전구체의 pH와 소성 온도가 실리카에 담지된 몰리브드늄 활성 종에 미치는 영향

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The Effect of Precursor pH and Calcination Temperature on the Molybdenum Species over Silica Surface

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Abstract The morphology of silica supported MoO_3 catalysts, which was prepared by impregnation of ammonium heptamolybdate(AHM) with various surface loadings up to 4 atoms Mo/nm^2, was studied using x-ray diffraction(XRD). All morphologies of silica supported MoO_3 appear to be thermodynamically driven. For high loaded catalysts there appeared three states: a sintered and well-dispersed hexagonal state at moderate temperature calcination(300°C), and a sintered orthorhombic state at high temperature calcination(500°C). Whereas the sintered orthorhombic phase is detected by XRD at loadings in excess of 1.1 atom Mo/nm^2, the well-dispersed hexagonal phase is not detected even until 4.0 atomsMo/nm^2. The higher apparent dispersion of the hexagonal phase may arise from some role of ammonia which results in a stronger MoO_3-SiO_2 surface interaction.

요 약 암모늄헵타몰리브데이트(ammonium heptamolybdate, AHM)를 전구체로 제조한 실리카 담지 몰리브드늄(MoO_3/SiO_2) 촉매의 구조적 특성을 x-ray 회절기(XRD)를 사용하여 자세히 고찰하였다. 몰리브드늄의 표면담지량은 0.2부터 4.0 atoms Mo/nm^{2}로 변화하였으며, 담지촉매의 소성온도는 300~500°C로 변화하여 열역학적으로 형성 가능한 모든 몰리브드늄 산화물의 구조를 고찰하였다. 담지량이 큰 경우(4 atoms Mo/nm2), 300°C소성에서는 뭉쳐있거나 잘 분산된 hexagonal 형태의 결정체가 형성되었으며, 500°C로 소성온도를 증가하면 뭉친 orthorhombic 형태의 MoO_3 결정체가 형성되었다. 뭉친 orthorhombic 형태의 결정체는 담지량이 1.1 atom Mo/nm^2 이상이 되면 형성된 반면 잘 분산된 hexagonal 형태의 결정체는 가장 큰 표면 담지량 4.0 atoms Mo/nm^{2}에서도 고찰하기가 어려웠다. 이러한 hexagonal 결정체의 담체 표면에서의 높은 분산은 암모니아로 인한 몰리브드늄 산화물(MoO_3)과 실리카(SiO_2) 담체 사이의 강한 표면작용에 기인한 것으로 생각된다.

Key Words : Sintered hexagonal MoO_3, Sintered orthorhombic MoO_3, Well-dispersed hexagonal MoO_3

1. Introduction

A recent series of comprehensive works performed with Raman and UV over a number of supports and molybdenum oxide and with a wide array of preparation procedures have synthesized many of 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(pzc) of the oxide.

Second, the amount of material deposited in well dispersed form depends on the number of reactive hydroxyl groups present.

There is still dispute for the nature of surface species of molybdenum over silica. Many reports suggest that the monomeric surface species exist at low loadings, polymeric at intermediate loadings, and bulk at high loadings[1-4].

More recent in situworks[5], in which only the polymeric species is observed before the formation of the bulk form at higher loadings, have brought this idea into question. According to the general synthesis theory as pertains silica[6], the pzc of silica is very low and so low pH values of the hydrated layer are

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always present giving rise only to the polymeric, octahedral species. Tetragonal signals were shown to arise from $NaMoO_3$ and $CaMoO_4$ crystalline impurities stemming from Na and Ca impurities in precipitated silica.

In all of the above referred work, molybdenum trioxide is produced by a calcination at temperatures in excess of 450°C, which produces the well known and well-characterized orthorhombic MoO_3 phase. The hexagonal phase can be produced in unsupported or supported form by adding concentrated acid to an AHM solution and drying at room temperature; it is stable to approximately 420°C in air[7, 8].

The hexagonal phase is actually yet a precursor to the orthorhombic phase, for it possesses small amounts of ammonium ions and varying degrees of water as interstitial impurities, depending on preparation and drying conditions[7]. The parent compound of various partially dehydrated and deammoniated phases is thought to be ammonium decamolybdate, $(NH_4)Mo_5O_{18}H_5$[7], which can be written as $((NH_4)_4O) \cdot 10MoO_3 \cdot 5(H_2O)$ or $((NH_4)_2O)0.1 \cdot MoO_3.(H_2O)_{0.5}$ to emphasize the stability of the hexagonal MoO_3 framework. The hexagonal phase is observed on silica, with no acid, when the impregnated ammonium molybdate precursor is calcined at a temperature of 300°C, but in the absence of the silica support the bulk orthorhombic phase is formed instead[8], and without the ammonia containing precursor the orthorhombic form is produced by a 300°C calcination over silica[8]. The present work has investigated the effect of the precursor pH and calcination temperature on the surface species of molybdenum over silica support.

2. Experimental

For high surface area catalysts, Degussa Aerosil(fumed) silica which had a surface area of 380 ± 30 m^2/g was used. 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 12h. Ammonium heptamolybdate(IV) tetrahydrate(AHM), $(NH_4)_6 \cdot Mo_7O_{24} \cdot 4H_2O$, 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. 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 MoO_3[9, 10]. MoO_3 surface loadings varied through 4 atoms Mo/nm^2. The slurries were thoroughly stirred and dried in air overnight, after they had been spread in a thin layer onto a watch glass. Calcinations were performed at either 300 or 500°C in air for 2h.

Siemens D5000 x-ray powder diffractometer was used to identify the various crystalline phases. Catalyst samples were ground to a fine powder, for most samples approximately 50 mg(about 2 cm by 3 cm in area and 0.2 cm in thickness) of loosely packed powder was backfilled into a zero background holder. Measurements were done at 50 kV, 30 mA, and suitable two theta range(8-33), theta step(0.05) and count time(3 sec).

3. Results and Discussion

XRD studies for the effect of the precursor pH(acidic, neutral and basic precursor), various loading of precursor, and calcination temperature are shown in Figs. 1-3. For acidic precursor and 300°C calcination samples, bulk hexagonal phase of MoO_3 was observed at and above 0.8 atom Mo/nm^2(patterns (b), (c) and (d) in Fig. 1). For neutral precursor and 500°C calcination samples, bulk orthorhombic MoO_3
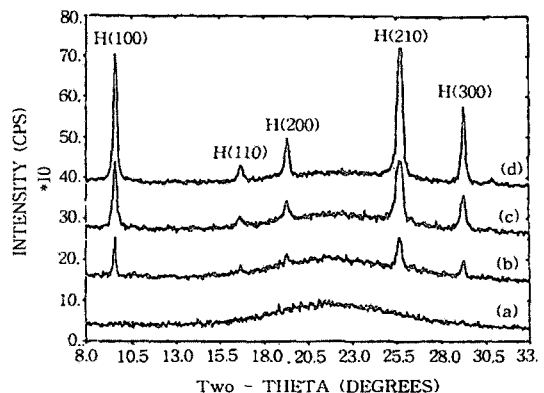

Fig. 1. XRD patterns of acidic precursor(AHM/SiO$_2$, impregnated with HNO$_3$(2.5 N)) and air calcination at 300°C for 2h: (a) 0.2, (b) 0.8, (c) 2.0, and (d) 4.0 atom Mo/nm^2.
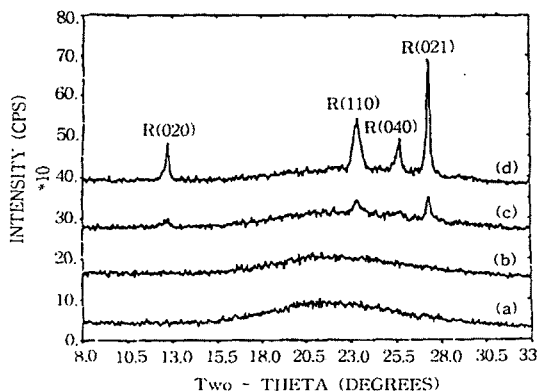
Fig. 2. XRD patterns of neutral precursor(AHM/SiO$_2$, impregnated with H$_2$O(pH 5)) and air calcination at 500°C for 2h: (a) 0.2, (b) 0.8, (c) 2.0, a nd (d) 4.0 atom Mo/nm^2.

Table 1. Supported Precursor and MoO$_3$ Patterns Resulting from Various Preparation Conditions for Supported MoO$_3$/SiO$_2$

Precusor	AHM/SiO$_2$		
Impregnation (Drying T)	Acida (25°C)	Waterb (25°C)	Basec (25°C)
Phase of MoO$_3$ Formed	Hexagonal	AHM	Triclinic
Calcination T (Time)	300°C(2h) in air	500°C(2h) in air	300°C(2h) in air
Phase of MoO$_3$ formed	Hexagonal	Orthorhombic	Dispersed Hexagonal

[a]Nitric acid, HNO$_3$(2.5 N), [b]Deionized water, H$_2$O(pH 5), [c]Ammonium hydroxide, NH$_4$OH(5 N)

was observed at and above 2 atom Mo/nm^2(patterns (c) and (d) in Fig. 2). And for basic precursor and 300°C calcination samples, both bulk hexagonal and orthorhombic phase of MoO$_3$ was observed only at 4 atom Mo/nm^2(pattern (d) in Fig. 3) and even them in small amounts. These three catalyst series will be designated as sintered hexagonal, SH, acid precursor with 300°C calcination, sintered orthorhombic, SO, neutral precursor with 500°C calcination, and dispersed hexagonal, DH, basic precursor with 300°C calcination. A summary of sample treatments and final phases of supported MoO$_3$ is given in Table 1.
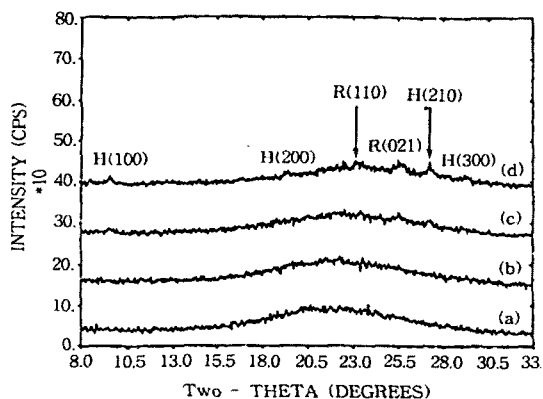

Fig. 3. XRD patterns of basic precursor(AHM/SiO$_2$, impregnated with NH$_4$OH(5.0 N)) and air calcination at 300°C for 2h: (a) 0.2, (b) 0.8, (c) 2.0, and (d) 4.0 atom Mo/nm^2.

The crystallite size of the fraction of crystallites observable by XRD was estimated from the Scherrer equation to be; 137Å(SH, 4 atom Mo/nm^2), 92Å(SH, 2 atom Mo/nm^2), 88Å(SO, 4 atom Mo/nm^2), 76Å (SO, 2 atom Mo/nm^2), and 59Å(DH, 4 atom Mo/ nm^2), using the full width at half maximum(FWHM) of the unsupported H(210)(hexagonal phase of MoO$_3$ crystal) and R(110)(orthorhombic phase of MoO$_3$ crystal) phases as standards for instrumental broadening. Since the integrated intensities of the DH(Fig. 3) are well below those of the sintered phases(Figs. 1 and 2), a good portion of the material also exists as very small(less than 40Å particles beyond the detection limit of XRD).

These could be amorphous or microcrystalline. No material was lost through volatilization in this series; a high degree of crystallinity can be re-established in the dispersed samples by subsequent high temperature treatment[11].

These three series of patterns from the same x-ray instrument using the same sample preparation and amount, definitely illustrate a lesser degree of crystallinity for the well-dispersed hexagonal samples(Fig. 3) compared to the sintered hexagonal and orthorhombic samples(Figs. 1 and 2). The surface loading for the onset of crystallinity as detected by XRD was about 4 or 2 times higher for the well-dispersedhexagonal phase than for the sintered hexagonal and orthorhombic phases, respectively.

Therefore, it is clear that except for the 0.2 atom Mo/nm^2, the trend in dispersion is SH<SO<DH.

4. Conclusions

The morphology of silica supported MoO_3 can be controlled at loadings at and over 0.8 atom Mo/nm^2 as follows: large hexagonal crystallites are produced with supported acid precursor at room temperature and with a 300°C air calcination for 2h, large orthorhombic crystallites are produced with supported neutral precursor by 500°C air calcination for 2h, and well dispersed MoO_3 and small hexagonal crystallites are formed with silica supported basic precursor by 300°C air calcination for 2h. At the low loading, 0.2 atom Mo/nm^2, final morphologies are independent of preparation technique.

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