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Atomic layer deposited zinc promoted copper catalysts for carbon dioxide hydrogenation to methanol: Influence of support

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ABSTRACT

Copper promoted with zinc is an active catalyst for carbon dioxide hydrogenation to methanol, a reaction relevant to carbon capture and utilization technologies. Previous work showed that inverse zinc-on-copper catalysts on zirconia supports, where zinc(II) is added via atomic layer deposition (ALD), are more active and selective in this reaction than copper-on-zinc catalysts on zirconia. This work continues exploring the inverse zinc-on-copper catalysts by varying the support, comparing zirconia support with alumina, titania and niobia, and with various combinations of the ceria-zirconia-lanthana mixed oxide family. Catalyst characterization was made with elemental analysis, temperature-programmed reduction, temperature-programmed desorption of carbon dioxide, nitrous oxide pulse titration, and transmission electron microscopy. Activity was measured in a fixed-bed flow reactor at 450–550 K. ALD of Zn(II) acetylacetonate gave a similar areal number density of ca. two zinc per square nanometer on all tested supports. Zinc promotion systematically increased the methanol production rate. Among the tested catalysts, the zinc-on-copper on zirconia support remained the most active, with other catalysts from the ceria-zirconia-lanthana mixed oxide family giving almost as good results.

1. Introduction

Converting carbon dioxide to methanol through reacting it with green hydrogen is among the potential methods of carbon dioxide capture and utilization (CCU), necessary for limiting the increase of atmospheric carbon dioxide levels and slowing down global warming [1]. In this exothermic reaction, one molecule of water is formed per reacted carbon dioxide molecule: $CO_2 + 3 H_2 \Rightarrow CH_3OH + H_2O$. Compared to the commercial process of methanol production from synthesis gas, carbon dioxide hydrogenation is more challenging due to a lower methanol equilibrium yield, and an increased product inhibition by water (generated from the CO_2 hydrogenation and the reverse water gas shift reactions) [2,3]. In addition, the formed water can accelerate catalyst deactivation through sintering. The traditional methanol production catalyst is copper on alumina, promoted with zinc [4–7]. Development

of catalysts for carbon dioxide hydrogenation that are resistant to deactivation in the presence of water is an active field of research, and zirconia has been recognized as a promising support for zinc-promoted copper catalysts [8–11].

Atomic layer deposition (ALD) is a catalyst preparation method with independent roots going back to the 1960s and 1970s [12–15], which has raised global interest especially in the past decade [16–20]. ALD is based on the repeated self-terminating (saturating and irreversible) reactions of at least two gaseous compounds on a solid surface [21–24], and it is a mainstream manufacturing technique in leading semiconductor devices [24]. ALD is regarded as a highly controlled catalyst preparation method that delivers uniform, reproducible catalyst preparation for nanoparticles (e.g. [25–28]), overcoatings (e.g. [29]) and single atoms (e.g. [18]) alike. The investment in ALD by the semiconductor industry benefits catalysis research as well: chemistry is at the

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core of ALD, and thanks to the ever-expanding semiconductor applications, new ALD reactants and processes are frequently discovered [30–33].

Zinc is among the metals frequently applied by ALD for catalysis [9, 34-38]. While the first catalysis ALD experiments in the end of 1980s used elemental zinc [34], the most commonly used ALD zinc reactant in catalysis ALD has been diethylzinc [35-38]. Diethylzinc is pyrophoric and requires handling in inert atmosphere. In recent work related to the current study, a new solid zinc reactant, Zn(II) acetylacetonate, was introduced, which does not require inert handling [9,39]. We found that at reaction temperature of 473 K, irrespective of the calcination temperature of zirconia and the resulting specific surface area, Zn(II) acetylacetonate gave consistently as areal number density ca. two zinc atoms per square nanometer [39]. Zinc-promoted copper catalysts on zirconia support were then made, varying the order of adding copper by impregnation and zinc by ALD, and tested for activity in carbon dioxide hydrogenation to methanol [9]. The most active catalysts were those, where zinc was added by ALD after impregnation of copper, as an in inverse zinc-on-copper catalyst [9].

This work continues earlier research [9], investigating whether the high activity observed for inverse zinc-on-copper catalysts on zirconia could be further increased by using other support materials instead of zirconia. Mesoporous supports of various types were used in addition to zirconia: γ -alumina, which is the traditional CO₂ hydrogenation catalyst support; titania and niobia, which are known for their reducible properties; and various combinations of the ceria-zirconia-lanthana family of supports. Copper was added by impregnation and zinc by ALD. The target was to have a 2:1 at. ratio for copper and zinc. The targeted areal loading was the same for all catalysts, defined by the ALD process for zinc.

2. Material and methods

2.1. Catalyst preparation

2.1.1. Supports

A total of seven supports were used in this study: monoclinic zirconia (ZrO₂, SZ 31164) was provided by Saint-Gobain NorPro as cylindrical extrudates (length 5 mm, diameter 3 mm); the mixed oxides 17ceria-zirconia (17 %CeO2-ZrO2, XZO1289), 25ceria-zirconia (25 %CeO2-ZrO2, XZO1290) and ceria-zirconia-lanthana (5 %La₂O₃-17 %CeO₂-ZrO₂, XZO1291) were provided by MEL Chemicals as powders; γ -alumina was provided by SASOL (γ -Al₂O₃, Puralox NWa-155) as particles ($d_{50} =$ 300 µm); anatase titania was provided by Alfa-Aesar (TiO2, CAS: 1317-70-0) as powder; and the niobia support was provided by Companhia Brasileira de Metalurgia e Mineração (CBMM) (Nb₂O₅, HY-340) as powder. A particle size of 250-420 µm was selected as optimal for the preparation of catalysts and, therefore, supports provided as powders were pelletized, crushed, and sieved, while extrudates were crushed and sieved to the desired particle size. The supports were then calcined in a muffle furnace (Nabertherm P330) under static air conditions at 773 K for 5 hours to remove impurities, prior to their use.

The porous properties of the different supports were analysed by nitrogen physisorption (77 K, liquid nitrogen) in a Thermo Scientific SURFER equipment. Approximately 200 mg of a calcined support was loaded to the equipment and degassed at 350°C (heating rate of 5°C/min) for 3 h before physisorption, except for niobia, degassing temperature of 150°C was used. The specific surface area (m² g⁻¹) and pore size distribution were calculated using Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively. The specific surface area, pore volume, and median pore diameter of each support are listed in Table 1. The specific surface area values varied from ~160 m²g⁻¹ for alumina to ~40 m²g⁻¹ for niobia. All supports were mesoporous, with the median pore diameter on the order of 10 nm.

Table 1

Nitrogen physisorption analysis of specific surface area, total pore volume, and median pore diameter of the supports, all calcined at 773 K (500 °C).

Code	Support	BET specific surface area (m^2g^{-1})	Pore volume (cm ³ g ⁻¹)	Median pore diameter (nm)
Zr	ZrO ₂	70	0.30	11.0
Al	γ -Al ₂ O ₃	158	0.54	9.1
Ti	TiO ₂	87	0.35	14.0
Nb	Nb ₂ O ₅	38	0.11	9.0
17CeZr	17 %CeO ₂ -ZrO ₂	89	0.19	7.2
25CeZr	25 %CeO2-ZrO2	104	0.26	9.8
CeZrLa	5 %La ₂ O ₃ -17 % CeO ₂ -ZrO ₂	98	0.25	12.0

2.1.2. Addition of Cu and Zn by impregnation and ALD

The supported zinc-copper samples were synthesized by following two methods. Copper was incorporated by the incipient wetness impregnation method (IWI), and zinc was added by ALD.

The copper and zinc precursors used were Cu nitrate trihydrate, Cu $(NO_3)_2$ ·3 H₂O (CAS: 10031–43–3, Sigma Aldrich, 99–104 % purity) and Zn(II) acetylacetonate, (Zn(acac)₂, CAS: 14024–63–6, Volatec). The targeted Cu:Zn atomic ratio was 2:1. One ALD cycle with Zn(acac)₂ was to be carried out, expected to give on average ~2 Zn/nm² [9,39], giving the areal number density target for copper as 4 Cu/nm². Noteworthily, because the areal number density targets were the same for all catalysts, but the specific surface areas of the supports different (Table 1), the catalysts would end up having significantly different weight-based Cu and Zn loadings.

Typically, the impregnation of copper started by dissolving the corresponding amount of Cu nitrate in the equal amount of deionized water needed to fill the pores of the supporting material. A known amount of dried support (393 K, overnight) was placed in an Erlenmeyer flask and approximately five drops of the solution were slowly added. Then, the flask was gently shaken for 2–3 minutes to ensure the homogenous distribution of the solution with the support. This step was repeated several times until the solution was completely incorporated into the supporting material. The impregnated support was then aged for 5 hours at room conditions and dried overnight at 393 K. The samples were finally calcined at 673 K for 2 h (5 K min⁻¹) in a tube furnace with a constant flow of synthetic air (100 mL min⁻¹, AGA 5.0 purity, 20 % O_2 , 80 % N_2).

For the deposition of Zn on the Cu/support samples by ALD, the procedure started by pretreating the calcined Cu/support (~2 g) in a flow-through fixed bed F-120 ALD reactor (ASM Microchemistry) at 523 K for 10 h to remove possible impurities before the actual ALD process and to ensure a successful deposition. Then, the solid zinc(II) acetylacetonate reactant (~0.5 g) was vaporized at 393 K in flowing nitrogen (100 sccm) and reacted with the pretreated sample at 473 K for 3 h, followed by a 2 h purge and cooling down. The pressure level in the ALD reactor was approximately 3–10 mbar (the fixed bed causes a pressure drop). After the addition of zinc, the sample was transferred to a tube furnace, where the reactant-originated acetylacetonate ligands were burned away by oxidative treatment. The sample was heated under synthetic air flow of 100 mL min⁻¹ with a ramp rate of 5 K/min to 773 K, where it was held for 2 h.

2.2. Catalyst characterization

2.2.1. Elemental analysis by ICP-OES

The copper and zinc loadings were analysed by inductively coupled plasma–optical emission spectroscopy (ICP–OES). The digestion method was developed further from [40]. About 0.05–0.1 g of sample powder was weighed into a Teflon bottle. Then 10 mL of H_2SO_4 acid (Sigma Aldrich, 99.999 %) and 5 mL of Milli-Q water were added. The bottle was sealed and placed into a microwave (Speedwave XPERT Microwave

Pressure Digestion System) to digest for 1 h with a maximum temperature of 463 K. The temperature and pressure were monitored with the help of the Berghof optical sensor system. After digestion, the sample was diluted to 50 mL with doubly distilled water. The sample was further diluted five times with distilled water. Measurements were conducted using the Agilent 5900 ICP SVDV system. The multi-element standard solution (Sigma Andrich, Germany, product code 1.11355) was used at 0–50 ppm concentrations during the measurement.

The weight percentages obtained from ICP-OES were converted to areal number density (metal atoms per square nanometre of catalyst, nm⁻²) using the specific surface are measured for the support $S (m^2 g^{-1})$ and molar mass M (g mol⁻¹) of the respective elements. In this calculation, it was assumed (as described in Eq. 25 of Ref. [22]) that the specific surface area of the sample decreases proportionally to the added mass of the catalyst preparation from the value measured for the support (m² g⁻¹_{sup}). ICP-OES analysis was made for catalyst in the oxidized state, so copper was assumed as CuO and zinc as ZnO. Note that areal number density represents an average value: all metal atoms are counted, whether they are on the outermost surface and accessible to catalysis.

2.2.2. Temperature-programmed reduction with H_2 (H_2 -TPR)

The reducibility of the Cu/support and the Zn/Cu/support samples were analysed with temperature programmed reduction of hydrogen (H2-TPR). Altamira (AMI-200) instrument was used, equipped with a thermal conductivity detector (TCD) and OmnistarTM mass spectrometer (MS) by Pfeiffer vacuum. Approximately 100 mg of the sample was placed in a U-tube quartz reactor. Prior to reduction with hydrogen, the sample was treated under a constant flow of 50 mL min⁻¹ (STP) of He (AGA 99.9999 % purity) at 473 K for 60 min to remove any impurities present on the surface. After He treatment, the sample was cooled down to 303 K with Ar flow (AGA 99.9999 % purity) at 50 mL min⁻¹. Finally, reduction was performed with 50 mL min⁻¹ flow of 2 % H₂/Ar (AGA 99.9999 % purity) with sample heated from 303 K to 1073 K at a heating rate of 5 K min⁻¹. Analysis was made with the MS, following the m/zsignals at 2 (H₂), 4 (He), 18 (H₂O), 32 (O₂), and 40 (Ar). Calibration of the signals was not made, meaning that the information obtained from H₂-TPR was merely semiquantitative.

2.2.3. Temperature programmed desorption of CO₂ (CO₂-TPD)

The interaction of carbon dioxide with the Cu/support and Zn/Cu/ support samples was investigated with temperature-programmed desorption of CO₂ (CO₂-TPD). The experiments were performed on Altamira (AMI-200) instrument equipped with a TCD and OmnistarTM MS by Pfeiffer vacuum. Mass spectrometer was used for the gas phase analysis. Approximately 100 mg of catalyst was placed in a U-tube quartz reactor. The catalyst was then treated under the He atmosphere flowing at 50 mL min⁻¹ (STP) at 473 K for 2 h, and then cooled back to 303 K. Then the metal oxide catalysts were reduced with constant flow of 2 % H_2 /Ar (AGA 99.9999 % purity) flowing at the rate of 50 mL min⁻¹ from 303 K to 623 K at heating rate of 10 K min⁻¹, with hold time of 1 h. The reduced catalyst was cooled to 323 K and then saturated with 0.5 %CO2/He for 1 h. The saturated sample was flushed with a flow of He (AGA 99.9999 % purity) for 1 h to remove any physisorbed CO₂. Finally, CO_2 was desorbed from 323 K to 1073 K at the heating rate of 10 K min $^{-1}$ under the flow of He (AGA 99.9999 % purity) at 50 mL min⁻¹. The MS signals were followed at m/z 44 for CO₂ and m/z 4 for He. The amount of CO₂ desorbed was quantified using a single-point calibration method, as described by Verkama et al. [41].

2.2.4. N_2O pulse titration

Copper surface area and dispersion were analysed with N_2O pulse titration in an AutoChem-III 2930 tool (Micromeritics Instrument Corporation) equipped with an external CirrusTM 3 mass spectrometer (MS; MKS Instruments). The analysis began by placing c.a. 100 mg of the sample in a U-shaped reactor. The sample was dried in He (Woikoski Oy,

99.995 %) under a flow rate of 50 mL min⁻¹ (STP) at 393 K for 60 minutes. The flow was then switched to Ar (Woikoski Oy, 99.999 %) at a flow rate of 50 mL min⁻¹ and cooled to 308 K. Then, the sample was reduced in a flow of 2 vol% H₂/Ar (50 mL min⁻¹) with a heating rate of 2 K min⁻¹ up to at 573 K, where reduction was continued for 30 min. After reduction, the sample was purged with He (50 mL min⁻¹) for 15 min at 573 K, followed by cooling to 333 K. Finally, N₂O pulse titration was carried out at 333 K by introducing 5 vol% N₂O/He pulses using a loop volume of 0.5185 mL which was kept at 383 K. Results were calculated from the N₂O signal at *m*/*z* of 44 followed with MS. An example of measurement data is shown in Figure S1 of the supporting information.

The cumulative quantity of volume adsorbed (V_{ads} , cm³g⁻¹ STP) was calculated in an automated way from peak areas by the AutoChem III Version 1.01 software. With input of the measured copper loading, and assuming copper atomic cross section a_{Cu} of 0.0680 nm² and density ρ_{Cu} of 8.96 g cm⁻³, the software also calculated the dispersion (D, %), metallic surface area A_{Cu} , and crystallite size d of copper assuming hemispherical particles. This calculation assumes stoichiometry of adsorption n of 2, corresponding to the surface reaction N₂O (g) + 2 Cu (0) (s) \rightarrow N₂ (g) + Cu₂O (deep oxidation is assumed to be avoided at the chosen temperature [42]).

2.2.5. Transmission electron microscopy

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of pre-reduced samples (623 K, 60 min, 50 mL min⁻¹ (STP) of 2 vol% H₂/Ar) were acquired using a double aberration corrected, high-resolution JEOL JEM-2200FS microscope, operated at 200 kV acceleration voltage. Elemental mapping was carried out with an energy-dispersive X-ray spectroscopy (EDS) detector. The samples were drop-casted using acetone onto a gold grid coated with an ultrathin holey carbon film.

2.3. Activity measurements

The catalytic activity tests were made in a fixed bed high-pressure continuous-flow reactor, as described previously [9]. One gram of catalyst was placed inside a stainless-steel tubular reactor (internal diameter: 15 mm, height: 40 cm), with a mesh positioned at the middle of the reactor to support the catalyst. Before the reaction, the catalyst was subjected to in-situ reduction at 623 K and 0.1 MPa for a duration of 60 min, using a continuous flow 5.0 L h^{-1} (STP) of 10 vol% H₂/N₂ (H₂: AGA 99.999 % purity, N₂: AGA 99.999 % purity). After reduction, the temperature was reduced to 450 K and pressure was increased to 3.0 MPa in the same flow of 10 the vol% H₂/N₂ mixture. Once the reaction conditions were stabilized, the catalyst was exposed to a feed of $H_2/CO_2/N_2$ at the volumetric ratio of 71/23/6 (H₂: AGA 99.999 % purity, CO₂: AGA 99.999 % purity; N₂: AGA 99.999 % purity). The volumetric flow rates were 6.3 L h^{-1} for H_2, 2.0 L h^{-1} for CO_2, and 0.6 L h^{-1} for N₂ (STP). After a period of 90 min at 450 K, temperature was increased first to 500 K and then to 550 K, with a heating rate of $10~{\rm K~min^{-1}}$ and a stabilization time of 90 min between. The activity tests were under total pressure of 3.0 MPa, and a gas hourly space velocity (GHSV) of 7500 h^{-1} (STP). The volume of catalyst utilized in each experiment was approximately 1.2 10^{-3} L.

The gas products were analyzed using an Agilent Micro Gas Chromatograph (microGC) equipped with a thermal conductivity detector (TCD) connected in line with the reactor. A gas sample from the gas product stream was automatically injected every ~3.7 min. The microGC consisted of two columns: (i) MS-5 molecular sieve column for the detection of permanent gases such as H₂, N₂, CH₄ and CO and, (ii) PoraPLOT U column for the detection of CO₂, CH₃OH and H₂O. The N₂ gas was used as an internal standard. The following equations were employed to calculate the CO₂ conversion (X_{CO2} , Eq. (1)), product yield (Y_i , Eq. (2)), relative product selectivity (RS_i , Eq. 3) and the methanol production rate per gram of copper (MPR, Eq. (4)).

$$X_{\rm CO2}(\%) = -\frac{F_{\rm CO2,in} - F_{\rm CO2,out}}{F_{\rm CO2,in}} \times -100\%$$
 (1)

$$Y_i (\%) = \frac{F_{i, \text{ out}}}{F_{\text{CO2,in}}} \times 100 \%$$
(2)

$$RS_{i}(\%) = \frac{F_{i, \text{ out}}}{F_{\text{CH3OH,out}} + F_{\text{CO,out}} + F_{\text{CH4,out}}} \times 100\%$$
(3)

$$MPR(mmol h^{-1}g_{Cu}^{-1}) = \frac{F_{CH3OH,out}}{m_{Cu}}$$
(4)

Here, F_{CO2} is the molar flow rate of CO₂, F_i is the molar flow rate of product compounds (i = CO, CH₄, CH₃OH) and m_{Cu} is the mass of copper in the catalyst. The methanol production rate based on the catalyst mass (mmolh⁻¹g_{cat}⁻¹) was also used in this work. The inlet gas composition was estimated from the analysis of the inlet gas stream (by-passing the reactor prior each experiment). The average of the analysis results of typically 7 stable data points was used to estimate the inlet gas composition while for the outlet gas composition, 10–20 stable data points at each reaction temperature were taken. Time-on-stream (TOS) data is provided in the electronic supplementary info.

3. Results

3.1. Catalyst preparation and characterization

3.1.1. Elemental analysis

Summary of the catalysts of this study along with the ICP–OES elemental analysis results is shown in Table 2. The targeted loadings were reached reasonably well. The copper loading varies from 1.4 to 6.0 wt% and the zinc loading from 0.9 to 3.7 wt%. When the weight-based loadings were converted to areal number density, the results are closer to each other. The areal number density of copper was within $3.5-5.1 \text{ Cu/nm}^2$, and the areal number density of zinc within $1.9-2.4 \text{ Zn/nm}^2$. The Cu:Zn atomic ratio was in all cases close to the targeted value of two (ranging within 1.5-2.2).

3.1.2. H₂ TPR

The temperature-programmed reduction profiles of the oxidized Cu/

Table 2



Sample	Code	Cu, wt%	Zn, wt%	Cu/ nm ²	Zn/ nm ²	Cu: Zn
Cu/ZrO ₂	Cu/Zr	3.33	-	4.7	-	-
Zn/Cu/ZrO ₂	Zn/Cu/Zr	3.17	1.61	4.5	2.2	2.02
Cu/Al ₂ O ₃	Cu/Al	5.99	-	3.9	-	-
Zn/Cu/Al ₂ O ₃	Zn/Cu/Al	5.20	3.67	3.5	2.4	1.46
Cu/TiO ₂	Cu/Ti	4.40	-	5.1	-	-
Zn/Cu/TiO ₂	Zn/Cu/Ti	3.47	2.09	4.0	2.4	1.71
Cu/Nb ₂ O ₅	Cu/Nb	1.48	-	3.7	-	-
Zn/Cu/Nb2O5	Zn/Cu/	1.40	0.92	3.6	2.3	1.57
	Nb					
Cu/17 %CeO2-ZrO2	Cu/	4.20	-	4.7	-	-
	17CeZr					
Zn/Cu/17 %CeO2-	Zn/Cu/	3.69	1.75	4.2	1.9	2.17
ZrO ₂	17CeZr					
Cu/25 %CeO2-ZrO2	Cu/	4.39	-	4.2	-	-
	25CeZr					
Zn/Cu/25 %CeO2-	Zn/Cu/	4.12	2.16	4.1	2.1	1.96
ZrO ₂	25CeZr					
Cu/5 %La2O3-17 %	Cu/	4.13	-	4.2	-	-
CeO ₂ -ZrO ₂	CeZrLa					
Zn/Cu/5 %	Zn/Cu/	4.02	2.05	4.2	2.1	2.02
La2O3-17 %CeO2-	CeZrLa					
ZrO ₂						

support and Zn/Cu/support samples are shown in Fig. 1. On all samples, the TPR profiles present either at least two maxima or one broadened peak. Reduction starts mainly after 400 K and is completed by 550 K, after which copper is fully reduced [9,43]. The presence of multiple peaks suggests that the reduction of CuO is a multi-step process. The features may represent different oxidation states of copper species with varying degrees of interaction with the support. Catalysts with copper supported on titania, niobia and 25ceria-zirconia present reduction features also at higher temperatures. The addition of zinc on Cu/supports modifies merely slightly the reduction profile of catalysts supported on zirconia, 17ceria-zirconia and ceria-zirconia-lanthana. In the case of alumina, titania and niobia, the effect is stronger: the presence of zinc notably shifts the reduction of copper to higher temperatures.

3.1.3. CO2 TPD

Interaction of carbon dioxide with the reduced Cu/support and Zn/ Cu/support catalysts was studied with CO₂ TPD. The TPD profiles measured after adsorption at 323 K are shown in Fig. 2. The measured CO₂ adsorption capacity per gram of catalyst varied significantly, from 18 µmol/g_{cat} on Cu/niobia to 193 µmol/g_{cat} on Zn/Cu/ceria-zirconialanthana (Table 3). Addition of zinc increased the CO₂ adsorption capacity in all cases for Zn/Cu/support vs. Cu/support samples. Comparing the areal CO₂ adsorption capacity between the samples shows that most of the CO2 adsorption capacity variation was caused simply by variation of the surface area of the sample (Table 3). When examined per unit area, the smallest CO2 adsorption capacity values were obtained for alumina, titania and niobia; zirconia and 17ceria-zirconia had intermediate values; and 25ceria-zirconia and ceria-zirconialanthana had the highest values. Interestingly, when examining the CO₂-TPD profile, the features observed within 450-550 K, where catalyst testing was made, differed significantly between the catalysts. All catalysts of the zirconia-based mixed oxide family, pristine zirconia included, contained significant desorption features in this temperature range. In contrast, for alumina, titania and niobia the features were insignificant or nonexistent.

3.1.4. N₂O titration

Surface copper was analysed by N_2O pulse titration. The results are summarized in Table 4. According to N_2O titration, the amount of N_2O reacted varied from 0.04 to 60 µmol/g_{cab} dispersion of copper varied from 0.01 % to 12.7 %, the average amount of surface copper atoms



Fig. 1. H₂-TPR profiles of metal oxide supported Cu/support and ZnCu/support catalysts. (Data shifted vertically for clarity.).



Fig. 2. CO₂-TPD profiles of metal oxide supported Cu/support and ZnCu/support catalysts, after adsorption at 323 K. (Data shifted vertically for clarity.).

Table 3

 CO_2 TPD characterization results for Cu/support and Zn/Cu/support samples (CO_2 adsorption at 323 K).

Support	pport S _{BET} Cu/ support		Zn/Cu/ support	Cu/ support ^{a)}	Zn/Cu/ support ^{a)}	
	${m^2 \over g_{sup}^{-1}}$	μ mol CO ₂ $(g_{cat})^{-1}$	$\mu mol CO_2$ $(g_{cat})^{-1}$	$\rm CO_2 \ nm_{cat}^{-2}$	${\rm CO}_2{\rm nm}_{\rm cat}^{-2}$	
ZrO ₂	70	85	94	0.76	0.88	
Al_2O_3	158	60	65	0.25	0.29	
TiO ₂	87	50	65	0.37	0.50	
Nb ₂ O ₅	38	18	51	0.29	0.84	
17 %CeO2-ZrO2	89	93	107	0.66	0.79	
25 %CeO2-ZrO2	104	137	193	0.84	1.25	
5 %La ₂ O ₃ -17 % CeO ₂ -ZrO ₂	98	101	148	0.65	1.01	

^{a)} The average number of CO_2 molecules adsorbed per unit surface area of catalyst was estimated by assuming that BET surface area measured for the support decreases in the catalyst preparation proportionally to the added mass. CO_2 TPD measurements were made for reduced samples, so copper was assumed as Cu(0) and Zn as ZnO.

from 0.0005 to 0.65 Cu/nm², copper surface area from 0.003 to $5.0 \text{ m}^2 \text{g}_{cu}^{-1}$ and 0.09–82 m² g_{cu}^{-1}, and copper particle size from nanoparticles of less than 10 nm in diameter up to micrometer-sized particles. The highest dispersion and smallest particles were achieved on alumina, while the smallest dispersion and largest particles were obtained on titania. Whether the addition of zinc decreased or increased the copper surface area, depended on the support: on zirconia, 17ceriazirconia and ceria-zirconia-lanthana, the addition of zinc increased the surface area and dispersion, while on alumina, titania and 25ceria-zirconia, the effect was the opposite.

3.1.5. Transmission electron microscopy

Representative STEM images with EDS mapping of the Zn/Cu/support samples are shown in Fig. 3. Overall, zinc seems uniformly distributed on the surface of all supports and samples. As for copper, some clustering into particles seems visible in the EDS maps, consistent with the particle size analysis by N_2O pulse titration. Copper seems rather uniformly distributed in the nanoscale of TEM on pure zirconia and on supports composed of varied combinations of ceria-zirconialanthana. Copper particles are seen on alumina and niobia and especially on titania supports. On titania, copper-containing particles reaching in size beyond 30 nm is seen. There seems to be no correlation between the local Cu and Zn contents: on copper-containing particles, the amount of zinc seems to be the same as elsewhere.

3.2. Activity measurements

The catalytic activity results are summarized in two figures: Fig. 4 for conversion and methanol production rate, and Fig. 5 for relative selectivity. In Fig. 4, panels (a) and (b) show the CO_2 conversion obtained at different temperatures (450, 500, 550 K) with Cu/support and Zn/Cu/support catalysts, respectively. Panels (c) and (d) show the methanol production rate expressed per gram of catalyst for Cu/support and Zn/Cu/support catalysts, and panels (e) and (f) the methanol production rate per gram of copper for Cu/support and Zn/Cu/support catalysts. While production per gram of catalyst is a standard way to express activity and allows straightforward comparison with literature values, among the self-made catalysts, production per gram of copper may be a meaningful measure, because of the significantly different loadings of copper (from ~1–6 wt%, see Table 1).

With increasing temperature, both carbon dioxide conversion and methanol production rate increase, as expected (Fig. 4). The relative selectivity to methanol decreases with increasing temperature, while the relative selectivity to carbon monoxide concurrently increases (Fig. 5). Promotion with zinc in general increases both methanol production rate and selectivity to methanol. The highest relative methanol selectivity values are obtained at 450 K (of \sim 90 %). Increasing temperature increases conversion and methanol production rate, but selectivity decreases: 70 % is a typical value for relative methanol selectivity at 500 K, and 20 %-30 % is a characteristic value at 550 K. In terms of conversion, all catalysts except those supported on titania and niobia show a favorable activity. In terms of methanol production rate, the catalysts supported on the ceria-zirconia-lanthana mixed oxide family perform well, while alumina-supported catalysts show lower methanol production rate as it favors carbon monoxide formation more than other catalysts.

4. Discussion

4.1. Addition of zinc on the supports by ALD

In this work, zinc promoter was added on Cu/support catalysts using a method not so frequently applied in catalysis literature, ALD. The same ALD process was used, which has been recently developed for zirconia supports [9,39]. To prepare the catalyst series for this work, an initial prediction was made that the Zn(II) acetylacetonate reactant would behave in rather similar way on the different supports, in that the resulting areal number density of zinc would be similar, approximately two atoms per square nanometre.

The areal number density values of zinc were indeed quite similar on all samples (1.9–2.4 Zn/nm²), although the weight-based loadings varied (0.9–3.7 wt%). The variation in the weight-based loadings was caused by the variation of the specific surface areas of the supports (because of the different surface area values of the supports, from ~40 to ~160 m²g⁻¹). These results are in line with earlier findings, where a series of experiments was made with zirconia calcined at different temperatures and having significantly different specific surface area values [39]. While the weight-based loading obtained for after Zn(II) acetylacetonate reaction differed for the catalysts (ca. 0.5–2.5 wt%), when the areal number density of copper was calculated, it was similar in all cases, about two Zn/nm² [39].

Table 4

N₂O characterization results for Cu/support and Zn/Cu/support samples (N₂O titration at 333 K).

Sample	Cu wt%	V _{ads} N ₂ O	n _{ads} N ₂ O		D _{Cu} (%)	Surface Cu/nm ^{2 b)}	A _{cu}	$A_{ m Cu}$	d_{Cu}
		$cm^3 g_{cat}^{-1}$ (STP)	$\begin{array}{l} \mu mol \; N_2O \\ g_{cat}^{-1} \end{array}$	nm _{cat} ^{a-2)}			$m^2 g_{cat}^{-1}$	$m^2 \ g_{Cu}^{-1}$	nm
Cu/ZrO ₂	3.33	0.360	15.8	0.14	6.2 %	0.29	1.31	39.8	16.8
Zn/Cu/ZrO2 ⁽⁾	3.0 ^{c)}	0.613	27.0	0.24	11.6 %	0.53	2.24	74.6	9.0
Cu/Al ₂ O ₃	5.99	1.348	59.4	0.24	12.7 %	0.49	4.93	82.1	8.2
Zn/Cu/Al ₂ O ₃	5.20	0.942	41.5	0.18	10.3 %	0.36	3.44	66.2	10.1
Cu/TiO ₂	4.40	0.0013	0.057	0.0004	0.017 %	0.00086	0.0047	0.11	6213
Zn/Cu/TiO ₂	3.47	0.00083	0.036	0.0003	0.013 %	0.00053	0.0030	0.086	7751
Cu/17 %CeO2-ZrO2	4.20	0.495	21.8	0.15	6.7 %	0.32	1.81	43.1	15.5
Zn/Cu/17 %CeO2-ZrO2	3.69	0.734	32.3	0.23	11.2 %	0.47	2.68	72.5	9.2
Cu/25 %CeO2-ZrO2	4.39	0.615	27.1	0.16	7.9 %	0.33	2.25	51.1	13.1
Zn/Cu/25 %CeO2-ZrO2	4.12	0.403	17.7	0.11	5.4 %	0.22	1.47	35.0	19.1
Cu/5 %La2O3-17 %CeO2-ZrO2	4.13	0.576	25.4	0.16	8.0 %	0.34	2.11	51.4	13.0
Zn/Cu/5 %La ₂ O ₃ -17 %CeO ₂ -ZrO ₂	4.02	1.128	49.7	0.33	15.6 %	0.65	4.12	100.6	6.7

^{a)}The average number of N₂O molecules reacted per unit surface area of catalyst was estimated by assuming that BET surface area measured for the support decreases in the catalyst preparation proportionally to the added mass. N₂O titration was made for reduced samples, so copper was assumed as Cu(0) and Zn as ZnO.

^{b)}The average amount of surface copper atoms has been calculated by multiplying the areal number density of copper (Table 2) with dispersion D_{Cu} measured by N₂O titration.

^{c)}The sample for which the analysis is reported is from a different batch than the one for which the other analysis and the catalytic testing were made but prepared in a similar way. The nominal Cu loading of 3.0 wt% is used for the calculation.

In conclusion, on the basis of the results of this work, the Zn(II) acetylacetonate based process appears as a predictable and reproducible way to add zinc on many different mesoporous oxide supports.

4.2. Trends in catalytic activity on different supports

All catalysts supported on zirconia and on supports from the ceriazirconia-lanthana mixed oxide family were found active and selective towards methanol production (Fig. 4, Fig. 5). Alumina-supported catalysts also actively converted carbon dioxide, but the selectivity to methanol was lower due to increased selectivity to carbon monoxide. Catalysts supported on titania and niobia were inferior to the others, in terms of activity. Zinc-promoted catalysts had an improved selectivity towards methanol, and higher methanol production rate, compared to non-zinc-promoted catalysts. At 500 K, which is in the middle of the tested temperature range, highest methanol production rates were 2.76 mmol g_{cat}^{-1} for Zn/Cu/25ceria-zirconia, and 71.8 mmol g_{cu}^{-1} for Zn/ Cu/zirconia (Table S1 in the supporting information). The order of magnitude of the turn-over-frequency of CO₂ to methanol was $10^{-2} s^{-1}$ (Table S1), which is comparable to literature values [5,44].

The supporting information contains various plots for the data obtained at 500 K, in search for correlations between activity and catalyst properties. One simple correlation to search for is with activity vs. Cu loading. As expected, there appears to be a positive correlation between copper loading and conversion, especially for the zinc-promoted catalysts (see supporting information, Figure S3b). This is as expected, as tests were made for one gram of catalyst, and the copper loading in them varied. Noteworthily, several properties in the system scaled with copper loading, because the area-based copper number density was kept ~constant, but the weight-based loading varied, and the increased conversion then also links with those properties (e.g. increasing zinc loading, increasing total surface area available in the catalyst bed). When the MPR is viewed per gram of catalyst, results are rather constant with increasing Cu loading (and thus those other properties) (Figure S3d). When the MPR per gram of copper is investigated vs. copper loading, a decreasing trend is seen, if any (Figure S3f). When the results are viewed as function of the total available copper surface area from N₂O titration, no simple increasing trend can be recognized (Figure S4). When the results are viewed as function of the average copper particle size derived from the N2O pulse titration and elemental analysis, we observe that increasing particle size (which corresponds to decreasing dispersion) seems to favor high MPR especially on non-zincpromoted catalysts (Figure S5a,c) and corresponds to an increased TOF

(Figures S5e,f). It has been shown in the literature that CO/CO_2 hydrogenation on zinc-promoted copper catalysts is structure-sensitive, with turn-over-frequency increasing up to particle size of about 10 nm, and being constant thereafter [5]. Our results seem to support a general conclusion of structure-sensitivity. However, in the current study, copper-particle-size-related properties were not changed independently of other properties, as all values were obtained on different supports, and therefore in addition to particle size, the nature of support may have influenced the activity comparison.

Because carbon dioxide adsorption on the catalyst must precede its conversion to methanol through reaction with hydrogen, one could expect CO2-TPD to give valuable information that can be related with catalytic activity. Investigating Table 3 shows that all catalysts that showed a favourable activity (zirconia and other supports from the ceria-zirconia-lanthana family), had a significant CO2 adsorption capacity (at 527 K) on the order of ~100 μ mol g_{cat}⁻¹. Also in terms of areal adsorption capacity, roughly about one CO2 molecule per square nanometer of the catalyst was adsorbed on these supports. Even more interestingly, when examining the CO₂-TPD profile (Fig. 2), it is seen that all the active catalysts present desorption features in the temperature range where the catalytic activity studies were made, 450-550 K. It seems therefore likely that there is a correlation between the TPD features in this temperature range and catalytic activity: CO2 binds strongly enough to adsorbed, but not too strongly to prevent desorption, or further catalytic reactions. This would be in line with the qualitative Sabatier's principle that interactions between the catalyst and reactants should be "just right": not too strong and not too weak.

When compared to the data of our previous publication [9], it is interesting to note that we did not reach the high values of methanol production rate per gram of copper as in the previous work. Comparing the results obtained at 500 K, previously, a methanol production rate of 165 mmol g_{Cu}^{-1} h⁻¹ was achieved [9], while in this work the highest reached was 71.8 mmol g_{Cu}^{-1} h⁻¹ (Table S1). A difference in this work compared to the previous work [9] was that here a targeted Cu/Zn ratio of 2:1 was used, while in the previous work the targeted Cu/Zn ratio was of 1:1. In both cases, one ALD cycle with Zn(acac)₂ was used giving a similar areal number density of zinc ($\sim 2 \text{ Zn/nm}^2$), with the consequence that in this work the copper loading was roughly double compared to the previous work. (Another small difference was that previously [9], prior to catalyst preparation, the support was calcined at 873 K, while here the supports were calcined at 773 K.) While the origin of the difference in the methanol production rate per g_{Cu} in the two works is not fully clear, the difference is consistent with the trend observed for catalysts on



Fig. 3. STEM images along with EDS mapping images of metal oxide supported Zn/Cu/support catalysts: (a) Zn/Cu/zirconia, (b) Zn/Cu/alumina, (c) Zn/Cu/titania, (d) Zn/Cu/niobia, (e) Zn/Cu/17ceria-zirconia, (f) Zn/Cu/25ceria-zirconia, and (g) Zn/Cu/ ceria-zirconia-lanthana. Note that the images have been obtained with varied magnifications.

different supports in this work, where the methanol production rate per g_{Cu} decreased with increasing copper loading.

When comparing our results to those obtained in unrelated studies per gram of copper, the current results show high activity level. For example, in an earlier work, where ZnCu/silica catalysts were made with ALD-added zinc (from diethylzinc) and tested for CO_2 hydrogenation to methanol, production of 10.6 mmol g_{Cu}^{-1} h⁻¹ was obtained at 523 K and 4 MPa [9,36], clearly less than in our current study. Compared to results obtained at 523 K and 3 MPa with ZnCu/alumina catalyst made with CVD (56 mmol g_{Cu}^{-1} h⁻¹) [9,45], our results are at a similar or slightly higher level.

5. Conclusion

In this work, we prepared a series of oxide-supported copper catalysts, with and without zinc promotion, and compared their activity for CO₂ hydrogenation to methanol.

Copper was added by impregnation, and zinc by ALD of zinc(II) acetylacetonate, targeting a 2:1 ratio for copper and zinc. While the metal loadings were close to targeted on all supports (based on areal number density of two zinc per square nanometre), the obtained particle size of copper varied. According to N₂O titration and TEM, the particle size was on the order of 10 nm for most supports, while on titania, the particles were orders of magnitude larger. Copper dispersion was on the order of 10 % for most supports, but only <1 % for titania. Zinc, however, according to TEM-EDX seemed in the nanoscale to be evenly distributed on all catalysts.

Zinc-promotion improved methanol selectivity and methanol production rate, as expected. All catalysts supported on zirconia or on oxides of the zirconia-based mixed oxide family (containing ceria and lanthana) were found active and selective. Common to all active catalysts was that they presented significant desorption features in CO₂-TPD



Fig. 4. Carbon dioxide conversion, methanol production rate per gram of catalyst, and methanol production rate per gram of copper of Cu/support catalysts (panels a, c and e) and Zn/Cu/support catalysts (panels b, d and f). Reaction conditions: p = 3.0 MPa, gas hourly space velocity (GHSV) = 7500 h⁻¹, feed vol%: H₂/CO₂/N₂ = 71/23/6. Data points for methanol production rates correspond to experimental data with noticeable CO₂ conversion.



Fig. 5. Relative selectivity of methanol, carbon monoxide, and methane of Cu/support catalysts (panels a, c and e) and Zn/Cu/support catalysts (panels b, d and f). Reaction conditions: p = 3.0 MPa, gas hourly space velocity (GHSV) = 7500 h⁻¹, feed vol%: H₂/CO₂/N₂ = 71/23/6. Data points correspond to experimental data with noticeable CO₂ conversion.

Catalysis Today 454 (2025) 115283

in the temperature range of catalytic activity studies (450–550 K). Based on methanol production rate at 500 K, zinc-promoted copper supported on zirconia remained the most active catalyst, although the difference was not large compared to other catalysts of the zirconia family.

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CRediT authorship contribution statement

Arandia Aitor: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Conceptualization. Velasco Jorge A.: Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation. Sajid Ahmed: Writing – original draft, Visualization, Investigation. Yim Jihong: Writing – original draft, Investigation. Shamshad Hammad: Writing – original draft, Investigaoriginal draft, Investigation. Singh Abhinash Kumar: Writing – original draft, Visualization, Validation, Formal analysis. Gonsalves Christine: Supervision. Karinen Reetta: Supervision. Puurunen Riikka L.: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Data curation, Conceptualization.

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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Appendices

Electronic supplementary information contains an example of N₂O titration results; tabular summary of the averaged catalytic activity results for the different temperatures; plots of the activity data at 500 K for relative selectivity vs. conversion; conversion and MPR vs. copper loading, copper surface area, and CO₂ desorbed (from CO₂-TPD analysis); MPR and TOF vs. copper particle size (from N₂O titration); and time-on-stream results for the catalysts (molar concentration of compounds, relative selectivity, conversion, yield of methanol, MPR per gram of catalyst and per gram of copper, carbon balance closure, and the calculated TOF values).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2025.115283.

Data availability

The data of this article is provided in the supplementary information.

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