Surface Lewis Acidity of Periphery Oxide Species as a General Kinetic Descriptor for CO₂ Hydrogenation to Methanol on Supported Copper Nanoparticles

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Experimental methods

Synthesis of mesoporous γ -Al₂O₃ substrate

High-purity dispersible pseudo-boehmite, (Sasol, 75 wt.% Al₂O₃), was used as precursor and a polyethyleneglycolether non-ionic surfactant (Tergitol 15-S-7, Sigma-Aldrich) was employed as porogen agent to synthesize the high-surface-area mesoporous γ -Al₂O₃ support. First, the pseudo-boehmite precursor and the porogen agent were co-dispersed in deionized water to obtain a synthesis gel with a molar composition of Al:EO:H₂O 1:1.51:43, where EO represents the ethylenoxide building units in the polymer (ca. 7 mol EO/mol surfactant). The gel was stirred vigorously with a laboratory vertical stirrer (400 rpm) for 3 hours at room temperature, and hydrothermally treated at 383 K in an oven for 48 h under static conditions in an autoclavable polypropylene bottle. Then, the gel was transferred to a ceramic evaporating dish which was then placed in an oven at 353 K for 48 hours to dry under internal air circulation. Last, the dish was transferred into a muffle oven, the solid was further dried at 393 K for 5 hours (10 K min⁻¹) and calcined in air at 873 K (3 K min⁻¹) in order to crystallize the pseudo-boehmite precursor into γ -Al₂O₃ and to remove the organic porogen via combustion. After calcination, the solid was sieved to retain particles in the 100-200 µm size range, which were used for further catalyst synthesis steps.

Synthesis of $MO_x@\gamma-Al_2O_3$ support materials

The surface Lewis acidity of the mesoporous γ -Al₂O₃ was modified via the deposition of an amount of different transition metal oxides (MO_x, M= Y, Sc, Zr and Ta) corresponding to the theoretical monolayer, i.e. ca. 4.5 M_{at} nm⁻².^[1-3] Metal precursors were selected on the basis of previous studies^[4-5] to achieve a high interaction with the γ -Al₂O₃ surface and thus a uniform oxide overlays. Sc(NO₃)₃·*x*H₂O (*x* ca. 4.0, 99.9%, Sigma Aldrich), Y(NO₃)₃·6H₂O (99.8%, Sigma Aldrich), Zr(OC₃H₇)₄ (70 wt. % in 1-Propanol, Sigma Aldrich) and Ta(OC₂H₅)₅ (99.98%, Sigma Aldrich) were used as received, without further purifications. Stock solutions of metal precursors were prepared by dissolving Sc(NO₃)₃·4H₂O or

Y(NO₃)₃·6H₂O in Milli-Q water, Zr(OC₃H₇)₄ in dry 1-propanol and Ta(OC₂H₃)₅ in dry ethanol, respectively. The nominal loading was adjusted in each case to achieve a surface coverage of 4.5 M_{at} nm⁻² on the γ -Al₂O₃ substrate. First, the γ -Al₂O₃ carrier was dried in a two-neck round-bottom flask at 523 K for 3 hours under dynamic vacuum (3 mbar). Then, impregnation was achieved at room temperature by admitting a predetermined volume of the precursor solution and enable equilibration by capillarity. In the case of ZrO_x@Al₂O₃, two incipient impregnation steps with the Zr(OC₃H₇)₄ stock solution were applied in order to achieve the desired nominal Zr surface content. The as-impregnated solid was transferred into a quartz packed-bed reactor, dried at 343 K for 10 hours and calcined at 773 K for 4 hours under flow of synthetic air (heating rates of 3 K min⁻¹). Next, the oven was let cool down to RT and the MO_x@ γ -Al₂O₃ solid transferred into a, Ar-filled glove-box under exclusion of air.

Synthesis of $Cu/MO_x@\gamma-Al_2O_3$ catalysts

Copper was incorporated on the surface of the $MO_x@\gamma-Al_2O_3$ catalysts by decomposition of copper nitrate. $Cu(NO_3)_3 \cdot 3H_2O$ (99%, Sigma-Aldrich) was dissolved in 0.25M $HNO_{3(aq)}$. The resulting solution impregnated to incipient wetness into the mesoporous support oxides. The Cu content was adjusted to achieve copper surface coverages in the range of 1.5-4.5 Cu_{at} nm⁻². The as-impregnated solid was transferred into a quartz packed-bed reactor, dried at 343K (3 K min⁻¹) for 10 hours and calcined at 623 K (3 K min⁻¹) for 4 hours under N₂ flow. Then, it was transferred into a U-shaped packed-bed glass tubular reactor in a glove box and reduced in an oven at 523 K (1 K min⁻¹) under flow of 10 vol% H₂/N₂. Last, the reactor was let cool down to RT and transferred into an Ar-filled glove box (O₂ < 0.1 ppm, H₂O < 0.1 ppm). The solid was recovered, ground finely in a mortar and stored under exclusion of air.

Characterization Methods

N₂-physisorption

Nitrogen isotherms were recorded in a Micromeritics ASAP instrument (3Flex) unit after degassing the sample (ca. 100 mg, 100-200 µm particle size) at 423 K under vacuum for 5 h. Specific

surface areas were derived using the Brunauer-Emmett-Teller (B.E.T) method applied in the relative pressure (P/P₀) regime of 0.05-0.30. Total mesopore volumes were obtained from the amount of N₂ taken up at a relative pressure P/P₀=0.95. Pore size distributions and average mesopore diameters were determined applying the Barrett-Joyner-Halenda (B.J.H) method to the desorption branch of the isotherms.

X-ray diffraction

Powder X-ray diffraction patterns were collected in a STOE Theta/Theta diffractometer using Cu-Ka radiation monochromatized by a graphite crystal monochromator ($\lambda = 1.5406$ Å). Data were collected from 20 to 80° (20) with a step size of 0.02° and a dwell time of 3 s/step.

Surface oxide Lewis acidity quantification: UV-vis spectroscopy with alizarin as surface probe.

The Lewis acidity of *cus* metal centers exposed on the surface of the $MO_x@\gamma-Al_2O_3$ support oxides was quantified by means of the intramolecular charge-transfer (IMCT) energy of alizarin adsorbed as a surface probe molecule following the procedure reported by Jeong et.al.^[6] Prior to spectra collection, the powdered solids were soaked in a stock alizarin solution in dry ethanol (0.15 mM) under the exclusion of air. After filtering off the solution, excess (unbound) alizarin was washed off with dry ethanol until colorless washing liquids were obtained and the solid was further dried at RT under vacuum (3 mbar) for 3 hours. Diffuse reflectance spectra were recorded in a Pelkin Elmer Lamda 365 spectrometer using BaSO₄ as reflectance standard and converted into absorption spectra using the Kubelka-Munk formalism. The peaking energy for the IMCT band (E_{IMCT}) of the adsorbed probe was determined after subtraction of the absorption spectra for the oxide support material prior to alizarin uptake.

Definition of theoretical oxide Lewis acidity.

Several correlations have been proposed to derive Lewis acidity scales for metal oxides from intrinsic, pre-bond physicochemical descriptors of the constituent elements. Most of them propose a linear dependence between the oxide Lewis acidity and the partial electron charge (δ) distribution within the

elements forming the oxide. Such a relationship was already proposed by Sanderson⁷ on the basis of his principle of *electronegativity equalization*. Later Bratsch⁸ correlated the universal oxide Lewis acidity parameter (*a*), as defined by Smith for binary oxides,⁹ with the partial electron charge on combined oxygen (δ_0), according to the linear function: *a*=m· δ_0 +b, where m and b were theoretically derived to be 33.7 and 9.2, respectively. One of the most comprehensive studies on Lewis acidity scales for oxides is the work of Jeong et al.⁶ They found an excellent and rather generally valid correlation of Lewis acidity, determined experimentally using UV-vis spectroscopy coupled to 1,2-dihydroxiantraquinone as a surface probe molecule, with the parameter (N_M-2 δ_M), where N_M is the metal formal oxidation state in the oxide, and δ_M is the Sanderson partial electron charge bored by the metal cations in the oxide, i.e. those leading to Lewis acid centers. The latter parameter is a function of the Sanderson electronegativities of the M cation and the O²⁻ anion, respectively, and the stoichiometry of the binary oxide. It follows from these results that the parameter N_M-2 δ_M might be used as a universal (and predictive) measure for Lewis acidity in binary metal and lanthanide oxides. This parameter has been used herein to establish a ranking of theoretical Lewis acidity for bulk-type binary oxides (see Figure 2b in the main manuscript).

Scanning-transmission electron microscopy (STEM)

Prior to analysis, catalysts were reduced at 523 K under flow of 10%H₂/N₂, transferred into a glove box and embedded in a low-viscosity resin (Spurr, Sigma-Aldrich) in a glove box. The resin was then cured in an oven at 333 K overnight. Specimen cross-sections with a nominal thickness of 50 nm were obtained using a DIATOME diamond knife mounted on a Reichert Ultracut ultramicrotome and collected on a nickel TEM grid (400 mesh) covered with a Lacey carbon film (PLANO). High-angle annular dark-field (HAADF) micrographs and energy-dispersive X-ray (EDX) elemental maps were acquired from the as-prepared cross-sectional specimens using a C_s-corrected dedicated Scanning Transmission Electron Microscope (Hitachi HD-2700) equipped with a cold-field emission gun and two EDAX Octane T Ultra W EDX detectors and operated at 200 kV.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra (XPS) were collected after in situ reduction in a customized spectrometer equipped with a hemispherical SPECS PHOIBOS 100 analyser using fixed transmission mode at 20 eV pass energy. Acquisition of the spectra was performed using a non-monochromatic dual Xray source (MgK or AlK radiation) with an anode current of 20 mA and a potential acceleration of 12 kV. As-calcined samples were pressed into small discs and evacuated in the pre-chamber of the spectrometer at 423 K and $<10^{-7}$ mbar before the measurement. In situ catalyst reduction was performed in a hightemperature, high-pressure SPECS HPC-20 reaction cell with IR heating. In this case, the samples were treated in a flow of 20% H₂/Ar (v/v), by heating from RT to 523 K at a heating rate of 3 K min⁻¹ and holding the final temperature for 2 hours. After reduction, the samples were allowed to cool down to room temperature, evacuated at $<10^{-7}$ mbar and transferred to the chamber of the spectrometer under ultra-high vacuum. Given the low surface carbon content after reduction treatments, binding energies (BE) were referred to the Al2p signal at 74.10 eV. To derive surface relative atomic ratios, peak intensities have been determined after nonlinear Shirley-type background subtraction and corrected by sensitivity factors (Scofield). Average Cu particle sizes were then derived from the experimental Cu/Al surface ratios using the Kerkhof-Moulijn model^[10] for high-surface-area supported catalysts, modified to consider a monolayer of the corresponding MO_x oxide on the surface of the Al_2O_3 carrier (modeled as slabs).

In situ Fourier-transform infrared spectroscopy (in situ FTIR)

In situ FTIR experiments were performed with a Bruker Vertex70 spectrometer using a homedesigned quartz cell fitted with an oven, KRS-5 windows and connected to a gas dosing system. Catalysts were pressed into self-supported wafers (5-10 mg cm⁻²) and reduced in the IR cell under flow of H₂ (Linde > 99.995%, 10 mL min⁻¹) at 523 K for 2 h (heating rate of 3 K min⁻¹). After *in situ* reduction, the sample was let cool down and an additional flow of CO₂ (Linde > 99.995%) was admitted to establish an overall flow of 20 mL min⁻¹ for a CO₂/H₂ mixture (1/3, v/v) through the cell at atmospheric pressure. Next the temperature was increased to 463 K at a heating rate of 2 K min⁻¹. This reaction temperature was held for 2 hours to let surface species relevant to steady-state reaction conditions develop, as evidenced by no further changes in the FTIR spectra with reaction time. Then, the sample was cooled down to 353 K. Finally, the relative stability of different carbon species developed on the catalyst surface was studied under a H₂ atmosphere. To this end, the CO₂ flow was ceased, the cell was flushed with H₂ and the temperature increased stepwise from 353 K to 503 K under hydrogen flow (15 mL min⁻¹). FTIR spectra were collected after 5 minutes dwell at each temperature. In order to gain insight into the sensitivity of different surface species to the hydrogenation temperature, the temperature-resolved FTIR spectra were deconvoluted in the selected relevant regions (see Figure S10). A Fourier self-deconvolution algorithm (gamma 35-40, smoothing factor 0.8) was first implemented (OriginPro 9.0) to get a first guess on the position of different convoluted IR peaks in the highest-coverage (T=353 K) and lowest-coverage (T=503 K) spectra. Next, the spectra were deconvoluted with multiple Voigt functions using a Levenberg-Marquart non-linear least-square algorithm. The position of the bands, as well as their FWHM were kept constant, within preset boundary intervals, while propagating the optimized deconvolution function to different spectra within the same experimental set. Variations in the optimal fitting band position and broadening lower than 5 cm⁻¹ and 10 %, respectively, were observed as a function of the surface coverage and hydrogenation temperature.

Catalytic Experiments

Catalytic experiments were performed in the liquid phase in order to ensure isothermal conditions and thus reduce the experimental error in the determination of apparent activation energies. A PTFE-lined 36 ml autoclave batch reactor was mounted on a heating plate equipped with temperature control and magnetic stirring. The pre-reduced catalyst (fine powder, $< 20 \ \mu$ m) was loaded into the reactor in a glove box, where the Ar overpressure was kept constant to 3 mbar relative to atmospheric pressure, in order to avoid oxidation of Cu species. In a typical experiment, 8 ml of anhydrous 1,4-dioxane as solvent (99.8%, Alfa-Aesar) and an amount of catalyst corresponding to 75 μ mol of Cu were added into the PTFE liner of the autoclave. The reactor was then sealed, taken out of the glove box and dosed with a CO_2/H_2 synthetic gas mixture ($H_2/CO_2=3.0$ (v), Air Liquid, 99.999%) to achieve a total pressure of 63 ± 3 bar at the final reaction temperature. All catalytic tests were performed using magnetic stirring (1000 rpm). The temperature in the reactor was increased from RT to the preset reaction temperature (433-493 K) using an aluminum heating jacket coupled to a heating plate (8 K min⁻¹) and the zero reaction time set upon achievement of the final reaction temperature. After selected reaction times the reactor was guenched by immersing the autoclave into an ice bath. The CO₂ conversion level was kept differential (<5%) at all reaction temperatures in order to determine initial product formation rates from a linear extrapolation of the experimental points to zero reaction time. After quenching the reaction in an ice bath, the gas phase was analyzed in an Agilent 7890B gas chromatograph equipped with two consecutive packed bed columns (Agilent HS-O 80/120, 1 and 3 m respectively) and a 13X molecular sieve column connected to two TCD detectors, respectively, and a Restek RTX-1 capillary column (60 m) connected to a FID detector for the analysis of permanent gases. The liquid phase was analyzed in an Agilent 6890-plus gas chromatograph equipped with a DB-WAXetr capillary column (15 m) and a TCD detector using 2-pentanol (0.028 M) as internal standard. Methanol and CO were the major carbon-containing reaction products Dimethylether (DME) was not detected in significant amounts under the set of reaction conditions applied in this study, i.e. relatively mild reaction temperatures and limited CO₂ conversion levels methanol which translate into methanol concentrations <15 mM in the reaction medium and hence disfavor a secondary and bimolecular reaction such as methanol dehydration to dimethylether. Control tests in which a higher methanol concentration of >100 mM was deliberately achieved in the reactor via hydrogenation of propylene carbonate, under otherwise identical reaction conditions, showed formation of DME, albeit in minor amounts, as product with the most Lewis acidic Cu/Al₂O₃ and Cu/TaO_x@Al₂O₃ catalysts at reaction temperatures \geq 473 K. The absence of DME within the products is in contrast with other studies, where higher DME formation rates were observed on Cu/Al₂O₃ under gas-phase CO₂ hydrogenation conditions at only slightly higher reaction temperatures and comparatively low CO₂ conversion levels.¹¹⁻¹² Performing the reaction in the presence of a solvent (as in the present study) might provide solvation stabilization effects, favoring the desorption of primary products (methanol in this case) and reducing the surface coverage of methoxy species, thus inhibiting bimolecular coupling reactions to DME. In line with this interpretation, a similar inhibition of DME formation on similar Cu/Al_2O_3 CO_2 hydrogenation catalysts have also been reported under reaction conditions favoring the aforementioned solvation effects, e.g. under supercritical CO_2 .¹² Apparent activation energies for the methanol synthesis and the *r*WGS reactions were determined according to the Arrhenius formalism from the initial methanol and CO formation rates, respectively, determined at four different reaction temperatures. Four data points, collected at reaction times in the range of 0-60 minutes, were used to determine initial reaction rates. As shown in Figure EM1 for the case of $Cu/ZrO_x@Al_2O_3$ as a representative example, CO_2 conversion showed a linear dependence with the reaction time in this range at all the reaction temperatures examined (433-493 K). For reactions performed at the lowest temperature of 433 K, additional experimental points were collected up to a reaction time of 120-180 min (in order to have data points with higher product concentrations) which did not modified the linear trend determined for reaction times of 0-60 min to any statistically relevant extent.



Figure EM1: Evolution of the CO_2 conversion with the reaction time for catalytic tests with $Cu/ZrO_x@Al_2O_3$ at various reaction temperatures in the range of 433-493 K. Each data point corresponds to an individual experiment, as

the reaction was quenched at every sampling time in order to analyze both liquid and gas phases. Lines correspond to linear regressions.

Assessment of kinetic significance of mass transport under catalysis conditions

In order to assess the kinetic significance of extra-particle mass transport processes a set of catalytic experiments were performed at various stirring rates in the range of 600-1000 rpm, maintaining constant the rest of experimental parameters. The catalyst loading was set to that corresponding to 75 µmol Cu, and the reaction temperature was the highest of those employed in this study (493 K), i.e. reaction conditions at which the maximum surface reaction rate is expected and thus the likelihood of transport kinetic control is also the highest. As shown in Figure EM2a, the initial methanol formation rate increased with increasing the stirring rate up to 800 rpm. Further increasing the stirring rate to 1000 rpm led to a statistically identical reaction rate. These results suggest that extra-particle mass transport is kinetically significant only for stirring rates lower than 800 rpm. Nevertheless, in order to rule out the existence of complex dependences of the stirring energy dissipation and thus the mass transport coefficient with the stirring rate, another set of experiments was performed where the catalyst-to-reactants ratio was varied systematically at the selected stirring rate of 1000 rpm. To this end, the amount of powder catalyst loaded into the reactor was set to 0, 44, 88 and 176 mg (values corresponding to 0 (blank test), 38, 75 and 150 μ mol Cu, respectively) while the initial gas-phase H₂ and CO₂ partial pressures were kept constant (P=65) bar (at reaction temperature), $H_2/CO_2=3/1$). As observed in Figure EM2b, the initial methanol formation rate increased linearly up to a catalyst loading of 75 µmol Cu, as expected for a reaction-controlled kinetics. Experiments performed at a 2-fold higher catalyst loading of 150 µmol Cu led to a slightly lower initial methanol formation rate than that expected upon extrapolation of the linear range, a result which might be ascribed to the onset of a contribution from extra-particle mass transport to the overall reaction kinetics. In view of these results, a catalyst loading corresponding to 75 µmol Cu and a mechanical stirring rate of 10^3 rpm were applied in all the reaction tests reported in this work to ensure a negligible contribution from extra-particle mass transport to the experimental reaction rates. The relevance of intraparticle mass transport was evaluated on the basis of the Weisz-Prater criterion¹³ for a *pseudo*-first order kinetics in CO₂. In the worst possible scenario, i.e. the highest reaction temperature of 493 K, the most active catalyst at this temperature (Cu/ZrO_x@Al₂O₃), and assuming a catalyst particle diameter of 20 μ m (the upper limit of the sieved fraction applied experimentally), the parameter N_{WP}, defined by eq. S1, took a value of 0.03 for the reactant with the slowest diffusivity under reaction conditions (CO₂). This value amply fulfills the criterion N_{WP}≤0.3, thus ruling out the contribution from intra-particle mass transport to the overall reaction kinetics (even lower values were obtained with the remaining catalysts). The parameters employed to estimate N_{WP} are gathered in Fig. EM2c. These tests show that under the reaction settings selected for those catalytic tests reported in this study (T=433-493 K, catalyst loading 75 µmol Cu, stirring rate 10³ rpm) mass transport limitations can be ruled out.

$$N_{W-P} = \frac{(-r)_{CO2} \cdot R_p^2}{C_{CO2,s} \cdot \mathfrak{D}_{CO2,eff}}$$
(eq. S1)

 N_{W-P} : Weisz-Prater parameter.

 $(-r)_{CO2}$: CO₂ consumption reaction rate per unit volume catalyst.

 R_p^2 : Solid catalyst particle radius.

 $C_{CO2,s}$: Concentration of CO₂ at the outer surface of catalyst particles (equal to CO₂ solubility in the absence of extra-particle (film) transport limitations.

 $\mathfrak{D}_{CO2,eff}$: Effective diffusion coefficient for CO₂ within the catalyst particles. $\mathfrak{D}_{CO2,eff} = \mathfrak{D}_{CO2} \cdot (\varepsilon/\tau)$, where ε denotes the catalyst porosity factor and τ the pore tortuosity.



Weisz-Prater criterion					
Parameter	Value	Units			
$(-r)_{CO2}^{a}$	$7.2 \cdot 10^{-4}$	$mol m^{-3} s^{-1}$			
R_p^{b}	10-5	т			
$C_{CO2,s}$ °	25	$mol m^{-3}$			
$\mathfrak{D}_{\mathcal{CO2}}{}^{\mathrm{d}}$	$1.9 \cdot 10^{-8}$	$m^2 s^{-1}$			
ε^{e}	0.67	-			
$ au^{ m f}$	1.2	-			

Figure EM2: Investigation of the influence of mass transport on experimental rate constants. a) Initial methanol formation rate as a function of the stirring rate applied in the reactor (Cu/Al₂O₃ catalyst mass corresponding to 75 μ mol Cu). b) Initial methanol formation rate as a function of the catalyst loading in the reactor (Cu/Al₂O₃, stirring rate of 10³ rpm). c) List of parameters determined/estimated to apply the Weisz-Prater criterion to assess the kinetic significance of intra-particle mass transport. ^aCO₂ consumption rate per unit volume catalyst registered with Cu/ZrO_x@Al₂O₃ at 493 K (equivalent to 1204 μ mol CO₂ g_{Cu}⁻¹ min⁻¹).^bCatalyst particle radius, assimilated to the upper limit of the applied sieved fraction (max. particle diameter: 20 μ m).^c Determined from solubility data for CO₂ in 1,4-dioxane¹⁴ extrapolated to reaction conditions, i.e. P_{CO2}=15 bar, T=493 K, assuming validity of Henry's law.^d Diffusion coefficient of CO₂ in 1,4-dioxane, estimated from literature values¹⁵ in the temperature range of 300-425 K, by extrapolation to a temperature of 493 K. ^eCatalyst porosity factor, determined as the fraction of the catalyst volume corresponding to pore volume, using the total pore volume determined by N₂ physisorption (0.56 cm³ g⁻¹) and assuming an overall catalyst skeleton density of 4.0 g cm⁻³.^f Pore tortuosity estimated as τ =1-(1/2)·Ln(ϵ). Reaction conditions: T=493 K, P=65 bar (at reaction temperature), H₂/CO₂=3/1. In panels a and b, lines are a guide to the eye.

Supplementary figures



Figure S1. X-ray diffractograms for the series of $MO_x@\gamma-Al_2O_3$ support materials.

Upon incorporation of monolayer amounts of the MO_x oxides on the surface of the γ -Al₂O₃ carrier, no diffractions ascribable to oxide crystallites other than those corresponding to the γ -Al₂O₃ substrate could be observed. Instead, a broad scattering band could be discerned in the 2 θ range 25°-35°, indicative of the amorphous character of the MO_x species.



Figure S2. N₂-physisorption isotherms for the pristine γ -Al₂O₃ mesoporous substrate and the series of MO_x@Al₂O₃ support materials synthesized thereof.



Figure S3: Parity plot for the Lewis acidity of surface *cus* determined using UV-vis spectroscopy coupled to 1,2dihydroxyanthraquinone as probe molecule for the series of MO_x oxides (M=Y, Sc, Zr, Ta) when dispersed as an overlay on the common γ -Al₂O₃ substrate and in their bulk form. The bulk ZrO₂ was the monoclinic polymorph (space group *P21/c*). The dotted line represents the diagonal of the parity plot.



Figure S4. Temperature-programmed reduction profiles for the series of $Cu/MO_x@Al_2O_3$ catalysts with a copper surface content of 1.5 Cu nm⁻², as indicated in brackets in the sample labels.



Figure S5. (cont.)



Figure S5: X-ray photoemission spectra for the Cu2p signal (left panels) and the corresponding spectral regions for the M element in the overlay MO_x oxides, i.e. Sc2p, Y3d, Zr3d, Al2p (catalyst synthesized on the neat Al₂O₃ support), and Ta4f, respectively for the series of Cu/MO_x@Al₂O₃: a) Cu/ScO_x@Al₂O₃; b) Cu/YO_x@Al₂O₃; c) Cu/ZrO_x@Al₂O₃; d) Cu/Al₂O₃, e) Cu/TaO_x@Al₂O₃, all with a surface copper content of 1.5 Cu nm⁻²; and f) Cu/TaO_x@Al₂O₃ (4.5 Cu nm⁻²). Spectra were recorded after *in situ* reduction in a thermal treatment cell coupled to the XPS setup. For comparison, spectra recorded for the catalyst prior to reduction (as-calcined) are shown for Cu/ScO_x@Al₂O₃. The inset to panel f-left corresponds to the Cu LMM Auger region (KE: kinetic energy).

XPS was employed to investigate the near-surface composition and oxidation state of various species in the series of Cu/MO_x@Al₂O₃ catalysts. After H₂ reduction, all Cu-based catalysts displayed Cu2p binding energies (BE) of 932±0.4 eV. These BEs, alongside the disappearance of the shake-up satellites typical of Cu(II), indicated the reduction of the Cu²⁺ species during catalyst activation. While the Cu2p BE alone does not enable an unequivocal distinction between Cu(I) and Cu(0) species, the Cu L₃M_{4,5}M_{4,5} Auger band, which was sufficiently defined for catalysts with higher surface Cu content (inset to panel f-left), appeared at kinetic energies of ca. 919 eV, which is characteristic for metallic copper. Hence, this analysis, in line with the temperature-programmed profiles, suggests the full reduction of Cu species to metallic Cu⁰ during the H₂ reduction treatment. On the other hand, overlay MO_x oxide species did not show signs of any noticeable change in the metal oxidation state. XPS BEs characteristic for Y(III) i.e. Y3d BE=157.9 eV, Sc(III), i.e. Sc2p BE=402.2 eV, Zr(IV), i.e. Zr3d BE=182.0 eV, and Al(III), i.e. Al2p BE=74.1 eV (used as reference for BE calibrations) were determined after reduction. Only in the case of catalysts supported on TaO_x@Al₂O₃ could a certain contribution from a surface tantalum sub-oxide, i.e. Ta(X), where 0<X<5, be detected after reduction (Ta4f BE=22.3 eV), in addition to the major contribution from Ta(V) (Ta4f BE=26.0 eV). The sub-oxide contribution was nevertheless determined to be <15%.



Figure S6: Representative spherical aberration-corrected high-angle annular dark-field scanning-transmission electron micrographs (C_s -HAADF-STEM, left panels) and the corresponding energy-dispersive X-ray spectroscopy compositional maps for a) Cu/YO_x@Al₂O₃, b) Cu/ScO_x@Al₂O₃, c) Cu/ZrO_x@Al₂O₃ and d) Cu/TaO_x@Al₂O₃ catalysts (copper surface content of 1.5 Cu nm⁻² in all cases) after H₂ reduction. For each sample, imaging has been performed at two magnification levels to obtain mesoscale overviews on elemental spatial distributions (top series of panels) and nanoscale details on Cu dispersion (bottom series of panels).



Figure S7: Arrhenius plots obtained from the initial methanol formation rates at various temperatures for CO_2 hydrogenation tests with a) different Cu/MO_x@Al₂O₃ catalysts with a surface copper content of 1.5 Cu nm⁻² on various oxide supports; and b) Cu/TaO_x@Al₂O₃ catalysts with copper surface contents of 1.5 and 4.5 Cu nm⁻² and average Cu nanoparticle sizes of ca. 4.2 nm and 15.2 nm, respectively (see main text). Reaction conditions: H₂/CO₂=3.0, T=433-493 K, P= 63 bar, CO₂ conversion <5%.

As shown in Figure S7, a temperature dependence analysis of the initial methanol formation rates (under differential CO_2 conversion conditions) showed an Arrhenius-type dependence in the entire temperature range examined. As shown in panel a, notable differences in the apparent activation energy as a function of the nature of the MO_x species were revealed. As evidenced in panel b, the Arrhenius analysis for catalysts displaying different Cu contents and average Cu nanoparticle sizes on the same oxide support (TaO_x@Al₂O₃) resulted in essentially identical apparent activation energies (statistically identical slopes), in spite of the differences in the density of active sites on the catalyst surface.



Figure S8: Comparison of apparent activation energies determined in this work for the series of Cu/MO_x@Al₂O₃ catalysts (full symbols, see legend) with those reported in the literature (open symbols) for the CO₂ hydrogenation reaction employing copper nanoparticles/monocrystals interfaced with different oxides, as a function of the oxide Lewis acidity. For the series Cu/MO_x@Al₂O₃ catalysts, the herein experimentally determined IMCT of adsorbed 1,2-dihydroxyanthraquinone (η spectroscopic parameter) has been employed as descriptor for the surface Lewis acidity (see experimental). For catalysts reported in previous literature studies, the IMCT of adsorbed 1,2-dihydroxyanthraquinone reported elsewhere^[6] for the most stable bulk structure of the corresponding oxide support has been employed. Literature results obtained on Cu/CeO₂ catalysts have been excluded owing to the highly reducible character of CeO₂ which leads to the co-existence of significant amounts of both Ce⁴⁺ and Ce³⁺ surface *cus* under reaction conditions, hampering a reliable prediction of the oxide surface Lewis acidity. References for literature data: $a^{[16]}$, $b^{[17]}$, $c^{[18]}$, $d^{[19]}$, $e^{[20]}$, $f^{[21]}$. Error bars along the y-axis corresponding to the current work, and the error reported in the corresponding reference for data points taken from literature. Error bars along the x-axis are smaller than the symbols in all cases. The gray-shaded area is a guide to the eye.

Analysis of the apparent activation energies determined in our study, together with those reported in previous studies for CO_2 hydrogenation with oxide-interfaced Cu catalysts, confirms a general correlation between the overall energy barrier for methanol formation and the relative Lewis acidity of the oxide at the periphery of the Cu nanoparticles.



Figure S9: Dependence of the apparent activation energy for CO formation with the relative Lewis acidity of the *cus* on the oxide overlay interfaced with the Cu nanoparticles, as described with the spectroscopic parameter η , for the series of Cu/MO_x@Al₂O₃ catalysts with different surface copper contents as indicated in the legend. Reaction conditions: H₂/CO₂=3.0, T=433-493 K, P= 63±3 bar, CO₂ conversion <5%.



Figure S10: Illustration of optimized band deconvolution results for the FTIR spectra in the carboxylic OCO stretching (left panels), alkoxidic CO stretching (center panels) and CH stretching (right panels) regions, respectively, for a) $Cu/YO_x@Al_2O_3$, b) $Cu/ZrO_x@Al_2O_3$, c) $Cu/TaO_x@Al_2O_3$ catalysts after having been exposed to CO_2 hydrogenation conditions for 2 hours. The spectra shown correspond to the highest surface coverage of carbonaceous species, i.e. right before starting the temperature-programmed hydrogenation tests (see experimental). The position for bands assigned to the asymmetric OCO stretching (left panels) and CH stretching (right panels) for bidentate surface formate species are indicated on the plots.



Figure S11: Temperature-resolved evolution of the intensity of the CO stretching FTIR band for surface methoxy species under H₂ flow for Cu/YO_x@Al₂O₃ (blue), Cu/ZrO_x@Al₂O₃ (green) and Cu/TaO_x@Al₂O₃ (red) catalysts which had been exposed to CO₂ hydrogenation conditions in the IR cell (see experimental details). Variations in band area are given as an "area decrease" in the y-axis, with reference to the spectra recorded at 353 K (the lowest temperature in the experiment). Negative "decrease" values indicate increments in the surface coverage of methoxy species during the heat treatment under H₂ flow. Lines are a guide to the eye.

Supplementary Tables

	Chemical composition		Textural properties ^a				<i>cus</i> Lewis acidity ^b
Sample	M ^c (wt%)	δ^{d} (at nm ⁻²)	$\frac{{{S_{BET}}^{e}}}{{\left({{m^2}{g_{{Al^2}{O^3}}^{-1}}} \right)}}$	V_{p}^{f} (cm ³ g ⁻¹)	V_{p}^{g} (cm ³ g _{Al²O³} -1)	d _p ^h (nm)	η ⁱ (eV)
Al_2O_3			265	0.80		11.5	2.50
$ScO_x@Al_2O_3$	9.4	4.5	255	0.59	0.65	9.4	2.45
YO _x @Al ₂ O ₃	14.5	4.6	270	0.66	0.78	9.9	2.40
$ZrO_x@Al_2O_3$	15.4	4.7	285	0.56	0.67	8.6	2.48
TaO _x @Al ₂ O ₃	24.1	4.5	310	0.54	0.71	8.4	2.56

Table S1. Chemical composition, textural and surface electronic properties of $MO_x@Al_2O_3$ oxide supports.

^a As determined by N₂ physisorption.

^b Relative Lewis acidity of surface-exposed coordinatively unsaturated metal sites (*cus*), determined by UV-vis spectroscopy with 1,2dihydroxyanthraquinone as surface probe molecule. ^c Loading of M, where MO_x stands for the overlay oxide.

^d Surface M coverage.

^e B.E.T. specific surface area, normalized per unit mass of Al₂O₃.

^f Total pore volume.

^g Total pore volume, normalized per unit mass of Al_2O_3 .

 ^h Average pore diameter, determined according to the B.J.H. formalism.
 ⁱ Lowest-energy intramolecular charge-transfer (IMCT) energy of adsorbed 1,2-dihydroxyanthraquinone as determined by UV-vis spectroscopy after surface-saturation with the probe molecule at room temperature.

Catalyst	$\frac{\delta_{Cu}{}^{a}}{(Cu nm^{-2})}$	Temperature (K)	X _{CO2, max} ^b (%)	$r_{MeOH,0}^{c}$ (µmol g _{Cu} ⁻¹ min ⁻¹)	$r_{CO,0}^{d}$ (µmol g _{Cu} ⁻¹ min ⁻¹)
Cu/YO _x @Al ₂ O ₃	1.5	433	0.1	7.3±0.5	3.8±0.6
Cu/YO _x @Al ₂ O ₃		453	0.2	28.0±2.0	17.2±2.6
Cu/YO _x @Al ₂ O ₃		473	0.4	82.5±6.0	61.4±9.5
Cu/YO _x @ Al ₂ O ₃		493	1.2	166.1±12.1	214.0±33
Cu/ScO _x @Al ₂ O ₃		433	0.3	23.1±1.7	9.8±1.5
$Cu/ScO_x@Al_2O_3$		453	0.4	93.7±6.8	37.4±5.8
$Cu/ScO_x@Al_2O_3$	1.5	473	1.1	216.2±15.8	136.0±20.9
$Cu/ScO_x@Al_2O_3$		493	2.2	440.3±32.1	440.0±67.8
Cu/ZrO _x @Al ₂ O ₃	1.5	433	0.5	57.5±4.2	13.4±2.1
Cu/ZrO _x @Al ₂ O ₃		453	0.7	146.1±10.7	57.6±8.9
Cu/ZrO _x @Al ₂ O ₃		473	1.3	280.2±20.4	147.8±22.8
Cu/ZrO _x @Al ₂ O ₃		493	3.9	627.5±45.8	577.0±88.9
Cu/Al ₂ O ₃	1.5	433	0.4	47.2±3.4	16.8±2.6
Cu/Al ₂ O ₃		453	0.5	112.0±8.2	51.6±7.9
Cu/Al ₂ O ₃		473	1.0	191.6±13.9	143.0±22.0
Cu/Al ₂ O ₃		493	1.9	335.0±24.5	392.0±60.4
Cu/TaO _x @Al ₂ O ₃	1.5	433	0.3	68.7±5.0	10.6±1.6
Cu/TaO _x @Al ₂ O ₃		453	0.5	108.0±7.9	42.4±6.5
Cu/TaO _x @Al ₂ O ₃		473	0.9	208.7±15.2	64.4±9.9
Cu/TaO _x @Al ₂ O ₃		493	1.5	284.0±20.7	249.0±38.3
3.0Cu/TaO _x @Al ₂ O ₃	3.0	433	0.2	51.4±3.8	9.0±1.4
3.0Cu/TaO _x @Al ₂ O ₃		453	0.3	80.0±5.8	28.0±4.3
3.0Cu/TaO _x @Al ₂ O ₃		473	0.6	139.7±10.2	71.4±11.0
3.0Cu/TaO _x @Al ₂ O ₃		493	1.6	263.2±19.2	249.8±38.5
4.5Cu/TaO _x @Al ₂ O ₃	4.5	433	0.2	30.2±2.2	6.0±0.9
$4.5 Cu/TaO_x @Al_2O_3 \\$		453	0.3	64.0±4.7	25.4±3.9
$4.5 Cu/TaO_x @Al_2O_3$		473	0.5	105.4 ± 7.7	57.6±8.9
4.5Cu/TaO _x @Al ₂ O ₃		493	1.1	165.0±12.0	196.6±30.3

Table S2. Initial methanol and CO formation rates obtained with the series of $Cu/MO_x@Al_2O_3$ catalysts at various reaction temperatures. Reaction conditions: $H_2/CO_2=3.0$, P= 63 bar, CO₂ conversion <5%.

^a Nominal surface copper content. ^bMaximum CO_2 conversion level considered to determine initial formation rates. ^c Initial methanol formation rate. ^d Initial CO formation rate. Standard errors for the formation rates have been determined from 3 independent tests with selected catalysts.

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