Priority Communication

Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products

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ABSTRACT

The rising concerns about global warming and imbalance in the carbon cycle urge rapid development of efficient CO_2 conversion processes. We report an exceptionally productive process for the synthesis of methanol via continuous catalytic hydrogenation of CO_2 under high-pressure conditions (up to 360 bar) over co-precipitated $Cu/ZnO/Al_2O_3$ catalysts. Outstanding one-pass CO_2 conversion (>95%) and methanol selectivity (>98%) were achieved under an optimized range of reaction conditions. At a very high GHSV of $182,000 \ h^{-1}$ over a commercial methanol synthesis catalyst, the process delivers $7.7 \ g_{MeOH} \ g_{cat}^{-1} \ h^{-1}$, which is by far the highest yield value reported to date, at the expense of lowered CO_2 conversion (65.8%) and methanol selectivity (77.3%). Using a mixed bed consisting of the $Cu/ZnO/Al_2O_3$ and H-ZSM-5 catalysts, one-step conversion of CO_2 into dimethyl ether with remarkable selectivity (89%) was attained at the equivalent or higher CO_2 conversion level. Furthermore, we demonstrate that the effluent stream of methanol, rich in H_2 and water, from the methanol synthesis reactor can be directly fed to a reactor containing the H-ZSM-5 catalyst for selective production of alkane (85%) or alkene (42%), depending on the operating pressure of the secondary reactor.

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1. Introduction

The global warming, mainly sourced from the human induced emission of CO_2, is one of the major environmental threats we are facing in the 21st century. In the past few decades, there has been growing scientific consensus to devise the strategy for CO_2 capture, fixation, and recycling technologies to level off the atmospheric CO_2 concentration. Nature has its own CO_2 fixation process which is extraordinarily selective in converting CO_2 into organic compounds. However, natural chemical transformation of CO_2 is not simply fast enough to cope with the increasing CO_2 emission rate of the industrialized world. Chemical transformation of CO_2 is not only about mitigating the global warming; rather it is about recycling of the carbon, irreversibly relocated in the form of CO_2 from the ground by burning fossil fuels such as coal, oil, and natural gas. In the light of the finite availability of fossil fuels, the production of commercially valuable chemicals and fuels from CO_2 is a promising strategy to simultaneously tackle the two major problems of the century, namely the global warming and fossil fuel depletion, for sustainable development. Among others, heterogeneous catalytic hydrogenation of CO_2 bears a strong potential to

treat large amount of CO_2 in a short time, rendering it an important mean for CO_2 conversion.

Methanol (MeOH) can be synthesized from CO_2 hydrogenation and is one of the most celebrated and widely suggested alternatives for chemical energy carrier [1,2]. It is an excellent fuel and a key starting material of the important industrial reactions. The use of methanol in fuel cells directly or indirectly as the source of hydrogen by a reforming reaction is well documented. Actively investigated hydrogen production by photocatalytic or electrocatalytic water splitting powered by renewable (e.g. solar and wind) energies can be regarded as future sources of hydrogen for CO_2 hydrogenation [3,4]. In addition, fundamental chemical products like olefins can be produced via a methanol-to-olefin (MTO) process [5] and various organic compounds like dimethyl ether (DME), that is, a potential substitute of diesel oil for its better combustion performance [6], can be produced from methanol. The commercially practiced processes of methanol synthesis from CO and CO_2 are operated at relatively low one-pass conversions and require separation and/or recycling of unconverted reactants to attain high conversions. Currently, the commercial methanol synthesis processes are operated typically at about 50–100 bar using copper- and zinc-based catalysts [7]. Lowering the reaction pressure is generally favoured because of the general perception of increased energy demands at high-pressure operation. However, a recent report on energetic aspects of CO_2 hydrogenation to

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methanol shows that the energy efficiency of the whole process is almost pressure independent and the dominant process in energy demand is the electrolysis of water which was assumed as the source of hydrogen [8]. Besides, high-pressure approaches can facilitate the reduction in reactor volume when reactants and/or products are compressive, reducing the plant area which consequently reduces capital costs, and possible improvements in handling dangerous chemicals such as hydrogen more safely when used in a small volume. Above all, such approaches may result in shifting equilibrium conversion and in the formation of unique phase and states of reaction mixture and catalysts, thus boosting catalytic activity.

The first high-pressure methanol synthesis process was commercialized by BASF in 1923, operated at pressure of 250–350 bar with a mixture of syngas with CO_2 as reactants [9]. The use of high pressure was necessary due to thermodynamics; decrease in temperature and increase in reaction pressure should favour the methanol formation. As mentioned above, modern processes are operated at lower reaction pressures of ca. 50–100 bar at comparably lower temperatures thanks to the highly active Cu–Zn-based catalysts [10]. Related to CO_2 hydrogenation, Ipatieff and Monroe reported high-pressure study up to 412 bar over Cu/Al_2O_3 catalysts in a fixed bed reactor, which showed remarkable selectivity to methanol and high conversion of CO_2 [11]. However, in their study, the gas hourly space velocity (GHSV), indicative of the productivity of the reaction, was very low (ca. 1000 h^{-1}) to make the process practically viable.

Herein, we report high-pressure (up to 360 bar) CO_2 hydrogenation to methanol over co-precipitated $Cu/ZnO/Al_2O_3$ catalysts at high GHSV (>10,000 h^{-1}). Under specific reaction conditions with conventional methanol synthesis catalysts, we will show that one can achieve close-to-full one-pass conversion of CO_2 to methanol. Furthermore, DME and hydrocarbons production from methanol can be directly incorporated or combined with the methanol synthesis process, outlining the high flexibility and versatility of the reported CO_2 hydrogenation process.

2. Experimental

2.1. Materials

Copper nitrate hexahydrate (⩾98%, Alfa Aesar), zinc nitrate hexahydrate (98%, Sigma–Aldrich), aluminium nitrate nonahydrate (⩾98%, Fluka), potassium hydroxide (⩾85%, Sigma–Aldrich), γ-Al_2O_3 (Bimodal, Alfa Aesar) and NH_4-ZSM-5 (SiO_2/Al_2O_3 = 50/1, Alfa Aesar) were used as received. Deionized water was used for catalyst synthesis. A commercial methanol synthesis catalyst was purchased from Alfa Aesar (Product ID: 45776). Liquid CO_2 (>99.9993%) and 10% Ar in H_2 (>99.999% for Ar or H_2, prior to mixing) were purchased from Linde.

2.2. Catalyst synthesis

For the synthesis of $Cu/ZnO/Al_2O_3$, aqueous solutions of copper nitrate hexahydrate (0.2 M), zinc nitrate hexahydrate (0.2 M) and aluminium nitrate nonahydrate (0.2 M) with potassium hydroxide (0.5 M) were slowly added together, in a round-bottom flask to precipitate the corresponding hydroxides. During the precipitation, the round-bottom flask was heated at 80 °C under constant stirring, and the pH of the solution with precipitate was maintained between 9.5 and 10.5. The precipitate was aged for 48 h, filtered and washed with water until the pH of the washed solution reached the value of 7.5. Then, the sample was dried at 100 °C overnight, crushed and calcined in air at 400 °C for 4 h to yield $Cu/ZnO/Al_2O_3$ (I). Following the same synthesis procedure, two

more catalysts, $Cu/ZnO/Al_2O_3$ (II) and Cu/Al_2O_3, were prepared using different compositions of precursor solutions. H-ZSM-5 was prepared by calcination of NH_4-ZSM-5 in air at 400 °C for 4 h. Another Cu/Al_2O_3 (18/82 wt%) catalyst was prepared by the incipient wetness impregnation method. The preparation method and catalyst properties are described elsewhere [12]. Prior to charging the catalysts into reactor, they were pelletized, crushed and sieved a size of 100–300 μm. Elemental composition, Cu surface area, CuO crystallite size and BET surface area of the synthesized and commercial catalysts are listed in Table S1 (Supplementary material).

2.3. Catalytic testing

CO_2 hydrogenation reaction was performed in the microreaction set-up and tubular reactors (ID: 1.74 mm, OD: 3.17 mm) were used throughout. Details of the set-up and method of product analysis are described elsewhere [12]. For methanol synthesis, 170 mg of $Cu/ZnO/Al_2O_3$ (I) was used. In the study of very low to high GHSVs using the commercial catalyst, 1000, 85 or 42.5 mg of the catalyst was used for the catalytic tests in the range of 425, 10,000–40,000 or 81,000–182,000 h^{-1}, respectively.

For the synthesis of DME, H-ZSM-5 (150 mg) was mixed with $Cu/ZnO/Al_2O_3$ (II) (170 mg) and charged into one reactor or the two catalysts were charged separately into two reactors connected in series.

For hydrocarbon synthesis, H-ZSM-5 (170 mg) was charged into a reactor connected in series after that containing $Cu/ZnO/Al_2O_3$ (II) for methanol synthesis. The temperature of the secondary reactor containing H-ZSM-5 was controlled independently from the first one. For alkane synthesis, the reactor with H-ZSM-5 was placed before the back pressure regulator, thus kept at the same pressure as the first one (Fig. S8). While in alkene synthesis, the secondary reactor was located after the back pressure regulator (Fig. S9) and kept at the atmospheric pressure. It should be noted that GHSVs for the combined processes (DME and hydrocarbon syntheses) were calculated based on the amount of the methanol synthesis catalyst in the reactor.

For the above three reactions, argon was used as an internal standard for gas chromatography (GC) analysis and product selectivity was calculated taking only carbon-containing products into account.

3. Results and discussion

Fig. 1 summarizes the effects of feed composition on CO_2 conversion and product selectivity over the $Cu/ZnO/Al_2O_3$ (I) catalyst
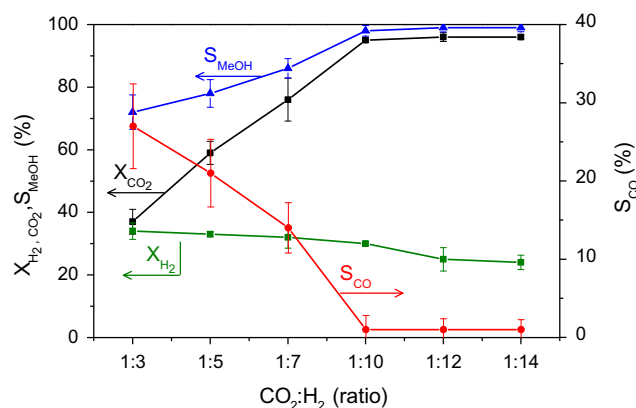

Fig. 1. Effects of the CO_2/H_2 feed ratio on CO_2 conversion (X_{CO2}), H_2 conversion (X_{H2}) and selectivity to CO (S_{CO}), and methanol (S_{MeOH}) in CO_2 hydrogenation over the $Cu/ZnO/Al_2O_3$ catalyst. Reaction conditions: T = 260 °C, P = 360 bar, GHSV = 10,471 h^{-1}.