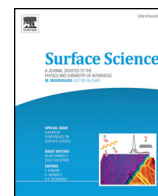




Contents lists available at ScienceDirect

Surface Science

journal homepage: [www.elsevier.com/locate/susc](http://www.elsevier.com/locate/susc)

## The surface of iron molybdate catalysts used for the selective oxidation of methanol

Benjamin R. Yeo<sup>a</sup>, Geoffrey J.F. Pudge<sup>a</sup>, Keith G. Bugler<sup>a</sup>, Alice V. Rushby<sup>a</sup>, Simon Kondrat<sup>a</sup>, Jonathan Bartley<sup>a</sup>, Stanislaw Golunski<sup>a</sup>, Stuart H. Taylor<sup>a</sup>, Emma Gibson<sup>b</sup>, Peter.P. Wells<sup>b</sup>, Catherine Brookes<sup>a,b</sup>, Michael Bowker<sup>a,b,\*</sup>, Graham J. Hutchings<sup>a,\*</sup>

<sup>a</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

<sup>b</sup> Rutherford Appleton Laboratory, UK Catalysis Hub, Research Complex at Harwell (RCAH), Harwell, Oxon OX11 0FA, UK

### ARTICLE INFO

Available online xxxx

#### Keywords:

Methanol oxidation  
Formaldehyde synthesis  
Iron molybdate  
Catalyst surface  
Catalyst preparation

### ABSTRACT

The oxidation of methanol to formaldehyde is a major chemical process carried out catalytically and iron molybdate is one of the major catalysts for this process. In this paper we explore the nature of the active and selective surfaces of iron molybdate catalysts and show that the effective catalysts comprise molybdenum rich surfaces. We conclude that it is therefore important to maximise the surface area of these active catalysts and to this end we have studied catalysts made using a new physical grinding method with oxalic acid. For superstoichiometric materials (Fe:Mo = 1:2.2) the reaction data show that physical mixing produces effective catalysts, possibly offering an improvement over the conventional co-precipitation method.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

Iron molybdate catalysts have been used for the industrial production of formaldehyde from methanol oxidation for many years. They are robust catalysts which are generally used in an unsupported form, and which operate in an oxygen rich environment. Interest in these materials has increased as the volume of formaldehyde production has increased, now reaching over 52 MT p.a. with an annual growth rate of 5% expected for the foreseeable future.

Two industrial processes for the production of formaldehyde have been used; i) the dehydrogenation of methanol over supported silver catalysts [1–3] or ii) the partial oxidation of methanol over mixed metal oxide catalysts such as iron molybdate [4–6]. The dehydrogenation reaction uses a high concentration of methanol in the feed (90%) and relatively high temperatures (600 °C), whereas the partial oxidation reaction uses a lower methanol concentration (<10%) at a lower temperature (300 °C). The lower operating temperature and robust nature of the mixed metal oxide catalyst has made the partial oxidation process more economically viable compared with the silver based catalytic system [7].

Iron molybdate has been established as an effective methanol partial oxidation catalyst since it was reported in 1931 [8]. The industrial catalysts are composed of two phases; Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> with an excess of MoO<sub>3</sub> [5]. The excess MoO<sub>3</sub> has recently been found to have a dual function.

First it increases the selectivity towards formaldehyde production by aiding the elimination of iron sites over the surface of the catalyst [9]. These iron sites have been conclusively shown to be detrimental towards the selective partial oxidation of methanol, by increasing selectivity towards carbon oxide products [10–12]. Secondly, whilst an excess of MoO<sub>3</sub> helps maintain high selectivity, it also extends the catalyst lifetime, as deactivation can occur by the loss of MoO<sub>3</sub> *via* sublimation. The loss of MoO<sub>3</sub> has been determined to lead to deactivation *via* the formation of iron oxide centres [4–6,13].

Many studies have focussed on the synthesis of iron molybdate catalysts using co-precipitation [6,11,14–16]. These catalysts have been successful in the production of formaldehyde from methanol and achieve high yields [14]. Synthesising iron molybdate catalysts in this way produces large volumes of aqueous waste containing unprecipitated iron and molybdenum and can result in phases containing only iron or molybdenum that do not contribute to the catalytic efficiency [9]. These factors, along with low active surface area of these materials, leads to a decreased catalytic performance as reoxidation of the catalyst is limited [17].

Alternative preparations of iron molybdates have been investigated, such as sol–gel methods [18] or supported iron on molybdenum nanorods [19]. These synthetic strategies aimed to achieve higher surface area materials with the aim of decreasing the occurrence of iron-dense regions responsible for total oxidation.

In recent years we have particularly been interested in the nature of the active surface of this material, that is, what is the surface composition and structure [9,11,12,14,16,20–25]? In addition, we are exploring novel ways of making such catalysts, and in making it in different morphologies [19].

\* Corresponding authors.

E-mail addresses: [bookworm@cardiff.ac.uk](mailto:bookworm@cardiff.ac.uk) (M. Bowker), [hutch@cardiff.ac.uk](mailto:hutch@cardiff.ac.uk) (G.J. Hutchings).

More recently, the production of iron molybdate nanoparticles using oxalic acid has been reported [26]. The solid state reaction, by grinding the salts together with oxalic acid, provides a cheaper and greener alternative, by eradicating the need for a solvent in the catalyst preparation procedure. These potential catalysts for the conversion of methanol to formaldehyde have been reported to exhibit a significant increase in the overall surface area compared with a conventional co-precipitation method.

In this study we investigate two features of this important catalyst. First, we report on the nature of the active surface of iron molybdate catalysts. From this it is clear that high surface area catalysts are required in which the surface is dominated by molybdenum. Secondly we investigate the new oxalic acid method of preparation to achieve materials with enhanced surface area. In particular we investigate the effect of varying the Fe:Mo ratio and assess the effect on the catalytic performance for the selective oxidation of methanol to formaldehyde. The performance of the oxalate solid state ground catalysts are compared with a conventional co-precipitation catalyst.

## 2. The nature of the surface of iron molybdate catalysts

We have examined the surface of iron molybdate catalysts that are active for selective methanol conversion by a range of techniques. The conclusions of this work are i) it is critically important that the surface is dominated by Mo, ii) Mo tends to segregate to the surface, even when present in the catalyst at very low levels. The performance of the catalyst is critically dependent on this surface level of Mo [9,23], as shown in Fig. 1. Here we have made catalysts of varying molar ratios of Mo by co-precipitation [23], and have measured the products from the surface after adsorbing methanol at ambient temperature. We see a particular pattern of behaviour with increasing Mo level. At very low bulk loadings  $\text{CO}_2$  is the main product since iron oxide is a combustor, and converts adsorbed methoxy through formate as the intermediate in the combustion pathway. Fig. 2 shows DRIFTS identification of the presence of methoxy on the catalyst surface [9]; this methoxy converts to formate upon heating, coinciding with  $\text{CO}_2$  evolution in TPD. As the Mo loading increases this combustion is reduced very quickly, so that by only 0.05 mol ratio of Mo the  $\text{CO}_2$  has been reduced to 50% selectivity. The major product at the intermediate loadings of Mo is CO, though formaldehyde begins to be made even at low loadings. Finally, as we approach stoichiometry of Mo:Fe 1.5 (mol fraction 0.6) for ferric

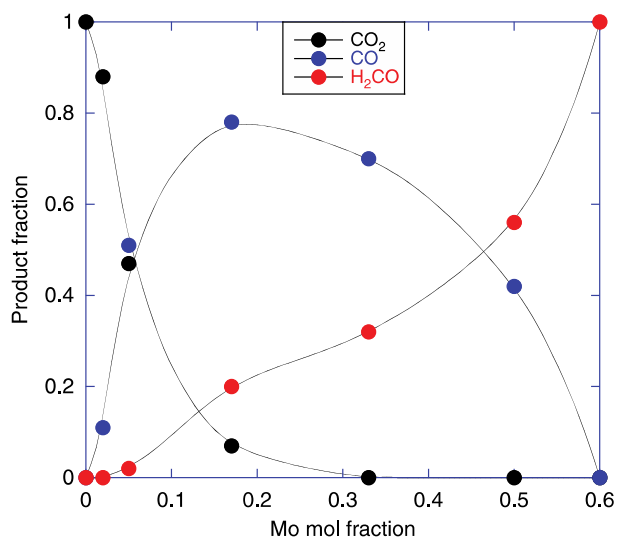


Fig. 1. The dependence of relative product yields in TPD upon the bulk loading of Mo in the oxide with Fe (from [9]).  
With permission of Taylor and Francis, [www.tandfonline.com](http://www.tandfonline.com).

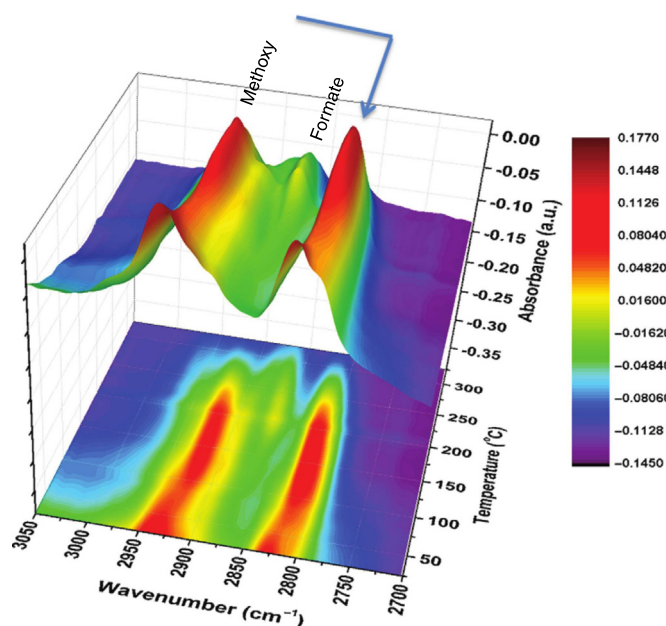


Fig. 2. Stacked temperature-programmed DRIFTS spectra for methanol adsorbed on an iron oxide surface (from [9]).

With permission of Taylor and Francis, [www.tandfonline.com](http://www.tandfonline.com).

molybdate, then CO is diminished and very high selectivity for formaldehyde is achieved.

So why do we have this distribution of products? We have very recently proposed that this is due to the nature of the ensembles on the surface [9]. If we imagine that the products are determined by pairs of Fe sites (which only produce  $\text{CO}_2$ ) and pairs of Mo sites (which are required for formaldehyde, as is proposed by a number of authors [27–29]), and that single sites of each produce CO, then the result of such a simple model, with a random statistical distribution is seen in Fig. 3.

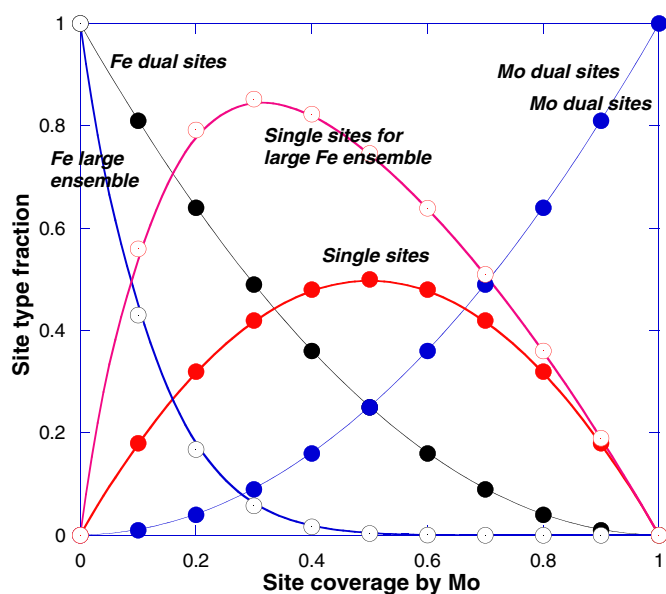


Fig. 3. The distribution of single and pair sites on a surface within a random distribution model for Mo coverage (solid data points). The open points are for the situation with larger ensembles of eight Fe atoms required for the combustion reaction, showing then the more severe effect on combustion sites (from [9]).

With permission of Taylor and Francis, [www.tandfonline.com](http://www.tandfonline.com).

Download English Version:

<https://daneshyari.com/en/article/5421644>

Download Persian Version:

<https://daneshyari.com/article/5421644>

[Daneshyari.com](https://daneshyari.com)