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Time evolution of the CO₂ hydrogenation to fuels over Cu-Zr-SBA-15 catalysts

Aylin Atakan^{1,*}, Edvin Erdtman², Peter Mäkie¹, Lars Ojamäe² and Magnus Odén¹

¹ Nanostructured Materials, Department of Physics, Chemistry and Biology, Linköping University, Linköping SE-58183, Sweden,

* aylin.atakan@liu.se

² Physical Chemistry, Department of Physics, Chemistry and Biology, Linköping University, Linköping SE-58183, Sweden

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ABSTRACT: Time evolution of catalytic CO₂ hydrogenation to methanol and dimethyl ether (DME) has been investigated in a high-temperature high-pressure reaction chamber where products accumulate over time. The employed catalysts are based on a nano-assembly composed of Cu nanoparticles infiltrated into a Zr doped SiO₂ mesoporous framework (SBA-15): Cu-Zr-SBA-15. The CO₂ conversion was recorded as a function of time by gas chromatography-mass spectrometry (GC-MS) and the molecular activity on the catalyst's surface was examined by diffuse reflectance in-situ Fourier transform infrared spectroscopy (DRIFTS). The experimental results showed that after 14 days a CO₂ conversion of 25% to methanol and DME was reached when a DME selective catalyst was used which was also illustrated by thermodynamic equilibrium calculations. With higher Zr content in the catalyst, greater selectivity for methanol and a total 9.5 % conversion to methanol and DME was observed, yielding also CO as an additional product. The time evolution profiles indicated that DME is formed directly from methoxy groups in this reaction system. Both DME and methanol selective systems show the thermodynamically highest possible conversion.

1. INTRODUCTION

CO₂ is a primary greenhouse gas with increasing concentration in the atmosphere: from 228 ppm as detected in 1750 to approximately 400 ppm as detected in 2016^{1,2}. Greenhouse gases promote global warming that has been predicted to cause climate shifts. Actions to diminish the human influence on the climate that started with the industrial revolution² are urgently called upon. There are two main strategies to reverse the increasing trend of CO₂ concentration in the atmosphere: reducing the amount of emitted CO₂ per unit time, and utilizing CO₂ that is currently being emitted in various processes²⁻⁴. For the second strategy, the CO₂ exhaust produced in industry can be redirected into processes where it will be used as a reactant and converted to less harmful molecules. CO₂ hydrogenation is such a process where methanol and dimethyl ether can be synthesized to be used as clean energy sources. This way, CO₂ can be reused and the obtained fuels can be combusted without net CO₂ emissions^{2,5}.

Methanol is one of the main CO₂ hydrogenation products^{2,6} which can be directly dehydrated to DME in a single batch reaction. Both these molecules are valuable alternative fuels^{2,7-9} and they are also used as feedstocks and intermediates for producing various chemicals and as energy carriers for fuel cells^{7,10-12}.

Methanol can typically be produced from synthesis gas at a pressure between 50-100 bar and at a temperature between 200-300 °C^{6,12-14}. It is well-established that both CO and CO₂ can be hydrogenated to methanol. More recently it has been claimed that CO₂ is the dominant carbon provider to the methanol molecule¹⁴ and the conversion occurs either through the formate or the hydrocarboxyl routes^{10,15} in existence of a competing reaction: reverse-water-gas-shift-reaction (RWGS) producing CO and water under the same conditions^{16,17}. Both the reaction routes (formate or hydrocarbox-

yl) of CO₂ hydrogenation yield water as a product and large amount of accumulated H₂O affects the CO₂ hydrogenation reaction. Trying to overcome the thermodynamical limitations^{18,19} are challenging tasks when converting CO₂ to methanol at large scale under reasonable and realistic conditions such as pressures lower than 50 bars or H₂/CO₂ < 5. To optimize the reaction under such conditions, it is a crucial task to investigate the reaction kinetics, i.e. the time-dependent evolution of the species during the reaction. Such knowledge can guide the development of new and more favorable processes. For these purposes, we chose to work with a batch (closed) reactor at a low pressure (33 bar) to slow down the reaction since each new product formed decreases the driving force for this reaction. The molecular activity was investigated under static conditions with diffuse reflectance in-situ Fourier transform infrared spectroscopy (DRIFTS) and gas chromatography-mass spectrometry (GC-MS). This type of study with a mesoporous Cu-based catalyst (see below) is extremely rare in the literature, and yet very promising to provide valuable information.

In this study, Cu-infiltrated Zr-doped SBA-15 (Cu-Zr-SBA-15) material was used to catalyze CO₂ hydrogenation²⁰ to methanol and dimethyl ether (DME) as direct and indirect products, respectively. SBA-15 acts as a highly stable and large surface support to improve the dispersion of the active components of this system^{21,22}. CO₂ hydrogenation can be achieved as a dual-site reaction. Zr was added to the support as active reaction sites for surface carbonate formation. The carbonate groups can then react with the atomic hydrogen generated by H₂ splitting over Cu to finally form carbon based fuels^{20,23-25}.

Two types of Cu-Zr-SBA-15 were synthesized. One is selective for methanol (Cat_Inf) and the other one for DME (Cat_EIWI). Both Cu-Zr-SBA-15 materials are similar in chemical properties

except for Zr content which is 2 times higher for Cat_EIWI than Cat_Inf.

The results were compared with theoretical calculations where the thermodynamic equilibrium concentrations of the species in the gas phase were obtained by minimizing the total Gibbs free energy of the system. According to the experimental results, the Cat_Inf catalyst yields 25% final conversion to methanol and DME whereas the Cat_EIWI catalyst yields 9.5% to methanol only. Both these results were determined to be the maximum thermodynamically possible values from the theoretical calculations. It was also determined that, in case of high methanol selectivity, where DME was not produced, CO was also a product of the reaction through RWGS which was concluded by comparing the experimental results with the thermodynamical calculations. The total CO₂ conversion (to methanol and DME) with Cat_Inf was determined to be 25% experimentally, consistent with the 23% theoretical yield. In the case of Cat_EIWI where CO is a final product we measure the CO₂ conversion to methanol to be 9.5% which is also consistent with the theoretical predictions. In this case, 11.5% of the CO₂ is converted to CO.

2. EXPERIMENTAL SECTION

Pluronic P123 block copolymer (EO₂₀PO₇₀EO₂₀, av. M_n~5800, Aldrich), ammonium fluoride (NH₄F) (≥98.0%, puriss p.a., ACS reagent, Fluka), HCl (≥37.0%, puriss. p.a., ACS reagent, fuming, Sigma-Aldrich), heptane (99%, ReagentPlus®, Sigma-Aldrich), tetraethyl orthosilicate (TEOS, 98%, reagent grade, Sigma-Aldrich), zirconium(IV) oxychloride octahydrate (ZrOCl₂·8H₂O, ≥98.0%, puriss p.a., Sigma-Aldrich), chlorotrimethylsilane (TMCS, ≥99.0%, Aldrich), (3-aminopropyl)trimethoxysilane (APTMS, 97%, Aldrich), toluene (≥99.7%, puriss p.a., ACS reagent, reagent ISO, reagent Ph Eur, Sigma-Aldrich), and copper(II) sulfate pentahydrate (CuSO₄·5H₂O, ≥99%, ACS reagent, reagent ISO, reagent Ph Eur, Sigma-Aldrich) and sodium borohydride (NaBH₄, >96%, gas volumetric) were used as received.

2.1. Catalyst Synthesis

The catalysts were synthesized in two steps: synthesis of Zr doped mesoporous silica framework (Zr-SBA-15) as the support and growth of Cu nanoparticles on this support via an infiltration (Inf) or evaporation induced wetness impregnation (EIWI) method. Zr-SBA-15 was prepared with the method described earlier²⁰. 2.4 g P123 and 28 mg NH₄F were mixed in 80 ml of 1.84 M HCl at 20 °C. Stirring was maintained for minimum 2 hours and upon complete dissolution of P123 in the acid solution 0.74 g zirconium oxychloride (ZrOCl₂) was dissolved in this mixture. Afterwards, 2 ml heptane and 5 ml of TEOS were premixed and added into the acid solution followed by 4 minutes vigorous stirring. When the stirring was turned off, the final solution was kept at 20 °C for 5 hours. The slurry was then left in an oven at 100 °C for 24 hours for hydrothermal treatment, followed by filtration. The obtained powder was calcined at 550 °C for 5 hours.

Cu infiltration was performed with the route reported earlier^{20,26} consisting of 4 steps: 1. outer functionalization, 2. inner functionalization, 3. Cu ion attachment, 4. reduction and growth of Cu nanoparticles.

Outer functionalization was done by passivating the outer surface of the Zr-SBA-15 particles with methyl (-CH₃) groups. For this,

uncalcined Zr-SBA-15 was suspended in 15 vol% TMCS (10 grams of powder in 1 L TMCS-toluene). The suspension was refluxed at 80 °C for 8 hours with vigorous stirring and then filtered and washed with toluene. The obtained material was calcined at 300 °C for 5 hours.

Inner functionalization was done by activating the pore surfaces with negatively charged amine (-NH₃⁺) groups. For this, the powder with outer functionalization was suspended in 6.25 vol% APTMS in toluene (6.25 g powder in 1 L of APTMS-toluene solution). The suspension was vigorously stirred at room temperature for 24 hours. Excess APTMS was removed by 5 hours of soxhlet extraction during which the toluene mixture was vigorously stirred. The suspension was then cooled, filtered, and the recovered powder was washed with toluene.

Cu ions were attached on the support by mixing dried APTMS and TMCS functionalized Zr-SBA-15 into 0.06 M CuSO₄ salt solution (20 g powder in 1 L solution). Stirring was performed overnight (16-20 hours) at room temperature. Afterwards, the mixture was filtered and the recovered powder was stirred with 0.1 M NaBH₄ (20 g powder in 1 L solution) to reduce the Cu ions and growing nanoparticles. Finally, the sample was calcined at 550 °C for 5 hours. The produced catalyst was labeled as Cat_Inf.

For EIWI, the Zr-SBA-15 powder was stirred with 0.06 M CuSO₄ salt solution (20 g powder in 1 L solution). Stirring was maintained at 80 °C until the water was completely evaporated. The material was reduced with NaBH₄ the same way as it is described above for Cat_Inf catalyst and calcined at 550 °C for 5 hours. This material is labeled as Cat_EIWI.

2.2. Characterization

A scanning electron microscope (SEM): LEO 1550 Gemini (3 kV operation voltage) and a transmission electron microscope (TEM): FEI Tecnai G2 was used for imaging of the catalyst. For TEM analysis, catalyst particles were attached on carbon coated copper grids using ethanol as the solvent. ZAF corrected atomic composition of the catalyst was detected by an EDS detector: Oxford X-Max 80 attached to SEM operated at 20 kV.

Pore structure of the catalyst was determined by measuring nitrogen sorption isotherms at -196 °C with a Micromeritics ASAP 2020 instrument. The pore size distribution (PSD) was calculated with Kruk Jaroniec Sayari (KJS) method²⁷ and specific surface area (SSA) with Brunauer Emmet Teller (BET) method²⁸ within a P/P₀ interval of 0.08-0.16.

The pore packing of the mesoporous structure of the catalyst was analyzed by small angle x-ray diffractometry (SAXRD) using a Panalytical Empyrean x-ray diffractometer equipped with Cu Kα x-ray source operated at 45 kV and 40 mA. The peaks obtained between 0-2.5 ° were used to calculate the d-spacing value of the catalyst.

A Panalytical X'Pert Pro x-ray diffractometer with Cu Kα radiation was operated between 0-70° and the obtained Cu peaks were later used to calculate the nanoparticle diameter employing the Scherrer equation²⁹.

NH₃ temperature programmed desorption (NH₃-TPD) was performed by a Micromeritics FLEX-3. Each reduced catalyst was dosed with 10 ml/min pure NH₃ flow for 10 min at 100 °C. The physisorbed NH₃ was flushed out by a 10 ml/min helium flow for 1 hour at 100 °C. The chemisorbed NH₃ is determined by continu-

ously increasing raising the temperature at a rate of 10°C/min to 750°C under 10 ml/min helium flow, while detecting the desorbed ammonia with a thermal conductivity detector.

2.3. Catalytic activity test

A Harrick Scientific 13 mL HPHT (high pressure-high temperature) cell was employed for CO₂ hydrogenation. The cell acts as a batch reaction and no reactant flow or recycling was applied. The catalyst, 0.4 g of each powder, was pressed under 8 tons for 15 min into a disc and placed in the cell horizontally. First, Cu in the catalyst was reduced with a H₂ flow at 400 °C for 9 hours. Afterwards, the reactants were fed into the cell with the ratio of CO₂/H₂ = 1/3. The reaction was carried out at 250°C and 33 bars for maximum 14 days. The reaction was then repeated by first emptying the cell and then directly filling it with a fresh CO₂-H₂ mixture. This meant that the repeated reactions were done with previously used catalysts that have not been in contact with air. The repeated reactions where run for 1-5 days and, in some cases, contained several repeats.

The surface reactions on the catalyst surface were detected by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with a Bruker Vertex 70 device which employs a glowbar MIR source (water cooled) and an integrated broad band MCT detector (LN₂ cooled). A resolution of 4 cm⁻¹ and an average of 128 scans were used for each spectrum. Background was taken with pure KBr.

The CO₂ conversion was calculated from the final gas mixture concentration values in the cell. For this, the reaction was terminated at a desired time and the gas mixture was transferred to a Bruker 450-GC gas chromatograph equipped with a flame ionization detector (FID) and a Bruker SCION mass spectrometer (GC-MS). The amount of the final gas mixture in the cell was sufficient for two to three GC-MS measurements, which were averaged and reported as the final CO₂ conversion value. These results are presented as the CO₂ conversion to methanol and DME, individually, and a total value. In this paper, the 'total' CO₂ conversion always indicates the combination of methanol and DME. The equations used are below.

$$\text{Synthesized MeOH and DME \%} = T_M = \text{MeOH\%} + 2 * \text{DME\%} \quad (1)$$

$$\text{Remaining CO}_2 \% = \frac{[100 - 2T_M]}{4} \quad (2)$$

$$\text{CO}_2 \text{ conversion to MeOH and DME \%} = \frac{T_M}{T_M + \frac{[100 - 2T_M]}{4}} \quad (3)$$

$$\text{CO}_2 \text{ conversion to DME \%} = \frac{2 * \text{DME\%}}{2 * \text{DME\%} + \frac{[100 - 2 * (2 * \text{DME\%})]}{4}} \quad (4)$$

$$\text{CO}_2 \text{ conversion to MeOH \%} = \frac{\text{MeOH\%}}{\text{MeOH\%} + \frac{[100 - 2 * (\text{MeOH\%})]}{4}} \quad (5)$$

3. THEORETICAL CALCULATIONS

In order to determine the total CO₂ conversion ratios, the distribution of the species involved in the CO₂ conversion to methanol and DME were calculated at the gas phase thermodynamical equilibrium conditions and then compared with the experimental results.

The introduced reactants for the system were CO₂ and H₂ with the molar ratio of CO₂/H₂=1/3. Different scenarios of final gas mixture content were tested and compared with the experimental results to obtain the scenario closest to the reality of our system.

The total Gibbs free energy (ΔG) of the system was minimized with respect to the distribution of the species in order to obtain the most thermodynamically stable (i.e. the equilibrium) composition of the system³⁰:

$$\min_{n_i} \Delta G(n_i) = \min_{n_i} (\sum_i \mu_i n_i) \quad (6)$$

with the boundary conditions

$$B \cdot \bar{n} = \bar{b}_0, 0 \leq \{n_i\} \leq \infty \quad (7)$$

where n_i and μ_i are the amount of molecule i and the chemical potential of molecule i , respectively. B is a matrix containing the stoichiometric content of the molecules, $\bar{n}$ is the column vector of n_i and $\bar{b}_0$ is a column vector with the total amounts of each atom type in the system. μ_i is dependent of the composition of the system and was given by

$$\mu_i = \Delta_f G_i^0 + RT \ln(p_i/p^0) \quad (8)$$

where tabulated Gibbs free energies of formation ($\Delta_f G_i^0$) are used as in the references³¹⁻³³. R is the gas constant, T is the temperature, p_i is the partial pressure of gas i as given by the ideal gas law, and p^0 is the standard pressure of 1 bar. The calculations were performed in MATLAB using the nonlinear equation system solver *fmincon*³⁴.

4. RESULTS

The catalyst support (Zr-SBA-15) was obtained with rod-shaped particle morphology, which was maintained after the Cu infiltration (Figure 1(a)). Cu nanoparticles can be observed not only in the pores but also on the outer surface of Zr-SBA-15 particles (Figure 1(b)). For both catalysts, the Cu nanoparticles on the outer surface have diameters between 10-30 nm and the Cu nanoparticles in the pores have diameters between 1-10 nm²⁰. The physisorption result in Figure 1(c and g) shows a type-IV isotherm with a H₁-type hysteresis loop and a narrow pore size distribution. The specific surface area (SSA), pore size, and pore volume (PV) were determined as 422 m²/g, 13.3 nm, and 0.84 cm³/g. For Cat_Inf the values were 316 m²/g, 13.0 nm, and 0.81 cm³/g, respectively. The final atomic ratio of Si/Zr was 20 for Cat_Inf whereas this value was 10 for Cat_EIWI. The Cu content in Cat_Inf was ~13%Wt and in Cat_EIWI was ~15 %Wt, which correspond to a total Cu weight of 0.052 g and 0.06 g for Cat_Inf and Cat_EIWI, respectively. NH₃-TPD results in Figure 1(i) show four peaks in each sample. Two of these peaks are between 200-300 °C and they are assigned to medium strength acid sites. The other two peaks are between 500-600 °C and these are assigned as strong acid sites. No peak was observed for weak acid sites that typically appear between 100-200 °C^{35,36}. The number of medium strength acid sites is larger for Cat_EIWI compared to Cat_Inf, while the number of strong acid sites is similar for both catalysts. An additional difference is that the medium strength acid sites are slightly stronger for Cat_Inf compared to Cat_EIWI, while an opposite situation is observed for the strong acid sites.

CO₂ hydrogenation over Cat_Inf catalysts resulted in methanol and DME with trace amounts of propane, butane, methoxy ethane,

and methyl formate as side products. The total amount of side products was less than 0.2 at.% in the final gas mixture. It is noteworthy that no methane was detected. The FID response and mass spectrum of the GC-MS measurement at the end of 14 days are presented in the Supporting Information.

A maximum of 25 % CO₂ conversion to MeOH (1.2·10⁻⁴ moles: 4.7 % CO₂ conversion) and DME (3·10⁻⁴ moles: 20.2 % CO₂ conversion) was reached at a pressure of 33 bars when using Cat_Inf as catalyst. The time evolutions of the CO₂ conversion with both catalysts are presented in Figure 2. In the case of Cat_Inf (Figure 2(a)) the equilibrium methanol concentration is reached fast compared to DME which keeps increasing during the entire measurement.

The trends in Figure 2(a) were further analyzed by fitting a logistic functions to the conversion data (using a MATLABTM curve function script). The logistic functions used is given below

$$y = A2 + \frac{(A1 - A2)}{1 + \left(\frac{t}{t_0}\right)^p} \quad (9)$$

where y is the conversion, A2 is the maximum (final) value, A1 the minimum (initial) value, t time [day], t₀ the time [day] to reach half of the full conversion, and p is an exponent.

These S-shaped logistic curves indicate an acceleration of the conversion rate that decelerates after a t₀ turn point and finally reaches an equilibrium value. The logistic functions of total and partial CO₂ conversion percentages to methanol and DME are given as Equation (10), (11), and (12).

$$\text{Conversion to MeOH and DME \%} = 25.45 - \frac{25.45}{1 + \left(\frac{t}{4.2}\right)^{2.4}} \quad (10)$$

$$\text{Conversion to MeOH \%} = 4.3 - \frac{4.3}{1 + \left(\frac{t}{2.1}\right)^{3.3}} \quad (11)$$

$$\text{Conversion to DME \%} = 20.2 - \frac{20.2}{1 + \left(\frac{t}{4.7}\right)^3} \quad (12)$$

The time evolutions of methanol and DME conversion are observed to be different. Figure 2(a) indicates that methanol was first detected in the gas mixture after 14 hours while DME was detected after 24 hours. The maximum conversion to methanol is reached during the third day while it took 14 days for the conversion to DME to reach its maximum. Despite this difference, the p exponent, which represents the rate of the functions in Eq. (10-12), is similar for DME and methanol formation. This is due to the larger amount DME formed compared to methanol. This is also seen as a higher A2 value for DME than methanol in Eq. (10-12) and at the end of the experiment the gas in the reaction cell contained a higher concentration of DME than methanol.

The Cat_EIWI catalyst yielded nearly no DME and showed a high selectivity for methanol. It catalyzed 6.5 % and 9.5 % CO₂ conversion to 2.0·10⁻⁴ and 2.9·10⁻⁴ moles of methanol after 5 and 14 days, respectively (Figure 2(b)).

Figure 1. SEM image (a), TEM image (b), physisorption isotherm and pore size distribution (c), and the small angle x-ray diffractogram (d) of Cat_Inf; SEM image (e), TEM image (f), physisorption isotherm and pore size distribution (g), the small angle x-ray diffractogram of Cat_EIWI (h), and the NH₃-TPD profiles of the catalysts (i).

Figure 2. CO₂ conversion % vs. time: total and to methanol and to DME for the catalyst Cat_Inf (a) and of Cat-EIWI (b).

The theoretical calculations were performed for various scenarios of the final gas mixture content. The conversion data of the scenarios, which include the larger hydrocarbons (such as propane, butane etc) and alcohols are listed in Table S1 in the Supporting information. Methane was also investigated as a potential product, although not detected by GC-MS, since it was reported earlier as a product of this type of a reaction^{2,5,18,37}. When all the detected molecules and methane were included in the calculations as products of the reaction, all CO₂ was found to be converted to methane. By removing methane from the product list, the calculations predicted the whole amount of CO₂ to be converted to only one or more of these higher hydrocarbon/alcohols without any methanol or DME formation. When both the larger molecules and methane were removed from the reaction product list in the calculations, DME and methanol could finally co-exist as thermodynamic equilibrium (this is equivalent to assuming that DME and methanol are catalyzed selectively) and suggests that the catalyst has no selectivity towards higher hydrocarbons or alcohols.

The scenarios with MeOH, DME, H₂O and CO as potential products of the reactions catalyzed with Cat_Inf and Cat_EIWI are presented in Table 1 and Figure 2. Accordingly, in the case of CO, MeOH and DME all being products of this reaction, the CO₂ conversion to methanol plus DME is 20.1 %. If we eliminate CO from the products, the conversion to methanol and DME increases to 23.0% (4.1% MeOH and 18.9% DME). This second scenario corresponds very well to our conversion results when using Cat_Inf as the catalyst.

In the GC-MS results, we have observed almost no DME produced with Cat_EIWI but only MeOH (Figure 2). For this type of a scenario, the theoretical CO₂ conversion to MeOH was calculated as 14.3%. On the other hand including CO as a product besides MeOH results in a 9.5% CO₂ conversion to methanol and this fits better to our Cat_EIWI data. The calculated total CO₂ conversion

to CO and MeOH was then 20.9% and almost half of this (11.4%) belongs to CO (Table 1).

Conversion changes caused by repeated use of the catalyst are presented in Figure 3(a-c) for 1-day, 3-day, and 5-day reactions. Repeating the 3- and 5-day reactions results in a conversion drop, and it is more pronounced for the 5-day reaction (Figure 3 (b,c)). Repeating the 1-day-reaction (Figure 3(a)) yields a higher conversion to both methanol and DME. However, this is not true if the reaction is extended for longer times, i.e. repeating the 1-day-reaction with the same catalyst sample a third, fourth, and fifth time results in decreased conversions (Figure 3(a)). We note that this decrease is less than for 3-day and 5-day reactions under similar conditions.

Table 1. Final mol amounts as a result of four different scenarios with the products: 1. MeOH, DME, CO, H₂O; 2. MeOH, DME, H₂O; 3. MeOH, CO, H₂O; and 4. MeOH, H₂O. The initial amounts of CO₂ and H₂ were 3.0·10⁻³ mol and 9.0·10⁻³ mol, respectively.

Scenario #	1	2	3	4
Component	n (mol) CO ₂ conv.*	n (mol) CO ₂ conv.*	n (mol) CO ₂ conv.*	n (mol) CO ₂ conv.*
CO ₂ (g)	2.2·10 ⁻³	2.3·10 ⁻³	2.4·10 ⁻³	2.6·10 ⁻³
H ₂ (g)	7.0·10 ⁻³	6.9·10 ⁻³	7.8·10 ⁻³	7.7·10 ⁻³
CO (g)	1.8·10 ⁻⁴	0.0	3.4·10 ⁻⁴	0.0
H ₂ O (g)	1.0·10 ⁻³	9.7·10 ⁻⁴	6.3·10 ⁻⁴	4.3·10 ⁻⁴
MeOH (g)	1.2·10 ⁻⁴ 3.93%	1.2·10 ⁻⁴ 4.14%	2.8·10 ⁻⁴ 9.45%	4.3·10 ⁻⁴ 14.34%
DME (g)	2.4·10 ⁻⁴ 16.18%	2.8·10 ⁻⁴ 18.87%	0.0 0.00%	0.0 0.00%
CO ₂ conversion to MeOH and DME	20.11%	23.01%	9.45%	14.34%
TOTAL CO ₂ CONVERSION	25.99%	23.01%	20.87%	14.34%

* CO₂ conversion to a component

Figure 3(d) shows the used catalyst after 14 days of a reaction. The external Cu nanoparticles are larger compared to the virgin catalyst, cf. Figure 1(a). This suggests coalescence of external Cu NPs to form larger ones during the 230 °C reaction. The high-temperature high-pressure reaction for 14 days also causes the pore size, pore volume, and SSA to decrease (Figure 3(e)). X-ray diffractograms of the as-synthesized and used catalysts are shown in Figure 3(f). The XRD peaks of the as-synthesized catalyst are all indexed to CuO (PDF#00-048-1548) whereas the used catalyst shows no CuO peaks but instead weak peaks that are indexed to only the reduced species of Cu: Cu₂O (PDF#01-071-3645) and Cu metal (PDF#00-004-0836).

DRIFTS spectra in Figure 4(a-d) and 5(a-d) show 3D and 2D representation of the time evolution for Cat_Inf and Cat_EIWI, respectively. The shown wavenumber range include the strongest and most characteristic bands of DME and methanol molecules in the gas state and adsorbed form, as well as the methoxy group (the surface intermediate of methanol). These bands are: C-O vibration of methoxy at 1054 cm⁻¹ 38-43, C-H vibration of methoxy/surface adsorbed methanol (methanol_{ads}) at 2854 cm⁻¹ 38,44, CH₃ antisymmetric vibration of gas phase methanol at 2978 cm⁻¹ 39,45-48, C-O vibration of gas phase DME at 1118 cm⁻¹ 40,49, and surface adsorbed DME molecule (DME_{ads}) at 2917 cm⁻¹ 49. The time evolutions of these peaks are presented in Figure 4(e) and 5(e) for Cat_Inf and Cat_EIWI, respectively.

In the reaction when Cat_Inf is used as the catalyst, the gas phase molecules methanol (2978 cm⁻¹) and DME (1118 cm⁻¹), as well as

surface adsorbed forms at 2854 and 2917 cm^{-1} show similar trends. They increase for the first ~ 7 days and then slightly decrease. The methoxy chemisorbed onto the catalyst surface (1054 cm^{-1}) demonstrates a different profile. The amount of chemisorbed methoxy increases rapidly during the first 14 hours and then exponentially decreases. The rate of methanol formation based on the intensity increase of the methanol bands at the 2854 and 2978 cm^{-1} (gas and adsorbed forms) changes after 14 hours and 3 days, which correspond to the first methanol appearance in the GC-MS results of the final gas mixture and when equilibrium is reached, respectively. We also note that the formation rate of surface methanol groups during the first 14 hours is higher than DME formation when comparing the 2854 and 2978 cm^{-1} methanol bands with the DME bands at 1118 and 2917 cm^{-1} .

Figure 3. CO₂ conversion % vs. time: total, to methanol and to DME with fresh and used Cat_Inf for 1 day (a), for 3 days (b) and for 5 days (c), reacted sample SEM micrograph (d), isotherms and pore size distributions of Cat_Inf before and after reaction (e), and X-ray diffractograms of Cat_Inf before and after reaction (f). (U: used, AR: after reaction, BR: before reaction)

The Cat_EIWI catalyst, on the other hand, yields only exponentially increasing methoxy and methanol bands at 2978 cm^{-1} , 2854 cm^{-1} and 1054 cm^{-1} . The intensity of these bands increases during the first 3 days and then stays constant. The initial evolution of methoxy and methanol correlates well with the initial evolution of the same molecules when catalyzed by the Cat_Inf. Moreover, in the case of Ref-EIWI, no DME peaks were observed in the DRIFTS spectra.

Surface attached methane was detected at 3015 cm^{-1} for reactions with either Cat_Inf or Cat_EIWI while no methane was detected in the gas phase. The band of adsorbed methane shows an increasing trend during the reaction.

Figure 4. Drifts spectra of Cat_Inf vs. time for the wavenumber ranges: 3300-2670 cm^{-1} and 1230-1020 cm^{-1} in 3D (a) and (b), in 2D (c) and (d), and time evolution of important peaks (e).

There are also other peaks in these regions which are indexed to other compounds and were detected in very small amounts in GC-MS (as mentioned above): methyl formate (MF)^{39,50,51}, ethyl methyl ether (EME)⁵², ethanol^{53–55}, propane^{56–58} and butane⁵⁹. This can be the result of random formation in the gas phase rather than the catalyst's activity. Theoretical calculations indicate that because of the high thermodynamic stability of these larger molecules, that if they were formed as reaction products, DME and methanol cannot be produced at all.

Methane^{60,61} that was determined on the surface of the catalyst by DRIFTS as well, however, wasn't observed in GCMS. The peaks for DME were detected for Cat_Inf whereas for Ref-EIWI no trace of DME was observed.

CO was also observed in the DRIFTS spectra. Based on the theoretical calculations we conclude that CO appears as an intermediate and not a product in the Cat_Inf catalytic reactions.

Figure 5. Drifts spectra of Cat_EIWI vs. time for the wavenumber ranges: 3300-2670 cm⁻¹ and 1230-1020 cm⁻¹ in 3D (a) and (b), in 2D (c) and (d), and time evolution of important peaks (e).

5. DISCUSSION

In this study, time evolution of CO₂ conversion to MeOH and DME was investigated via DRIFTS and GC-MS techniques. For this, two catalysts (Cat_Inf and Cat_EIWI) were synthesized and compared. Cat_Inf yields both MeOH and DME while Cat_EIWI preferentially yields MeOH.

The CO₂ conversion to methanol and DME is higher for Cat_Inf (25 %) compared to Cat_EIWI (9.5 %) and the difference stems mostly from DME formation indicating that higher DME selectivity can boost the conversion to fuels^{18,19}. Our thermodynamic calculations predict well these experimental findings for the two scenarios with and without DME formation. In addition, the calculations predict CO as a product when no DME is formed. In contrast when DME is formed no CO exists in the final gas mixture although some CO surface groups appeared in the DRIFT spectra. Since gas phase CO is formed as a final product during MeOH synthesis, during DME synthesis the surface CO groups must then contribute and be consumed in the formation of DME. The Zr concentration of Cat_EIWI is higher than Cat_Inf and it has been shown earlier that Zr is selective for CO as a product via RWGS and methanol^{62–64}. The selectivity caused by Zr in the SiOx-network stems from its effect on the electron/oxygen mobility such that a larger number of medium acid sites are provided and thus a larger number of surface species such as H atoms and methoxy groups can be held⁶⁵. It has been reported that medium acid sites holding methoxy are responsible of DME formation from methanol³⁵. In our study we see that Cat_Inf is selective to DME formation. Based on this we infer that the stronger medium acid strength sites increases the surface affinity to methoxy, which is related to the electronegativity of its oxygen³⁶. An increased surface methoxy concentration facilitates interaction between neighboring methoxy groups to form DME.

Other molecules detected in the final gas mixture (higher hydrocarbons and alcohols as well as methane) have remained as impurities due to the fact that the thermodynamical state in the reaction cell formed by Cat_Inf catalyst did not promote their formation and instead yielded MeOH and DME. This is supported by our thermodynamical calculations, which predicts that no conversion to MeOH or DME would occur if one or several of these molecules were reaction products.

During the reaction over Cat_Inf, the methoxy peak (1054 cm⁻¹) shows a rapid intensity increase during the first half day and thereafter an exponential decay. This is in contrast to the reaction over Cat_EIWI, where the intensity of the methoxy band remains constant after the first day even though the amount of methanol formed is higher for Cat_EIWI than for Cat_Inf. These observations indicate that DME formation involves an intermediate reaction of two surface methoxy groups in the CO₂ hydrogenation reaction. In this context, we propose a different last step of the formate route^{2,10,19} for direct CO₂ hydrogenation to DME, which is schematically depicted in Figure 6(a,b). Formed methoxy remains on the catalyst surface until its concentration is high enough to facilitate surface reaction of methoxy groups to form DME. At low methoxy concentrations methanol formation is primarily triggered since just one methoxy is needed. Above a certain threshold con-

centration of methoxy, DME starts to form. This is the reason why the reaction gas contains methanol earlier than DME. In addition, the evolution of our DRIFTS-spectra shows no indication of any consumption of the produced methanol molecules. This is in contrast to what has been reported earlier when formation of DME was associated with combining CH_3OH and CH_3O^- that were attached on acidic and basic sites of the catalyst's surface, respectively^{8,35,36,66}. The catalysts studied here show a preference for methoxy attachment that apparently suppresses surface attachment of methanol and changes the DME formation route.

DRIFTS results indicate methane formation on the surface, which was not detected in the final reaction gas. We can therefore not rule out that surface methane is an intermediate molecule in the transition from surface attachment to the gas phase. Another reason for the methane signal can be a weak interaction between CH_3^- and H atoms in surface groups or the detected methane could be spent during the reaction by steam reforming since it is in contact with the formed water⁶⁷.

The affinity of methanol to the catalyst surface and also to the surfaces of the reaction vessels is expected to be higher than for DME since DME is more volatile than methanol⁶⁸. This shows up as a discrepancy between DRIFTS and GC-MS measurements of the methanol yield. The DRIFTS results indicate an increase of the methanol yield for the first 7 days while GC-MS measurements indicate a maximum yield on the second day. Such difference is not observed for DME. The same effect was observed during the GC-MS measurements. The entire content of the reaction vessel cannot be analyzed by one single injection in the GC-MS spectrometer. Instead this is done by several injections. All the injections show the same DME content while the methanol content is the highest for the last injection. Such higher adsorption capacity was previously shown for methanol compared to DME on a SAPO-34 zeolite, especially at elevated temperatures⁶⁹.

Figure 6. Illustration of the methanol and DME formation from methoxy groups (a) and schematic representation of the simplified

formate route^{2,10,19} including the proposed formation of methanol and DME from methoxy as the last step (b).

The time evolution of the CO_2 conversion ratios (Figure 2(a)) can be described by sigmoidal logistic functions (Eq. 10-12). The reaction rate is characterized by t_0 and p , which represent the incubation time and acceleration of the reaction, respectively⁷⁰. When comparing the values of t_0 and p for methanol and DME formation it is clear that methanol formation starts earlier and then the two reactions then proceeds at similar rate. The rate controlling mechanism is likely the combination of methoxy groups on the surface to form DME, which also affects methanol formation. Equilibrium is reached when sufficient amount of DME is formed.

Sigmoidal curves have been used to describe different types of two-step kinetic processes, e.g. formation of nanoparticles including nucleation and autocatalytic surface growth which are dominated by different rate constants⁷¹⁻⁷³. In this study, the two-step process of CO_2 conversion corresponds to an incubation period where the concentration of the surface intermediate species are increased on the catalyst surface and a second step where formation and release of the final MeOH and DME molecules into the gas phase occurs.

In a flow reactor operating at steady state the conversion during the start-up. From a technological view-point the use of flow reactors is advantageous in terms of reaction rate and conversion ratio since the incubation time can be avoided by running in the reactor or by pre-seeding. In a flow reactor the reaction products are continuously removed, which keeps the thermodynamic driving force for the reaction at its maximum. Further improvements can be achieved by optimizing the reaction conditions of the flow reactor for example by increasing the working pressure. Thus, CO_2 conversions and reaction rates obtained from this study performed in a batch reactor is not comparable with others done in flow reactors⁷⁴⁻⁷⁸.

The performance of the Cat_Inf catalyst changes as it is used repeatedly. The performance increased by 50% if a 1-day reaction is repeated, which is a pre-seeding effect of methoxy groups on the catalyst's surface. For longer repeated reaction times coalescence of Cu-nanoparticles causes clogging of the pores that diminishes the active catalytic surface and decreases the performance of the catalyst.

In summary, the time evolution of the CO_2 -conversion over Cu-Zr-SBA-15 studied here points out the importance of optimizing the reaction conditions. From an energy saving point of view our data shows that reducing the reaction time by half from 14 to 7 days decreases the energy spent by half but only reduces the conversion by 4%. Moreover no large hydrocarbons or alcohols such as ethanol, propane, butane etc., are formed and instead Cat_Inf is selective to DME and methanol and Cat_EIWI to just methanol, which show their potential for applications where selectivity is required.

6. CONCLUSIONS

The catalyst Cu-Zr-SBA-15, with Cu nanoparticles in a mesoporous framework, yields MeOH and DME from CO_2 hydrogenation where the selectivities are dependent on the catalyst content. The reaction mechanism involves an intermediate step where surface methoxy groups combine to form DME. This step can be controlled by the Zr-content of the catalyst. The time evolution of the

reaction shows that CO₂ hydrogenation into MeOH and DME is initially an accelerating reaction. This first step of the reaction is rate-controlled by the availability of methoxy groups on the catalysts surface. The decelerating second step of the reaction is rate-controlled by the decreasing driving force for the reaction as the reaction mixture content approaches its thermodynamic equilibrium.

ASSOCIATED CONTENT

Supporting Information. Table of the peaks observed in the DRIFTS analysis, table of the results from theoretical calculations, and figure of the FID signal are presented in the Supporting Information.

AUTHOR INFORMATION

Corresponding Author

* E-mail: aylin.atakan@liu.se

Notes

The authors have no competing financial interest.

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REFERENCES

- Blasing, T. J. Recent Greenhouse Gas Concentrations. **2009**, No. August 2016, 1–5.
- Wang, W.; Wang, S.; Ma, X.; Gong, J. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. *Chem Soc Rev* **2011**, *40* (7), 3703–3727.
- Raudaskoski, R.; Turpeinen, E.; Lenkkeri, R.; Pongrácz, E.; Keiski, R. L. Catalytic Activation of CO₂: Use of Secondary CO₂ for the Production of Synthesis Gas and for Methanol Synthesis over Copper-Based Zirconia-Containing Catalysts. *Catal Today* **2009**, *144* (3–4), 318–323.
- Liang, X.-L.; Dong, X.; Lin, G.-D.; Zhang, H.-B. Carbon Nanotube-Supported Pd–ZnO Catalyst for Hydrogenation of CO₂ to Methanol. *Appl. Catal. B Environ.* **2009**, *88* (3–4), 315–322.
- Liu, X.-M.; Lu, G. Q.; Yan, Z.-F.; Beltramini, J. Recent Advances in Catalysts for Methanol Synthesis via Hydrogenation of CO and CO₂. *Ind. Eng. Chem. Res.* **2003**, *42* (25), 6518–6530.
- Fisher, I. a; Bell, A. T. In-Situ Infrared Study of Methanol Synthesis from H₂/CO₂ over Cu/SiO₂ and Cu/ZrO₂/SiO₂. *J. Catal.* **1997**, *172* (1), 222–237.
- Hosseiniadjad, S.; Afacan, a.; Hayes, R. E. Catalytic and Kinetic Study of Methanol Dehydration to Dimethyl Ether. *Chem. Eng. Res. Des.* **2012**, *90* (6), 825–833.
- LCL, J.; CMBM, B.; L, N.; JR, R. Catalytic Dehydration of Methanol to Dimethyl Ether (DME) Using the Al₆₂2Cu₂₅3Fe₁₂5 Quasicrystalline Alloy. *J. Chem. Eng. Process Technol.* **2013**, *4* (5), 1–8.
- Olah, G. a. Beyond Oil and Gas: The Methanol Economy. *Angew. Chem. Int. Ed. Engl.* **2005**, *44* (18), 2636–2639.
- Zhao, Y.-F.; Yang, Y.; Mims, C.; Peden, C. H. F.; Li, J.; Mei, D. Insight into Methanol Synthesis from CO₂ Hydrogenation on Cu(111): Complex Reaction Network and the Effects of H₂O. *J. Catal.* **2011**, *281* (2), 199–211.
- Samson, K.; Śliwa, M.; Socha, R. P.; Góra-Marek, K.; Mucha, D.; Rutkowska-Zbik, D.; Paul, J.-F.; Ruggiero-Mikołajczyk, M.; Grabowski, R.; Słoczyński, J. Influence of ZrO₂ Structure and Copper Electronic State on Activity of Cu/ZrO₂ Catalysts in Methanol Synthesis from CO₂. *ACS Catal.* **2014**, *4* (10), 3730–3741.
- Tidona, B.; Koppold, C.; Bansode, A.; Urakawa, A.; Rudolf Von Rohr, P. CO₂ Hydrogenation to Methanol at Pressures up to 950 Bar. *J. Supercrit. Fluids* **2013**, *78*, 70–77.
- Skrzypek, J.; Lachowska, M.; Grzesik, M.; Słoczyński, J.; Nowak, P. Thermodynamics and Kinetics of Low Pressure Methanol Synthesis. *Chem. Eng. J. Biochem. Eng. J.* **1995**, *58* (2), 101–108.
- Kandemir, T.; Friedrich, M.; Parker, S. F.; Studt, F.; Lennon, D.; Schlögl, R.; Behrens, M. Different Routes to Methanol: Inelastic Neutron Scattering Spectroscopy of Adsorbates on Supported Copper Catalysts. *Phys. Chem. Chem. Phys.* **2016**, No. 4, 17253–17258.
- Grabow, L. C.; Mavrikakis, M. Mechanism of Methanol Synthesis on Cu through CO₂ and CO Hydrogenation. *ACS Catal.* **2011**, *1* (4), 365–384.
- Ma, J.; Sun, N.; Zhang, X.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y. A Short Review of Catalysis for CO₂ Conversion. *Catal. Today* **2009**, *148* (3–4), 221–231.
- an, X.; Zuo, Y.; Zhang, Q.; Wang, J. Methanol Synthesis from CO₂ Hydrogenation with a Cu/Zn/Al/Zr Fibrous Catalyst. *Chinese J. Chem. Eng.* **2009**, *17* (1), 88–94.
- Arakawa, H. *Advances in Chemical Conversions for Mitigating Carbon Dioxide, Proceedings of the Fourth International Conference on Carbon Dioxide Utilization*; Studies in Surface Science and Catalysis; Elsevier, 1998; Vol. 114.
- Jadhav, S. G.; Vaidya, P. D.; Bhanage, B. M.; Joshi, J. B. Catalytic Carbon Dioxide Hydrogenation to Methanol:

- A Review of Recent Studies. *Chem. Eng. Res. Des.* **2014**, *92*(11), 2557–2567.
- (20) Atakan, A.; Mäkie, P.; Söderlind, F.; Keraudy, J.; Björk, E. M.; Odén, M. Synthesis of a Cu-Infiltrated Zr-Doped SBA-15 Catalyst for CO₂ Hydrogenation into Methanol and Dimethyl Ether. *Phys. Chem. Chem. Phys.* **2017**, *19*(29), 19139–19149.
 - (21) van den Berg, R.; Zečević, J.; Sehested, J.; Helveg, S.; de Jongh, P. E.; de Jong, K. P. Impact of the Synthesis Route of Supported Copper Catalysts on the Performance in the Methanol Synthesis Reaction. *Catal. Today* **2016**, *272*, 87–93.
 - (22) de Jongh, P. E.; Adelhelm, P. Nanosizing and Nanoconfinement: New Strategies Towards Meeting Hydrogen Storage Goals. *ChemSusChem* **2010**, *3*(12), 1332–1348.
 - (23) Arena, F.; Italiano, G.; Barbera, K.; Bordiga, S.; Bonura, G.; Spadaro, L.; Frusteri, F. Solid-State Interactions, Adsorption Sites and Functionality of Cu-ZnO/ZrO₂ Catalysts in the CO₂ Hydrogenation to CH₃OH. *Appl. Catal. A Gen.* **2008**, *350*(1), 16–23.
 - (24) Witoon, T.; Numpilai, T.; Phongamwong, T.; Donphai, W.; Boonyuen, C.; Warakulwit, C.; Chareonpanich, M.; Limtrakul, J. Enhanced Activity, Selectivity and Stability of a CuO-ZnO-ZrO₂ Catalyst by Adding Graphene Oxide for CO₂ Hydrogenation to Methanol. *Chem. Eng. J.* **2018**, *334* (November 2017), 1781–1791.
 - (25) Phongamwong, T.; Chantaprasertporn, U.; Witoon, T.; Numpilai, T.; Poo-arporn, Y.; Limphirat, W.; Donphai, W.; Dittanet, P.; Chareonpanich, M.; Limtrakul, J. CO₂ Hydrogenation to Methanol over CuO-ZnO-ZrO₂-SiO₂ Catalysts: Effects of SiO₂ Contents. *Chem. Eng. J.* **2017**, *316*, 692–703.
 - (26) Escalera, E.; Ballem, M. A.; Córdoba, J. M.; Antti, M.-L.; Odén, M. Synthesis of Homogeneously Dispersed Cobalt Nanoparticles in the Pores of Functionalized SBA-15 Silica. *Powder Technol.* **2012**, *221*, 359–364.
 - (27) Jaroniec, M.; Solovyov, L. A. Improvement of the Kruk-Jaroniec-Sayari Method for Pore Size Analysis of Ordered Silicas with Cylindrical Mesopores. *Langmuir* **2006**, *22*(16), 6757–6760.
 - (28) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*(2), 309–319.
 - (29) Patterson, A. L. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.* **1939**, *56*(10), 978–982.
 - (30) Erdtman, E.; Andersson, M.; Lloyd Spetz, A.; Ojamäe, L. Simulations of the Thermodynamics and Kinetics of NH₃ at the RuO₂(110) Surface. *Surf. Sci.* **2017**, *656* (June 2016), 77–85.
 - (31) Atkins, P. W.; Paula J. *Physical Chemistry*, 7th ed.; Oxford University Press Inc., 2002.
 - (32) Haynes, W. M. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*; Boca Raton: CRC Press, 2009.
 - (33) NIST Chemistry WebBook, NIST Standard Reference Database Number 69.
 - (34) MATLAB R2015a. The MathWorks Inc.: Natick, MA 2015.
 - (35) Asthana, S.; Samanta, C.; Bhaumik, A.; Banerjee, B.; Voolapalli, R. K.; Saha, B. Direct Synthesis of Dimethyl Ether from Syngas over Cu-Based Catalysts: Enhanced Selectivity in the Presence of MgO. *J. Catal.* **2016**, *334*, 89–101.
 - (36) Witoon, T.; Permsirivanich, T.; Kanjanasontorn, N.; Akkaraphataworn, C.; Seubsai, A.; Faungnawakij, K.; Warakulwit, C.; Chareonpanich, M.; Limtrakul, J. Direct Synthesis of Dimethyl Ether from CO₂ Hydrogenation over Cu-ZnO-ZrO₂/SO₄²⁻-ZrO₂ Hybrid Catalysts: Effects of Sulfur-to-Zirconia Ratios. *Catal. Sci. Technol.* **2015**, *5*(4), 2347–2357.
 - (37) Sakurai, H.; Haruta, M. Carbon Dioxide and Carbon Monoxide Hydrogenation over Gold Supported on Titanium, Iron, and Zinc Oxides. *Appl. Catal. A Gen.* **1995**, *127*(1–2), 93–105.
 - (38) Loyd J. Burcham, †; Laura E. Briand, ‡ and; Israel E. Wachs*, §. Quantification of Active Sites for the Determination of Methanol Oxidation Turn-over Frequencies Using Methanol Chemisorption and in Situ Infrared Techniques. 1. Supported Metal Oxide Catalysts. *Langmuir* **2001**, *17*(20), 6164–6174.
 - (39) Chuang, C.-C.; Wu, W.-C.; Huang, M.-C.; Huang, I.-C.; Lin, J.-L. FTIR Study of Adsorption and Reactions of Methyl Formate on Powdered TiO₂. *J. Catal.* **1999**, *185*(2), 423–434.
 - (40) Kecskeméti, A.; Barthos, R.; Solymosi, F. Aromatization of Dimethyl and Diethyl Ethers on Mo₂C-Promoted ZSM-5 Catalysts. *J. Catal.* **2008**, *258*(1), 111–120.
 - (41) Flores-Escamilla, G. a.; Fierro-Gonzalez, J. C. Infrared Spectroscopic Study of Dimethyl Ether Carbonylation Catalysed by TiO₂-Supported Rhodium Carbonyls. *Catal. Sci. Technol.* **2015**, *5*(2), 843–850.
 - (42) Chen, L.; Wang, S. Infrared Spectra of Methanol Desorption in a He Stream and under Vacuum on CeO₂ and ZrO₂ Catalyst Surfaces. *RSC Adv.* **2016**, *6*(24), 19792–19793.
 - (43) Xu, L.-H.; Lees, R. M.; Wang, P.; Brown, L. R.; Kleiner, I.; Johns, J. W. C. New Assignments, Line Intensities, and HITRAN Database for CH₃OH at 10 μm. *J. Mol. Spectrosc.* **2004**, *228*(2), 453–470.
 - (44) Erdohelyi, A.; Hancz, A.; Tóth, M.; Novák, É. Oxidation of Methanol on Different Silica Supported

- Lithium Molybdates. *Catal. Today* **2004**, *91–92*, 117–120.
- (45) Yu, Y.; Wang, Y.; Lin, K.; Hu, N.; Zhou, X.; Liu, S. A Complete Raman Spectral Assignment of Methanol in C-H Stretching Region. *J. Phys. Chem. A* **2013**, *47* (May), 1385–1393.
- (46) Ladera, R.; Finocchio, E.; Rojas, S.; Fierro, J. L. G.; Ojeda, M. Supported Niobium Catalysts for Methanol Dehydration to Dimethyl Ether: FTIR Studies of Acid Properties. *Catal. Today* **2012**, *192* (1), 136–143.
- (47) Forester, T. R.; Howe, R. F. In Situ FTIR Studies of Methanol and Dimethyl Ether in ZSM-5. *J. Am. Chem. Soc.* **1987**, *109* (17), 5076–5082.
- (48) Yu, J.; Mao, D.; Han, L.; Guo, Q.; Lu, G. Synthesis of C2 Oxygenates from Syngas over Monodispersed SiO₂ Supported Rh-Based Catalysts: Effect of Calcination Temperature of SiO₂. *Fuel Process. Technol.* **2013**, *106*, 344–349.
- (49) G. N. Bondarenko, E. A. Volnina, M. A. Kipnis, A. S. Rodionov, P. V. Samokhin, G. I. L. Surface Reactions of Dimethyl Ether on γ -Al₂O₃. *Russ. J. Phys. Chem. A* **2016**, *90* (2), 458–465.
- (50) Burke, D. J.; Puletti, F.; Woods, P. M.; Viti, S.; Slater, B.; Brown, W. A. Adsorption and Thermal Processing of Glycolaldehyde, Methyl Formate, and Acetic Acid on Graphite at 20 K. *J. Phys. Chem. A* **2015**, *119* (26), 6837–6849.
- (51) Lochar*, V. FT-IR Study of Methanol, Formaldehyde and Methyl Formate Adsorption on the Surface of Mo/Sn Oxide Catalyst. *Appl. Catal. A Gen.* **2006**, *309* (1), 33–36.
- (52) Senent, M. L.; Ruiz, R.; Villa, M.; Domínguez-Gómez, R. CCSD(T) Study of the Far-Infrared Spectrum of Ethyl Methyl Ether. *J. Chem. Phys.* **2009**, *130* (6).
- (53) Yu, A.; Lin, K.; Zhou, X.; Wang, H.; Liu, S.; Ma, X. New C-H Stretching Vibrational Spectral Features in the Raman Spectra of Gaseous and Liquid Ethanol. *J. Phys. Chem. C* **2007**, *111* (25), 8971–8978.
- (54) Drobyshev, A.; Aldiyarov, A. IR-Spectroscopy of Ethanol Formed by Recondensation from a Nitrogen Cryomatrix. *Low Temp. Phys.* **2011**, *37* (8), 718–724.
- (55) Drobyshev, A.; Aldiyarov, A.; Katpaeva, K.; Korshikov, E.; Kurnosov, V.; Sokolov, D. On the Stability of Ethanol Nanoclusters in a Nitrogen Cryomatrix. *Low Temp. Phys.* **2013**, *39* (11), 961–966.
- (56) Solymosi, F.; Nemeth, R.; Ovari, L.; Egri, L. Reactions of Propane on Supported Mo₂C Catalysts. *J. Catal.* **2000**, *195* (2), 316–325.
- (57) Subbotina, I. R.; Kazanskii, V. B. Use of the IR Spectra of Adsorbed Ethane and Propane Molecules to Characterize the Strength of Active Sites in Zeolites and to Analyze the Activation of C-H Bonds in These Paraffins. *Kinet. Catal.* **2008**, *49* (1), 138–148.
- (58) Larsson, R. Propane Dehydrogenation Catalyzed by ZSM-5 Zeolites. A Mechanistic Study Based on the Selective Energy Transfer (SET) Theory. *Molecules* **2015**, *20* (2), 2529–2535.
- (59) Pele, L.; Šebek, J.; Potma, E. O.; Benny Gerber, R. Raman and IR Spectra of Butane: Anharmonic Calculations and Interpretation of Room Temperature Spectra. *Chem. Phys. Lett.* **2011**, *515* (1–3), 7–12.
- (60) Aoki, Y.; Tominaga, H.; Nagai, M. Hydrogenation of CO on Molybdenum and Cobalt Molybdenum Carbide Catalysts - Mass and Infrared Spectroscopy Studies. *Catal. Today* **2013**, *215*, 169–175.
- (61) Weng, W. Z.; Chen, M. S.; Wan, H. L. Mechanistic Study of Partial Oxidation of Methane to Syngas Using in Situ Time-Resolved FTIR and Microprobe Raman Spectroscopies. *Chem. Rec.* **2002**, *2* (2), 102–112.
- (62) Yang, C.; Ma, Z.; Zhao, N.; Wei, W.; Hu, T.; Sun, Y. Methanol Synthesis from CO₂-Rich Syngas over a ZrO₂ Doped CuZnO Catalyst. *Catal. Today* **2006**, *115* (1–4), 222–227.
- (63) Saeidi, S.; Amin, N. A. S.; Rahimpour, M. R. Hydrogenation of CO₂ to Value-Added products—A Review and Potential Future Developments. *J. CO₂ Util.* **2014**, *5*, 66–81.
- (64) Daza, Y. A.; Kent, R. A.; Yung, M. M.; Kuhn, J. N. Carbon Dioxide Conversion by Reverse Water–Gas Shift Chemical Looping on Perovskite-Type Oxides. *Ind. Eng. Chem. Res.* **2014**, *53* (14), 5828–5837.
- (65) Sato, A. G.; Volanti, D. P.; Meira, D. M.; Damyanova, S.; Longo, E.; Bueno, J. M. C. Effect of the ZrO₂ Phase on the Structure and Behavior of Supported Cu Catalysts for Ethanol Conversion. *J. Catal.* **2013**, *307*, 1–17.
- (66) MAO, D.; YANG, W.; XIA, J.; ZHANG, B.; SONG, Q.; CHEN, Q. Highly Effective Hybrid Catalyst for the Direct Synthesis of Dimethyl Ether from Syngas with Magnesium Oxide-Modified HZSM-5 as a Dehydration Component. *J. Catal.* **2005**, *230* (1), 140–149.
- (67) Angeli, S. D.; Monteleone, G.; Giaconia, A.; Lemonidou, A. A. State-of-the-Art Catalysts for CH₄ Steam Reforming at Low Temperature. *Int. J. Hydrogen Energy* **2014**, *39* (5), 1979–1997.
- (68) Luyben, W. L. *Distillation Design and Control Using Aspen™ Simulation*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2006.
- (69) Kobayashi, Y.; Li, Y.; Wang, Y.; Wang, D. Adsorption Isotherms of Methanol and Dimethyl Ether on SAPO-34 Measured Together with Differential Adsorption Heat Measurement. *Chinese J. Catal.* **2013**, *34* (12), 2192–2199.

- (70) Hodgson, E. *A Textbook of Modern Toxicology*; Hodgson, E., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2004.
- (71) Mondloch, J. E.; Yan, X.; Finke, R. G. Monitoring Supported-Nanocluster Heterogeneous Catalyst Formation: Product and Kinetic Evidence for a 2-Step, Nucleation and Autocatalytic Growth Mechanism of Pt(0)_n Formation from H₂PtCl₆ on Al₂O₃ or TiO₂. *J. Am. Chem. Soc.* **2009**, *131* (18), 6389–6396.
- (72) Zahmakiran, M.; Özkar, S. Dimethylammonium Hexanoate Stabilized rhodium(O) Nanoclusters Identified as True Heterogeneous Catalysts with the Highest Observed Activity in the Dehydrogenation of Dimethylamine-Borane. *Inorg. Chem.* **2009**, *48* (18), 8955–8964.
- (73) Durak, H. .; Gulcan, M. .; Zahmakiran, M. .; Ozkar, S. .; Kaya, M. . Hydroxyapatite-Nanosphere Supported ruthenium(0) Nanoparticle Catalyst for Hydrogen Generation from Ammonia-Borane Solution: Kinetic Studies for Nanoparticle Formation and Hydrogen Evolution. *RSC Adv.* **2014**, *4* (55), 28947–28955.
- (74) Yang, Y.; Mims, C. A.; Mei, D. H.; Peden, C. H. F.; Campbell, C. T. Mechanistic Studies of Methanol Synthesis over Cu from CO/CO₂/H₂/H₂O Mixtures: The Source of C in Methanol and the Role of Water. *J. Catal.* **2013**, *298*, 10–17.
- (75) Takeishi, K.; Akaike, Y. Direct Synthesis of Dimethyl Ether (DME) from Syngas. *Recent Adv. ENERGY Environ.* **2010**, 408–411.
- (76) Sun, J.; Yang, G.; Yoneyama, Y.; Tsubaki, N. Catalysis Chemistry of Dimethyl Ether Synthesis. *ACS Catal.* **2014**, *4* (10), 3346–3356.
- (77) Wilkinson, S. K.; Van De Water, L. G. A.; Miller, B.; Simmons, M. J. H.; Stitt, E. H.; Watson, M. J. Understanding the Generation of Methanol Synthesis and Water Gas Shift Activity over Copper-Based Catalysts-A Spatially Resolved Experimental Kinetic Study Using Steady and Non-Steady State Operation under CO/CO₂/H₂ Feeds. *J. Catal.* **2016**, *337*, 208–220.
- (78) Ereña, J.; Garoña, R.; Arandes, J. M.; Aguayo, A. T.; Bilbao, J. Effect of Operating Conditions on the Synthesis of Dimethyl Ether over a CuO-ZnO-Al₂O₃/NaHZSM-5 Bifunctional Catalyst. *Catal. Today* **2005**, *107–108*, 467–473.

Supporting Information for 'Time evolution of the CO₂ conversion to fuels over Cu-Zr-SBA-15 catalysts'

Aylin Atakan*, Edvin Erdtman, Peter Mäkie, Lars Ojamäe and Magnus Odén

Nanostructured Materials, Department of Physics, Chemistry and Biology, Linköping University, Linköping SE-58183, Sweden, aylin.atakan@liu.se

Table S1. List of peaks in the infrared spectrum in the wavenumber ranges: 3300-2670 cm⁻¹ and 1230-1020 cm⁻¹

Wavenumber (cm ⁻¹)	Compound ID	Wavenumber (cm ⁻¹)	Compound ID	Wavenumber (cm ⁻¹)	Compound ID
3015	Methane ¹⁻³ MF ^{4,5}	2907	EME Ethanol	1193	DME MF
2978	Methanol EME Ethanol Butane Propane	2890	DME EME Ethanol Butane	1176	DME EME
2967	Methanol ⁴ EME Ethanol Butane Propane MF	2877	Butane Propane	1170	MF
2957	Methoxy MF Propane EME	2854	Methoxy	1118	DME
2947	Methanol Butane Propane	2845	Methanol	1100	DME EME
2935	EME Butane Propane MF	2834	DME EME Methanol	1090	DME Methoxy
2926	Methoxy DME MF	2818	Methoxy DME	1054	Methoxy Propane Ethanol
2917	DME	2806	Methoxy	1031	Methanol

The bands of, methane^{1,3,2}, methyl formate (MF)^{1,4,5}, methanol^{1,4,6-10}, dimethyl ether (DME)^{1,11,12}, methoxy^{1,8,12,13}, ethyl methyl ether (EME)^{1,13}, ethanol^{1,14-16}, butane^{1,17,18} and propane^{1,19,20} were obtained from references.

Table S2. Results of the theoretical thermodynamic equilibrium distribution calculations

Reactant	n (mol)															
CO ₂ initial	3.00E-03															
H ₂ initial	8.93E-03															
Product Scenario	ALL	ALL except for CH ₄		ALL except for CH ₄		ALL except for Et, Pr, Bu		CO, H ₂ O, MeOH, DME		H ₂ O, MeOH, DME		CO, H ₂ O, MeOH		H ₂ O, MeOH		
Component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component	n (mol)	CO ₂ conversion to the component
CO ₂ (g)	7.56E-04		4.76E-04		3.86E-04		1.20E-03		2.22E-03		2.31E-03		2.37E-03		2.57E-03	
H ₂ (g)	2.79E-05		1.70E-04		3.01E-04		3.63E-03		7.01E-03		6.92E-03		7.80E-03		7.70E-03	
CO (g)	4.73E-08		1.79E-07		2.51E-07		1.68E-05		1.76E-04		0.00E+00		3.42E-04		0.00E+00	
H ₂ O (g)	4.48E-03		5.04E-03		5.22E-03		2.99E-03		1.02E-03		9.72E-04		6.25E-04		4.30E-04	
CH ₄ (g)	2.24E-03		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
MeOH (g)	3.24E-12	0.00%	4.06E-12	0.00%	1.54E-12	0.00%	3.00E-06	0.10%	1.18E-04	3.93%	1.24E-04	4.14%	2.83E-04	9.45%	4.30E-04	14.34%
DME (g)	1.01E-12	0.00%	1.20E-12	0.00%	1.90E-13	0.00%	4.70E-08	0.00%	2.43E-04	16.18%	2.83E-04	18.87%	0.00E+00	0.00%	0.00E+00	0.00%
H ₂ CO (g)	2.07E-12		1.93E-12		3.13E-13		1.01E-11		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
EME (g)	8.26E-13		1.10E-12		1.85E-13		5.93E-04		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
HCOO-Me (g)	1.14E-12		1.18E-12		1.75E-13		8.03E-12		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
Et (g)	1.08E-08		1.25E-03		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
Pr (g)	3.31E-12		6.31E-06		8.20E-04		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
Bu (g)	1.62E-12		6.28E-08		3.75E-05		0.00E+00		0.00E+00		0.00E+00		0.00E+00		0.00E+00	
CO ₂ conversion to MeOH and DME		0.00%		0.00%		0.00%		0.10%		20.11%		23.01%		9.45%		14.34%
TOTAL CO ₂ CONVERSION		74.77%		84.12%		87.11%		60.05%		25.99%		23.01%		20.87%		14.34%

Figure S1. FID chromatograms obtained from GCMS.