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INFLUENCE OF MOLYBDENA ON THE DISPERSION AND ACTIVITY OF VANADIA IN $V_2O_5/\gamma\text{-}Al_2O_3$ CATALYSTS **

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The influence of molybdenum oxide on the dispersion and activity of vanadium oxide supported on alumina was investigated. A series of MoO_3 catalysts were prepared using monolayer $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts by impregnation method. The catalysts were characterized by X-ray diffraction and oxygen chemisorption at −78 °C. The catalytic properties were evaluated for the vapour-phase oxidation of methanol. The addition of MoO_3 to $V_2O_5/\gamma\text{-}Al_2O_3$ results in the decrease of dispersion of vanadia and also the activity for the oxidation reaction. However, the selectivity of formaldehyde was found to increase with MoO_3 loading indicating that MoO_3 created additional sites for partial oxidation reaction.

1. Introduction

Supported vanadium oxides have been widely investigated as they catalyse a number of selective oxidation [1–3], ammoxidation reactions [4–6] as well as for the reduction of NO by NH_3 [7]. The catalytic properties of vanadia in the oxidation reactions are strongly influenced by the method of preparation, nature of support and the type of promoter. It has been shown that the addition of molybdena improves the selectivity of vanadia catalysts [8]. The presence of molybdena in the catalyst system induces changes in the phase composition of surface layers [8,9]. Recently, Satsuma et al. [10] have reported the surface active sites of $V_2O_3\text{-}MoO_3$ catalysts as determined by NO-NH_3 rectangular pulse method.

Previous studies from our laboratory showed that V_2O_5 forms a monolayer on the surface of $\gamma\text{-}Al_2O_3$ support at 10% w/w of V_2O_5 [11]. Evidence for the monolayer formation of vanadia was also provided by the characterization results

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using ^{51}V solid state NMR spectroscopy [12], radial electron distribution (RED) analysis [13], X-ray diffraction and low temperature oxygen chemisorption [11]. Further the presence of two types of chemically distinct V^{4+} species was observed by ESR investigations of these catalysts [14]. In the present communication we report the results of the influence of molybdenum oxide on the dispersion of V_2O_5 on Al_2O_3 and its consequential effect on the activity and the selectivity of the catalysts towards partial oxidation of methanol to formaldehyde.

2. Experimental methods

The catalyst preparation involves two steps. In the first step a 10% V_2O_5 (w/w) supported on γ-Al_2O_3 was prepared by wet impregnation of Al_2O_3 support using an aqueous solution containing ammonium metavanadate. The catalysts were dried and calcined in air at 500 °C for 6 h. In the second step a series of V_2O_5-MoO_3 catalysts with varying MoO_3 content from 1–5 wt% were prepared by wet impregnation of previously prepared 10% V_2O_5/γ-Al_2O_3 catalyst using stoichiometric amounts of an aqueous solution containing ammonium heptamolybdate. The samples were dried and calcined for 6 h at 500 °C. Oxygen chemisorption experiments were performed on pre-reduced catalysts using a static high vacuum adsorption apparatus following the method of Parekh and Weller [15]. Briefly, the catalyst sample was reduced at 500 °C in a continuous flow of hydrogen (40 ml/min) for 6 h and evacuated at the same temperature for an hour prior to oxygen adsorption at −78 °C. The amount of oxygen chemisorption was determined by the difference between two oxygen adsorption isotherms at −78 °C. The details of experimental procedure are described elsewhere [11].

A flow micro-reactor operating at atmospheric pressure was used for the catalytic oxidation of methanol to formaldehyde. About 0.25 g of the catalyst plugged with glass wool in a glass reactor was fed with methanol vapour at 175 °C. The feed gas (air) was passed through two saturators containing methanol at a flow rate of 40 ml/min. The reaction products, formaldehyde and dimethyl ether were analysed by an on-line gas chromatograph using a column containing 10% carbowax 20M on chromosorb.

3. Results and discussion

Results of oxygen chemisorption by various V_2O_5-MoO_3/γ-Al_2O_3 catalysts were plotted as a function of MoO_3 loading in fig. 1. It is clear that oxygen uptake decreases linearly with the increase of MoO_3 content in the catalyst. The dispersion of vanadia was calculated by the number of V-oxide units present in the sample and number of 'O' atoms chemisorbed, with the assumption that one

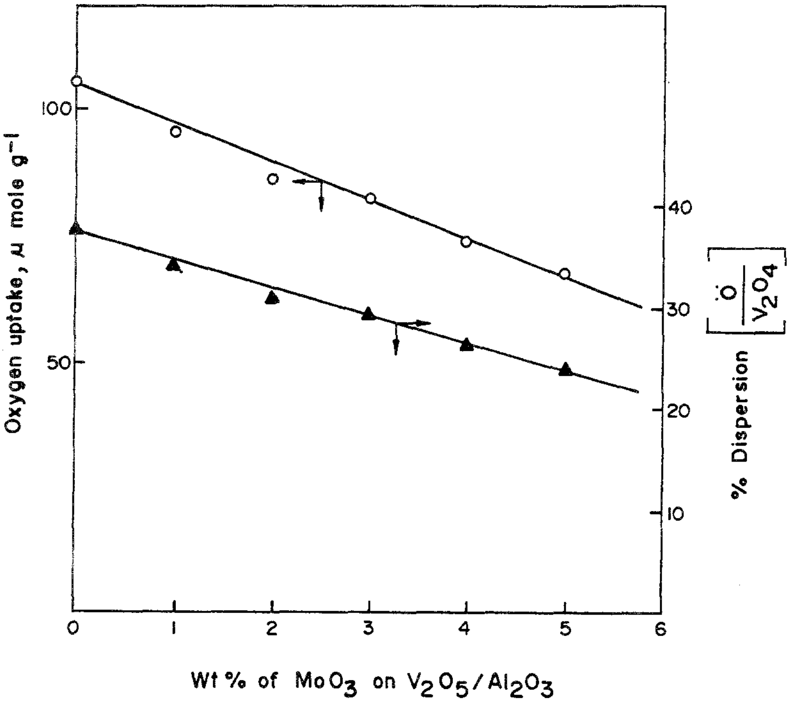

Fig. 1. Oxygen uptake and dispersion of vanadia as a function of MoO_3 loading on V_2O_5/γ-Al_2O_3.

'O' atom corresponds to two V atoms as per the equation.

$$V_2O_5 + H_2 \rightarrow V_2O_4 + H_2O$$

$$V_2O_4 + O \rightarrow V_2O_5.$$

The dispersion of vanadia is found to decrease linearly with increase of MoO_3 content (fig. 1). Powder X-ray diffraction patterns of these samples reveals that no characteristic XRD peak is found either due to V_2O_5 or MoO_3 or a new compound formed, indicating the amorphous nature of these catalysts. However, it can not rule out the possibility of formation of intermediate surface compounds such as V_2MoO_8 or $V_9Mo_6O_{40}$ [16] etc. with crystallite size smaller than 40 Å which is beyond the detection capacity of X-ray diffraction method. The percentage conversion of methanol during partial oxidation is plotted as function of MoO_3 loading in fig. 2. The percentage conversion decreases as a function of MoO_3 content. This further supports the decrease of dispersion of vanadia with addition of MoO_3. The selectivities of formaldehyde (due to partial oxidation) and dimethyl ether (due to dehydration) during methanol oxidation reaction at 175 °C by various catalysts are plotted as a function of MoO_3 content in fig. 3. The selectivity of formaldehyde is found to increase linearly with MoO_3 content in the catalyst. However, the selectivity for dimethyl ether decreases linearly as a function of MoO_3. Under the similar experimental conditions V_2O_5/Al_2O_3 cata-

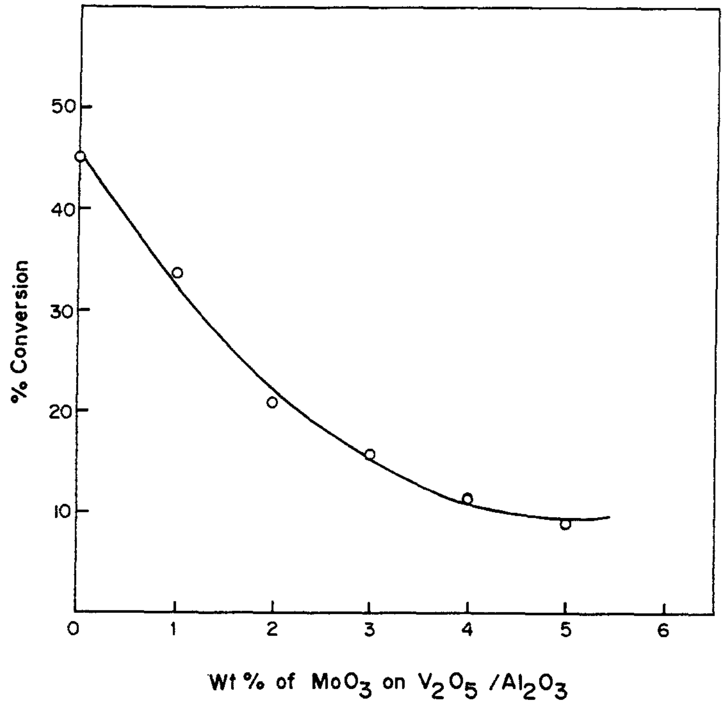

Fig. 2. Percentage conversion of methanol as a function of MoO_3 loading on V_2O_5/γ-Al_2O_3.

lysts have shown both dehydration and partial oxidation functionalities. However, with the increase of MoO_3 loading in the catalyst, the selectivity of formaldehyde increases. It is also observed that the selectivity of MoO_3-V_2O_5/Al_2O_3 catalysts towards formaldehyde is higher than the corresponding V_2O_5/Al_2O_3 catalysts. It is instructive to consider what can possibly happen to the molybdena added to the V_2O_5/Al_2O_3 monolayer catalysts. Three possibilities can be conceived – (i) part of the added molybdena can interact with hydroxyl groups on alumina left after vanadia impregnation, because it is well known that molybdena interacts with the hydroxyl groups on alumina [17,18], (ii) the molybdena may cover part of the monolayer vanadia, (iii) the molybdena might interact with vanadia to form a surface compound which is difficult to reduce. Now let us consider the influence of the above possibilities on oxygen uptake. According to the first possibility the oxygen chemisorption should increase as it is known that the reduced molybdena on aluminum oxide chemisorb oxygen [15]. It is experimentally found that oxygen chemisorption decreases with the addition of molybdena. Therefore, the first possibility seems to be ruled out if the molybdena reduces as does the vanadia. The second possibility predicts a more or less constant oxygen chemisorption with the increase of molybdena, if the molybdena covering V_2O_4 units chemisorb oxygen, otherwise a decrease is visualised. The third possibility indicates a decrease in oxygen chemisorption since the surface

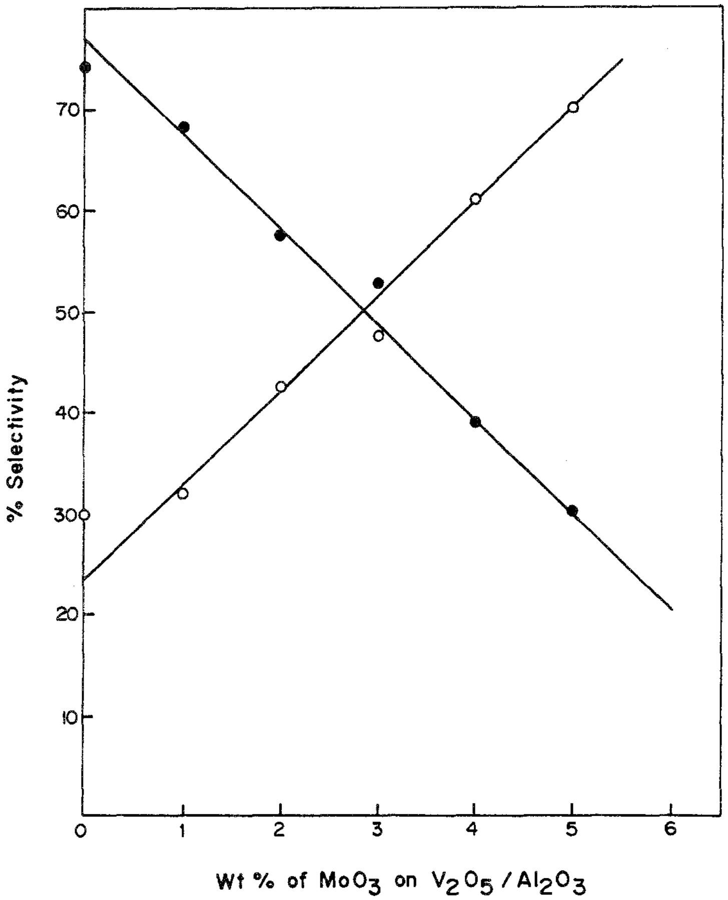

Fig. 3. Selectivity of formaldehyde and dimethyl ether as a function of MoO_3 loading on V_2O_5/γ-Al_2O_3. a) O-formaldehyde, b) O-dimethyl ether.

compound formation is expected to decrease the dispersion of both the components. In reality all of the three possibilities may simultaneously occur to different extents. The decrease in oxygen chemisorption indicates that the third possibility is the most important one. However, one can not rule out the possibility that a small fraction of molybdena interacts with the hydroxyl groups of bare alumina surface left out on the monolayer V_2O_5/Al_2O_3. Because of this phenomena the increase in oxygen chemisorption is expected to be small. Therefore, the net decrease in oxygen chemisorption led us to believe that the third possibility predominates. The increase of formaldehyde selectivity with MoO_3 content might be due to the promotion by Mo species. The decrease in dehydration activity with the addition of molybdena might be a consequence of decrease in acidity of the support as a result of elimination of hydroxyl groups. Thus addition of molybdena to V_2O_5/Al_2O_3 catalyst considerably increases the selectivity to formaldehyde during the partial oxidation of methanol.

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