



Title	Supported Re Catalysts for the Transformation of CO ₂ to Value-added Chemicals [an abstract of dissertation and a summary of dissertation review]
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Supported Re catalysts for the transformation of CO₂ to value-added chemicals
(担持レニウム触媒を用いた二酸化炭素変換反応による高付加価値化合物の合成)

The growing concern on climate change and the depletion of fossil fuels has prompted the search for alternative carbon sources for power generation and chemical production. Carbon dioxide (CO₂), which accounts for approximately 76% of global greenhouse gases emissions, is widely regarded as the major contributor to the acceleration of global warming that leads to the deterioration of the climate situation around the world. Therefore, there is an urgent need to contain and mitigate the ever-rising anthropogenic CO₂ emission. Despite all the negative connotations surrounding CO₂, it is a promising prospective for potential applications as a raw material for the production of fuels and chemicals. To this day, a great deal of effort has been dedicated to the study of CO₂ valorization, in pursuit of carbon neutrality to ensure the materialization of a truly sustainable society.

In recent years, the direct synthesis of methanol (MeOH) via CO₂ hydrogenation has attracted significant interest in both academic and industrial sector, owing to the concept of methanol economy as advocated by George Olah, the late Nobel laureate. Conventionally, MeOH is exclusively produced from fossil-derived syngas (gas mixture of carbon monoxide and hydrogen) by employing Cu-based catalyst, typically under relatively extreme conditions (T > 200 °C, P = 5-10 MPa). The hydrogenation of CO₂ to MeOH is exothermic, which means that a lower reaction temperature is more favorable for the formation of MeOH. In this work, TiO₂-supported Re (Re/TiO₂) catalyst was found to be highly active and selective for CO₂ hydrogenation to MeOH, which was conducted in batch system (T = 150 °C, P_{CO₂} = 1 MPa, P_{H₂} = 5 MPa), achieving the highest turnover number (TON) and MeOH selectivity. The catalyst was also found to be superior to the conventional Cu-based methanol synthesis catalyst when tested in a fixed-bed continuous flow reactor (T = 150 °C, P = 36 MPa, H₂/CO₂ = 3, GHSV = 2000 h⁻¹), showing comparable or higher CO₂ conversion, and exceptional selectivity for MeOH. Through the means of various *in situ/operando* characterization methods such as DRIFTS, AP-XPS, XAS together with isotopic labelling experiment, important reaction intermediates and the behavior of catalytically active Re species were able to be determined. It was found that Re species were reduced under H₂ atmosphere and re-oxidized upon exposure to CO₂, in which the oxidation state of Re fluctuates between Re⁰ and Re⁴⁺. Metallic Re species was responsible for the activation of H₂, whereas the formation of formate species occurs on cationic Re species for subsequent hydrogenation to form MeOH.

Aside from the direct synthesis of useful C1 chemicals via CO₂ hydrogenation, the application of CO₂, often together with H₂ as a methylating agent has emerged as a promising strategy to achieving a higher equilibrium conversion of CO₂. Although methanol production from the hydrogenation of CO₂ has recently been tested out industrially, this process usually suffers from a low equilibrium conversion of CO₂ due to thermodynamic limitations. One possible approach to achieve high CO conversion is using a lower reaction temperature to produce MeOH. However, the development of a highly active and selective catalyst for low temperature MeOH synthesis is not an easy feat. Therefore, by employing CO₂/H₂ as a methylating agent for the one-pot synthesis of value-added products, we can bypass this issue surrounding low equilibrium conversion of CO₂. In this study, a combined catalyst system consisting of Re/TiO₂ and zeolite catalyst was used for the catalytic methylation of aromatic hydrocarbons in batch reactors, namely benzene, toluene, and *m*-xylene. These substrates were chosen due to their lower demand in the petrochemical industries. The combination of Re/TiO₂ and H-MOR(90) is highly active for the methylation of benzene (T = 250 °C, P_{CO₂} = 1 MPa, P_{H₂} = 5 MPa) whereas Re/TiO₂ and H-Beta(40) is the most suitable for the methylation of toluene and

m-xylene ($T = 240\text{ }^{\circ}\text{C}$, $P_{\text{CO}_2} = 1\text{ MPa}$, $P_{\text{H}_2} = 5\text{ MPa}$), exhibiting the highest overall yield and selectivity of methylated products. ML approaches were also used to improve the performance of the catalytic methylation process, and a 1.8 wt% of Re/TiO₂ was found to surpass the activity of previous best catalyst which was 1 wt% Re/TiO₂.

Metal-support interactions (MSIs) influence the behavior of catalyst by changing the properties of the metal, its interface, and its perimeter sites. The nature of the active sites created by the metal-support environment can be affected by the size, shape, and degree of dispersion of the metal species. The MSI also affects the resistance of metal to sintering, a process that often leads to the deactivation of catalyst. Therefore, understanding how MSIs behave depending on the metal and oxide used is essential for tailoring the activity, selectivity, and stability of oxide-supported metal catalysts. Driven by the interest of unveiling the precise nature of supported Rhenium catalysts, which has been performing relatively well in our previous studies, a systematic investigation is conducted with the aim of describing the MSIs between Re and oxide supports such as TiO₂, SiO₂, Al₂O₃, MgO, V₂O₅, ZrO₂, Nb₂O₅, and CeO₂. The excellent catalytic properties of Re catalysts are often ascribed to the high dispersion of Re on its oxide support. A combined experimental and computational approach was employed to investigate the MSIs of supported Re catalysts. The results suggests that the degree of dispersion and aggregation of Re atoms on the surface of oxide supports is correlated to the electronic properties of both species. Metal oxide supports that have higher electron affinity (EA) than the work function (WF) of Re (TiO₂, V₂O₅ and CeO₂) can accept electrons from Re into their conduction band (CB), which induces strong MSIs and results in a relatively high Re-adsorption energy (E_{ads}) that leads to a higher degree of dispersion of supported Re metal. Conversely, metal oxides that has EA smaller than the WF of Re (MgO and Al₂O₃) do not incorporate electrons from Re into their CB, showing only weak MSIs and a correspondingly low E_{ads} for Re. Ultimately, this leads to low degree of dispersion of Re metal. These findings are further corroborated with the results from XRD and HAADF-STEM.

As an ending note, TiO₂-supported Re was found to be highly promising as a catalyst for CO₂ valorization reaction, showing high activity for low temperature hydrogenation of CO₂ to methanol and the catalytic methylation of aromatic hydrocarbons. The precise nature of the Re/TiO₂ was investigated using both computational and experimental method and the high dispersion of Re species on TiO₂ was attributed to the strong MSI between the two.