



Review

Valorization of greenhouse carbon dioxide emissions into value-added products by catalytic processes

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ABSTRACT

Complete oxidation or combustion of any carbon-based organic matter produces CO₂, which is known to cause global warming and climate changes. To mitigate the concentration of CO₂ in the atmosphere various strategies have been implemented such as separation, storage, and valorization of CO₂. The focus of this review was on the catalytic processes of the chemistries involved in the conversion of CO₂ into value-added products. The various valorization technologies which include conversion of CO₂ into fuel, valorization of CO₂ as a feedstock for chemicals were discussed. Also, an overview regarding the challenges and opportunities for future research in CO₂ valorization was provided.

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Nomenclature

GHG	green house gas
H ₂	hydrogen
C	carbon
VOCs	volatile organic compounds
EOR	enhanced oil recovery
ECBMR	enhanced coal bed methane recovery
UCG	underground coal gasification
CCS	carbon capture and storage
EGR	enhanced gas recovery
DME	dimethyl ether
DMC	dimethylcarbonate
DMP	2,2-dimethoxy propane
EC	ethylene carbonate
PC	propylene carbonate
PO	propylene oxide
PPC	poly(propylene carbonate)
PCHC	poly(cyclohexene carbonate)
DMC	dimethyl carbonate
DPC	diphenyl carbonate
MPC	methyl phenyl carbonate
RWGS	reverse water gas shift reaction
FT	Fischer–Tropsch
CHP	combined heat and power
DMF	N,N-dimethylformamide
TAGs	triacylglycerols
HVPs	high value products
ICEs	internal combustion engines
VAPs	value added products
POM	partial oxidation of methane
TOE	ton of oil equivalent
MMTCE	million metric tons of carbon equivalent
MTCE	metric ton of carbon equivalent
ppmv	parts per million by volume
CHP	combined heat and power
ATP	adenosine triphosphate
WGS	water gas-shift
RWGS	reverse water gas shift
BMI _m -Br	butyl methyl imidazolium bromide
[EMI _m] ⁺	ethylmethylimidazolium cation
K ₂ CO ₃	potassium carbonate
ILs	ionic liquids
OOIP	original oil in place
scCO ₂	supercritical carbon dioxide
GTL	gas to liquid
CTL	coal to liquid
ERC	electrochemical reduction of carbon dioxide
GDEs	gas diffusion electrodes
GSV	gas space-velocity
SHE	standard hydrogen electrode
SCE	standard calomel electrode
NHE	normal hydrogen electrode
CEM	cation exchange membrane
SPE	solid polymer electrode

1. Introduction

While greenhouse gases emissions are reaching alarming rates, fossil fuels still represent more than 80% of the world energy portfolio and 95% of our organic-based chemicals rely on non-renewable resources, such as hydrocarbons. The largest source of CO₂ emissions is from consumption of fossil fuels. Besides, heavy dependence on fossil fuels causes problems in energy security since many of our fossil fuels are imported and they are inherently nonrenewable. One approach for reducing CO₂ emissions that has received a lot of attention in recent years is carbon capture and sequestration (CCS) [1–6]. In this process, CO₂ is removed from the flue gases of large emitters, such as power plants, using membrane separation or an absorbent/adsorbent, e.g. monoethanolamine (MEA) [7]. The captured CO₂ is then stored either in deep ocean or underground in geological formations such as depleted oil and gas reservoirs. While this has the potential for reducing the amount of CO₂ entering the atmosphere, this approach has a number of issues. First, CCS requires a suitable sequestration site located near the CO₂ source or the CO₂ must be transported to a suitable site. Also, to reduce our dependence on imported petroleum, the development and expansion of natural gas to liquid (GTL) and coal to liquid (CTL) technology has been proposed. GTL and CTL yield syngas, a mixture of hydrogen and carbon monoxide, which is then converted into liquid fuels via the Fischer–Tropsch process [8,9] and both are well developed technologies [7,10–12]. While the implementation of CSS will decrease emissions and CTL and GTL would allow the use of relatively abundant coal and natural gas to decrease our dependence on imported oil for transportation fuels, such a solution does not address the nonrenewable nature of fossil fuels. Because of this issue, CCS and GTL/CTL will likely serve as bridging technologies to a more sustainable energy supply needed for the long-term [11]. An attractive alternative to CO₂ sequestration is the use of captured carbon as a reagent for producing useful chemicals either through biological, chemical or electrochemical methods.

In this context, conversion of CO₂ rather than its sequestration is presently being explored as one potential alternative solution to CO₂ emissions into the atmosphere. Production of useful value-added chemicals, like ethanol from CO₂ as an alternative to petrochemistry appears promising as it has a double advantage of reusing CO₂ while sparing fossil resources and avoiding CO₂ emissions from their use. The development of new catalytic processes is thus needed and intensive research efforts are necessary to find new ways of functionalizing carbon dioxide.

Value-added carbon management technologies can generate value-added carbonaceous products such as: fuels, fertilisers, materials and chemicals. These value-added products may thus offset costs associated with carbon management. Besides, the introduction of such carbonaceous products to markets might significantly improve world economy by lowering production costs of several intermediates and providing massive and cheap production of some final products. The high versatility nature of CO₂ has been exploited in numerous industrial applications, although the thermodynamic stability of CO₂ also hampered its utility as a reagent for chemical synthesis [13,14]. There are generally two types of product derivable from CO₂: fully reduced carbon derivatives such as hydrocarbons; and products where a C=O fragment or even a complete O=C=O moiety is introduced into the molecule. These approaches will be discussed in the following section. This paper will be limited to catalyzed organic reactions, however it should be noted that considerable research work is on-going in inorganic chemistry, including accelerated mineralization reactions [4,14].

This article will consider a range of approaches to chemical, electrochemical and biological transformations of CO₂ into

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