[Review Paper]

Carbon Dioxide Utilization by Using Organic or Metal Catalysts

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Technology for the utilization of carbon dioxide (CO2) is expected to gain importance in the near future. This review of studies describes the catalytic conversion of CO2 to chemically useful molecules. Catalysts have been used for the hydrosilylation of CO2, for the synthesis of formic acid (from hydrogen and CO2), for selective decomposition of formic acid to hydrogen and CO2, and for the synthesis of urea from ammonium ions and CO2. These catalytic systems will facilitate the sustainable recycling of CO2.

Keywords
Carbon dioxide, Catalytic reduction, Hydrosilylation, Formic acid, Urea

1. Introduction

Reduction or effective utilization of excessive carbon dioxide (CO2) emissions is essential for countering the onset of manmade global warming. Energy conservation in private and public surroundings and manufacturing sites, and CO2 capture and storage are potential effective measures for reducing CO2 emissions. Promotion of crop growth in agriculture, enhanced crude oil recovery, and chemical conversion of CO2 to other useful compounds are other possibilities for the effective utilization of CO2. Chemical conversion of CO2 has a high energy requirement because CO2 is a stable compound. Consequently, the synthesis using CO2 as a raw material is often involves the use of highly reactive molecules, targeting oxygen-containing or carbonyl compounds, or using catalysts to reduce the activation energy. Highly reactive compounds generally contain functional groups, such as epoxides, dienes, hydrogen, hydroxilanes, and amines, and are used to synthesize cyclic carbonates, carboxylates, formic acid and carbon monoxide (CO), silyl formate, and amides, respectively (Fig. 1). This review discusses the reaction of CO2 and hydroxilanes, interconversion of CO2 + hydrogen and formic acid, and synthesis of urea using CO2 and ammonium cations.

Fig. 1 Reaction of CO2 with Highly Reactive Molecules

2. Synthesis of Silyl Formate via Hydrosilylation

Reduction of CO2 can be achieved under mild reaction conditions using highly reactive hydrosilanes (Fig. 2). The product, silyl formate, is also highly reactive, so can be converted to various useful substances. Metal-complex catalysts have high activity for the hydrosilylation of CO2, and catalysts based on noble and base metals have been widely studied. In particular, Pd-based catalysts are highly active with TOF as high as 19,300 h–1. Organocatalysts, including NHCs, frustrated Lewis pairs, and polymeric cata-
lysts\textsuperscript{14} have also been actively investigated\textsuperscript{11}. Simple fluoride or carbonate salts also act as high-activity catalysts in the reaction\textsuperscript{15}. According to the proposed reaction mechanism, fluoride anion, hydrosilane, and CO\textsubscript{2} first react to produce silicon fluoride and formate (Fig. 3). The generated formate is considered to act as a catalyst, supported by the observation that the reaction occurs after formate is directly introduced into the system\textsuperscript{16}. Counter-cations with small size and high charges are effective in increasing the basicity of the formate anion. Since formate anion is the active species in such systems, cationic polymer can be used to prepare a polymer-supported catalyst, with subsequent improvements in handling\textsuperscript{17,18}.

The use of hydrosilane as a reductant is effective for CO\textsubscript{2} reduction, but preparation of hydrosilanes is complex, thereby limiting industrial applications. Hydrosilylation reaction has been observed using silicon crystals\textsuperscript{19}. Metallic silicon (Si-Si bond) and water first react, and convert silicon to hydrosilane (Fig. 3). The as-prepared hydrosilane is considered to function as an effective reductant. Metallic silicon is discarded as scraps and shavings in the manufacturing process of solar panels. Consequently, a large amount of silicon will be available from discarded solar panels in the future. Therefore, use of industrial waste silicon for CO\textsubscript{2} reduction would serve as a green approach.

3. Interconversion between Formic Acid and CO\textsubscript{2} + Hydrogen

Reaction of CO\textsubscript{2} with hydrogen forms CO and water or formic acid. Reaction of CO and water to form CO\textsubscript{2} and hydrogen is the well-known shift reaction, and the reverse reaction of CO\textsubscript{2} and hydrogen to produce CO and water is the reverse shift reaction. Formic acid is known to occur in an intermediate state between the conversion of CO\textsubscript{2} and CO. In other words, formic acid has the potential to decompose into both CO\textsubscript{2} and CO (Fig. 4). Moreover, formic acid is easy to handle in the liquid state at room temperature and ambient pressure, and the molecule contains two hydrogen atoms (4.3 wt\%) so has recently been regarded as a hydrogen storage molecule or so-called hydrogen carrier\textsuperscript{20}. Effective use of formic acid as a hydrogen carrier will require selective conversion of formic acid to hydrogen and CO\textsubscript{2}.

Two studies on the selective decomposition of formic acid to hydrogen and CO\textsubscript{2} achieved breakthroughs in 2008, and have motivated extensive research in the field of formic acid usage\textsuperscript{21,22}. Various review articles have been published, so we describe our research on...
complex catalysts based on iridium. An iridium-based bipyridine complex with a metal center can selectively decompose formic acid\(^{23}\). Subsequent modifications of the ligands improved its activity\(^{24} - ^{27}\). The half-sandwich complex formed by the combination of iridium and bidentate ligands is the basis of the high activity and selectivity. The proposed reaction mechanism involves ionization of formic acid, and reaction of the generated formate anion with the catalyst to form a formato complex. This formato complex undergoes a \(\beta\)-hydrogen elimination reaction, and CO\(_2\) is released to form a hydride complex. Finally, the hydride complex reacts with the protons to produce hydrogen, which is considered to regenerate the catalyst (Fig. 5).

The combination of iridium and bidentate ligands is highly active for the selective decomposition of formic acid and for the reduction of CO\(_2\) with hydrogen\(^{28}\). Therefore, the catalyst can be used for CO\(_2\)-based hydrogen storage and supply (Fig. 6). In practice, the pH of the reaction system must be maintained to control the reduction and oxidation, but the reaction system can store and deliver hydrogen under mild conditions.

Iridium bipyridine complexes also produce high-pressure hydrogen gas because of their high reaction selectivity\(^{29},^{30}\). Heating of formic acid and catalyst in a sealed vessel forms hydrogen gas and CO\(_2\), generated by the selective decomposition in the reactor, which increase the internal gas pressure. Consequently, high-pressure gas exceeding 100 MPa can be produced. Effective hydrogen supply in applications including domestic use require pressurization of the hydrogen gas, but the high cost of a hydrogen pressure booster limits the wide-scale application of hydrogen gas. The use of a formic acid-iridium complex system has the potential to eliminate the need for hydrogen pressure boosters.

4. Synthesis of Urea from Ammonium Salts

Urea is probably the most widely used chemical product produced from CO\(_2\). Industrial synthesis uses CO\(_2\) and ammonia (NH\(_3\)) gas under high temperature and pressure in the absence of a catalyst\(^{31}\). Urea can be synthesized from ammonium ions and CO\(_2\) (or carbonates) instead of ammonia gas\(^{32}\). Ammonium salts, which are an environmental pollutant arising from wastewater and sewage, could be effectively utilized by using ammonium ions as the raw material for urea synthesis (Fig. 7).

Synthesis of urea from ammonium salts is possible using various catalysts with Lewis basicity (Fig. 8)\(^{33}\). Strongly basic catalysts with a pK\(_a\) of \(>20\) for the conjugate acid in acetonitrile were active in the synthesis of urea from ammonium carbamate. Screening of reaction solvents showed that the yield of urea was correlated with the dielectric constant of the solvent, i.e., solubility of NH\(_3\), but not with the solubility of CO\(_2\). This suggests that promoting the nucleophilic attack of NH\(_3\) is important for the reaction. Various investigations of the reaction mechanism have been based on the use of diazabicycloundecene (DBU), which showed the high-

![Fig. 5 Estimated Reaction Mechanism of Selective Formic Acid Dehydrogenation on Ir Catalyst](image1)

![Fig. 6 Hydrogen Storage System Based on CO\(_2\) Utilization](image2)

![Fig. 7 Urea Synthesis Using Ammonium Cation and CO\(_2\)](image3)
Carbon-13 nuclear magnetic resonance (¹³C NMR) spectroscopy showed that cation exchange occurred between the substrate and DBU, which had not been predicted. Fourier-transform infrared (FT-IR) spectroscopy suggested a reaction mechanism in which the carbonyl group of the substrate was activated via cation exchange (Fig. 9).

Urea can be synthesized using bases, so we also investigated the synthesis of urea by acids. Catalysts with Lewis acidity for organic synthesis were screened, and Ni compounds were found to be active (Table 1). Nickel acetate and nickel hydroxide exhibited good catalytic activity. X-ray absorption fine structure (XAFS) spectroscopy showed that the Ni-O-Ni bond intensity of nickel hydroxide decreased after the catalytic reaction. In contrast, Ni K-edge Fourier-transform extended...
XAFS (FT-EXAFS) spectrum found the Ni-O bond intensity did not change (Fig. 10). This result suggests that addition of the substrate, ammonium carbamate, cleaves the Ni-O-Ni bond of nickel hydroxide and promotes the coordination of ammonia and carbamate with the catalyst (Fig. 11). The carbonyl group of the coordinated carbamate is activated by Ni acting as a Lewis acid, and becomes susceptible to nucleophilic attack.

5. Conclusion

Catalytic reactions using CO₂ as a feedstock are extensively reviewed. Some of these reactions are already in industrial operation, whereas many other interesting reactions are still being investigated at the laboratory scale. Further development of CO₂ conversion reactions is desired for the achievement of a more sustainable society.

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Table 1 Results of Urea Synthesis Using Metal Compounds

| Entry | Metal salt | Yield [mmol] | Yield [%] |
|-------|------------|--------------|-----------|
| 1     | Ni(AcO)₂·4H₂O | 0.20         | 6         |
| 2     | Ni(OH)₂     | 0.12         | 3         |
| 3     | NiCl₂       | 0.10         | 3         |
| 4     | Ni(acac)₂   | 0.09         | 2         |
| 5     | NiO         | trace        | trace     |
| 6     | FeO         | 0.06         | 2         |
| 7     | FeCl₃       | trace        | trace     |
| 8     | SnCl₄       | 0.05         | 1         |
| 9     | SnCl₂       | trace        | trace     |
| 10    | Sn(Of)₂     | trace        | trace     |
| 11    | Cu(Of)₂     | 0.04         | 1         |
| 12    | MnCl₂       | trace        | trace     |
| 13    | Bi(Of)₃     | trace        | trace     |
| 14    | Nd(Of)₃     | trace        | trace     |

Fig. 10 FT-EXAFS Spectra of Ni(OH)₂ and Ni Foil before and after the Catalytic Reaction (k = 3-12 Å⁻¹)

Fig. 11 Proposed Reaction Pathway of Urea Synthesis Using Metal Catalyst

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要 旨

有機分子触媒もしくは金属触媒を用いた二酸化炭素変換反応

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二酸化炭素の利用は今後必須になる技術である。このレビューでは、触媒を用いて二酸化炭素を化学的に有用な分子へと変換する研究を紹介する。トピックとしては、(1) ヒドロシランによる二酸化炭素のヒドロシル化反応に活性を示す触媒、中でも特に単純な塩類による触媒反応とジアノ酸反応を触媒とする反応機構、(2) 水素と二酸化炭素によるジアノ酸製造によるジアノ酸の選択的分解による水素製造に活性を示すイリジウム錯体触媒とその反応機、(3) アンモニウムイオンと二酸化炭素による尿素合成に活性を示す有機塩基触媒とその反応機、金属触媒による反応、を取り上げた。これらの技術は二酸化炭素を循環利用する持続可能な社会の実現に寄与すると期待される。

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