Review Article

Advances in catalytic homogeneous hydrogenation of carbon dioxide to methanol

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ABSTRACT

Increase in atmospheric CO$_2$ concentration due to the combustion of fossil fuels has been linked to the presently observed global warming phenomenon. In order to mitigate excessive emissions, efforts are underway to capture CO$_2$ from various emission sources and sequester it underground. In parallel, utilization of the captured CO$_2$ to produce value added products and fuels has also been advocated. Among these products, methanol, which can be used as a fuel and fuel additive, is of particular interest. Methanol can be synthesized by hydrogenation of CO$_2$ and could therefore lead to a carbon neutral cycle in the frame of a methanol economy, as proposed by the late professor George Olah. In this review, we reflect upon the recent advances in homogeneous reduction of CO$_2$ to methanol using molecular H$_2$. This research area has seen significant progress over the last five years and the recent studies for this challenging transformation are discussed herein. Catalyst activity, selectivity, reaction mechanism and other aspects are analyzed. We also comment on future prospects awaiting exploration to improve the catalytic systems for this reduction. We hope that this review will provide the reader with an overview of the current state of the art on homogeneous CO$_2$ hydrogenation to methanol in a concise manner and provide potential directions in which further investigations can be undertaken in order to eventually make this process economically viable.

1. Introduction

It is now commonly agreed by most scientists that excessive anthropogenic CO$_2$ emission is a main contributor to global warming and the associated climate change phenomenon. The intergovernmental panel on climate change (IPCC) predicts a global temperature rise of up to 4.8 °C over the next century. The expected consequences of climate change are for the most part negative with significant environmental, societal and economical costs [1]. However, despite the dire situation and the ominous predictions, about 80% of our energy consumption still originates from the burning of fossil fuels (coal, natural gas and petroleum oil), resulting in the emission of more than 35 billion metric tonnes of CO$_2$ into the environment in 2015 alone. As the world's human population is predicted to grow from 7.3 billion today to 9.7 billion by 2050 and 11.2 billion by 2100, along with increasing standard of living, a steadily increasing global energy demand seems inevitable. In this context, utilization of cleaner renewable energy sources and limiting CO$_2$ emission into the atmosphere are paramount in order to avoid the adverse consequences of excessive anthropogenic carbon emissions.

One way to avoid increasing CO$_2$ concentration in the atmosphere is by capturing CO$_2$ from emission point sources as well as from dilute sources like ambient air [2,3]. The captured CO$_2$ can then be pressurized and stored underground in geological formations, in a process called carbon capture and sequestration (CCS) [4,5]. An alternate and attractive pathway is carbon capture and recycling (CCR), where the concentrated CO$_2$ obtained after capture is used to make new materials and fuels. For instance, fuels such as methanol, dimethylether and formic acid can be obtained by hydrogenation of CO$_2$ captured from the atmosphere [6–9]. Upon utilization of these fuels, CO$_2$ would be released back to the atmosphere, from where it can again be captured and converted to fuels, leading to a carbon neutral cycle (Fig. 1). Producing methanol through CCR is an essential part of the proposed "Methanol Economy" concept championed by late professor and Nobel Laureate George A. Olah [9,10].

Methanol can be directly used as a fuel in internal combustion engines (ICE), gas turbines and direct methanol fuel cells (DMFC), as a feedstock for numerous chemicals, and as a precursor for the production of higher hydrocarbons [9]. Another way to harness the energy stored in methanol is through methanol reforming, where H$_2$ and CO$_2$ are produced from a methanol/water mixture. Hydrogen is a clean fuel since its only combustion product is water. Hydrogen has also a high gravimetric energy density. However, due to its gaseous nature and thus low volumetric density, storage and handling of pure hydrogen

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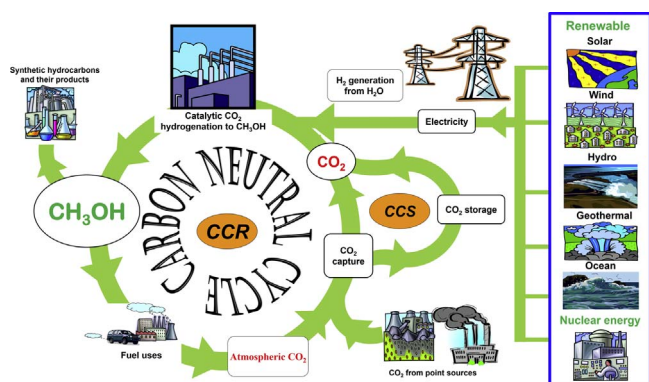
Fig. 1. Carbon neutral cycle in the context of this review.

CO$_2$ hydrogenation

$$CO_2 + 3H_2 \;\underset{\text{Reverse}}{\overset{\text{Forward}}{\rightleftharpoons}}\; CH_3OH + H_2O \qquad (1)$$

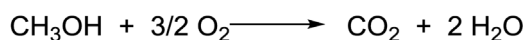Aqueous methanol reforming
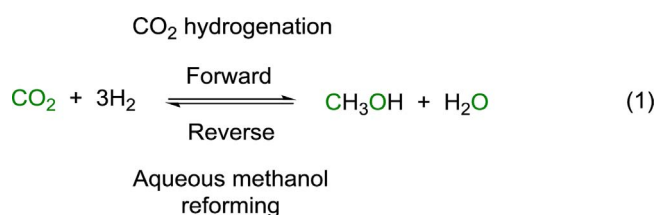
Scheme 1. CO$_2$ hydrogenation to methanol and methanol reforming.

remains a challenge [11,12]. In practice, the use of a LOHC (liquid organic hydrogen carrier) would be preferable, as these LOHC are much more user friendly, safer and easier to use compared to pure hydrogen [13]. Methanol is a convenient LOHC since it can be produced through CO$_2$ hydrogenation, and the stored H$_2$ can be conveniently extracted through aqueous reforming (Scheme 1).
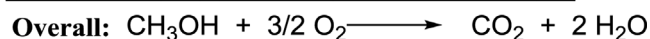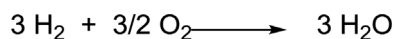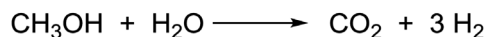
The produced H$_2$ can then be fed to a hydrogen fuel cell for electrical power generation. This two-step process, methanol reforming and subsequent use of generated H$_2$ in proton exchange membrane (PEM) fuel cells, has been named a "reformed methanol fuel cell (RMFC)" and constitutes essentially an indirect methanol combustion route as shown in Scheme 2. Ideally, for a "methanol economy" to be sustainable, the hydrogen must be obtained by water electrolysis or any other water splitting method using renewable or nuclear energy to achieve an overall carbon neutral cycle [14–18]. As such, methanol acts not only as an energy carrier, but also an energy storage medium for intermittent and fluctuating renewable energy sources such as solar and wind.

Heterogeneous Cu-based catalysts are known for both CO$_2$ hydrogenation to methanol/water and the reverse reaction, methanol reforming, but require high temperature (> 200 °C) and/or high pressure (> 50 bar) for both forward and reverse reactions [19–23]. In contrast, homogeneous catalytic systems can operate at temperatures below 150 °C [24]. Since the hydrogenation reaction is entropically unfavorable, performing it at lower

Methanol Oxidation in ICE or DMFC

$$CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

Methanol Oxidation in RMFC

$$CH_3OH + H_2O \longrightarrow CO_2 + 3\,H_2$$
$$3\,H_2 + 3/2\,O_2 \longrightarrow 3\,H_2O$$

Overall: $CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2\,H_2O$

Scheme 2. Comparison of methanol oxidation in ICE, DMFC and RMFC.

temperature would improve the overall theoretical yield. In addition, the homogeneous catalyst can be rationally designed by studying the mechanism on a molecular level and thus the overall catalytic activity can be improved. An ideal industrial or practical catalyst for the synthesis of CH$_3$OH (derived from CO$_2$) and the reverse reaction is expected among others to have the following properties/benefits: (i) be preferably non-noble metal-based, (ii) operate at low temperatures and low pressures, (iii) have high TON/TOFs, and (iv) have a long lifetime. This would reduce the operational cost and energy input to the system. Henceforth, the recent advances in the synthesis of methanol from CO$_2$ at low temperature with homogenous catalysis will be discussed.

## 2. Catalytic homogeneous hydrogenation of CO$_2$ to methanol

Back in 1995, the first homogenous metal catalyzed hydrogenation of CO$_2$ to methanol was performed by Tominaga et al. using molecular hydrogen, Ru$_3$(CO)$_{12}$ and potassium iodide in a N-methylpyrrolidone solution at 240 °C under 80 bar of a 3H$_2$:CO$_2$ mixture (Scheme 3) [25]. In the absence of potassium iodide, Ru$_3$(CO)$_{12}$ decomposed to ruthenium metal causing methanation of CO$_2$. However, in the presence of a halide, CO$_2$ was first converted to CO (through the reverse water-gas shift reaction) at about 200 °C and then subsequent hydrogenation of CO formed methanol at about 240 °C. Below 160 °C, no trace of CO or CH$_3$OH was observed and above 240 °C, the formed methanol further hydrogenated to methane. Other transition metal complexes such as Rh$_3$(CO)$_{12}$, Ir$_4$(CO)$_{12}$, W(CO)$_6$, Mo(CO)$_6$, Fe$_2$(CO)$_9$ and Co$_2$(CO)$_8$ gave no CO$_2$ hydrogenation products. From the mechanistic study, it was identified that the tetranuclear ruthenium cluster formed during the reaction first converts CO$_2$ to CO. Under the CO atmosphere, the tetranuclear ruthenium cluster is converted to [HRu$_3$(CO)$_{11}$]$^-$ and [Ru(CO)$_3$I$_3$]$^-$ complexes, which catalyze the CO hydrogenation to methanol. However, this system suffers from significant drawbacks in terms of selectivity and the need for high operating temperature.

For more than a decade after this study, no other homogenous catalytic system for the conversion of CO$_2$ to methanol was reported. In 2011, the Milstein group described the successful hydrogenation of carbonates, carbamates and formate esters to methanol in the presence of Ru-PNN pincer catalysts [26]. While direct CO$_2$ hydrogenation wasn't achieved, this process, however, enabled an indirect approach for CO$_2$ to methanol reduction, since carbonates, carbamates, and formates can be easily synthesized from CO$_2$ and alcohols or amines. (Scheme 4). It should be noted that such a two-step sequential process, from CO$_2$ to carbonate, carbamate and formate and then to MeOH, would be mechanistically very different than the system developed by Tominaga, which proceeds through reduction of in situ formed CO.

The ability of complexes **C-1** and **C-2** to catalyze the hydrogenation reaction with molecular H$_2$ stems from their capacity to split hydrogen on a molecular level through metal-ligand cooperation (Scheme 5). The monohydride complex **C-1** can react with molecular hydrogen to form the dihydride complex **C-1A**, the driving force for the reaction being supplied by the aromatization of the pyridine moiety of the ligand. Complex **C-1A** in turn can transfer the proton and hydride to a suitable acceptor molecule with carbonyl/imine functional groups, regenerating the complex **C-1** in the process. Thus, through metal ligand cooperation and ligand aromatization and de-aromatization, complex **C-1** and **C-2** can effectively hydrogenate organic molecules using molecular H$_2$.

In a similar pattern as Milstein et al., Ding et al. demonstrated in

Tominaga et al., 1995
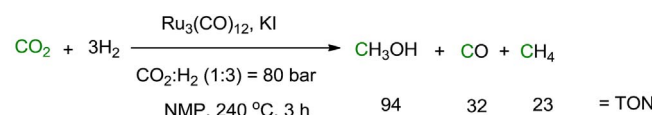
Scheme 3. First example of homogeneous CO$_2$ hydrogenation to MeOH.