Total oxidation of naphthalene using copper manganese oxide catalysts

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ABSTRACT

A series of copper manganese oxide catalysts have been investigated for the total oxidation of naphthalene, selected as a model compound for oxidation of polyaromatic hydrocarbons. Catalysts were prepared by coprecipitation and were calcined at 300, 400, 500 and 600 °C. The catalyst most active and selective towards CO_2 was calcined at 400 °C, and this was related to the formation of a high surface area poorly crystalline $CuMn_2O_4$ phase. Catalysts calcined at 500 and 600 °C were less effective in oxidising naphthalene to CO_2, and their composition of more highly crystalline $CuMn_2O_4$, with Mn_2O_3 for the 600 °C catalyst, formed partial oxidation products. There was also a direct relationship between the extent of reduction from temperature programmed reduction and catalyst performance.

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1. Introduction

Catalytic oxidation of volatile organic compounds (VOCs) is recognised as being a highly effective process for controlling their aerial emissions [1]. Whilst catalytic total oxidation of VOCs have been studied widely, some specific types of VOCs have received less attention. One such example is poly-aromatic hydrocarbons (PAHs), which are produced from a wide range of combustion processes and have been linked with serious health risks [2,3]. However, more recently, attention has started to focus on the catalytic total oxidation of PAHs [4]. Naphthalene has often been selected as a model PAH for study, as it is relatively less toxic to handle and its behaviour during catalytic oxidation can be extrapolated to more complex higher molecular weight PAHs.

In one of the earliest studies on naphthalene catalytic oxidation, Zhang et al. [5] used a series of metal catalysts supported on γ-Al_2O_3. The most effective were those containing platinum, and initial studies focused on precious metals, showing that they were generally more active than metal oxide catalysts [6,7]. The effect of support was also important and studies have shown that platinum supported on silica is exceptionally active for naphthalene oxidation [8]. Alongside the investigation of supported metals, there has also been a drive to develop more active metal oxide-based catalysts, as they are cheaper and supplies are more abundant. Previously, we investigated Co_3O_4, Mn_2O_3, ZnO, CuO, Fe_2O_3 and

CeO_2, prepared by precipitation, for naphthalene catalytic oxidation [9]. Nanocrystalline CeO_2 with a small crystallite size and high surface area was the most active [10], and it has also been demonstrated that activity could be improved further by the addition of copper to CeO_2 [11]. Mn_2O_3 also showed appreciable activity for naphthalene oxidation, and more in depth studies using high surface area Mn_2O_3, prepared by nanocasting, have identified that it is potentially a catalyst worth further investigation [12]. Against this background, it is interesting to consider the influence of adding copper to manganese oxide for naphthalene oxidation.

Mixed copper manganese oxide (Hopcalite) is well known as an active low-temperature catalyst for the oxidation of carbon monoxide to carbon dioxide [13,14]. Hopcalite has also been studied for the oxidation of a limited range of VOCs including propane [15], toluene [16] and chlorinated VOCs including chlorobenzene [17]. However, to date, mixed copper manganese oxide catalysts have not been studied for the total oxidation of PAHs. In this study, we have, for the first time, investigated the performance of Hopcalite for the total oxidation of the model PAH naphthalene, in order to establish if this inexpensive and readily available catalyst is potentially suitable for control of PAH emissions.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using an automated coprecipitation technique. Copper and manganese nitrate solutions (0.25 M) were premixed in a 1:2 ratio. Using a Metrohm titrando autotitrator, the

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nitrate solution was mixed with a sodium carbonate solution (2 M) at an appropriate rate to maintain a pH of 8.3 in a stirred precipitation vessel maintained at 80 °C. The resulting precipitate was left to age for 30 min at 80 °C before recovery by filtration, thoroughly washed and then dried for 16 h at 110 °C. Catalysts were generated by calcination of the precursor material in static air for 2 h at 300, 400, 500 and 600 °C. The heating ramp rate was 2 °C min^{-1} starting from ambient temperature

2.2. Catalyst characterisation

Structural phase information on the materials was determined using powder X-Ray diffraction. The data was gathered using a PANalytical X'Pert Pro powder X-ray diffractometer and compared with the ICDD database. The diffractometer was fitted with a Cu source operating at 40 kV and 40 mA.

Thermal gravimetric analysis of the precursor was undertaken using a Setram Labsys TGA/DTA instrument. The sample was heated from 30 to 700 °C under flowing air (15 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The mass change and the heat flow of the sample was monitored.

Temperature-programmed reduction (TPR) analysis of the catalysts was performed using a Quantachrome ChemBET TPD/R/O apparatus. In total, 30 mg sample of each catalyst was heated to 600 °C at a rate of 15 °C min^{-1} under a flow of 10%H$_2$/Ar at a flow rate of 30 mL min^{-1}.

The surface area of the catalysts was determined using the BET method. The catalysts were degassed by flushing with dry N$_2$ for 0.5 h at a temperature of 120 °C to avoid catalysts becoming nonstoichiometric by degassing under vacuum. A 5-point N$_2$ adsorption isotherm was measured at −196 °C using a Micromeritics Gemini 2360 instrument.

2.3. Catalytic activity determination

Catalyst activity was determined using a standard fixed-bed gas flow microreactor. A 100 vppm flow of naphthalene was generated by heating naphthalene (scintillation grade, Sigma–Aldrich) in a tube furnace under a flow of helium. Oxygen was then added to give a total flow of 40 mL min^{-1} (20% O$_2$ balance He). This was flowed through a fixed bed of the catalyst, which was packed to a constant volume to give a gas hourly space velocity of 60,000 h^{-1}. The catalyst temperature was controlled by a thermocouple placed in the catalyst bed, and activity was measured over the temperature range 150–350 °C using incremental temperature steps. At each temperature, the catalyst was allowed to stabilise and steady-state activity was measured. The gaseous effluent was measured using an on-line Varian 3400 gas chromatograph fitted with OV-17 and Carbosive columns with flame ionisation and thermal conductivity detectors.

In order to analyse the stability of the catalysts on-stream, a sample was tested at a constant temperature of 350 °C and products analysed every hour for 48 h. To investigate the reusability of the catalyst, a sample was tested for three successive cycles, raising the catalyst temperature to a maximum of 350 °C for each cycle, before cooling and restarting the cycle.

3. Results and discussion

3.1. Catalyst and precursor characterisation

Fig. 1a shows the X-ray diffraction pattern of the catalyst precursor (material obtained after drying the precipitate before calcination). The only phase observed was that of the hexagonal-rhombohedra MnCO$_3$ phase. This was indicated by the principle reflection at 32° corresponding to the (114) set of lattice planes. The reflection associated with the (012) plane was also clearly observed at 24.5°, as was the (116) at 52.2°. No evidence was observed for reflections that corresponded to a copper-containing phase. However, when compared with a standard MnCO$_3$ diffraction pattern, the peaks appear shifted to higher 2θ angles by around 0.5°. In the standard MnCO$_3$ sample, the (114) plane is observed at 31.4°, the (012) plane at 24.3° and the (116) plane at 51.7. This is consistent with previous work by Porta et al., who demonstrated that when copper is substituted into the MnCO$_3$ lattice, the unit cell contracts due to the smaller ionic radius of copper, site distortion due to the d^9 electron configuration as well as the higher covalency of the copper–oxygen polyhedral [18]. Indeed, previous work on related copper manganese oxide catalysts prepared mechanochemically
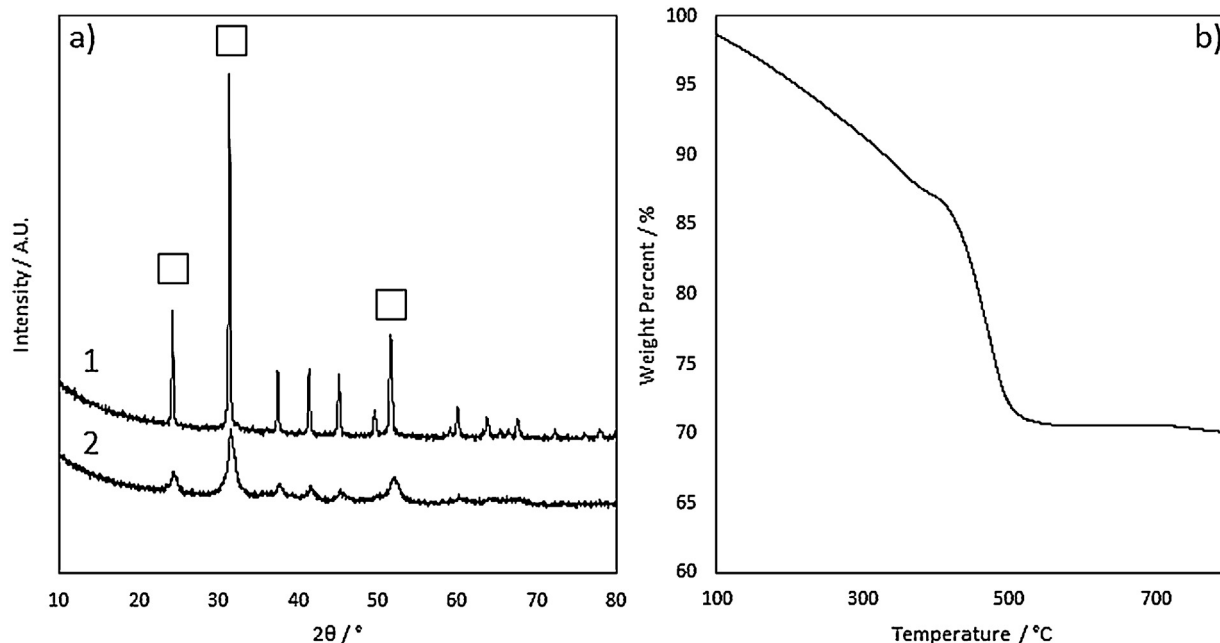

Fig. 1. a. Powder X-ray diffraction patterns of precursor materials 1. Standard MnCO$_3$, 2. Copper manganese oxide catalyst precursor. □ = MnCO$_3$. b. Thermal gravimetric analysis profile of the catalyst precursor.