Silica accelerates the selective hydrogenation of CO₂ to methanol on cobalt catalysts

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The reaction pathways on supported catalysts can be tuned by optimizing the catalyst structures, which helps the development of efficient catalysts. Such design is particularly desired for CO₂ hydrogenation, which is characterized by complex pathways and multiple products. Here, we report an investigation of supported cobalt, which is known for its hydrocarbon production and ability to turn into a selective catalyst for methanol synthesis in CO₂ hydrogenation which exhibits good activity and stability. The crucial technique is to use the silica, acting as a support and ligand, to modify the cobalt species via Co–O–SiOₙ linkages, which favor the reactivity of spectroscopically identified *CH₃O intermediates, that more readily undergo hydrogenation to methanol than the C–O dissociation associated with hydrocarbon formation. Cobalt catalysts in this class offer appealing opportunities for optimizing selectivity in CO₂ hydrogenation and producing high-grade methanol. By identifying this function of silica, we provide support for rationally controlling these reaction pathways.
The increasing atmospheric CO$_2$ concentration originating from anthropogenic emissions has caused global warming and related climate issues. Progress to reduce fossil fuel consumption and reduce CO$_2$ emissions is substantial but insufficient, and research is underway to develop processes for large-scale CO$_2$ sequestration, but validated technology is still lacking. Additional prospects for CO$_2$ reduction on a significant scale include processes for conversion of CO$_2$ as a feedstock for manufacturing of platform chemicals and fuels, including CO$_2$-olefins$^{12}$, alcohols$^{8-10}$, and hydrocarbon fuels$^{11}$. The most promising candidate routes are catalytic, including the hydrogenation of CO$_2$ to produce methanol, a large-scale platform chemical for the production of olefins, gasoline, aromatics$^{12}$, and other chemicals$^{13}$. Further, methanol is a fuel in its own right and also promising for the storage of hydrogen$^{14}$, with the prospect of playing a significant role in hydrogen fuel cells$^{15}$. The CO$_2$-to-methanol transformation is challenging because of the chemical inertness of CO$_2$ and the difficulty of converting it selectively to desired products.

Catalysts for the hydrogenation of CO$_2$ to methanol include supported Au particles$^{16}$, In$_2$O$_3$$^{17}$, Ni-Ga$^{18}$, Pd-Ga$^{19}$, Zn-Zr$^{20}$, and Mn-Co$^{21}$. Copper, which has the advantage of being earth-abundant, has been widely investigated and applied$^{22-28}$. Numerous copper catalysts have been designed recently to optimize interfaces between copper and metal oxide supports, because copper alone is less effective in bonding and activating CO$_2$. Successful examples include Cu/ZnO/Al$_2$O$_3$ (used industrially for hydrogenation of CO and CO$_2$)$^{22-25}$, Cu/ZrO$_2$$^{26}$, Cu/CoO$_2$$^{27}$, and Cu/Al$_2$O$_3$$^{28}$. In these cases, a wide scope of reaction intermediates and pathways have been identified by using the supported copper as models$^{22-24,26,28}$, but how to optimize the catalyst structure for turning the selectivity is still in need of investigation. In addition, supported copper usually suffers from deactivation caused by nanoparticle sintering under harsh reaction conditions$^{29,30}$.

Consequently, researchers have been motivated to find replacements for supported copper catalysts, focusing on inexpensive and earth-abundant metals that work effectively, such as cobalt. Cobalt is widely used in industry as a catalyst for Fischer-Tropsch synthesis$^{31}$, also drawing attention for CO oxidation$^{32}$ and ammonia synthesis$^{33}$. But cobalt is regarded as inappropriate for the selective methanol formation, because of the high activity for C-O dissociation$^{34}$, and CO and hydrocarbons usually form instead of methanol$^{35}$. On the other hand, recent efforts on selectivity optimization in CO$_2$ hydrogenation have focused on engineering metal oxide supports with redox properties and electronic metal-support interactions$^{2,12,36-38}$, but the promotion role of inert supports, such as silica, has been largely overlooked.

Herein, we report how cobalt can be optimized to give efficient catalysts for methanol production by choice of a silica support. The catalyst is synthesized by incorporating cobalt nanoparticles onto amorphous silica (Co@Si$_x$) to construct abundant Co-O-Si$_n$ interfaces, which stabilize methoxy (–CH$_3$O) species as intermediates in CO$_2$ hydrogenation. Optimizing the cobalt-to-silica ratio gives superior catalysts, even outperforming those expensive noble-metal catalysts$^{19}$ as well as the supported copper catalysts$^{25,28}$ employed for hydrogenating CO$_2$ to methanol.

### Results

**Synthesis.** The method for synthesizing Co@Si$_x$ is summarized in Fig. 1. To construct the Co-O-Si$_n$ linkage, the hydrolysis of tetraethoxysilane (TEOS) was performed in a basic liquor containing Co(NO$_3$)$_2$, followed by calcination of the resultant solid at 500 °C to form a product containing predominantly Co$_2$O$_4$, as shown by X-ray diffraction (XRD) crystallography (Co$_2$O$_4@$Si$_n$). Supplementary Fig. 1). The final product was obtained by reduction with hydrogen at 600 °C. The composition was adjusted by changing the amount of TEOS in the starting solution, giving Co@Si$_x$, where x is the molar ratio of silica to cobalt (Supplementary Tables 1 and 2). For comparison, a conventional catalyst consisting of cobalt nanoparticles supported on silica (Co/SiO$_2$) was synthesized by a deposition method (details in the SI), the cobalt loading was 43 w%.

**Catalysis in CO$_2$ hydrogenation.** Fig. 2 shows the performance of a set of cobalt catalysts in CO$_2$ hydrogenation with a feed gas at a pressure of 2.0 MPa containing CO$_2$ and H$_2$ (H$_2$/CO$_2$ = 3:1, molar). The products, besides methanol, were CO and methane, formed respectively by the reverse water-gas shift and methanation reactions. A cobalt catalyst without silica (Co$_x$O$_y$) was characterized under our conditions by a CO$_2$ conversion of 6.7%, with CO and methane as the dominant products, and a slight amount of methanol (Fig. 2a). Significantly, the inclusion of silica in the cobalt catalyst improved both the CO$_2$ conversion and methanol selectivity. For example, the Co@Si$_{0.52}$ catalyst gave CO$_2$ conversion and methanol selectivity of 9.0% and 47.9%, respectively. The methanol selectivity was further optimized by changing the cobalt/silica ratio, with the methanol selectivity of 70.5% at a CO$_2$ conversion of 8.6% for Co@Si$_{0.95}$ (Supplementary Table 1, Fig. 2b and c). In the catalytic reaction experiment, methanol was the sole carbon-containing liquid product (condensed in a cold trap downstream of the reactor) without any C$_2$ by-products, which are usually formed in conversions with cobalt-containing catalysts$^{5,7}$, revealing a potentially valuable methanol production process.

In contrast, more silica in the catalyst led to decreased CO$_2$ conversions and lower methanol selectivity, illustrated by data characterizing the performance of Co@Si$_{0.18}$ and Co@Si$_{0.27}$, which might be due to changes in the state of cobalt and/or blocking of cobalt active sites by silica. In contrast, the conventional cobalt catalyst (Co/SiO$_2$) gave a CO$_2$ conversion of 7.3% and a methanol selectivity at 16.6%, with CO being the dominant product under the equivalent reaction conditions. These data confirm the unusual catalytic performance of Co@Si$_{0.95}$ in the CO$_2$ hydrogenation.

As expected, increased operating temperatures of the Co@Si$_{0.95}$ catalyst (Supplementary Fig. 4) gave higher conversions, with the methanol selectivity being >70% at 260–320 °C but decreasing at temperatures >320 °C. Similar trends were observed with the other Co@Si$_x$ catalysts (Supplementary Figs. 2–7). In these cases, the Co@Si$_x$ catalysts exhibited a marked decrease in selectivity to the undesired methane compared with the conventional cobalt catalysts (Supplementary Fig. 8). The conventional Co/SiO$_2$ was characterized by methanol selectivity generally <25% at temperatures in the range of 260–380 °C (Supplementary Figs. 9 and 10), where the C$_2$ by hydrocarbons were also detected with selectivity of 4.0%–8.5% at 260–380 °C. As shown in Fig. 2b, Co@Si$_{0.95}$ catalyst gave methanol productivity of 3.0 mmol g$_{cat}$$^{-1}$ h$^{-1}$, outperforming Co/SiO$_2$ and even the other supported copper and noble-metal catalysts that have been reported to be excellent for the CO$_2$–to-methanol transformation (Supplementary Table 3)$^{19,25,28}$. For example, the methanol productivity of Co@Si$_{0.95}$ was found to be comparable to that of Cu/SiO$_2$ under comparable conditions$^{39}$.

The conventional supported metal nanoparticle catalysts generally suffer from the poor stability$^{29,30}$. For example, the standard commercial Cu/ZnO/Al$_2$O$_3$ catalyst (Supplementary Figs. 11–13) for synthesis of methanol from CO$_2$ hydrogenation, evaluated in a wide temperature range (200–380 °C, Supplementary Fig. 12), gave the performances that are sensitive to the reaction temperatures. The best methanol yield appeared at
Fig. 1 Synthesis and catalysis strategies of Co@Siₙ catalysts. The procedures with cobalt phyllosilicates as intermediates for synthesizing Co@Siₙ. Within the highlighted square, the CO₂-to-methanol transformation on Co@Siₙ catalysts.

Fig. 2 Performance of Co@Siₙ catalysts in CO₂ hydrogenation. a Performance of catalysts, standard reaction conditions for Co@Si₀.₉₅: 0.2 g of catalyst, pressure = 2.0 MPa; H₂/CO₂ feed ratio = 3:1, molar; temperature = 320 °C; GHSV = 6000 mL/g h. The mass of the other Co@Siₓ catalysts was chosen to give the same cobalt content in the reactor. b Dependences of methanol yield on temperature. Each reaction was performed three times, and the corresponding data points are provided in the bar charts. Error bounds for the conversion and selectivity are ± 0.3% and ± 0.5%, respectively. c CO₂ conversion and CH₃OH selectivity of Co@Siₓ catalysts at 260–320 °C. d Stability test of Co@Si₀.₉₅ catalyst operated for 100 h in a flow reactor.
240 °C, giving productivity of 3.5 mmol g_{cat}^{-1} h^{-1} with CO_{2} conversion of 15.2% and methanol selectivity of 47.6%, which is higher than that of the Co@Si0.95 catalyst (3.0 mmol g_{cat}^{-1} h^{-1}). However, the Cu/ZnO/Al_{2}O_{3} was characterized by a markedly inferior performance in the reaction life test, losing almost half of the methanol yield after reaction at 240 °C for 50 h (Supplementary Fig. 13). This result is in agreement with the knowledge of the Cu/ZnO/Al_{2}O_{3} catalyst, whereby the Cu nanoparticles easily sinter into larger ones and cause deactivation^{29,30}. Significantly, Co@Si0.95 underwent almost negligible decay in the CO_{2} conversion and methanol selectivity in 100 h of onstream operation (70 h at 320 °C and 30 h at 380 °C, Fig. 2d).

To the best of our knowledge, this excellent performance of Co@Si0.95 catalyst in the CO_{2} hydrogenation to methanol is unmatched. We are led to hypothesize that the silica support plays a key role, because the comparable silica-supported catalyst, Co/SiO_{2}, did not show this behavior. We were thus motivated to investigate the catalysts in depth and to determine catalytic structure-performance relationships.

Catalyst structure study. A transmission electron microscopy (TEM) image of Co@Si0.95 (Fig. 3a) shows a lamellar structure of cobalt phyllosilicates. A high-angle annular dark field scanning transmission electron microscopy image (HAADF-STEM, Fig. 3b) and EDX elemental maps (Fig. 3c-e) demonstrate uniform dispersions of cobalt and silicon. The TEM image of Fig. 3f shows cobalt nanoparticles with an average diameter of 3.9 nm supported on the silica. A high-resolution TEM (HRTEM) image reveals the co-existence of metallic Co and CoO phases on the cobalt nanoparticles present in Co@Si0.95 (Fig. 3g), which is further confirmed by the fast Fourier-transform (FFT) analysis (Fig. 3h) and XRD patterns. The cobalt nanoparticles on a series of Co@Si_{x} samples have similar diameters, as evidenced by the HRTEM characterization. In contrast, the CoO_{x} and Co/SiO_{2} catalysts incorporate metallic Co as the dominant phase (Supplementary Figs. 14–18). These data indicate a role of silica controlling the dispersion and the oxidation state of cobalt.

The cobalt-silica interaction on Co@Si_{x} samples was investigated with FT-IR spectroscopy, with the bands at 665 and 1025 cm\(^{-1}\), assigned to the Co-O-Si_{n} linkage (Fig. 3i and Supplementary Fig. 19)^{40}. In contrast, these bands are undetectable in the FT-IR spectrum of Co/SiO_{2}, consistent with the lack of substantial interactions between cobalt and silica. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded to characterize the oxidation states and coordination environments of Co in the Co@Si_{x} catalysts. The Co K-edge XANES spectra of Co@Si_{x} samples exhibit pre-edge features of the Co 1s-3d absorption transition at 7709.5 eV, with absorption edge positions of 7721.6 ± 0.2 eV (Fig. 3j) and Supplementary Fig. 20)—these features are characteristic of cobalt oxides^{41}. In contrast, the Co K-edge XANES of Co/SiO_{2} is represented by an edge position of 7709.0 eV, assigned to metallic cobalt. These results point to the presence of cationic cobalt bonded to the silica, with Co-O-Si_{n} linkages at the Co-SiO_{2} interfaces stabilizing the dispersed cobalt species in Co@Si_{x}. X-ray absorption spectra (XAS) recorded at the O K-edges of Co@Si_{x} provide evidence confirming the hypothesis: the spectra include peaks assigned to Co-O bonds, at 532.5 and 539.8 eV^{42}, whereas the Co/SiO_{2} exhibits an extremely weak Co-O signal because of its metallic feature (Supplementary Fig. 21).

In contrast, EXAFS spectra of Co/SiO_{2} recorded at the Co K-edge (Fig. 3k), include a Co-Co shell with a distance determined in the fitting to be 2.50 5 Å, with a coordination number of 9.3, indicating the dominant presence of metallic cobalt (Supplementary Table 4). Consistent with our interpretation, the Co-Co contributions characteristic of metallic cobalt are extremely weak in the spectra of Co@Si_{x} samples. The EXAFS spectra indicate Co-O and Co-Co shells at distances of 2.05 and 3.02 Å, respectively, for Co@Si0.95 with coordination numbers of 4.2 and 10.7, consistent with the presence of nonmetallic cobalt bonded to silica.

![Fig. 3 Structural characterization of Co@Si0.95 catalyst.](image-url)
To further characterize these dispersed cobalt species, we did in situ Co 2p XPS experiments with the samples undergoing reductive treatments (Fig. 3f) and Supplementary Figs. 22–25). The as-synthesized CoOx@Si0.95 sample characterized by a dominant signal assigned to Co2+ (782.4 eV, Supplementary Fig. 26), which was resistant to reduction and unchanged even after exposure to H2 at 500 °C. Reduction at 600 and 650 °C gave spectra indicating the predominant presence of Co2+ (781.5 eV) with some Co0 (777.8 eV), indicating that the surface of CoOx@Si0.95 incorporated predominantly cobalt oxide species and a small amount of metallic cobalt after vigorous reduction. Although the in situ XPS was performed using hydrogen with a lower pressure than that of the practical reduction treatment because of the XPS technique limitations,43, it is sufficient to reduce the cobalt species. For example, the Co2+ on CoOx@SiO2 was easily reduced to Co2+ at a temperature of only 300–400 °C, and Co0 was the only cobalt species detected after reduction at 500 and 600 °C (Supplementary Figs. 27 and 28). This result is in good agreement with the H2-TPR measurement of the cobalt oxide sample (Supplementary Fig. 29). These results support the conclusion that the cobalt species in Co/SiO2 are strongly resistant to reduction.

In order to provide more evidence, we treated the CoOx@Si0.95 sample with relatively high-pressure H2 at 600 °C for 2 h (10% H2 in Ar, 2 MPa), which should provide enough hydrogen for reducing the cobalt species. Significantly, the treated CoOx@Si0.95 still contained cobalt oxide as the dominant phase with a small amount of metallic cobalt, as confirmed by the XRD (36.4°, 42.5° and 61.5° assigned to CoO phase) and XPS characterizations (781.5 eV assigned to Co2+ and 777.8 eV assigned to Co0) (Supplementary Fig. 30). The conclusion is further confirmed by in situ Raman spectra (Supplementary Fig. 31). By increasing reduction temperature to 600 °C, CoOx@Si samples still showed a typical Raman signal of Co-O species, which was undetectable on the reduced Co/SiO2. Even after reaction for 100 h under the practical CO2 hydrogenation conditions (Fig. 2d), the CoOx@Si0.95 sample still exhibited the dominant CoO phase with a relatively small amount of metallic Co (XRD and XPS in Supplementary Fig. 32), confirming the difficult-to-reduce cobalt species on the CoOx@Si0.95 catalyst, in good agreement with the in situ XPS investigation.

On the basis of these results, we propose that the silica influences the cobalt oxidation state, resulting in structures that are active and selective catalysts for methanol formation and not for methane and CO formation.35 The relationships between the methanol yield in CO2 hydrogenation and Co9/Co2+ ratio for various catalysts are presented in Supplementary Fig. 24f. Compared with CoOx catalyst, the CoOx@Si0.52 and CoOx@Si0.95 with Co2+ species exhibited enhanced methanol yields. Further decreasing the Co9/Co2+ ratio reduced the methanol yields over CoOx@Si0.48 and CoOx@Si0.97 catalysts. These data confirm the balanced metallic Co and CoO phases on the catalysts are important for the methanol production. More Co0 species cause the formation of a large amount of methane with poor methanol selectivity. Consistent with this picture, the hydrogen dissociation ability was evaluated by the catalysis in HD production by the reaction of H2 with D2 (a measurement of activity for activation of dihydrogen) over the CoOx@SiO2 and CoOx@Si0.95 catalysts. The product of the former contained 85% HD and only 27% HD for the latter (Supplementary Fig. 33), suggesting the H2 dissociation ability of CoOx@Si0.95 was weakened because such ability was strongly related to the metallic Co. The surprising finding is that the CoOx@Si0.95 with lower H2 dissociation ability even exhibits higher CO2 conversions than the CoOx@SiO2 catalysts with high activity in H2 activation. The sole CoO phase is known to have poor activity for the hydrogenation. Therefore, the CoOx@Si0.95 catalyst with balanced phases exhibited the best performance among these samples (Supplementary Figs. 34–36). Apart from influencing the cobalt oxidation state, more silica species might block more surface sites of the Co@Si, catalysts, which would also influence the catalytic performance. These data might explain why the various Co@Si catalysts with similar cobalt nanoparticle sizes have markedly different catalytic performance.

We conclude that the silica acts as an effective support for turning the cobalt nanoparticles from catalysts for methanation/CO formation into catalysts for methanol production, exhibiting simultaneously high activity, selectivity, and durability for the CO2→methanol transformation. Such different catalytic features compared with the conventionally supported cobalt catalysts are associated with the Co-O-SiO2 linkage. It is reasonable to understand this linkage stabilizes the cobalt nanoparticles and hinders the sintering during the calcination/reduction/reaction under harsh conditions. For example, after reaction for 100 h, the used CoOx@Si0.95 catalyst still incorporated the cobalt nanoparticles with an average diameter of 3.9 nm, which is almost unchanged compared with the as-synthesized catalyst (Supplementary Fig. 37). The CoOx@Co species are undetectable on CoOx@Si0.95, as confirmed by the XRD pattern and HRTEM images (Supplementary Figs. 32 and 37). In contrast, the used CoOx@SiO2 contained predominantly metallic Co accompanied by Co2+ species (Supplementary Figs. 38 and 39) after the equivalent test for 100 h, in good agreement with expectation.44,45 The remarkably different phenomena of CoOx@Si0.95 compared with the conventional cobalt catalysts are attributed to the Co-O-Si linkage on the CoOx@Si0.95 catalyst, which hindered the carbonization of cobalt species.46,47

**Mechanism study.** In order to gain insight into how the silica modification influences the reaction pathways, we characterized the samples using IR spectroscopy in CO2 adsorption and hydrogenation. Supplementary Fig. 40 shows the spectra of various catalysts after exposure to CO2, with the CoOx characterized by bands at 1260, 1530, 2850, 2945, and 3015 cm−1, assigned to carboxylate (Co2−), 1260 cm−1, CO3− (1435 cm−1), and *CH2 species (3015 cm−1), respectively.28,48–50 The Co2+ is from the chemisorbed CO species on the cobalt sites, and the *HCOO and *CH2 are from the interaction of chemisorbed CO2 with hydrogen adatom on cobalt sites resulted from the H2 pretreatment. The *CH2 species, which are known intermediates in methane formation, confirm that deep hydrogenation occurs on the CoOx catalyst.50 It is significant that the *CH3 band (3015 cm−1) was almost undetectable in the spectra of the CoOx@Si catalysts, consistent with the suppression of deep hydrogenation of CO2 which requires metallic sites.35 The spectra further show that more silica species in CoOx@Si correspond to lower intensity of *HCOO (2850 and 2945 cm−1), also being correlated with those of the chemisorbed CO2 (Co2−: 1244–1276 cm−1).

To identify reaction intermediates, we collected in situ DRIFTS spectra (Fig. 4a and Supplementary Figs. 41–43), bringing the catalysts in contact with feed gases having varied CO2 and H2 concentration at 350 °C. Exposure of CoOx@Si0.95 to CO2 without H2 gave rise to bands, mainly including those of CO2− (1246, 1592 cm−1), CO2− (1435 cm−1), and *HCOO (1337, 2850, 2945 cm−1).28 When H2 was present (CO2:H2, molar ratio = 3), the bands of CO2− (1246, 1592 cm−1) were markedly weakened and those of *HCOO (1360, 1560 cm−1) enhanced. Simultaneously, new bands appeared at 1048, 1462, 2830, and 2928 cm−1, assigned to *CH3O species. Continuous feeding of H2 (switch off CO2) markedly increased the *HCOO and *CH3O band intensities (Fig. 4b), 0–12 min). After 12 min, the *HCOO signal was constant, but the *CH3O signal continued
to increase. In contrast with the spectra of Co@Si0.95, the comparable spectra Co/SiO2 and CoO give evidence of only trace of *CH3O (in contrast to the stronger bands of *HCOO and/or *CHx species). The *CH3O species are readily converted into methanol by hydrogenation 22,24, and the high methanol selectivity of Co@Si0.95 is ascribed to these species as reaction intermediates. The trace of *CH3O signal on Co/SiO2 and CoO is consistent with their low methanol selectivity.

Further investigation of the reaction intermediates on Co@Si0.95 was performed with ambient-pressure (AP) XPS. Although the CO2 and H2 pressure was much lower than that in the practical tests, it is sufficient to react with the catalyst surface. Changes in the surface and reaction intermediates were shown by X-ray photoelectron spectra 16,27,50. CO2 is readily adsorbed on this catalyst, giving rise to C 1s bands at 293.0, 290.6, 289.2, 288.4, and 287.2 eV, assigned to gaseous CO2, CO32−, *HCOO, CO2δ−, and HCO3− species, respectively (Fig. 4c)51.

When the sample was exposed to H2 (CO2:H2, molar ratio = 3), signals characteristic of CO2δ− and HCO3− were reduced and that of *HCOO enhanced. Concomitantly, a signal appeared at 286.3 eV and became dominant, indicating the formation of abundant *CH3O species. More H2 in the feed gas (CO2:H2 ratio = 1/3, molar) markedly reduced the bands of chemisorbed CO2 (CO2δ− and CO32−), which were quickly transformed to *CH3O species by feeding sufficient hydrogen, whereas the signal of *HCOO remained almost unchanged. When the feed gas was switched to pure H2 without CO2, the *CH3O signal disappeared immediately—this species was evidently further hydrogenated to form methanol. However, the *HCOO signal remained essentially constant, as this species was resistant to hydrogenation on the catalyst (Supplementary Figs. 44 and 45). In contrast, the Co/SiO2 catalyst was also characterized by chemisorbed CO2, but with extremely weak *CH3O bands under the equivalent conditions (Supplementary Fig. 46), in good agreement with the DRIFTS spectra. These data confirm the importance of the silica-supported species containing cationic cobalt for *CH3O formation and stabilization, even when the reaction atmosphere contains only little H2 (CO2/H2, molar ratio = 10:1, Supplementary Figs. 47 and 48).

The easily detected abundant *CH3O signals in the in situ DRIFTS and XPS characterization confirm the fast formation and slow further transformation of *CH3O on the Co@Si catalyst (Supplementary Figs. 49 and 50). Apart from the hydrogenation to *CH3OH, the *CH3O species might also undergo C–O cleavage and the subsequent hydrogenation to CH424,28,52, as well as the dehydrogenation to CO. With regard to the *CH3O transformation, multiple reaction pathways have been proposed in the formation of *CHx intermediates, that are ready to proceed the methanation 50. In this route, the C–O cleavage is always regarded to be the rate controlling step 24,28,52. Reported density functional theoretical calculations have revealed that the cleavage of the C–O bond in *CH3O requires the metallic Co surface or the CoO.

**Fig. 4 Mechanism of CO2 hydrogenation on Co@Si0.95 catalyst.** a In situ DRIFTS spectra of Co@Si0.95 catalyst at 350 °C in contact with CO2 + H2. b Time-dependent DRIFTS band intensities characterizing surface *HCOO and *CH3O species during the CO2 + H2 reaction on Co@Si0.95 at 350 °C. c In situ C 1s XPS spectra of Co@Si0.95 in contact with 1.2 mbar of CO2 + H2 atmosphere with controlled ratios at 250 °C.
Discussion

A central result emerging from the in situ DRIFTS and XPS data is that the \( ^\circ \text{CH}_3\text{O} \) species on Co@Si0.95 act as intermediates for methanol formation. The observation of abundant \( ^\circ \text{CH}_3\text{O} \) species indicates that they are stable intermediates. The results suggest that the CO2 hydrogenation on Co@Si0.95 might proceed by a mechanism similar to that occurring on the well-known Cu/ZnO catalyst\(^{34}\), whereby the transformation of \( ^\circ \text{CH}_3\text{O} \) is crucial for the selective formation of methanol. Another central result is the catalyst performance data showing that methanol forms with much less accompanying CO and methane—their formation from \( ^\circ \text{CH}_3\text{O} \) would require deep dehydrogenation and breaking of the C-O bond, respectively, which readily occurs on metallic cobalt but not on the cobalt oxide surface with unredoxable oxygen, according to the reported simulation results\(^{35}\). Thus, we infer that the dominant cobalt oxide phase on Co@Si0.95 provides a nearly optimum structure for hindering the side reactions and facilitating methanol formation.

Catalysts in this class offer a compelling example showing the key role of a nominally inert support—silica—turning cobalt from a nonselective catalyst into highly selective catalyst for methanol production. We suggest this work may open the way to new control of catalysts by supports and help guide the design of improved catalysts for selective hydrogenation of CO.

Methods

Materials. Co(NO\(_3\)\(_2\))\(_6\)\(_2\)\(_H_2\)O (99.0%), CoO\(_x\) (99.5%, 100 nm), CO(NH\(_2\))\(_2\) (99.5%), and tetraethyloxysilicate (TEOS, 99.0%) were obtained from Aladdin Chemical Reagent Company. NaOH (96.0%), NH\(_4\)\(_2\)\(_H_2\)O (25.0%-28.0%) and amorphous SiO\(_2\) were obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd. Cu/ZnO/Al\(_2\)O\(_3\) was provided by Beijing Sanju Environmental Protection & New Materials Co. Ltd. Pure Ar, CO, CO\(_2\), CH\(_4\), H\(_2\)\(_2\)/Ar, 10% CO/CO\(_2\)/H\(_2\)/Ar (25%/50%/25%, 20%/60%/20%, and 19%/76%/5%) and CO/H\(_2\)/Ar (30%/60%/10%) were provided by Hangzhou Jingong Special Gases Co. Ltd.

Catalysts preparation. Synthesis of Co\(_3\text{O}_4@\text{Si}_{0.95}\) and Co@Si0.95 catalysts: The Co(NO\(_3\)\(_2\))\(_6\)\(_2\)\(_H_2\)O (40 mmol) and TEOS (40 mmol) were dissolved in 200 mL mixed liquid containing water and ethanol with the volume ratio of 3/1, followed by adding 20 mL of NH\(_3\)_\(_2\)\(_H_2\)O. After stirring at room temperature for another 8 h, the precipitate was separated by filtration, washed with deionized water, and dried at 100 °C overnight to obtain Co phyllosilicates. The Co\(_3\text{O}_4@\text{Si}_{0.95}\) was obtained by calcining the Co phyllosilicates at 500 °C in air for 4 h. After reducing Co\(_3\text{O}_4@\text{Si}_{0.95}\) in flowing hydrogen (10% H\(_2\)/Ar, 60 mL/min) for 3 h at 600 °C, the Co@Si0.95 catalyst was obtained.

Synthesis of Co@Si0.95 and Co@Si0.95 catalysts with different Si/Co ratios: The Si/Co ratio was adjusted to obtain a series of Co@Si\(_x\) catalysts, where x is the Si/Co ratio. The Co@Si\(_x\) catalysts with different initial Si/Co ratios of 0.52, 1.48, and 1.87 were synthesized by procedures similar to those used for Co\(_3\text{O}_4@\text{Si}_{0.95}\) and Co@Si0.95 catalysts except for changing the amount of TEOS to 20, 60, and 80 mmol.

Synthesis of Co\(_x\) catalyst: The Co\(_x\) catalyst was synthesized following the similar synthesis procedures for Co@Si\(_x\) catalysts without using TEOS.

Synthesis of Co\(_x\) catalyst: 1.2 g of SiO\(_2\) was dispersed into 100 mL of aqueous solution containing 20 mmol of Co(NO\(_3\)\(_2\))\(_6\)\(_2\)\(_H_2\)O and 100 mmol of CO (NH\(_2\))\(_2\), followed by stirring at 80 °C for 4 h, then the precipitate was separated by filtration and washed with deionized water. After drying at 100 °C overnight, calcining at 400 °C in air for 4 h and reducing in flowing hydrogen (10% H\(_2\)/Ar, 60 mL/min) for 3 h at 600 °C, the Co\(_x\) catalyst was obtained.

Synthesis of Co\(_x\) catalyst: 1.2 g of Co@Si\(_x\) catalyst was dispersed into 100 mL of aqueous solution containing 1 mmol of NaOH, followed by stirring at room temperature for 3 h. Then the catalyst was separated by filtration and washed with deionized water. After drying at 100 °C overnight and reducing in flowing hydrogen (10% H\(_2\)/Ar, 60 mL/min) for 3 h at 600 °C, the Co@Si\(_x\) catalyst was obtained.

Characterization. X-ray diffraction (XRD) patterns were collected on a Rigaku D/ MAX 2500 diffract meter with Cu Ka radiation (\(\lambda = 1.5406 \text{Å}\)). The Fourier-transform IR (FT-IR) spectra were recorded on a Bruker Vector 22 in the range of 4000-400 cm\(^{-1}\). The composition of Co@Si\(_x\) catalysts was measured by an inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), images and selected area electron diffraction (SAED) were obtained on a JEM-2100F electron microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectra were collected on a Thermo Fisher Nicolet iS50 FT-IR spectrometer equipped with a MCT/A detector and ZnSe windows and a high temperature reaction chamber under ambient pressure. In a typical run, 50 mg of solid sample was loaded into the chamber and pretreated at 200 °C for 30 min in flowing Ar (20 mL/min). Then, the chamber was adjusted to the desired temperature (250 °C) and CO (10% H\(_2\)/Ar) and CO\(_2\) (10% CO in Ar) as a feed was flowed through the sample for 30 min. After removing the physically adsorbed CO, by pure Ar gas, the DRIFTS signals were recorded (Supplementary Fig. 40).

In situ DRIFTS characterization. DRIFTS were recorded using a Thermo Fisher Nicolet iS50 FT-IR spectrometer equipped with an MCT/A detector and ZnSe windows and a high temperature reaction chamber under ambient pressure. In a typical run, 50 mg of solid sample was loaded into the chamber and pretreated at 200 °C for 30 min in flowing Ar (20 mL/min). Then, the chamber was adjusted to the desired temperature (250 °C) and CO (10% H\(_2\)/Ar) and CO\(_2\) (10% CO in Ar) as a feed was flowed through the sample for 30 min. After removing the physically adsorbed CO, by pure Ar gas, the DRIFTS signals were recorded (Supplementary Fig. 40).

In order to observe the reaction intermediates on the catalyst surface, the similar procedures were repeated except using mixed gases of H\(_2\) and CO\(_2\) (10% CO in Ar) and H\(_2\) (10% H\(_2\)/ Ar) with controlled ratios were continuously introduced to the chamber (40 mL/min) at 350 °C, and the data were collected (Figs. 4a, b and Supplementary Figs. 41–43).

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In situ Raman characterization. Raman spectra were recorded using a HR800 Raman spectrometer equipped with an Ar excitation source (λ = 488 nm). The spectra were collected (Supplementary Fig. 31). For investigating the CO2 adsorption, the samples were pretreated with H2 at 250 °C and then the feed gases were introduced. For investigating the reaction on the sample, the above-mentioned procedures were repeated except using mixed gas of CO2 and H2 (1:3) in the treatment at 250 °C (Supplementary Fig. 45).

In situ XPS characterization. XPS spectra were recorded using a SPECS NAP-XPS with a monochromatic Al Ka source. The exposure to reaction gas was done by backfilling the NAP-XPS chamber. The binding energies were calibrated on the basis of the C 1s (284.8 eV) peak. In a typical run, 50 mg of solid sample was molded in advance and fixed in the chamber, then the sample chamber was evacuated. The blank XPS spectra were collected at 25 °C, followed by reducing the solid samples at controlled temperatures (300, 400, 500, 600, and 650 °C) in a hydrogen atmosphere (pure H2, 0.1 mbar) for 10 min, then the data were collected to identify the changes of Co and O (Fig. 31 and Supplementary Figs. 23, 27 and 28).

For investigating the CO2 adsorption on the samples, the chamber was evacuated again to eliminate the excess hydrogen, and another feed gas (pure CO2, 1.0 mbar) was introduced for 10 min at 250 °C. The XPS spectra were recorded in the meantime. For investigating the CO2 hydrogenation reaction on the samples, the above-mentioned procedures were repeated except using mixed gas of CO2 and H2 with the desired gas ratio (CO2:H2 = 3:1; 1:1 and 1:3, total pressure was 1.2 mbar) in the treatment at 250 °C (Fig. 4c and Supplementary Figs. 44 and 46). In the end, 1.0 mbar of hydrogen was introduced to regain a fresh sample. The XPS spectra were recorded following the above-mentioned procedures. The CO2 hydrogenation activity of the catalysts was further studied at a low hydrogen pressure. A mixed gas containing 0.1 mbar of hydrogen and 1.0 mbar of CO2 was introduced into the chamber for 5 min. Then the gas was switched off and slowly evacuated from the chamber, and the XPS spectra were recorded (Supplementary Figs. 47 and 48).

CO2 hydrogenation. The CO2 hydrogenation was carried out in a tubular fixed-bed continuous-flow reactor equipped with gas chromatography (GC). 0.2 g of catalyst (40–60 mesh) was diluted with 0.4 g of quartz sand (40–60 mesh) in the catalyst bed. The reaction was conducted under reaction conditions of 1.0–4.0 MPa, 260–380 °C, V(H2:CO2:Ar) = 50:25:25, 60:20:20, or 75:19:5, GHSV = 3000–12,000 mL·g−1·h−1. The emission gas (Ar, CO, CH4, CO2, and C2H4, hydrocarbons) from the reactor was maintained at 130 °C and immediately transported to the sample valve of a Fu Li-9790 GC equipped with a thermal conductivity detector (TCD) and a Fu Li-9790 GC equipped with a flame ionization detector (FID). The liquid phase products (CH4,CO) were collected in a cold trap and then analyzed with a Fu Li-9790 GC equipped with FID, with benzyl alcohol as an internal standard. Error bounds for the conversion and selectivity are ±0.3% and ±0.5%, respectively.

Data availability

The source data underlying Figs. 2–4 are provided as a Source Data File. The other primary data that support the plots within this paper and findings of this study are available from the corresponding author on reasonable request.

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Author contributions

L.X.W. performed the catalyst preparation, characterization, and catalytic tests. E.G. and B.C.G. did the EXAFS/XANES experiments and analysis. Y.W. participated the catalyst preparation and characterization. Z.G. and Y.C. performed the XPS investigation. X.M. provided helpful discussions. L.W. and F.-S.X. designed this study, analyzed the data, and wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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