



Review

Insight into catalytic reduction of CO₂: Catalysis and reactor designPeter Adeniyi Alaba^{a,*}, Ali Abbas^b, Wan Mohd Wan Daud^{a,**}^a Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia^b School of Chemical and Biomolecular Engineering, University of Sydney, NSW 2006, Australia

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ABSTRACT

Catalytic reduction of CO₂ to produce specialty chemicals or renewable energy sources has attracted immense attention because of the possibility of renewable, sustainable alternative energy, and safer environment. Utilization of CO₂ as an alternative feedstock for synthesis of biorenewable fuel is one of the numerous strategies essential for mitigation of the greenhouse gases emission into the atmosphere. CO₂ reduction occurs at temperature above 413 K and pressure above 1 MPa by using a suitable hydrogenation catalyst. This study investigates the recent advances in catalytic reduction of CO₂ via hydrogenation, focusing on catalysis, reactor, and process intensification. Several factors for the effective catalytic reduction of CO₂ and recent progress in the reactor design for the system are also highlighted.

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Nomenclature

GHG	Greenhouse gas	Al ₂ O ₃	Aluminum oxide
IPCC	International Panel on Climate Change	γ-Al ₂ O ₃	Gamma alumina
CCS	Carbon dioxide capture and storage	ZrO ₂	Zirconium oxide
RWGS	Reverse water-gas-shift	ZnO	Zinc oxide
GHSV	Gas hourly space velocity	HCO ₂ ⁻	Formate
DME	Dimethyl ether	CH ₄	Methane
TMC	Transitional metal carbide	CaO	Calcium oxide
PSA	Pressure swing adsorption	WC	Tungsten carbide
CNT	Carbon nanotube	Mo ₂ C	Molybdenum carbide
KMC	Kinetics Monte Carlo	SiC	Silicon carbide
ZPE	Zero-point energy	TaC	Tantalum carbide
DFT	Density functional theory	Fe ₃ C	Iron carbide
CO	Carbon monoxide	MnO	Manganese oxide
CO ₂	Carbon dioxide	Cr ₂ O ₃	Chromium oxide
CH ₃ OH	Methanol	La ₂ O ₃	Lanthanum oxide
CuO	Copper oxide	Ga ₂ O ₃	Gallium oxide
		MCM-41	Mobil Composition of Matter No. 41
		K ₂ O	Potassium oxide

1. Introduction

Global warming is currently the foremost environmental concern faced by mankind (Valipour, 2012a, 2012b; Yannopoulos et al., 2015). Carbon dioxide, extracted from combustion of fossil fuel, is the chief greenhouse gas (GHG) in the atmosphere that immensely contributes to global climate change (Budzianowski, 2012; McCollum et al., 2014; Roy et al., 2010). CO₂ capture from petrochemical process streams and flares is necessary for reduction of GHG emission into the atmosphere (Alaba, Sani and Daud, 2015b; Ravanchi and Sahebdehfar, 2014; Sani, Alaba, Raji-Yahya, Aziz and Daud, 2016b). The global temperature increase via absorption and re-emission of infrared light is due to the effect of GHG. The GHG effect has global and significant aspects including rising precipitation throughout the earth, ice melting on the Earth pole, and fast increasing sea level (Abnisa and Daud, 2015; Khatib, 2012). International Panel on Climate Change (IPCC) predicted that the level of release of CO₂ to the atmosphere may possibly increase to 590 ppm by 2100 and the average global temperature could increase by ~1.9 °C (Change, 2007). To avoid this, IPCC proposed 50%–85% reduction of global CO₂ emissions relative to 2000 levels by the year 2050 (McGlade and Ekins, 2015). Generation of energy via combustion of fossil fuel is the main source of CO₂ emission, thus depleting fossil fuel. The major challenge for adequate reduction of CO₂ emissions is disposing or utilizing the captured CO₂. A prospected and appealing method for utilizing captured CO₂ is CO₂ sequestration into biorenewable fuels or specialty chemicals (Jeong et al., 2012). Consequently, it is crucial to discover a renewable and sustainable energy source to alleviate the effect of global warming as well as meeting the rising energy need (Alaba, Sani and Daud, 2015a; Alaba et al., 2016a,b,c,d; Mikkelsen et al., 2010; Yui et al., 2011). Furthermore, researchers need to work extensively toward CO₂ storage and utilization to stabilize the atmospheric CO₂ level.

Theoretically, reduction of CO₂ emission in the atmosphere is mainly categorized into three routes, including CO₂ utilization, direct reduction of CO₂ emission, and CO₂ capture and storage (CCS) (Hurst et al., 2012; Windle and Perutz, 2012). Increasing industrialization (Alaba et al., 2016a,b,c,d; Bauer et al., 2013) combined with population growth cause the daily increase of fossil fuel

consumption (Alaba et al., 2016a,b,c,d; Sani, Alaba, Raji-Yahya, Aziz and Daud, 2016a); therefore, the mitigation of CO₂ emission and the development of carbon-neutral renewable energy source appear unachievable. In addition, environmental hazard because of leakage, cost of gas compression, and transportation is the major disadvantage of the CCS (K. Li, An, Park, Khraisheh and Tang, 2014). Therefore, CO₂ reduction into fuels or specialty chemicals via major techniques, such as thermochemical, photochemical (Bai et al., 2015; Berardi et al., 2014; Qu and Duan, 2013), electrochemical (Back et al., 2015; Costentin et al., 2013; S. Ma and Kenis, 2013), inorganic transformation, (Sanna et al., 2014) and biological methods, is the growing concern of researchers since the past decade.

As commercially available CH₃OH from CO₂ technology uses Cu/Zn-based formulation and Cu/Zn/Al/Zr-based catalysts the catalysts should be improved. CO₂ is a stable compound and thus requires a substantial energy and highly stable and active catalyst for conversion into specialty chemicals. This finding requires developing suitable catalysts and intensifying CO₂ conversion for economical production. The techniques, prospects of the synthesis, and material and reactor design of using CO₂ as the main starting material for an economically viable renewable and sustainable energy source are investigated. The basic catalytic reduction of CO₂ is discussed first. The rational design of catalysts with remarkable activity as well as the critical factors for efficient catalytic reduction of CO₂ is emphasized. The progress in using CO₂ reduction catalytic reactors for clean fuel and specialty chemicals production is also discussed.

2. CO₂ reduction and its mechanism

In recent time, atmospheric CO₂ utilization engendered the replacement of CO with CO₂ as a feedstock for CH₃OH synthesis. The process is necessary to alleviate the GHG effect associated with considerable rise in the amount of CO₂ in the atmosphere (Olah, 2004; C. Yang et al., 2006). Catalytic reduction of CO₂ to CH₃OH is a remarkable approach toward green environment. Generally, CH₃OH synthesis from CO₂ starts in hydrogenation using suitable hydrogenation catalyst at temperature above 413 K and pressure above 1 MPa (J. Ma et al., 2009). When CO₂ is activated at high temperature and pressure for hydrogenation, the desired reaction

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