

## Effect of an Adsorbed Residual Chlorine at Adlineation Sites over Formation of Pt/HxMoO<sub>3</sub>

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### 활성점에 흡착된 잔존 chlorine이 Pt/HxMoO<sub>3</sub> 생성에 미치는 영향

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**Abstract** Kinetics of H-spillover over Pt/MoO<sub>3</sub> was greatly affected by the amount of residual chlorine differing by calcination temperature. Multifaceted techniques for characterization were dedicated to elucidate the faster reduction of chlorine in the isothermal reduction (ITR) at 50°C after calcination. Reduction of residual chlorine over platinum resulted in opening the more channel of hydrogen pathway into more MoO<sub>3</sub> particles and controlling the kinetics of hydrogen uptake.

**요약** Pt/MoO<sub>3</sub>로의 수소 이동 속도론은 소성 온도에 따라 변하는 잔존 Cl량에 의하여 영향을 받았다. 선택적 CO 화학흡착법을 사용하여 소성 온도의 증가에 따른 Pt 표면적의 감소를 측정하였다. 50°C 등은 실험에서 소성 후에 Cl 량의 빠른 감소 현상을 규명하기 위하여 여러 특성화 분석을 실시하였다. Pt 결정 표면에서 잔존 Cl 량의 감소는 MoO<sub>3</sub>로의 수소 공급을 증가시켰고, 수소 흡착 속도론을 조절하였다.

**Key Words** : H-spillover, Pt/MoO<sub>3</sub>, Calcination, H<sub>2</sub> uptake, residual chlorine

### 1. Introduction

Calcination of Pt/MoO<sub>3</sub> increased the rate of H<sub>2</sub> uptake from Pt to support MoO<sub>3</sub> resulting in hydrogen molybdenum bronze (H<sub>x</sub>MoO<sub>3</sub>) [1,2]. The concept of hydrogen spillover was applied to explain the kinetics of H<sub>2</sub> uptake over Pt/MoO<sub>3</sub>. It is well documented that the rate determining step in bronze formation is the actual spillover step [3], in which atomic H migrates from the Pt surface to the trioxide lattice.

Molecules adsorbed at the metal-trioxide interface have been documented to increase the rate of this H<sub>2</sub> spillover step [1]. It was reported that water molecule present at adlineation sites between Pt and MoO<sub>3</sub> increased to uptake H<sub>2</sub> into Pt/MoO<sub>3</sub>.

Residual chlorine was also considered to be one of possible factors to affect H-spillover from Pt to

MoO<sub>3</sub>. Chemisorption study over Ru/SiO<sub>2</sub> showed that the amount of residual Cl greatly influenced the chemisorptive capacity of Ru for CO, O<sub>2</sub> and especially H<sub>2</sub> which adsorbs dissociatively on Ru [4]. Reduction study of PtCl<sub>x</sub> over SiO<sub>2</sub> increased the temperature at which reduction of PtCl<sub>x</sub> in H<sub>2</sub> starts from 140°C and finished at 190°C [5]. According to these notions, it is expected that reduction at 50°C of PtCl<sub>x</sub> precursor impregnated onto MoO<sub>3</sub> might not serve to eliminate all chlorine.

### 2. Experimental Procedure

Ammonium heptamolybdate (AHM, Aldrich Co., USA) was dried in an oven at 500°C overnight. The AHM was completely changed to an orthorhombic crystalline MoO<sub>3</sub> [6]. An appropriate weight of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Aldrich Co., USA) 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

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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 overnight and then ground into a fine powder. 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% H<sub>2</sub> in N<sub>2</sub> was used for reduction experiment at 50°C and the progress of reduction was monitored using a thermal conductivity detector. After purging reactor with He, a pulse chemisorption by CO was continued to measure free Pt surface area.

In situ XPS spectrometer (SSX 100, Amoco Co. USA) was employed to analyze the chemical state of the surface of calcined Pt/MoO<sub>3</sub> in reduced condition. Reduction has been performed in 30 ml/min of H<sub>2</sub> for 15 min at 50°C during pretreatment.

### 3. Result and Discussion

To explain the effect of Pt precursor on hydrogen spillover over Pt/MoO<sub>3</sub>, kinetics of hydrogen spillover as shown in Fig. 1 and 2 have been performed under the condition of isothermal temperature at 50°C and

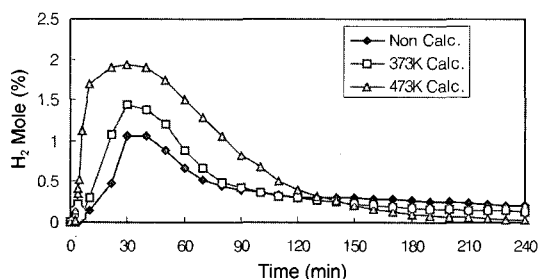


Fig. 1. Effect of calcination on H<sub>2</sub> uptake at an elevated high temperature

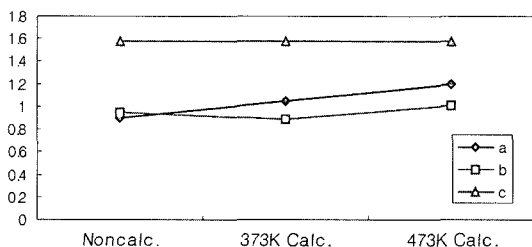


Fig. 2. Effect of an elevated calcination temperature on morphology of Pt/MoO<sub>3</sub> (a) Ratio of H/MoO<sub>3</sub> (b) free Pt surface area (unit: mmole) (c) Pt crystallite size (unit: nm)

at atmospheric pressure, after Pt/MoO<sub>3</sub> was pretreated in an oven as a function of an elevated calcination temperature.

With a MoO<sub>3</sub> sample only, no H<sub>2</sub> uptake occurs since MoO<sub>3</sub> cannot activate to uptake hydrogen at 50°C without presence of Pt [3,7]. CO does not adsorb since there is no active site available. The noncalcined Pt containing MoO<sub>3</sub> exhibits a relatively slow initial reduction rate and has a slow long tail. For noncalcined and 100°C calcined samples, the initial sinuous curves of H<sub>2</sub> uptake in 15 minutes indicate the very significant “auto-accelerative” behavior [8,9]. Calcination at 200°C temperatures increases the initial reduction rate, and decreases the size of the spectral tail. With 200°C calcined Pt/MoO<sub>3</sub>, the amount of specific CO uptake is approximately constant or increases slightly while the ITR spectra show the increased initial reduction rate.

As shown in Fig. 1, it was found that the rate of H<sub>2</sub>-uptake increased as the temperature of calcination of the Pt/MoO<sub>3</sub> samples was increased. Two factors might be considered for an account for the reason of these trends; physisorbed water or water formed during the reduction and residual chlorine on Pt.

The presence of water has been reported to increase the H<sub>2</sub> spillover rates [10]. Rate of hydrogen spillover at 50°C is expedited by the presence of water on the adlineation sites [1]. It might be considered that even with feeding the completely dry hydrogen gas, hydration of surface of Pt/MoO<sub>3</sub> produces a small amount of water, which acts as a carrier.

However, in this Fig. 3, water was not seemed to play a role to control H-spillover as shown in Fig. 1, because there were large differences in H<sub>2</sub> uptake kinetics by changing calcination temperature. Therefore, this possibility can be eliminated because this

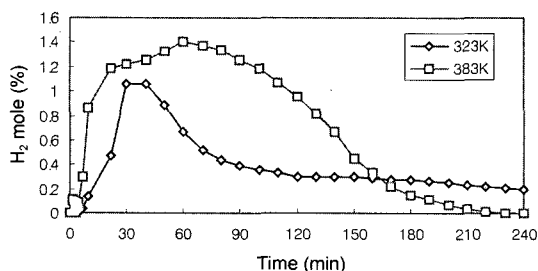


Fig. 3. Effect of water on H<sub>2</sub> uptake over Pt/MoO<sub>3</sub>

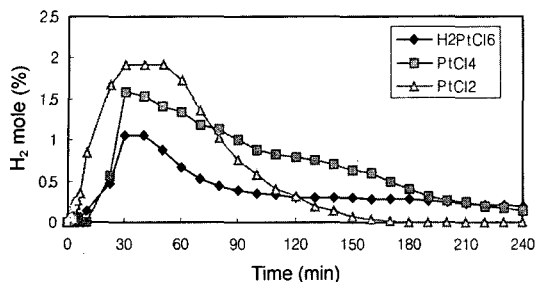


Fig. 4. Effect of residual chlorine on H<sub>2</sub> uptake

would have affected all the experiments if it did. Gravimetric measurements and differential thermal analysis by Sermon and Bond [3] have shown that lower oxide formation does not occur below 200°C. [3] The volumetric measurements of water released during the bronze formation and NMR study results by Fripiat showed again that there was no noticeable formation of a hydrated lower oxide such as Mo<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O below 200°C [11]. According to this notion, it was accepted that water would not be formed under the reduction condition of this set of experiments at 50°C. Thus, it is believed that water formation does not affect the H<sub>2</sub> uptake kinetics.

The effect of residual chlorine on H-spillover was investigated with partially physical mixtures of MoO<sub>3</sub> and different Pt chloride precursors. ITR pattern at 50°C of these samples are shown in Fig. 4.

As the ratio of Cl/Pt decreased, initial rate of H<sub>2</sub> uptake increased and amount of H<sub>2</sub> uptake became higher. This indicated that the chlorine played the dominant role to control the kinetics if H-spillover over Pt/MoO<sub>3</sub>.

Effect of residual chlorine on H-spillover is now discussed via Cl/Pt ratio and electronic state of Pt crystallite. XPS result as shown in Fig. 5 and Fig. 6 has been dedicated to investigate chemical composition of PtCl<sub>x</sub> precursor over surface of Pt crystallites.

Effect of reduction on the change of Cl/Pt ratio as shown in Fig. 5 has appeared to be very drastic for the 200°C calcined Pt/MoO<sub>3</sub> compared to noncalcined Pt/MoO<sub>3</sub>. Cl/Pt ratio has changed from 4.1/1 to 4.7/1 for the noncalcined Pt/MoO<sub>3</sub>, which is not significant. In contrast to this, this number has dropped to almost to trace levels for 200°C calcined Pt/MoO<sub>3</sub>. Reduction of Cl/Pt ratio in the XPS experiment is expected

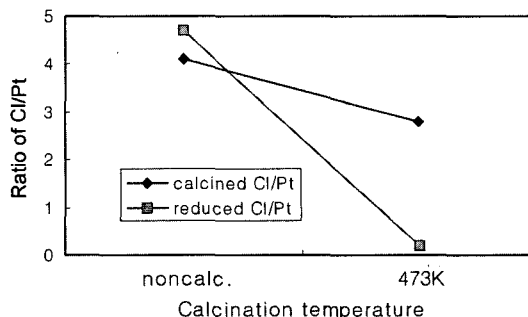


Fig. 5. Cl/Pt ratio of Pt/MoO<sub>3</sub>

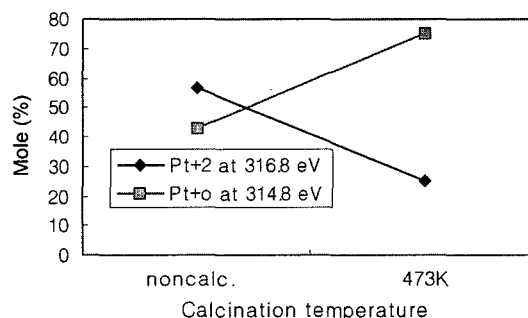


Fig. 6. XPS result for an electronic state of Pt as a function of calcination temperature

to be similar to the trend from the results of ITR experiment. This results indicated that Cl play a role to dominate the H-spillover rates from Pt to surface of MoO<sub>3</sub>.

Electronic state of Pt crystallite as shown in Fig. 6 has been in the state of Pt<sup>+2</sup> for all Pt/MoO<sub>3</sub> samples before reduction. After reduction, 43% of Pt has changed into metallic Pt<sup>0</sup> for noncalcined Pt/MoO<sub>3</sub>, while 75% of Pt has changed into metallic Pt<sup>0</sup> for 200°C calcined Pt/MoO<sub>3</sub>. This results indicated that Cl play a role to dominate the H-spillover rates from Pt to surface of MoO<sub>3</sub>.

#### 4. Conclusion

Calcination results in faster hydrogen uptake, even if dispersion of Pt crystallites did not change. Amount of residual chlorine analyzed by characteristic techniques of XPS and CO chemisorption reduced more faster in ITR at 50°C after calcination at higher temperature. This lessening of residual chlorine resulted in opening the more channel of hydrogen pathway into more MoO<sub>3</sub> particles and controlling the kinetics of hydrogen uptake.

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