수소 spillover 속도론 - I. Pt/MoO₃ 촉매의 표면 형상 변화

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Hydrogen Spillover Kinetics - I. Effect of Surface Morphology on Pt/MoO₃ Catalyst

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Abstract H_2 uptake into Pt/MoO₃ was enhanced with an increased calcination temperature. Selective CO pulse chemisorption demonstrated that free Pt surface area was decreased as calcination temperature was increased. Characteristic techniques were dedicated to elucidate the closer contact at adlineation sites between Pt and MoO₃ substrates. Calcination resulted in supplying the hydrogen access into more MoO₃ particles and controlling the kinetics of hydrogen uptake.

요 약 소성 온도 증가 시 Pt/MoO₃로의 수소 흡착이 증가하였다. 선택적 CO 화학 흡착 법을 사용하여 소성 온도의 증가에 다른 백금 표면적의 감소를 측정하였다. 특성화 분석법에 의하여 Pt와 MoO₃간의 접촉 활성 점의 접촉이 개선됨을 측정하였다. 소성은 MoO₃로의 수소 공급을 증가시켰고, 수소 흡착 속도론을 조절하였다.

Key Words : H-spillover, Pt/MoO₃, Calcination, H₂ uptake, overlayer

1. Introduction

It was recognized that calcinations of Pt/MoO₃ increased the rate of H_2 uptake into support such as MoO₃ [1,2]. The role played by donor is to supply H-spillover species in a continuous way. Otherwise, if this species are absent, rapid poisoning by coking is registered with the Pt-free eronite catalyst in the hydrocracking reaction. The role of donor is assumed to serve as 'shuttle molecule' transporting the H-spillover species as inferred by Thomas [3]. H-spillover species was found to initiate the reversible interconversion of Br φnsted (protonic) sites into Lewis sites. This concept has been reported for an isomerization of n-heptane under Pt/WO$_x$/ZrO₂ [4] and for cumene cracking reaction under zeolites

or Pt containing supports [5,6].

The formation of oxide overlayer on noble metal placed the system in the realm of strong metal support interaction (SMSI), a phenomenon discovered in 1978 for Ni/TiO$_x$ [7]. In a work by Dumesic and Vannice, they accepted the model which proposed the migration of TiO$_x$ species onto the Pt surface and creation of new sites for CO hydrogenation at titania surface [8,9]. From their XRD results, they concluded that the presence of x-ray pattern for TiO$_x$/Pt multiple layers, although weak, showed that TiO$_x$ species existed in the form of crystallites and did not cover the metal surface entirely. The formation of TiO$_x$ overlayer after reduction was found to be a chemically specific effect driven by the interaction between TiO$_x$ and metal surfaces.

It has been reported that calcinations increased forward H-spillover rate and reverse H-spillover rate on the (100) face of a MoO₃ single crystal in ethylene hydrogenation. This is not be confused with ordinary sintering which leads to a decrease in the total surface area. Under these concepts, the

increased rate of H_2 uptake over Pt/MoO_3 will be investigated in terms of the concept of hydrogen spillover and morphological change after calcination. According to this notion, the role of spillover was studied as a function of calcination temperature over Pt/MoO_3 and this can be dedicated to catalyst's longevity, stability of activity and selectivity in an environmental and industrial catalysis.

2. Experimental Procedure

X-ray diffraction identified that the phase of MoO_3 was orthorhombic after calcination of ammonium heptamolybdate (AHM, Aldrich Co., USA) at 500°C overnight. An appropriate weight of $H_2PtCl_6 \cdot 6H_2O$ (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 impregnation was adjusted to give a nominal metal loading of 1 wt% Pt for supported MoO_3 catalysts. 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_2 in N_2 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.
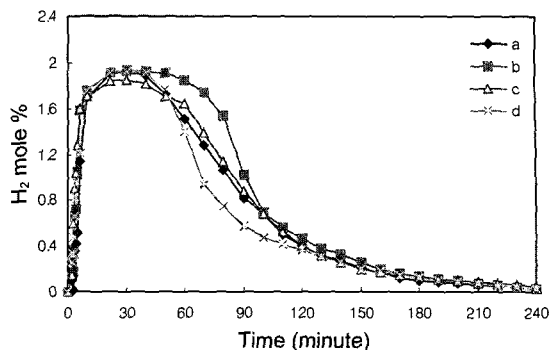

Fig. 1. Effect of calcination temperature over kinetics of H_2 uptake over Pt/MoO_3.
(a) 200°C (b) 300°C (c) 400°C (d) 500°C

JEOL 100CX (UIC, USA) 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_3. The same area was imaged and photographed before and after calcinations. In situ XPS spectrometer (SSX 100, Amoco Co., USA) was employed to analyze surface chemical state of calcined Pt/MoO_3 in reduced condition. Reduction condition has been done in 30 ml/min of H_2 during pretreatment for 15 minutes at 50°C.

3. Result and Discussion

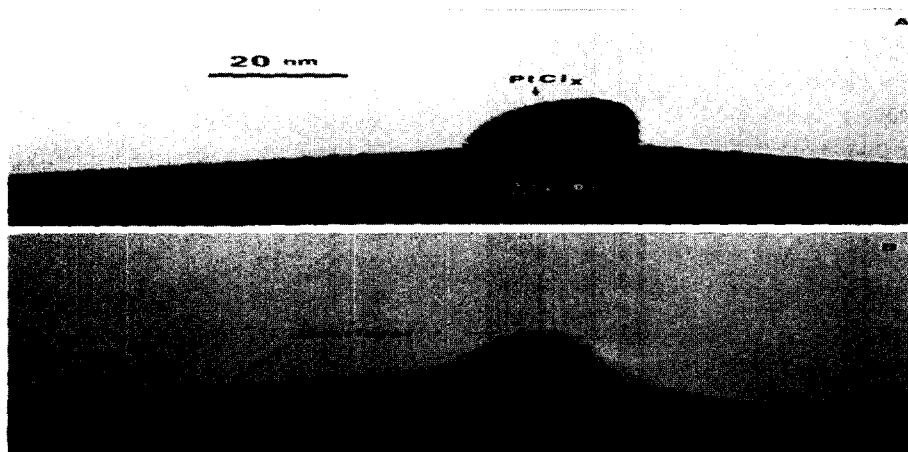To investigate the morphological effect of hydro-

Fig. 2. Electro micrograph of calcined Pt/MoO_3 at 300°C for 1 hour. (a) before calcination (b) after calcination

gen spillover over Pt/MoO₃, kinetics of hydrogen spillover have been shown under the condition of isothermal temperature at 50°C and at an atmospheric pressure, after Pt/MoO₃ was pretreated in oven as a function of an elevated calcination temperature. With a MoO₃ sample only, no H_2 uptake occurs since MoO₃ cannot activate to uptake hydrogen at 50°C without presence of Pt [3]. Also, CO is not adsorbed since there is no active site available. With 200°C calcined Pt/MoO₃ the amount of specific CO uptake is approximately constant or increases slightly while the isothermal reduction (ITR) spectra show the increased initial reduction rate. At 300°C calcined Pt/MoO₃, the amount of hydrogen uptake at 50°C shows the maximum ($H_{1.45}MoO_3$), while CO uptake decreases than the amount before. The spectra of samples calcined at 400°C and 500°C exhibits the same high reduction rate but turns up more quickly, so that total H2 uptake is decreased. Also, CO chemisorption uptake drops drastically from 21.8 μl for the 200°C calcined sample to 9.4 μl for the 400°C calcined sample and to 3.4 μl for the 500°C calcined sample.

An electro micrograph of calcined Pt/MoO₃ at 300°C for 1 hour demonstrated the swelling effect of adlineation sites between Pt and MoO₃, which is called as necking effect, while MoO_x overlayer does not appear to exist over surface of Pt and MoO₃ before calcination. Pt aggregates shown before calcination became multiplying twinned particles.

After calcination at 400°C, H_2 uptake as shown in Fig. 3 became larger compared to noncalcined Pt° and MoO₃, while free Pt surface area became smaller as shown from CO chemisorption. Moreover, these trends became more significant after reoxidation at 150°C.

The chemical composition of hydrogen bronze determined by XPS and ITR are demonstrated in Fig. 4, where the amount of H_2 uptake is calculated from integrating the areas of H_2 uptake of ITR results in Fig. 1.

This is approximately the same trend as bulk Mo reduction observed with ITR. XPS is acknowledged to be surface sensitive technique, so that this is dedicated to analyze the amount of H_2 uptake over sur-
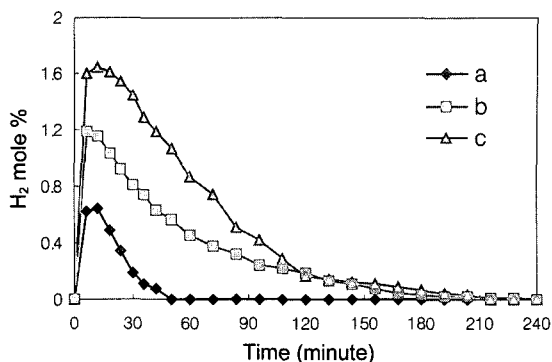

Fig. 3. Effect of pretreatment on H_2 Uptake for Pt°/MoO₃. a. noncalcined Pt°/MoO₃ b. 400°C calcined Pt°/MoO₃ c. reoxidizaton at 150°C of 'b'.
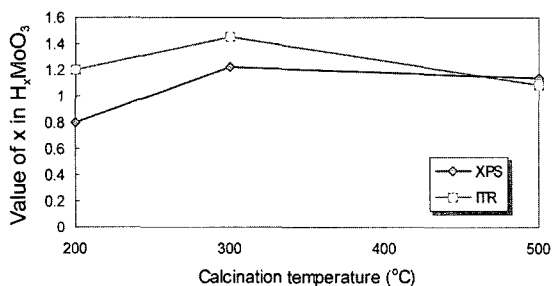

Fig. 4. Ratio of H/MoO₃ measured by XPS and ITR.

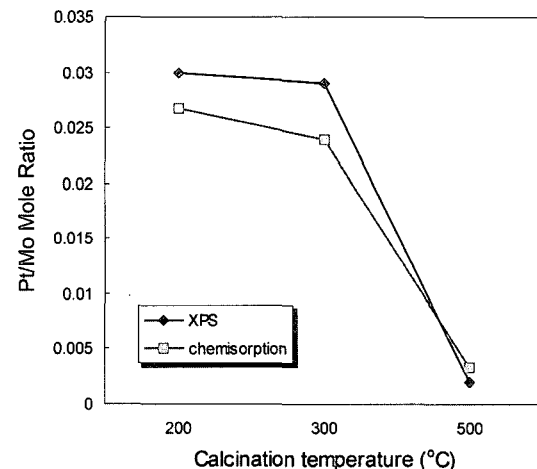Fig. 5. Mole ratio of Pt/Mo of calcined Pt/MoO₃.

face of Pt/MoO₃.

Pt/Mo ratios of 200°C and 300°C calcined Pt/MoO₃ determined by XPS and chemisorption as shown in Fig. 5 showed good agreeable numbers in the range of experimental error, whereas those of

300°C and 500°C calcined Pt/MoO$_3$ decreased by a factor of 10 approximately. These XPS results supported the formation of MoO$_3$ overlayers during calcination.

4. Conclusion

Kinetics of hydrogen storage of Pt/MoO$_3$ was greatly controlled by calcinations, where rate of hydrogen uptake into Pt/MoO$_3$ became faster after calcination, even if free surface area of Pt crystallites became less. Characteristic techniques of XPS, CO chemisorption and TEM demonstrated that MoO$_x$ overlayer formed over Pt and MoO$_3$ substrates after calcinations. This induced closer contact at adlineation sites between Pt and MoO$_3$ substrates. It resulted in supplying the hydrogen access into more MoO$_3$ particles and controlling the kinetics of hydrogen uptake.

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