieved and three analyses were made and the data averaged. The catalyst was then increased to the next temperature and the process

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