



# Power-law kinetics of methanol synthesis from carbon dioxide and hydrogen on copper–zinc oxide catalysts with alumina or zirconia supports



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## ARTICLE INFO

### Article history:

Received 1 July 2015

Received in revised form 30 October 2015

Accepted 10 November 2015

Available online 23 December 2015

### Keywords:

Methanol synthesis

Carbon dioxide hydrogenation

Kinetics

Copper catalyst

Zirconia

Alumina

## ABSTRACT

Kinetics of methanol synthesis from carbon dioxide and hydrogen were studied on two catalysts, a copper–zinc oxide–alumina catalyst (CuZA) and a copper–zinc oxide–zirconia (CuZZ) catalyst. Although both catalysts show similar turnover frequencies for the methanol synthesis reaction, CuZZ is more selective for methanol synthesis because the reverse water gas shift reaction occurs more slowly on this catalyst. The results of the catalytic tests were modeled with power-law equations which highlight the strong positive impact of hydrogen partial pressure on methanol synthesis activity and selectivity. The comparison of the experimental results with thermodynamic equilibrium allows separating thermodynamic and kinetic driving forces.

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## 1. Introduction

In order to limit global warming, worldwide efforts to reduce anthropogenic CO<sub>2</sub> emissions are underway [1]. This is particularly relevant to the energy sector, which accounts for over 60% of global greenhouse gas emissions [2]. While the share of renewable energies for electricity generation is getting more and more important in the global energy mix, the actual electricity production from renewable sources like wind or solar energy is intermittent, causing a negative impact on electric grid stability if production and demand do not match [3,4]. To address these interrelated problems, the French research project VItESSE2 was initiated [5]. Its goal is to couple two objectives, valorization of CO<sub>2</sub> emissions and electricity grid stabilization, via a flexible methanol synthesis process. In delocalized units, CO<sub>2</sub> captured from major industrial emission sources would react with hydrogen produced by water electrolysis from available decarbonized excess electricity from the grid [6].

With a worldwide production of around 60 Mt in 2013, methanol is an important basic chemical [7]. It is produced indus-

trially from synthesis gas mixtures (CO/CO<sub>2</sub>/H<sub>2</sub>) over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts at 50 to 100 bar total pressure and at a temperature between 200 and 300 °C [8]. Pilot and commercial plants for methanol synthesis using only CO<sub>2</sub> as a carbon source and operating in steady-state have already been launched [9,10]. Among the requirements for a flexible design of the novel process envisaged here, sufficiently active and selective catalysts adapted to the intermittency of the process are needed [11]. Furthermore, for reactor design, knowledge of the kinetics of the catalytic chemical transformation is necessary [12].

Methanol synthesis from carbon oxides can be described using the following reaction equations: methanol synthesis from CO<sub>2</sub> (Eq. (1)), the reverse water gas shift reaction (RWGS, Eq. (2)) and methanol synthesis from CO (Eq. (3)).



As a consequence of the industrial importance of methanol, numerous kinetic models already exist to describe the reaction. Early models exclusively accounted for methanol synthesis from CO in CO/CO<sub>2</sub> synthesis gas mixtures [13–16]. For these models, it

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was assumed that methanol is produced from CO only. This implies that they cannot be used with pure CO<sub>2</sub> feed streams. Subsequently, complex kinetic models have been developed, which take into account the experimental fact that methanol is produced mainly from CO<sub>2</sub> even using CO-containing feeds [16–20]. Power-law models, on the other hand, require no hypothesis about the reaction mechanism, which is still under debate in the literature [21,22]. Such models have been proposed by Peter et al. and Ledakowicz et al. [23,24]. However, these empirical models can only be used in a defined range of partial pressures, conversions and temperatures.

This work aims to provide recent input data for reactor and process design for the intermittent CO<sub>2</sub> valorization process described above. Kinetic data of methanol synthesis from CO<sub>2</sub>/H<sub>2</sub> feeds over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and a Cu/ZnO/ZrO<sub>2</sub> catalyst were collected and power-law models were developed.

## 2. Experimental

### 2.1. Catalyst characterization

Catalysts 30 wt% Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (CuZA) and 30 wt% Cu/ZnO/ZrO<sub>2</sub> (CuZZ) were prepared by coprecipitation of nitrate solutions of the respective metals with Na<sub>2</sub>CO<sub>3</sub> solution [11].

The copper surface area of the catalysts was measured by the N<sub>2</sub>O reactive frontal chromatography method using a Micromeritics AutoChem II analyzer with TCD detector at a total flow rate of 50 mL<sub>SATP</sub> min<sup>-1</sup> [25]. After reduction of 400 mg of the sample at 280 °C, ramp 1 °C min<sup>-1</sup>, isotherm for 12 h under 10% H<sub>2</sub>/Ar flow, N<sub>2</sub>O chemisorption was carried out at 50 °C under a 2% N<sub>2</sub>O/Ar flow.

Specific surface areas measurements were performed by nitrogen adsorption–desorption at 196 °C using the Brunauer–Emmet–Teller (BET) method on a Micromeritics ASAP 2420 apparatus. Samples were previously outgassed at 250 °C for 3 h to remove adsorbed moisture.

### 2.2. Reaction setup

A gas mixture bottle of molar composition 31.5% CO<sub>2</sub>, 63.5% H<sub>2</sub> and 5.0% N<sub>2</sub> was purchased from Air Liquide. Gas bottles of H<sub>2</sub>, N<sub>2</sub> and Ar were purchased from Air Liquide and SOL France.

Catalytic tests were carried out on a stainless steel reaction setup. Gas flows of the mixture bottle, of pure H<sub>2</sub>, N<sub>2</sub> and Ar were regulated by Brooks SLA 5850S mass flow controllers connected to Brooks 0254 secondary electronics. Pressure was controlled by a Brooks 5866 back pressure regulator. The catalyst bed was placed between two pieces of quartz wool retained by a quartz tube and a metallic grid with gas flows pointing downwards. Temperature was regulated by a PID controller with the regulation thermocouple touching the catalyst bed at the effluent side. Liquid products (methanol and water) were trapped during the reaction in a first trap at room temperature and afterwards in a second, water-cooled trap at 15 °C and analyzed offline using an Agilent 6890 N gas chromatograph equipped with a Solgelwax column and FID detector.

Gases CO<sub>2</sub>, CO, H<sub>2</sub>, N<sub>2</sub> and Ar were analyzed online once per hour by an Inficon 3000 microchromatograph equipped with Molsieve 5 Å and Poraplot Q columns and TCD detectors.

No traces of methane or other hydrocarbons, dimethylether or other alcohols than methanol were detected.

### 2.3. Catalytic tests

The catalytic tests were carried out using the catalyst beds described in Table 1. A Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (CuZA) and a Cu/ZnO/ZrO<sub>2</sub> (CuZZ) catalyst were used. The catalyst powders were sieved to a 50–125 μm particle fraction, yielding apparent densities of 0.44 g cm<sup>-3</sup> for CuZA and 1.51 g cm<sup>-3</sup> for CuZZ. As the

**Table 1**  
Catalyst and catalyst bed properties.

	CuZA	CuZZ
Mass fraction Cu (%)	30	30
Mass fraction CuO (%)	37.5	37.5
Mass fraction ZnO (%)	41	41
Mass fraction support (%)	21.5	21.5
Support type	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
Apparent density (g cm <sup>-3</sup> )	0.44	1.51
Catalyst mass (mg)	135	135
Particle size (μm)	50–125	50–125
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	82	71
Cu <sup>0</sup> surface area (m <sup>2</sup> g <sup>-1</sup> )	9.6	8.3
SiC mass (mg)	–	387
Bed volume (cm <sup>3</sup> )	0.307	0.307
Bed height (cm)	0.382	0.382
Internal reactor diameter (cm)	1.01	1.01
External reactor diameter (in)	0.5	0.5

catalyst mass was fixed to 135 mg and CuZZ exhibits a higher apparent density than CuZA, CuZZ was diluted with inert SiC in order to obtain the same GHSV for both catalysts. The reaction conditions are summarized in Table 2. The following procedure was used for the experiments: the catalyst was reduced under H<sub>2</sub> flow (6.4 mL<sub>SATP</sub> min<sup>-1</sup>) at atmospheric pressure (ramp from room temperature to 280 °C, rate 1 °C min<sup>-1</sup>, isotherm for 12 h). The reduced catalyst was then cooled down to 100 °C under the same flow. The desired reaction gas flow rates were adjusted to a total volumetric flow rate of 40 mL<sub>SATP</sub> min<sup>-1</sup> and verified using an Agilent ADM 1000 flow meter. Then the reactor was pressurized to the desired total pressure (usually 50 bar) under reaction flow and the gas phase composition was allowed to stabilize. The temperature was ramped at 1 °C min<sup>-1</sup> to the desired reaction temperature. The moment when this temperature was reached was defined as the starting point of the reaction.

### 2.4. Data treatment

For the calculation of conversions and selectivities, the amount of substance integrated over the entire duration of the experiment was used. For liquid products, the weighed mass of product *i* was converted to amount of substance using  $n_i = m_i/M_i$ . For gases, the amount of substance  $n_i$  was calculated by integrating the molar flow rate  $F_i$  over the duration  $t_R$  of the experiment.

$$n_i = \int_0^{t_R} F_i dt \quad (4)$$

Conversions (*X*) were calculated as average values for the total test duration.

$$X_{\text{CO}_2} = 100\% \times \frac{n_{\text{CH}_3\text{OH}} + n_{\text{CO}}}{n_{\text{CO}_2, \text{in}}} \quad (5)$$

$$X_{\text{H}_2} = 100\% \times \frac{2n_{\text{CH}_3\text{OH}} + n_{\text{H}_2\text{O}}}{n_{\text{H}_2, \text{in}}} \quad (6)$$

Selectivities (*S*) were calculated with respect to carbon-containing products.

$$S_{\text{CH}_3\text{OH}} = 100\% \times \frac{n_{\text{CH}_3\text{OH}}}{n_{\text{CH}_3\text{OH}} + n_{\text{CO}}} \quad (7)$$

$$S_{\text{CO}} = 100\% - S_{\text{CH}_3\text{OH}} \quad (8)$$

Methanol was assumed to be produced directly from CO<sub>2</sub> (Eq. (1)). This assumption is based on literature data [26–28] and on the fact that the experiments were conducted at low conversions. CO production was attributed to the reverse water gas shift reaction (Eq. (2)). In addition, on a catalyst of similar composition to our

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