Enhanced CH_3OH selectivity in CO_2 hydrogenation using Cu-based catalysts generated via SOMC from Ga^III single-sites†

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Small and narrowly distributed nanoparticles of copper alloyed with gallium supported on silica containing residual Ga^III sites can be obtained via surface organometallic chemistry in a two-step process: (i) formation of isolated Ga^III surface sites on SiO_2 and (ii) subsequent grafting of a Cu^I precursor, [Cu(O^Bu)]_4, followed by a treatment under H_2 to generate CuGa, alloys. This material is highly active and selective for CO_2 hydrogenation to CH_3OH. In situ X-ray absorption spectroscopy shows that gallium is oxidized under reaction conditions while copper remains as Cu^0. This CuGa material only stabilizes methoxy surface species while no formate is detected according to ex situ infrared and solid-state nuclear magnetic resonance spectroscopy.

Introduction

The transformation of CO_2 into value-added products is a promising strategy to mitigate the further increase of CO_2 in the earth’s atmosphere that is connected to environmental changes. In that context, the hydrogenation of CO_2 yields CH_3OH that can be used as a base chemical for the production of fuels or as a fuel itself, thus generating a closed carbon-fuel cycle, provided that efficient CO_2 capture and storage, and efficient H_2 production from renewable energy sources are available. Major issues associated with the hydrogenation of CO_2 into CH_3OH are the selectivity of the process and the long-term stability of catalysts. Regarding selectivity, the hydrogenation of CO_2 can also yield CO via, for instance, the reverse water gas shift (RWGS) reaction or the decomposition of methyl formate, that can be formed in situ via secondary reactions. Heterogeneous catalysts that are able to form CH_3OH with good selectivity and activity mainly consist of copper-based catalysts together with zinc oxide (e.g. Cu/ZnO or Cu/ZnO/Al_2O_3), gallium oxide (e.g. Cu/ZnO/Ga_2O_3) or zirconium oxide (Cu/ZrO_2). In the case of ZrO_2, it has been shown that the Lewis acidic surface Zr^IV sites stabilize reaction intermediates (CO_2, formates and methoxy) and improve the activity and methanol selectivity. The origin of the promotional effect of zinc or gallium oxide is, however, not fully understood. For instance, the formation of highly active CuZn surface alloys or interfacial sites between Cu and ZnO have both been proposed. The promotional effect of gallium oxide has been far less studied.

Recently, it has been shown that surface organometallic chemistry (SOMC) combined with thermolytic molecular precursors (TMP) constitutes a powerful synthetic strategy to generate supported metal nanoparticles surrounded by well-defined isolated promoter sites that allows investigating the role of interfacial sites via in situ spectroscopic methods. This approach can also yield supported alloyed nanoparticles, depending on the selection of metal and promoters (vide infra). The SOMC/TMP approach can be summarized as follows: in a first step, the support, SiO_2, is dehydroxylated at 700 °C to obtain isolated surface silanol (Si-OH) groups (1 OH, nm^2) that are used as anchoring groups to graft the TMP. Post-thermal treatment at high temperature generates isolated low-coordinated metal surface sites, that are free of organic ligands, and restores Si-OH groups (Scheme 1a), onto which a second molecular precursor is grafted. Subsequent post-treatment under reducing conditions (H_2) generates metal nanoparticles interfacing low-coordinated metal surface sites (Scheme 1b). This approach has allowed the generation of highly active and selective CO_2 hydrogenation catalysts by supporting Cu nanoparticles on SiO_2 containing isolated Zr^IV and Ti^IV sites. These catalysts show high activity and CH_3OH selectivity, but also suffer from the decrease of CH_3OH selectivity at high conversion as observed for other CO hydrogenation catalysts. The outstanding activity and CH_3OH selectivity of copper supported on silica containing Ti^IV isolated sites is particularly noteworthy, considering that Cu/TiO_2 performs very poorly in CH_3OH synthesis by favoring CO formation. This difference of catalyst performance has been ascribed to the site isolation of Ti^IV and the use of a non-reducible support, SiO_2, thus allowing...
TiIV to play exclusively the role of a Lewis acid, that stabilizes reaction intermediates at the interface with Cu particles.25 Using a similar approach, i.e., the treatment under H2 of a grafted platinum[II] molecular precursor on isolated GaIII sites generates small and narrowly distributed PtGaIII nanoparticles stabilized by remaining GaIII sites that show high activity, selectivity and stability for propane dehydrogenation.40

Here, we reasoned that the SOMC/TMP approach would be a useful tool to investigate the behavior of gallium promoters in CO2 hydrogenation catalysts (Scheme 1c). We thus prepared Cu-based nanoparticles by grafting [Cu(OBu)]4 on a silica support containing GaIII single-sites, followed by a treatment under H2. This approach yields nanoparticles consisting of CuGaIII alloys that evolved under CO2 hydrogenation conditions into Cu0 and GaIII according to in situ X-ray absorption spectroscopy (XAS). Such Cu-Ga/SiO2 catalysts display enhanced activity and selectivity at higher conversions in the hydrogenation of CO2 into CH3OH, by comparison to other Cu-based catalysts. These improved performances are attributed to Cu0/GaIII interfaces that only stabilize methoxy and not formate intermediates, according to infrared (IR) and solid state nuclear magnetic resonance (NMR) spectroscopy.

Results and discussion

Catalyst synthesis and characterization

We first prepared well-defined GaIII sites on SiO2 with ca. 1.0 GaIII nm−2 by grafting and thermolysis of [Ga(OSi(OBu))3(THF)]4 GaIII@SiO2 (ref. 42) [MIII@SiO2 denoted as isolated M surface sites in its x oxidation state] via a SOMC/TMP approach and then grafted [Cu(OBu)]4 on residual surface silanols present in GaIII@SiO2. The IR spectra show the consumption of Si–OH groups (3747 cm−1) and the appearance of C–H stretching (2700–3000 cm−1) and bending (1300–1500 cm−1) bands, consistent with grafting of [Cu(OBu)]4 via protonolysis of the Si–OH group (Fig. S1†). Next, reduction under H2 at 500 °C removes all the organics and regenerate the Si–OH groups, as shown by IR spectroscopy, yielding Cu-Ga/SiO2 (Fig. 1a). Based on inductively coupled plasma optical emission spectroscopy (ICP-OES), a metal loading of 1.61 wt% gallium and 3.88 wt% copper is obtained for Cu-Ga/SiO2 (corresponding to a 5 : 2 Cu : Ga atomic ratio).

A specific surface area of ca. 200 m2 g−1 – determined by N2 physisorption isotherms and Brunauer–Emmett–Teller (BET) analysis (Table S1†) – is obtained, similar to this of the initial material. Transmission electron microscopy (TEM) studies show the formation of small and narrowly distributed nanoparticles on SiO2 (4.6 ± 1.4 nm) (Fig. 1b), which corresponds to Cu–Ga alloy nanoparticles (vide infra). These particles are slightly larger than what was found for the corresponding Cu/SiO2 (2.9 ± 1.3 nm) prepared via a similar approach.34 Energy-dispersive X-ray (EDX) mapping of as-prepared Cu-Ga/SiO2 was introduced to the microscope without exposure to air using a vacuum transfer TEM sample holder, shows that gallium is found in the same region as the copper nanoparticles, but it is also dispersed throughout the support (Fig. S2†). In addition, the particle size distribution of Cu-Ga/SiO2 from TEM of samples with and without exposure to air does not change, indicating the absence of copper and gallium redispersion under oxidizing conditions (Fig. S3†). N2O titration at 90 °C, that selectively titrates the surface of Cu nanoparticles, was performed, resulting in around 55 μmol gcat−1 surface sites for Cu-Ga/SiO2 (assuming a 1 : 2 stoichiometry between N2O and the Cu surface site) (Table S1†), which is similar for what is obtained for Cu/SiO2 (50 μmol gcat−1),34 despite the larger particle sizes for Cu-Ga/SiO2. It is possible that N2O reacts with reduced gallium sites leading to a higher N2O uptake similar to what is observed with zinc in case of Cu/ZnO/Al2O3.34 Chemosorption experiments using H2 at 40 °C indicate around 60 μmol gcat−1 surface sites (assuming a 1 : 2 stoichiometry between H2 and the surface site) for Cu-Ga/SiO2, consistent with the number obtained via N2O titration (Table S1 and Fig. S4†). No crystalline phases are observed by powder X-ray diffraction, as expected from the amorphous nature of the SiO2 support and the presence of small metal nanoparticles (Fig. S5†). The presence of residual Lewis acidic gallium sites is supported by pyridine adsorption and IR spectroscopy,41 by the presence of ring vibrational bands of pyridine at 1621 cm−1, characteristic for Lewis acidic surface sites, likely associated with GaIII sites (Fig. S6†). Upon adsorption of pyridine, it persists even at 500 °C under high-vacuum (10−5 mbar) indicating strongly bound pyridine (for details see ESI†). IR spectroscopy (Fig. S7†) of the catalysts upon adsorption of CO (90 mbar) at room temperature shows stretching bands at 2102 cm−1 for Cu-Ga/SiO2 corresponding to CO bonded to the metal nanoparticle which are slightly red-shifted with respect to what is observed for pure Cu/SiO2 at 2106 cm−1.

Further information regarding the oxidation states and structural environment of copper and gallium in Cu-Ga/SiO2 is obtained by the XAS spectra at the copper and gallium K-edges for the as-prepared catalysts stored under inert conditions (Fig. 1c). The Cu K-edge X-ray absorption near-edge structure

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**Scheme 1**  (a) General SOMC strategy to generate isolated sites or supported nanoparticles. (b and c) Utilizing isolated metal site supports generated from SOMC for metal and metal–alloy nanoparticle formation.
Fig. 1 (a) Schematic procedure for grafting of [Cu(O’Bu)]₄ on GaIII@SiO₂ followed by reduction under H₂ at 500 °C. (b) Particle size distribution and TEM images of Cu-Ga/SiO₂. (c) First derivative of the XANES spectra at the Ga K-edge of Cu-Ga/SiO₂ and reference samples.

The XANES spectrum of Cu-Ga/SiO₂ shows an edge energy at 8979 eV consistent with reduced Cu⁰ but the near edge features of Cu-Ga/SiO₂ are different from the Cu/SiO₂ or Cu foil spectrum (Fig. S8†). Fitting of the extended X-ray absorption fine structure (EXAFS) shows the presence of gallium (N = 4 ± 3 at 2.57 Å) and copper (N = 7 ± 2 at 2.34 Å) scattering paths (Table 1 and Fig. S9†), suggesting the formation of a CuGa alloy phase. The XANES spectrum of Cu-Ga/SiO₂ at the gallium K-edge shows an edge energy of 10 368 eV, which is 5 eV lower than the edge energy of GaIII@SiO₂ or Ga₂O₃, as reference samples (Fig. 1c). The shift in the edge energy indicates the presence of reduced gallium species, while the feature observed in GaIII@SiO₂ or Ga₂O₃ at 10 373 eV is still present, albeit lower in intensity, in Cu-Ga/SiO₂ as shown in the first derivative of the XANES spectrum (Fig. 1c). Further analysis and fitting of the EXAFS (Table 1) at the Ga K-edge reveals the presence of Cu neighbors (N = 8 ± 2 at 2.57 Å) consistent with the EXAFS fitting result at the K-edge with part of the gallium forming a metal alloy phase with copper. In addition, there are oxygen neighbors (N = 2 ± 1 at 1.81 Å), which are attributed to remaining isolated GaIII sites (Fig. S11†), consistent with pyridine adsorption and IR spectroscopy (vide supra). Considering the number of oxygen neighbors (N = 4) found in GaIII@SiO₂, we estimated that approx. 50% of Ga is in the form of GaIII sites in Cu-Ga/SiO₂. This indicates formation of CuGa alloy with x ≈ 0.2 based on respective copper (3.88 wt%) and gallium (1.61 wt%) loadings and taking into account that ca. 50% of gallium sites are present in its reduced form.

Overall, the XAS spectra show that reduction of the samples after Cu grafting (500 °C under H₂) leads to a partial reduction of GaIII with the formation of CuGa alloys along with remaining GaIII sites. These finding contrast with what was observed for Cu-Ti/SiO₂ (ref. 35) and Cu-Zr/SiO₂ (ref. 34) prepared in a similar fashion from TiIV and ZrIV single-sites that remained isolated upon Cu nanoparticle formation.

### Catalytic performance in CO₂ hydrogenation

The catalytic performance of Cu-Ga/SiO₂ in CO₂ hydrogenation was evaluated at 230 °C under a total pressure of 25 bar and 3 : 1 H₂ : CO₂. Following exposure to air, the material is reduced at 300 °C under H₂ in the reactor prior to catalysis. The effect of contact time on the catalytic activity/selectivity by varying the gas flowrate and the intrinsic formation rates extrapolated to zero contact time are evaluated and compared with Cu/SiO₂ and Cu-Zr/SiO₂ benchmark materials (Fig. S12 and S13†). Catalytic

### Table 1 EXAFS fits parameters of Cu-Ga/SiO₂ at the Cu and Ga K-edges

<table>
<thead>
<tr>
<th>Edge</th>
<th>Neighbor, N</th>
<th>r [Å]</th>
<th>σ² [Å²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu K-edge</td>
<td>Ga, 4 ± 3</td>
<td>2.57 ± 0.01</td>
<td>0.012 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Cu, 7 ± 2</td>
<td>2.54 ± 0.02</td>
<td>0.0100 ± 0.0009</td>
</tr>
<tr>
<td>Ga K-edge</td>
<td>O, 2 ± 1</td>
<td>1.81 ± 0.03</td>
<td>0.012 ± 0.009</td>
</tr>
<tr>
<td></td>
<td>Cu, 8 ± 2</td>
<td>2.57 ± 0.01</td>
<td>0.012 ± 0.002</td>
</tr>
</tbody>
</table>

* Number of specified neighbors. * Distance to corresponding neighbor.  
† Debye-Waller factor.
tests are carried out at conversions below 7%, which are far from thermodynamic equilibrium (15% with a CH₃OH selectivity of 43%) under the given reaction condition. The intrinsic formation rate for CH₃OH is 1.3 g h⁻¹ g⁻¹Cu for Cu-Ga/SiO₂ that is 4 times higher than Cu/SiO₂ and also slightly higher than Cu-Zr/SiO₂ (Fig. 2a). Note that the product formation rates on the support itself (GaIII@SiO₂) are below detection limits. The intrinsic CO formation rate of Cu-Ga/SiO₂ (0.1 g h⁻¹ g⁻¹Cu) is 3 times lower as compared to Cu/SiO₂ or Cu-Zr/SiO₂ (0.3 g h⁻¹ g⁻¹Cu), making Cu-Ga/SiO₂ a better catalysts with an improved selectivity to CH₃OH products of 93% (CH₃OH/DME = 30) with only 7% of CO. The formation of DME likely arise from the subsequent dehydration of CH₃OH, indicating a significant Lewis acidity for this support (vide supra). ⁴³ Remarkably, Cu-Ga/SiO₂ shows a higher CH₃OH selectivity than unpromoted Cu/SiO₂ (48%) or even Cu-Zr/SiO₂ (77%). ⁴⁴ At longer contact times (Fig. S14†), both CH₃OH and CO formation rates decrease (with a slightly larger decrease for CH₃OH formation rates (Fig. S14†)), suggesting product inhibition for both processes for Cu-Ga/SiO₂. The decrease of activity with contact time is a key limiting factor for a high productivity of CH₃OH for the Cu-Ga/SiO₂ catalyst. The product inhibition is likely associated with the blocking of Lewis acidic GaIII sites by H₂O/CH₃OH that in turn reduces CH₃OH and CO formation rates. Note that in case of Cu/SiO₂, where no Lewis acidic (interfacial) sites are present to assist the conversion of CO₂, CH₃OH and CO formation rates remain independent of contact time. Product inhibition was also observed for the related Cu-Ti/SiO₂ and Cu-Zr/SiO₂ catalysts. However, the major difference between Cu-Ti/SiO₂ or Cu-Zr/SiO₂ and Cu-Ga/SiO₂ is that in the former cases, the contact time affects the CH₃OH formation rates more than CO formation rates, leading to a decrease of CH₃OH selectivity. This dramatic decrease of selectivity is not observed for Cu-Ga/SiO₂, also indicating that CO likely forms via different mechanisms. A high selectivity toward CH₃OH is maintained for Cu-Ga/SiO₂ (>89%; taking into account DME that is initially formed from CH₃OH) at ca. 3% conversions vs. 71% and 60% selectivity for Cu-Ti/SiO₂ and Cu-Zr/SiO₂, respectively at the same conversion (Fig. 2b and S15†). After 30 hours of reaction, Cu-Ga/SiO₂ deactivates for both CH₃OH and CO formation by 75% and 80%, respectively. Analysis of the spent catalyst shows a similar particle size distribution by TEM for Cu-Ga/SiO₂ of 4.9 ± 1.6 nm compared to the fresh catalyst (Fig. S16†). The absence of any crystalline phases by powder X-ray diffraction (Fig. S3†) further indicates the absence of significant sintering throughout the catalytic testing. The deactivation of the catalyst could originate from a slightly decreased amount of accessible metal sites as shown by N₂O titration of the fresh/spent catalyst (Table S1†).

**In situ X-ray absorption spectroscopy**

The role of gallium, especially the effect of metal alloy formation and its consequence in promoting the selective formation of CH₃OH, were further investigated by in situ XAS at the copper K-edge and the gallium K-edges for Cu-Ga/SiO₂ (Fig. 3). The X-ray absorption spectra are first recorded after oxidation of the catalyst in air, followed by reduction at 300 °C under H₂. The reduced catalyst was then cooled down to 230 °C and the reaction gas consisting of CO₂ and H₂ (1 : 3) was introduced at 1 bar and then pressurized to 5 bar.

The XANES spectrum of Cu-Ga/SiO₂ at the gallium K-edge after reduction under H₂ shows a decreased white line intensity and the appearance of a feature at lower energy (10 368 eV) indicative of reduced gallium sites. ⁴⁵ The XANES spectrum has a lower intensity of the feature at that energy (10 368 eV) compared to the as-prepared catalyst, indicating that the gallium sites are more difficult to reduce following exposure to air. The feature toward lower energy associated with reduced gallium sites only appears when copper is present and is not observed for GaIII@SiO₂ treated under H₂ (Fig. S17†). Changes in GaIII@SiO₂ during in situ XAS is only due to changes in the oxygen coordination number upon heating at high temperature most likely due to removal of water (due to exposure to air) according to EXAFS fitting (Table S2 and Fig. S18–S20†). The absence of reduced gallium sites for the material without copper (GaIII@SiO₂) suggests that copper, most likely in close interaction with gallium, is necessary to reduce GaIII to Ga⁰. Under reaction conditions at 5 bar (1 : 3 ratio of CO₂ : H₂), the white line intensity increases and the feature toward lower energy disappears, indicating full oxidation of gallium sites (Fig. 4).

Copper is fully reduced upon reaction with H₂ at 300 °C and under reaction condition according to XAS (Fig. S21†). Furthermore, Lewis acidic surface sites are present in the catalysts after exposure to air followed by reduction as shown by

![Fig. 2](Image) (a) Intrinsic formation rates for CO, CH₃OH and DME and (b) overall CH₃OH selectivity vs. conversion for Cu/SiO₂, Cu-Zr/SiO₂ and Cu-Ga/SiO₂.
pyridine adsorption and IR spectroscopy (Fig. S22†). This data suggests that the Lewis acidic sites from Ga\textsuperscript{III} would be responsible for the promotion of CH\textsubscript{3}OH synthesis, similarly to what is observed for Cu/ZrO\textsubscript{2} or related Cu-Ga/SiO\textsubscript{2} systems.

**Ex situ solid state NMR spectroscopy**

In order to determine possible intermediates on gallium under reaction conditions, \textsuperscript{1}H-\textsuperscript{13}C HETCOR spectra of Cu-Ga/SiO\textsubscript{2} (reduced after exposure to air) are recorded after reacting the catalyst with 5 bar of \textsuperscript{1}H\textsubscript{2} : \textsuperscript{13}CO\textsubscript{2} (3 : 1) for 12 hours at 230 °C followed by evacuating the gas phase under high vacuum (10\textsuperscript{–5} \text{mbar}) at room temperature. The NMR spectra of Cu-Ga/SiO\textsubscript{2} shows a cross-peak at around 3/50 ppm (\textsuperscript{1}H/\textsuperscript{13}C), which is indicative of methoxy species (Fig. S23f) and the presence of dimethyl ether as evidenced by the additional cross-peak at 3/60 ppm (\textsuperscript{1}H/\textsuperscript{13}C) (Fig. S23f), consistent with the observed formation of dimethyl ether during catalysis. Notably, no formate species on Lewis acidic gallium sites (present in the case of Cu/ZrO\textsubscript{2}, Cu-Zr/SiO\textsubscript{2}, Cu-Ti/SiO\textsubscript{2}, or Cu/Al\textsubscript{2}O\textsubscript{3} systems)\textsuperscript{17,34,35} are observed, indicating that Ga\textsuperscript{III} Lewis acidic sites possibly favor the subsequent hydrogenation of formate into methoxy species and/or increase the thermodynamic stability of methoxy in comparison to formate species. This is also confirmed by the IR spectra of the ex situ Cu-Ga/SiO\textsubscript{2} sample after reacting with \textsuperscript{1}H\textsubscript{2}/\textsuperscript{13}CO\textsubscript{2} (Fig. S24f) showing the \textsuperscript{13}C–H stretches at around 2954 and 2855 cm\textsuperscript{–1} indicating the presence of methoxy, while no band associated with formate species are observed. While formate species are also likely formed as reaction intermediates on Cu-Ga/SiO\textsubscript{2} under reaction condition, the lower stability of formate compared to methoxy would be consistent with (and explains) the higher CH\textsubscript{3}OH selectivity of this material in contrast to other systems. Indeed, stable formate species have been shown to be able to generate methyl formate that readily decomposes into CO. Further work is needed to investigate the formation (or not) of formate species as key intermediate in this Cu-Ga/SiO\textsubscript{2} system.

**Conclusions**

The use of SOMC was explored in order to understand the promotional effect of gallium in Cu-based CO\textsubscript{2} hydrogenation catalysts, starting from well-defined silica-supported Ga\textsuperscript{III} sites as an initial support. This approach generates small and narrowly distributed silica-supported CuGa\textsubscript{x} nanoparticles along with residual Ga\textsuperscript{III} Lewis acidic sites. This is in contrast to previously studied well-defined isolated Zr\textsuperscript{IV} and Ti\textsuperscript{IV} sites on SiO\textsubscript{2} that yield Cu nanoparticles surrounded with isolated metal interfacial sites\textsuperscript{34,35}. These materials are readily oxidized to generate the corresponding CuO and Ga\textsuperscript{III} sites upon exposure to air, but can be partially reduced back to CuGa\textsubscript{x} alloys under H\textsubscript{2}. These CuGa\textsubscript{x} systems display improved catalytic performances in the hydrogenation of CO\textsubscript{2}, allowing the increase in the overall CH\textsubscript{3}OH (CH\textsubscript{3}OH + DME) selectivity (up to ca. 90%) at higher conversion (3%) by comparison with the benchmark catalysts, Cu-Zr/SiO\textsubscript{2} and Cu-Ti/SiO\textsubscript{2}. Under reaction conditions, the silica-supported CuGa\textsubscript{x} de-alloys yielding Cu nanoparticles and Ga\textsuperscript{III} sites indicating that the increased activity and selectivity is likely due to an increased interfacial area between Cu\textsuperscript{0} and Ga\textsuperscript{IIIO} that would promote CH\textsubscript{3}OH formation. In fact, methoxy surface species are the only observed intermediates according to ex situ solid state NMR or IR. This study overall shows the subtle differences of interest between promoters; it opens new ways to tailor CH\textsubscript{3}OH selective catalysts. We are currently exploring other promoters to understand their role and to design improved CO\textsubscript{2} hydrogenation catalysts via a more rational design.

**Conflicts of interest**

There are no conflicts to declare.
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