

# Pt/MoO<sub>3</sub> 촉매에 형성된 MoO<sub>x</sub> 박막이 수소 전이 속도론에 미치는 효과

김진걸\*, 김성수\*\*, 유승준\*\*\*†

\*순천향대학교 나노화공과, \*\*한국에너지기술연구소 대체연료 연구실, \*\*\*서남대학교 환경·화학공학부

## Effect of MoO<sub>x</sub> Overlayer on Hydrogen Spillover Kinetics over Pt/MoO<sub>3</sub>

JINGUL KIM\*, SEONGSOO KIM\*\*, SEUNGJOON YOO\*\*\*†

\*Dept. of Chemical Eng., Soonchunhyang Univ., Asan 337-745

\*\*Alternate Fuel Research Center, Korea Institute of Energy Research, Yusongku, Daejeon

\*\*\*Dept. of Env. and Chemical Eng., Seonam Univ., Namwon

### ABSTRACT

투과 전자 현미경(TEM)을 사용하여 소성 후 Pt와 MoO<sub>3</sub> 표면 위에 MoO<sub>x</sub> 박막층이 형성되는 것을 조사하였다. 연속된 CO 화학 흡착법에 의하여 표면된 노출된 Pt 표면적의 변화를 관찰하였으며, XPS 분석으로 부터 Pt 표면에 형성된 MoO<sub>x</sub> 박막층 두께는 소성 온도 증가에 따라 증가하는 것으로 측정되었다. 소성 과정은 Pt와 MoO<sub>3</sub> 간에 개선된 접촉을 유도하였으며, Pt/MoO<sub>3</sub> 촉매에서 수소 전이현상을 조절하는 것으로 나타난다.

**KEY WORDS** : H-spillover(수소전이), Calcination(소성), Overlayer(박막층), Pt/MoO<sub>3</sub>

### 1. Introduction

It was recognized that calcination of Pt/MoO<sub>3</sub> increased rate of H<sub>2</sub> uptake into support such as MoO<sub>3</sub>. This happens when a metal is in a close contact with MoO<sub>3</sub> or WO<sub>3</sub>, where the products are hydrogen molybdenum oxide (H<sub>x</sub>MoO<sub>3</sub>) or hydrogen tungsten oxide (H<sub>x</sub>WO<sub>3</sub>), respectively<sup>1,2)</sup>. The concept of hydrogen spillover can explain this phenomenon more clearly. According to this concept, the hydrogen atoms may not only occupy

the host lattice of supported metal, but also remain on the surface of MoO<sub>3</sub><sup>3)</sup>.

Concept of hydrogen spillover can be adapted as a tool in an important implications and a potential utilization in catalyst involving hydrogen transfer or storage, for reactions such as hydroconversion of n-heptane, FCC regeneration, dehydrogenation of propanol and etc<sup>3-8)</sup>. The role played by donor is to supply H-spillover species in a continuous way. Otherwise, if this species are absent, hydrocracking followed by a rapid poisoning by coking is registered with the Pt-free eronite catalyst<sup>8)</sup>. The role of donor such as Pt is assumed to

†Corresponding author : sjyoo@tiger.seonam.ac.kr

serve as 'shuttle molecule' transporting the H-spillover species as inferred by Thomas<sup>9)</sup>. H-spillover species was found to initiate the reversible inter-conversion of Brönsted (protonic) sites into Lewis ones. This concept has been reported for an isomerization of n-heptane under Pt/WO<sub>x</sub>/ZrO<sub>2</sub> and for cumene cracking reaction under zeolites or Pt containing supports<sup>10-12)</sup>. According to this notion, the role of spillover can be dedicated to catalyst's longevity, stability, activity and selectivity in an environmental and industrial catalysis.

The formation of oxide overlayer on noble metal placed the system in the realm of strong metal support interaction (SMSI), a phenomenon discovered for Ni/TiO<sub>x</sub> in 1978<sup>13)</sup>. After it was found that the properties of group VIII metals could be altered drastically by supporting these metals on reducible supports such as TiO<sub>2</sub>, study on metal support interaction has been done over different supports with comparing the turnover frequency (TOF) and selectivity. In a work by Dumesic and Vannice, they accepted the model, which proposed the migration of TiO<sub>x</sub> species onto the Pt surface and creation of new sites for CO hydrogenation at titania surface<sup>14,15)</sup>. From their XRD results, they concluded that the presence of x-ray pattern for TiO<sub>x</sub>/Pt multiple layers, although weak, showed that TiO<sub>x</sub> species existed in the form of crystallites and did not cover the metal surface entirely. The formation of TiO<sub>x</sub> overlayer after reduction was found to be a chemically specific effect driven by the interaction between TiO<sub>x</sub> and metal surfaces.

It has been reported that calcinations increased forward spillover rate and reverse spillover rate on the (100) face of a MoO<sub>3</sub> single crystal in ethylene hydrogenation<sup>16)</sup>. They observed that the calcination of the bronze improved the catalytic performance markedly and the rate of reverse

spillover. Regalbuto and Wolf observed that calcination caused WO<sub>x</sub> overlayer in Pt/WO<sub>3</sub>/SiO<sub>2</sub> catalysts for the reaction of involving NO with CO<sup>17,18)</sup>. MoO<sub>x</sub> overlayers have been reported on Rh/MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysis<sup>19,20)</sup>. This is not to be confused with ordinary sintering which leads to a decrease in the total surface area.

Under these concepts, the rate of H<sub>2</sub> uptake over Pt/MoO<sub>3</sub> will be investigated and MoO<sub>3</sub> overlayer formed at newly created contact sites between Pt and MoO<sub>3</sub>.

## 2. Experimental Procedure

### 2.1 Catalyst Preparation

Ammonium heptamolybdate called as AHM (Aldrich) was dried in an oven at 500°C overnight. The AHM was completely changed to an orthorhombic crystalline MoO<sub>3</sub> phase as verified by X-ray diffraction<sup>21)</sup>. An appropriate weight of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Aldrich Co.) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the support. The concentration of the metal precursors in the solution used for impregnation was adjusted to give a nominal metal loading of 1 wt% Pt for supported MoO<sub>3</sub> catalysts. The slurry became Pt/MoO<sub>3</sub> after drying in an oven open to air at 100°C for 12 hour and then ground into a fine powder. Catalyst was calcined at an elevated temperature starting from 400°C to 500°C before the use.

### 2.2 Reaction Kinetics

Reactor was made with a pyrex tube (0.55" ID \* 10" L), which was held in place by O-ring joints and clamp. Temperature programmed controller (Cole-Parmer, model 2010) controlled the temperature of the furnace. The reactor was run in the recirculation mode with a nominal flow rate of 30 sccm

and a recycle ratio of 70. The thermocouple inside catalyst bed measures the temperature of gas stream. A mixture of 2 vol% H<sub>2</sub> in N<sub>2</sub> was used for hydrogen uptake experiment at 50°C called as Isothermal Reduction (ITR) and the progress of hydrogen uptake was monitored using a thermal conductivity detector. After purging reactor with He, pulse chemisorption by CO was continued to measure free Pt surface area and size of Pt crystallites assuming the hemispherical geometry. Crystallite size of Pt with overlayer of MoO<sub>3</sub> was not calculated.

### 2.3 Catalyst Characterization

X-ray powder diffractometer (Siemens D5000) was used to identify the crystalline phase. Catalyst was ground to a fine powder and backfilled into zero background holder. Measurement was done at 50 KV, 30 mA, 8 to 33 degree, 0.05 degree step size, and 3.0 second count time. Pt/MoO<sub>3</sub> was identified as an orthorhombic phase using the x-ray diffraction file.

JEOL 100CX was employed at 100KV up to 250,000 times magnification in condition of transmission mode (TEM) to investigate the effect of calcination over the morphological change of Pt/MoO<sub>3</sub>. The bright field mode was chosen to record the TEM images. The amount of beam exposure to this area was kept very low. Substrate free gold grid was used to mount the samples. The same area was imaged and photographed before and after calcinations.

In situ XPS spectrometer (SSX 100) was employed to analyze the chemical state of the surface of calcined Pt/MoO<sub>3</sub> in reduced condition. Reduction condition has been done in 30 ml/min of H<sub>2</sub> for 15 minutes at 50°C during pretreatment. Spot size was 600 micro spot size at 100 eV of an

analyzer pass energy, which would usually yield a half width of the Au 4f<sub>7/2</sub> of 1.0 eV. During in situ analysis, flood gun was used at about 2 eV for charge neutralization. All binding energies were referenced to C1s of hydrocarbons at 284.6 eV.

## 3. Result and Discussion

### 3.1 Surface Morphology

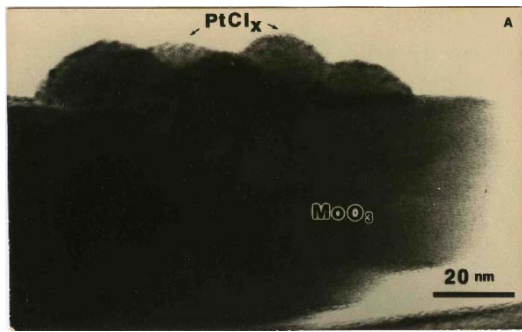
X-ray diffraction (Siemens D5000) identified that the phase of MoO<sub>3</sub> was orthorhombic after calcination of AHM at 500°C over 12 hours<sup>21</sup>. Non-calcined PtCl<sub>x</sub>/MoO<sub>3</sub> was electro-micrographed in Figure 1(a) as multiple Pt aggregates. Pt aggregates shown before calcination became multiply twinned particles after calcination at 400°C. Amorphous MoO<sub>x</sub> overlayer formed extensively over surface of Pt and MoO<sub>3</sub> after calcinations at 400°C for 3 hour.

The Pt crystallites are not of the 'snowball' morphology with higher chemisorption area that can be produced with supported rhodium crystallites after oxidation and reduction<sup>22</sup>. From TEM results, it is seen that the PtCl<sub>x</sub> precursors deposit onto MoO<sub>3</sub> in a large isolated agglomerates, and redispersion of these agglomerates does not occur as a result of calcination. Rather, it appears that Pt crystallites size is not significantly affected by calcination temperature.

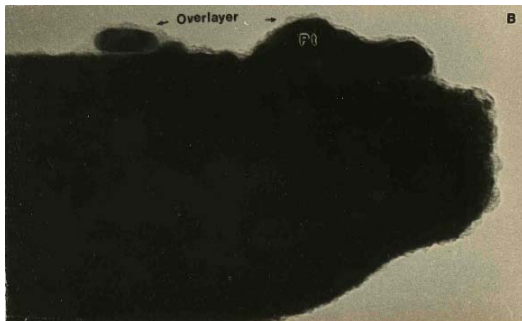
### 3.2 Evaluation and Characterization

Calcined Pt/MoO<sub>3</sub> at 400°C in a successively longer time (1, 2 and 6 hour) and values of successively chemisorbed CO were enlisted in Figure 2 and Figure 4. These H<sub>2</sub> uptakes in spectra were relatively independent of calcination time.

This proves good reproducibility of experimental procedure and shows number of Pt sites not



(a) before calcination



(b) after calcination

Fig. 1 TEM micrograph of calcined 1% Pt/MoO<sub>3</sub> at 400°C for 3 hour (a) before calcination (b) after calcination

critical in this range. This also suggests well that chemical state of Pt crystallites have little effect on the rate of H<sub>2</sub> uptake. Otherwise, the kinetics of calcined sample for 1 hour should be very different with the kinetics of calcined samples for longer time.

As shown in Figure 3 and Figure 4, calcination at 500°C with different time demonstrated that the amount of H<sub>2</sub> uptake into the oxide does vary with CO uptake and CO uptake is always very low in all of these latter runs. This indicates that H<sub>2</sub> uptake of 500°C calcined Pt/MoO<sub>3</sub> is limited by free Pt surface area.

While the average crystallite size (145Å) of Pt is calculated from CO chemisorption of noncalcined sample, the typical size photographed by TEM as in Figure 1 is about 150Å. After 400°C

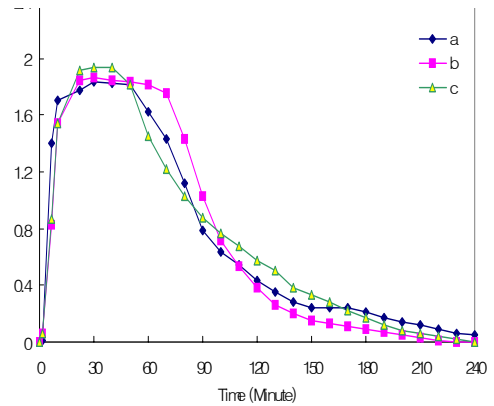


Fig. 2 Effect of calcination at 400°C as a function of time (a) 1 hour calc. (b) 2 hour calc. (c) 6 hour calc.

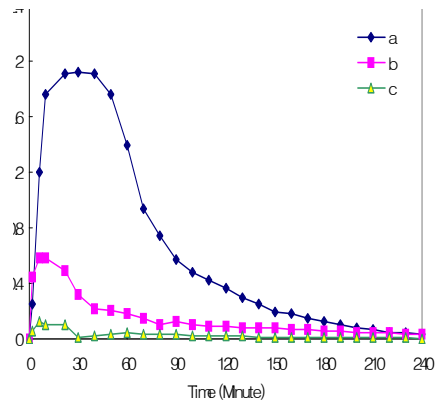


Fig. 3 Effect of calcination at 500°C as a function of time (a) 1 hour calc. (b) 2 hour calc. (c) 3 hour calc.

calcination, there are necking effects at contact sites between Pt and MoO<sub>3</sub> indicated by TEM results as shown in Figure 1, which show a closer contact between Pt crystallites and the MoO<sub>3</sub>.

This necking effect causes H<sub>2</sub> uptake high for calcined samples such 400°C as shown in Figure 1. The decrease of free Pt surface area can be explained as blockage of the Pt surface by the formation of MoO<sub>x</sub> overlayer. Like the earlier report on Pt/WO<sub>3</sub>/SiO<sub>2</sub><sup>17,18</sup>, overlayers form during the calcination step, and remained relatively unchanged

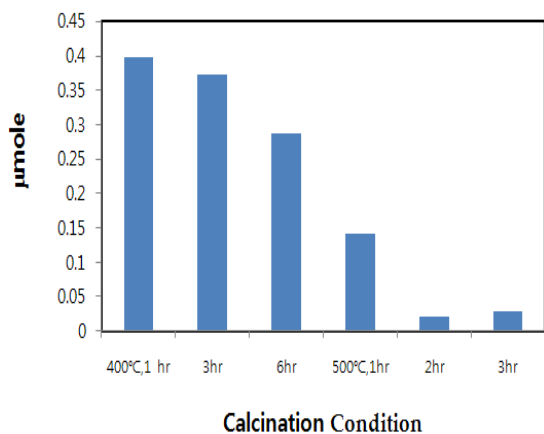


Fig. 4 Effect of calcination temperature and duration

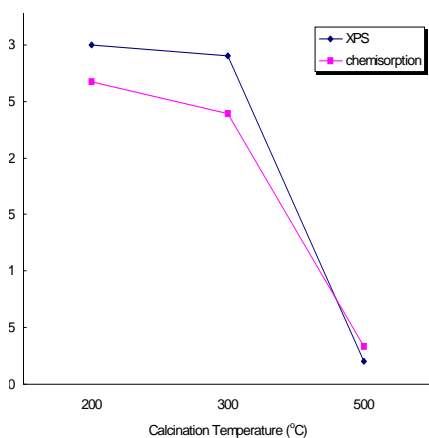


Fig. 5 Pt/Mo mole ratio as function of calcination temperature

during the reduction step. This is different from the behavior of materials such as  $\text{TiO}_2$  typically associated with the decoration effects, in which the mobile species are provided by the reduction step<sup>23)</sup>.

As shown in Figure 5, Pt/Mo ratios of 300 °C and 500 °C calcined Pt/MoO<sub>3</sub> decreased by a factor of 10 approximately. These XPS results also support the formation of MoO<sub>3</sub> overlayers during calcination. A decrease in the Pt/Mo ratio after calcination could be due to particle sintering or to

coverage of Pt by MoO<sub>x</sub>.

These results have concurred with the formation of more extensive MoO<sub>x</sub> overlayer found from TEM work as shown in Figure 1. In the report by Gerstein, 1Hself-diffusion within the bulk is 107 times greater than that calculated for the overall spillover process in Pt/MoO<sub>3</sub><sup>24)</sup>. According to this notion, MoO<sub>x</sub> overlayer is seemed to control the hydrogen spillover rate, which is assumed to be the rate determining step from Pt surface to surface MoO<sub>3</sub><sup>1,2,13)</sup>.

## 4. Conclusion

Results of XPS and CO chemisorption support TEM observation in which MoO<sub>x</sub> overlayers form in greater quantities after calcination at higher temperature, where the amount of the free Pt surface area decreases by a factor of an almost 10.

## Acknowledgement

This work was supported by grants 2006-02-1920000-3-020 of Korean Ministry of Commerce, Industry and Energy.

## References

- 1) P. A. Sermon and G. C. Bond, *J. Chem. Soc. Faraday I*, Vol. 72, 1976, p. 730.
- 2) J. J. Fripiat and D. Tinet, *J. De Chimie Phys. et de Phys. Chim. Bio.*, Vol. 76, 1979, p. 867.
- 3) G. M. Pajonk, *Appl. Catal. A*, Vol. 202, 2000, p. 157.
- 4) B. Delmon, *Heterog. Chem. Rev. No. 1*, 1994, p. 219.
- 5) 심규성, 김종원, 김연순, 박기배, “2-propanol의 탈수소화에 의한 수소제조연구”, *한국수소에너지학회지*, Vol. 6, No. 1, 1995, p. 11.
- 6) W. C. Corner and J. L. Falconer, *Chem. Rev.*

- No. 1, 1994, p. 329.
- 7) A. El Tanany, G. M. Pajonk, K. H. Steinberg, and S. J. Teichner, *Appl. Catal.*, Vol. 39, 1988, p. 89.
  - 8) A. M. Stumbo, P. Grange, and B. Delmon, *Catal. Lett.*, Vol. 31, 1995, p. 173.
  - 9) C. Thomas, L. Vivier, A. travert, F. Mauge, S. W. Kasztelan, and G. Petrot, *J. Catal.*, Vol. 179, 1998, p. 495.
  - 10) D. G. Barton, S. L. Soled, G. D. Meitzner, G. A. Fuentes, and E. Iglesia, *J. Catal.*, Vol. 181, 1999, p. 57.
  - 11) T. Shishido, and H. Hattori, *Appl. Catal. A.*, Vol. 146, 1996, p. 157.
  - 12) T. Shishido, and H. Hattori, *J. Catal.*, Vol. 161, 1996, p. 194.
  - 13) S. J. Tauster, and S. C. Fung, *J. Catal.*, Vol. 55, 1978, p. 29.
  - 14) J. A. Dumesic and B. J. Tatarchuk, *J. Catal.*, Vol. 70, 1981, p. 308.
  - 15) M. A. Vannice and C. Sudhkar, *J. Phys. Chem.*, Vol. 88, 1984, p. 2429.
  - 16) J. P. Marcq, X. Wispennickx, G. Poncelet, D. Keravis, and J. J. Fripat, *J. Catal.*, Vol. 73, 1982, p. 309.
  - 17) J. R. regalbuto, T. H. Fleisch, and E. E. Wolf, *J. Catal.*, Vol. 107, 1987, p. 114.
  - 18) J. R. Regalbuto, C. W. Allen, and E. E. Wolf, *J. Catal.*, Vol. 108, 1987. p. 304.
  - 19) B. J. Kip, J. Wolput, N. Hermans, and R. Prins, *Appl. Catal.*, Vol. 35, 1987, p. 109.
  - 20) F. Van der Berg, J. Clezer, and W. H. Satchler, *J. Catal.*, Vol. 93, 1985, p. 340.
  - 21) J. G. Kim, *J. Korean Ind. Eng. Chem.*, Vol. 10, No. 8, 1999, p. 1109.
  - 22) J. Burkhead and L. D. Schmidt, *J. Catal.*, Vol. 116, 1989, p. 240.
  - 23) S. J. Tauster, *Amer. Chem. Soc. Symp. Ser.*, Vol. 298, 1986, p. 1.
  - 24) B. C. Gerstein and R. E. Taylor, *J. Catal.*, Vol. 62, 1980, p. 401.