



High-pressure advantages in stoichiometric hydrogenation of carbon dioxide to methanol



Rohit Gaikwad, Atul Bansode, Atsushi Urakawa*

Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

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ABSTRACT

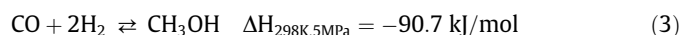
Interplay between three important reaction parameters (pressure, temperature, and space velocity) in stoichiometric hydrogenation of carbon dioxide (CO₂:H₂ = 1:3) was systematically investigated using a commercial Cu/ZnO/Al₂O₃ catalyst. Their impacts on reaction performance and important ranges of process conditions toward full one-pass conversion of CO₂ to methanol at high yield were rationalized based on the kinetics and thermodynamics of the reaction. Under high-pressure condition above a threshold temperature, the reaction overcomes kinetic control, entering thermodynamically controlled regime. Ca. 90% CO₂ conversion and >95% methanol selectivity were achieved with a very good yield (0.9–2.4 g_{MeOH} g_{cat}⁻¹ h⁻¹) at 442 bar. Such high-pressure condition induces the formation of highly dense phase and consequent mass transfer limitation. When this limitation is overcome, the advantage of high-pressure conditions can be fully exploited and weight time yield as high as 15.3 g_{MeOH} g_{cat}⁻¹ h⁻¹ could be achieved at 442 bar. Remarkable advantages of high-pressure conditions in terms of reaction kinetics, thermodynamics, and phase behavior in the aim to achieve better methanol yield are discussed.

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1. Introduction

The ever-increasing energy demand to sustain the industrialization and modern lifestyle has led to depletion of world's current primary energy supply, finite and non-renewable fossil fuels. In parallel, their irreversible consumption resulted in accumulation of carbon dioxide (CO₂) in the atmosphere, causing the climate to change. For sustainable development of mankind, the carbon cycle has to be closed, and conversion of CO₂ into chemical fuels and feedstocks serves as an effective strategy to cope with the interrelated energetic and environmental problems [1]. Heterogeneous catalytic conversion of CO₂ to fuels and industrially important chemicals, such as methanol by hydrogenation reaction, offers a unique path to transform a large amount of CO₂ in a short span of time by the high reaction rates. The vital roles of methanol as chemical energy carrier and starting material or chemical intermediates are well recognized [2]. However, CO₂ is a thermodynamically stable and relatively inert molecule. Its activation typically requires energy inputs, e.g. by the use of elevated pressure and temperature as well as effectual strategies such as innovative catalytic processes [3–6].

CO₂ hydrogenation to methanol is exothermic (reaction (1)), while the competing reaction, reverse water–gas shift (RWGS, reaction (2)), is endothermic [7]. Moreover, CO produced by RWGS may undergo exothermic hydrogenation to form methanol (reaction (3)).



In accordance with Le Châtelier's principle, high-pressure and low-temperature reaction conditions are favorable to achieve high CO₂ conversion and methanol selectivity [8]. In fact, the advantage and necessity of high-pressure conditions in the synthesis of methanol from syngas (CO and H₂ mixture typically containing some fraction of CO₂) have been known over the last 90 years [9]. Since 1966, the trend has shifted to lower pressure methanol synthesis (<100 bar) using highly active and economic Cu–ZnO based catalysts [10]. For this family of catalysts that are most common for methanol synthesis nowadays, high-pressure advantages in methanol synthesis by the hydrogenation of CO and particularly CO₂ had not been explored and documented for a long time, except the excellent work reported by Ipatieff and Monroe in 1945 for Cu-based catalysts [5]. Recently, we reported a range of high-pressure

* Corresponding author.

E-mail address: aurakawa@iciq.es (A. Urakawa).

reaction conditions, yielding remarkable almost-full one-pass conversion of CO₂ to methanol with high selectivity using Cu/ZnO/Al₂O₃ catalysts and also to methanol-derived products such as dimethyl ether (DME) by co-presence of an acidic zeolite [11]. The elevated H₂ partial pressure (molar ratio, CO₂:H₂ = 1:≥10), higher than the stoichiometric one (CO₂:H₂ = 1:3, reaction (1)), was found kinetically as well as thermodynamically beneficial for methanol synthesis. Employing the reaction pressure of 360 bar (reactant pressure of 331 bar due to the presence of Ar for GC analysis), outstanding CO₂ conversion (>95%) and methanol selectivity (>98%) were achieved at 260 °C at relatively high gas hourly space velocity (GHSV) of ca. 10,000 h⁻¹. With a commercial Cu–ZnO based methanol synthesis catalyst, exceptionally high methanol yield of 7.7 g_{MeOH} g_{cat}⁻¹ h⁻¹ was attained at the expense of lower CO₂ conversion (65.8%) and methanol selectivity (77.3%). Energy-demanding high-pressure conditions are not necessarily disadvantageous in this reaction because of smaller geometrical requirements for the reactor and plant area, which lower the capital cost and possibly improve safety aspects [4,11]. Moreover, the energetic cost associated with compression of the reactants is less significant than that required for hydrogen production in the overall process of CO₂ hydrogenation to methanol when water electrolysis is assumed as the mean to produce H₂ [12].

Despite the exceptionally high CO₂ conversion and methanol selectivity under high-pressure conditions and also high process viability in terms of costs and methanol productivity, the reported reaction condition requires recycling or further conversion of unreacted H₂ fed in excess. In addition, CO produced by RWGS should be recycled if methanol selectivity is not sufficiently high. Recycling of precious H₂ can only be avoided by achieving its full conversion. In other words, the challenge in this respect is to achieve complete conversion of both CO₂ and H₂ with high methanol productivity. This goal naturally requires the operation of the reaction at the stoichiometric CO₂ to H₂ ratio.

Herein, we have thoroughly examined high-pressure reaction conditions (50–480 bar; in reactant pressure of 46–442 bar) at 220–300 °C for stoichiometric CO₂ hydrogenation, in the aim to identify reaction conditions maximizing CO₂ and H₂ conversions with high methanol selectivity and/or productivity. A commercial Cu/ZnO/Al₂O₃ catalyst, optimized for the conversion of syngas to methanol, was employed as catalyst due to its high activity in CO₂ hydrogenation to methanol [11]. Tendency and effects of kinetic and thermodynamic controls over the reaction performance are discussed along with the trends in theoretical thermodynamic equilibria to critically evaluate what is achievable with the optimized Cu/ZnO/Al₂O₃ catalyst and to highlight possible directions of future research in CO₂ hydrogenation to methanol.

2. Experimental

The details of high-pressure fixed-bed reactor and analytical systems are described elsewhere [4]. Specificity of this work about reactor system, catalyst material, activation procedure and product analysis by gas chromatography is described in [Supplementary Material](#). Continuous CO₂ hydrogenation to methanol was tested at five different pressure conditions of 50, 100, 200, 360, 480 bar (considering 8% Ar in feed composition, actual total pressure of CO₂ and H₂ was 46, 92, 184, 331, and 442 bar, respectively). In this work, GHSV is defined by the volumetric flow rate of inlet stream at normal pressure divided by the reactor volume where the catalyst is packed (including the catalyst volume). A wide range of GHSV conditions (650–100,000 h⁻¹) were examined. GHSV is also shown in catalyst-mass-normalized unit, in which the value ranges 0.37–49.85 NL g_{cat}⁻¹ h⁻¹. For the GHSV calculation in both units, the total flow rate at normal pressure including Ar was used. The

vaporized outlet stream was injected to GC every ca. 12 min for 3 h at each condition of temperature, pressure and GHSV and an averaged values were taken. The standard deviation of the quantification is presented in [Figs. S3–S5 in Supplementary Materials](#). No catalyst deactivation was detected for the duration of catalytic tests performed.

Equilibrium conversion and product selectivity were calculated by the Soave–Redlich–Kwong (SRK) equation of state (EOS) using Aspen HYSYS V8.6. Modified SRK-EOS binary interaction parameters for CO, CO₂, H₂, methanol and water were taken from the optimized values reported by Heeres and coworkers for methanol synthesis [13]. The calculations were performed by minimization of Gibbs free energy. Methane was not considered in all calculations.

3. Results and discussion

3.1. Effects of temperature under high-pressure conditions

First, the effects of temperature on CO₂ conversion and methanol selectivity were examined at the reactant pressure of 46, 92, 184, 331, and 442 bar ([Fig. 1](#)). The catalytic tests were performed at a constant GHSV of 10,000 h⁻¹, although, as discussed in [Section 3.2](#), this reaction parameter can directly influence the residence time of the reactants in the reactor and thus catalytic performance. CO₂ conversion and methanol selectivity are presented in comparison with the thermodynamic equilibrium values.

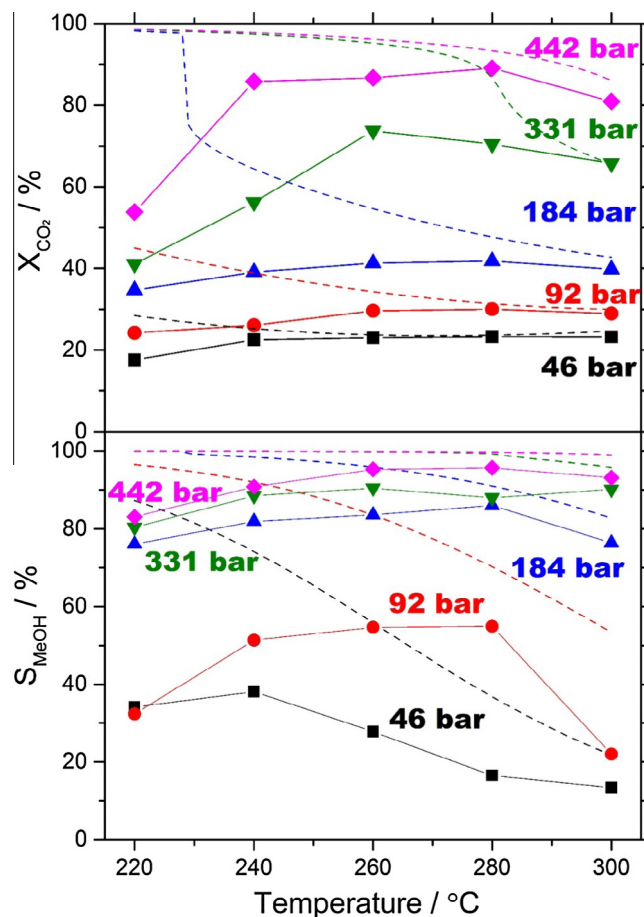


Fig. 1. Effects of reaction temperature and pressure on CO₂ conversion (X_{CO_2}) and methanol selectivity (S_{MeOH}) in high-pressure stoichiometric CO₂ hydrogenation using commercial Cu/ZnO/Al₂O₃ catalyst at constant GHSV of 10,000 h⁻¹ (5.87 NL g_{cat}⁻¹ h⁻¹). Dotted lines show the theoretical equilibrium CO₂ conversion and methanol selectivity.

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