

Supplementary Information

The role of copper particle size in low pressure methanol synthesis via CO₂ hydrogenation over Cu/ZnO catalysts

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S1. Mass and heat transfer limitations

In order to obtain meaningful reaction rates, these have to be measured in the absence of mass transport limitations or temperature gradients. There exist experimental and theoretical methods to study the magnitude of the transport processes in fixed bed reactors to verify if the reaction rates are effectively kinetically controlled. In this work equations proposed in [1] were used for this purpose.

Intraparticle temperature gradients

In the case of heat transfer, the verification of the following equation permits to conclude that the intraparticle temperature gradients are insignificant:

$$\frac{|\Delta H| r R_p^2}{\lambda T_S} < \frac{0.75 T_S R}{E_t} \quad (\text{S.1})$$

Where $|\Delta H|$ is the absolute enthalpy of reaction, r corresponds to the measured rate of reaction, R_p is the radius of the catalyst particles, λ stands for the thermal conductivity of the support material, T_S is the temperature on the external part of the particles, R is the gas constant and E_t the apparent activation energy.

Data used corresponds to methanol formation at 225°C for the most active catalyst (Cu(15)ZnO), and using the most pessimistic values of the variables.

$$|\Delta H| = 49.5 \text{ kJ/mol}$$

$$r = 0.10 \text{ } \mu\text{mol/g/s} * 5600 \text{ g/cm}^3 = 0.56 \text{ mol/m}^3/\text{s}$$

$$R_p = 158 \text{ } \mu\text{m}$$

$$\lambda = 4 \text{ W/K/m}$$

$$T_S = 225^\circ\text{C}$$

$$R = 8.314 \text{ J/mol/K}$$

$$E_t = 42 \text{ kJ/mol}$$

Using equation S.1 it is observed that the inequality is largely satisfied:

$$3.45 \times 10^{-7} < 7.39 \times 10^{-2}$$

Consequently, the temperature gradients in the catalysts particles are assumed to be negligible.

Intraparticle concentration gradients

For intraparticle mass transfer the Weisz-Prater dimensionless number is calculated. It relates the rate of reaction to that of diffusion in the particle pores. If the Weisz-Prater number is lower than or equal to 0.3 the internal diffusional limitations can be considered negligible:

$$\frac{r R_p^2}{C_S D_{eff}} \leq 0.3 \quad (\text{S.2})$$

Besides the terms already defined, here C_S is the concentration of reactant on the catalyst surface and D_{eff} is the effective diffusion coefficient. For the experiments of this work the values are:

$$r = 0.56 \text{ mol/m}^3/\text{s}$$

$$R_p = 158 \text{ } \mu\text{m}$$

$$C_S = 2.58 \text{ mol/m}^3$$

$$D_{eff} = 2.1 \times 10^{-6} \text{ m}^2/\text{s}$$

In this case the criterion is largely satisfied since Weisz-Prater number amounts 0.003

Interphase concentration gradients

In the case of gradients between the bulk gas phase and the surface of catalyst particles, an effectiveness factor has been defined (ψ) which relates the measured rate of reaction with the reaction rate without diffusional limitations. The product of the effectiveness factor with the Damköhler number (Da_0) which relates the rate of reaction with the rate of transport from the bulk of the fluid to the catalyst surface is composed of observable magnitudes:

$$\psi Da_0 = \frac{r}{k_g a C_0} \quad (\text{S.3})$$

Where k_g is the mass transfer coefficient between the fluid and the surface of catalyst particles, a is the ratio area/volume of catalyst particles and C_0 the concentration of reactant in the bulk of the fluid.

Data for the system studied here are the following:

$$r = 0.56 \text{ mol/m}^3/\text{s}$$

$$k_g = 0.00007 \text{ m/s}$$

$$a = 10587 \text{ m}^2/\text{m}^3$$

$$C_0 = 19.6 \text{ mol/m}^3$$

Consequently, the product ψDa_0 equals 0.04, and ψ is approximately 0.96, which means that external mass transfer artifacts are negligible.

Taking into account the above results one can safely assume that the reaction took place in fully kinetic regime.

S2. Thermodynamic equilibrium assessment

The formation of CO and methanol by CO₂ hydrogenation could be affected by thermodynamic equilibrium. Since methanol synthesis reaction is exothermic, the equilibrium tends to be unfavorable when temperature is increased. The equilibrium yields of methanol and CO were calculated by Gibbs free energy minimization using HSC

Chemistry 4.0 software [2], considering the following chemical species: CO, CO₂, CH₃OH, H₂O and H₂. The feed ratio (H₂/CO₂ = 9), the pressure (7 bar) and the temperature were the input variables. The equilibrium yields and conversion are plotted in the following figure.

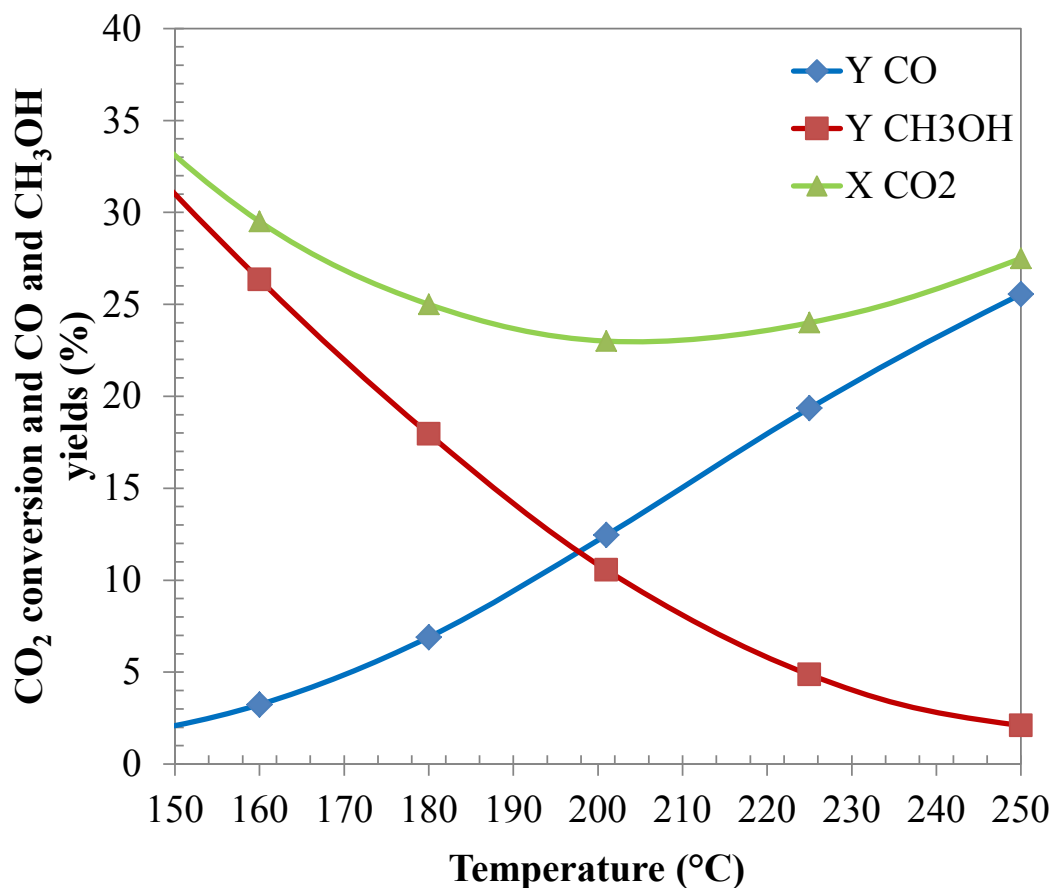
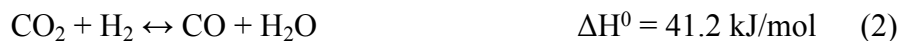


Figure S1: Equilibrium yield of methanol and CO as well as CO₂ conversion for the conditions of this study. H₂/CO₂ = 9, Pressure = 7 bar.

The reactions involved are the following:



It is worth noting that reaction (3) is a linear combination of reactions (1) and (2).

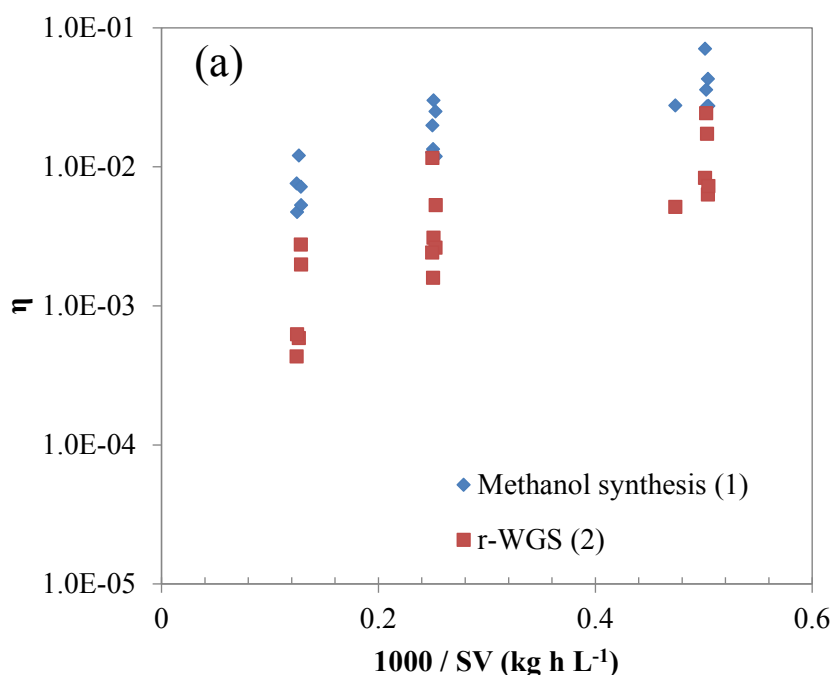
From the above equations one can observe that methanol can be produced by reaction 1 as well as by the reverse of reaction 3. CO can be produced by reverse water gas shift (2) and

by methanol decomposition (3). Taking into account that equilibrium methanol yield goes to very low values as temperature is raised (Figure S1), the approach to equilibrium factor (η) is a useful parameter to measure the kinetic consequences of the thermodynamic equilibrium over a given reaction [3]. η is defined as the ratio of product and reactant concentrations and the equilibrium constant:

$$\eta_1 = \frac{1 P_{CH_3OH} P_{H_2O}}{K_1 P_{CO_2} P_{H_2}^3}$$

$$\eta_2 = \frac{1 P_{CO} P_{H_2O}}{K_2 P_{CO_2} P_{H_2}}$$

The calculated values of η for each reaction are plotted against the inverse of residence time expressed as the inverse of space velocity.



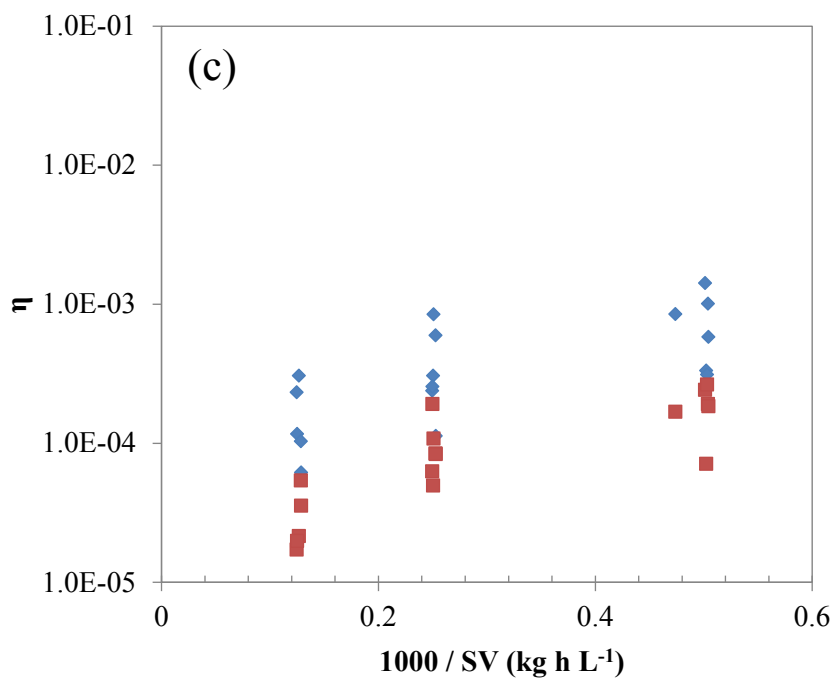
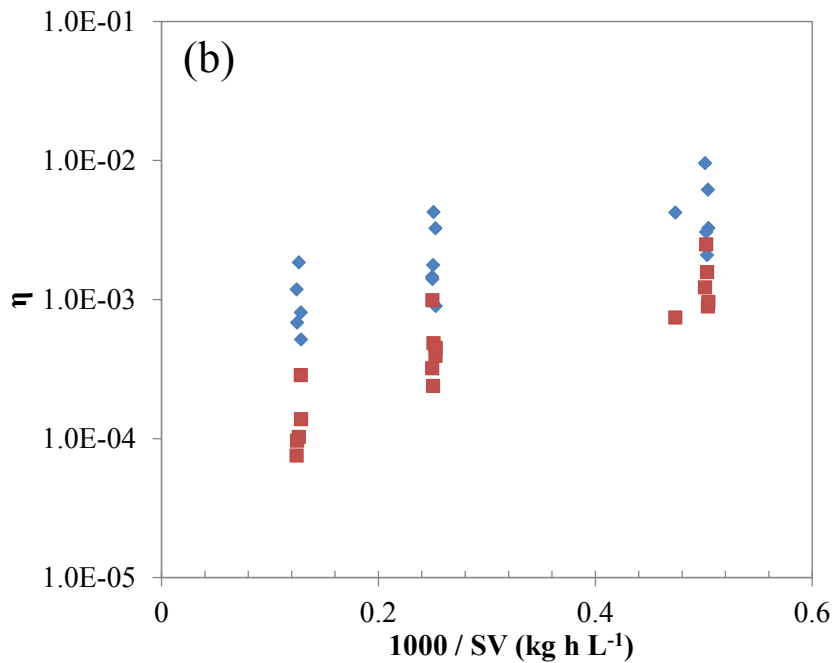


Figure S2: Approach to equilibrium values (η) calculated for each reaction as a function of residence time expressed as the inverse of space velocity. Temperature: 225°C (a), 200°C (b) and 180°C (c).

S3. N₂ adsorption isotherms

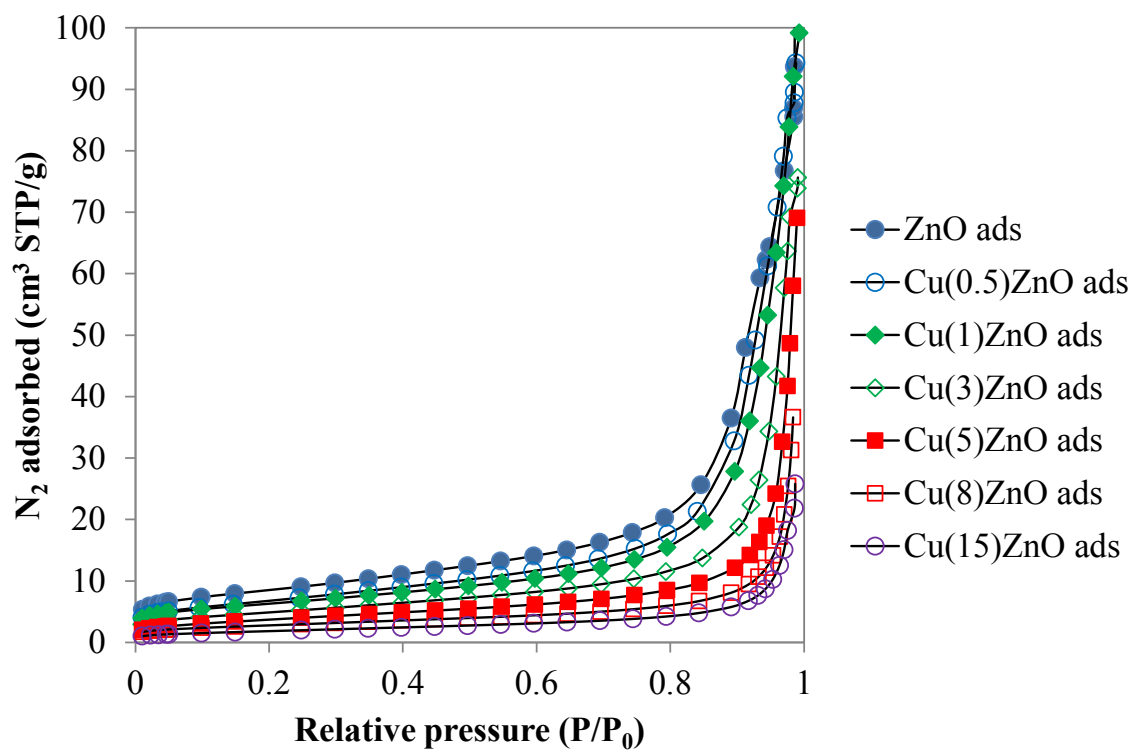


Figure S3: N₂ adsorption isotherms obtained at -196°C for all the samples studied.

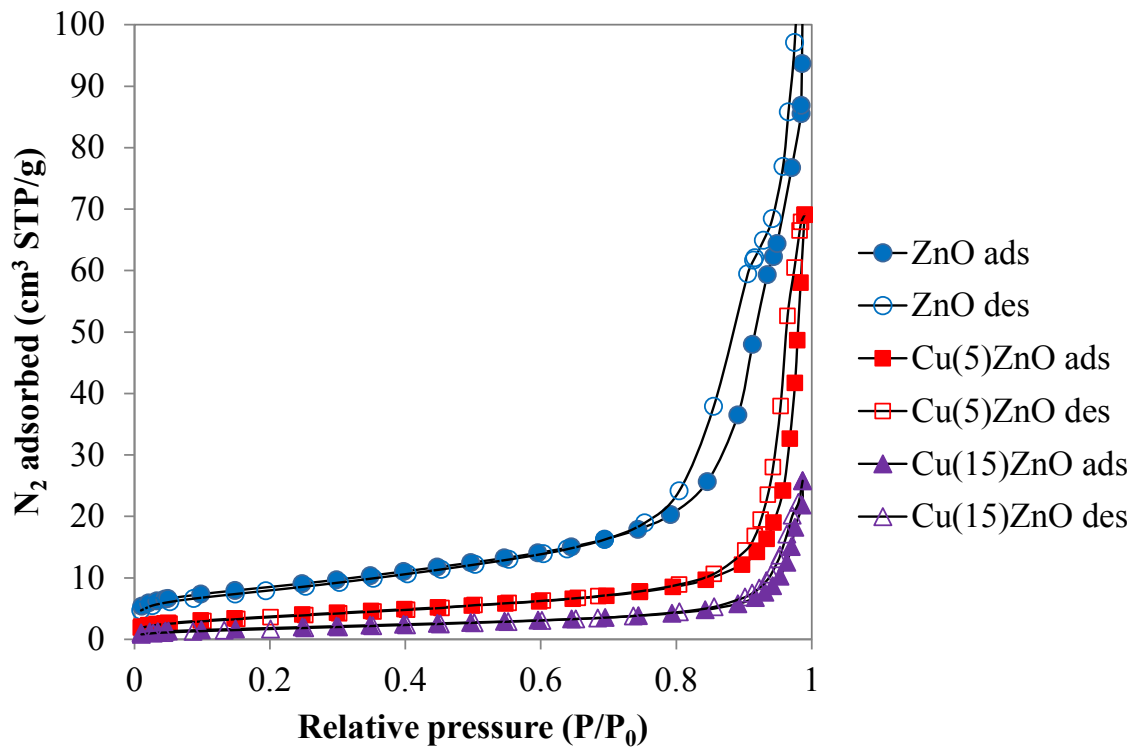


Figure S4: N₂ adsorption and desorption isotherms for selected samples.

S4. XPS results

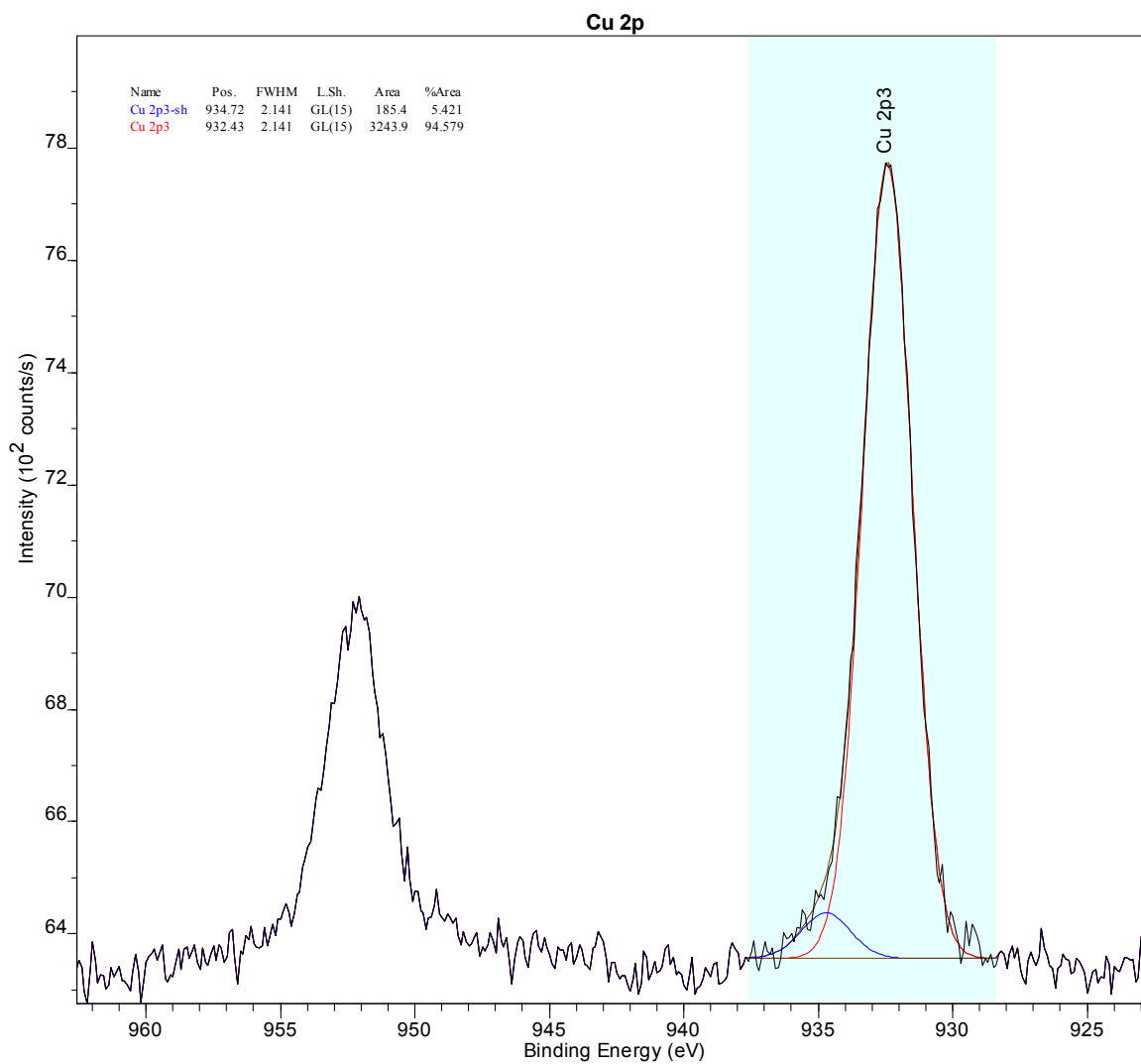


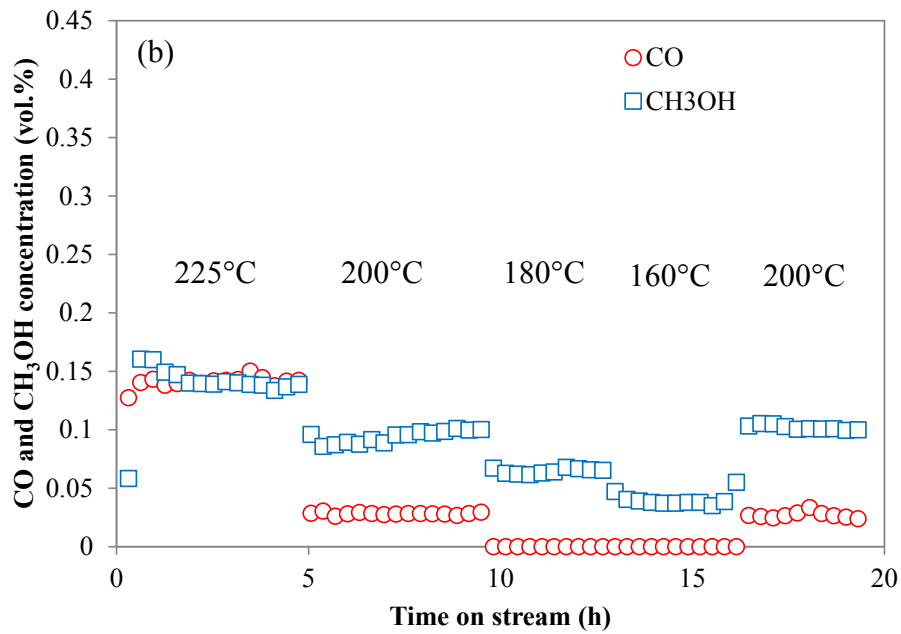
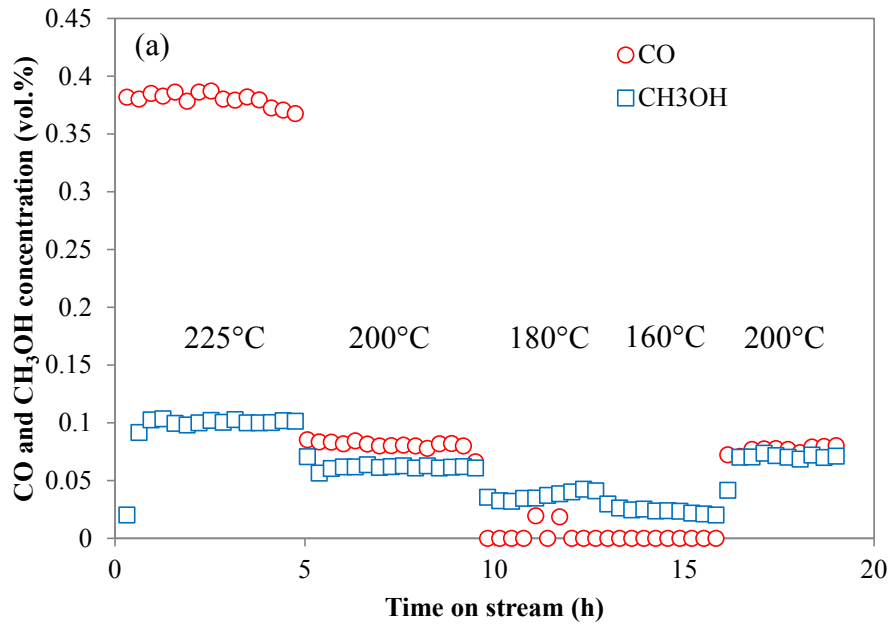
Figure S5: XPS results for the Cu 2p region for Cu(1)ZnO. Cu2p3/2 peak was used for Cu quantification.

Table S1: Summary of XPS results. Comparison of molar ratios obtained by XPS vs. the bulk ones. Binding energies of Zn 2p_{3/2} and Cu 2p_{3/2} and their full width at half maximum (FWHM). The samples were analyzed after reaction tests.

Sample	Molar ratio	Molar ratio	BE (eV)	FWHM	BE (eV)	FWHM
	Cu/Zn (XPS)	Cu/Zn (bulk)	Zn 2p _{3/2}	(eV)	Cu 2p _{3/2}	(eV)
Cu(0.5)ZnO	0.026	0.006	1021.5	2.25	932.5	2.35
Cu(1)ZnO	0.048	0.014	1021.5	2.22	932.4	2.14
Cu(3)ZnO	0.060	0.036	1021.5	2.23	932.3	2.22
Cu(5)ZnO	0.063	0.064	1021.5	2.24	932.2	2.20
Cu(8)ZnO	0.091	0.104	1021.6	2.24	932.2	2.11
Cu(15)ZnO	0.087	0.205	1021.6	2.27	931.9	2.00

S5. Stability of the catalysts.

The reaction rates were always obtained at stable conditions. In Figure S6 is shown as an example, the evolution of CO and CH₃OH concentrations with time on stream for three catalysts. The space velocity of the experiments shown was the lowest (2000 L kg⁻¹ h⁻¹), because in these experiments the stabilization of the concentrations was slower. Reaction rates were calculated by averaging the 3 to 6 concentration values at the end of each temperature interval. It is worth noting that the concentrations in both segments at 200°C are very similar, which shows that not significant deactivation occurred at the length scale of these measurements. In the case of Cu(8)ZnO sample (Figure S6-c), the concentration of methanol decreases strongly the first hour of reaction. This could be due to sintering of copper. However, since catalysts were characterized after reaction, the catalyst properties (surface area, copper dispersion) take that into account.



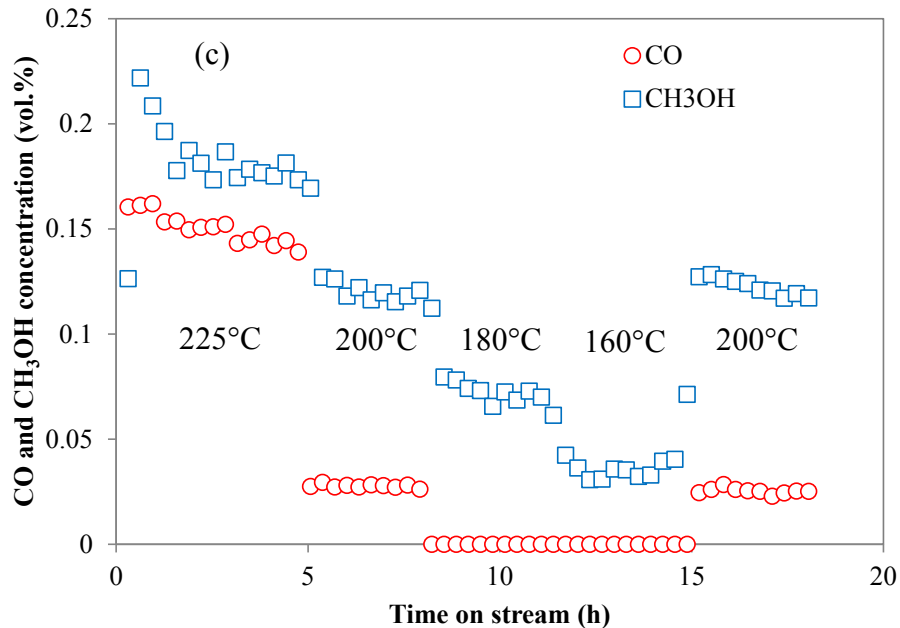


Figure S6: Measured CO and CH₃OH concentrations (vol. %) at the exit of the reactor, as a function of time on stream. H₂/CO = 9. Space velocity = 2000 L kg⁻¹ h⁻¹. Cu(1)ZnO (a); Cu(5)ZnO (b); Cu(8)ZnO (c).

S6. Estimation of forward reaction rates

In order to obtain the forwards reaction rate for methanol synthesis (1) and reverse water gas shift (2), the rates of methanol and CO formation were extrapolated to zero residence time (which is equivalent to extrapolate to zero CO₂ conversion, as shown in Figures S7 and S8). At zero residence time, methanol decomposition reaction (3) is assumed to be negligible: all CH₃OH and CO are produced from reactions (1) and (2) respectively.



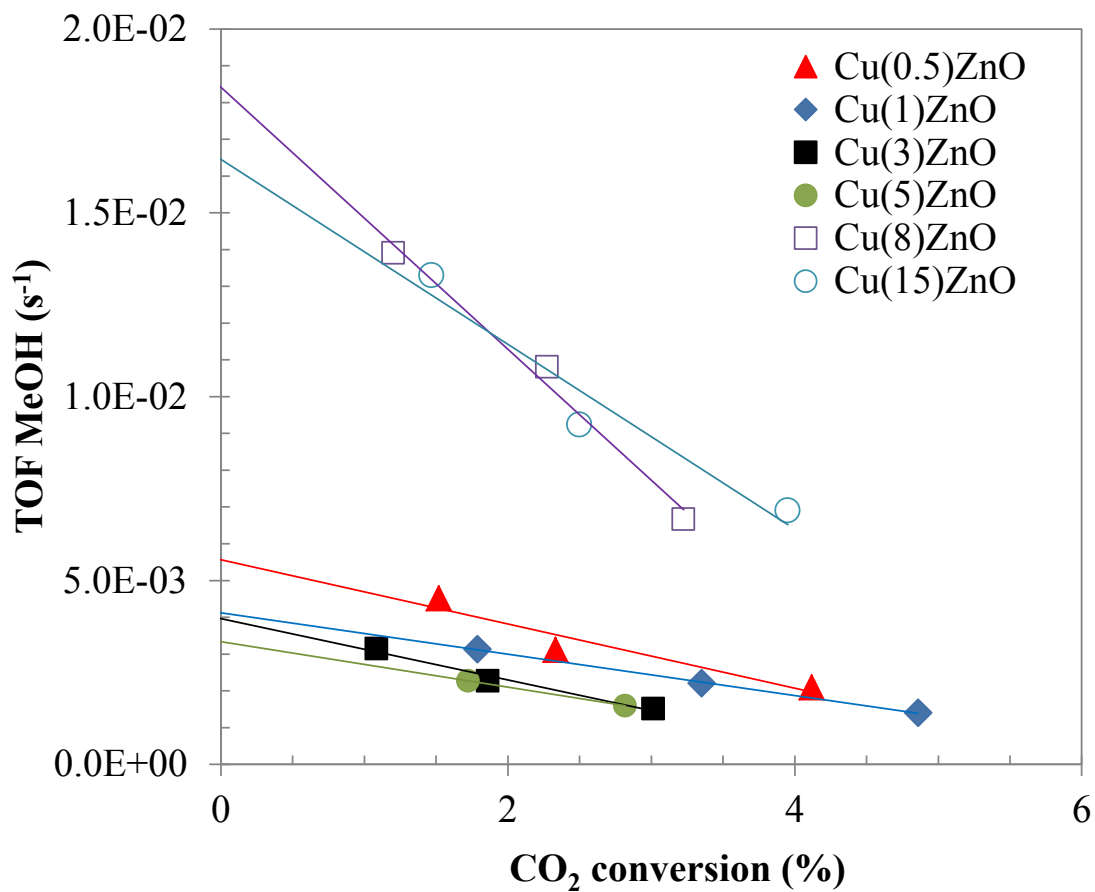


Figure S7: Turnover frequency for methanol formation as a function of CO₂ conversion at 225°C. A linear fit was extrapolated to zero CO₂ conversion. This gives the forward rate of methanol synthesis reaction.

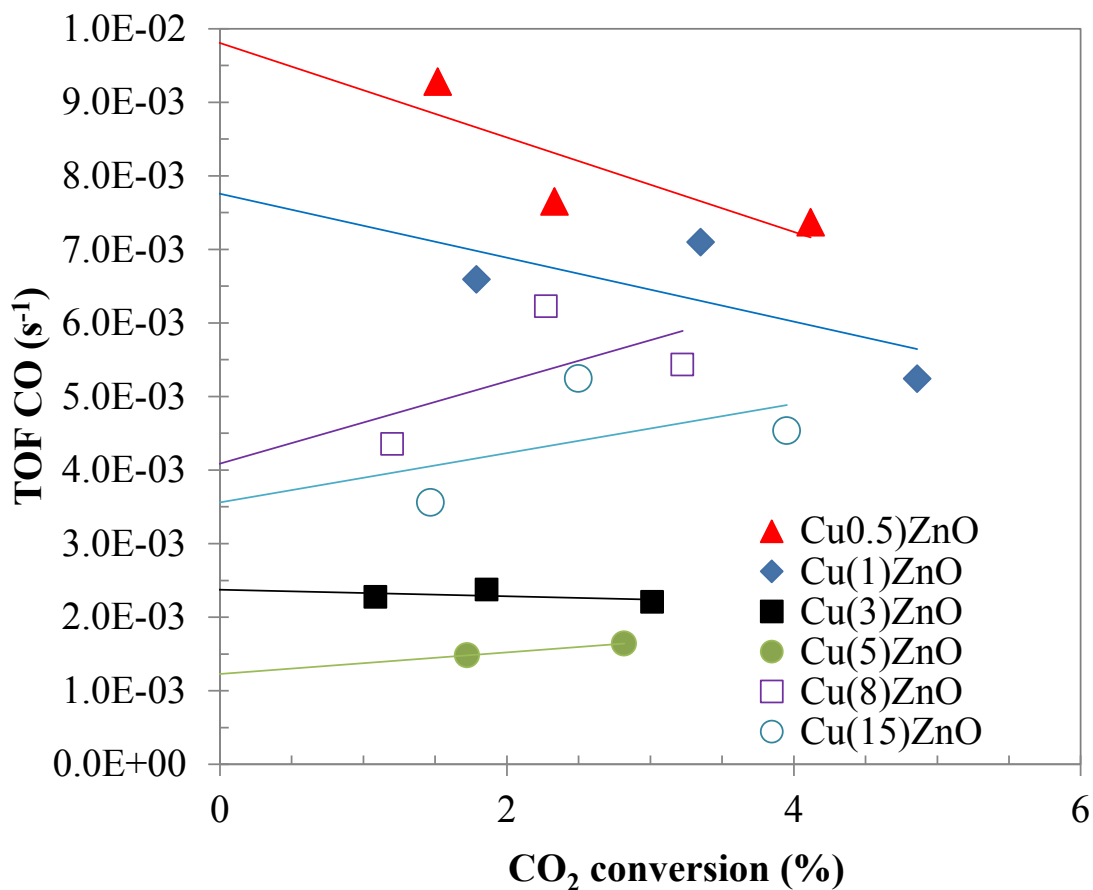


Figure S8: Turnover frequency for CO formation as a function of CO₂ conversion at 225°C. A linear fit was extrapolated to zero CO₂ conversion. This gives the forward rate of reverse water gas shift reaction.

S7. Comparison with catalysts prepared by coprecipitation

The model catalysts of this study were prepared by wet impregnation technique and present low copper surface areas compared with catalysts similar to the ones used in industry, which are prepared by coprecipitation. In an attempt to compare the performance of our catalysts with those more representative of industrial conditions, Figure S9 shows the selectivity to methanol as a function of CO₂ conversion for the catalysts prepared for this study compared with other catalysts prepared by coprecipitation method at similar reaction conditions.

It can be observed that a typical industrial Cu/ZnO/Al₂O₃ catalyst [4] presents a performance that is comparable with the samples presented here. Although its conversion is higher (10%, versus up to 4% in the case of Cu/ZnO catalysts of our study), the selectivity

is similar and one should expect that at higher CO₂ conversion the more selective samples prepared by wet impregnation (Cu(8)ZnO and Cu(15)ZnO) would show similar selectivities compared to industrial catalyst. This means that one could expect that the conclusions of this work would be valid for industrial-like catalysts.

Figure S9 also shows the results for other catalysts prepared by coprecipitation technique. Cu/ZnO/ZrO₂ present similar methanol selectivities compared to Cu/ZnO/Al₂O₃ [4]. When ZnO is absent, which is the case of Cu/ZrO₂ catalysts presented by Nitta et al. [5], the selectivity to methanol is lower. The selectivity of the Cu/ZnO samples prepared by wet impregnation is significantly higher compared to the Cu/ZrO₂ catalyst prepared by Nitta et al.

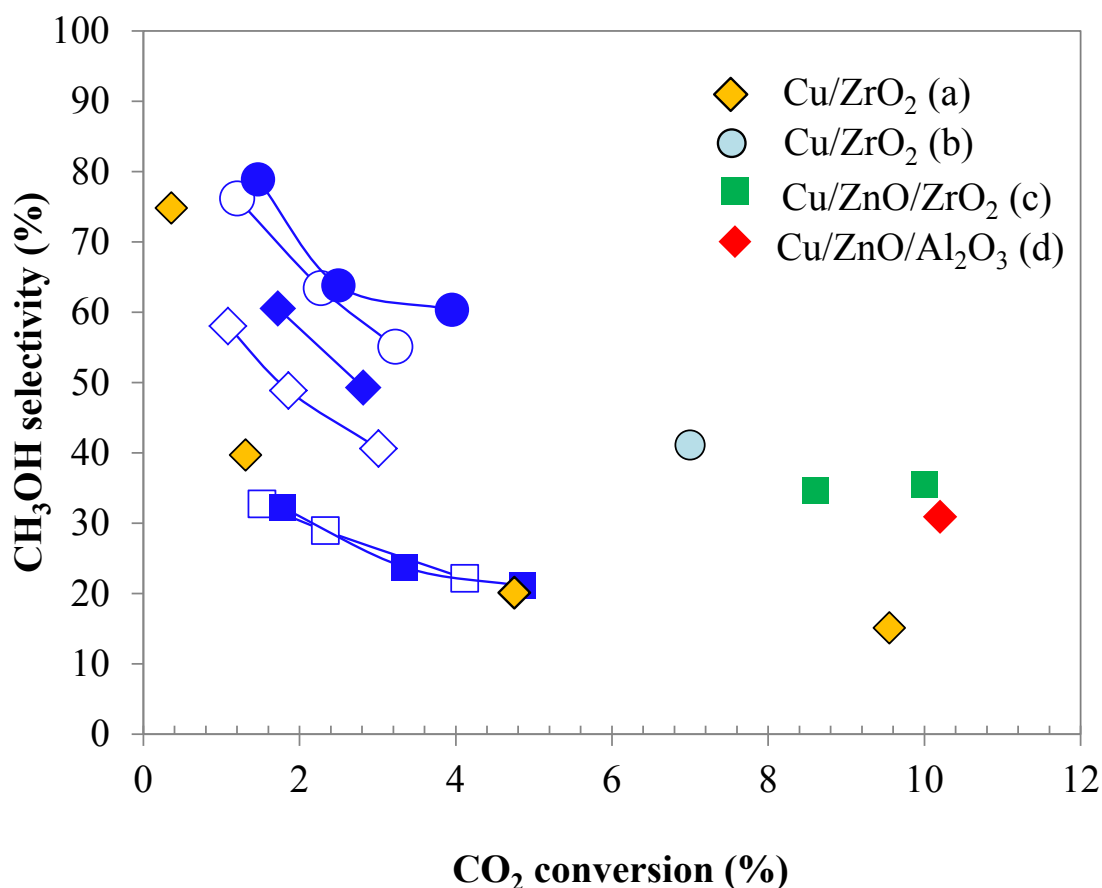


Figure S9: Selectivity to methanol as a function of CO₂ conversion. Points connected with blue lines correspond to experimental data of this work obtained at 225°C and 7 bar. (see caption of Figure 4 for more details). (a) Data obtained from reference [5] for Cu/ZrO₂ catalysts. Reaction conditions: Temperature: 220°C, Pressure 9 bar, H₂/CO₂ = 3; (b, c, d)

Data presented by Arena et al. [4]: Temperature 220°C, Pressure 10 bar, H₂/CO₂ = 3 for Cu/ZrO₂ (b), Cu/ZnO/ZrO₂ (c) and commercial Cu/ZnO/Al₂O₃ (d). Note: As all these new points correspond to different catalysts we did not attempt to draw a correlation line.

References

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