



Title	Hydrogenation of Carbon Dioxide over Doped Metal Oxide Catalysts [an abstract of dissertation and a summary of dissertation review]
Author(s)	Shaikh, Nazmul Hasan Mohammad Dostagir
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学位論文内容の要旨

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ハーメッド ドスタギル

学位論文題名

Hydrogenation of Carbon Dioxide over Doped Metal Oxide Catalysts
(ドーピング型金属酸化物触媒による二酸化炭素の水素化)

Fossil fuels have been the primary source of energy for over a century. As a result, concentration of CO₂, a major greenhouse gas, has been increasing in the atmosphere. This increase in the atmospheric CO₂ content is having adverse effect on environment such as global warming, ocean acidification and rise in sea level. Therefore, at this time it is vital to make strategies for reduction of CO₂ emission in the atmosphere. One effective way is to use CO₂ as a chemical feedstock to produce fuels and chemicals instead of relying on fossil fuels. This will not only reduce emission of CO₂ but also provide necessary chemicals and fuels from a waste resource. In this direction, production of methanol and CO from hydrogenation of CO₂ is important because they are precursors for many industrially important chemicals and liquid fuels.

The major challenge in CO₂ hydrogenation to methanol or CO is to achieve high productivity along with high selectivity. The current industrial catalyst for methanol synthesis, Cu-ZnO/Al₂O₃, produces methanol with low activity and the catalyst gets deactivated rapidly. Conventional supported metal catalysts are not effective because metal nanoparticles tend to over-hydrogenate methanol and CO to produce methane, which is not a desired product. Selective hydrogenation of CO₂ often happens at the interface of a metal and metal oxide. Therefore, careful design of interfacial sites on a metal oxide support is essential to achieve desired activity and selectivity in CO₂ hydrogenation reaction. Keeping these things in mind, I chose to design metal oxide catalysts doped with metal atoms for selective CO₂ hydrogenation. Doping of metal atoms in the crystal is expected to increase the stability of isolated atoms via strong interaction with oxide and create a specific catalytic site. In addition to the catalyst design for high activity, the parameter that influences the selectivity of different products was also investigated.

Chapter 1 provides the background of the study and the objective of this dissertation in detail. A broad overview is provided to establish the benefits of methanol and CO production from CO₂ using thermochemical process along with thermodynamic consideration of the reaction. Current research in catalyst design for CO₂ hydrogenation to methanol and CO is discussed in the context of selectivity and activity considering the factors affecting them. This discussion is followed by the problem formulation in the field and framing the objective of this thesis.

In Chapter 2, CO₂ hydrogenation to methanol is studied using an indium oxide (In₂O₃) that was reported as a stable and selective catalyst for this reaction. However, the methanol productivity was low due to poor CO₂ conversion over pure In₂O₃. This chapter shows the synthesis and use of In₂O₃ catalysts doped with several transition metal atoms. Among all the dopants used, Rh doped In₂O₃ showed the highest methanol productivity without reduction in methanol selectivity. Over Rh doped In₂O₃ catalyst, a methanol productivity of 1.0 gMeOH h⁻¹ gcat⁻¹ was achieved, which is one of the highest reported. Extensive characterization was carried out to understand this promotional effect. It was found that Rh atoms were atomically dispersed throughout the In₂O₃ crystal and under hydrogenation condition, high density of oxygen vacancies were formed around Rh atoms via reduction. This created Rh-Vo-In (Vo = oxygen vacancy) interfacial active sites, which promoted strong CO₂ adsorption. Rh atoms also helped in H₂ dissociation and transfer of hydrogen to C of CO₂ formed formate species. Formate underwent further hydrogenation to form methanol. This chapter shows that atomically dispersed metal atom having oxygen vacancy near it can improve CO₂

hydrogenation ability.

In Chapter 3, the concept of atomically dispersed metal atom having oxygen vacancy near it was applied for reverse water gas shift (RWGS) reaction. Co doped ZrO₂ catalysts were prepared and CO selectivity over 95% was achieved with CO₂ conversion around 20%. Oxygen vacancies formed near Co atoms as result of charge imbalance between Co²⁺ and Zr⁴⁺. This oxygen vacancies helped in the chemisorption of CO₂ as carbonate species. H₂ dissociation happened over Co single atoms and formate intermediate formed at the interfacial site. Stabilization of formate over the interfacial site was confirmed by in-situ characterization. Over this catalyst, formate decomposed selectively to CO instead of forming methanol via further hydrogenation. Methane production via further hydrogenation of CO was suppressed by weak interaction of CO over the active site. As a result, high CO selectivity was achieved with high activity over an oxygen vacant interfacial site.

In Chapters 2 and 3, it was clear that the interfacial sites with similar oxygen vacancy can dramatically control the selectivity of products. While the influence of dopant or active metal is also always crucial, there is little information on the importance of oxide over product selectivity. Therefore, in Chapter 4, I focused on the role of support in controlling CO₂ hydrogenation pathway. Two indium doped catalysts, In-TiO₂ and In-ZrO₂, were synthesized with different supports. It was found that the CO₂ hydrogenation pathway and selectivity are dependent on the nature of the support metal at the interfacial site. Over In-TiO₂ catalyst, indium species were reduced under hydrogenation condition due to the presence of easily reducible TiO₂. As a result, the interface could not hydrogenate the adsorbed CO₂ to formate species. Instead, indium and neighboring partially reduced Ti species were oxidized by CO₂ and produced CO selectively through the redox mechanism. On the other hand, due to non-reducible nature of ZrO₂, the indium species in In-ZrO₂ were able to hydrogenate the adsorbed CO₂ to methanol through the formate formation. This chapter shows the importance of support metal atom at the interfacial site of the doped oxide catalysts in CO₂ hydrogenation.

Chapter 5 of this thesis summarizes the important results. This dissertation has shown that doped metal oxide catalysts are highly active and selective for CO₂ hydrogenation to methanol and CO in the presence of unique interfacial sites. High productivity of methanol with high selectivity can be obtained under industrially relevant conditions. High CO selectivity was achieved at lower temperature, which can open the possibility of the combination of RWGS reaction and the downstream reactions from CO to produce valuable products directly from CO₂. Moreover, mechanistic insight considering the parameters that influence the activity and selectivity was discussed. I believe that this dissertation will help in the development of new highly active and selective catalysts for CO₂ hydrogenation.