

# Methanol intermediated catalytic hydrogenation of CO<sub>2</sub> to fuels: A critical review

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## Introduction

One of the global problems that need to be solved as soon as possible is the environmental pollution. The reduction of greenhouse gases (GHG) emissions is one of the main solutions that the fields of technology and research focus on, and more specifically the reduction of carbon dioxide which is the major GHG (77% of total GHG emissions)[1]. Multiple technologies have been developed targeting this goal by capturing, storing and further converting CO<sub>2</sub> (Carbon Capture and Storage, CCS and Carbon Capture and Utilization, CCU)[1]. CO<sub>2</sub> can be valorized in many ways such as when it is used directly for example in food industry or oil recovery, when biological fixation is used such as for microalgae growth, when mineralization takes place, for instance for direct carbonation and finally through catalytic reduction for example for methanation or the synthesis of chemicals, fuels etc[2].

This work focuses on the last pathway and more specifically on the hydrogenation of CO<sub>2</sub> to the production of fuels. For this process the feed gases are CO<sub>2</sub> and hydrogen. The source of hydrogen is of high importance as the way it is produced could cause extra GHG emissions. Consequently, hydrogen is divided in 5 categories: grey hydrogen, blue hydrogen, brown hydrogen, turquoise hydrogen and green hydrogen which have different carbon footprints[6]–[11]. It should be noted that Green hydrogen could have potentially the lowest footprint but this is highly dependent (on the source of electricity (for instance when electricity is produced from nuclear power the emissions are the lowest, followed by wind and solar energy)[8].

Valorizing C1 compounds such as CO and CO<sub>2</sub> to hydrocarbons is possible through 2 main processes that have been developed which are the Fischer-Tropsch (FT) process and the methanol to hydrocarbons (MTH) route[9], [10]. In the FT synthesis, CO is hydrogenated to hydrocarbons directly or CO<sub>2</sub> is first converted to CO through the reverse Water-Gas-Shift (RWGS) reaction and then CO is hydrogenated to targeted products[11]. With the MTH process, methanol is the important intermediate that can be further converted to hydrocarbons. For this purpose, a first step is necessary in order to convert CO or CO<sub>2</sub> to methanol. The CO to methanol route (with syngas) is commercial and catalytic. Starting with CO<sub>2</sub> conversion is of course more interesting from a GHG point of view. Going to fuels from methanol has some advantages compared to the FT synthesis route. First of all, the hydrocarbons produced this way are of a smaller range maximum with 11 carbon atoms while the production of C1 hydrocarbons such as CH<sub>4</sub> is very low. Another important reason is that the selectivity and yield are high increasing the quality of the fuel produced[9]. On the other hand, when combining CO<sub>2</sub> hydrogenation to methanol process with MTG process some difficulties arise (such as limited selectivity and yield) as well. Developing highly effective materials that catalyze this reaction towards certain products selectively and optimizing the reaction conditions are needed in order for this system to be scaled up.

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## Methodology

CO<sub>2</sub> to fuels through the methanol synthesis route is a catalytic process as it has been mentioned before. Not so much research has been done on this particular, very complex reaction which leads to the demand of a critical comparison between the catalysts and reaction conditions in order to find useful conclusions and optimum conditions.

First of all it must be explained here that the catalysts needed for this reaction are tandem catalysts that consist of a part that converts CO<sub>2</sub> to methanol (usually an oxide) and a second part for the methanol to fuels reaction (usually a zeolite). The conventional system for CO<sub>2</sub> (and CO) to methanol that has been studied is Cu-Zn-Al while recently, In, Zr and Zn-containing oxides are coming to the fore. Such decent methanol synthesis catalysts can be combined with ZSM-5 or other zeolites[12]–[15]. For the purpose of this paper the latest system will be discussed and used for extracting useful information by collecting data from previous works and comparing them in a critical way, leading to conclusions.

## Results and Discussion

To start with, it should be mentioned that the groups who have studied this system have, as main product, alkanes C<sub>5</sub>+ or aromatics in mind, and work with a feed of H<sub>2</sub> and CO<sub>2</sub> of a ratio equal to 3 (H<sub>2</sub>/CO<sub>2</sub>). The temperature chosen is always higher than 300°C and more specifically 315-340°C. As for the pressure, 30-40 bar is the preferred for the system. Different synthesis methods for the oxide have been tested as well as different Si/Al ratios for the ZSM-5, which relates to its acidity. The Gas Hourly Space Velocity (GHSV) applied to the system lays between the range of 1020-9000 ml/gcat/h. As shown in Figure 1, different Si/Al ratios of the zeolite do not influence the conversion of CO<sub>2</sub> as this is mainly performed at the oxide part of the dual catalyst system. On the other hand, this ratio has an effect on the Space Time Yield (STY) of the target fuels which seems to benefit from low ratios (Si/Al=25 shows the highest STY), while a drop is observed for Si/Al=65 and reaching a plateau with further increase. As it is also worth noticing in Figure ,1 the main determinator of the space time conversion is the GHSV (of course linked with the nature of the oxide).

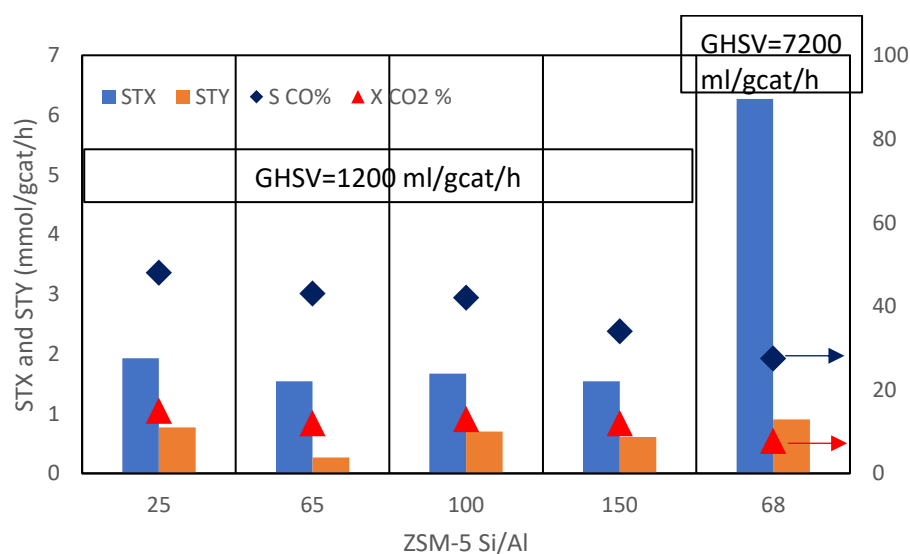


Figure 1. Effect of Si/Al ratio of ZSM-5 zeolite on Space Time Conversion (STX) and Space Time Yield (STY) in a system with dual catalysts physically mixed: ZnZrO<sub>x</sub> + ZSM-5 Based on data from [12], [13], [14].

Thus, Figure 2 represents the effect of GHSV for the same systems working at 2 different pressures. The main assumption that can be extracted from this comparison is that pressure does not play a major role in STX especially compared to GHSV. However when GHSV is higher, the pressure contributes more to STX because as we can see at 3000 and 3060 ml/g<sub>cat</sub>/h a big difference is observed. The same behavior is observed for Space Time Yield of fuel-range products even though as it can be seen in Figure 3 there is some data missing.

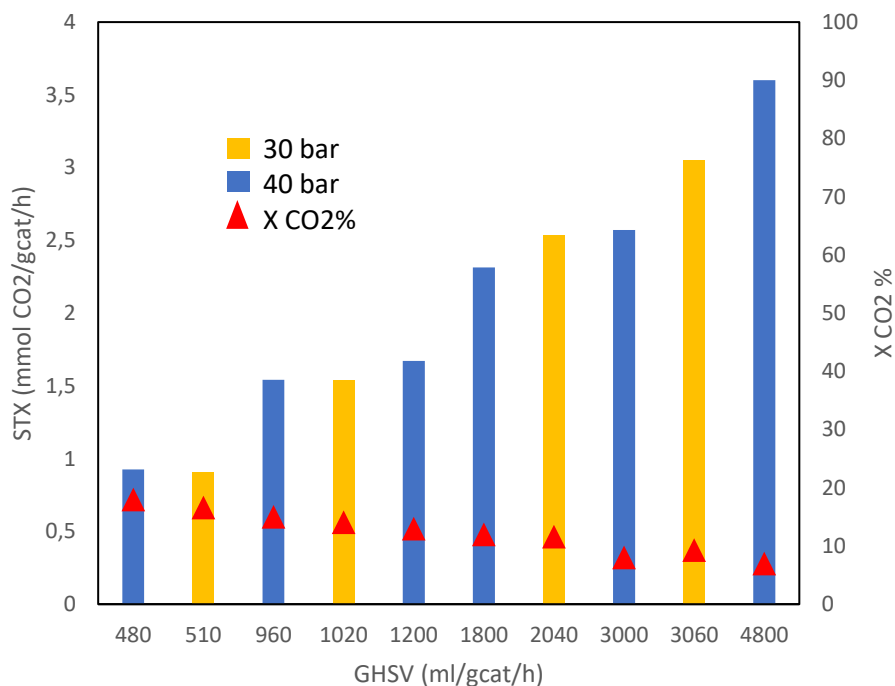


Figure 2. Effect of pressure and GHSV in Space Time Conversion of CO<sub>2</sub> in system ZnZrOx+ZSM-5 [12], [13]

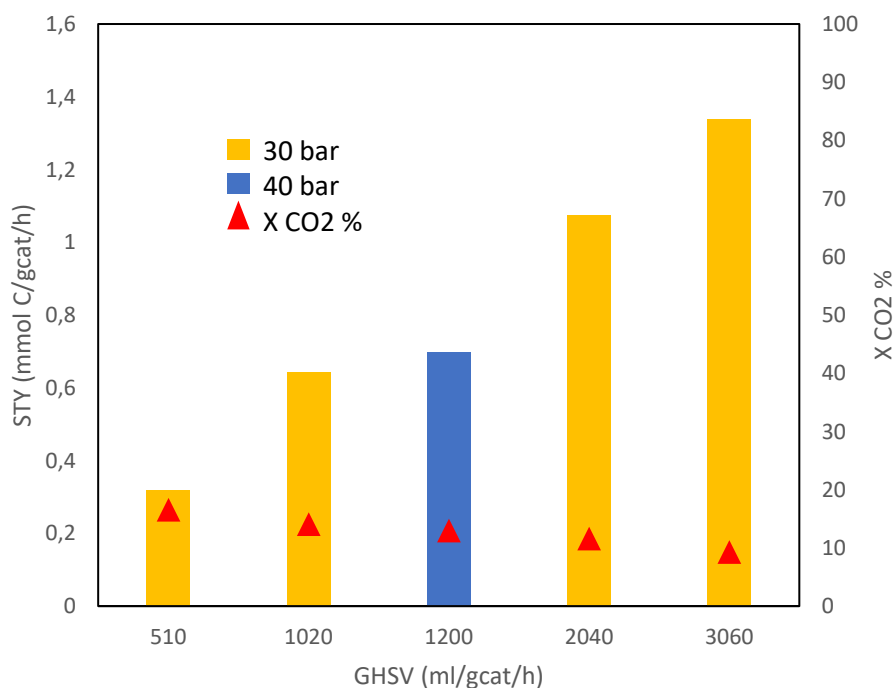


Figure 3. Effect of pressure and GHSV in Space Time Yield in fuel products in system ZnZrO<sub>x</sub>+ZSM-5 [12], [13]

## Conclusions

Based on the preliminary results from this critical review there are some assumptions that can be extracted safely. First of all, the difference in the acidity of the zeolite part, as indicated based on the Si/Al ratio is one of the main contributors for altering the experimental results in the CO<sub>2</sub> conversion to fuels reaction on the part of what happens to the intermediate methanol. Moreover, GHSV plays a crucial role since it is the main way to increase the STX of the CO<sub>2</sub> and at the same time increase the STY of the targeted products. It is important to find an optimum GHSV to work with because increasing the flow has also a negative impact on the conversion of CO<sub>2</sub> with a higher rate compared to the rate of the increase noticed in STYs. In addition, increase of the pressure (30-40) has a slightly positive effect on the system in higher GHSVs. Lower pressures (<20 bar) would lower the conversion of the CO<sub>2</sub>/H<sub>2</sub> mixture. However, there is still a lot of research that needs to be done in order to make sure that these assumptions are general conclusion and more contribution is needed towards the study of the mechanism and kinetics of such a complex system. In further work, our research will focus on developing tandem catalysts by improving the zeolites and studying the proximity between the 2 materials (oxide-zeolite), in order to increase the selectivity of gasoline range hydrocarbons and more specifically, C<sub>5</sub>+ alkanes, while at the same time avoiding the production of aromatics.

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