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Selective Hydrogenation of CO₂ to CH₃OH on Supported Cu Nanoparticles Promoted by Isolated Ti^{IV} Surface Sites on SiO₂

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Abstract: Small and narrowly distributed Cu nanoparticles, supported on SiO₂ decorated with isolated Ti^{IV} sites, prepared via surface organometallic chemistry, show significantly improved CO₂ hydrogenation activity and CH₃OH selectivity compared to the corresponding Cu nanoparticles supported on SiO₂. We propose that these isolated Lewis acid Ti^{IV} sites, evidenced by UV-Vis spectroscopy, stabilize surface intermediates at the interface between Cu nanoparticles and the support.

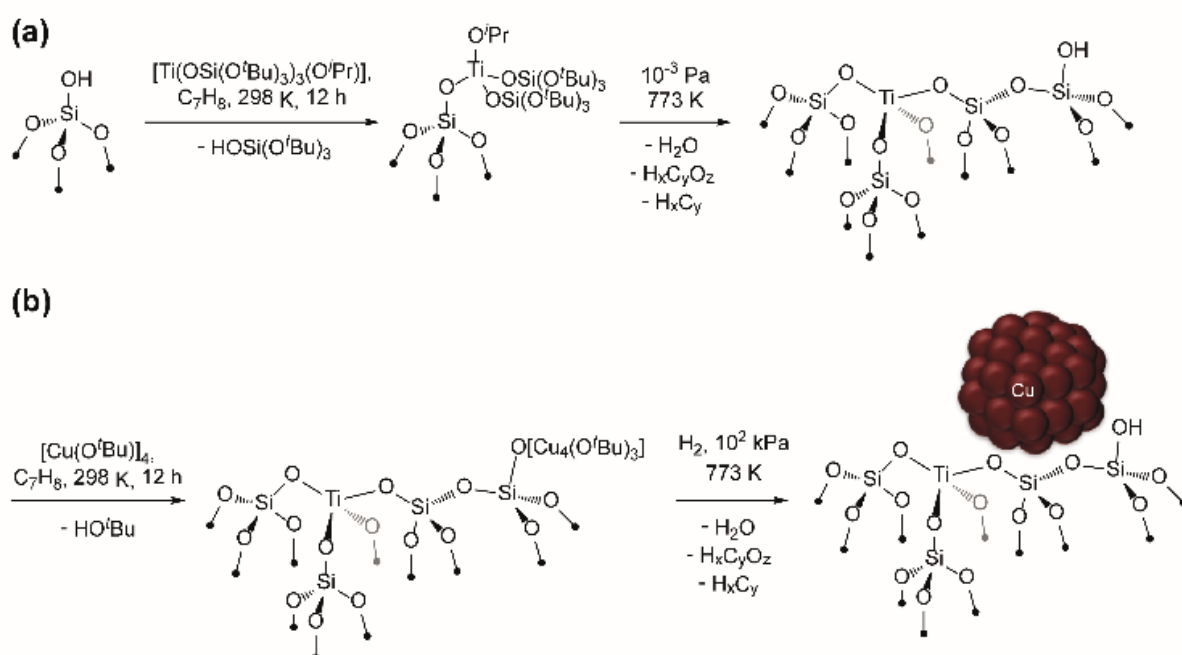
The selective hydrogenation of CO₂ to CH₃OH, together with the production of H₂ from renewable sources—e.g., intermittent excess energy generated from wind or solar power—is essential to a virtuous sustainable closed-carbon fuel cycle.^[1-4] Its practice, however, is complicated by the parasitic reverse water-gas-shift (RWGS) reaction, which forms CO instead. The most prominent catalysts for selective CO₂ hydrogenation to CH₃OH are Cu-based, although their activity and CH₃OH selectivity dramatically depend on the oxide support.^[5-8] Cu supported on ZrO₂ (Cu/ZrO₂, where “Cu/X” denotes Cu nanoparticles dispersed on support X) has shown promising activity and high CH₃OH selectivity compared

to Cu/SiO₂.^[9–12] While SiO₂ can be considered as an inert support for the Cu nanoparticles that catalyze the reaction, ZrO₂ provides Zr^{IV} sites interfacing Cu nanoparticles that act as Lewis acid sites and promote CH₃OH synthesis.^[9] In fact, Cu nanoparticles supported on SiO₂ decorated with isolated Zr^{IV} sites show CO₂ hydrogenation activity and CH₃OH selectivity nearly identical to those for Cu/ZrO₂,^[13] underscoring the importance of these Lewis acid sites at the periphery of Cu nanoparticles for the selective hydrogenation of CO₂ to CH₃OH.

In contrast, Cu/TiO₂ has been observed to be a very poor CO₂ hydrogenation catalyst with low reaction rates and CH₃OH selectivity,^[7,8,14] in spite of the ability of Ti^{IV} metal centers, which are noteworthy Lewis acids,^[15–21] to play the same role in principle as the aforementioned Zr^{IV} surface sites present in ZrO₂. This striking difference may be due to the greater reducibility of TiO₂ compared to ZrO₂, which can lead to the formation of oxygen vacancies concomitant with the reduction of Ti^{IV} to Ti^{III} and/or to strong metal-support interactions that may lead to the coverage of Cu surface atoms by TiO_x species.^[22] Recent work from our group has demonstrated the ability to mitigate the reducibility of Ga₂O₃ by dispersing Ga^{III} species on the surface of an insulating support (i.e., SiO₂).^[23] We therefore reasoned that the atomic dispersal of Ti^{IV} sites at the surface of SiO₂, upon which Cu nanoparticles were then supported, could promote the selective hydrogenation of CO₂ to CH₃OH by generating isolated Lewis acid sites decoupled from the bulk properties of the native oxide. We demonstrate here that such sites can be generated via a surface organometallic chemistry (SOMC) approach^[24,25] to form a material – Cu/Ti@SiO₂ (where “M@SiO₂” denotes isolated metal centers M on SiO₂) – that selectively hydrogenates CO₂ to CH₃OH. In fact, the CH₃OH formation rates and CH₃OH selectivity are greater for Cu/Ti@SiO₂ than those for the reported Cu/Zr@SiO₂ materials.^[13]

The catalytic material (Cu/Ti@SiO₂) was prepared in two steps by SOMC (Scheme 1) as follows: first, isolated Ti^{IV} sites that are free of organic ligands were generated on SiO₂ (dehydroxylated at 973 K, 10⁻³ Pa; Supporting Information, Section S1) by grafting of a Ti^{IV}

molecular precursor, $\text{Ti}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\text{O}^i\text{Pr})$,^[26] followed by thermal treatment under high vacuum (10^{-3} Pa, 773 K) (Scheme 1a; Supporting Information, Section S1; this material is denoted $\text{Ti}@/\text{SiO}_2$). This process generates isolated Ti^{IV} sites (vide infra) and surface silanols, which are used to subsequently graft $[\text{Cu}(\text{O}^t\text{Bu})_4]$; treatment under H_2 (101 kPa H_2 , 773 K) of the resulting material (Scheme 1b; Supporting Information, Section S1) yields supported Cu nanoparticles dispersed on $\text{Ti}@/\text{SiO}_2$ (referred to as $\text{Cu}/\text{Ti}@/\text{SiO}_2$).



Scheme 1. SOMC approach to synthesize **(a)** $\text{Ti}@/\text{SiO}_2$ and **(b)** $\text{Cu}/\text{Ti}@/\text{SiO}_2$. Experimental methods and details in the Supporting Information, Section S1.

^1H -Nuclear magnetic resonance (NMR) spectroscopy of the supernatant used for grafting (Supporting Information, Section S1) and infrared (IR) spectroscopy of the dried solids indicate that grafting of $\text{Ti}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\text{O}^i\text{Pr})$ occurs through protonolysis and the release of one $\text{HOSi}(\text{O}^t\text{Bu})$ ligand, as evidenced by the decrease of intensity of the O-H stretching bands at 3747 cm^{-1} (Fig. 1a) and the concomitant appearance of C-H stretching ($2700\text{-}3100 \text{ cm}^{-1}$) and bending ($1300\text{-}1500 \text{ cm}^{-1}$) bands associated with the presence of the remaining organic ligands.

Upon thermal treatment, these C-H bands disappear while the O-H bands re-appear (Fig. 1a). This Ti@SiO₂ material contains 0.73 wt % Ti, which corresponds to an areal density of 0.45 Ti/nm². The isolated nature of these Ti atoms is confirmed by the narrow band at 210 nm in the diffuse reflectance UV-Vis (DRUV) spectrum (Fig. 1b), which is characteristic of the ligand-to-metal charge transfer (LMCT) from O to isolated tetrahedral Ti^{IV} centers^[27,28] (spectrum for tetrahedral Ti^{IV} molecular precursor Ti(OSi(OⁱBu)₃)₃(OⁱPr) in Supporting Information, Section S4; crystal structure included in Supporting Information, Section S2), in contrast with the features at ~390 and ~410 nm observed for TiO₂ (anatase and rutile, respectively; DRUV spectra in Supporting Information, Section S4) and the broad d-d transition band of d¹ Ti^{III} at ~700 nm (seen for the Ti^{III} molecular complex Ti(OSi(OⁱBu)₃)₃;^[29] DRUV spectrum in Supporting Information, Section S4). The absence of this d-d transition band (Fig. 1b), together with X-band electron paramagnetic resonance (EPR) spectroscopy that shows the absence of the line characteristic of Ti^{III} [*g* = 1.94-1.98;^[30,31] spectrum in Supporting Information, Section S6 shows only a very narrow feature characteristic of C-centered radicals or free-electrons (*g* = 2.0023),^[32] likely carbon residues formed during catalyst synthesis], indicates that the Ti@SiO₂ material contains isolated Ti^{IV} sites dispersed on SiO₂.

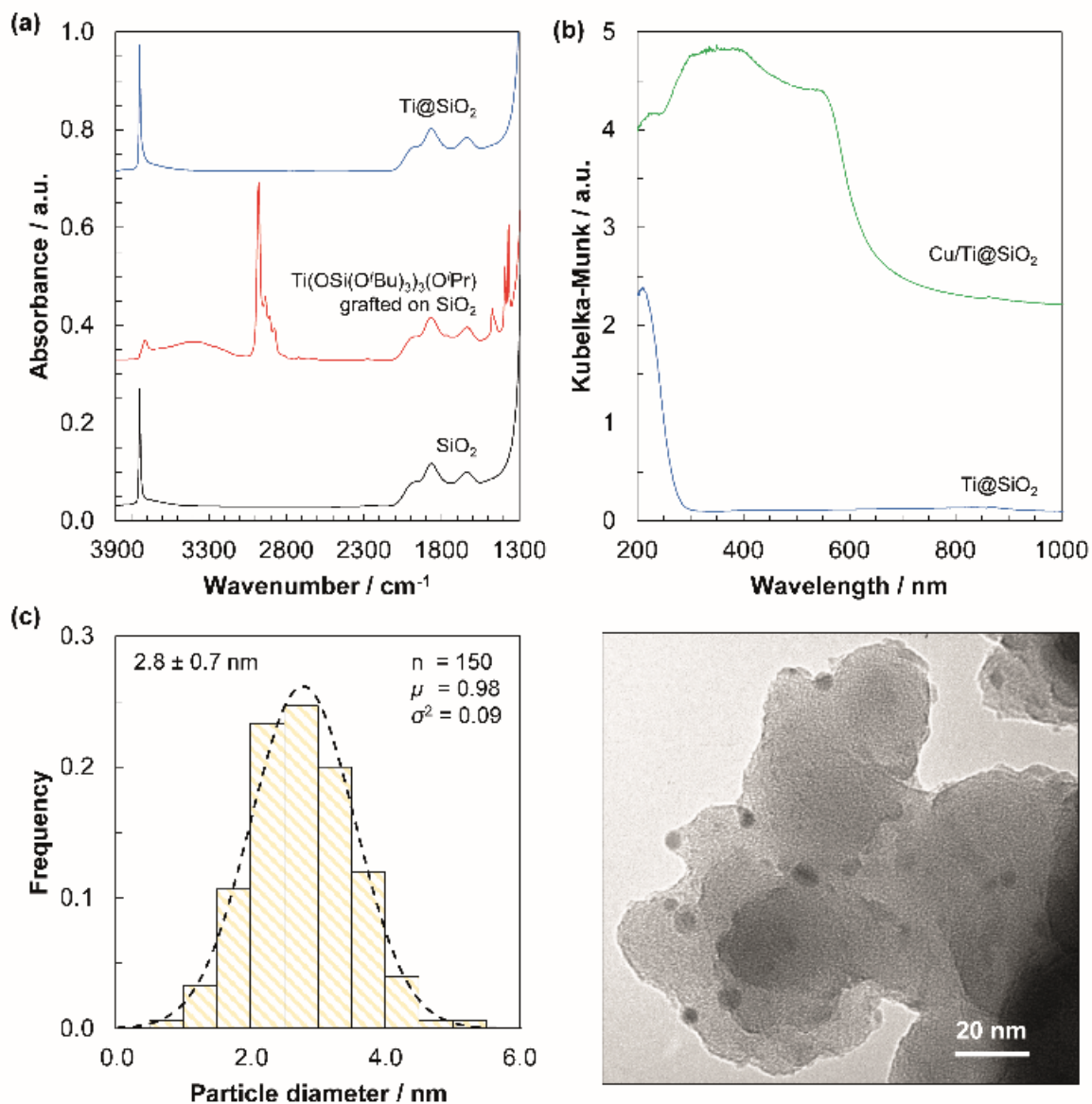


Figure 1. (a) IR spectra of (bottom) SiO₂ dehydroxylated at 973 K (discussed in the Supporting Information, Section S1), (middle) Ti(OSi(O'Bu)₃)(O'Pr) grafted on SiO₂, and (top) isolated Ti sites decorating SiO₂ (Ti@SiO₂). Analogous spectra for grafting of [Cu(O'Bu)₄] onto Ti@SiO₂ and SiO₂ are included in the Supporting Information (Section S3). (b) DRUV spectra of (bottom) Ti@SiO₂ and (top) Cu/Ti@SiO₂. (c) Histogram of Cu nanoparticle diameters (2.8 ± 0.7 nm diameter; n = 150 particles) and representative micrograph for Cu/Ti@SiO₂. Dashed line overlaying the histogram represents the regressed lognormal distribution ($\mu = 0.98$, $\sigma^2 = 0.09$); scale bar represents 20 nm.

Upon reaction of $[\text{Cu}(\text{O}^t\text{Bu})_4]$ with Ti@SiO_2 , the O-H stretching bands decrease in intensity (spectra in Supporting Information, Section S3) due to grafting and reappear following treatment under H_2 (773 K) as Cu nanoparticles are generated (vide infra). The Cu/Ti@SiO_2 material contains 4.5 wt % and 0.7 wt% Cu and Ti, respectively, and is free of organic ligands, as indicated by the absence of the C-H stretching ($2700\text{-}3100\text{ cm}^{-1}$) and bending ($1300\text{-}1500\text{ cm}^{-1}$) bands (spectra in Supporting Information, Section S3). Transmission electron microscopy (TEM) of Cu/Ti@SiO_2 shows the formation of small and narrowly distributed Cu nanoparticles with $2.8 \pm 0.7\text{ nm}$ diameter (Fig. 1c). The isolated Ti^{IV} sites retained their oxidation state after the reduction of the material to form Cu nanoparticles, as demonstrated by the absence of Ti^{III} features in the EPR spectra for Cu/Ti@SiO_2 (Supporting Information, Section S6). The DRUV spectrum (Fig. 1b) for Cu/Ti@SiO_2 shows the narrow LMCT band for O-Ti and the broad band attributed to the localized surface plasmon resonance (LSPR) for fully reduced Cu nanoparticles ($520\text{-}580\text{ nm}$;^[33] Supporting Information, Section S4 shows DRUV spectrum for Cu/SiO_2). For comparison, Cu/SiO_2 (4.6 wt %) was prepared using the same approach (Scheme 1b; Supporting Information, Section S1; IR spectra in Supporting Information, Section S3) and also shows small and narrowly distributed Cu nanoparticles of similar size ($2.8 \pm 0.3\text{ nm}$ diameter; Supporting Information, Section S5). The nearly identical IR spectra of Cu/Ti@SiO_2 and Cu/SiO_2 with adsorbed CO (3.5 kPa CO, 298 K; spectra in Supporting Information, Section S7) suggest that the metal nanoparticles of both materials are composed of Cu^0 . Both supported Cu materials were further characterized using N_2O frontal chromatography^[34] to evaluate the number of accessible surface Cu sites (Cu_s); these similar values ($\text{Cu}_s = 46$ and $55\text{ }\mu\text{mol.g}^{-1}$ for Cu/Ti@SiO_2 and Cu/SiO_2 , respectively, assuming 2:1 Cu/ N_2O stoichiometry), together with similar particle size distributions from TEM, indicate that Cu nanoparticles are similar in size and in accessible surface area, irrespective of whether they are supported on Ti@SiO_2 or SiO_2 .

With these materials in hand, we evaluated their catalytic performance in CO₂ hydrogenation. The rates and product selectivities were measured at various CO₂ residence times (0.2-12 s.g_{Cu}.μmol⁻¹; 0.5 MPa CO₂, 1.5 MPa H₂, 2.5 MPa, 503 K; Supporting Information, Section S1) for Cu/Ti@SiO₂, Ti@SiO₂, and Cu/SiO₂. Reactant conversion and products were undetectable in the reactor effluent for Ti@SiO₂, indicating that isolated Ti^{IV} metal sites alone are unable to catalyze CO₂ hydrogenation. Rates were extrapolated to zero residence time (i.e., zero reactant conversion; extrapolation discussed in Supporting Information, Section S1) to obtain initial formation rates, in order to account for the significant effects of residence time on product formation rates (Fig. 2b; vide infra) and thus to permit accurate comparison among catalysts. Initial CH₃OH formation rates (Table 1; Fig. 2a) were more than a factor of four greater for Cu/Ti@SiO₂ than for Cu/SiO₂ (18 μmol.s⁻¹.g_{Cu}⁻¹ vs. 3.6 μmol.s⁻¹.g_{Cu}⁻¹). Similarly, molar CH₃OH selectivities decreased from 85% for Cu/Ti@SiO₂ to 49% for Cu/SiO₂. In contrast, initial CO formation rates are nearly the same for Cu/Ti@SiO₂ and Cu/SiO₂ (3.1 and 3.8 μmol.s⁻¹.g_{Cu}⁻¹, respectively). Compared to previously reported initial rates for Cu/Zr@SiO₂^[13] (included in Table 1), which were collected at similar reaction conditions, CO formation rates are nearly identical (3.9 μmol.s⁻¹.g_{Cu}⁻¹ for Cu/Zr@SiO₂), while CH₃OH formation rates are nearly a factor of two greater for Cu/Ti@SiO₂ than Cu/Zr@SiO₂ (18 and 10.8 μmol.s⁻¹.g_{Cu}⁻¹, respectively).

Table 1. Initial CH₃OH and CO formation rates and CH₃OH molar selectivities for supported Cu catalysts.

Catalyst	CH ₃ OH formation rate ^[a]	CO formation rate ^[a]	Molar CH ₃ OH selectivity
Cu/Ti@SiO ₂	18	3.1	0.85
Cu/SiO ₂	3.6	3.8	0.49
Ti@SiO ₂ ^[b]	--	--	--
Cu/Zr@SiO ₂ ^[c]	10.8	3.9	0.73

^[a] units: $\mu\text{mol} \cdot (\text{g}_{\text{Cu}} \cdot \text{s})^{-1}$

^[b] products in reactor effluent below detection limits

^[c] Ref: ^[13]; extrapolated to zero CO₂ residence times (Supporting Information, Section S1).

The effects of reactor residence time on CH₃OH synthesis rates and RWGS rates are also revealing. CH₃OH synthesis rates (Figure 2b) and RWGS rates (Figure 2c) for Cu/Ti@SiO₂ decrease dramatically with increasing residence time, while those for Cu/SiO₂ are much less sensitive to changes in residence time. Such trends for Cu/Ti@SiO₂ are consistent with product inhibition, whereby product H₂O or CH₃OH inhibits formation rates by competitively adsorbing to active sites at higher CO₂ conversions; nearly identical decreases in CH₃OH rates with increasing residence time were observed for Cu/ZrO₂^[9] and Cu/Zr@SiO₂,^[13] suggesting that the same pathways mediate CO₂ hydrogenation on these materials. The near absence of these residence time effects for Cu/SiO₂, a material in which Cu nanoparticles alone are responsible for conversion of the reactant and the support itself can be considered innocent, indicates that these active sites that are affected by product inhibition cannot be located solely on the Cu surface.

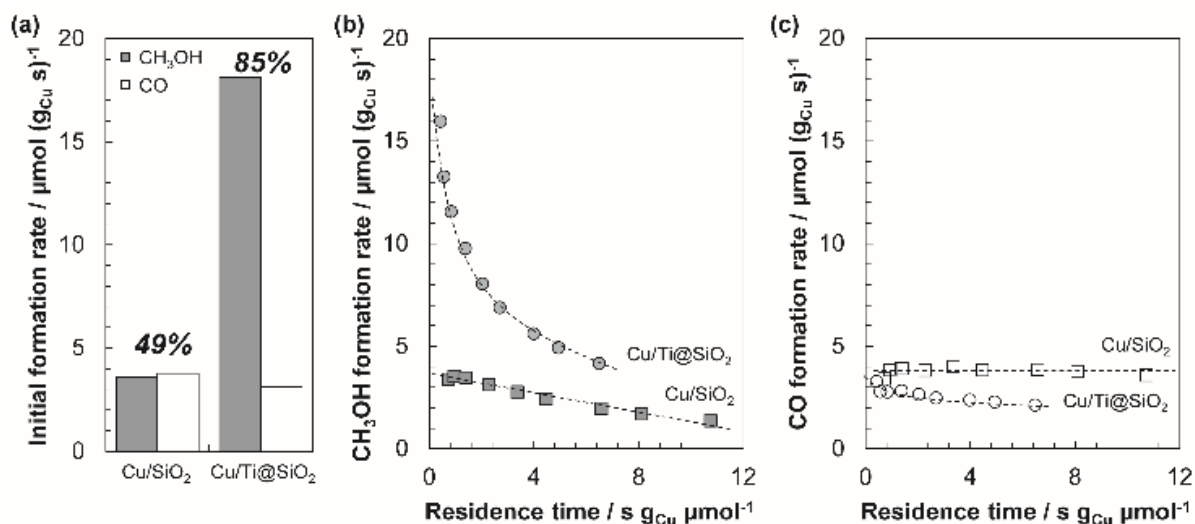


Figure 2. (a) Initial formation rates for CO (white) and CH₃OH (grey) for Cu/SiO₂, Cu/Ti@SiO₂, and Cu/Zr@SiO₂. Percentages indicate molar selectivity to CH₃OH; (b) CH₃OH and (c) CO formation rates as a function of residence time on Cu/SiO₂ (triangles) and Cu/Ti@SiO₂ (circles). Dashed lines represent trends. 503 K, 2.5 MPa, 0.5 MPa CO₂, 1.5 MPa H₂. Experimental details in the Supporting Information, Section S1.

The presence of residence time effects on rates for Cu/Ti@SiO₂ but not Cu/SiO₂ suggests that these Ti sites decorating SiO₂ play a critical role in CH₃OH synthesis. EPR spectroscopy of the Cu/Ti@SiO₂ catalyst following catalytic testing revealed that Ti^{IV} sites retain their oxidation state, as indicated by the absence of features indicative of Ti^{III} (Supporting Information, Section S6). These data together are consistent with the expectations based on previous conclusions of the role of Zr^{IV} sites in Cu/ZrO₂ and Cu/Zr@SiO₂^[9,13] that Lewis acid sites at the periphery of Cu nanoparticles promote CH₃OH synthesis.

To confirm the Lewis acid nature of these isolated Ti^{IV} sites, IR spectra were collected during the desorption of pre-adsorbed pyridine – a well-known titrant for Lewis acid sites^[35] – at different temperatures (details in the Supporting Information, Section S1) for Cu/Ti@SiO₂ and Cu/SiO₂. Vibrational bands associated with hydrogen-bonded pyridine^[35] ($\nu = 1599 \text{ cm}^{-1}$

and 1447 cm^{-1}) were observed in the IR spectra for Cu/SiO₂ and Cu/Ti@SiO₂ (Supporting Information, Section S7). The spectra for Cu/Ti@SiO₂ (Supporting Information, Section S7) shows an additional band at higher frequency ($\nu = 1608\text{ cm}^{-1}$), indicative of the coordination of pyridine to Lewis acid sites.

Ex situ solid-state NMR experiments further demonstrated the importance of such Lewis acid sites by investigating the presence and identity of surface intermediates on Cu/Ti@SiO₂; these surface species are similar to those observed for Cu/Zr@SiO₂ and Cu/ZrO₂.^[9,13] The ¹H-¹³C HETCOR spectrum (Figure 3) of the Cu/Ti@SiO₂ catalyst contacted with 5 bar of ¹³CO₂ and ¹H₂ (in 1:3 ratio) for 12 h at 503 K (experimental details and additional solid-state NMR spectra in the Supporting Information, Section S8) shows the presence of signals assigned to methoxy (correlation peaks at $\delta(^{13}\text{C})/\delta(^1\text{H}) = 48\text{ ppm}/2\text{ ppm}$ and $65\text{ ppm}/3\text{ ppm}$) and formate (correlation peaks at $\delta(^{13}\text{C})/\delta(^1\text{H}) = 170\text{ ppm}/8\text{ ppm}$).^[9] Such signals are not observed in the absence of Lewis acidic single sites for Cu/SiO₂^[9] or in the absence of Cu nanoparticles for Ti@SiO₂, indicating that both these Lewis acidic single sites and Cu nanoparticles are required for their formation. We thus propose that the promotional role of Ti^{IV} in the selective hydrogenation of CO₂ to CH₃OH is the same as that of Zr^{IV}, based on similar site requirements and surface species.

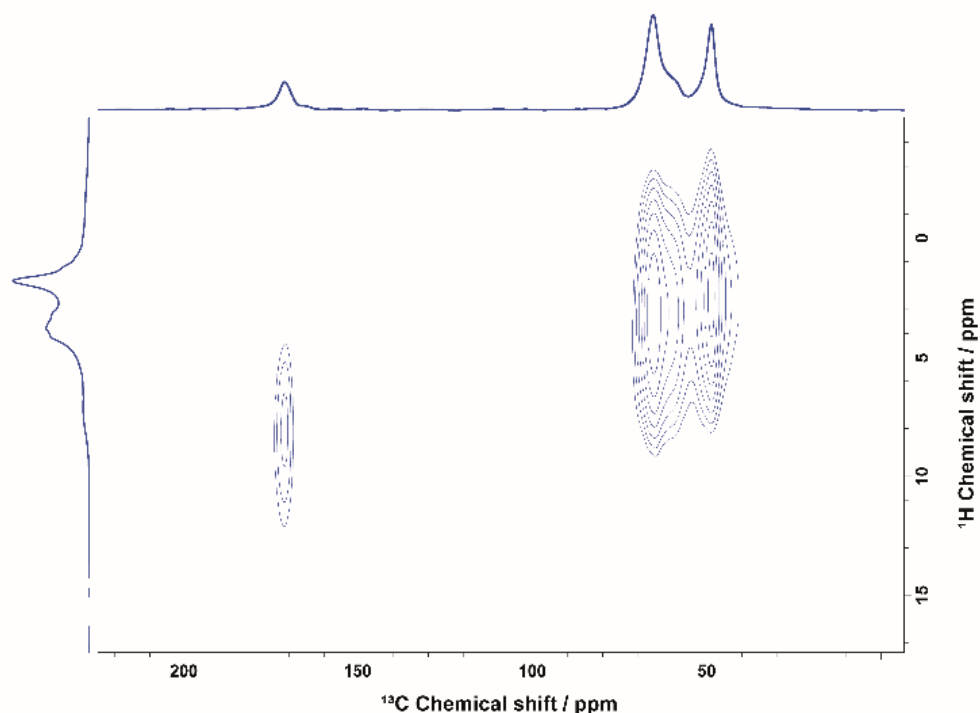


Figure 3. Ex situ ^1H - ^{13}C HETCOR spectrum of Cu/Ti@SiO₂ after exposure to $^{13}\text{CO}_2$ and $^1\text{H}_2$ (1:3 ratio; 5 bar total pressure, 503 K, 12 h). Experimental details in the Supporting Information, Section S8.

We have demonstrated here the synthesis of a tailored catalyst with isolated Ti^{IV} sites on SiO₂ and dispersed Cu nanoparticles. The presence of isolated Ti^{IV} Lewis acid sites at the periphery of Cu nanoparticles promote CH₃OH synthesis. The SOMC approach used here takes advantage of the Lewis acid character of Ti^{IV} isolated metal centers on a SiO₂ surface, while avoiding the bulk properties of the parent oxide (e.g., the reducibility of TiO₂). Such an approach can be used to develop tailored supports to target characteristics of single metal sites to promote CO₂ hydrogenation and other heterogeneously catalyzed reactions.

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CCDC 1882540 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Keywords: CO_2 hydrogenation • surface organometallic chemistry • CH_3OH synthesis • heterogeneous catalysis • titanium

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