Oxygen Chemisorption & X-Ray Diffraction Studies on Molybdena-Titania Catalysts

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A series of titania-supported molybdena catalysts with various Mo loadings ranging from 2 to 12 wt% have been prepared and characterized by means of low temperature oxygen chemisorption (LTOC) and X-ray powder diffraction methods. X-ray data indicate that the amount of anatase and rutile forms of titania support undergo changes with increase in Mo concentration. The LTOC results suggest the formation of monolayer MoO_2 patches at about 6 wt% Mo and the anataserutile phase transformations are also found to correlate with this loading on the support.

Titania is an important catalyst material not only because of its effectiveness in photoassisted reactions but also in the enhancement of activity and selectivity of transition and noble metals when used as a support[1,2]. The structural transformations of vanadia − titania catalysts have been extensively investigated by several workers using XRD, EPR, ESCA and other techniques[3,4]. Similar studies on molybdena-titania catalysts are very limited. In the present investigation an attempt is made to characterize the $MoO_3 - TiO_2$ catalysts having various amounts of molybdena in their unreduced and reduced states. In particular, the effect of loading on the structure of the support as well as the dispersion of active component on support surface have been looked into using low temperature oxygen chemisorption (LTOC) and XRD techniques. The LTOC technique has recently been proved to be an important method for measuring specific catalytic surface areas of supported molybdenum oxides and sulfides[5,6].

Materials and Methods

Titanium dioxide (Harshaw-Ti-0720; surface area 169 m^2g^{-1}; pore volume 0.36 ml g^{-1}) supported catalysts with Mo loadings ranging from 2 to 12 wt% were prepared by incipient wetting technique. An appropriate amount of ammonium heptamolybdate (spectroscopic grade, JT Baker, USA) corresponding to the desired Mo loading on the support was dissolved in that volume of water which corresponded exactly to the total pore volume of the quantity of support used for impregnation. The ammonium heptamolybdate solution thus prepared was added to the support, well mixed for 30 min and then allowed to stand for 1 hr. The impregnated samples thus prepared were dried at 120°C for 16 hr and calcined at 540°C for 12 hr in an open air furnace.

LTOC measurements were performed at − 78°C on catalysts, prereduced in a flow of hydrogen (35 ml/min) at 500°C for 6 hr, in a specially designed cell attached to a static volumetric high vacuum system. The details of experimental procedure have been given elsewhere[7]. After the chemisorption experiment BET surface area of the catalyst was determined by N_2 adsorption at − 196°C and the sample was saved after evacuation for XRD measurements. The X-ray diffractograms were recorded on a Philips PW 1051 diffractometer using Ni-filtered CuK_α radiation.

Results and Discussion

Oxygen uptake values and BET surface areas of the reduced MoO_3-TiO_2 catalysts as a function of Mo loading are presented in Fig. 1. Oxygen uptake (g^{-1} catalyst) increases linearly as a function of Mo loading upto about 6 wt% Mo and thereafter levels off with further loading. On the other hand, BET surface areas of the reduced catalysts decrease linearly with Mo loading upto 12 wt%. The saturation in oxygen uptake at 6 wt% Mo loading is indicative of completion of monolayer coverage of the active support surface by Mo oxide phase. A similar trend in oxygen uptake capacities and BET surface areas were also observed on $MoO_3 - Al_2O_3$ (ref. 6), $MoO_3 - C$ (ref. 8) and $MoO_3 - ZrO_2$ (refs. 9, 10) catalyst systems at different Mo loading. The initial increase and subsequent levelling off in oxygen uptake capacities of the catalysts as a function of Mo loading on different supports are interpreted in terms of Hall's patch model[11]. Based on this model, it is proposed that at low Mo loading small two-dimentional patches of Mo oxide and Mo in octahedral coordination are formed on the support surface. The same structure, however, remains on the support surface as small patches of MoO_2 with coordinately unsaturated Mo sites (CUS) upon reduction in hydrogen. The CUS are the locations on which oxygen chemisorption takes place at

low temperatures[12]. As the Mo loading increases the number of these MoO_2 patches increases with attendant increase in the number CUS upto the monolayer level. Hence, oxygen uptake increases linearly with Mo loading upto the monolayer level. Beyond monolayer level these patches grow three-dimensionally, thus decreasing the dispersion of Mo oxide on the support surface. This growth in size of small patches rather in number is expected not to add new CUS per unit of Mo as a function of Mo loading. Therefore, saturation in oxygen uptake beyond monolayer is observed. An important point to note here is that the LTOC technique clearly indicates the Mo loading where the monolayer formation attains completion.

X-ray diffractograms of the unreduced and reduced $MoO_3 - TiO_2$ catalysts are shown in Figs 2 and 3 respectively. In accord with its X-ray profile, the pure TiO_2 support used in this study contains about
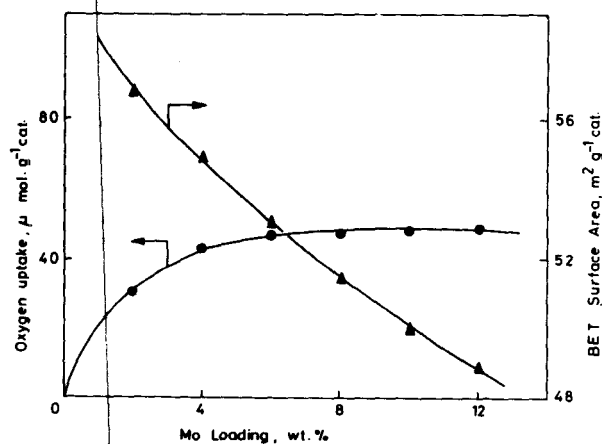

Fig. 1 — Oxygen uptake at $-78°C$ and BET surface area of the catalysts as a function of Mo loading.

85% anatase and 15% rutile phases of TiO_2 but badly crystallized ones. The most intense peaks at $25.3°(2\theta)$ corresponding to diffraction by planes (101) of anatase and at $27.4°(2\theta)$ corresponding to the diffraction by planes (110) of rutile are detected in all the samples[13]. The other prominent observable peaks in the spectra are the triplet at $37.4°(2\theta)$ due to diffraction by planes (103), (004) and (112), as well as the doublet at $53.9°(2\theta)$ due to the diffraction by planes (105) and (211) of anatase, but these are not well-defined indicating lack of good crystallinity. No XRD lines due to MoO_3 phase and also due to compound formation between MoO_3 and TiO_2 are observed in the spectra.

As can be seen from Fig. 3 the prominant peak at $25.3°$ due to the anatase phase is predominant in all the spectra. The intensity of the peaks are due to rutile phase decreases with Mo loading upto 6 wt% Mo, where the formation of monolayer is observed from LTOC data (Fig. 1), and then starts rising slowly with further Mo loading upto 12 wt%. However, in the case of unreduced samples (Fig. 2) no definite trend in transformation of anatase – rutile phase can be seen in the XRD. This is an interesting observation in this study, but the real significance of these results are not clearly known at present. Bond et al.[3] have investigated some of the physicochemical properties of $V_2O_5 - TiO_2$ catalysts using a number of anatase and rutile containing catalysts differing in calcination temperatures and concentration of impurities such as Na^+ and SO_4^{2-}. They reported that during the transformation of anatase to rutile, the vanadia phase was reduced and became incorporated in the rutile structure as $V_xTi_{(1-x)}O_2$ (rutile solid solution). According to Vejux and Courtine[4] the simultaneous reduction of
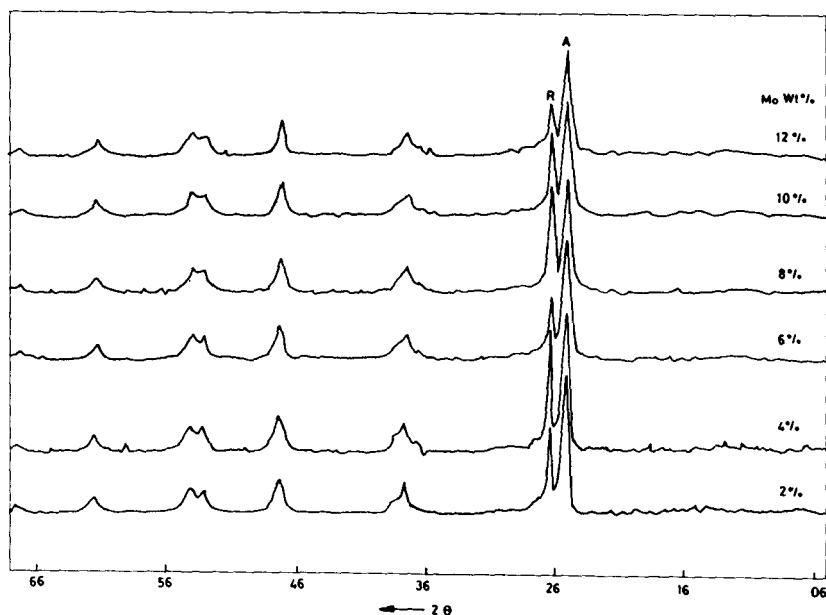

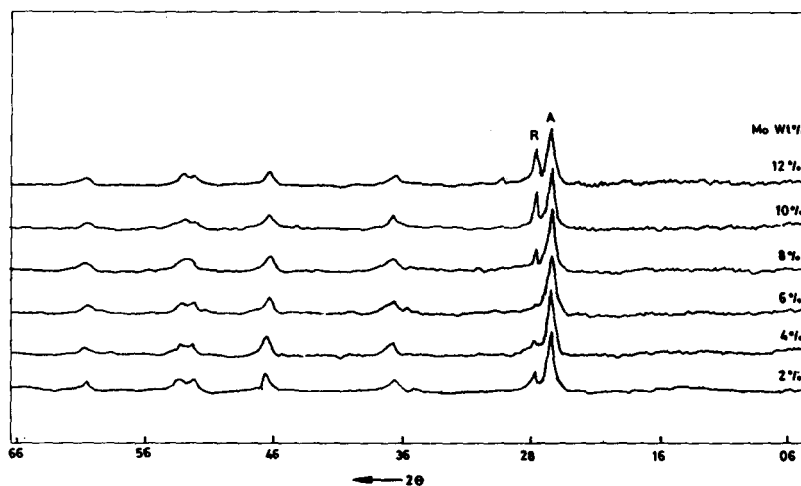Fig. 2 — X-Ray diffractograms of unreduced $MoO_3 - TiO_2$ catalysts.

Fig. 3 — X-Ray diffractograms of reduced $MoO_3 - TiO_2$ catalysts.

V_2O_5 and transformation of anatase into rutile are topotactic reactions activated by the remarkable fit of the crystallographic patterns of V_2O_5 and anatase phase of TiO_2. With respect to MoO_3, Bordes et al.[14] have claimed that the (110) and (010) planes of MoO_3 can be 'anchored' on the (010) and (001) planes of anatase, thus suggesting facile growth of reduced MoO_3 layers on these faces of TiO_2 crystallites. Chary et al.[15] in their recent study on $V_2O_5 - TiO_2$ catalysts have also observed this anomalous occurrence of the anatase-rutile phase transformation, classically observed at much higher temperature than 500°C employed in the present study. The similar detailed studies on $MoO_3 - TiO_2$ catalysts are scarce in the literature. However, it is worth assuming at present that a similar mechanism operates in the $MoO_3 - TiO_2$ catalyst system, and the present results can also be explained with the help of same concepts proposed for $V_2O_5 - TiO_2$ catalysts. Vanadium pentoxide and MoO_3 form layer structures on the anatase phase of TiO_2 support surface because of the remarkable fit of their crystallographic planes[13]. Thus the present X-ray study on the MoO_3 catalysts once again points to the existence of so called 'interfacial synergetic effect' — a catalysis of the topotactic reduction of MoO_3 and a significant lowering of the activation energy for the anatase-rutile transformation which develops concurrently and cooperatively with loading.

Acknowledgement

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