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CO_2 utilization: Developments in conversion processes

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ABSTRACT

Carbon dioxide capture, utilization and storage (CCUS) –including conversion to valuable chemicals-is a challenging contemporary issue having multi-facets. The prospect to utilize carbon dioxide (CO_2) as a feedstock for synthetic applications in chemical and fuel industries -through carboxylation and reduction reactions-is the subject of this review. Current statute of the heterogeneously catalyzed hydrogenation, as well as the photocatalytic and electrocatalytic activations of conversion of CO_2 to value-added chemicals is overviewed. Envisaging CO_2 as a viable alternative to natural gas and oil as carbon resource for the chemical supply chain, three stages of development; namely, (i) existing mature technologies (such as urea production), (ii) emerging technologies (such as formic acid or other single carbon (C1) chemicals manufacture) and (iii) innovative explorations (such as electrocatalytic ethylene production) have been identified and highlighted. A unique aspect of this review is the exploitations of reactions of CO_2 –which stems from existing petrochemical plants-with the commodity petrochemicals (such as, methanol, ethylene and ethylene oxide) produced at the same or nearby complex in order to obtain value-added products while contributing also to CO_2 fixation simultaneously. Exemplifying worldwide ethylene oxide facilities, it is recognized that they produce about 3 million tons of CO_2 annually. Such a CO_2 resource, which is already separated in pure form as a requirement of the process, should best be converted to a value-added chemical there avoiding current practice of discharging to the atmosphere.

The potential utilization of CO_2, captured at power plants, should also been taken into consideration for sustainability. This CO_2 source, which is potentially a raw material for the chemical industry, will be available at sufficient quality and at gigantic quantity upon realization of on-going tangible capture projects. Products resulting from carboxylation reactions are obvious conversions. In addition, provided that enough supply of energy from non-fossil resources, such as solar [1], is ensured, CO_2 reduction reactions can produce several valuable commodity chemicals including multi-carbon compounds, such as ethylene and acrylic acid, in addition to C1 chemicals and polymers. Presently, there are only few developing technologies which can find industrial applications. Therefore, there is a need for concerted research in order to assess the viability of these promising exploratory technologies rationally.

1. Introduction

CO_2 emissions into atmosphere is a global concern and a recent theoretical model provides a quantitative approach for its connection with global warming and climate change [2]. Combustion stoichiometry gives that burning 1 ton of carbon in fossil fuels results more than 3.5 tons of CO_2; whose accumulation in the atmosphere is now approaching 1 tera ton [3]. According to a model developed by IEA [4], in order to limit the temperature increase within 2 °C by 2050, the CO_2 levels should not exceed 15 giga tons annually. In this quest, increasing both the energy

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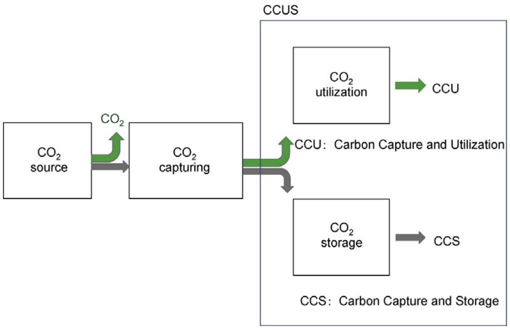
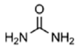
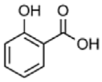
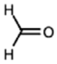
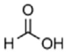
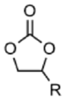
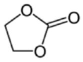
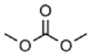
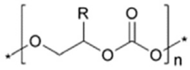
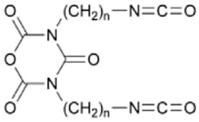


Fig. 1. The schematic representation of concept of carbon capture, utilization and storage (CCUS) (adapted from Ref. [27]).

efficiency and the use of renewable sources is going to have the most profound effects. However, the share of carbon dioxide capture is estimated to be about 14% which means that mammoth amount of relatively pure CO_2 will be available [4].

Hence, the past concept of CCS is no longer adequate and it has already been amended to CCUS involving significant carbon dioxide utilization as illustrated in Fig. 1. Utilization itself should be divided into two parts. First, CO_2 alone without any conversion has certain uses, such as, enhanced oil recovery by CO_2 flooding [5] or physical solvent applications—especially in the supercritical state [6]. Indeed, injection of CO_2 into an oil reservoir increases the production due to high mutual dissolving capability of supercritical CO_2 and hydrophobicity of oil. Also, the increase in pressure lowers the viscosity of the CO_2—oil mixture. Consequently, CO_2 flooding can raise the production by about 15%. The oil containing dissolved CO_2 is then brought to the surface and the gases are flashed and CO_2 is separated for reinjection. In the second class of utilization, CO_2 moiety is converted to chemicals [7] and fuels [8] via carboxylation or reduction avenues. Indeed, using CO_2 as a viable feedstock for the chemical industry has been the foresight of visionary scientists and the pioneering studies towards converting CO_2 to C1 building block chemicals have already made significant achievements [9–13]. Table 1 shows some of the chemicals produced from CO_2, but this list is only the tip of the iceberg. Already, around 130 Mt (mega or millions tons) CO_2 are used annually to manufacture urea, salicylic acid, cyclic carbonates, and polycarbonates. Among them, urea process consumes most of the CO_2 industrially [7]. Urea is produced at around 185–190 °C and at pressure range of 180–200 atm by reacting

Table 1
Some of the chemicals which can be produced from CO_2.

Chemical	Molecular formula	Annual production [7]	Annually utilised CO_2 as feedstock [7]
Urea (commodity)		150 million tons	112 million tons
Methanol	CH_3OH	100 million tons	2 million tons
Salicylic acid		70 thousand tons	30 thousand tons
Formaldehyde		9.7 million tons	
Formic acid		700 thousand tons	
Cyclic carbonates		80 thousand tons	40 thousand tons
Ethylene carbonate			
Di-methyl carbonate		10 million tons	
Copolymers			
Polymer building blocks			
Fine chemicals (for instance, biotin)