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Kinetic modelling of the methanol synthesis from CO$_2$ and H$_2$ over a CuO/CeO$_2$/ZrO$_2$ catalyst: The role of CO$_2$ and CO hydrogenation

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1. Introduction

The combustion of hydrocarbons to produce energy entails a critical global challenge that needs to be tackled with urgency. The usage of fossil fuels correlates directly to the release of greenhouse gasses – especially CO$_2$ – into the atmosphere, which is the main responsible of global warming [1,2]. Hence, in the last century research has been focusing on the development of carbon capture and storage technologies (CCS) first and, more recently, on the alternatives for CO$_2$ utilization (CCU) [3–6]. An interesting approach for CCU is the CO$_2$ reduction with renewable H$_2$ to produce valuable chemicals and/or energy carriers [7]. In this context, the CO$_2$ conversion to methanol is particularly appealing due to the high methanol demand worldwide (i.e. about 200 kton of methanol are used every day as chemical feedstock and transportation fuel) [8]. Indeed, methanol could be used directly as an alternative fuel or as intermediate for the production of dimethyl ether, olefins, gasoline and aromatics [9–11]. The CO$_2$ hydrogenation to methanol is a catalytic gas phase process which follows three main reactions: the direct hydrogenation of CO$_2$ to methanol (reaction 1), the production of CO through the r-WGS reaction (reaction 2) and the hydrogenation of CO to methanol (reaction 3).

\[
\text{CO}_2 \text{ hydrogenation: } \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_\circ = -49.5 \text{ kJ/mol} \tag{1}
\]

\[
\text{Reverse water gas shift: } \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H_\circ = +41.2 \text{ kJ/mol} \tag{2}
\]

\[
\text{CO hydrogenation: } \text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta H_\circ = -90.5 \text{ kJ/mol} \tag{3}
\]

Among these reactions, the CO$_2$ hydrogenation to methanol is the most desired. Inevitably, the r-WGS takes place in parallel, accelerating the H$_2$ depletion and, at the same time, contributing to the production of water. As a matter of fact, water is the main reaction by-product, which limits the system thermodynamically and causes catalyst deactivation [12]. Depending on the catalyst, the CO hydrogenation to methanol (reaction 3) could take place simultaneously, partially balancing the negative effect of the r-WGS. Nowadays, methanol is produced industrially from syngas feedstock (i.e., mixture of CO, H$_2$ and c.a. 3% of CO$_2$) at pressures of 50–80 bar and temperatures of 200–300 °C, over CuO/ZnO/Al$_2$O$_3$ catalytic beds [13,14]. Since the benchmark technology involves only traces of CO$_2$ in the feedstock [15], the corresponding
catalyst is not necessarily optimal when using pure CO$_2$, i.e., a thermodynamically very stable molecule, as the sole carbon source. Usually CO$_2$ adsorption is not strong enough [16] and efforts are required specifically on novel catalyst formulations [17]. Over the years, researchers have proposed a variety of different catalysts for the CO$_2$ hydrogenation to methanol, with particular focus on Cu-based systems, in combination with different metal oxides as carrier and/or promoters [18–21]. First, important research efforts aimed at replacing the hydrophilic Al$_2$O$_3$ support, which could deactivate in presence of the large amounts of water produced in all the reactions [22]. In most of the catalyst formulations, the Zno oxide still acts as main promoter, since it guarantees both a higher Cu dispersion and the formation of Cu$^{4+}$ sites at the Cu-ZnO interface [23–25]. On the other hand, various carriers/promoters have been proposed in literature such as ZrO$_2$ [17,25–29], CeO$_2$ [22,30–34], Fe$_2$O$_3$ [34–36], SiO$_2$ [37–39], and TiO$_2$ [30,40–43]. Most recently, the synergistic effect of CeO$_2$-ZrO$_2$ mixed oxides has received particular attention due to their high redox ability, improved thermal stability [44] and superior oxygen storage capacity (OCS) [45], properties that have proved highly beneficial for different reactive systems, such as the oxidation of aliphatic C2 [46], the conversion of NOx [47], the reduction of NO by propene [48] and, most recently, for the CO$_2$ hydrogenation to methanol [49–51]. The introduction of smaller Zr$^{4+}$ ions into the CeO$_2$ tetrahedron creates a defective fluorite structure, which facilitates the adsorption of oxygen [52]. Shi et al. [49] proposed for the first time a ternary CuO/CeO$_2$/ZrO$_2$ catalyst for the CO$_2$ hydrogenation to methanol. They found that a Ce:Zr mass ratio of 1 optimizes the basicity of the system in favour of the CO$_2$ adsorption capacity. Their Cu$_{3}$Zr$_{5}$O$_{12}$-ZrO$_2$ mixed oxides showed excellent reducibility and Cu dispersion, as well as a balanced distribution of Cu$^{0}$ and strong basic sites to enhance the H$_2$ dissociative-adsorption and the formation of the H$_2$CO intermediate, which preferentially hydrogenates to form methanol. Wang et al., [50] investigated the reaction pathway via in situ DRIFTS analysis. They showed that a calcination temperature of 450 °C increases the CuO surface area and the formation of Cu-Oe-Zr sites, which favour the formation of H$^+$ and bi/m-HCOO$^-$, responsible for the high selectivity to methanol.

In any catalytic process, kinetic modelling is an essential tool to support efforts on catalyst development, to elucidate reaction mechanisms as well as to aid reactor design and process optimization. Numerous kinetic models have been proposed over the years to describe the methanol synthesis, mostly on commercial catalysts [13,53–57]. However, the majority of the kinetic models trace back to the works of Graaf et al., [58] and Bussche and Froment [59]. Both models propose a Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism with the

\begin{align*}
 & b_i \quad \text{Adsorption constant of component } i, \text{ (depending on model)} \\
 & K^q_i \quad \text{Equilibrium constant of reaction } j, \text{ (depending on reaction)} \\
 & \Delta H_{ads, i}^\circ \quad \text{Standard enthalpy of adsorption of component } i, \text{ (J·mol}^{-1}) \\
 & \Delta S_{ads, i}^\circ \quad \text{Standard entropy of adsorption of component } i, \text{ (J·mol}^{-1}·K^{-1}) \\
 & E_a_{ij} \quad \text{Activation energy of reaction } j, \text{ (J·mol}^{-1}) \\
 & R \quad \text{Gas constant, (J·mol}^{-1}·K^{-1}) \\
 & C_a \quad \text{Carberry’s number, (–)} \\
 & D_{Dit} \quad \text{Second Damkohler number, (–)} \\
 & D_x \quad \text{Effective diffusivity, (m}^2\cdot\text{s}^{-1}) \\
 & r_{obs, V} \quad \text{Observed reaction rate per volume of catalyst, (mol}^{-1}·\text{m}^{-3}\cdot\text{s}^{-1}) \\
 & n_i \quad \text{Order of reaction with respect to component } i, \text{ (–)} \\
 & k_{sp} \quad \text{Gas-solid mass transfer coefficient, (m}^{-1}) \\
 & r_{i}^* \quad \text{Forward rate of reaction of component } i, \text{ (mol}^{-1}·\text{m}^{-3}\cdot\text{s}^{-1}) \\
 & c_i \quad \text{Concentration of species } i \text{ in the bulk phase, (mol}^{-1}) \\
 & C_i \quad \text{Concentration of species } i \text{ on the catalyst surface, (mol}^{-1}) \\
 & F_{statistic} \quad \text{Statistic indicator of the F-test, (–)} \\
 & F_{critical} \quad \text{Critical value of } F_-, \text{ from Fisher distribution tables, (–)} \\
 & s_{i}^2 \quad \text{Variance of the lack of fit, (–)} \\
 & s_{i}^2 \quad \text{Variance of the experimental error, (–)} \\
 & N_i \quad \text{Number of variables (parameters of kinetic models), (–)} \\
 & p_i \quad \text{Partial pressure of component } i \text{, (bar)} \\
 & \beta_i \quad \text{Adsorption term of Bussche and Froment kinetic model, (–)} \\
 & \Theta_1, \Theta_2 \quad \text{Adsorption terms of Graaf’s kinetic model, (bar}^{-0.5}) \\
 & \Theta^*, \Theta^+ \quad \text{Adsorption terms of Seidel’s kinetic model, (–)} \\
 & \phi_i \quad \text{Total amount of reduced centers, (–)} \\
 & \eta_i \quad \text{Relative contact free energy of Cu and CeZr, (–)} \\
 & \nu_i \quad \text{Inlet reactor condition} \\
 & 1 \quad \text{CO}_2 \text{ hydrogenation to methanol reaction} \\
 & 2 \quad \text{Reverse water gas shift reaction} \\
 & 3 \quad \text{CO hydrogenation to methanol reaction} \\
 & \exp \quad \text{Experimental value} \\
 & \text{calc} \quad \text{Calculated value}
\end{align*}
dissociative adsorption of H₂. Graaf et al., established a dual-sites mechanism (i.e., one for CO and CO₂ and one for H₂O and H₂) where methanol is produced from CO₂ and CO simultaneously. On the contrary, Bussche and Froment considered a mechanism where Cu is the sole active site and CO₂ is the only carbon source for the methanol production. Even today, literature shows disagreements on the relative contribution of CO and CO₂ to the methanol synthesis. For example, Liu et al., [60] propose at least four parallel reactions: CO-CO₂ exchange, CO hydrogenation, CO₂ hydrogenation and WGS, while Bowker et al., [61] proposed that CO₂ is the only responsible of methanol synthesis, even when feeding CO/CO₂/H₂ mixtures. Interestingly, Yang et al., [62] proved that the CO₂ and CO contributions to methanol synthesis varies with the operating conditions. More recently, Niels et al., [63] found that CO₂ is the immediate source for methanol (i.e., CO₂ pathway is one order of magnitude faster), whereas the presence of CO is inhibitory at low conversion due to competitive adsorption, and beneficial at higher conversion due to the removal of water via the WGS. Finally, L.C. Graaf et al., [64] showed through DFT calculations that about 2/3 of the methanol comes from CO₂ in the conventional process (i.e., syngas feed). However, the situation could be completely different with CO₂-rich streams and other catalyst formulations.

More recently, Park et al., [65] developed a model considering three-sites adsorption, where CO₂ and CO adsorb on two distinct sites. In this study the authors carried out a rate determining step analysis (RDS) based on the mechanistic hypotheses earlier proposed by Graaf et al., to find the rate expressions that best fit the experimental data. Seidel et al., [56] reviewed the elementary steps involved in the three-sites adsorption mechanism, proposing an even more complex kinetic model. This was recently simplified by Slotboom et al., [66], who reduced the reaction mechanism, proposing an even more complex kinetic model. This allows to the methanol synthesis. As a result, only reaction (1) and (2) take place on the Cu surface of the catalyst, where both H₂ and CO₂ undergo dissociative adsorption. According to the authors, the rate determining steps are: 1) the CO₂ dissociation on the active sites, which releases surface oxygen for the rWGS reaction and 2) the hydrogenation of the formate species for the CO₂ hydrogenation to methanol. The rate equations are reported in Eq. 3–5.

\[
r_1 = k_1 \rho_{\text{CO}_2} \rho_{\text{H}_2} \left(1 - \frac{1}{K_1} \frac{P_{\text{H}_2} \rho_{\text{CO}_2}}{P_{\text{H}_2} \rho_{\text{CO}_2}} \right) \beta^\theta (\Theta_1, \Theta_2) \tag{3}
\]

\[
r_2 = k_2 \rho_{\text{CO}} \left(1 - \frac{1}{K_2} \frac{P_{\text{H}_2} \rho_{\text{CO}}}{P_{\text{H}_2} \rho_{\text{CO}}} \right) \beta (\Theta_1, \Theta_2) \tag{4}
\]

\[
\beta = \left(1 + b_{\text{H}_2/O:H_2} + b_{\text{H}_2/O:H_2} \right)^{-1} (\Theta_1, \Theta_2) \tag{5}
\]

The Bussche and Froment model considers three adsorption states (i.e., \( b_{\text{H}_2/O:H_2} \) and \( b_{\text{H}_2/O:H_2} \)) and two kinetic constants (i.e., \( k_1 \) and \( k_2 \)), for a total of 10 parameters to be optimized.

2.2. Dual-site adsorption mechanism

The most important and widely employed kinetic model describing the methanol synthesis is the model developed by Graaf et al., [58] in 1988. In their first publication, the authors had already recognized the lack of agreement in the literature on whether the carbon source for the methanol production is CO or CO₂. As a result, they developed a model including both pathways (reaction 1, 2 and 3). All the reactions are assumed to be based on a dual-site LHHW mechanism, where CO and CO₂ adsorb competitively on one site (S₁) and H₂ and H₂O adsorb competitively on a second site (S₂), with dissociation of H₂. The adsorption of methanol is once again neglected. The rate equations are reported in Eq. 6–8, with the two adsorption terms (i.e., \( \Theta_1 \) and \( \Theta_2 \)) related to the site \( s_1 \) and site \( s_2 \) described in Eq. 9–10.

\[
r_1 = k_1 \rho_{\text{H}_2} \rho_{\text{CO}} \Theta_1, \Theta_2 \tag{6}
\]

\[
r_2 = k_2 \rho_{\text{H}_2} \rho_{\text{CO}} \Theta_1, \Theta_2 \tag{7}
\]

\[
r_3 = k_3 \rho_{\text{H}_2} \rho_{\text{CO}} \Theta_1, \Theta_2 \tag{8}
\]

\[
\Theta_1 = \left(1 + b_{\text{H}_2/O:CO} + b_{\text{H}_2/O:CO} \right)^{-1} (\Theta_1, \Theta_2) \tag{9}
\]

\[
\Theta_2 = \left(1 + b_{\text{H}_2/O:CO} + b_{\text{H}_2/O:CO} \right)^{-1} \tag{10}
\]

where A, B, and C represent the driving force of the CO hydrogenation, r-WGS and CO₂ hydrogenation to methanol, respectively. As a matter of fact, the authors provided also different expressions for the driving forces terms, which depends on the particular RDS for the specific
reaction. All the (48) combinations are reported in Table 1 and were tested in this study.

The model from Graaf et al.,1 includes 3 kinetic constants (i.e., \(k_1\), \(k_2\) and \(k_3\)) and 3 adsorption constants (i.e., \(b_{\text{co}}\), \(b_{\text{co2}}\) and \(\frac{b_{\text{co}}}{\sqrt{b_{\text{co}}}}\)), for a total of 12 kinetic parameters.

More recently, Henkel modified the model developed by Graaf et al., excluding the CO hydrogenation to methanol \([54]\). His reparameterization was based on two sets of experimental results, obtained from two distinct set-ups: 1) a Berty reactor and 2) a micro-fixed bed reactor, from which he obtained two different set of kinetic parameters \([55]\).

The rate equations proposed for the CO2 hydrogenation and the rWGS are reported in Eq. 11–12, which lead to a total of 10 kinetic parameters.

\[
r_1 = \frac{k_1 b_{\text{co}2} P_{\text{co}2} P_{\text{H2}}}{(1 + b_{\text{co}2} P_{\text{co}2} + b_{\text{co}2} P_{\text{co}2} P_{\text{H2}})\left(P_{\text{H2}}^2 + b_{\text{co}2} P_{\text{co}2} + b_{\text{co}2} P_{\text{co}2} P_{\text{H2}}\right)}
\]

\[
r_2 = \frac{k_2 b_{\text{co}2} P_{\text{co}2} P_{\text{H2}}}{(1 + b_{\text{co}2} P_{\text{co}2} + b_{\text{co}2} P_{\text{co}2} P_{\text{H2}})\left(P_{\text{H2}}^2 + b_{\text{co}2} P_{\text{co}2} + b_{\text{co}2} P_{\text{co}2} P_{\text{H2}}\right)}
\]

### 2.3. Three-sites adsorption mechanism

In 2014, Park et al.,\([65]\) proposed a reaction pathway, based on the mechanism developed by Graaf et al., with the introduction of a third adsorption site exclusively for CO2. The authors considered the methanol dehydration to dimethyl ether in their reaction scheme, which was discarded in our analysis since no traces of DME were detected during the experimentation. The rate equations are summarized in Eq. 13–15.

The model from Park et al., involves 14 kinetic parameters to be optimized.

\[
r_1 = \frac{k_1 b_{\text{co}} P_{\text{co}} P_{\text{H2}}^2}{(1 + b_{\text{co}} P_{\text{co}} + b_{\text{co}} P_{\text{co}} P_{\text{H2}})\left(P_{\text{H2}}^2 + b_{\text{co}} P_{\text{co}} + b_{\text{co}} P_{\text{co}} P_{\text{H2}}\right)}
\]

\[
r_2 = \frac{k_2 b_{\text{co}} P_{\text{co}} P_{\text{H2}}}{(1 + b_{\text{co}} P_{\text{co}} + b_{\text{co}} P_{\text{co}} P_{\text{H2}})\left(P_{\text{H2}}^2 + b_{\text{co}} P_{\text{co}} + b_{\text{co}} P_{\text{co}} P_{\text{H2}}\right)}
\]

\[
r_3 = \frac{k_3 b_{\text{co}} P_{\text{co}} P_{\text{H2}}}{(1 + b_{\text{co}} P_{\text{co}} + b_{\text{co}} P_{\text{co}} P_{\text{H2}})\left(P_{\text{H2}}^2 + b_{\text{co}} P_{\text{co}} + b_{\text{co}} P_{\text{co}} P_{\text{H2}}\right)}
\]

### Table 1

| RDS | Driving force |
|-----|--------------|
| A1 | \(k_{1}\)Co + Ha2 ⇌ \(k_{1}\)CoH3 + s2 | \(k_{1}\)CoH3 ⇌ \(k_{1}\)CoH3/pco2/k3 |
| A2 | \(k_{2}\)CoH3 + Ha2 ⇌ \(k_{2}\)H2 + CoH3 + s2 | \(k_{2}\)H2 + CoH3 ⇌ \(k_{2}\)H2/pco2/k3 |
| A3 | \(k_{3}\)H2 + CoH3 ⇌ \(k_{3}\)H2 + CoH3/pco2/k3 |
| A4 | \(k_{4}\)CoH3 + Ha2 ⇌ \(k_{4}\)CoH3 + s2 | \(k_{4}\)CoH3 + s2 |
| B1 | \(k_{5}\)CoH3 + Ha2 ⇌ \(k_{5}\)CoH3 + s2 | \(k_{5}\)CoH3 + s2 |
| B2 | \(k_{6}\)CoH3 + Ha2 ⇌ \(k_{6}\)H2 + CoH3 + s2 | \(k_{6}\)H2 + CoH3 + s2 |
| C1 | \(k_{7}\)CoH3 + Ha2 ⇌ \(k_{7}\)CoH3 + s2 | \(k_{7}\)CoH3 + s2 |
| C2 | \(k_{8}\)CoH3 + Ha2 ⇌ \(k_{8}\)CoH3 + s2 | \(k_{8}\)CoH3 + s2 |
| C3 | \(k_{9}\)CoH3 + Ha2 ⇌ \(k_{9}\)CoH3 + s2 | \(k_{9}\)CoH3 + s2 |
| C4 | \(k_{10}\)CoH3 + Ha2 ⇌ \(k_{10}\)CoH3 + s2 | \(k_{10}\)CoH3 + s2 |

\[\text{Φ}_\text{r} = \frac{1}{2} \left(1 - \frac{\text{c}_\text{r}}{\text{c}_\text{r}}\right)\]

\[\text{c}_\text{r} = 1 - \sqrt{\frac{K_{\text{pco2/pco2,co2}}}{K_{\text{pco2/pco2,co2}}}}\]

\[K_{\text{i}} = \exp\left(\frac{\Delta G_{\text{i}}}{RT}\right)\]
Table 2

| RDS | Driving force |
|-----|---------------|
| 2: CO$_2$ + 2 H + ⊙ → HCO$_2$ + ⊙ | $r_1 = k_{t,ppOH_{p}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 3: HCO$_2$ + H + ⊙ → HCOOH + 2 ⊙ | $r_1 = k_{t,ppOH_{p}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 4: HCOOH + ⊙ → HCO + OH ⊙ | $r_1 = k_{t,ppOH_{p}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 5: HCO + H + ⊙ + H$_2$CO + ⊙ | $r_1 = k_{t,ppOH_{p}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 6: H$_2$CO + H + ⊙ → HCO + ⊙ | $r_1 = k_{t,ppOH_{p}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 7: H$_2$CO + H + ⊙ → CH$_3$OH + ⊙ | $r_1 = k_{t,ppOH_{p}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 11: CO$_2$ + ⊙ → CO$_2$ ⊙ | $r_2 = k_{g,ppCO_{2}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 12: CO + ⊙ + ⊙ → CO ⊙ + O ⊙ | Equal to 11 |
| 13: CO + ⊙ → CO ⊙ | $r_2 = k_{g,ppCO}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 14: CO$_2$ + ⊙ + ⊙ → COOH + ⊙ + ⊙ | Equal to 11 |
| 15: COOH + ⊙ + ⊙ + ⊙ → OH ⊙ | $r_2 = k_{g,ppCO_{2}}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 16: CO$_2$ + ⊙ + ⊙ → CO + ⊙ | $r_2 = k_{g,ppCO}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |
| 17: CO + ⊙ + ⊙ → CO ⊙ + O ⊙ | Equal to 11 |
| 18: COOH + ⊙ + ⊙ → CO + ⊙ | $r_2 = k_{g,ppCO}$ (1 $\frac{P_{CO_2} P_{pOH_{p}}}{P_{CO_2} P_{pOH_{p}}}^{a}$) $\eta^{2}$ |

\[ \theta = \left( \frac{b_h p_{H_2}^{0.5} + b_{H_2} 0.5 p_{H_2} + p_{CH_2} + p_{OH}}{FWHM\cos(\theta)} \right)^{1/2} \tag{26} \]

3. Experimental

3.1. Catalyst synthesis and characterization

The Cu-Ce-Zr mixed oxides catalyst was prepared with a CuO loading of 50 wt%, to be comparable to the benchmark formulation, and a CeO$_2$:ZrO$_2$ mass fraction of 1, as recently optimized by Shi et al. [49]. The catalyst was synthesized via the gel-oxide coprecipitation method [27]. The required amount of metal nitrate precursors (i.e., Cu(NO$_3$)$_2$·2H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, and ZrO(NO$_3$)$_2$·6H$_2$O) were solubilized in ethanol and coprecipitated by adding an oxalic acid solution (20 wt% excess) dropwise, at room temperature and under continuous stirring. The precipitate was stirred for 3 h, aged overnight, centrifuged and washed with deionized water, dried at 95°C for 16 h and calcined at 450 °C for 4 h. The catalyst was pelletized, crushed and sieved to produce 50–125 µm particle size, to be used for the characterization techniques and reaction tests. The chemical composition of the synthesized catalyst was measured via microwave plasma atomic emission spectroscopy, using an Agilent MP-AES 4200 elemental analyzer. Prior to the analysis, about 0.1 g of catalyst sample was digested in 70 v.% HNO$_3$ solution at 80 °C overnight and then diluted with 5 v.% HNO$_3$ solution (i.e., blank solution), to reach ppm values of the metal content. The specific surface area (S.A.) and pore volume (P.V.) were determined via the BET and BJH elaboration of the N$_2$ adsorption-desorption isotherms at -196 °C, obtained using a Micromeritics ASAP 2020 gas adsorption device. Before the measurement, the sample was degassed at 250 °C for 2 h. The catalyst reducibility was studied via temperature programmed reduction (TPR) analysis performed using a Micromeritics AutoChem 2020 equipment with a TCD detector. The analysis was carried out in the range 50–400 °C with a heating rate of 10 °C min$^{-1}$, feeding 50 mL min$^{-1}$ of a 10% H$_2$/Ar mixture. Prior to the TPR analysis, the sample was outgassed under inert conditions as for the N$_2$ physisorption.
10–40 bar, respectively, feeding H₂/CO₂/N₂ mixtures in different proportion, to have a H₂/CO₂ molar ratio from 3 to 7, and a GHSV ranging from 7500 to 24000 NL·kg⁻¹·h⁻¹. The carbon balance in the reaction was respected with a maximum error of 3%. The catalyst stability was observed within a long-term (100 h) test performed at 250 °C, 30 bar, H₂:CO₂ molar ratio of 3 and a GHSV of 9600 NL·kg⁻¹·h⁻¹. The CO₂ conversion (X_CO₂), product yield (Y_i), product space time yield (STY) and product selectivity (S_i) were calculated according to Eqs. 30–33, where i is either methanol or CO and w_cat is the catalyst weight. Methanol and CO where detected as the sole carbon species in the product mixture.

\[
X_{CO_2} = \frac{F_{CO_2}^{\text{in}} - F_{CO_2}^{\text{out}}}{F_{CO_2}^{\text{in}}} \tag{30}
\]

\[
Y_i = \frac{F_i^{\text{out}}}{F_{CO_2}^{\text{in}}} \tag{31}
\]

\[
STY_i = \frac{F_i^{\text{out}}}{w_{\text{cat}}} \tag{32}
\]

\[
S_i = Y_i \cdot X_{CO_2} \tag{33}
\]

A commercial Cu/ZnO/Al₂O₃ catalyst from Johnson Matthey (i.e. Katako-S1) was tested in the exact same conditions, to compare the novel catalyst with the benchmark technology.

4. Modeling

4.1. Fitting procedure and model discrimination

The fitting procedure was carried out entirely in MATLAB R2019a. The kinetic parameters were determined via the fminsearch optimization procedure, based on the Nelder-Mead simplex algorithm [69], which minimizes an error objective function (OF) that we defined as the sum of the root mean square errors (RMSE) between the experimental and calculated molar fraction of the carbon containing species (i.e., CO₂, CO and methanol) as follows:

\[
RMSE_i = \sqrt{\frac{\sum_{j=1}^{N_{\text{data}}} (y_{i,j}^{\text{calc}} - y_{i,j}^{\text{exp}})^2}{N_{\text{data}}}} \tag{34}
\]

\[
OF = RMSE_{CO_2} + RMSE_{CO} + RMSE_{\text{methanol}} \tag{35}
\]

Where \(N_{\text{data}}\) is the number of experimental data used for the kinetic fitting and \(y_{i,j}^{\text{calc}}\) and \(y_{i,j}^{\text{exp}}\) are the molar fractions of the component \(i\) at the exit of the catalytic bed determined experimentally and via the model prediction, respectively. The experimental data were imported in terms of \(y_{i,j}^{\text{exp}}\), together with the corresponding boundary conditions, such as inlet flow (\(F_i\)), inlet composition (\(y_j^{\text{in}}\)), temperature (T) and total pressure (P). On the other hand, the \(y_{i,j}^{\text{calc}}\) were determined, within the algorithm iterations, via the integral analysis method, thus solving the ODEs describing the mole balance equations in a fixed bed reactor (Eq. 36).

\[
\frac{dF_i}{dw_{\text{cat}}} = \sum_{j=1}^{N} (r_j) \tag{36}
\]

where \(F_i\) is the molar flow rate of the component \(i\), \(w_{\text{cat}}\) is the catalyst weight, \(N_r\) is the total number of the reactions involved, \(r_j\) is the stoichiometric number of the component \(i\) in the reaction \(j\), and \(r_j\) is the corresponding reaction rate expression, which is unknown. The mole balance equations were solved under the hypothesis of steady state regime, isothermal operation, negligible pressure drop along the catalytic bed and absence of internal diffusion and external mass transfer limitation. The first three hypothesis were confirmed experimentally: 1) the reaction performance was evaluated at steady state (i.e., when no changes in the outlet composition were recorder over time); 2) the temperature difference between the gas inlet and outlet positions was less than 1 °C and 3) the pressure difference between the gas inlet and outlet positions was less than 0.2 bar. The absence of mass transfer limitations was explored with preliminary experiments (details in S.I.) and was later confirmed with the Mear’s [70] and Weisz-Prater [71] testing criteria.

The reaction rates \(r_j\) are function of the partial pressure of the components, and parameters such as kinetic (\(k_j\)), adsorption (\(b_i\)) and equilibrium constants (\(K_j^{\text{eq}}\)). The equilibrium constants (Table 3) were retrieved from literature [72].

The kinetic constant of each reaction (\(k_j\)) and adsorption constants of the components (\(b_i\)) are the parameter to be optimized throughout the algorithm. The kinetic constants were described as a function of a pre-exponential factor and an activation energy, following the Arrhenius’

| Table 3 | Equilibrium constant of all the reactions as a function of temperature [72]. |
|---|---|
| Equilibrium constant | Expression | Units |
| \(K_1^{\text{eq}}\) | \(\log_{10} K_1 = \frac{-2066}{T} - 10.592\) | \(\text{bar}^{-2}\) with T in K |
| \(K_2^{\text{eq}}\) | \(\log_{10} K_2 = \frac{-2073}{T} + 2.029\) | dimensionless with T in K |
| \(K_3^{\text{eq}}\) | \(\log_{10} K_3 = \frac{-5139}{T} - 12.6291\) | \(\text{bar}^{-2}\) with T in K |
law (Eq. (37) [73]). The adsorption constants, instead, were expressed as a function of the standard entropy ($\Delta S^0_{\text{ads},i}$) and enthalpy of adsorption ($\Delta H^0_{\text{ads},i}$), according to the van’t Hoff equation (Eq. (38)). However, in some of the kinetic models considered in this study, the dependency on the temperature of the adsorption constants is neglected (i.e., $\Delta H^0_{\text{ads},i} \approx RT$) [5666]. Furthermore, to reduce the number of fitting parameters, some authors lumped the adsorption constants of some components together.

$$k_i = k_0 \exp \left( \frac{E_{\text{act},i}}{RT} \right)$$  (37)

$$b_i = \exp \left( \frac{\Delta S^0_{\text{ads},i}}{R} \right) \exp \left( - \frac{\Delta H^0_{\text{ads},i}}{RT} \right)$$  (38)

The selected algorithm (fminsearch) requires an initial guess for the fitting parameters. Kinetic constant found in literature for the Cu-Zn-Al catalyst were implemented as initial guess, assuming these are likely of similar order of magnitude that the corresponding for our Cu-Ce-Zr catalyst [5513]. This minimizes the strong dependence that the algorithm has on the initial guess itself, and therefore increases the probability of obtaining meaningful results. To increase robustness of the model results, we setup a routine that evaluated the sensitivity of the model to the initial guess. This procedure consists of running the optimization algorithm in a loop, with newly obtained results as the initial guess. Thus, the convergence was reached when the difference between the algorithm output and the initial guess was less than 1%. Once the parameters of the best fit were obtained, the covariance matrix was computed with a second algorithm based on Levenberg-Marquardt method (lsqnonlin). From the covariance matrix, the standard deviation and the 95% confidence intervals, first indicators of the quality of the fit, were determined using the nlparci function in MATLAB. However, model discrimination techniques were necessary to find the set of rate expressions that best describe our system and, therefore, to gain insight into the reaction mechanism. A model was discarded at first when the physicochemical constraints (Table 4) were not respected. Thereafter, the significance of the model was assessed via the comparison of the analysis of the variance (Eq. (41), i.e., probability that the data belong to the non-critical area of the Fisher distribution), assuming 95% level of confidence (i.e., $a = 0.05$). The $F_{\text{statistic}}$ was first calculated according to Eq. 39, where $s_1^2$ is the variance of the lack of fit and $s_2^2$ is the variance of the experimental error. The $F_{\text{critical}}$ was retrieved from the Fisher distribution tables, considering $N_{\text{var}}$ and $(N_{\text{data}} - N_{\text{var}})$ as degree of freedom, where $N_{\text{var}}$ is the number of variables (parameters). The $F_{\text{statistic}}$ was then compared to the $F_{\text{critical}}$ (F-test, Eq. (40)).

$$F_{\text{statistic}} = \frac{s_1^2}{s_2^2}$$  (39)

$$F_{\text{statistic}} < F_{\text{critical}} = F_{(1-a)}(N_{\text{var}}; N_{\text{data}} - N_{\text{var}})$$  (40)

$$p > a$$  (41)

As a result, the kinetic models fulfilling the physicochemical constraints were evaluated according to: 1) the value of the objective function, 2) the parity plots of the experimental and calculated flow rates of the carbon species, and 3) the outcome of the F-test and $p$-value.

### 4.2. Testing criteria for mass transfer limitation

The absence of mass transfer (MT) limitations was evaluated according to the criteria reported in Table 5, where the Carberry (C) and the second Damkohler number ($D_{\text{DA}}$) are defined per component. The order of reaction with respect to the component ($n_i$) was estimated with Eq. 42, where $r^*_i$ is its forward reaction rate [74]. Such derivation is specifically defined for complex reaction rates equation such as a LHHW kinetic. The correlations used for the mass transfer coefficient ($k_g$) and the effective diffusivity ($D_e$) are reported in SI.

$$n_i = p \frac{\partial \ln(r^*_i)}{\partial \ln(p)}$$  (42)

### 5. Results

#### 5.1. Catalyst properties and reaction performance

Table 6 summarizes the main physical properties of the Cu/CoO/ZrO$_2$ catalyst. The textural properties of the catalyst are in line with the literature [49,50]. The $N_2$ physisorption analysis revealed an isotherm of type IV with hysteresis (Figure S1), which is typical of a mesoporous material (i.e., pores in the range of 2–50 nm). The TPR profile (Figure S4a) exhibits two peaks at 204 °C and 231 °C, after deconvolution. No further reduction of the support, due to H$_2$ spillover, was measured. As a result, a reduction temperature of 250 °C is believed to be sufficient to reduce all the CuO, prior to the reaction tests. The XRD spectra on the calcined and reduced catalyst (Figure S2) show the typical diffraction peaks of CuO at 2θ of 35.5° and 38.7° and of Cu at 2θ of 43.3° and 50.4°, respectively. The disappearance of the CuO peak in the XRD spectrum of the reduced sample (Figure S2b) does not necessarily indicate the presence of sole metallic Cu, as CuO crystals smaller than 3–5 nm cannot be detected, as well as the Cu that is in contact with the Ce-Zr phases via O-bridges. The more complex Ce-Zr oxide phase was analyzed via XPS (Figure S3). We confirmed the presence of the Ce$^{3+}$ valence, which is introduced by the zirconia phase, as reported elsewhere [49,50]. The CuCeZr catalyst of this study is characterized by a Cu$^{2+}$/Ce$^{3+}$ ratio of c.a. 3.53, which was calculated through the integration of the corresponding peaks of the XPS spectra. A detailed discussion on the XPS results is given in S.I. The catalyst composition according to the MP-AES method is 52 wt% of CuO, 22 wt% of CeO$_2$ and 26 wt% of ZrO$_2$. This composition is very close to the theoretical value, indication of the reliability of the synthesis method. In Fig. 2a the catalyst performance during CO$_2$ hydrogenation is compared to that of the benchmark formulation (i.e., the CuZnAl from JM). The CuCeZr catalyst shows a much higher methanol production compared to CO$_2$, with a crossover temperature (i.e., $T_{\text{CO2}}$) beyond which STY$_{CO}$ > STY$_{MeOH}$ of ca. 240 °C. On the contrary, the benchmark catalyst shows a STY$_{CO2}$ larger than STY$_{MeOH}$ over the entire temperature range. Since our catalyst formulation and preparation methods is a reproduction of previous works [49,50], we also compare the performance of this catalyst with that of the original reports by Shi et al., [49] (Fig. 2b). The catalyst synthesized in this work shows higher methanol yield with respect to the different formulations proposed by Shi et al., However, the physicochemical properties of our CuCeZr are further

### Table 4

| Parameter          | Physicochemical constraint |
|--------------------|-----------------------------|
| Pre-exponential factor, $k_0$ | $k_0 > 0$          |
| Activation energy, $E_{\text{act},i}$ | $E_{\text{act},i} > 0$          |
| Enthalpy of adsorption, $\Delta H^0_{\text{ads},i}$ | $\Delta H^0_{\text{ads},i} < 0$          |
| Entropy of adsorption, $\Delta S^0_{\text{ads},i}$ | $0 < \Delta S^0_{\text{ads},i} < S^0_i$          |

### Table 5

Testing criteria for the exclusion of internal (intraparticle) and external (gas-solid) mass transfer limitation.

| Criteria         | Formula-test | Type of MT excluded  |
|------------------|--------------|----------------------|
| Carberry’s [70]  | $C_a - \frac{r_{\text{obs},i} \cdot d_p}{2 \cdot \Delta S^0_{\text{ads},i}} < 0.15$ | External mass transfer |
| Weisz-Prater [71] | $\frac{D_{\text{DA},i}}{D_e} < 0.3$ | Internal diffusion |
Table 6

Physical properties of the Cu/CeO2/ZrO2 catalyst.

| Property                     | Value |
|------------------------------|-------|
| BET surface area, \( S_{BET} \) (m²·g⁻¹) | 79    |
| Pore volume, \( P/V \) (cm³·g⁻¹)         | 0.26  |
| Pore diameter, \( D_p \) (nm)          | 9.5   |
| Average Cu diameter, \( d_{Cu} \) (nm) | 10.4  |
| Surface-to-volume Cu diameter, \( d_{SV}^{Cu} \) (nm) | 11.6 |
| Cu dispersion, \( D_{Cu} \) (%)         | 8.56  |
| Cu specific surface area, \( S_{Cu} \) (m²·g⁻¹) | 58    |
| Catalyst apparent density, \( \rho_\text{app} \) (g·cm⁻³) | 7.53  |
| Catalyst porosity, \( \varepsilon_\text{cat} \) (m³·m⁻³) | 0.66  |
| Catalyst apparent density, \( \rho_{\text{Capp}} \) (g·cm⁻³) ** | 2.56  |

* Determined via XRD; **Include the solid porosity.

improved with the calcination temperature (i.e., 450 °C), according to the optimization reported by Wang et al., [50]. Unfortunately, insufficient details on the results reported by Wang et al., made a direct comparison with our results unreliable. However, assuming a catalyst density of 2.56 g·cm⁻³ (i.e., value we measured), the STY\(_{\text{MeOH}}\) they obtained at the same conditions is ca. 6.6 mmol·h⁻¹·g⁻¹, which compares with the value reported in Fig. 2b. The agreement of our results with literature underline the credibility of the method. Furthermore, they emphasize the promising performance of the CuCeZr catalyst with respect to the benchmark technology, in view of the CO₂ valorization to methanol.

5.2. Model discrimination and proposed reaction mechanism

Table 7 reports the information required for the model discrimination procedure, as discussed in Section 4.1. The rate determining step analysis (RDS) is carried out only when the author(s) reported the details behind the model derivations (i.e., Graaf and Slotboom). The discrimination between the different options proposed by Graaf and Slotboom is reported in S.I. and is based on the same criteria shown here. Both the models developed by Park and Seidel did not fulfill all the physicochemical constraints, thus, the statistics analysis was not carried out. It is worth noticing that all the models which do not consider the formation of methanol from CO (reaction 3), resulted in a low \( p\text{-MeOH} \) (i.e., \( p \)-value for methanol) which indicates the tendency of the model towards a scarce prediction of the methanol outlet molar fraction. This result anticipates the importance of considering the contribution of both CO and CO₂ to the methanol synthesis, especially when CO₂ is the sole carbon source.

The model with the lowest RMSE (which corresponds to the final value of the objective function) and the largest \( p \)-values for the carbon species is the one proposed by Graaf. As a result, we select this model (Graaf-A₂B₂C₃, where \( A_2B_2C_3 \) refer to the specific combination of RDS) to be the most representative of our system. The kinetic parameters obtained from the fitting procedure are provided in Table 8. The accuracy of the parameter estimation is represented by the parity plots of \( \text{CO}_2, \text{H}_2 \) and methanol (Fig. 3). The orders of magnitude of all the parameters are in line with the literature, especially when compared to the values retrieved from Graaf et al. Nevertheless, given the differences in the reaction rate expressions (i.e., \( A_2B_2C_3 \) for our CuCeZr catalyst versus the \( A_2B_2C_3 \) for the CuZnAl reported by Graaf), the comparison between the two kinetic models – and catalyst – is fair when observed in terms of reaction rates, rather than kinetic constants. Such analysis is addressed in Section 5.5. On the other hand, the adsorption term corresponding to the first and second active sites (i.e., \( \Theta_1 \) and \( \Theta_2 \), respectively) do not differ from the original model. Therefore, in Table 9 we compare the values of our adsorption constants to the same constants.

Table 7

Comparison of the kinetic models reparametrized for the CuCeZr catalyst.

| Property | BF [59] | Graaf [58] | Henkel [54] | Park [65] | Seidel [56] | Slotboom [66] |
|----------|---------|------------|-------------|-----------|-------------|---------------|
| RDS      | ✓ ✓ ✓ ✓ | ✓ ✓ ✓ ✓ ✓ ✓ | ✓ ✓ ✓ ✓ ✓ ✓ | ✓ ✓ ✓ ✓ | ✓ ✓ ✓ ✓ ✓ ✓ | ✓ ✓ ✓ ✓ ✓ ✓ |
| RMSE     | 1.684   | 1.512      | 1.541       | 1.650     | 1.030       | 1.720         |
| \( V_{\text{max}} \) | 0.5419 | 0.2450 | 0.2871 | – | – | 0.4344 |
| \( V_{\text{oral}} \) | 1.993 | 1.917 | 1.993 | – | – | 2.254 |
| \( p\text{-CO} \) | 0.9761 | 0.9035 | 0.8919 | – | – | 0.9826 |
| \( p\text{-MeOH} \) | 0.5157 | 0.9601 | 0.9453 | – | – | 0.4903 |

* The result of the Rate-Determining-Step (RDS) analysis is reported for the models which provided such tool, as described in section 3.
** Physicochemical constraints: if not fulfilled, statistics analysis is not carried out.

Fig. 2. Methanol (MeOH) and CO space time yield (STY) as a function of temperature for the CuCeZr and the benchmark CuZnAl catalyst (a) and comparison of the methanol space time yield (STY\(_{\text{MeOH}}\)) at 250 °C with the performance of CuCeZr retrieved from literature [49] (b). Other experimental conditions: total pressure of 30 bar, H₂:CO₂ molar ratio of 3.
Kinetic parameters for the Graaf model (A_1B_1C_1). The adsorption constants b_i need to be calculated according to Eq. 13, considering $b_i = \exp\left(\Delta S_{ads}^i/R\right)$.

| Kinetic parameter | Value                        | Units          |
|-------------------|------------------------------|----------------|
| $k_{10}$          | $(7.103 \pm 0.351) \times 10^{-1}$ | mol kg\(^{-1}\) s\(^{-1}\) bar\(^{-2.5}\) |
| $k_{20}$          | $(2.765 \pm 0.118) \times 10^{1}$ | mol kg\(^{-1}\) s\(^{-1}\) bar\(^{-1.5}\) |
| $k_{30}$          | $(1.416 \pm 0.097) \times 10^{2}$ | mol kg\(^{-1}\) s\(^{-1}\) bar\(^{-2.5}\) |
| $E_{a1}$          | $(3.378 \pm 0.224) \times 10^{4}$ | kJ mol\(^{-1}\) |
| $E_{a2}$          | $(1.342 \pm 0.089) \times 10^{5}$ | kJ mol\(^{-1}\) |
| $E_{a3}$          | $(1.204 \pm 0.094) \times 10^{5}$ | kJ mol\(^{-1}\) |
| $b_{CO,0}$        | $(6.173 \pm 0.327) \times 10^{-7}$ | bar\(^{-1}\) |
| $\Delta H_{ads,CO}$ | $–(5.668 \pm 0.451) \times 10^{4}$ | J mol\(^{-1}\) |
| $b_{CO,0}$        | $(3.561 \pm 0.296) \times 10^{-3}$ | bar\(^{-1}\) |
| $\Delta H_{ads,CO}$ | $–(8.438 \pm 0.364) \times 10^{3}$ | J mol\(^{-1}\) |
| $b_{H_2,O,H_2}$   | $(3.521 \pm 0.511) \times 10^{-12}$ | bar\(^{-0.5}\) |
| $\Delta H_{ads,H_2,O,H_2}$ | $–(1.242 \pm 0.105) \times 10^{3}$ | J mol\(^{-1}\) |

1 Parameters to determine the combined adsorption constant of H\(_2\)O and H\(_2\) ($b_{H_2,O}/\sqrt{b_{H_2}}$).

calculated by Graaf at 200 and 260 °C. From the reaction rate expressions (Eq. 6–10), we see that the adsorption constants of CO\(_2\) and CO contribute also to the driving force (i.e., numerator of the reaction rate). As a result, the prediction of their effect on the reaction rate is not straightforward. On the contrary, the combined adsorption of H\(_2\)O and H\(_2\) (i.e., $b_{H_2,O}/\sqrt{b_{H_2}}$) contributes only to the adsorption term in the denominator, hindering the reaction rate. Since our constant is order of magnitude higher than the one derived by Graaf, this leads to the conclusion that our catalyst is either more sensitive to water or to H\(_2\) adsorption.

The model discrimination allows us not only to identify a model which better predicts the performance of our catalyst, but, most importantly, to gain some insights into the reaction mechanism itself. According to the assumptions behind the model developed by Graaf.

Table 9
Comparison of the values of the adsorption constants obtained in this work and by Graaf at 200 and 260 °C.

| Adsorption constant | This work (200–260 °C) | Graaf (200–260 °C) |
|---------------------|-------------------------|--------------------|
| $b_{CO}$, bar\(^{-1}\) | $1.117 \pm 0.2207$ | $4.571 \pm 0.7823$ |
| $b_{CO}$, bar\(^{-1}\) | $(3.042 \pm 2.389) \times 10^{-2}$ | $3.171 \pm 0.8313$ |
| $b_{H_2,O}/\sqrt{b_{H_2}}$, bar\(^{-0.5}\) | $181.4 \pm 5.19$ | $(5.389 \pm 4.238) \times 10^{-8}$ |

Fig. 3. Parity plot representing the accuracy of the parameter estimation for the outlet flow rate of CO\(_2\) (a), CO (b), Methanol (c) and H\(_2\) (d). The corresponding experimental data points are reported in S.I.
et al., we can distinguish between two active centers in the structure of the CuCeZr catalyst, which is in agreement with what was hypothesized in literature [49]: 1) the metallic copper (i.e., Cu), where the dissociative adsorption of H₂ occurs and 2) the oxygen defects within the Ce/Zr interface, where the CO₂ molecule adsorbs and activates. The H species spill over towards the carbon atom of the activated CO₂ to begin a series of hydrogenation steps, known as “formate” route. The reaction pathway is sketched in Fig. 4. According to the formate path, methanol can be either synthesized directly from CO₂ (direct route) or indirectly from the CO produced via the rWGS reaction. The two routes overlap when the H₂CO intermediate forms, sharing the last two steps which then lead to the formation of methanol. However, at the point where the CO₂ (i.e., CO adsorbed) intermediates appears, an equilibrium between the adsorbed CO and the CO released to the gas phase explains a certain selectivity to CO. The relative contribution of CO and CO₂ to the methanol synthesis depends on different factors such as temperature, H₂ concentration and the distribution of the Cu⁹ active sites with respect to the oxygen vacancies. Nevertheless, for a fixed catalyst composition, only reaction conditions can affect the fraction of methanol produced via the direct and indirect paths. A detailed discussion on this aspect is given in Section 5.5.

In Fig. 4, the limiting steps of the three reactions are also marked. In particular, the slowest steps are the formation of the H₂CO₃, HCOO⁻, and H₂CO₂ intermediates for the reaction 1, 2 and 3, respectively. This result is in agreement with the in situ DRIFT studies carried out by Wang et al., [50], where the formation of the formate (i.e., HCOO⁻) through the first hydrogenation of the carbon atom is defined as “the slowest and key step”.

At this stage, being the reaction rate expressions determined, we could estimate the order of the reaction with respect to CO₂ (nCO₂) and evaluate the Ca and Dₐ₂ numbers. We observed that in our experimental conditions, nCO₂ ranges between 0.094 and 0.62. Furthermore, both the external mass transfer and internal diffusion limitation resulted to be negligible, being the maximum value of Ca and Dₐ₂ of 1.4×10⁻³ and 7.1×10⁻⁵, respectively. This result confirms our earlier conclusion that the experiments were carried out under kinetic regime.

5.3. Analysis of the catalyst performance: Experiments vs model prediction

In this section, we discuss the catalyst performance as a function of the reaction conditions explored both experimentally and via model predictions. Experimental points and simulation results are combined in the same graphs, to show at the same time the quality of the fit. A detailed analysis of the thermodynamic equilibrium is reported in S.I.. Furthermore, to underline the compatibility of our results with the adopted equilibrium constant, the catalyst performance as a function of temperature and pressure – both experimental and modeling data – are reported together with the corresponding thermodynamic limit in Figure S10.

First, from Fig. 5, we observe that the kinetic model (solid lines) describes accurately the experimental reaction performance (points), in terms of XCO (Fig. 5a), YMethOH (Fig. 5b) and YCO (Fig. 5c) as a function of the space velocity (GHSV) at various temperatures. As expected from a kinetically controlled system, the conversion decreases with the space velocity, being the contact time of the gases with the catalytic bed shorter. Furthermore, YMethOH and YCO show the same trend as XCO, leading to the conclusion that the contact time does not affect the product distribution in the range we explored. As a result, when employing a GHSV in the range 7500–24000 h⁻¹, the CO contribution to the formation of methanol appears instantaneously, so that CO does not require additional contact time to react with the adsorbed hydrogen. Indeed, if that was the case, we would have observed an optimum in YCO as a function of GHSV. Additionally, XCO₂, YMethOH and YCO all show a clear increase with temperature, resulting from the positive effect that temperature has on all the reaction rates. Finally, it is important to notice that at the lowest GHSV (Fig. S10), the catalyst performance approach the thermodynamic equilibrium only at 260 °C (i.e., highest reaction rate), where the thermodynamic value of XCO₂, YMethOH and YCO at 30 bar is 21.1 %, 8.04 % and 13.1 %, respectively. As a result, in the temperature region 200–260 °C XCO₂, YMethOH and YCO still displays an exponential increase with temperature (i.e., kinetic regime).

Fig. 6 displays the effect of temperature and total pressure on the CO yield (YMethOH) and CO yield (YCO). As anticipated from Fig. 5, temperature positively affects all the reactions, since the effect of kinetics (i.e., Arrhenius type) overcomes the thermodynamics. Besides, we observe that the effect of temperature on YMethOH (Fig. 6a) is more significant as total pressure increases (i.e., the increase in YMethOH from 200 to 260 °C is of 91% and 193% at 10 and 40 bar, respectively). On the contrary, YCO decreases with pressure and, at the same time, it keeps the same trend vs temperature, independently on the total pressure. As a result, the temperature of crossover shifts to higher values when pressure increases: at 10 bar the crossover occurs at c.a. 216 °C, while at 40 bar YMethOH > CO in the temperature region we explored (i.e., 200–260 °C).

In Fig. 6b the effect of total pressure in the range of 10–40 bar is underlined. YCO and YMethOH exhibit two opposite trends, and the effect becomes more significant at higher temperatures (i.e., faster increase/ decrease vs pressure). As discussed in section 4.2, methanol is formed via two parallel routes: 1) the direct one, which involves only reaction 1 and 2) the indirect one, which involves reaction 2 and 3, in series. As a result, when feeding only CO₂ and H₂ or, more generally, with CO₂-rich streams, the direct route is faster than the indirect, since the latter needs the formation of CO first (i.e., r₅ is negligible for low values of PCO₂). As soon as CO is formed, r₅ increases, causing an increase in methanol formation and, at the same time, a consumption of CO₂, which acts both
as a product and a reactant. Such an effect is more noticeable at greater temperatures, because of faster reactions (i.e., the effect of pressure anticipates).

Besides the effect of total pressure, a higher H$_2$ concentration in the feed (i.e., higher molar feed ratio H$_2$:CO$_2$) causes an increase in both $Y_{\text{MeOH}}$ and $Y_{\text{CO}}$ (Fig. 7a), independently of temperature. However, $Y_{\text{MeOH}}$
increases more than $Y_{\text{CO}}$, shifting again the crossover point towards higher temperatures. As shown in Fig. 7a, the model describes quite precisely the crossover point ($T_{\text{cross}}$). Therefore, we used the model to predict the reaction performance in a wider range of $H_2:CO_2$ (1–10). We found that $T_{\text{cross}}$ monotonically increases up to an asymptotic value of 258°C at around $H_2:CO_2$ of c.a. 7 (Fig. 7b). As a matter of fact, a higher $H_2$ concentration facilitates its adsorption on the active sites, increasing the surface concentration of $H_2$. As a result, as soon as CO forms, its hydrogenation is faster than its desorption to the gas phase, which enhances the indirect pathway once again (i.e., higher $Y_{\text{MeOH}}$). However, when all the active sites for $H_2$ adsorption (i.e., Cu) are saturated with $H_2$, a further increase in its partial pressure does not affect the reaction rates anymore.

5.4. Predictive capability of the kinetic model

Once defined the reaction rates, we tested the predictive capability of the model by using the model to calculate both $X_{\text{CO}_2}$ and $Y_{\text{MeOH}}$ and comparing those values to an independent set of experiments (i.e., experimental data not used for the kinetic fitting). The kinetic model predicts quite accurately the experimental points obtained at lower GHSV (i.e., 2880 NL·kg$^{-1}$·h$^{-1}$, last 4 points) and at lower pressure (i.e., 28 bar, first two points), with a maximum deviation of 2.1% and 2.2% for $X_{\text{CO}_2}$ and $Y_{\text{MeOH}}$, respectively (Fig. 8).

5.5. Analysis of the reaction rates: Role of CO and CO$_2$ hydrogenation

In this section, we analyse in more details the reaction rates and the relative contribution of the CO$_2$ and CO hydrogenation (i.e., direct and indirect pathway, respectively) to the methanol formation. First, we calculate the reaction rates at different temperatures, via a theoretical differential analysis (i.e., assuming conversion values lower than 5%) at 30 bar and $H_2:CO_2$ ratio of 3 (Fig. 9a). We observe that $r_1$ is the highest reaction rate at temperatures below c.a. 240°C. Therefore, at low temperatures, the CO$_2$ hydrogenation to methanol is the fastest reaction, being its activation energy the lowest (Table 8). However, $r_1$ is the only reaction rate showing an optimum in the temperature range we explored. It is clear indeed, that $r_1$ approaches the equilibrium as temperature increases, being its value very close to zero at 260°C. As a result, we observe here the two opposite effects of kinetics and thermodynamics of an exothermic reaction. On the contrary, $r_2$ and $r_3$ are

![Fig. 7. Methanol (solid lines with circles) and CO (dashed lines with stars) as a function of temperature at $H_2:CO_2 = 3$ (fr3, light blue lines) and $H_2:CO_2 = 6$ (fr6, red lines); markers and lines represent experimental points and simulation results, respectively (a). Temperature of crossover between methanol and CO yield ($T_{\text{cross}}$) as a function of the $H_2:CO_2$ molar ratio, as predicted by the kinetic model (b). Other experimental/modeling conditions: total pressure of 30 bar, GHSV of 9600 NL·kg$^{-1}$·h$^{-1}$.

![Fig. 8. Parity plot representing the validation of the kinetic model, reporting the predicted $X_{\text{CO}_2}$ vs the experimental $X_{\text{CO}_2}$ (a) and the predicted $Y_{\text{MeOH}}$ vs the experimental $Y_{\text{MeOH}}$ (b). The corresponding experimental data are reported in S.I. (Table S1).](image-url)
quite far from the equilibrium and both display the typical exponential behaviour of kinetically controlled reactions. In addition, reaction 2 and 3 proceed with similar velocities, with \( r_2 \) being slightly faster as temperature increases (i.e., \( r_2/r_3 = 1.1 \) at 260 °C). We clearly see that the two pathways for methanol formation behave differently with temperature. As a result, the relative contribution of CO\(_2\) and CO to methanol synthesis changes as temperature increases (Fig. 9b). At 200 °C, CO and CO\(_2\) contribute almost equally (i.e., 51.5% and 47.4% at 200 °C, respectively). As temperature increases, CO-to-MeOH and CO\(_2\)-to-MeOH exhibit opposite trends, with CO-to-MeOH reaching a value of c.a. 100% at 260 °C. This result reveals why methanol selectivity does not decay with temperature as fast as it does on the CuZnAl catalyst (Fig. 2a) and underlines the importance of designing a catalyst in such a way that CO adsorption is strong enough, to be able to proceed with the hydrogenation steps and form methanol, rather than desorb to the gas phase and contaminate the product stream.

In Fig. 10a, instead, we report the reaction rates as a function of the H\(_2\):CO\(_2\) molar ratio at 200 °C and 30 bar. All the reaction rates remarkably increase with the H\(_2\) concentration. In particular, when H\(_2\):CO\(_2\) goes from 1 to 10, \( r_1 \), \( r_2 \) and \( r_3 \) increase by ca. 30, 17 and 60%, respectively. As a matter of fact, all the direct reactions exhibit a positive order with respect to H\(_2\). However, expectedly, when the Cu\(^0\) active sites are saturated with H\(_2\), a further increase in the H\(_2\) concentration corresponds to a dilution of the carbon species, such as CO\(_2\) and CO, which also influence positively the reaction rates. This explains the slight decrease of the reaction rate (more noticeable for \( r_2 \) and \( r_3 \)) beyond H\(_2\):CO\(_2\) of c.a. 7, which is in agreement with the result reported in Fig. 7b. For completion, in Fig. 10b we also report the relative contribution of CO\(_2\)-to-MeOH and CO-to-MeOH crosses at H\(_2\):CO\(_2\) of c.a. 1.5, with CO showing the predominant contribution beyond the crossing point. This is a clear consequence of the influence that the H\(_2\):CO\(_2\) ratio has on the reaction rate. For H\(_2\):CO\(_2\) larger than 1.5, \( r_3 > r_1 \) and the contribution of CO surpasses that of CO\(_2\), following a trend which corresponds to the reaction rates \( r_3 \) and \( r_1 \), respectively.

To underline the potential of the CuCeZr catalyst, we propose here a comparison with the benchmark formulation (i.e., CuZnAl) in terms of reaction rates. First, the model derived by Graaf et al., was implemented and validated with the experimental results obtained for the CuZnAl catalyst (details on the validation are given in S.I.). Therefore, the kinetic model we adopted for such comparison is representative of the CuZnAl system and can be used for predictive studies. As depicted in Fig. 11a, the CO\(_2\) consumption rate (\(-r_{CO_2}\)) increases exponentially with temperature and it is quite similar for both catalysts, with the CuCeZr catalyst showing a slightly faster consumption. However, the CuCeZr catalyst
converts CO₂ more selectively to methanol – including both direct and indirect route – than the CuZnAl catalyst. As shown in Fig. 11b, methanol formation rate (r_{MeOH}) its higher for the CuCeZr and crosses with CO (r_{CO}) only at c.a. 256 °C. On the contrary, the CuZnAl shows a much faster production of CO than methanol over the entire temperature range, which indicates that the CO hydrogenation does not contribute significantly to the synthesis of methanol, being CO the main reaction product. This demonstrates that the CuCeZr catalyst allows for a delay in the selectivity decay with increasing temperature when compared to the benchmark. It is clear that, in principle, lower temperatures favour the methanol production over CO. On the contrary, a higher temperature would correspond to much faster reactions, requiring less amount of catalyst to achieve equilibrium. In the end, when the desired product – in this case methanol – comes from an exothermic reversible reaction, the choice of the optimal temperature lies on a trade-off between reaction performance and economics. However, it is clear that the CuCeZr would facilitate the conflict between the demand of higher performance and catalyst/reactor costs, since it allows to achieve higher methanol selectivity and faster CO₂/CO conversion at higher temperature, when compared to the benchmark formulation.

6. Conclusions

In this work, we investigate the kinetics of the CO₂ conversion to methanol over a Cu/CoO/ZrO₂ catalyst, which remarkably outperforms the conventional Cu/ZnO/Al₂O₃ in terms of methanol yield/selectivity. The cross-over temperature (i.e., T_{cross}, defined as the temperature above which the yield to CO exceeds that of methanol) increases up to 240 °C for the CuCeZr, while CuZnAl shows a higher selectivity to CO in the entire temperature range.

We analyse in detail the one-site, dual-site and three adsorption sites kinetic models, based on hypothesis retrieved from literature, and accordingly derived the kinetic parameters of all the models via an optimization algorithm based on the minimization of the RMSE (root mean square error). Physicochemical constraints and statistical indicators were used as tool for model discrimination. The best performing kinetic model (i.e., dual-site model of Graaf et al.,) suggests that the reaction mechanism proceeds via the adsorption of one of the oxygens of CO₂ on the oxygen vacancies of the CeO₂-ZrO₂ phase (i.e., 1st active site), while H₂ adsorbs and dissociate on the metallic copper (i.e., 2nd active site). The adsorbed hydrogen preferentially hydrogenates the carbon atom giving rise to the formate route. According to this mechanism, methanol can be formed either directly from CO₂, or indirectly from the CO produced via the RWGS. The resulting kinetic model (i.e., rate expressions and fitted parameters) predicts the experimental data quite accurately, particularly the cross-over temperature (i.e., the model predicts that T_{cross} stabilizes at 258 °C at around H₂/CO₂ of c.a. 7.) Further, analysis of the individual reaction rates and the relative contributions of CO₂ and CO to the methanol synthesis (i.e., COx-to-MeOH) reveal that CO₂ and CO contribute evenly at 30 bar, H₂/CO₂ of 3 and 200 °C (i.e., 51.5% and 47.4%, respectively), while the pathway CO-to-MeOH takes over at higher temperatures and/or higher H₂ concentration. For H₂/CO₂ above 1.5, the CO contribution is predominant and exhibits an optimum at c.a. H₂/CO₂ of 7 (at 30 bar and 200 °C), which likely corresponds to the saturation of the Cu⁰ sites. This analysis underlines the importance of the indirect CO hydrogenation pathway in the reaction mechanism.

In conclusion, these findings lead to a deeper understanding of the reaction mechanism of CO₂ hydrogenation to methanol on novel CuCeZr systems, and serve as basis for future research into this catalyst formulation. For example, a more hydrophobic surface (i.e., weaker H₂O adsorption and faster desorption from Cu⁰ sites) could lead to faster reaction rates and lower H₂ requirement in the feed. Furthermore catalyst modification that lead to stronger CO binding would facilitate CO hydrogenation and, thus increase the selectivity to methanol even at higher temperatures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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