Vanadium promoted molybdenum phosphate catalysts for the vapour phase partial oxidation of methanol to formaldehyde

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ABSTRACT

The catalytic properties of $(MoO_2)_2P_2O_7$ promoted with vanadium have been investigated for the partial oxidation of methanol, and structure-activity relationships probed using a range of characterization techniques. All unpromoted and promoted molybdenum phosphate catalysts were active, with higher vanadium content achieving both high activity and high formaldehyde selectivity at reaction temperatures around 400 °C. The association between increasing vanadium content and the enhanced activity towards methanol oxidation was attributed to the formation of mixed phase catalysts, in particular $VOHPO_4 \cdot 0.5H_2O/VOPO_4 \cdot 2H_2O$ with $(MoO_2)_2P_2O_7$. The dispersion of vanadium phosphate phases on the surface of $(MoO_2)_2P_2O_7$ was found to substantially enhance the catalytic properties of the molybdenum phosphate catalyst. The data from this study indicate that molybdenum phosphate based catalysts are promising candidates for selective oxidation, and hence worthy of further investigation.

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1. Introduction

Formaldehyde is an important intermediate in the chemical industry, as it is used in the production of thermosetting resins, antiseptics, and adhesives. It is also essential for the manufacture of a range of other materials such as plywood, carpeting, paper and fertilizers amongst others [1]. Presently there are two competing industrial processes to produce formaldehyde from the oxidation of methanol, which are based on silver and ferric molybdate catalysts [1–5]. The silver process uses a methanol-rich feed (around 40%) and reaction temperatures around 650 °C, whereas the ferric molybdate process uses a methanol-lean feed (around 8%), and reaction temperatures in the region of 300 °C [6,7]. Both catalysts produce a high yield of formaldehyde, and the choice of process is determined by the operating and capital costs, as well as product end use, plant size and type of operation [5,8,9]. Over the last decade, the ferric molybdate-catalysed process has dominated the market as a consequence of the higher formaldehyde selectivity.

This paper reports for the first time, the use of molybdenum phosphate catalysts for methanol oxidation to formaldehyde. Molybdenum phosphate materials (MoPO) have received increasing interest in the last decade for use as new cathode materials for

lithium and sodium batteries [10]. For catalysis, they are mainly reported for use in the partial propane oxidation reaction, where they are usually promoted by metals such as silver or cerium, and they produce high selectivity to propene at relatively low conversion [11–15]. In general, MoPO phases are usually comprised of $(PO_4)^{3-}$ tetrahedra linked mostly with $(MoO_6)^{6-}$ octahedra [16]. One of the main characteristics of these phosphate materials is their ability to stabilize molybdenum in various oxidation states, i.e. Mo^{6+}, Mo^{5+}, Mo^{3+} and even mixed valencies such as Mo^{5+}/Mo^{6+}. These redox properties make them ideal catalysts for oxidation reactions, such as the partial oxidation of propane, and potentially for the partial oxidation of methanol. Transition metal phosphate catalysts have been reported in the literature to be active for numerous partial oxidation reactions, e.g. vanadyl pyrophosphate for butane oxidation to maleic anhydride [17,18], and iron phosphate for the oxidative dehydrogenation of isobutyric acid into methacrylic acid [19,20]. There is some evidence to suggest that the role of phosphate tetrahedra is to enhance the redox properties of the catalyst, possibly due to the increase in mobility of the lattice oxygen through the bulk to the surface, where it can re-oxidise the reduced surface during the reaction [21]. Hence, considering the high selectivity to formaldehyde using molybdenum oxide based catalysts, and considering the possible improvement as an oxidation catalyst by incorporating phosphate groups, the investigation of molybdenum phosphates as catalysts for methanol oxidation is an interesting concept.

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Against this background we have started to investigate the efficacy of molybdenum phosphate catalysts for the selective oxidation of methanol to formaldehyde. The effect of adding vanadium into the molybdenum phosphate structure has also been investigated and the affect on catalyst performance evaluated. Catalysts have been prepared using a relatively simple co-precipitation technique, and physico-chemical properties have been studied using a range of characterisation techniques. Catalytic activity for selective methanol oxidation is reported for the first time with these catalyst formulations, and performance is related to the structure of the catalysts.

2. Experimental

2.1. Catalyst Preparation

2.1.1. Unpromoted molybdenum phosphates

The precursor $MoO_2 \cdot HPO_4 \cdot H_2O$ was obtained by dissolving MoO_3 (15 g, Sigma–Aldrich, >99.5%) in H_3PO_4 (45 ml, Aldrich, 85% in H_2O, 99.99%) at 180 °C. Upon cooling of the viscous solution, concentrated HNO_3 was added (300 ml, Fisher Chemical, 70% Analytical grade) and the mixture refluxed for 16 h. After completion of the reaction, the solid phase was recovered by filtration and washed with water and acetone, before drying overnight at 110 °C in air. $MoO_2 \cdot HPO_4 \cdot H_2O$ was calcined (650 °C, 6 h, ramp rate 20 °C min^{-1}) to form $(MoO_2)_2P_2O_7$. The nomenclature for the unpromoted precursor is Mo-HPO, and for the unpromoted $(MoO_2)_2P_2O_7$ catalyst, MoPO.

Vanadium promoted molybdenum phosphate catalysts were prepared by adding the desired amount of V_2O_5 (Sigma–Aldrich, >98%) during the phosphation step of the precursor synthesis, where MoO_3 and V_2O_5 were dissolved in H_3PO_4, prior to refluxing with HNO_3. The same procedure was then followed as for the unpromoted precursor and MoPO preparation. The nomenclature of V promoted $(MoO_2)_2P_2O_7$ is MoPO-Vx, where x denotes either 1, 5, 10 or 20 mol % V, in relation to the molar quantity of Mo.

2.2. Catalyst characterisation

Catalyst surface areas were analysed using a Micromeretics Gemini 2360 analyser and were determined by multi-point nitrogen adsorption at −196 °C, prior to data analysis in accordance with the BET method. All catalysts were degassed under a helium atmosphere (120 °C, 2 h) before analysis. Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. XRD patterns were collected using a PANalytical XPert diffractometer, with a graphite monochromator and a Cu X-ray source operated at 40 kV and 40 mA. Phases were identified by matching the experimental patterns to the ICCD PDF database. Raman spectroscopy was carried out using a Renishaw inVia Raman microscope equipped with a 514 nm laser (argon ion) with an average laser power of 25 mW. Before acquisition of catalyst spectra the system was calibrated using a silicon reference sample. Catalyst samples were flattened onto an aluminium plate before being analysed.

Scanning electron microscopy (SEM) was conducted using a Carl Zeiss EVO 40 microscope, with each sample dispersed on an adhesive carbon disc. Temperature programmed reduction (TPR) experiments were performed using a Quantachrome ChemBET chemisorption analyzer equipped with a TCD detector. Samples were pre-treated in an argon atmosphere at 120 °C for 1 h, prior to analysis under a reducing atmosphere of 10% H_2 in Ar, with a flow rate of 50 ml min^{-1}. The temperature ranged from room temperature to 750 °C, at a specific ramp rate. XPS analysis was performed using a Kratos Axis Ultra DLD photoelectron spectrometer, equipped with an aluminium monochromatic source and a
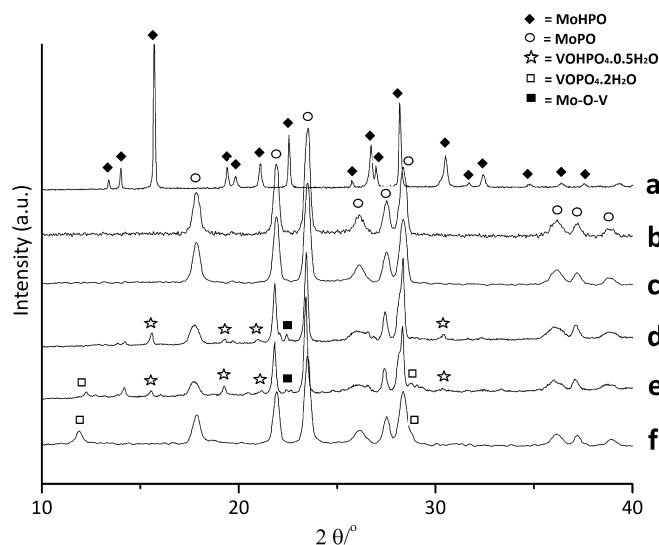

Fig. 1. Powder X-ray diffraction patterns: (a). MoHPO; (b). MoPO; (c). MoPO-V1; (d). MoPO-V5; (e). MoPO-V10; (f). MoPO-V20.

dual Al/Mg achromatic source. Spectra were acquired over an area of $700 \times 300 \mu m$ at a pass energy of 40 eV for high resolution scans. All spectra were calibrated to the C(1s) line of adventitious carbon at a binding energy of 284.7 eV.

2.3. Methanol oxidation

Catalytic activity for partial gas phase methanol oxidation, was performed in a fixed bed microreactor. 0.3 g of catalyst was held between plugs of quartz wool in the centre of a 5 mm i.d. quartz tube, which was placed vertically into a Carbolite tube furnace, with the outlet line heated to prevent condensation of products such as formaldehyde. Mass flow controllers were used to supply the reactant feed mixture of MeOH:O_2:He with a molar ratio of 5:10:85, and a total flow rate of 60 ml min^{-1} (GHSV = 12000 h^{-1}). To achieve 5 mol. % methanol, helium was passed through a saturator containing liquid methanol (Aldrich, 99.5%) which was maintained at 8 °C using a thermostatically controlled water bath. The reactor temperature was varied from 25 to 500 °C in incremental steps, at each interval the catalyst was allowed to attain steady state operation before data were collected. Product analysis was carried out using a Varian Star 3400 C_x on-line gas chromatograph, which used two columns in a series/bypass configuration to provide separation of all reactants and products (calibrated using gas reference standards). A Carbosieve S-11 (3 m) column was used for the analysis of O_2 and CO, accompanied by a Porapak Q (1 m) column to separate methanol (MeOH), dimethyl ether (DME), methyl formate (MF), formaldehyde (FA) and CO_2. A TCD was used in series with an FID for product identification and quantification. Methanol conversion in an empty reactor tube reached around 1% at 500 °C.

3. Results and discussion

3.1. Catalyst characterisation

The diffraction patterns of both Mo-HPO and MoPO are shown in Fig. 1. The pattern of the highly crystalline Mo-HPO material was observed, and corresponds well with that of the monoclinic structure reported by Kierkegaard [22]. The structure consists of parallel chains, where each chain of PO_4 tetrahedra binding together MoO_6, are linked by hydrogen atoms. The calcination of the Mo-HPO precursor produced a crystalline orthorhombic $(MoO_2)_2P_2O_7$ phase, (Fig. 1b). In contrast to the parallel chains of the precursor, MoPO