Kinetic modelling of the catalytic hydrogenation of CO_2 to methanol at moderate pressures

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1. Introduction

Methanol is considered one of the most important basic chemicals in industry, being a raw material for the production of acetic acid, formaldehyde and di-methyl ether. It has recently attracted interest as a chemical energy carrier, depicting itself as a potential hydrogen storage source for fuel cells, or directly as a liquid fuel [1]. CO_2 conversion into methanol would serve to reduce CO_2 emissions, as well as to produce a high valued chemical. Because of CO_2 high molecular stability, the choice and use of a proper reactive system in order to maximise its conversion into methanol is necessary. Catalytic systems are among the most used ones, as they can decrease the activation energy necessary for the reaction.

A wide array of powder catalysts (mostly copper-alumina based) has already been synthesised, characterised, and their performance analysed over conventional fixed-bed reactors at a laboratory scale [2]. However, powder catalysts are not used in industry because of the prohibitively high pressure losses this would provoke. A proper catalyst pellet sizing becomes thus vital. This pellet would need to be able to deliver product yields similar to those of its precursor powder.

Our aim is to study the kinetics of CO_2 catalytic hydrogenation under pressures ranging from 20 to 35 bar, over a home-made copper-zinc on alumina catalyst and study its heat and mass transfer limitations. In this paper, a rate law for the catalytic powder is going to be presented. A study of the heat and transfer limitations over an increasing particle size, concluding with the pellet, is going to be carried out. Ultimately, a kinetic model of the reaction under moderate pressure, where parameters such as kinetic constants and activation energies will be optimised, is going to be delivered.

2. Methods

A bimetallic (copper-zinc) catalyst supported over alumina was synthesised by wet impregnation. This catalyst was prepared as extrudates of 2 mm x 5 mm. The experimental set-up (shown below) consists of a 200 mm x 4 mm (i.d.) stainless steel reactor placed inside a resistive heating furnace. Gas fed into the reactor are H_2, CO_2 and N_2. Nitrogen is used as an inert vector gas for quantification purposes and to control the heat production of the reaction. Products are analysed using a GC apparatus.
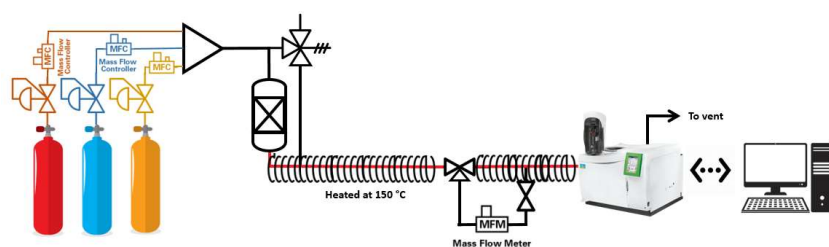

Figure 1. Experimental Setup

3. Results and discussion

Initial catalytic tests, where the influence of the spatial velocity over CO_2 conversion and methanol selectivity have been carried out. Figure 2 shows how an increase in spatial velocity improves methanol selectivity with a $CO_2/H_2/N_2$ (1:3:4) feed at 26 bars. This could be explained from the two mechanisms for CH_3OH production: either by direct CO_2 hydrogenation (Eq. 1), or by CO generation from the reversed water-gas-shift (RWGS) reaction (Eq.2), which would later be hydrogenated into CH_3OH (Eq. 3). Methanol production from Eq. 3 would need Eq. 2 to occur first, providing the necessary CO. However, because methanol selectivity is increasing with space velocity, it can be concluded that this methanol is in fact being produced by Eq. 1, and that an increased space velocity favours Eq. 1 in spite of Eq. 2, apparently indicating this route (Eq. 1) to be faster. This is confirmed by the decrease in CO_2 conversion observed with the increase of the space velocity.
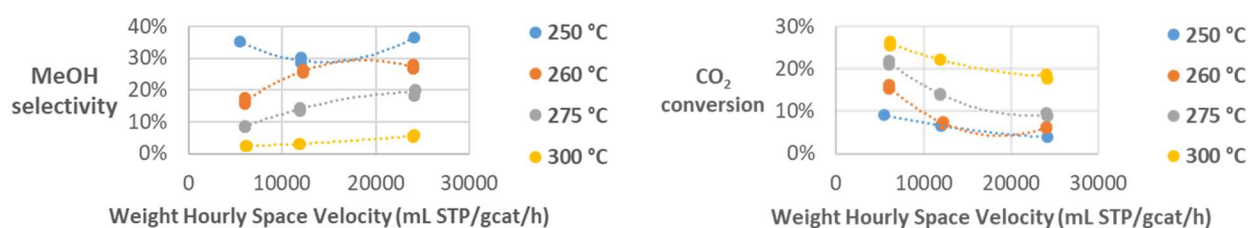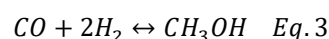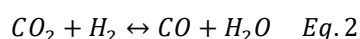
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad Eq.1$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad Eq.2 \qquad CO + 2H_2 \leftrightarrow CH_3OH \quad Eq.3$$
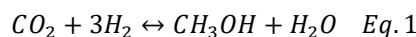

Figure 2. Influence of the WHSV on methanol selectivity and CO_2 conversion

A wide range of parameters has been varied in order to assess and identify all the necessary catalytic aspects concerning our reactive system: temperature (between 200 and 300 °C), total pressure (20-35 bar), molar feed composition (CO_2/H_2 from 1:1 to 1:9) and space velocity (5,000 – 25,000 mL STP/g_{cat}h). The obtained results are used to validate the kinetic model. In the initial approach, both the power law and the Langmuir-Hinshelwood kinetic models are analysed, and the thermodynamics equilibrium approach is used. These optimised kinetic parameters will serve as a solid base for posterior reactor modelling work.

4. Conclusions

The conversion of CO_2 to methanol over a copper-zinc catalyst has been experimentally studied for the production of methanol under moderate pressure (20-35 bar). The kinetic modelling of this reaction was carried out taking into consideration heat and mass transfer diffusional limitations obtained in pellets, which were examined and discussed. The multiplicity of reactions involved and the thermodynamic equilibria had to be taken into account to obtain a correct kinetic representation of the experimental results. This work, which is preliminary to any reactor sizing attempt, is an essential step in CO_2 valorisation into methanol using carbon-free hydrogen.

References

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