

Influence of nature of support on the catalytic activity of supported molybdenum-oxo species in benzyl alcohol conversion

Shanty Mathew^a, C. Shiva Kumara^b, N. Nagaraju^{a,*}

^a *St. Joseph's College, Research Centre, 46 Langford Road, Shanthi Nagar, Bangalore 560027, India*

^b *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*

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Abstract

Supported catalysts containing 15 wt.% of molybdenum have been prepared by the incipient wetness impregnation method. CaO, MgO, Al₂O₃, Zr(OH)₄ and Al(OH)₃ have been used as supports for the preparation of supported Mo catalysts. Characterisation of all the materials prepared has been carried out through BET surface area measurement, X-ray diffractometry and FT-IR spectroscopy. Catalytic activity measurements have been carried out with reference to structure-sensitive benzyl alcohol conversion in the liquid phase. The percentage conversion of benzyl alcohol to benzaldehyde and toluene varied over a large range depending on the support used for the preparation of catalysts, indicating the importance of the support on catalytic activity of Mo catalysts. Al(OH)₃ has been found to be the best support for molybdenum among all the supports used. Support–metal interaction (SMI) has been found to play an important role in determining the catalytic activity of supported catalysts.

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1. Introduction

Even though MoO₃ as such is a very well-known catalyst, due to its instability at higher temperature, it is often used in a supported form. Supported molybdenum oxide catalysts have been used in petroleum, chemical and pollution control industries [1]. Earlier alumina, TiO₂, ZrO₂, SiO₂ and MgO were used as supports for molybdenum oxide by various authors and studied their various physico-chemical and catalytic properties [2–6]. It is a well-known fact that, in several reactions, catalysts based on multicomponent oxides exhibit a better performance than when component oxides were used separately [7]. The catalytic activity of a supported catalyst depends not only on the ion supported but also on the support. Even though various parameters are collectively responsible for the unique catalytic activity of the catalysts, SMI plays a major role [8–11]. It was earlier reported by Kim et al. that in the oxidation of methanol, TiO₂ supported molybdenum oxide catalyst is superior to other oxide

supports in the increasing order, MgO, SiO₂, Al₂O₃, ZrO₂ and TiO₂, when prepared by equilibrium adsorption method [12]. In our earlier work with varied amount of molybdenum supported on Al(OH)₃, it was observed that 15 wt.% molybdenum containing Al(OH)₃ converts 98% of benzyl alcohol to benzaldehyde and toluene [13]. In order to investigate the influence of the nature of the support on the distribution of the catalytically active species, we have used different types of supports like CaO, MgO, Zr(OH)₄, Al(OH)₃ and alumina. Molybdenum (15 wt.%) containing supports have been prepared and tested in the conversion of benzyl alcohol.

2. Experimental

2.1. Preparation of supports

Zr(OH)₄, Al(OH)₃ and CaO were obtained commercially and dried at 120 °C overnight prior to their use. MgO was prepared by treating commercial MgCO₃ at 350 °C. Alumina (Al₂O₃) was prepared by the calcination of commercial Al(OH)₃ at 750 °C for 5 h.

* Corresponding author.

E-mail address: nagarajun@yahoo.com (N. Nagaraju).

2.2. Preparation of supported 15 wt.% molybdenum catalysts

Each support obtained as mentioned above was mixed with required amount of a solution of ammonium heptamolybdate at natural pH to obtain 15 wt.% molybdenum containing catalysts. Incipient wetness impregnation at natural pH was adopted to prepare these catalysts. The mixture was ground well for an hour and treated at 120 °C in an air oven overnight and finally calcined at 550 °C for 5 h. Since uncalcined Al(OH)₃ and Zr(OH)₄ were used as supports, these two supports containing Mo will be represented as Mo/Al(OH)₃ and Mo/Zr(OH)₄, respectively.

2.3. Characterisation

BET surface areas of all the materials were measured by N₂ adsorption at 77 K on a NOVA-1000 (VER: 3.7) instrument. The crystallographic phases of the supported catalysts were detected by recording powder X-ray diffraction patterns (PXRD) on a Philips X'pert Pro diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) using a graphite monochromator to filter the K β lines. Data were collected at a scan rate of 2°/min with a 0.02° step size for 2θ ranging from 5° to 70°. To check the nature of molybdenum-oxo species, IR absorption spectra of the catalysts were recorded following the KBr pellet method in the range 4000–600 cm⁻¹ on a Jasco FT-IR-410 instrument.

2.4. Catalytic activity

In a typical reaction, 5 ml of benzyl alcohol was refluxed for 6 h with 0.5 g of catalyst in a round bottom flask fitted with an ice-cold water condenser. After the stipulated time, the round bottom flask was cooled and the reaction mixture was separated from the catalyst by centrifugation. Components in the reaction mixture was analyzed by TLC first and later analyzed by a Netel gas chromatograph using a 10% SE 30 Chromosorb column. The products were further identified by ¹³C NMR, ¹H NMR and GC–MS.

3. Results and discussion

3.1. Surface area

The specific surface area of all supports and supported Mo catalysts determined by nitrogen physisorption is presented in Table 1. The surface areas of supports and supported molybdenum catalysts vary over a wide range. Among all the supports, the CaO support had the lowest surface area and Al(OH)₃ had the highest. The decrease in the surface area of Al(OH)₃ on calcination to 750 °C can be attributed to partial change from the γ phase to the more crystalline σ phase as shown by their powder XRD patterns.

Incorporation of molybdenum species reduced the surface area of all the supports, except for CaO supported catalysts where the increase was only marginal. The decrease in the surface area of Mo/Al(OH)₃, Mo/Al₂O₃ and Mo/Zr(OH)₄ compared to pure supports is due to the penetration of molybdenum species into

Table 1
Specific surface area of various supports and Mo supported catalysts

Support	Surface area (m ² /g)	Supported catalyst	Surface area (m ² /g)
Al(OH) ₃	191 (181)	Mo/Al(OH) ₃	139
Al ₂ O ₃	124	Mo/Al ₂ O ₃	109
Zr(OH) ₄	176 (32)	Mo/Zr(OH) ₄	22
MgO	43 (179)	Mo/MgO	136
CaO	8 (12)	Mo/CaO	16

Surface area of supports calcined at 550 °C are given in parenthesis.

the pores of the support, resulting in the dispersion of active species on the support [14]. This is confirmed by the absence of MoO₃ peaks in XRD of these supports. In the case of Mo/MgO there was an increase in the surface area compared to the MgO support obtained by the decomposition of MgCO₃ at 350 °C. However, this was not true when compared to 550 °C calcined MgO support. The change in the surface area of Mo/MgO is due to the formation of Mg(OH)₂ upon contact of MgO with water during incipient impregnation and its subsequent decomposition to high surface area MgO upon calcination [15].

The drastic decrease in the surface area of Mo/Zr(OH)₄ compared to the pure support can be attributed to the conversion of amorphous Zr(OH)₄ to ZrO₂ during calcination. Difference in the kind of phases present (monoclinic and tetragonal) in the presence of molybdenum species is also responsible for the decrease in surface area [16].

3.2. Powder X-ray diffraction

Powder X-ray diffraction patterns of all the supports and those containing 15 wt.% Mo are shown in Fig. 1. Mo/CaO showed a different crystallographic phase from that of the pure support. Apart from characteristic peaks of CaO the molybdenum containing CaO also showed a sharp peak at 28.8° which represents the compound CaMoO₄ (JCPDS No. 29-0351). Hence it can be inferred from X-ray diffraction patterns of CaO support and CaO supported molybdenum catalysts that CaO being basic in nature reacts with molybdenum species to form the compound CaMoO₄ [12]. Hence some of the peaks characteristic of CaO have disappeared and new peaks corresponding to CaMoO₄ appeared in the XRD pattern of the Mo/CaO catalyst.

Similarly, in the case of MgO, the PXRD showed peaks typical of MgO (JCPDS 01-1235) corresponding to d values of 2.1, 1.49 and 1.21 nm. Formation of α -MgMoO₄ in the Mo/MgO sample was indicated by a peak at $d = 3.1$ nm (JCPDS 31-0796) [17].

Aluminum hydroxide support (calcined at 550 °C) exhibited a diffraction pattern, typical of γ -alumina (JCPDS, Card No. 5-0508) [18]. Mo/Al(OH)₃ also exhibited a similar diffraction pattern, except for a slight deflection of the base line indicating the incorporation of molybdenum species in the support. Absence of peaks typical of crystalline MoO₃ at 2θ values of 27.3° and 25.6° indicates that these phases are not formed over the aluminum hydroxide support. This is in agreement with the fact that interaction between aluminum hydroxide support and

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