MoO₃ 분말의 수소환원거동

구원범 · §유경근 · §김행구

한국해양대학교 에너지자원공학과

The Hydrogen Reduction Behavior of MoO₃ Powder

Won Beom Koo, §Kyoungkeun Yoo and §Hanggoo Kim

Korea Maritime & Ocean University, Busan, Korea

요 약

수평관상로를 사용하여 산화몰리브덴의 수소환원거동을 연구하였으며, 환원은 MoO₃ → MoO₂과 MoO₂ → Mo의 두 단계로 진행되었다. 첫 번째 단계에서는 높은 발열반응을 고려하여 MoO₃ 환원을 위해 30 vol% H₂와 70 vol% Ar의 혼합 가스를 선택하였다. 온도 범위는 550~600°C이고 체류 시간 범위는 30~150분으로 진행하였다. 두 번째 단계에서는 MoO₂의 환원을 위해 순수한 H₂ 가스를 사용하였으며, 온도와 체류시간의 범위는 각각 700~750°C와 30~150분이었다. 몰리브덴 산화물의 두 단계의 수소환원과정에서 각각 다른 환원거동이 관찰되었다. 1단계에서는 반응속도의 온도 의존성이 관찰되었으며, 본 연구의 조건에서 중간 산화물의 존재에도 불구하고 표면반응을 속 메커니즘이 결과와 잘 일치하는 것으로 나타났다. 이 메커니즘을 기반으로 활성화 에너지와 빈도인자는 각각 85.0 kJ/mol 및 9.18×10^7 로 계산되었다. 또한, 입자 내 기공 크기는 온도 및 체류 시간에 따라 증가했다. 2단계 환원의 경우 반응속도의 온도 의존성이 관찰되었으나 표면반응을 속 메커니즘은 초기에만 부합하였다. 이는 환원과정 후반부에 상변태 MoO₂ → Mo가 진행됨에 따라 부피 변화에 의한 산화물 결정구조의 붕괴에 기인한다고 생각할 수 있다.

주제어 : 몰리브덴, 수소환원, 2단계 환원, 삼산화몰리브덴, 이산화몰리브덴

Abstract

The hydrogen reduction behavior of molybdenum oxides was studied using a horizontal-tube reactor. Reduction was carried out in two stages: MoO₃ → MoO₂ and MoO₂ → Mo. In the first stage, a mixed gas composed of 30 vol% H₂ and 70 vol% Ar was selected for the MoO₃ reduction because of its highly exothermic reaction. The temperature ranged from 550 to 600 °C, and the residence time ranged from 30 to 150 min. In the second step, pure H₂ gas was used for the MoO₂ reduction, and the temperature and residence time ranges were 700–750 °C and 30–150 min, respectively. The hydrogen reduction behavior of molybdenum oxides was found to be somewhat different between the two stages. For the first stage, a temperature dependence of the reaction rate was observed, and the best curve fittings were obtained with a surface reaction control mechanism, despite the presence of intermediate oxides under the conditions of this study. Based on this mechanism, the activation energy and pre-exponential were calculated as 85.0 kJ/mol and 9.18×10^7 , respectively. In addition, the pore size within a particle increases with the temperature and residence time. In the second stage, a temperature dependence of the reaction rate was also observed; however, the surface reaction control mechanism fit only the early part, which can be ascribed to the degradation of the oxide crystals by a volume change as the MoO₂ → Mo phase transformation proceeded in the later part.

Key words : Molybdenum, Hydrogen Reduction, 2- stage Reduction, MoO₃, MoO₂

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§ Corresponding Author : Kyoungkeun Yoo (E-mail : kyoo@kmou.ac.kr) / Hanggoo Kim (E-mail : hanggoo_kim@kmou.ac.kr)

Department of Energy and Resources Engineering, Korea Maritime and Ocean University, 727 Taejong-ro, Youngdo-gu, Busan 49112, Korea

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1. Introduction

In the recycling of molybdenum-containing sources, the hydrogen reduction of molybdenum trioxide to molybdenum is the last step in producing molybdenum powders. Most of important properties of the resulting powder such as average grain size and specific surface area are determined by this step. The reduction of molybdenum oxide is necessarily carried out in two steps to prevent the melting and the sublimation loss of MoO_3 at temperatures above about 600°C and to prevent the formation of coarse metal powder due to the presence of water vapor developed during the reaction¹⁻⁵⁾. In the first-stage, molybdenum trioxide is reduced at a temperature in the range of $500\text{--}550^\circ\text{C}$ to produce molybdenum dioxide ($\text{MoO}_3 + \text{H}_2 \rightarrow \text{MoO}_2 + \text{H}_2\text{O}$), and in the second-stage, the molybdenum dioxide is reduced to molybdenum in the temperature range of $750\text{--}900^\circ\text{C}$ ($\text{MoO}_2 + 2\text{H}_2 \rightarrow \text{Mo} + 2\text{H}_2\text{O}$). For the first-stage, the direct reduction (MoO_3 -to- MoO_2) had been considered in early times⁶⁻⁸⁾, but the formation

of Mo_4O_{11} via the parallel reaction mechanism (comproportionation) of MoO_3 and MoO_2 ($\text{MoO}_3 + \text{MoO}_2 \rightarrow \text{Mo}_4\text{O}_{11}$) has been reported in recent literature^{9,10)}, although its driving force is not explained by Gibbs free energy change. According to the data base of Outokumpu HSC Chemistry 5.11, three low-volatility intermediate oxides such as $\text{MoO}_{2.889}$ (or Mo_8O_{23}), $\text{MoO}_{2.875}$ (or $\text{Mo}_{17}\text{O}_{47}$) and $\text{MoO}_{2.75}$ (or Mo_4O_{11}) can be formed during the first-stage reduction, and they disappear at temperatures above 900°C , as shown in the Fig. 1.

For the second-stage hydrogen reduction, a few of papers¹²⁻¹⁴⁾ have reported on the reduction kinetics, but thought to be insufficiently studied.

In this study, thermodynamics, kinetics, and morphology of the two stage hydrogen reductions were investigated from a different standpoint, and the three aspects were compared between the two stages. The objective of this study is to obtain experimental data which could be effectively used in a commercial operation of the two stage hydrogen reduction process.

Fig. 1. Phase diagrams of Molybdenum oxides at temperatures of 600°C , 700°C , 850°C , and 900°C (created using the software of Outokumpu HSC Chemistry 5.11).

2. Experimental

High purity (99.9 wt%) MoO₃ and MoO₂ powders from Cisa, Japan were used in this study in the first and second-stages, respectively. The oxide powders were isothermally reduced by hydrogen gas using a horizontal tube furnace (ID 60 x L 1000). An alumina boat loaded with 10 gram of a sample was placed in the middle of the tube and the total gas flow rate was fixed at 1 L/min. In the first-stage, a mixed gas composed of 30 vol% H₂ and 70 vol% Ar was selected for the reduction of MoO₃, in the consideration of its high exothermic reaction. The temperatures range was from 550 to 600°C, and the residence time ranged from 30 to 150 min. In the second step, a pure H₂ gas was used for the reduction of MoO₂, and the ranges of temperature and residence time were from 700 to 750°C and from 30 to 150 min, respectively. The fractional conversion was calculated by a weight loss, and the phase change was characterized by X-ray diffraction (XRD, D/Max 2500, Rigaku, Japan) and scanning electron microscopy (SEM, S-2400, HITACHI, Japan).

3. Results and Discussion

The isothermal stepwise process can be expressed as a route represented in Fig. 2, which was created using the software of Outokumpu HSC Chemistry 5.11.

According to the figure, the intermediate oxides can exist at a temperature lower than around 870°C and at a partial pressure ratio of H₂O to H₂ higher than 10⁵.

For the first-stage, the experimental results were represented in Figs. 3 to 5. The fractional conversions at different temperatures are shown in Fig. 3 (a). A temperature dependence of reaction rate was observed, and the best curve fittings were obtained with a surface reaction control mechanism in spite of the presence of the intermediate oxides at the conditions of this study as represented in Fig. 3 (b). Based on this mechanism, the activation energy and the pre-exponential were calculated as 85.0 kJ/mol and 9.18×10⁷, respectively. The changes

Fig. 2. A route of the stepwise hydrogen reduction of MoO₃ (created using the software of Outokumpu HSC Chemistry 5.11).

Fig. 3. Reaction rates of MoO₃ at 550°C, 575°C, and 600°C during the first-stage hydrogen reduction: (a) fractional conversion (b) curve fittings with a surface reaction control mechanism.

Fig. 4. Changes in XRD patterns the during the first-stage hydrogen reduction of MoO₃: (a) change with residence time at 575°C (b) change with temperature at the residence time of 60 min.

Fig. 5. SEM images of the molybdenum oxides before the hydrogen reduction and after the first-stage hydrogen at 600°C.

in XRD patterns are shown in Fig. 4. As can be seen in the figure, only Mo₄O₁₁ was detected as an intermediate oxide, and this phase disappeared at a temperature higher than 600°C or even at a lower temperature like 575°C with a long resident time. The formation of Mo₄O₁₁, however, seemed to have little effect on the

reaction kinetics as can be seen in Fig. 3. Although the other intermediate oxides were not detected in this study, a similar rate-controlling step to that by Wang et al. was obtained⁽¹¹⁾, and in their study CO-15 vol% CO₂ mixed gases were used in the temperature range of 628–675°C. Fig. 5 shows SEM images of the MoO₃ powder

Fig. 6. Evidences of the metallic part in the molybdenum oxide reduced at 600°C; (a) XRD analysis (b) SEM-EDX analysis for the reduction time of 150 min.

Fig. 7. Reaction rates of MoO₂ at 700°C, 725°C, and 750°C during the second-stage hydrogen reduction: (a) fractional conversion (b) curve fittings with a surface reaction control mechanism.

before the hydrogen reduction and after the reduction times of 30 min and 90 min at 600°C. As can be seen in the images, the pore size increased with the reduction time (i.e. with the conversion), which support the surface reaction control mechanism.

On other hand, metallic parts of molybdenum was overserved even in the first-stage reduction by hydrogen at 600°C at a reduction time longer than 120 min, as can be seen in the Figs. 6 (a) and 6 (b). This formation of metallic Mo, however, is not important because the formation rate is too slow to be meaningful in terms of a process concept.

For the second-stage reduction, the experimental results were represented in Figs. 7 to 9. In this study, a high purity MoO₂ of reagent grade was used, instead of the produced MoO₂ from the first-stage of this study, to avoid any residual effect from the first-stage reduction. The fractional conversions at different temperatures are shown in Fig. 7 (a). The temperature dependence of the reaction rate was also observed in the second-stage hydrogen reduction, but the surface reaction control mechanism fit only the early part of the second-stage reduction as represented in Fig. 7 (b).

The changes in XRD patterns are shown in Fig. 8. As

Fig. 8. Changes in XRD patterns the during the second-stage hydrogen reduction of MoO₂: (a) change with residence time at 725°C (b) change with temperature at the residence time of 60 min.

Fig. 9. SEM images of the molybdenum oxides before the hydrogen reduction and after the second-stage hydrogen at 750°C.

can be seen in the figure, MoO₂ was completely reduced into metallic Mo at a high temperature above 750°C or at a lower temperature like 725°C with a long resident time. Fig. 9 shows SEM images of the MoO₂ powders before the hydrogen reduction and after the reduction

times of 30 min and 90 min at 750°C. As shown in the images, the morphologies were quite different from those observed in the first-stage reduction.

The original MoO₂ powder was composed of many small platelet-shaped MoO₂ particles. The platelet shape

was broken as the MoO₂ was reduced to metallic Mo, and when the MoO₂ is completely reduced to metallic Mo, there were found to be many cracks and broken pieces, which resulted from the tension stress due to a volume change during the phase transformation, and this degradation may change the later part mechanism of the hydrogen reduction as can be seen in the Fig. 7b. This degradation was also reported by Dang et al.¹²⁾, and a pseudomorphic transformation mechanism was introduced in their study.

4. Conclusion

Hydrogen reduction behaviors of molybdenum oxides were studied using a horizontal tube reactor. The reduction was carried out in two stages: MoO₃ → MoO₂ and MoO₂ → Mo. The temperatures range was from 550 to 600°C, and the residence time range was from 30 to 150 min. In the second step, a pure H₂ gas was used for the reduction of MoO₂, and the ranges of temperature and residence time were from 700 to 750°C and from 30 to 150 min, respectively. The hydrogen reduction behaviors of the molybdenum oxides was found to be somewhat different between the two stages.

- (1) For the first-stage, a temperature dependence of reaction rate was observed, and the best curve fittings were obtained with a surface reaction control mechanism, in spite of the presence of the intermediate oxides at the conditions of this study. Based on this mechanism, the activation energy and pre-exponential were calculated as 85.0 kJ/mol and 9.18×10^7 , respectively. In addition, the pore size within a particle was increased with temperature and residence time.
- (2) For the second-stage, on the other hand, the temperature dependence of the reaction rate was also observed in the second-stage hydrogen reduction, but the surface reaction control mechanism fit only the early part of the second-stage reduction. Although this may be ascribed to cracks and broken pieces

resulted from the volume change by the phase transformation from MoO₂ to Mo during the hydrogen reduction, a more active research is planned to obtain a more clear reaction mechanism.

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구원범

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