Characterization and reactivity of MoO_3 supported on $AlPO_4$ ☆

L. Jhansi Lakshmi and P. Kanta Rao [1]

Catalysis Section, Physical and Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 20 March 1993; accepted 24 May 1993

A series of $MoO_3/AlPO_4$ catalysts with molybdena content varying from 2 to 16 wt% were prepared and characterized by low temperature oxygen chemisorption (LTOC), ammonia chemisorption, X-ray diffraction (XRD) and electron spin resonance (ESR). Maximum O_2 uptake was observed at 6 wt% MoO_3 loading indicating the completion of monolayer. The ESR results are in conformity with LTOC and XRD data. The activities of the catalysts were tested in methanol partial oxidation and are correlated with their surface characteristics wherever possible.

Keywords: $MoO_3/AlPO_4$; characterisation (LTOC, XRD, ESR, NH_3 adsorption); dispersion

1. Introduction

Supported oxides and sulfides of molybdenum have been extensively studied and applied as catalysts for various reactions like partial oxidation, hydrotreating of petroleum crudes and alkane metathesis [1–3]. Phosphate anion is known to be an effective modifier for γ-Al_2O_3, resulting in higher MoO_3 dispersion in HDS catalysts [4,5]. The $AlPO_4$ like species formed upon phosphate modification of γ-Al_2O_3 were thought to be responsible for increased molybdena dispersion [5]. Both stoichiometric and non-stoichiometric aluminum phosphates have been used as supports for various metals like Ni, Rh, Pt, Pd because of their thermal stability over a broad range of temperatures and their surface acid–base character [6]. These properties in turn are dependent on the condition in which $AlPO_4$ is prepared and also on Al/P ratio. However, studies on $MoO_3/AlPO_4$ have not so far been carried out.

Probe molecules like CO_2, NO, O_2 have been used for measuring the active sites in reduced/sulfided molybdena supported on various oxides [7–9]. Among them the oxygen chemisorption is a versatile and simple technique for measuring the

☆ IICT Communication No. 3188.

[1] To whom correspondence should be addressed.

© J.C. Baltzer AG, Science Publishers

active molybdena sites on various supports [9,10]. The amount of O_2 chemisorbed has been correlated with the catalytic activity for hydrodesulphurization, hydrogenation and dehydrogenation [11]. It has recently been reported [12] that ESR is a useful technique to measure the dispersion of Mo^{5+}.

2. Experimental

$AlPO_4$ was prepared by coprecipitation using ammonium hydroxide as hydrolysing agent [13]. Aluminum nitrate (Loba AR grade) was dissolved in deionized water and then mixed with the required quantity of 85% H_3PO_4 (BDH Chemicals AR grade) in order to attain an Al/P ratio of unity. To the resulting solution aqueous ammonia was added dropwise with vigorous stirring to precipitate $AlPO_4$. The pH of the solution was maintained at ~ 8 during the precipitation process. Then the precipitate was filtered, washed with deionized water and dried at 110°C for 16 h and finally calcined at 600°C for 5 h. The resulting material has a N_2 BET SA of 63 m^2/g. $AlPO_4$ supported molybdena catalysts with MoO_3 loadings ranging from 2–16 wt% were prepared by impregnating $AlPO_4$ with requisite quantity of aqueous solution of ammonium hepta molybdate (Fluka Chemie, Switzerland). The samples were dried at 110°C for 16 h and calcined in air at 500°C for 6 h. The molybdena contents in the samples were estimated by atomic adsorption spectroscopy. An all glass high vacuum apparatus (capable of attaining 10^{-6} Torr) with the facility to reduce the samples in situ has been used to carry out low temperature oxygen chemisorption experiments. The O_2 uptakes at −78°C were determined according to the procedure of Parekh and Weller [14]. Oxygen chemisorption was determined as the difference between two adsorption isotherms at −78°C. Prior to first adsorption isotherm the catalyst sample (200 mg) was reduced for 5 h at 500°C in flowing purified hydrogen (40 cm^3/min), degassed for 1 h at the reduction temperature and then cooled under vacuum (10^{-6} Torr) to the temperature of adsorption. Between the first and second adsorption isotherms the sample was evacuated for 1 h at −78°C. After chemisorption experiment the BET SA of the catalyst was determined by N_2 physisorption at −196°C by taking 0.162 nm^2 as the cross sectional area of N_2. The same system used for oxygen chemisorption was employed to carry out NH_3 chemisorption experiments. The details of the experimental procedure are described elsewhere [15]. In a typical experiment about 300 mg of catalyst sample was placed in a glass adsorption cell and evaluated at 150°C (10^{-6} Torr) for 2 h. The ammonia uptakes were measured at ambient temperature using the double isotherm method. The X-ray diffraction patterns were recorded on a Philips PW 1051 diffractometer using Ni filtered Cu Kα radiation. The ESR spectra were recorded on a Bruker ER 200 D-SRC X band spectrometer with 100 kHz modulation at ambient temperature. For recording the ESR spectra of the reduced samples the procedure reported earlier was followed [16]. Activity studies for partial oxidation reaction of methanol were carried out at 175°C taking

200 mg of the catalyst packed in a fixed bed continuous flow tubular glass reactor of 6 mm i.d. Catalyst particles of the same size (0.5 mm) were taken in all the experiments. The feed gas consisting of 72, 24 and 4% by volume of nitrogen, oxygen and methanol vapour respectively was passed through the reactor. The conversions were kept below 10%. The rates were measured under steady state conditions with the help of the equation

$$X = rW/F,$$

where r is the rate in moles h^{-1} g^{-1} catalyst, X is the fractional conversion of methanol, W is the weight of the catalyst in gram, and F is the flow rate of the feed in mol h^{-1}. The products were analysed by on-line GLC.

3. Results and discussion

X-ray diffraction patterns of $MoO_3/AlPO_4$ catalysts are shown in fig. 1. XRD pattern of pure $AlPO_4$ support is also included in the figure. According to its XRD profile the $AlPO_4$ support is in amorphous state. A broad hump with 2θ value between 20–30° could be seen for the samples upto 10 wt% molybdena loading. At higher loadings small crystalline peaks corresponding to bulk MoO_3, $Al_2(MoO_4)_3$ were noticed [17]. Below 10 wt% also the aggregates of molybdena may be present but they may be microcrystalline particles of less than 40 Å which are undetectable by XRD. Oxygen uptake values, BET surface areas of the reduced catalysts, dispersion, crystallite size calculated from the amount of O_2 chemisorbed are listed as a function of catalyst composition in table 1. There is an increase in O_2 uptake upto 6 wt% MoO_3 loading beyond which it declined possibly due to the three-dimen-

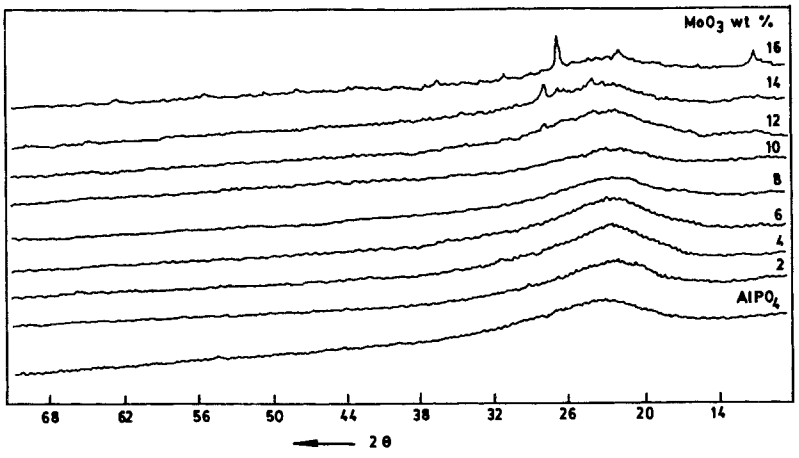


Fig. 1. X-ray diffractograms of $MoO_3/AlPO_4$ and $AlPO_4$ samples.

Table 1
Composition, oxygen and ammonia uptakes, crystallite size, surface coverage, methanol conversion rate and product selectivities of $MoO_3/AlPO_4$ catalysts

Catalyst composition MoO_3 (wt%) on $AlPO_4$	O_2 uptake (ml STP/g)	NH_3 uptake (mol/g)	BET surface area (m^2/g)	Crystallite size [a] (Å)	Surface coverage [b] (%)	CH_3OH conversion rate (mol/h/g-cat $\times 10^{-3}$)	Selectivity (%)	
							DME	HCHO
0	–	612	63	–	–	10.9	100	–
2	0.99	372	49.9	13.7	0.27	21.2	69.7	30.4
4	1.33	283	40.2	20.6	0.45	25.3	61.0	36.1
6	1.67	232	37.0	24.6	0.61	32.6	58.2	39.0
8	1.43	178	35.5	38.2	0.55	26.5	60.6	33.9
10	1.17	312	34.0	58.5	0.46	22.0	61.9	32.7
12	0.92	335	32.8	89.00	0.38	17.60	64.3	32.0
14	0.77	351	30.7	124.5	0.34	16.6	68.0	30.0
16	0.69	409	25.8	185.0	0.31	15.5	70.0	25.7

[a] Crystallite size $= (6 \times 10^4)/(M \times \rho)$, where M is the EMA per g of MoO_3, ρ is the density of MoO_2 g/cm^3.
[b] Defined as EMA/surface area of reduced catalyst (equivalent molybdena area (EMA) = O_2 uptake (ml STP)/g $\times$ 13.6 (factor) [9]).

sional growth of molybdena crystallites. The decline in reducibility of MoO_3 in the post monolayer region may be due to the inaccessibility of all the molybdenum oxide units in the bulky crystallites to the reducing gas. It can be noted that the crystallite size is small at lower MoO_3 loadings and increases with molybdena loading upto 180 Å. These values are in conformity with the XRD results where at higher loadings small peaks corresponding to MoO_3 bulky crystallites were detected. The amount of active component required to react with all the surface hydroxyl groups of support to form a uniform layer is known as monolayer loading. The 6 wt% loading can be considered as monolayer capacity of $AlPO_4$ support for MoO_3. This is about 60% of the theoretical monolayer capacity based on the theoretical requirement of 0.16 wt% of MoO_3 per m^2 of support surface [18]. The monolayer may be depicted as a patchy one with islands of Mo-oxide units attached to the active support surface by a strong chemical force. Any further addition of active component leads to multilayer growth on the monolayer and eventual formation of bulky crystallites while a fraction of the support surface remains bare.

The ESR spectra of the reduced $MoO_3/AlPO_4$ catalysts recorded at 25°C are presented in fig. 2. Due to short spin lattice relaxation times arising from less extent of tetragonal distortion a very broad resonance absorption attributed to Mo^{5+} could be seen. No hyperfine splittings due to ^{95}Mo and ^{97}Mo ($I = 5/2$) isotopes were observed because the natural abundance of these isotopes is only 25%. The axially anisotropic g values, peak to peak line widths (ΔH) and α which gives the electron density in d_{xy} orbital of Mo^{5+} for all catalysts have been calculated. The above said parameters for monolayer loaded catalyst are $g_{\|} = 1.911, g_{\perp} = 1.955$, $\Delta H = 74, 1/\alpha = 0.565$. The g tensor of Mo^{5+} has axial symmetry with parallel component $g_{\|} = g_{zz}$ smaller than $g_{\perp} = g_{xx} = g_{yy}$. The intensities of the peaks corresponding to Mo^{5+} calculated from ESR signals is plotted as a function of molybdena composition in fig. 3. The intensity is maximum at monolayer loading of 6 wt% MoO_3 and decreased with further increase in loading which may be due to presence of bulky MoO_3 crystallites which get reduced to a lesser extent. These results are in conformity with LTOC results.

The acidities of the $AlPO_4$ and $MoO_3/AlPO_4$ catalysts determined from ammonia chemisorption are shown in table 1. At low and high molybdena loadings the acidities of $MoO_3/AlPO_4$ catalysts are high, because at low molybdena loadings a large number of surface hydroxyl groups of $AlPO_4$ will be left unreacted resulting in high acidity. At medium molybdena loadings the acidities of the catalysts are low because the molybdena reacts with increased quantities of surface hydroxyl groups of $AlPO_4$ support and at these loadings only the Lewis and Brønsted acidities of molybdena and OH group of $AlPO_4$ inaccessible to molybdena exist. However, at higher molybdena loadings again an increase in acidities of catalysts could be seen because bulk MoO_3 is formed at the expense of small amounts of dispersed molybdena species. Bulk MoO_3 is also known [19] to exhibit acidity resulting in increased total acidity of the catalysts at higher loadings.

The methanol conversion rate and selectivities of HCHO and DME are pre-

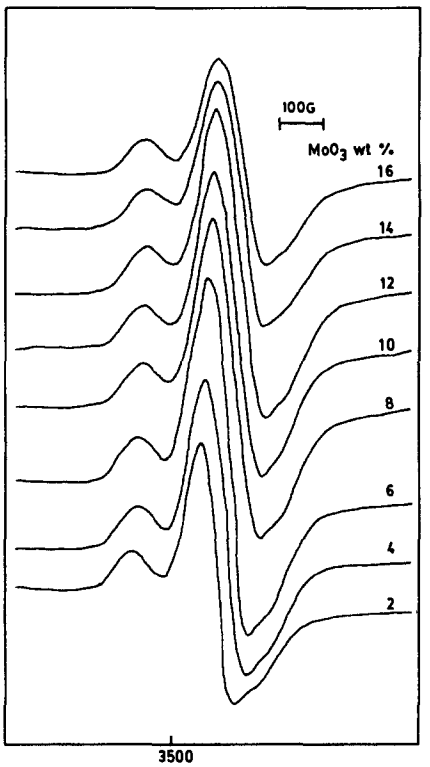
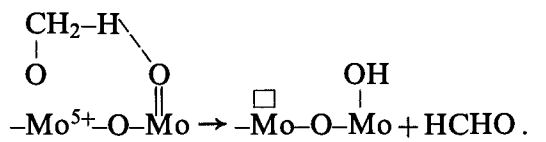


Fig. 2. ESR spectra of reduced $MoO_3/AlPO_4$ catalysts.

sented in table 1. It can be observed that at monolayer loading of 6 wt% MoO_3 there is maximum dehydrogenation activity which may be attributed to highly dispersed active molybdena phase. On pure $AlPO_4$ total selectivity to the dehydration product, DME, was observed with very low activity. However, reducible interacted species of MoO_3 and $AlPO_4$ impart dehydrogenation activity to the catalysts. Thus, maximum selectivity to HCHO is associated with maximum O_2 uptake. Both unsupported and supported molybdena act as a dehydrating as well as dehydrogenating catalyst [20].

A close look at table 1 reveals that the rate of methanol conversion directly correlates with O_2 uptakes indicating that oxygen chemisorption is a measure of active sites upon which partial oxidation of methanol takes place. Methanol is known to dissociatively chemisorb on dioxomolybdenum species,



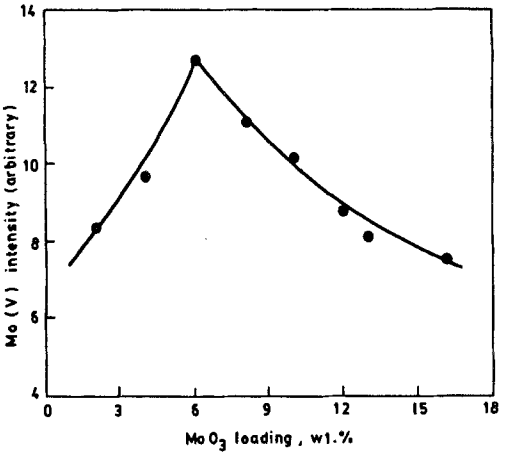
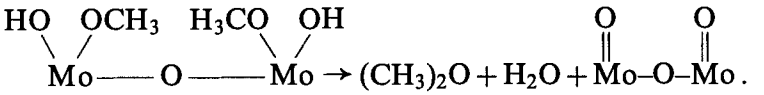


Fig. 3. Variation of ESR signal intensity with Mo loading on $AlPO_4$.

The multifunctionality of both acidic ("O" vacancy) and basic (oxygen) sites are required to produce formaldehyde [21]. Bridge oxygen vacancy sites were found to be responsible for higher order product DME.

The formation of dimethyl ether needs no oxidative dehydrogenation and leaves the catalyst in its original oxidized state. Its formation is more probable (compared to other products) at high conversion when less oxygen is available on the surface than at low conversion,



The cyclic mechanism proposed for CH_3OH oxidation to formaldehyde on MoO_3 involves all the molybdenum oxidation states like +4, +5, +6 [22]. It has been found that at steady state MoO_3, Mo_2O_5, MoO_2 all are active and highly selective for HCHO. In $MoO_3/AlPO_4$ catalysts both the types of molybdenum species may be present to different extent depending upon the MoO_3 loading resulting in different selectivities to formaldehyde and dimethyl ether. The molybdena species responsible for oxidative dehydrogenation of methanol to formaldehyde appears to be maximum at the monolayer loading of 6 wt% MoO_3 on $AlPO_4$.

4. Conclusions

Molybdena is well dispersed on $AlPO_4$ support. Monolayer loading capacity of $AlPO_4$ for MoO_3 is 6 wt%. This is equivalent to 60% of the theoretical requirement. Reaction of methanol over $MoO_3/AlPO_4$ catalysts yields both dimethyl ether and

formaldehyde. Methanol conversion rate as well as selectivity to formaldehyde is maximum on monolayer catalyst. On $AlPO_4$ methanol converts to dimethyl ether (dehydration product) only. Upon loading of MoO_3 on $AlPO_4$ methanol conversion rates increased by 2 to 3 times with formaldehyde selectivities ranging from 25 to 40%.

Acknowledgement

Thanks are due to Dr. A.V. Rama Rao, Director, IICT for his encouragement. Mrs. Jhansi Lakshmi wishes to thank the University Grants Commission, New Delhi for the award of a Senior Research Fellowship.

References

[1] F.E. Massoth, in: *Advances in Catalysis*, Vol. 27, eds. D.D. Eley, H. Pines and P.B. Weisz (Academic Press, New York, 1978) p. 265.
[2] J. Haber, *The Role of Molybdenum in Catalysis* (Climax Molybdenum Co., London, 1981).
[3] T.C. Ho, J. Catal. 138 (1992) 357.
[4] S.M.A.M. Bouwens, A.M. van der Kraan, V.H.J. de Beer and R. Prins, J. Catal. 128 (1991) 559.
[5] J.M. Lewis and R.A. Kydd, J. Catal. 136 (1992) 478.
[6] A. Blanco, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and A.A. Romero, J. Catal. 137 (1992) 51.
[7] W. Zmierczak, Q. Qader and F.E. Massoth, J. Catal. 106 (1987) 65.
[8] D.S. Kim, K. Seqawa, J. Soeya and I.E. Wachs, J. Catal. 136 (1992) 539.
[9] K.V.R. Chary, H. Ramakrishna, K.S. Rama Rao, G. Muralidhar and P. Kanta Rao, Catal. Lett. 10 (1991) 27.
[10] G. Muralidhar, B.E. Concha, G.L. Bartholomew and C.H. Bartholomew, J. Catal. 89 (1984) 274.
[11] W.S. Millman and W.K. Hall, J. Catal. 59 (1979) 311.
[12] C. Louis, J.M. Tatibouët and M. Che, J. Catal. 109 (1988) 354.
[13] W.L. Kehl, US Patent 4 080 311 (1978).
[14] B.S. Parekh and S.W. Weller, J. Catal. 47 (1977) 100.
[15] L. Jhansi Lakshmi, K. Narsimha and P. Kanta Roa, Appl. Catal. 94 (1993) 61.
[16] L. Jhansi Lakshmi and P. Kanta Rao, Appl. Catal., in press.
[17] C.L. Young, C.H. Yang, S.J. De Canio, M.S. Patel and D.A. Storm, J. Catal. 113 (1988) 307.
[18] G.C. Bond, S. Flamerz and L.V. Wijk, Catal. Today 1 (1987) 229.
[19] A. Gervasini and A. Auroux, J. Catal. 113 (1991) 190.
[20] G.C. Bond, S. Flamerz and R. Shukri, Faraday Discussions Chem. Soc. 87 (1989) 65.
[21] J.S. Chung, R. Miranda and C.O. Bennet, J. Catal. 114 (1988) 398.
[22] T.-J. Wang and J.H. Lunsford, J. Catal. 103 (1987) 55.