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Zr(IV) surface sites determine CH₃OH formation rate on Cu/ZrO₂/SiO₂ - CO₂ hydrogenation catalysts

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ABSTRACT

Cu/ZrO₂/SiO₂ are efficient catalysts for the selective hydrogenation of CO₂ to CH₃OH. In order to understand the role of ZrO₂ in these mixed-oxides based catalysts, in situ X-ray absorption spectroscopy has been carried out on the Cu and Zr K-edge. Under reaction conditions, Cu remains metallic, while Zr is present in three types of coordination environment associated with 1) bulk ZrO₂, 2) coordinatively saturated and 3) unsaturated Zr(IV) surface sites. The amount of coordinatively unsaturated Zr surface sites can be quantified by linear combination fit of reference X-Ray absorption near edge structure (XANES) spectra and its amount correlates with CH₃OH formation rates, thus indicating the importance of Zr(IV) Lewis acid surface sites in driving the selectivity toward CH₃OH. This finding is consistent with the proposed mechanism, where CO₂ is hydrogenated at the interface between the Cu nanoparticles that split H₂ and Zr(IV) surface sites that stabilizes reaction intermediates.

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1. Introduction

The hydrogenation of CO₂ to CH₃OH is a promising approach to mitigate the increasing amount of CO₂ in the atmosphere and to incorporate CO₂ into a carbon cycle by using renewable H₂ derived from intermittent excess energy coming from wind and solar power [1–7]. Copper-based catalysts promoted by ZnO or ZrO₂ are typically preferred because of their superior catalytic performances compared to other metals in addition to the relatively large availability and cheap price of Cu [3,6], while alternative catalysts have also been reported for the hydrogenation

of CO₂ to CH₃OH consisting of different metals and/or alloys such as Pd/ZnO, Pd-Cu/SiO₂ or Ni₅Ga₃/SiO₂ as well as systems without any metals in their metallic form as in the case of In₂O₃/ZrO₂ or ZnO-ZrO₂ [8–12]. Catalysts consisting of copper nanoparticles supported on ZrO₂ or ZrO₂/SiO₂ [13–24], are promising due to their high selectivity for CH₃OH vs. CO. The origin of this improved selectivity has been discussed over the years; with proposals ranging from Lewis acidic Zr(IV) sites, formation of oxygen vacancies associated to formation of Zr(III) sites, or electronic charge transfer between Cu and Zr [14,19,25–27]. Thus, the exact role of Zr to mediate CH₃OH

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synthesis is still under debate. We have recently shown by a combined computational and experimental approach that the role of ZrO_2 in Cu/ZrO_2 is to provide Lewis acidic Zr(IV) surface sites that helps with the stabilization and the conversion of reaction intermediates to CH_3OH [19]. In parallel, it was also shown that these interfacial sites have a positive influence on the catalytic conversion of ethanol to ethyl acetate on Cu-ZrO_2 [28]. Moreover, we have recently shown that Cu nanoparticles supported on silica doped with isolated Zr(IV) surface sites, prepared by a Surface Organometallic–Thermolytic precursor approach [29–31], obey the same principle: the Zr(IV) ions, likely situated at the periphery of Cu nanoparticles, drives the selective hydrogenation of CO_2 to CH_3OH [24].

We therefore reasoned that the presence of Zr surface sites are likely involved in the selective hydrogenation of CO_2 to CH_3OH in $\text{Cu}/\text{ZrO}_2/\text{SiO}_2$ mixed oxides and have thus investigated this system by in situ X-ray absorption spectroscopy (XAS). Furthermore, the use of high surface area SiO_2 , which is considered as an inert support compared to ZrO_2 , allows for the formation of mixed oxides with varying Zr loadings and a high surface Zr density. Here we show a direct connection between CH_3OH activity with the number of under-coordinated Zr surface sites, further pointing to the role of Lewis surface sites in the promotion of Cu/Zr -based CH_3OH synthesis catalysts.

2. Experimental

2.1. General

SiC (FisherEU), CuCl (Acros Organics), LiO^iBu (Aldrich-Fine Chemicals), and $\text{ZrO}(\text{NO}_3)_2$ hydrate (Aldrich-Fine Chemicals), CaH_2 (Aldrich-Fine Chemicals) were used as received. Monoclinic ZrO_2 was obtained from Daiichi Kigenso Kagaku Kogyo Co. Pentane was purified over two solvent purification alumina columns (MBraun) and degassed prior to use. H_2 for catalysts preparation was purified over activated R3-11 BASF catalyst and activated 4 Å molecular sieves. SiO_2 (AEROSIL 200) was purchased from Evonik. Pyridine (Across Organics) was dried over CaH_2 and degassed prior to use. Unless otherwise specified all preparations of catalysts were carried out under argon using standard Schlenk techniques and gloveboxes. $[\text{Cu}(\text{O}^i\text{Bu})]_4$ [32] and Cu/SiO_2 [19] were synthesized according to literature procedure and stored in an argon filled glovebox. All the details concerning material characterization, catalytic testing and X-ray absorption spectroscopy are similar to Ref. [24] and repeated here for the sake of clarity.

2.2. Preparation $\text{ZrO}_2/\text{SiO}_2$ (SZ_xO)

SiO_2 was impregnated with an aqueous solution of $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ 1 mL g^{-1} corresponding to the porous volume of SiO_2 , dried at room temperature, prior to calcination under a flow of synthetic air at 500 °C for 12 h (60 °C h^{-1}), evacuated hot under high vacuum and stored in an argon filled glovebox. The Zr loading was controlled by the concentration of the $\text{ZrO}(\text{NO}_3)_2$ solution.

2.3. Representative procedure for supported copper nanoparticle synthesis.

A solution of $[\text{Cu}(\text{O}^i\text{Bu})]_4$ (220 mg, 0.4 mmol) in 20 mL of pentane was added to 2 g of the $\text{ZrO}_2/\text{SiO}_2$ mixed oxide (SZ_xO) wetted with pentane. The suspension was stirred for 4 hours, washed three times with pentane (5 mL) and dried at 10^{-5} mbar for 1 h. The solid was then reduced under H_2 at 500 °C for 5 h (100 °C h^{-1}) cooled down to room temperature under H_2 , evacuated under high vacuum (10^{-5} mbar) and stored in an argon filled glovebox.

2.4. Material characterization

Elemental analyses of all materials were performed by the Mikroanalytisches Labor Pascher, Remagen, Germany. Powder X-ray diffraction (pXRD) patterns were recorded on a PANalytical X'Pert PRO-MPD diffractometer at a voltage of 40 kV and a current of 40 mA by applying $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54060$ Å) or on a STADI P diffractometer in transmission mode equipped with a Mythen 1K detector (DECTRIS) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54060$ Å). Catalyst morphology was obtained by transmission electron microscopy (TEM) on a Hitachi HT7700 or a Talos F200X microscope within the facilities of ScopeM at ETH Zurich. For the determination of the particle size distribution, an average of at least 100 individual particles were considered, and the mean particle size and standard deviation are given according to a lognormal distribution function. Fourier-Transform Infrared (FTIR) spectroscopy experiments were performed on self-supporting wafers using a Bruker Alpha FT-IR spectrometer in transmission mode (24 scans, 4 cm^{-1} resolution) under exclusion of air. Intensities were normalized to the Si-O-Si overtones from the silica. The specific surface area of the catalysts was measured from a N_2 physisorption isotherm recorded at 77 K on a BEL JAPAN BELSORP-mini II apparatus. The samples were degassed at 300 °C under vacuum (10^{-3} mbar) for 3 h prior to measurement. The data was analyzed by the BET method with a p/p_0 range between 0.1 and 0.3. Copper surface area was determined by N_2O titration. In a typical experiment 30–50 mg of the sample were weight into a U-shape quartz tube and connected to the instrument (BEL Japan, INC., BELCAT-B). Prior to analysis, the samples were pretreated under a flow of 50% H_2/He at 300 °C for 2 h, after which 25–30 successive pulses of the titration gas mixture (1% N_2O in He) were introduced by a calibrated injection valve (2.77 $\mu\text{LN}_2\text{O}$ (stp) per pulse). The amount of N_2O consumed is determined by monitoring the amounts of N_2O and N_2 in the exhaust with a thermal conductivity detector. The quantity of surface copper is then determined assuming the titration equation:

Pyridine adsorption experiments were performed on a self-supporting pellet of the Cu -based catalysts and monitored by infrared spectroscopy. After exposure of pyridine in the gas phase, the pellet was subsequently placed under high vacuum (10^{-5} mbar) at room temperature (rt), 100, 200, 300 and 400 °C (300 °C min^{-1}) for 15 min. prior to measurement of the IR

spectrum.

2.5. X-ray absorption spectroscopy (XAS)

X-ray absorption spectra at the Cu and Zr *K*-edge were measured at the SuperXAS beamline at the Swiss Light Source (SLS). The SLS is operating in top-up mode at a 2.4 GeV electron energy and a current of 400 mA. The incident photon beam provided by a 2.9 T super bend magnet source was selected by a Si(111) quick-EXAFS monochromator [34] and the rejection of higher harmonics and focusing were achieved by a silicon (for Cu *K*-edge) or a rhodium-coated (for Zr *K*-edge) collimating mirror at 2.5 mrad. During the measurements the monochromator was rotating with 10 Hz frequency and XAS spectra were collected in transmission mode using ionization chambers specially developed for quick data collection with 1 MHz frequency [34]. The resulting spectra were averaged over 5 min. Calibration of the monochromator energy position was performed by setting the inflection point of a Cu or Zr foil spectrum recorded simultaneously with the sample to 8979 or 17998 eV for Cu or Zr *K*-edges, respectively.

In a typical in situ experiment, about 10–20 mg of the powder sample was packed into a 3-mm thick quartz capillary (0.1 mm wall thickness), which was connected with a pressurizable gas flow system. The catalysts were reduced under a H₂/N₂ mixture (15%, 1 bar) at 300 °C for 60 min, and then cooled down to reaction temperature (230 °C). The reduction gas was flushed with N₂ for 15 min and then changed to the reaction gas mixture (CO₂:H₂:N₂ = 1:3:1). Under reaction gas, the set-up was pressurized to 5 bar using a back-pressure regulator before recording the spectra. The spectra were background-corrected and normalized using the Demeter software package. References (ZrO₂, CuO and Cu₂O) were mixed with cellulose, pressed into wafers and sealed in kapton tape.

2.6. Catalytic testing in CO₂ hydrogenation

CO₂ hydrogenation reactions were conducted in a fixed-bed tubular reactor (9.1 mm ID) in down-flow configuration (PID Eng&Tech). In a typical experiment 250 mg of catalyst powder oxidized in air was mixed with 5.0 g of SiC and loaded in the reactor under ambient conditions. First, the catalyst was reduced for 1 h under a flow of 15% H₂/N₂ (50 mL min⁻¹) at 300 °C and atmospheric pressure. After cooling down to 270 °C a flow of CO₂:H₂:N₂ (1:3:1, 50 mL min⁻¹) at 25 bar was passed through the catalyst for 3 h to ensure steady-state thereafter. The reactor was then set to measurement conditions (230 °C, 25 bar) and the gas phase was analyzed via online gas chromatography (Agilent 7890B) equipped with an FID for CH₃OH, CH₃OCH₃ and TCD for N₂, CO₂, CO and CH₄. Different contact times were probed by changing the gas flow rate from 100 mL (STP) min⁻¹ to as low as 6 mL (STP) min⁻¹. Finally, activity data was collected at the initial flow rate of 100 mL min⁻¹ to check for potential deactivation of the catalyst. The reaction rates, conversions and selectivities were calculated using the following set of Eqs. (1–4):

$$F_{out} [mol\ h^{-1}] = \frac{F_{in} \cdot c_{N_2,in}}{c_{N_2,out}} \quad (1)$$

$$r_{Cu,x} [mol_x\ h^{-1}\ g_{Cu}^{-1}] = \frac{F_{out} \cdot c_{x,out}}{m_{cat} \cdot w_{Cu}} \quad (2)$$

$$S_x = \frac{F_{x,out}}{\sum_{i=1}^n F_{i,out}} \quad (3)$$

$$X_{CO_2} = \frac{\sum_{i=1}^n F_{i,out}}{F_{CO_2,in}} \quad (4)$$

where F_{in} is the total gas inlet flowrate (mol h⁻¹), F_{out} is the total gas outlet flow rate (mol h⁻¹), $c_{x,in}$ is the inlet gas fraction of species x , $r_{Cu,x}$ is the formation rates of species x per gram copper ($g_x\ h^{-1}\ g_{Cu}^{-1}$), m_{cat} is the mass of catalyst in the reactor

Fig. 1. (a) Schematic representation of grafting and reduction of [Cu(OⁱBu)]₄ on SZ_xO for generating Cu nanoparticles. (b) Particle size distribution and TEM images of Cu/SZ₁O (left) and Cu/SZ₂O (right).

Table 1Physicochemical properties of the prepared copper-based catalysts Cu/SZ_xO (*x* = 1 or 2) vs. reported Cu/ZrO₂ and Cu/Zr_{0.9}@SiO₂.

Entry	Catalyst	Zr loading ^a (wt%)	Cu Loading ^a (wt%)	Specific surface area ^b (m ² g ⁻¹)	Cu Surface area ^c (μmol g ⁻¹)	Particle size Distribution ^d (nm)
1	Cu/SZ ₁ O	1.07	3.66	177	63/36	3.3 ± 1.2
2	Cu/SZ ₂ O	2.32	3.97	177	63/32	3.7 ± 1.2
3[24]	Cu/ZrO ₂	N/A	2.33	115	33/17	— ^e
4[24]	Cu/Zr _{0.9} @SiO ₂	0.96	4.19	206	50/50	2.6 ± 1.3
5[24]	Cu/SiO ₂	N/A	4.19	197	50/34	2.9 ± 1.3

^a Determined by ICP-OES; ^b Determined from N₂ physisorption isotherms applying the BET method; ^c Determined from N₂O chemisorption on fresh/spent catalyst; ^d Determined by TEM of fresh catalyst; ^e Poor contrast between Cu and Zr did not allow TEM analysis

(*g*_{cat}), *w*_{Cu} the weight loading of copper (wt_{Cu}%), *S_x* the product based selectivity of product *x*, *F*_{i,out} the flowrates of the products, and *X*_{CO₂} the conversion of CO₂. Intrinsic formation rates (with respect to the contact time) and selectivity (with respect to CO₂ conversion) are obtained by using a second order polynomial fit on the experimental data.

3. Results and discussion

Mixed oxide ZrO₂/SiO₂ supports with different Zr loadings are prepared by incipient wetness impregnation of silica (SiO₂) with a ZrO(NO₃)₂ solution, followed by calcination at 500 °C. Reaction of [Cu(OⁱBu)]₄ with the surface Si-OH and Zr-OH groups on the calcined mixed oxide support allows the formation of grafted copper complexes as evidenced by the consumption of Si-OH (3745 cm⁻¹) and Zr-OH groups (3790 cm⁻¹) and the appearance of C-H stretches (around 3000 cm⁻¹) in the infrared spectra (Figs. S1–S4). Subsequent reduction under H₂ at 500 °C removes all the organic ligands and leads to the re-appearance of Si-OH and Zr-OH groups (Figs. S1–S4) yielding supported copper nanoparticles on the ZrO₂-SiO₂ mixed oxide supports (Fig. 1) denoted as Cu/SZ_xO (with *x* corresponding to the weight loading of Zr). Catalysts consisting of Zr loadings ranging from 1 wt% to 9wt% and a Cu loading of around 4 wt% are generated (Tables 1 and S1) according to inductively coupled plasma optical emission spectrometry (ICP-OES). In all cases, small and narrowly distributed copper nanoparticles of around 2–4 nm (Figs. 1(b) and S5–S6) are formed according to transmission electron microscopy (TEM). Chemisorption experiments of the Cu surface sites using N₂O also show similar amounts of Cu surface sites of ca. 63 μmol g⁻¹ for Cu/SZ_xO (*x* = 1 and 2) (Tables 1 and S1), confirming the similar copper dispersion; the Zr loading being the only varying parameter. Such data are similar to what is observed for Cu supported on SiO₂, ZrO₂, and isolated Zr(IV) surface sites on SiO₂ prepared by the same approach [19,32,33]. Powder XRD shows no presence of crystalline Cu and Zr phases consistent with a high dispersion of both Cu and ZrO₂ at low Zr loading (Fig. S7).

The existence of similar physicochemical properties for all samples allow to directly study the effect of the support, namely the Zr loading. These catalysts are tested in CO₂ hydrogenation in a fixed bed plug-flow reactor at 230 °C and 25 bar using a CO₂:H₂:N₂ ratio of 1:3:1 at different contact times, generating CH₃OH and CO as main reaction products (Table 2). Extrapolating the conversion to 0% show selectivities toward CH₃OH of

78% and 83% for Cu/SZ₁O and Cu/SZ₂O, respectively, similarly to what is obtained for Cu/ZrO₂ (68%) [19]. The intrinsic formation rates of CH₃OH normalized by the mass of copper are 1.47 and 1.32 g h⁻¹ g_{Cu}⁻¹ for Cu/SZ₁O and Cu/SZ₂O, respectively and thus decreases slightly with higher Zr content (Cu/SZ₂O) (Table 2). By comparison, the intrinsic CO formation rates are 0.51 and 0.38 g h⁻¹ g_{Cu}⁻¹ for Cu/SZ₁O and Cu/SZ₂O, respectively, in relation to the observed selectivities. Noteworthy the CH₃OH formation rates decrease at longer contact times for all Cu/SZ_xO catalysts, indicating inhibition of CH₃OH formation at higher conversion (Fig. S8). In addition, the mixed oxide catalysts with higher Zr loading that show similar physicochemical properties (Table S1) do not lead to further enhancement in CH₃OH activity (Table S2). The tested catalysts show no deactivation after 2 days of reaction (Figs. S9 and S10) and similar particle size distributions of the spent catalyst is obtained according to TEM, while the Cu surface sites determined by N₂O chemisorption slightly decrease (Table 1, Table S1 and Figs. S5–S6 and S11–S12). Overall the prepared catalysts show to be selective toward CH₃OH in line with the previous results on Cu/ZrO₂/SiO₂ and Cu/ZrO₂ based CO₂ hydrogenation catalysts [14,19,24].

However, the similar CH₃OH activity for the Cu supported catalysts on ZrO₂/SiO₂ mixed oxides with varying Zr loading may seem surprising as a higher amount of promoter is expected to further enhance the CH₃OH formation rate. We have thus decided to investigate these catalysts by in situ XAS on the Cu and Zr *K*-edge with the goal to evaluate the speciation of Cu and Zr under reaction condition for Cu/SZ_xO (*x* = 1 and 2), where a high dispersion of Zr is expected. The XAS spectra of Cu/SZ_xO are recorded under different conditions. (1) after exposure to air, (2) after heating at 300 °C under a flow of N₂ at 1 bar, (3) under a flow of N₂ at 230 °C and 1 bar after reduction

Table 2Catalytic activity data in the hydrogenation of CO₂ of copper-based catalysts Cu/SZ_xO vs. reported Cu/ZrO₂ and Cu/Zr_{0.9}@SiO₂.

Entry	Catalyst	CH ₃ OH Sel. ^a	CO Sel. ^a	<i>r</i> _{Cu,CH₃OH} ^b (g h ⁻¹ g _{Cu} ⁻¹)	<i>r</i> _{Cu,CO} ^b (g h ⁻¹ g _{Cu} ⁻¹)
1	Cu/SZ ₁ O	78	20	1.47	0.51
2	Cu/SZ ₂ O	83	17	1.32	0.38
3[24]	Cu/ZrO ₂	68	28	0.97	0.37
4[24]	Cu/Zr _{0.9} @SiO ₂	77	23	1.06	0.41
5[24]	Cu/SiO ₂	47	52	0.27	0.26

Reaction conditions: CO₂:H₂:N₂ = 1:3:1, 230 °C, 25 bar. ^a Obtained by extrapolation to 0% conversion; CH₃OCH₃ and traces of CH₄ were detected by GC-FID; ^b Extrapolated to a contact time of 0 s g mL⁻¹.

with H₂, and (4) under CO₂ hydrogenation conditions (CO₂:H₂:N₂ in a 1:3:1 ratio, 230 °C and 5 bar) (Fig. S13). The Cu K-edge shows that copper is present as CuO after exposure to air. CuO is reduced and present as metallic Cu under H₂ at 300 °C and remains so under CO₂ hydrogenation conditions for both Cu/SZ_xO samples (Fig. S14). It is however not possible to draw more specific conclusions regarding the state of surface Cu since the XAS signal is mostly dominated by bulk Cu.

The Zr K-edge under air indicates the presence of Zr(IV) for both Cu/SZ_xO ($x = 1$ and 2) samples. Upon heating at 300 °C under N₂ a pre-edge appears for Cu/SZ₁O. This feature was previously assigned to under-coordinated Zr(IV) surface sites in Cu/Zr_{0.9}@SiO₂, which contain only surface Zr(IV) sites; they are generated upon desorption of adsorbates (such as H₂O) on the surface Zr(IV) sites when heated to 300 °C [24]. The same feature is also observed with Cu/SZ₂O but with a lower intensity, most likely due to a smaller ratio of surface Zr atoms compared to bulk ZrO₂ with increasing ZrO₂ loading. After reduction under H₂ at 230 °C, no changes in the Zr K-edge XANES for both Cu/SZ_xO ($x = 1$ and 2) samples are observed, similar to the samples heated to 300 °C under N₂. Under reaction conditions, at 5 bar and 230 °C, the pre-edge is reduced in intensity on both samples, which likely corresponds to the partial coordination of reaction intermediates/products (CH₃OH, formate, H₂O...) on Zr surface sites (Fig. 2), as we proposed for Cu/Zr_{0.9}@SiO₂, where only isolated Zr surface sites are present on the SiO₂ support [24]. Overall, no change in the position of the inflexion point of the XANES spectra are observed pointing to Zr remaining mainly in a 4+ oxidation state (Table S3). All the changes in the XANES spectra can thus be assigned to coordination and de-coordination of adsorbates, i.e., reaction intermediates/products on the Zr(IV) surface sites. The presence of Lewis acidic Zr surface sites are further evidenced by pyridine adsorption experiments by the appearance of additional bands (1608 cm⁻¹) in the IR spectra (Fig. S15) when comparing to Cu/SiO₂ (Fig. S16). In particular, while on Cu/SiO₂ all the pyridine is removed at 300 °C under high vacuum (10⁻⁵ mbar), pyridine coordinated to Lewis acid sites are still present on the

Fig. 3. Representation of three types of Zr sites used for XANES fitting.

zirconium containing sample.

In order to obtain a quantitative assessment of the number of Zr surface sites present on the Cu/SZ_xO as well as the ratio of Zr surface sites that are fully coordinated under reaction condition, the X-ray near edge structure (XANES) spectra are further fitted by a linear combination of three reference XANES spectra (Fig. 3). Monoclinic ZrO₂ (*m*-ZrO₂) is used to represent bulk ZrO₂, and well-defined isolated Zr(IV) surface sites (prepared using a Surface Organometallic Chemistry (SOMC) approach [24]) representing either coordinatively saturated or under-coordinated Zr surface sites with a coordination number of 5 (Fig. 3 and Table 3). All the XANES spectra can be adequately fitted using these three reference spectra (Fig. S17–S18).

For Cu/SZ₁O (Table 3 and Fig. S13) 21%–31% of the Zr is present as bulk ZrO₂ throughout all the in situ XAS experiment. Under air at room temperature 57% of the Zr is present as coordinatively saturated Zr surface sites, while 12% are coordinatively unsaturated. Upon heating under N₂ at 300 °C all the surface Zr sites become under-coordinated and remains so after reduction and at 230 °C. Under CO₂ hydrogenation conditions, the fraction of coordinatively saturated Zr increases (26%) along with decreasing fraction of under-coordinated sites (45%). On Cu/SZ₂O (Table 3 and Fig. S14), the linear combination fit shows that 39%–52% of the Zr is present as bulk ZrO₂ under all experimental conditions, consistent with a higher ratio of bulk ZrO₂ when increasing the Zr loading in compar-

Fig. 2. Zr K-edge XANES spectra recorded at different stages under different reaction conditions for Cu/SZ₁O and Cu/SZ₂O.

Table 3

Results of the linear combination fit of the in situ Zr K-edge XANES spectra (%).

Sample	Reaction step	Reference		
		Coordinated Zr(IV) Surface Sites	Under-coordinated Zr(IV) Surface Sites	m-ZrO ₂
Cu/SZ ₁ O	Air, rt, 1 bar	57	12	31
	N ₂ , 300 °C, 1 bar	0	79	21
	Reduced, 230 °C, 1 bar	3	73	24
	CO ₂ /H ₂ /N ₂ (1:3:1), 230 °C, 5 bar	26	45	29
Cu/SZ ₂ O	Air, rt, 1 bar	48	0	52
	N ₂ , 300 °C, 1 bar	24	37	39
	Reduced, 230 °C, 1 bar	28	33	39
	CO ₂ /H ₂ /N ₂ (1:3:1), 230 °C, 5 bar	36	19	45

ison to Cu/SZ₁O. 48% of Zr correspond to coordinatively saturated Zr surface sites, which become in part under-coordinated at 300 °C under N₂ (37%), while 24% remain coordinatively saturated. After reduction and cooling to 230 °C a similar ratio of under-coordinated and coordinated Zr surface sites are present (28% and 33%). Finally, under CO₂ hydrogenation conditions the fraction of sites that are coordinatively saturated increases to 36%, while 19% are still present as under-coordinated sites.

Overall, the linear combination fit of the XANES spectra allows the evaluation of the amount of surface and bulk Zr sites for Cu/SZ₁O and Cu/SZ₂O. For each individual sample, the ratio of bulk vs. Zr surface species remains similar indicating no extensive restructuring of ZrO₂ during the tested conditions. It is noteworthy that while Cu/SZ₂O has a higher Zr loading than Cu/SZ₁O, they display both similar concentration of under-coordinated Zr surface sites per gram of catalyst (around 90 μmol g⁻¹) at the reaction temperature of 230 °C under N₂, which thus correlates with similar CH₃OH formation rates for Cu/SZ₁O and Cu/SZ₂O. Such a finding is consistent with our previous proposal that Lewis acidic Zr surface sites are key for increasing the CH₃OH formation rate[24] and shows that the role of Zr dopants is similar for all Cu/ZrO₂ based CO₂ hydrogenation catalysts.

4. Conclusions

All in all, copper supported on ZrO₂/SiO₂ mixed oxides, with varying Zr loading at similar copper loading, particle size distribution and specific surface area, are selective toward CH₃OH in CO₂ hydrogenation with no significant difference in catalytic performance at different Zr loadings. In situ XAS reveals that the reactivity of supported copper nanoparticles on the ZrO₂/SiO₂ mixed oxides for CO₂ hydrogenation to CH₃OH correlates with the number of under-coordinated Zr surface sites, rather than the Zr loading, thus indicating that a high dispersion of Zr is likely a key descriptor to enhance the CH₃OH formation rate. Such type of molecular level structure-activity relationship paves the way towards more rational design of CO₂ hydrogenation catalysts.

Supporting Information.

Additional data including IR and XAS spectra, catalytic data,

X-ray powder diffractograms and TEM images (PDF)

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Graphical Abstract

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Zr(IV) surface sites determine CH₃OH formation rate on Cu/ZrO₂/SiO₂ - CO₂ hydrogenation catalysts

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Density and role of Lewis acidic Zr(IV) surface sites in Cu/SiO₂/ZrO₂ based catalyst to promote CO₂-to-CH₃OH synthesis is elucidated by in-situ X-ray absorption spectroscopy.

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CO₂加氢催化剂Cu/ZrO₂/SiO₂上Zr(IV)表面位对甲醇生成速率的影响

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摘要: Cu/ZrO₂/SiO₂是有效的CO₂选择加氢制甲醇催化剂。为了理解混合氧化物基催化剂中ZrO₂的作用, 在Cu和Zr的K边进行了原位X-射线吸收光谱测试。在反应条件下, Cu保持金属态, 而Zr以三类配位环境的形式存在: 体相ZrO₂, 配位饱和的、以及不饱和的Zr(IV)表面位。配位不饱和Zr表面位可通过线性拟合参比的X射线吸收近边结构光谱进行定量, 发现其数量与甲醇生成速率有关, 因而表明Zr(IV) Lewis酸表面位在驱动选择生成甲醇反应中的重要性。这与提出的机理是一致的: 在裂解H₂的Cu纳米颗粒与稳定反应中间体的Zr(IV)表面位之间的界面上进行CO₂加氢。

关键词: CO₂加氢; ZrO₂/SiO₂负载的Cu纳米颗粒; Lewis酸表面位; 原位X射线吸收光谱

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