

Pt/MoO₃ 촉매에서 MoO₃ 상변화가 수소 spillover에 미치는 효과

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Effect of Phase Change of MoO₃ on H₂ Spillover Kinetics over Pt/MoO₃

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ABSTRACT

수소가 Pt/MoO₃로 흡장되는 현상을 XRD, TEM, CO 화학흡착 분석방법을 사용하여 조사하였다. 소성과정은 Pt/MoO₃ 촉매의 Chlorine 함유량을 감소하며 박막을 형성하였다. 소성전과 비교하여 수소 흡장량은 소성 후에 증가하였다. Orthorhombic Pt/MoO₃은 Hexagonal Pt/MoO₃보다 항상 수소 흡장량이 증가하였다. 상대적으로 Hexagonal Pt/MoO₃에서 수소 흡장량이 감소하는 이유는 Hexagonal 결정격자 내에 존재하는 NH₄⁺ 이온에 기인하는 것으로 판단된다. 결정격자 내부로의 수소 침투시 암모늄 이온이 수소내부 기공에 장애물 역할을 하므로, 수소 흡장량이 감소하는 것으로 판단된다.

KEY WORDS : Pt/MoO₃(백금담지 몰리브덴산화물), Orthorhombic(사각기둥), Hexagonal(육각기둥), H₂ spillover(수소 전이), H₂ uptake(수소 흡장)

1. Introduction

In a mixture between a metal that adsorb a diatomic molecule dissociatively and a nonmetal which itself cannot dissociate the molecule at the temperature of observation, the metal can act as an activator of atoms which migrate to the non-metal and participate there in various process: oxidation, reduction or adsorption. Such a tran-

sport has been called spillover. Spilt over hydrogen creates catalytic centers on the surfaces of mixed oxides which can use molecular hydrogen as the reactant¹⁻⁵.

It has drawn wide attention in systems ranging from the high temperature Pt catalyzed oxidation of graphite to the low temperature Pt catalyzed reductions of CuO and WO₃¹⁻³. Others have addressed the influence of hydrogen spillover in reactions involving hydrogen, such as cyclohexane dehydrogenation, benzene hydro-

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generation and ethylene hydrogenation⁴⁻⁹⁾.

This study explored this phenomenon for low temperature spillover. The platinum catalyzed reduction of MoO₃ to H_xMoO₃ at 110°C and different phase of acceptor was dedicated to investigate the effect of activator on spillover rate. Since hydrogen spillover was reported to be affected by several factors, the changes in kinetics of H₂ spillover with Pt/MoO₃ catalysts will be studied in the terms of the effects of chlorine, overlayer and different MoO₃ phase.

2. Experimental Procedure

2.1 Catalyst preparation

Two different phases of hexagonal MoO₃ and orthorhombic MoO₃ were prepared using monoclinic ammonium heptamolybdate oxide hydrate (AHM, (NH₄)₆Mo₇O₂₄·4H₂O) and the detailed procedure was explained in Figure 1. Pt/MoO₃ was prepared by impregnation of MoO₃ with a solution of PtCl₆, evaporating excess water and drying at 100°C overnight. Metal concentrations were kept to be 10 wt%.

2.2 Kinetics Evaluation

30 mg of catalyst was placed in the reactor and calcined at a given temperature for 1 hour. Before ITR(isothermal temperature reduction) started, a steady state concentration of 0.5% H₂/N₂ in the recycle loop was reached at atmospheric pressure while the reactor was bypassed and filled with nitrogen. The uptake of hydrogen subject to calcination treatments was measured at 110°C via ITR.

After reduction was complete, catalyst was treated in He at 200°C for 2 hour. After catalyst was cooled to room temperature and base line of

TC cell was stabilized, CO chemisorption by pulse of 50 µl sample loop was followed to measure active Pt surface area.

2.3 Characterization

X-ray powder diffractometer (Siemens D5000) was used to identify the crystalline phases in the condition of 50KV and 30 mA. To explain the overlayer formation induced by calcination, TEM (JEOL 100CX) has been used to investigate the morphology for 10% Pt/ orthorhombic MoO₃. Comparing the same area before and after calcined treatments, morphological changes were photographed using bright field imaging. All the electron micrographs were photographed at the magnification of 250,000 and then enlarged by two times.

3. Result and Discussion

XRD result shown in Figure 1 explained the preparation procedure of two different MoO₃ phases using AHM precursor. The untreated pure precursor shown in Figure 1-(a) was AHM. The hexagonal phase was prepared by; first, impregnation of pure precursor with nitric acid, second, drying at room temperature overnight, and third, calcination at 300°C for 2 hours in air. The orthorhombic phase was prepared simply by calcination of the precursor at 500°C for 18 hours⁷⁾.

A study of the effect of calcination on unsupported samples is shown in Figure 2. The dried sample in a) was the hexagonal phase with a small amount of impurity, possibly suboxide or precursor displaying peaks at 2θ equal to 18.3, 22.7 and 29.0. As shown in b), upon calcination, the impurity was removed and pure hexagonal phase was observed while the peak intensity

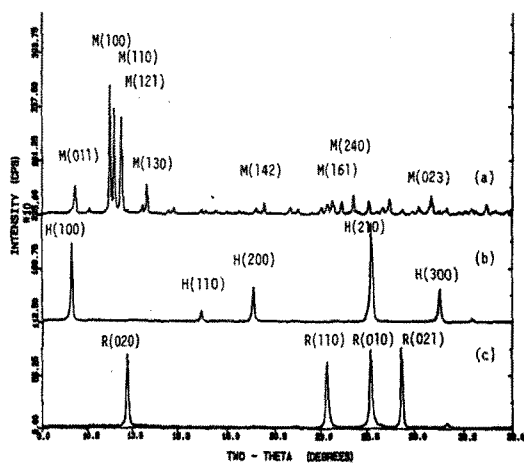


Fig. 1 Production of bulk hexagonal and orthorhombic MoO₃ a) pure precursor, b) hexagonal MoO₃, c) orthorhombic MoO₃.

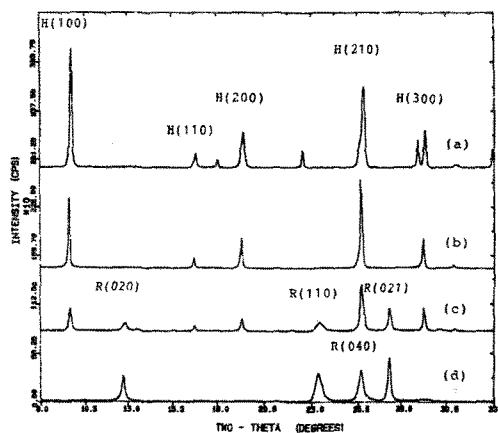


Fig. 2 Effect of calcination on transformation of phase of unsupported sample a) AHM in acid for 3 weeks and dried at 25°C overnight, b) calcination of (a) at 300°C for 2 hours, c) calcination of (a) at 300°C for 3 hours, d) calcination of (c) at 500°C for 1 hour.

ratio of planes(100) and(210) was reversed. Upon continued calcination, some of the hexagonal crystallites convert to the orthorhombic phase observed in c). This transformation of phase becomes complete after calcination for 1 hour at 500°C, as seen in d).

Morphological change of Pt crystallite and its

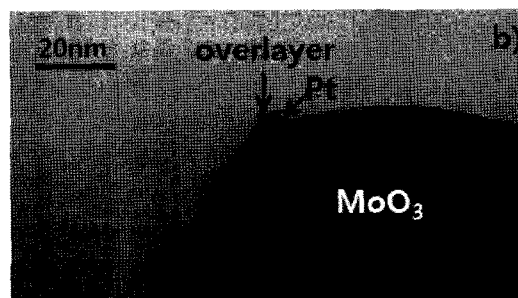
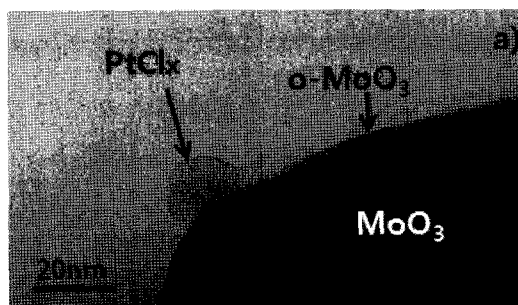


Fig. 3 Effect of 400°C calcination on morphology of 10% Pt/o-MoO₃: a) amorphous precursor before calcination, b) after 400°C calcination in O₂ for 1 hour.

surroundings upon calcination at 400°C for 1 hour is illustrated in Figure 3. Before calcination, PtCl_x deposits on MoO₃ as aggregated bundle. Upon calcination, the Pt particle shrinks due to the loss of chlorine¹²⁾. Pt surface appears to be partially covered by amorphous overlayers after calcination. The thickness of the overlayer on Pt crystallite is approximately 40Å. The hydrogen uptakes of the different morphologies as shown in Figure 4 are measured before and after calcination. In these samples, there was no prior reduction pretreatment.

The noncalcined samples exhibited lower total hydrogen uptake, and slow rates of H₂ uptake. In contrast to this, both of calcined catalyst showed higher H₂ uptake than noncalcined catalysts did. All the patterns were repeated at least twice and were reproducible within about five percent. The

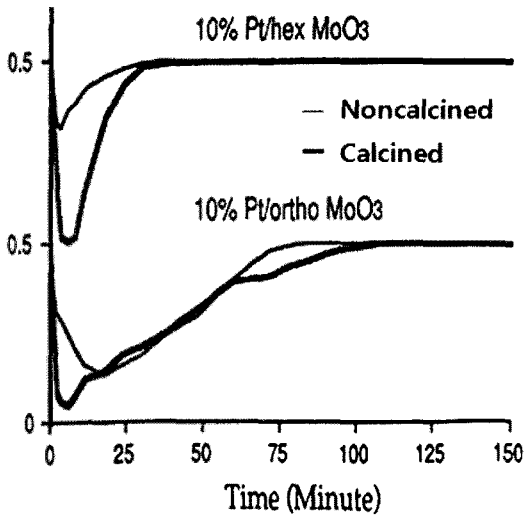


Fig. 4 ITR experiment of Pt/MoO₃ at 110°C.

maximum calculated stoichiometry was H_{1.17}MoO₃ for Pt/MoO₃ after calcination.

Interestingly, unsupported hexagonal phase, showed relatively lower H₂ uptake. These materials was reported that it might contain the unremoved NH₄⁺ ions in interstitial sites of the lattice of MoO₃, because ammonium ions in precursor was not fully removed during calcination step at 300°C¹⁰. It is postulated that this occluded NH₄⁺ ion blocks subsurface diffusion of H. For this reason the H₂ uptake of hexagonal phases is lower than the corresponding orthorhombic phase as shown in Figure 4. In contrast to this, thermodynamically stable orthorhombic phase made after calcination at 500°C overnight showed higher H₂ uptake than hexagonal phase did, because orthorhombic phase did not contain some of the NH₄⁺ ion in the MoO₃ lattice, as reported by Datta¹⁰.

In this study, calcination at high temperature resulted in an extensive overlayer formation as shown in Figure 3. To measure the uncovered Pt surface area by overlayer, pulse CO chemi-

Table 1 CO Chemisorption in ITR experiments

CO uptake (μl/g cat.)		
Catalyst	noncalcined sample	calcined sample
hexagonal phase	110.0	6.7
orthorhombic phase	203.3	26.7

sorption was performed. The decreased amount of CO chemisorption for calcined catalysts as shown in Table 1 would be due to the overlayer formation over Pt surface. Result of CO chemisorption suggested that overlayer covered Pt surface area by 94% for hexagonal phase and 84% for orthorhombic phase after calcination.

Since multi-grained Pt crystallites did not disintegrated with the calcination treatment as shown in Figure 3, it can be said that Pt dispersion (0.29% for hexagonal phase and 0.53% for orthorhombic phase) would not be changed after calcination. Therefore, Pt dispersion would be same regardless of calcination step for each individual phase.

The calcination step was reported to cause both removal of chlorine of PtCl_x precursor and overlayer formation over Pt surface area resulting in newly created adlenation sites¹¹. These conditions were found to be calcination at 400°C for 1 hour for Pt/orthorhombic MoO₃.

Because the PtCl_x precursor was in relatively poor contact with MoO₃ catalysts, H₂ uptake of all noncalcined samples exhibited slower rates and lower amounts than H₂ uptake of calcined samples did, where calcination contributed to induce good contact between Pt and MoO₃.

There were reports implying that the MoO₃ containing samples are easier to reduce. PtCl_x in PtCl_x/MoO₃ sample reduces even at 50°C⁸. The chloride precursor became more easily decomposable after calcination, so that increased

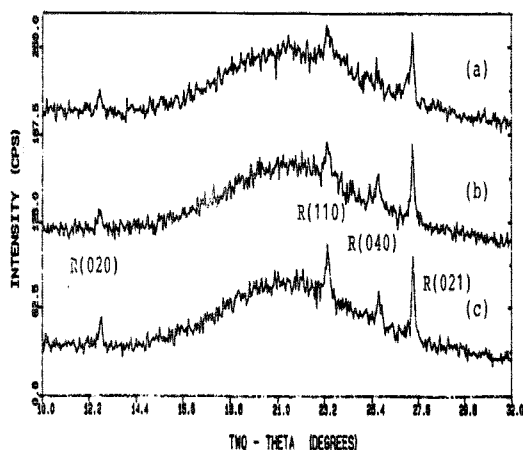


Fig. 5 Effect of reduction temperature for SiO₂ supported Pt/MoO₃, a) fresh MoO₃ b) reduced in H₂ at 100°C for 1 hour c) reduced in H₂ at 150°C for 1 hour.

spillover rates was reported due to the loss of Cl⁻ caused by calcination¹²⁾. Based on this study, overlayers indicated by TEM study shown in Figure 3 and the decreased CO chemisorption uptake shown in Table 1, would contribute to enhance the total H₂ access into each individual Pt/MoO₃ phase by improving the contact between Pt and MoO₃.

Water has been reported to accelerate the H₂ spillover rate. The effect of water on H₂ spillover, which could come from gas impurities or from reaction between H₂ and MoO₃, has been discounted based on reported paper^{5,8)}. And also, to demonstrate the stability of Pt/MoO₃ in ITR experiment at 110°C of Figure 4, catalyst was treated at 150°C in H₂. As shown in Figure 5, all the XRD pattern does not change, which means that MoO₃ is stable after H₂ treatment and does not lose oxygen as water in ITR experiment at 110°C.

4. Conclusion

H₂ spillover over Pt/MoO₃ was clearly investigated with multifaceted techniques of catalyst

characterization such as XRD, TEM, and CO chemisorption.

The calcination step increased H₂ spillover rate, where removal of chlorine of PtCl_x precursor and overlayer formation was the dominating factors to control spillover rate in each individual MoO₃ phase.

H₂ spillover rate over orthorhombic phase was faster than hexagonal phase, where NH₄⁺ ion occluded the H diffusion between the hexagonal MoO₃ lattice.

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