Total oxidation of naphthalene using an amorphous copper manganese oxide catalyst

Tomos J. Clarke[1*], Simon. Kondrat[1], Thomas. Davies[1] Stuart H. Taylor[1]
[1]*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK*
**corresponding author:clarketj1@cf.ac.uk*

Introduction

Volatile organic compounds are the subject of strict European legislation limiting their release into the environment. Poly aromatic hydrocarbons are a class of VOC's that are produced during the incomplete combustion of wood and other fuels. PAH's consist of multiple fused aromatic systems. The simplest PAH, Naphthalene, is widely studied as a model compound. The most widely studied naphthalene oxidation catalysts are supported noble metals[1]. However due to the rare nature of platinum there is a niche for a base metal catalyst for naphthalene oxidation. Hopcalite ($CuMn_2O_4$) is a mixed copper manganese oxide catalyst most commonly used as a CO oxidation catalyst. However in recent years investigations into alternative uses have shown it to have appreciable activity in a variety of total oxidation applications. We have investigated the activity of hopcalite for naphthalene total oxidation.

Materials and Methods

The catalysts were prepared by a co-precipitation method. Copper and manganese nitrate solutions (0.25M) were premixed in a 1:2 ratio. Using a Metrohm titrando autotitrator the nitrate solution was mixed with a sodium carbonate solution at an appropriate rate to maintain a pH of 8.3. The resulting precipitate was left to age for 30mins at 80°C before recovery by filtration and drying for 16h at 110°C. The active materials were generated by calcination in static air.

Materials were tested for naphthalene oxidation in a fixed bed reactor and analyzed by thermal conductivity measurements using a Varian 3400 gas chromatograph. The testing gas consisted of v100ppm naphthalene in air was flowed over the catalyst bed at a GSHV of 60 000h^{-1}.

Results and Discussion

The catalysts were calcined at a range of temperatures in order to investigate the relationship between the phase generated and the activity of the catalyst. Table 1 contains information referring to the physical properties of the catalysts. Surface area was observed to increase with calcination as the precursor material broke down before decreasing at higher calcination conditions as sintering occurred. X-ray diffraction identified residual carbonate precursor in the sample calcined at 300°C. There was no precursor evident by 400°C with only one broad reflection corresponding to $CuMn_2O_4$ observed. As calcination temperature was increased the evidence of crystalline $CuMn_2O_4$ along with Mn_2O_3 reflections was observed as expected from the literature [2].

Table 1: Properties of the calcined catalysts

Calcination Temperature/°C	Surface area/ m^2g^{-1}	Phases observed	T90 CO_2/°C
300	9	CuMn2O4, MnCO3	278
400	72	CuMn2O4	238
500	54	CuMn2O4	270
600	9	CuMn2O4, Mn2O3	301

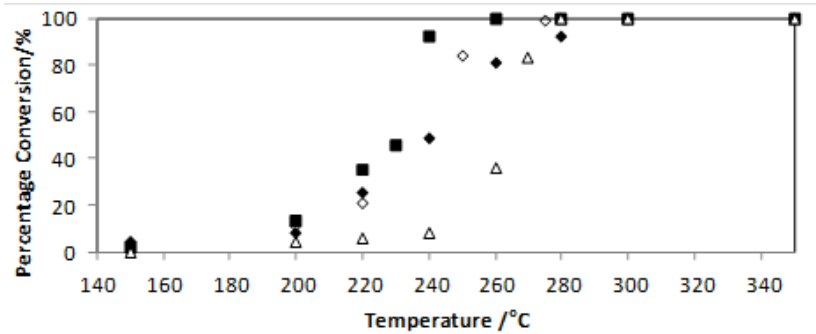

Figure 1. Temperature dependent naphthalene oxidation activity of copper manganese oxide catalysts calcined at different temperatures as a function of CO2 production**.**

300C: ◆ 400C: ■ 500C: ◇ 600: ▲

Naphthalene oxidation activity of the catalysts as a function of CO_2 conversion is detailed in Figure 1. No evidence of partial naphthalene oxidation was observed. It was found that the catalyst calcined at 400°C was the most active, this was attributed to the generation of the amorphous spinel phase. As calcination temperature increased and the catalyst became more crystaline in nature along with the associated decrease in surface area the activity of the catalyst declined.

Significance

Copper manganese oxide has been shown to be an active catalyst for naphthalene oxidation. It exhibits promising low temperature activity. XRD of the catalyst suggests the amorphous CuMn2O4 phase is the more active phase for naphthalene oxidation as activity decreases with increased crystalline character.

References

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