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# Ultra-small Mo-Pt Subnanoparticles for $CO_2$ Hydrogenation at Room Temperature and Atmospheric Pressure

by

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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 $CO_2$ conversion at these ambient conditions. Here, for the first time, I have demonstrated a partially-oxidized Mo-Pt subnanoparticles ($Mo_4Pt_8O_x$) that catalyzes $CO_2$ hydrogenation at room temperature and atmospheric pressure.

In Chapter 1 “Introduction”, I described the background about subnanoparticles, their synthesis methods, and the strategy to employ them for achieving $CO_2$ hydrogenation at room temperature and atmospheric pressure.

In Chapter 2 “Low-temperature $CO_2$ Hydrogenation: A Case of Pt Subnanoparticles”, I investigated low-temperature $CO_2$ hydrogenation using $TiO_2$-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 $Pt/TiO_2$ 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 $Pt/TiO_2$ 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 $CO_2$ Hydrogenation at Room Temperature and Atmospheric Pressure”, I described an alloy subnanoparticle of Mo and Pt for $CO_2$ hydrogenation at room temperature and atmospheric pressure. It is designed to create a specific active site combining their respective function for $CO_2$ and $H_2$ 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 $Mo_4Pt_8O_x/TiO_2$ SNPs was characterized using XPS and X-ray Absorption Near Edge Structure (XANES) measurements. While the $Pt_{12}/TiO_2$ SNPs showed CO production beginning from 40 °C, the $Mo_4Pt_8O_x/TiO_2$ 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 $CO_2$ Hydrogenation at Room Temperature and Atmospheric Pressure”, I elucidated the mechanism of the full catalytic cycle of the reaction from $CO_2$ activation to catalyst reactivation. *In situ* XANES measurements revealed the reversibility of Mo oxidation-reduction in $Mo_4Pt_8O_x/TiO_2$ 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 $Mo_4Pt_8O_x/TiO_2$ SNPs. It also explained the reason why $Mo_4Pt_8O_x/TiO_2$ SNPs enable the reaction at RT and 1 bar while $Pt_{12}/TiO_2$ 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 $Mo_4Pt_8O_x/TiO_2$ SNPs.

In conclusion, for the first time, I have successfully achieved thermally-driven $CO_2$ hydrogenation at room temperature and atmospheric pressure by employing ultra-small $Mo_4Pt_8O_x$ subnanoparticles supported on $TiO_2$. 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 $CO_2$ conversion to fuels.

**Keywords**: subnanoparticles, molybdenum, platinum, room temperature, $CO_2$ hydrogenation, CO desorption

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