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Spectroscopic Study on Mo Species of Mo-SBA-15 Synthesized Hydrothermally from H_2MoO_4 and Tetraethylorthosilicate

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Mo-SBA-15 (mesoporous silica SBA-15 containing molybdenum oxides) was hydrothermally synthesized with H_2MoO_4 , P123 as the template and tetraethylorthosilicate (TEOS). Mo species of precursor solutions and final products were characterized by Raman spectroscopy. Mo-P123 complexes are formed in solution by reaction of MoO_2Cl_2 dissolved in concentrated HCl and P123, but MoO_2Cl_2 does not react with TEOS. N_2 adsorption-desorption analysis and small angle X-ray diffraction reveal that the SBA-15 framework is formed in Mo-SBA-15 synthesized. This is explained that the Mo-P123 complexes act to form the SBA-15 framework as an effective template in the hydrothermal aging. The formed molybdenum oxides are expected to be dispersed in the SBA-15 channels and their structures are affected by the volume of concentrated HCl. UV-Vis spectroscopy indicates that the tetrahedrally coordinated mono-molybdates dominate in Mo-SBA-15 when 20 mL of concentrated HCl (HCl/ H_2MoO_4 weight ratio = 16.0) is added.

Keywords

Molybdenum dichloride dioxide, Molybdenum-surfactant complex species, SBA-15, Mono-molybdate

1. Introduction

Molybdenum base catalysts are interesting candidates for a large variety of catalytic reactions such as olefin metathesis, selective oxidation of alkane or alcohols and partial oxidation of alkene^{1,2}. The crystal structure of molybdenum trioxide was determined in 1931 by Brakken³ and independently by Wooster⁴ which gave a similar result. The structure was described as a layer structure in which each layer is built up of MoO_6 octahedra which were interconnected in one direction (c axis) by common edges and corners so as to form zigzag rows which, in turn, are link to each other via common corners in a perpendicular direction (a axis). The structure of MoO_3 evidently represents a transitional stage between octahedral and tetrahedral coordination. Thus, although usually regarded as an octahedral structure, it may alternatively be considered as built up of MoO_4 tetrahedra connected by the sharing of two oxygen corners with two neighboring tetrahedral to form the chains⁵. The crystals of MoO_3 usually grow in the form of needles with the direction of c axis as needle axis. Although octahedral coordination seems to be most common, tetrahedral coordination occurs frequently in oxygen compounds of hexavalent

molybdenum, such as in anhydrous ortho- and di-molybdates^{6,7} and also in some reduced molybdenum oxides⁸.

The structure of molybdenum oxide described above is regarded as normal thermodynamically stable phase which is called $\alpha\text{-MoO}_3$. Another phase of molybdenum trioxide was firstly detected in 1985 by Rao *et al.* who observed an electron diffraction pattern characteristic of the ReO_3 -type structure during a dehydration process of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ by an electron beam. $\beta\text{-MoO}_3$ is now known as metastable phase of molybdenum oxide, crystallized in monoclinic structure in which the MoO_6 octahedra share only the corners with each other. It transforms to $\alpha\text{-MoO}_3$ at around 400 °C. $\beta\text{-MoO}_3$ has a high catalytic activity in oxidation of methanol to formaldehyde and an ability to form lithium molybdenum bronzes as an active material for a lithium battery⁹. In order to reveal the partial oxidation activity of $\beta\text{-MoO}_3$ and also $\alpha\text{-MoO}_3$ transformed through silicomolybdic acid (SMA), we have been investigating on the properties of SMA and obtained that SMA on solids with high surface areas is a useful catalyst for the improvement of physico-chemical performance^{10)~12}. We have synthesized SMA using molybdic acid and SiO_2 . The impregnation of SMA and/or the solid state reaction between MoO_3 and SiO_2 in the presence of water vapor are also useful methods. When the molybdic acid is employed as Mo precursors, it is pointed out that

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the structure of the molybdic acid under several conditions is affected to the generation of SMA with active centers.

Structure of Mo(VI) species in aqueous solution changes upon pH value from MoO_4^{2-} at pH 8 to $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$ at pH ~1.5; however, at pH ~0.9, Mo(VI) tends to precipitate as white slurry because of zero point charge at concentration higher than 10^{-3} M ($1 \text{ M} = 1 \text{ mol} \cdot \text{dm}^{-3}$)¹³. Recently, Cruywagen *et al.* investigated the equilibrium of Mo(VI), derived from sodium molybdate, in highly concentrated perchloric acid and discovered the formation of $\text{MoO}_2(\text{OH})(\text{H}_2\text{O})_3^+$ at low Mo(VI) concentration, 10^{-3} M ¹⁴. From then, some research groups were trying to introduce Mo into SBA-15 in term of mono- or di-molybdate by using the above stated solution because these structures did not formed without the addition of alkaline ion (*i.e.* Na^+ , K^+) but only formed di- and poly-molybdates species in the presence of ammonium ion^{15,16}. We found a new way to prepare single Mo(VI) containing solution without using ammonium hepta molybdate (AHM), therefore avoiding the interference of ammonium ion into the formation of Mo structure, which is totally adapted to the low pH value of SBA-15 synthesis medium.

Zholobenko *et al.* used small angle X-ray diffraction and small angle neutron diffraction to study the initial stages of SBA-15 formation¹⁷. The formation of SBA-15 was divided into three stages: the presence of spherical of templates in the first stage, the formation of hybrid organic- inorganic micelles and the transformation from spherical to cylindrical micelles, finally, the aggregation of cylindrical micelles to two dimensional hexagonal structures leading to the precipitation of SBA-15. That was one of the very rare studies on SBA-15 formation mechanism in term of time-resolved observation. SBA-15 supported Mo catalysts have been still current of interest as the partial oxidation and polymerization catalysts^{18)~20)} but the catalysts were prepared the impregnation of AHM to SBA-15.

In this paper, we attempt to synthesize directly SBA-15 containing molybdenum oxides (Mo-SBA-15) from H_2MoO_4 , tetraethylorthosilicate (TEOS) and P123. Raman spectroscopy is very sensitive to analyze Mo species of solid and even in aqueous media. A few Raman studies, however, were reported. The details of behavior of Mo species are reported.

2. Experimental

Chemicals (H_2MoO_4 , HCl and TEOS) were purchased of reagent grade (Kishida Chemical) and Pluronic P123 (P123: $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich) was used as structure directing agent. All chemicals were used without further purification.

Mo-SBA-15 was synthesized according to the modification in Mo resource preparation¹⁵. 4.0 g of P123

was dissolved into 100 mL distilled water, and then stirred for 3 h. Mo containing solution was prepared by immersing 0.525 g H_2MoO_4 in x mL of 35.5 % HCl solution and shaking overnight. Three x values (20, 10 and 5 mL) were employed; HCl/ H_2MoO_4 weight ratios were corresponding to 16.0, 8.0 and 4.0, respectively. It is known that H_2MoO_4 is hard to dissolve in acidic aqueous solutions except for concentrated hydrochloric acid which is usually employed as the acid to synthesize SBA-15. This is the reason why H_2MoO_4 was employed as a Mo source material. Those solutions were mixed, and then y mL distilled water was added. The mixed solution was stirred for 30 min, resulting in a pale yellow transparent solution. A total volume of x and y was held constant at 25 mL in all experiments. After complete dissolution of H_2MoO_4 , 6.753 g of TEOS was added to the mixture at room temperature, and the precursor solution was stirred at 40 °C for 20 h. The resulting suspension was transferred into a Teflon bottle placed in an autoclave and hydrothermally aged at 100 °C for 24 h. Powders after filtration and washing treatments were air-dried overnight at 110 °C. As-made powders were calcined to remove the template at 400 °C for 12 h in air with a heating rate of 10 °C $\cdot$ min⁻¹. The nominal loading of MoO_3 was adjusted to be 19 wt% in all catalysts. For example, when 20 mL of HCl is used, the composition by weight is H_2MoO_4 : HCl : P123 : TEOS = 0.525 g : 8.38 g : 4.0 g : 6.753 g and 105 mL of H_2O . Final products are denoted as Mo-SBA-15 x mL, where x means the volume of HCl used. Pure siliceous SBA-15 was also synthesized with 20 mL HCl by using the same process for comparison.

Samples were characterized with Raman spectroscopy, N_2 adsorption-desorption isotherm, small angle X-ray diffraction (XRD) and UV-Vis spectroscopy. Raman measurements were carried out at ambient condition using a JASCO NRS-3100 spectrometer. A green laser beam of 532 nm was focused using an objective lens (20X). Small angle XRD patterns were obtained by X-ray powder diffractometer (Rigaku RINT2000) with a $\text{CuK}\alpha$ radiation operated at 40 kV and 20 mA. UV-Vis spectra were recorded with Shimadzu UV-2400PC from 800 to 200 nm. Nitrogen adsorption-desorption isotherm was measured by using a Belsorp mini (BEL Japan). Prior to N_2 adsorption, samples were degassed at 300 °C for 1 h in a He stream. BET surface area and pore size distribution (BJH method) were determined.

3. Results and Discussion

3.1. Raman Spectroscopy

Figure 1 shows Raman spectra (wavenumber region from 1200 to 700 cm^{-1}) of different precursor solutions during the preparation process of Mo-SBA-15 20 mL. As shown in Fig. 1e, no peaks of P123 in the aqueous

Fig. 1 Raman Spectra of Different Solutions during Preparation Procedure; a) filtrate after hydrothermal step, b) precursor solution (addition of TEOS into solution of P123 and MoO_2Cl_2), c) mixture of P123 solution and MoO_2Cl_2 solution, d) H_2MoO_4 in concentrated HCl and e) P123 aqueous solution

solution were detected in range of 200–1300 cm^{-1} . The spectrum (**Fig. 1d**) of H_2MoO_4 in concentrated HCl solution with peak at 956 and 920 cm^{-1} proves the formation of MoO_2Cl_2 species²¹. The mixture of P123 solution and MoO_2Cl_2 solution gives new peaks at 981 and 950 cm^{-1} (**Fig. 1c**) as compared with **Fig. 1e** and **Fig. 1d**. This suggests the reaction of MoO_2Cl_2 with bridge oxygen species in P123. Addition of TEOS into the solution shown in **Fig. 1c** provides a new spectrum in **Fig. 1b**, in which peaks of TEOS and EtOH at 874, 1041 and 1083 cm^{-1} , respectively, were observed. However, Mo related peaks at 981 and 950 cm^{-1} were not affected by the addition of TEOS. This means that Mo species do not react with SiO_2 :SMA as a reaction product was not generated in this condition. The filtrate after the treatment under autogenous pressure shows Raman spectrum (**Fig. 1a**) as same as **Fig. 1b** and **Fig. 1c** except for the disappearance of peak at 981 cm^{-1} . Consequently, there were two complexes containing Mo(VI) in Mo-P123 solution: one will be incorporated in SBA-15 channels as the template and the other still remains in solution.

Raman spectra of products after the calcination are shown in **Fig. 2**. All spectra have similar profile with shoulder at around 950 and peak at 997 cm^{-1} . Those are of surface polymolybdate or MoO_3 oligomer^{21,22}. The typical peaks assigned to MoO_3 phase were not observed, indicating no formation of MoO_3 crystallized after the calcination. The Mo concentration of products seems to be lower than theoretical value (19 wt% as MoO_3) because the Mo species were observed in the filtrate and the color of product was somewhat white.

Fig. 2 Raman Spectra of Mo-SBA-15 after Calcination; a) Mo-SBA-15 20 mL, b) Mo-SBA-15 10 mL and c) Mo-SBA-15 5 mL

3. 2. Nitrogen Adsorption-desorption Isotherm and Small Angle X-ray Diffraction

Figure 3 shows nitrogen adsorption-desorption isotherm and pore size distribution. The pure siliceous SBA-15 shows the type IV adsorption isotherm with hysteric loops type H1 which is a characteristic profile of SBA-15 (**Fig. 3d**). BET surface area and pore radius of the pure siliceous SBA-15 are 646 $\text{m}^2\cdot\text{g}^{-1}$ and 4.03 nm, respectively. Shown in **Figs. 3a** and **3b**, Mo-SBA-15 20 mL and 10 mL provide the similar adsorption-desorption profiles as observed in the pure siliceous SBA-15, indicating the formation of SBA-15 framework even in the presence of Mo species. BET surface area and pore radius are estimated to 952 $\text{m}^2\cdot\text{g}^{-1}$, 4.6 nm for Mo-SBA-15 20 mL and 798 $\text{m}^2\cdot\text{g}^{-1}$, 5.6 nm for Mo-SBA-15 10 mL, respectively. When the sample was prepared using 5 mL HCl solution, Mo-SBA-15 5 mL provided somewhat different isotherm and pore distribution curve (**Fig. 3c**); BET surface area and pore radius were found to be 436 $\text{m}^2\cdot\text{g}^{-1}$ and 1.2 nm, respectively. This suggests that the framework of SBA-15 collapsed, resulting in low surface area and small pore radius of Mo-SBA-15 5 mL. Those mean that the volume of concentrated HCl is an important factor for the synthesis of Mo-SBA-15 together with the formation of Mo-P123 complexes.

Small angle XRD patterns of Mo-SBA-15 20 mL as well as Mo-SBA-15 10 mL gave typical peaks due to mesoporous structure (**Figs. 4a** and **4b**). The same peaks were also observed in pure siliceous SBA-15 as shown in **Fig. 4c**. Mo-SBA-15 5 mL provided no peaks in this region, which is consistent with the N_2 adsorption-desorption analysis. Results of wide angle XRD indicated that all SBA-15 gave only a broadened XRD peak at 15–40° and peaks related Mo species were not observed.

N_2 adsorption-desorption and XRD results indicate that Mo-SBA-15 with the framework of SBA-15 were

Fig. 3a N₂ Adsorption-desorption Isotherm of Mo-SBA-15 20 mL Fig. 3c N₂ Adsorption-desorption Isotherm of Mo-SBA-15 5 mL Fig. 3b N₂ Adsorption-desorption Isotherm of Mo-SBA-15 10 mL Fig. 3d N₂ Adsorption-desorption Isotherm of SBA-15

prepared except for Mo-SBA-15 5 mL. Raman data show that Mo ions react with only P123 and the formation of Si-O-Mo bond corresponding to SMA does not occur (Fig. 1). This means that Mo-P123 complexes seem to incorporate and disperse in SBA-15 channels as a template. Consequently, Mo species will be dispersed in SBA-15 channels after the decomposition of the template. In addition, the increase of BET surface areas seems that the existence of molybdenum oxides in SBA-15 channels thus act to suppress the collapse of SBA-15 pores during the calcination process.

3. 3. UV-Vis Spectroscopy

The further characterization of Mo species in synthesized samples was investigated by UV-Vis spectroscopy in order to determine the symmetry and the environment of supported Mo ions^{(23)~(25)}. Spectra observed were converted from reflection to absorbance by the Kubelka-Munk function. Figure 5 displays that no absorption band around 310 nm, which was assigned to MoO₃^{(23),(24)}, was observed. This is consistent with the

Raman results mentioned above and it is confirmed that no crystalline MoO₃ was formed in Mo-SBA-15, too. The absorption bands at 215 and 240 nm were detected from Mo-SBA-15 20 mL, which suggests the presence of mono-molybdate species only. Mo-SBA-15 10 mL and 5 mL have absorption bands at 215, 240 and 290 nm, respectively, suggesting the co-existence of mono- and poly-molybdates. However, it is difficult to clearly distinguish between tetrahedral and octahedral coordinated Mo(VI) from UV-Vis spectroscopy. As another approach, the spectra were transformed to the energy edge⁽²⁵⁾ and the result is shown in Fig. 6. According to Fig. 2 of ref. 25, the absorption energy edge between *ca.* 3.8 eV and *ca.* 4.2 eV is due to tetrahedrally coordinated poly-molybdate and over *ca.* 4.2 eV is due to tetrahedrally coordinated mono-molybdate. The absorption energy edge below *ca.* 3.8 eV is due to octahedrally coordinated poly-molybdates. The absorption edge energy is estimated to be 4.7 and 3.6 eV for Mo-SBA-15 5 mL and 4.7, 4.0, and 3.6 eV for Mo-

Fig. 4a Small Angle XRD Diffraction of Mo-SBA-15 20 mL

Fig. 4c Small Angle XRD Diffraction of SBA-15

Fig. 4b Small Angle XRD Diffraction of Mo-SBA-15 10 mL

Fig. 5 UV-Vis Spectra of Mo-SBA-15 after Calcination; a) Mo-SBA-15 5 mL, b) Mo-SBA-15 10 mL, c) Mo-SBA-15 20 mL and d) SBA-15

SBA-15 10 mL, indicating the co-existence of tetrahedrally and octahedrally coordinated molybdates. On the other hand, the tetrahedrally coordinated monomolybdate is dominant in Mo-SBA-15 20 mL. This method is effective to characterize molybdates which are hard to detect by XRD and Raman measurements.

4. Conclusion

Mo-SBA-15 was successfully synthesized using H_2MoO_4 , template (P123) and tetraethylorthosilicate (TEOS). Raman spectroscopy revealed that Mo-P123 complexes are formed in solution by reaction of MoO_2Cl_2 dissolved in concentrated HCl and P123, but MoO_2Cl_2 does not react with TEOS. The Mo-P123 complexes lead to the formation of SBA-15 framework in Mo-SBA-15 and the resultant molybdenum oxides are dispersed in the SBA-15 channels. The structure is affected by the volume of concentrated HCl added and the tetrahedrally coordinated monomolybdates

dominate in Mo-SBA-15 when 20 mL of concentrated HCl (HCl/ H_2MoO_4 weight ratio = 16.0) is added.

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Fig. 6a UV Absorption Edge of Mo-SBA-15 5 mL

Fig. 6c UV Absorption Edge of Mo-SBA-15 20 mL

Fig. 6b UV Absorption Edge of Mo-SBA-15 10 mL

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要 旨

ケイ酸エチルと H_2MoO_4 から水熱合成した Mo-SBA-15 の Mo 種に関する分光法による同定

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我々は、ケイ酸エチル (TEOS) とモリブデン酸 (H_2MoO_4), テンプレートとして P123 を用いて Mo 酸化物を含む Mo-SBA-15 を水熱合成した。調製過程や最終生成物のモリブデン種はラマン分光法を用いてキャラクタライズした。濃塩酸中で生成した MoO_2Cl_2 はテンプレート (P123) と反応して Mo 錯体を形成したが、TEOS との反応は見られなかった。窒素吸着等温線や小角での X 線回折法から、合成した Mo-SBA-15 が SBA-15 構造を維持していることが明らかとなり、濃塩酸中で生成

したモリブデン錯体 (Mo-P123) がテンプレートとして作用し、SBA-15 構造を形成したものと説明される。そのため、酸化モリブデンは SBA-15 のチャンネル内に分散していると考えられる。酸化モリブデンの構造は添加する濃塩酸の量に依存し、20 mL (塩酸/モリブデン酸重量比=16.0) を加えた Mo-SBA-15 では、四面体構造を持つ単核のモリブデン酸塩として主に存在していることが、UV-Vis 分光法により明らかになった。

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