

Energimyndighetens titel på projektet – svenska <b>Grönt jet bränsle från en integrerade katalytisk process</b>	
Energimyndighetens titel på projektet – engelska <b>Green jet fuel from an integrated catalytic process</b>	
Universitet/högskola/företag <b>Chalmers Tekniska Högskola AB</b>	Avdelning/institution <b>Kemiteknik</b>
Adress <b>412 96 Göteborg</b>	
Namn på projektledare <b>Louise Olsson</b>	
Namn på ev övriga projektdeltagare <b>Derek Creasar, Poonam Sharma, Sreetama Ghosh, Joby Sebastian</b>	
Nyckelord: 5-7 st <b>Jet fuel, CO<sub>2</sub> hydrogenation, Alcohol to Jet (AtJ), catalysis, kinetic modelling</b>	

## Preface

This project is funded by the Swedish Energy agency. The focus of the project is to produce Jet-fuels by catalytic CO<sub>2</sub> hydrogenation. There has been three post-docs working in the project Dr. Poonam Sharma, Dr. Joby Sebastian and Dr. Sreetama Ghosh. The project has been supervised by Prof. Derek Creaser and Prof. Louise Olsson. The project was conducted at Chemical Engineering, Chalmers University of Technology.

## Table of content

Preface .....	1
Table of content .....	1
Sammanfattning .....	2
Summary .....	2
Introduction.....	3
Methods .....	4
Results.....	7
Discussion.....	11
Publications.....	12
References.....	12
Appendix.....	13

## Sammanfattning

I detta projekt har vi studerat koldioxid hydrogenering till kolväten, via metanol som mellanprodukt. Målet var att öka utbytet av kolväten inom området för jetbränsle (C<sub>8</sub>-C<sub>16</sub>). Vi har utvecklat ett nytt katalytiskt tvåbäddssystem där den första bädden innehåller en In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>-katalysator för metanolsyntes och ZSM-5 för bildning av metanol till kolväte (MTH=methanol to hydrocarbons). Den andra bädden placerades nedströms och innehöll katalysatorn för oligomerisering. Med tillägget av oligomeriseringskatalysatorn, som polymeriserar små kolväten till större kolväten, ökade vi selektiviteten för kolväten inom jetbränsleintervallet (C<sub>8</sub>-C<sub>16</sub>) från 29% till 42.5%. Dessutom har vi utvecklat en kinetikmodell för CO<sub>2</sub>-hydrogenering till kolväten, som väl kan beskriva C<sub>2</sub>-C<sub>4</sub>, C<sub>5</sub>-C<sub>8</sub> och C<sub>9+</sub> selektivitet samt CO-bildning vid olika temperaturer. En kinetik modell är viktig för att göra simuleringar för uppskalning av processen. Vidare, oligomeriseringskatalysatorn förbättrade mängden av kolväten inom jetbränsleområdet och vi tror att ytterligare forskning inom detta område kan resultera i ytterligare ökad selektivitet för längre kolväten i jetbränsleområdet. Sammantaget är koldioxidhydrogenering till bränslen en lovande väg framåt och när man använder koldioxid som bildas från omvandling av biomassa kan det till och med ge negativa koldioxidutsläpp.

## Summary

In this project we have studied CO<sub>2</sub> hydrogenation to hydrocarbons, via methanol as an intermediate. The aim was to increase the yield of jet fuel range hydrocarbons (C<sub>8</sub>-C<sub>16</sub>). We have developed a novel two-bed catalytic system where the first bed contained a In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst for methanol synthesis and ZSM-5 for methanol to hydrocarbon (MTH) formation. The second bed, placed downstream, contained the oligomerization catalyst. With the addition of the oligomerization catalyst, which polymerizes small hydrocarbons to larger hydrocarbons, we could increase the selectivity for jet-fuel range hydrocarbons (C<sub>8</sub>-C<sub>16</sub>) from 29% to 42.5%. In addition, we have developed a kinetic model for CO<sub>2</sub> hydrogenation to hydrocarbons, which can well describe the C<sub>2</sub>-C<sub>4</sub>, C<sub>5</sub>-C<sub>8</sub> and C<sub>9+</sub> selectivity as well as CO formation at different temperatures. A kinetic model is important in order to make simulations for up-scaling of the process. Moreover, the oligomerization catalyst improved the jet-fuel range hydrocarbons and we believe that further research in this area can result in further increase of the selectivity to longer hydrocarbons in the Jet-fuel range. Overall, CO<sub>2</sub> hydrogenation to fuels is a promising way forward and when using CO<sub>2</sub> formed from bio-mass conversion it can even give negative CO<sub>2</sub> emissions.

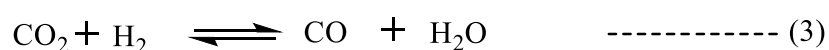
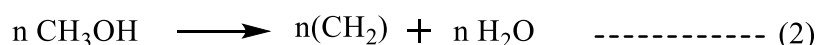
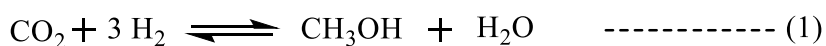
## Introduction

### Background

The large emission of CO<sub>2</sub> to the atmosphere by anthropogenic activities (36.5 gigatons per annum) is the major reason for global warming. To alleviate global warming, several key CO<sub>2</sub> recycling technologies were proposed.<sup>1</sup> The abundant nature of CO<sub>2</sub> endows itself as a C<sub>1</sub> feedstock for chemicals and fuels. If CO<sub>2</sub> formed from biomass is used, even negative CO<sub>2</sub> emissions can be achieved. Thus, many technologies based on photochemistry, electrochemistry, biochemistry, plasma chemistry, and solar thermochemistry were emerged to convert CO<sub>2</sub> to valuable chemical products. In this context, the conversion of CO<sub>2</sub> to fuels is highly desirable to reduce our dependence on fossil resources and reduce the global warming. CO<sub>2</sub> to fuel process has a huge and important market<sup>2</sup>, and can thereby significantly reduce the CO<sub>2</sub> emissions from the transport sector.

The conversion of CO<sub>2</sub> to fuel range compounds, also for jet-fuel, involves a reduction process with H<sub>2</sub>. Since jet-fuel is composed of C<sub>8</sub> to C<sub>16</sub> hydrocarbons,<sup>3</sup> a large amount of H<sub>2</sub> is needed. Hydrogen can be produced e.g. by solar water-splitting<sup>4</sup> or hydrolysers using electricity (the use of renewable electricity is of utmost importance). There is a vast amount of research currently ongoing in this field. CO<sub>2</sub> could be captured from the air or industries (cement, ammonia, ethylene oxide, etc., or by combustion of waste biomass).<sup>5</sup> Altogether, this makes the CO<sub>2</sub> to hydrocarbons (jet fuel) process a green and sustainable process.

In this report, the CO<sub>2</sub> to hydrocarbons process is investigated through the methanol intermediate as shown in equations (1) and (2). The entire process involves two independent catalysts working in synergy to generate hydrocarbons in a single step.



Industrially, methanol is produced over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst from a gas mixture composed of both CO<sub>2</sub> and CO, where high selectivity for CO and fast catalyst deactivation are the major drawbacks.<sup>6</sup> The direct hydrogenation of CO<sub>2</sub> to methanol is more difficult due to the chemically inert and thermodynamically stable nature of CO<sub>2</sub>. This necessitates a high reaction temperature for a high CO<sub>2</sub> conversion (300-450°C). But, at higher reaction temperatures, the main challenge is to control the CO formation (eq. 3) occurring through the reverse water-gas shift reaction (RWGS), thereby reducing the methanol selectivity.<sup>6</sup> Recent studies based on both theory and experiments have shown that ZrO<sub>2</sub> supported In<sub>2</sub>O<sub>3</sub> is a promising catalyst for the methanol synthesis from CO<sub>2</sub> under the same industrially relevant conditions as the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>7</sup> Almost 99.8% selectivity to methanol could be achieved over this catalyst at a GHSV of 16000 h<sup>-1</sup>. Oxygen vacancies observed on In<sub>2</sub>O<sub>3</sub> are the active sites for the reaction. The presence of

H<sub>2</sub> can increase the number of these vacancies,<sup>8</sup> thereby paving the way for the possibility of improving the CO<sub>2</sub> conversion. The methanol production is also limited by thermodynamic restrictions, especially at high temperature and low pressure. The CO<sub>2</sub> conversion can therefore be further improved by consuming the produced methanol on-site (converting into valuable products), by this allowing the equilibrium to shift to the product side.

Methanol to hydrocarbons (MTH) is a well-known industrial process for converting methanol to olefins (MTO), methanol to aromatics (MTA), and methanol to gasoline (MTG) range compounds. The reaction is realized through zeolite catalysis performed at atmospheric pressures and in a temperature range of 350-500°C.<sup>9, 10</sup> The shape-selectivity of zeolites, the strength of its acid sites, acid site distribution, crystallite size, etc., control the number of carbon atoms within a hydrocarbon product.<sup>11</sup> The zeolite catalysts are known to be deactivated by coking. Studies have shown that in the presence of H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, the stability of the zeolite catalysts could be largely improved.<sup>12-14</sup> Since these gases are involved in the CO<sub>2</sub> to methanol reaction, a combination of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and a zeolite catalyst provides a bifunctional catalyst, which could be an efficient method to increase the CO<sub>2</sub> conversion in the methanol synthesis step by consuming it immediately over the zeolite catalyst for the hydrocarbon synthesis. This bifunctional catalyst system can convert CO<sub>2</sub> to hydrocarbons in a single step.

### Objectives

The aim of this project is to increase the selectivity for Jet-fuel range hydrocarbons. Here, we used oligomerization process with CTH (CO<sub>2</sub> to Hydrocarbon) process to increase the fraction of Jet-Fuel range hydrocarbons. There are various reports where this process was separately used for oligomerization of ethylene, propylene, butene and hexene over modified zeolites.<sup>15, 16</sup> Along with this, a fundamental understanding of the entire process through kinetic modelling, which involves reaction mechanism and the corresponding rate constants, is also aimed in this project. These modelling studies are vital for the future up-scaling. In essence, this project-report discusses these aspects, catalyst modifications, process parameter optimization, and kinetic modelling for advancing the knowledge on CO<sub>2</sub> to hydrocarbon process, more specifically aiming for hydrocarbons in the jet fuel range.

### Methods

#### Catalyst preparation

ZrO<sub>2</sub> (monoclinic phase, extrudates, SZ 31164, NORPRO), In(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (Alfa Aesar, 99.99%), and HZSM-5 with SAR-27 and SAR-27 (Zeolyst) were used. ZrO<sub>2</sub> supported In<sub>2</sub>O<sub>3</sub> was prepared by a Incipient wetness-impregnation method where the bifunctional catalyst was prepared by physical mixing of pellets/granules (250-500 μm) of In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and HZSM-5/desilicated-HZSM-5 in 1:1 ratio. HZSM-5 was desilicated using an alkaline solution of NaOH. The indium loading on ZrO<sub>2</sub> was kept 13 wt.% for methanol synthesis and hydrocarbons synthesis.

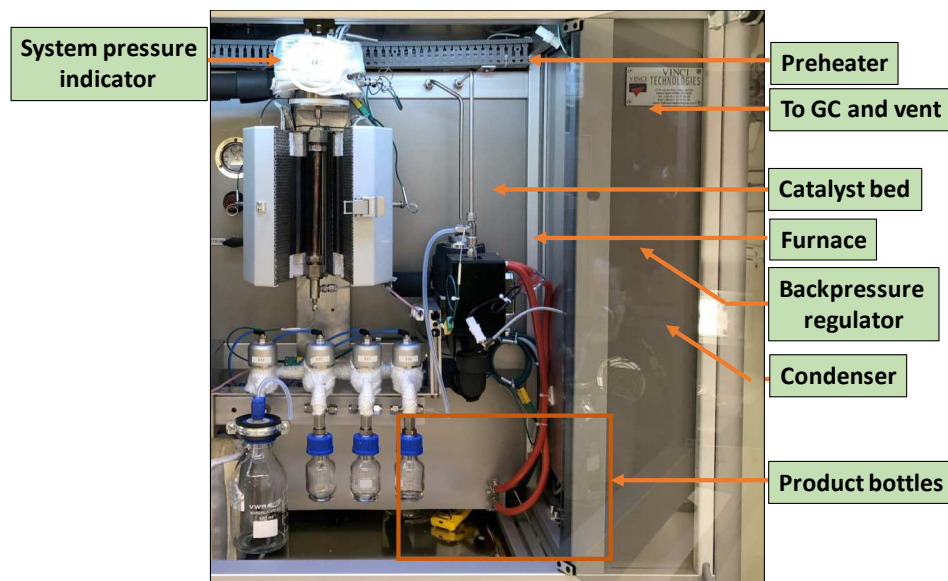
In addition, unsupported indium catalysts were synthesized and investigated. Indium hydroxide ( $\text{In}(\text{OH})_3$ ) was first synthesized by the standard precipitation method.  $\text{In}(\text{OH})_3$  was then calcined at 300 °C to obtain crystalline  $\text{In}_2\text{O}_3$  powder.<sup>17</sup> Commercial ZSM-5 zeolite (with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 23) in ammonium form was calcined at high temperature to obtain the acid form HZSM-5 catalyst. The  $\text{In}_2\text{O}_3$  and the HZSM-5 thus obtained were individually pressed, crushed and sieved to granules. Then the desired mass ratio of  $\text{In}_2\text{O}_3$  and HZSM-5 granules were mixed together and used as a bifunctional catalyst.

### **Catalysts Characterization**

$\text{In}_2\text{O}_3$  (13 wt.%) /  $\text{ZrO}_2$  was synthesized and combined with HZSM-5 and used as a bifunctional catalyst. The catalysts were characterized in detail using (i) BET for surface area, (ii) X-ray photo emission spectroscopy (XPS) for getting insight relating to formed compounds, e.g. if the metals are in oxidic or in metallic form, (iii) X-ray fluorescence (XRF) to determine the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, (iv) X-ray diffraction (XRD) for determining crystal structure (v) High-resolution transmission electron microscopy (HR-TEM) coupled with Energy-dispersive X-ray spectroscopy (EDS) to image the active catalyst particles on atomic level as well as retrieving the metal dispersion, (viii) Ammonia temperature-programmed desorption ( $\text{NH}_3$ -TPD) experiments to determine Lewis and Bronsted acid sites. By combining these techniques, detailed information relating to the material characteristics of these catalysts was found. In-situ DRIFT spectroscopy was used to investigate the intermediates to get a further understanding of the mechanism.

### **Flow Reactor**

The  $\text{CO}_2$  hydrogenation experiments were performed in a high-pressure fixed bed vertically positioned tubular stainless-steel reactor (VINCI Technologies, France). The Micro Catalyst Bed (MCB) unit is shown in Figure 1. The system pressure can be monitored using the pressure indicator. The stainless-steel reactor is placed in a ceramic furnace. A back-pressure regulator is fitted in the system that can maintain a steady pressure during the reaction. The effluent gas from the reactor was quantitatively analyzed online using a gas chromatograph (GC, SCION 456) equipped with both thermal conductivity (TCD) and flame ionization detectors (FID). The bed consists of a mixture of the catalyst particles and solid inert carborundum SiC with an average particle diameter according to catalysts granule size to maintain the bed isothermicity. The reactor was placed inside a furnace.  $\text{H}_2$  and  $\text{CO}_2$  were fed through separate mass flow controllers.



**Figure 1.** Picture showing the continuous flow reactor.

### Catalytic tests

The activity and selectivity of catalysts were examined in the continuous high-pressure reactor (Figure 1). Two processes were performed in the continuous reactor: (1) CO<sub>2</sub> hydrogenation to form methanol and (ii) CO<sub>2</sub> hydrogenation to hydrocarbons. First, the activity of In<sub>2</sub>O<sub>3</sub> (13 wt.%)/ZrO<sub>2</sub> was tested for methanol synthesis at various temperatures and used for optimizing the reaction parameters. Further, this catalyst was combined with zeolite HZSM-5 to form hydrocarbons from the methanol. Then, this bifunctional catalyst was tested at various temperature ranges. To get higher selectivity for longer hydrocarbons, lower olefins were oligomerized to form larger amount of hydrocarbons in the jet fuel range. For that, catalysts were tested using three configurations (A, B and C), which are shown in Figure A1 (Appendix 2). Briefly configuration A consists of one bed with In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/HZSM-5, configuration B consists of two beds the first with In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/HZSM-5 and the second bed with desilicated-HZSM-5 and finally configuration C consists of one bed with In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/desilicated-HZSM-5.

Also flow reactor experiments were performed for the kinetic modelling. Before reaction, the catalyst was activated at 400 °C in Ar atmosphere. The reactor was then allowed to cool down to the desired reaction temperature before the feed gas was switched to CO<sub>2</sub> and H<sub>2</sub> and pressurized to the desired total pressure. Tests were conducted at a temperature of 250 – 400 °C, a total pressure of 20 – 40 bar and with different H<sub>2</sub>:CO<sub>2</sub> molar feed ratios and Weight Hourly Space Velocities (WHSV). The quantification and identification of the product stream was performed using the online GC based on calibration standards of known concentration.

### Modeling methodology

The mass conservation equation is given by eq. 4:

$$\frac{dF_j}{dw} = \sum_{i=1}^n v_{ij} r_i \quad (4)$$

where  $w$  represents the catalyst weight,  $F_j$  the molar flow rate of species  $j$ ,  $v_{ij}$  the stoichiometric coefficient of species  $j$  in reaction  $i$  and  $r_i$  the rate of the reaction  $i$ . The nonlinear least square function 'lsqnonlin' subroutine in MATLAB R2019b's optimization package was used for carrying out non-linear regression. This non-linear least square solver uses a gradient-based optimization method to minimize the residual sum of squares (SSR) function (eq. 5) between the experimental and simulated results to optimize the kinetic parameters to find the best fit of model predictions to experimental measurements.

$$SSR = \sum_i w_i \sum_j R_j (y_{i,j}^{exp} - y_{i,j}^{sim})^2 \quad (5)$$

where  $y_{i,j}^{exp}$  represents the experimental mole fractions of each  $i$  lump for the  $j$  experimental condition and  $y_{i,j}^{sim}$  represents those calculated by numerical solution of the system of ordinary differential equations that are solved by the ode15s solver using MATLAB.  $w_i$  represents the weighting factor for each  $i$  lump of the kinetic scheme used typically to weigh up minority lumps in the reaction medium.

## Results

### CO<sub>2</sub> hydrogenation to methanol

In this project we are converting CO<sub>2</sub> to hydrocarbons, through methanol as an intermediate. We aim to increase the amount of hydrocarbons in jet-fuel range and also to develop a kinetic model for the process. We started with examining the CO<sub>2</sub> to methanol step by using an In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst. The synthesized catalyst was characterized in detail. The XRD patterns show that In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> has good crystallinity after preparation (Figure A2). The BET surface area of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> was found to be 60 m<sup>2</sup>/g with 0.21 cm<sup>3</sup>/g in pore volume (Figure A3). The presence of oxygen vacancies in catalyst was observed by XPS analysis (Figure A4). Hydrogen temperature programmed reduction (TPR) was used to examine the reduction behavior of the catalyst. The H<sub>2</sub>-reduction temperature was observed at 253.3 °C and 609.2 °C for the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst (Figure A5). TEM analysis was performed to examine the shape of the particles (Figure A6). EDS mapping shows the homogeneous dispersion of In<sub>2</sub>O<sub>3</sub> over ZrO<sub>2</sub> support (Figure A7). Carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) species were found on the surface of In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> during in-situ DRIFT analysis (Figure A8).

The catalytic activity of In<sub>2</sub>O<sub>3</sub> (13 wt.%)/ZrO<sub>2</sub> was tested in a continuous reactor. The In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst gave 100 % CH<sub>3</sub>OH selectivity with 0.6 % CO<sub>2</sub> conversion at 493 K whereas, at 553 K, we found 7.9 % CO<sub>2</sub> conversion with 73.5 % CH<sub>3</sub>OH selectivity while keeping pressure 30 bar (Figure A9a). The catalyst also exhibited a temperature-sensitive selectivity toward CO of up to 26 % at 553K (Figure A9d). CO<sub>2</sub> conversion, methanol and CO selectivity were also tested at lower loading of In (1 wt.%), on ZrO<sub>2</sub> and, In<sub>2</sub>O<sub>3</sub> without support. Efficient results were observed at higher loading of In on ZrO<sub>2</sub> (In<sub>2</sub>O<sub>3</sub> (In 13 wt.%)/ZrO<sub>2</sub>) (Figure A9b, c & d). The

catalyst stability was tested up to 50 h time-on-stream and the activity was found to be constant.

### **Increasing the selectivity for Jet fuel range hydrocarbons using a bifunctional catalyst**

Hydrocarbons were produced during hydrogenation of CO<sub>2</sub>. Initially a methanol catalyst (In<sub>2</sub>O<sub>3</sub> (13 wt.%)/ZrO<sub>2</sub>) was combined with an MTH-catalyst (ZSM-5 zeolite). We used two ZSM-5 zeolites with different Silica to alumina Ratio (SAR), SAR = 27 and SAR = 57. We produced a mixture of hydrocarbons over this bifunctional catalyst which was the combination of lower alkanes, lower alkene, aromatics and C<sub>5+</sub> hydrocarbon. Since the aim of our project is to increase the jet-fuel range hydrocarbons, we aimed to decrease the fraction of lower olefins using an oligomerization catalyst. As a oligomerization catalyst, we modified the ZSM-5 by removing some of the Si inside the zeolite by alkaline treatment. This results in increase the BET surface area, average pore volume, and acid strength. The acid strength of HZSM-5 was tested using NH<sub>3</sub>-TPD and found that the number of weak acid site and strong acid sites was increased after desilication (Figures A10-A11). SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was measured using XRF after desilication and found that it decreased in both HZSM-5 (SAR = 27 and SAR = 57). It was observed that the extent of desilication increased with SAR ratio.

Further to form hydrocarbons, HZSM-5 with SAR = 27 and 57 were physically mixed with In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> in a ratio of 1:1 and tested at 30/40 bar at 280, 300 and 350 °C (Configuration A, i.e. In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and HZSM-5 was mixed in one bed). At this reaction condition, the C<sub>5</sub>-C<sub>12</sub> selectivity among hydrocarbons reached up to 65.2 % with only 0.6 % for CH<sub>4</sub> selectivity at a CO<sub>2</sub> conversion of 5.7 % (Figure A12). It was observed that the CO<sub>2</sub> conversion and CO selectivity increased with temperature while the selectivity of hydrocarbons decreased.

In the oligomerization process, the desilicated zeolites were placed below the catalysts bed of In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/HZSM-5 (Configuration B). With desilicated zeolite, the lower olefins oligomerized and formed longer hydrocarbon (C<sub>5</sub>-C<sub>12</sub>) where the selectivity of C<sub>5</sub>-C<sub>12</sub> increased up to 70 % among hydrocarbons (Figure A13) whereas the selectivity of lower olefins (up to 5 %) decreased after oligomerization (Figure A15 & A20). Maximum C<sub>5</sub>-C<sub>12</sub> selectivity was found in case of configuration B compared to A and C for both HZSM-5 (with SAR = 27 and 57) while the C<sub>5</sub>-C<sub>12</sub> selectivity was higher in case of HZSM-5 (57) than HZSM-5 (27) (Figure A13 and Figure A18).

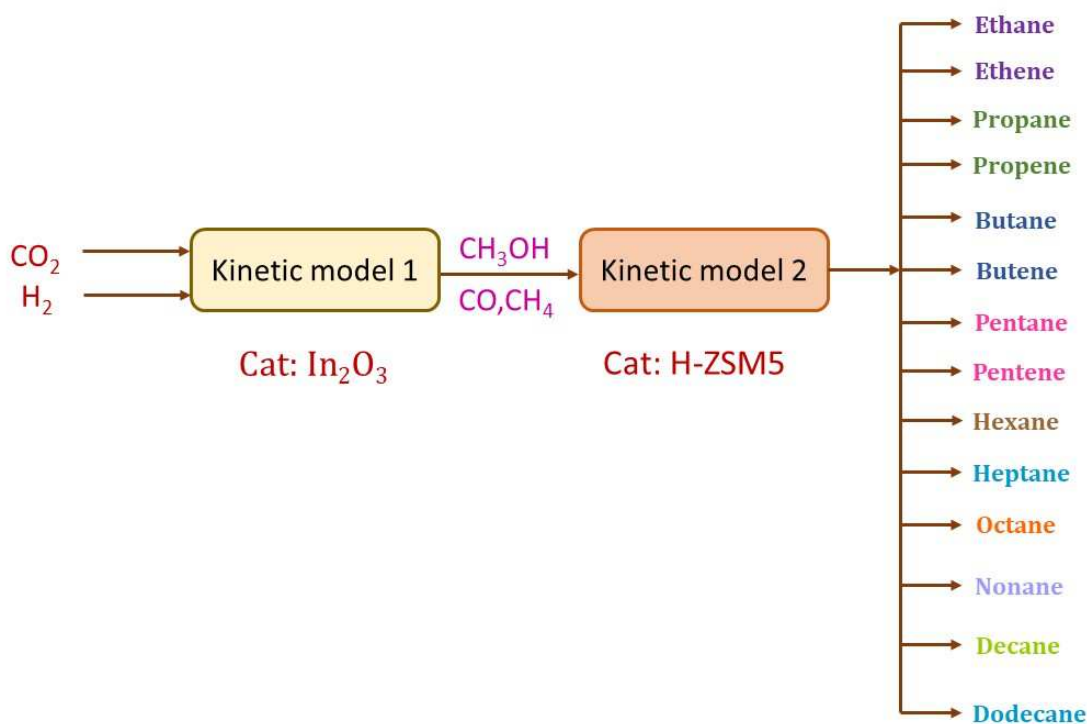
We also examined the distribution of hydrocarbons in the C<sub>5</sub>-C<sub>12</sub> fraction, since jet fuel range is in the range of C<sub>8</sub>-C<sub>16</sub>.<sup>3</sup> The results are shown in Figure A16 and A21. The fraction of C<sub>8</sub>-C<sub>12</sub> selectivity among C<sub>5</sub>-C<sub>12</sub> was higher in case of HZSM-5 (SAR=27) (Figure A16) than HZSM-5 (SAR=57) (Figure A21). The selectivity of longer hydrocarbons was also decreased with temperature as the formation rate of methanol decreased with the temperature. The best reaction condition was observed



at 280 °C, 40 bar with feed gas ratio of H<sub>2</sub>: CO<sub>2</sub> =3:1. In this experiment the CO<sub>2</sub> conversion was 7.3%, the CO selectivity was 11% and the hydrocarbon selectivity was 87%. For the formed hydrocarbons, the C<sub>5</sub>-C<sub>12</sub> selectivity was 68% and the C<sub>8</sub>-C<sub>12</sub> (jet fuel range) was 42.5%. It is very interesting to see that the addition of an oligomerization catalyst below the catalyst bed significantly improved the yield of jet-fuel range hydrocarbons, from 29% selectivity to 42.5%.

***Kinetic modelling of CO<sub>2</sub> hydrogenation to fuel through alcohol mediated path  
Proposed kinetic scheme***

Detailed knowledge of the performance and mechanisms of CO<sub>2</sub> hydrogenation reactions can be obtained from kinetic modelling. The kinetic models can have widely different levels of detail and are mainly based on different approximations related to the rate-determining steps and the nature of surface intermediates of the reaction. Kinetic modelling studies are separately reported for CO<sub>2</sub> hydrogenation to methanol and methanol to hydrocarbon (MTH) systems, but there are no kinetic models for the integrated catalytic reaction. Hence, a kinetic model is necessary to model and evaluate the application of such a synthesis process as a part of the full-scale process to produce jet fuels from CO<sub>2</sub> directly.



**Figure 2.** Schematic showing the kinetic model for direct CO<sub>2</sub> hydrogenation to hydrocarbons.

A methanol to hydrocarbon (MTH) kinetic model has been added to the developed CO<sub>2</sub> to methanol model (see Appendix 4). The basic lumped-type MTH kinetic model is adapted from that reported by Uriarte *et al.* for DME to olefin reaction

kinetics.<sup>18</sup> Our experimental results showed that the  $\text{In}_2\text{O}_3/\text{H-ZSM-5}$  catalyst produces more alkanes than alkenes unlike the model proposed by Uriarte *et al.*<sup>18</sup> So, alkene hydrogenation reactions have been added to the model. Also, we supplemented the model so that it could predict three ranges (or lumps) of hydrocarbon products, namely  $\text{C}_1\text{-C}_4$ ,  $\text{C}_5\text{-C}_8$  and  $\text{C}_{9+}$  products. This provides the model with a better ability to predict the selectivity for hydrocarbon products in the jet fuel range. The following reaction steps have been considered in the model:

- *Step 1-3*: the reaction of  $\text{CO}_2$  and  $\text{H}_2$  to form methanol (M), CO and  $\text{CH}_4$  respectively liberating water (W) as a by-product
- *Step 4*: dehydration of methanol (M) to produce DME (D) and water (W)
- *Step 5*: the reaction of methanol to olefins [ethylene ( $\text{E}^-$ ), propylene ( $\text{P}^-$ ) and butylene ( $\text{B}^-$ )] with water liberation (W)
- *Step 6*: the reaction of DME to olefins and water
- *Step 7-12*: autocatalytic reactions of olefins with the oxygenates
- *Step 13*: olefin hydrogenation forming ethane (E), propane (P) and butane (B)
- *Step 14*: secondary reactions of oligomerization of olefins to form  $\text{C}_5\text{-C}_8$  ( $\text{C}_{5-8}$ ) hydrocarbons ( $\text{C}_{5-8}$ )
- *Step 15*: Further reaction of  $\text{C}_5\text{-C}_8$  compounds with olefins to form  $\text{C}_{9+}$  hydrocarbons.

The resulting reaction scheme is presented in Figure A22. The rate constants for steps 1-3 have been directly taken from the  $\text{CO}_2$  to methanol model (kinetic model 1) that was developed by our group, partly in this project and partly in project (48387-1), see Appendix 4.

Figure A23 illustrates the validity of the proposed kinetic model and compare the concentrations of the different lumps of the major and minor products at different reaction temperatures over  $\text{In}_2\text{O}_3/\text{H-ZSM-5}$  bifunctional catalyst. The experimental results are represented by points and those calculated using the model by lines. With the increase in temperature from 200 to 400 °C (keeping other reaction conditions identical to the standard one), the concentration of methanol and methane are seen to increase with temperature as they continue to remain in their kinetic regime. It should be noted that in this range of temperatures, the concentration of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$  and DME are much less. CO also increases as reverse water gas shift reaction progresses with the increase in temperature. The composite catalyst showed a high selectivity towards alkanes rather than olefins. The concentrations of the lump for light paraffins and olefins ( $\text{C}_2\text{-C}_4$ ) as well as the higher hydrocarbons ( $\text{C}_5\text{-C}_8$  and  $\text{C}_{9+}$ ) increases with temperatures and passes through a maximum around 370 °C after which it starts to reduce.

Figure A24 shows a comparison between the experimental and simulated conversions/selectivities and hydrocarbon (HC) distributions. Experimentally at the reference temperature of 320 °C, a  $\text{CO}_2$  conversion of 8.8 % could be achieved. A  $\text{C}_2\text{-C}_4$  concentration of 63 % and  $\text{C}_5\text{-C}_{12}$  concentration of 35 % was obtained at the same temperature under the standard reaction conditions of 40 bar,  $\text{WHSV} = 9000$

$\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$  and molar  $\text{H}_2:\text{CO}_2 = 3:1$ . Moreover, a maximum  $\text{CO}_2$  conversion of 33 % with a corresponding CO concentration of 55 % was obtained at 400 °C with the composite catalyst. The model also predicts similar trend with hydrocarbon selectivity decreasing with the increase in temperatures and  $\text{CO}_2$  conversion and CO selectivity correspondingly increasing with temperatures. In addition, the HC distribution obtained from the model was compared with the experimental results and they showed similar trends. Table A1 shows the kinetic parameters with the kinetic rate constants and corresponding the activation energies for the proposed kinetic scheme shown in Figure A22. Overall, the kinetic model can well describe the experiment for  $\text{CO}_2$  hydrogenation to hydrocarbons for different temperatures.

## Discussion

The direct catalytic hydrogenation of  $\text{CO}_2$  to hydrocarbons in a single reactor step is significant because the two steps ( $\text{CO}_2 \rightarrow \text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OH} \rightarrow$  hydrocarbon) are not mutually exclusive. In literature, extensive experimental studies are reported for direct  $\text{CO}_2$  hydrogenation to hydrocarbons. Previous works show that metal oxides such as  $\text{In}_2\text{O}_3$  act as an efficient catalyst for the  $\text{CO}_2$  hydrogenation to methanol in which the presence of oxygen vacancies plays a key role. On the other hand, the acidic sites of zeolites are responsible for the conversion of methanol into valuable hydrocarbons. This project is focusing on the utilization, i.e. converting  $\text{CO}_2$  to fuels. The overall goal with the current project is to hydrogenate  $\text{CO}_2$  to hydrocarbons through methanol mediated route. The aim was to increase the yield of jetfuel range hydrocarbons ( $\text{C}_8\text{-C}_{16}$ ), and also to develop a kinetic model. First, we examined  $\text{CO}_2$  to methanol reaction using different conditions over indium supported catalysts. We continued with using the  $\text{In}_2\text{O}_3/\text{ZrO}_2$  catalyst and combined with the zeolite ZSM-5 to further convert the methanol to hydrocarbons. We thereafter developed a novel two-bed catalytic system to increase the selectivity of Jet-fuel range hydrocarbons ( $\text{C}_8\text{-C}_{16}$ ). We used a configuration where the first bed contained a  $\text{In}_2\text{O}_3/\text{ZrO}_2+\text{ZSM-5}$  catalyst well mixed. Downstream was a second bed placed with an oligomerization catalyst (desilicated-ZSM-5). The oligomerization catalyst polymerizes small hydrocarbons (mainly lower olefins) to larger hydrocarbons. This addition was successful and we could increase the selectivity for jet-fuel range hydrocarbons ( $\text{C}_8\text{-C}_{16}$ ) from 29% to 42.5%. In addition, we have developed a kinetic model for  $\text{CO}_2$  hydrogenation to hydrocarbons via methanol. The developed model can well describe the  $\text{C}_2\text{-C}_4$ ,  $\text{C}_5\text{-C}_8$  and  $\text{C}_9+$  selectivity and also the CO formation at different temperatures. For up-scaling of the process it is important to have a kinetic model in order to determine reactor dimensions, etc. Since the oligomerization catalyst improved the jet-fuel range hydrocarbons, we believe that further research in this area can result in even further increase of the selectivity to Jet-fuel range hydrocarbons. To summarize, we suggest that  $\text{CO}_2$  hydrogenation to fuels is a promising for the future in order to reduce the global warming. It can even give negative  $\text{CO}_2$  emissions, when using  $\text{CO}_2$  originating from biomass.

## Publications

1. P. Sharma, J. Sebastian, S. Ghosh D. Creaser, L. Olsson, Effect of support material for CO<sub>2</sub> hydrogenation to methanol over indium-based catalysts, *Catalysis Science and Technology*, 11 (2021) 1665.
2. S. Ghosh, J. Sebastian, L. Olsson, D. Creaser, Experimental and kinetic modelling studies of methanol synthesis from CO<sub>2</sub> hydrogenation using In<sub>2</sub>O<sub>3</sub> catalyst, *Chemical Engineering Journal*, 416 (2021) 129120.
3. P. Sharma, D. Creaser, L. Olsson, Effect of support material for CO<sub>2</sub> hydrogenation to methanol over indium-based catalysts, In preparation (2021).
4. P. Sharma, D. Creaser, L. Olsson, Addition of oligomerization catalysts to increase the selectivity for higher hydrocarbons during CO<sub>2</sub> hydrogenation, In preparation (2021).
5. S. Ghosh, L. Olsson, D. Creaser, Experimental and kinetic modelling studies of CO<sub>2</sub> hydrogenation to fuels, In preparation (2021).

## References

1. S. Das, J. Pérez-Ramírez, J. Gong, N. Dewangan, K. Hidajat, B. C. Gates and S. Kawi, *Chemical Society Reviews*, 2020, **49**, 2937-3004.
2. A. Mustafa, B. G. Lougou, Y. Shuai, Z. Wang and H. Tan, *Journal of Energy Chemistry*, 2020, **49**, 96-123.
3. G. Hemighaus, T. Boval, J. Bacha, F. Barnes, M. Franklin, L. Gibbs, N. Hogue, J. Jones, D. Lesnini and J. Lind, *Chevron Corporation*, 2006.
4. M. Z. Rahman, M. G. Kibria and C. B. Mullins, *Chemical Society Reviews*, 2020, **49**, 1887-1931.
5. J. H. Edwards, *Catalysis Today*, 1995, **23**, 59-66.
6. K. C. Waugh, *Catalysis Today*, 1992, **15**, 51-75.
7. O. Martin, A. J. Martín, C. Mondelli, S. Mitchell, T. F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré and J. Pérez-Ramírez, *Angewandte Chemie International Edition*, 2016, **55**, 6261-6265.
8. J. Ye, C. Liu, D. Mei and Q. Ge, *ACS Catalysis*, 2013, **3**, 1296-1306.
9. I. Yarulina, A. D. Chowdhury, F. Meirer, B. M. Weckhuysen and J. Gascon, *Nature Catalysis*, 2018, **1**, 398-411.
10. U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T. V. W. Janssens, F. Joensen, S. Bordiga and K. P. Lillerud, *Angewandte Chemie International Edition*, 2012, **51**, 5810-5831.
11. S. Teketel, M. Westgård Erichsen, F. Lønstad Bleken, S. Svelle, K. Petter Lillerud and U. Olsbye, in *Catalysis: Volume 26*, The Royal Society of Chemistry, 2014, vol. 26, pp. 179-217.
12. S. S. Arora, Z. Shi and A. Bhan, *ACS Catalysis*, 2019, **9**, 6407-6414.
13. X. Zhao, J. Li, P. Tian, L. Wang, X. Li, S. Lin, X. Guo and Z. Liu, *ACS Catalysis*, 2019, **9**, 3017-3025.
14. F. Magzoub, X. Li, J. Al-Darwish, F. Rezaei and A. A. Rownaghi, *Applied Catalysis B: Environmental*, 2019, **245**, 486-495.
15. W. Monama, E. Mohiuddin, B. Thangaraj, M. M. Mdleleni and D. Key, *Catalysis Today*, 2020, **342**, 167-177.

16. A. de Klerk, *Industrial & engineering chemistry research*, 2005, **44**, 3887-3893.
17. M. S. Frei, C. Mondelli, R. García-Muelas, K. S. Kley, B. Puértolas, N. López, O. V. Safonova, J. A. Stewart, D. C. Ferré and J. Pérez-Ramírez, *Nature communications*, 2019, **10**, 1-11.
18. P. Pérez-Uriarte, A. Ateka, A. T. Aguayo, A. G. Gayubo and J. Bilbao, *Chemical Engineering Journal*, 2016, **302**, 801-810.

## Appendix

### Appendix 1: Administrative appendix

Appendix 2-4 contains sensitive information and is therefore not open (Copy right reasons).

**Appendix 2:** Figures showing experimental and modelling results from this work. These figures will be used in papers that will be submitted during spring 2021 and is therefore not open (Copy right reasons).

**Appendix 3:** Published review. This is an extensive review with 33 pages covering 268 references. “Recent advances in hydrogenation of CO<sub>2</sub> into hydrocarbons via methanol intermediate over heterogeneous catalysts” by Poonam Sharma, Joby Sebastian, Sreetama Ghosh, Derek Creaser and Louise Olsson, *Catalysis Science and Technology*, 11 (2021) 1665.

**Appendix 4:** “Experimental and kinetic modeling studies of methanol synthesis from CO<sub>2</sub> hydrogenation using In<sub>2</sub>O<sub>3</sub> catalyst” by Sreetama Ghosh, Joby Sebastian, Louise Olsson and Derek Creaser, *Chemical Engineering Journal*, 416 (2021) 129120. This work is done partly in this project and partly in project 48387-1.