

論文 / 著書情報
Article / Book Information

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Title(English)	Ultra-small Mo-Pt Subnanoparticles for CO2 Hydrogenation at Room Temperature and Atmospheric Pressure
著者(和文)	アウギアトコ
Author(English)	Augie Atqa
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種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

系・コース : Chemical Science
Department of, Graduate major in and Engineering

系
コース

申請学位 (専攻分野) : 博士
Academic Degree Requested Doctor of (Engineering)

学生氏名 :
Student's Name Augie Atqa

審査員主査 : Prof. Kimihisa
Chief Examiner Yamamoto

要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Subnanoparticles (SNPs), with just a size of 1 nm, display unique properties endowing them with exceptional reactivity not seen in their bulk- or nano-analogs. They are also free of phase separation, achieving various mixtures of metals that create a synergistic effect, maximizing their utility as catalysts. Additionally, subnanoparticles enable atomic dynamics suggested as the source of high reactivity. This makes subnanoparticles promising catalyst candidates for room-temperature conversion of carbon dioxide. Contrary to these expectations, there were no studies of subnanoparticles to realize CO₂ conversion at these ambient conditions.

In Chapter 1 “Introduction”, I described the background about subnanoparticles, their synthesis methods, and the strategy to employ them for achieving CO₂ hydrogenation at room temperature and atmospheric pressure.

In Chapter 2 “Low-temperature CO₂ Hydrogenation: A Case of Pt Subnanoparticles”, I investigated low-temperature CO₂ hydrogenation using TiO₂-supported Pt particles with various sizes (1 nm, 2 nm, 4 nm, and 15 nm). Their sizes and electronic states were measured using High-Angle Annular-Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) and X-ray Photoelectron Spectroscopy (XPS), respectively. The smallest 1-nm Pt/TiO₂ SNP had the highest catalytic activity and started the reaction from 40 °C. It demonstrated the lowest apparent activation energy of 53 kJ/mol amongst all samples. Electron Spin Resonance (ESR) measurements revealed that 1-nm Pt/TiO₂ SNP has the most amount of oxygen vacancies, due to its high dispersion and excellent hydrogen spillover ability. ESR also indicated that while the number of oxygen vacancies influences the catalytic reactivity, it is not the sole determining factor.

In Chapter 3 “Mo-Pt Subnanoparticles for CO₂ Hydrogenation at Room Temperature and Atmospheric Pressure”, I described an alloy subnanoparticle of Mo and Pt for CO₂ hydrogenation at room temperature and atmospheric pressure. It is designed to create a specific active site combining their respective function for CO₂ and H₂ adsorption-dissociation. From the initial catalyst screening, a Mo:Pt molar ratio of 1:2 was found to be the most active. Based on this screening result, the precise synthesis using a dendrimer template was conducted. The Mo₄Pt₈O_x/TiO₂ SNPs was characterized using XPS and X-ray Absorption Near Edge Structure (XANES) measurements. While the Pt₁₂/TiO₂ SNPs showed CO production beginning from 40 °C, the Mo₄Pt₈O_x/TiO₂ SNPs enabled the reaction from room temperature (RT). It has the lowest apparent activation energy of 49 kJ/mol and the catalytic activity at RT was observed for 49 h. The decrease of the catalytic activity after 24 h was

possibly due to water formation, which was confirmed using a quadrupole mass spectrometer and *operando* DRIFTS measurements.

In Chapter 4 “Mechanistic Studies of CO₂ Hydrogenation at Room Temperature and Atmospheric Pressure”, I elucidated the mechanism of the full catalytic cycle of the reaction from CO₂ activation to catalyst reactivation. *In situ* XANES measurements revealed the reversibility of Mo oxidation-reduction in Mo₄Pt₈O_x/TiO₂ SNPs, which plays a crucial role in enabling the reaction from RT. *In situ* DRIFTS measurements showed the CO formation-onto & desorption-from the Pt surfaces of Mo₄Pt₈O_x/TiO₂ SNPs. It also explained the reason why Mo₄Pt₈O_x/TiO₂ SNPs enable the reaction at RT and 1 bar while Pt₁₂/TiO₂ SNPs cannot, because of the easier CO desorption. This idea was supported by the result of Density Functional Theory (DFT) calculations of Pt-CO adsorption energies in both SNPs, pointing out the average weakening CO adsorption by a 15.2 kcal/mol in Mo₄Pt₈O_x/TiO₂ SNPs.

In conclusion, for the first time, I have successfully achieved thermally-driven CO₂ hydrogenation at room temperature and atmospheric pressure by employing ultra-small Mo₄Pt₈O_x subnanoparticles supported on TiO₂. Comprehensive mechanistic study, including advanced spectroscopical measurements and theoretical calculations, were performed. This study helps us to understand the nature of the catalytic process at room temperature and atmospheric pressure, and could be a stepping stone in designing a catalyst that enables low-cost CO₂ conversion to fuels.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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