The Use of X-ray Diffraction for Solid and Catalyst Characterization

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Abstract: The morphology of silica supported catalysts, prepared by impregnation of ammonium heptamolybdate (AHM) and for various weight loadings up to 35 wt%, was studied using X-ray diffraction. In addition to the orthorhombic phase, the behavior of the rarely studied hexagonal phase was fully characterized. All morphologies of silica supported MoO₃ appear to be thermodynamically driven. For high loaded catalysts there appeared three states: a metastable sintered hexagonal state and a well dispersed hexagonal state at moderate temperature calcinations (300°C), and the sintered orthorhombic state at high temperature (500°C). Whereas the sintered orthorhombic phase is detected by XRD at loadings in excess of 1.1 atom Mo/nm², the well dispersed hexagonal phase is not even until 4.0 atoms Mo/nm². It is possible to produce the well dispersed hexagonal phase from the sintered orthorhombic phase with an ammonia impregnation and subsequent calcination at 300°C. The apparently higher dispersion of the hexagonal phase may arise from some role of ammonia which results in a stronger MoO₃-surface interaction.

1. Introduction

Supported molybdenum trioxide catalysts have a vast abundance of industrial uses. Continual effort is put into characterization of the types of Mo oxide species which exist over various supports, their stability, and the optimal preparation techniques to obtain them. Various morphology influencing factors have been proposed for the impregnation and calcination steps of preparation[1-6]. A recent series of comprehensive works performed with Raman and UV over a number of supports and supported oxides and with a wide array of preparation procedures, including all those listed above, have synthesized many of these concepts into a general theory. First, it was postulated that the surface species of molybdenum present in the air exposed, hydrated catalyst is only a
function of pH in the hydrated layer, which can be calculated from the point of zero charge (or "pzc," which is equivalent to the isoelectric point in the absence of specific adsorption) of the oxide, adjusted for the surface composition of molybdenum oxide or other oxide. The types of surface species are independent of the preparation procedure and complex. Second, the amount of material deposited in well dispersed form depends on the number of reactive hydroxyl groups present.

The present work with silica supported MoO₃ has centered on investigating and exploiting the behavior of the little studied hexagonal phase of MoO₃.

2. Experimental

For high surface area catalysts, Degussa Aerosil (fumed) silica was used. The powder was 99.8% pure with traces of Al₂O₃, Fe₂O₃, TiO₂ and HCl. Na and Ca impurities in fumed silica are typically on the order of 2 ppm. The silica had a surface area of 380 ± 30 m²/gm. To increase its bulk density, it was washed with deionized water and vacuum dried overnight at 40°C and then air dried at 110°C for 12 hr. Ammonium heptamolybdate (IV) tetrahydrate (NH₄)₆Mo₇O₃₄·4H₂O,(AHM), was purchased from Aldrich. High loading samples were prepared by physically mixing the desired amount of dry support and precursor, and then adding sufficient water to reach incipient wetness. This technique circumvents the problem at high loadings that the amount of water added to the SiO₂ is insufficient to dissolve all of the AHM. This is typically resolved by performing successive impregnations with a lower concentration solution, whereas a single step was employed here. Acid or base impregnations were conducted with concentrated nitric acid (2.5 N) or ammonium hydroxide (5 N) in place of water. The acid preparation follows a standard procedure to produce hexagonal MoO₃. MoO₃ weight loadings varied through 35.3 wt% MoO₃. The most common weight loading studied, 26.7 wt%, corresponds to a surface loading of 4 Mo atoms/nm². The slurries were thoroughly stirred and dried in air Overnight, after they had been spread in a thin layer onto a watch glass. When samples were placed in a small crucible at depths of 1-2 cm, the top 2-3 mm of the sample turned darker (green) than the bulk of the sample after drying and calcination. Presumably some of the Mo containing phase migrated toward the surface during pretreatment. The final distribution of material appeared homogeneous with the use of watchglasses. X-ray diffraction was performed on one of two Siemens D 5000 diffractometers, at either 50 or 40 kV and 30 mA. For most samples, approximately 50 mg of loosely packed powder was backfilled into a Zero background holder.
3. Results and discussions

The dispersion of the supported hexagonal MoO₃ phase, produced by a 300 °C calcination, was compared to that of the supported orthorhombic phase, produced at 500 °C by treating a series of increasingly loaded samples at the respective calcination temperatures, and observing the MoO₃ loading at which crystallinity is first evidenced by XRD. The weight percent loading at which the orthorhombic phase is observed is 8.8 wt%, which translates to a surface loading of 1.1 atom Mo/nm² and is in good agreement with the average of reported values of 1.1 atom Mo/nm². However, the weight percent loading at which hexagonal crystallites are detected is 26.7 wt% (4.0 atoms Mo/nm²). These two series of catalysts, analyzed on the same X-ray instrument, definitively illustrate a lesser degree of crystallinity for the hexagonal samples compared to the orthorhombic samples. The surface loading for the onset of crystallinity as detected by XRD is about 4 times higher for the well dispersed hexagonal phase than for the orthorhombic samples. The dramatic effect of ammonia on the dispersion of silica supported MoO₃ was found in a series of experiments with physical mixtures of silica and hexagonal MoO₃ (formed by the acid precursor and 300 °C calcination) and orthorhombic MoO₃. Equilibrium phase model of MoO₃ containing phases supported on silica is illustrated in following Fig.

The interconversion between the hexagonal and orthorhombic phases for 26.7 wt% samples, starting with the dispersed hexagonal phase, the small hexagonal peaks had diminished completely. The dramatic effect of ammonia on the dispersion of silica supported MoO₃ was found in a series of experiments with physical mixtures of silica and hexagonal MoO₃ (formed by the acid precursor and 300 °C calcination) and orthorhombic MoO₃. The reversibility of MoO₃ wetting of silica via ammonia reimpregnation and the hexagonal to orthorhombic phase change were examined in a
further XRD experiment. Finally, the redispersion mechanism of the sintered hexagonal and orthorhombic phases was investigated by preparing XRD samples of the ammonia reimpregnated samples just after drying. These data indicate that the equilibrium form of MoO₃ subjected to an ammonium solution and dried at 25°C is the ammonia rich precursor phases. The SiO₂ supported samples are mainly monoclinic, while small amounts of triclinic also form in the unsupported materials. The reammoniation of a hydrous orthorhombic MoO₃ to this extent has not been reported, although hexagonal MoO₃ has been produced from mixing MoO₃·2H₂O with excess liquid solution containing NH₄Cl. The pathway from the sintered hexagonal or orthorhombic phases to the well dispersed hexagonal phase. From there it becomes parallel to decomposition of the impregnated basic precursor.

4. Conclusions

All morphologies of silica supported MoO₃ appear to be thermodynamically driven. At low loadings there appears to be one stable morphology and dispersion, which agrees with recent in situ Raman data. For high loaded calcined catalysts there appear three states: a metastable sintered hexagonal state and a well dispersed hexagonal state at moderate temperatures, and a sintered orthorhombic state at high temperatures (≤400-500°C). It is possible to produce the well dispersed hexagonal phase from the sintered orthorhombic phase with an ammonia impregnation, which forms the ammonium rich precursor phases, and subsequent calcination at 300°C. The apparent increase in dispersion of the hexagonal phase may arise from some role of ammonia which results in a stronger MoO₃-SiO₂ interaction.

References