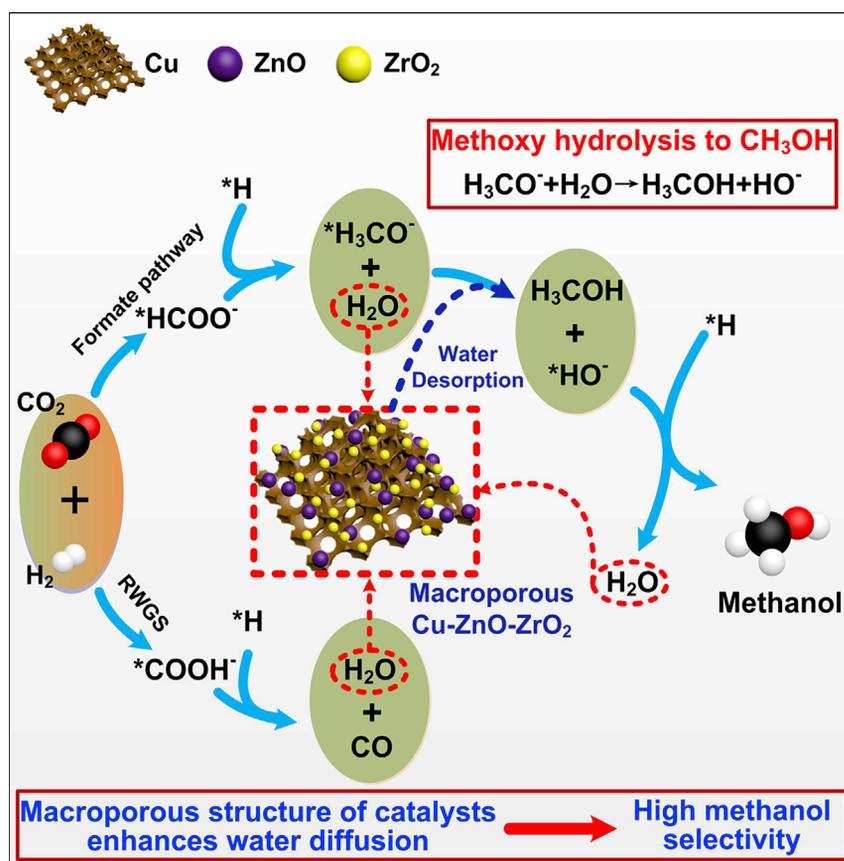**Article**

Strong Evidence of the Role of H_2O in Affecting Methanol Selectivity from CO_2 Hydrogenation over Cu-ZnO-ZrO$_2$

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HIGHLIGHTS

Methanol formation via CO_2 hydrogenation originates from methoxy hydrolysis

Suitable amount of additional water promotes methanol production

Macroporous structure increases methanol selectivity by enhancing water diffusion

Hydrogenation of CO_2 is attractive to reduce CO_2 emissions and produce value-added chemicals (e.g., methanol) with renewable energy. However, the mechanistic understanding of the role of water, a byproduct of CO_2 conversion to methanol, is still missing. Here, we identify that water directly participates in methanol formation via methoxy hydrolysis, and the enhancement on the water vapor diffusion strongly improves methanol selectivity and yield.

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Strong Evidence of the Role of H_2O in Affecting Methanol Selectivity from CO_2 Hydrogenation over Cu-ZnO-ZrO$_2$

Yuhao Wang,[1,2] Wengui Gao,[1,2] Kongzhai Li,[1,3,*] Yane Zheng,[1] Zhenhua Xie,[4] Wei Na,[2,5] Jingguang G. Chen,[4,6,7,*] and Hua Wang[1,5,*]

SUMMARY

CO_2 hydrogenation to methanol with renewable H_2 is an ideal process for coupling reduction of greenhouse gas and development of sustainable methanol economy, and Cu-ZnO-ZrO$_2$ is regarded as a promising catalyst for this process. Identification of the key descriptors that control the catalytic activity and selectivity is one of the most important issues for this reaction. Here, we identify the role of water in the hydrogenation of CO_2 to methanol, which strongly affects the selectivity and yield of methanol. Our results reveal that methanol is generated via the hydrolysis of methoxy formed by the hydrogenation of formate, and the desorbed water vapor facilitates the hydrolysis of methoxy. A suitable amount of water in the feed can promote the formation of methanol. The enhancement on the water vapor diffusion in catalysts by structural and/or surface modification offers a new strategy for tuning the selectivity and yield of methanol.

INTRODUCTION

Methanol is a potential liquid energy or hydrogen carrier as well as an important feedstock to produce commodity chemicals and key chemical intermediates.[1] The catalytic conversion of CO_2 to methanol has been considered as a highly desirable process in a sustainable methanol-based economy because it is also an important approach to mitigate this greenhouse gas when hydrogen is obtained from CO_2-free sources.[2–4] Supported copper materials (e.g., Cu-ZnO, Cu-ZrO$_2$, and Cu-ZnO-ZrO$_2$ [CZZ]) have emerged as promising catalysts for this transformation owing to their high performance.[5–9] Among them, CZZ catalysts are the most attractive ones because they usually show much higher catalytic activity than the Cu-ZnO and Cu-ZrO$_2$ catalysts, especially at relatively low temperatures (180°C–240°C).[10–14] The weak hydrophilic character of the ZrO$_2$ support would inhibit the poisoning effect of water on the active sites during methanol synthesis.[11]

Substantial progress suggests that the structure sensitivity of Cu (e.g., dispersion and particle size), the interaction between Cu and the oxide support (e.g., formation of interface or Cu alloy), as well as the material morphology play critical roles in controlling the activity and selectivity for CH$_3$OH synthesis by modifying the adsorption and activation of reactants (CO_2 and H_2) and the transformation of key reaction intermediates.[6,9,15–22] By optimizing the preparation methods or synthesis procedures, the Cu surface area, particle uniformity, surface basicity, and Cu-oxides interaction of catalysts can be tuned, which result in high CO_2 conversion and methanol selectivity.[23–26] CZZ catalysts with narrow mesopores size

The Bigger Picture

CO_2 hydrogenation to methanol is an ideal process for coupling reduction of greenhouse gas and development of sustainable methanol economy with renewable energy. As one of the most important byproducts in the CO_2 hydrogenation reactions, H_2O plays a crucial role in determining the CO_2 conversion and methanol selectivity. However, at present, the mechanistic understanding of the role of water in affecting the formation of methanol is still missing. Here, we provide strong evidence for a fundamental understanding of the role of water during CO_2 hydrogenation over Cu-ZnO-ZrO$_2$ (CZZ) catalysts. Our results reveal that methanol is generated via the hydrolysis of methoxy formed by the hydrogenation of formate, and the desorbed water vapor facilitates the hydrolysis of methoxy. Enhancement on water diffusion via preparing macroporous catalysts increases the methanol selectivity, and addition of suitable amount of water in the feed gas can promote the methanol yield.

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distributions also exhibit high methanol selectivity owing to the larger metal-oxide interfacial area.[27]

At present, the mechanistic understanding of methanol synthesis over Cu-ZnO-ZrO₂ is insufficient. In general, formate (*HCOO) produced by the reaction between CO₂ and adsorbed atomic H and CO generated from the reverse water-gas shift (RWGS) are considered to be two major intermediates.[9,28] Regardless of the formate and RWGS + CO hydrogenation pathways, methanol is finally generated from the methoxy (*CH₃O) intermediate, but there is still lack of basic knowledge on how methoxy is converted to methanol. In addition, the role of water, which is a byproduct in both the hydrogenation process ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) and in the main side reaction (RWGS: $CO_2 + H_2 \rightarrow CO + H_2O$), in affecting the formation of methanol and intermediates is not well understood.

It has been reported that the presence of water in the hydrogenation of CO could help in maintaining the catalyst in an active state (a partially oxidized state) under a steady-state operation, enhancing the methanol yield.[29] When using CO-CO₂-H₂ as the feed, either positive or negative effect of water in the feed on methanol synthesis is observed, which mainly depends on the ratio of CO to CO₂ and the partial pressure of water.[30–32] For the CO₂+H₂ system, the methanol formation is suppressed with the presence of water in the feed, which is presumably because of the competitive adsorption on the active sites.[31,33] It is also found that water produced during methanol synthesis from a CO₂-rich feed could accelerate the crystallizations of Cu and ZnO in the catalyst, leading to the deactivation of the catalyst.[34] On the other hand, a thermodynamic analysis reveals that the *in situ* water adsorption on the CO₂ hydrogenation process could lead to 15% higher methanol production.[35]

The role of water in the reaction pathway of CO₂ hydrogenation to methanol is also under debate. Surface hydroxyl group originating from water might directly react with CO to produce formate, and alternatively active surface oxygen could be produced by the H₂O-H₂ redox mechanism that promotes methanol synthesis from CO₂ via carbonate.[32] In addition, it is proposed that some water-derived adsorbates might assist in the hydrogenation of adsorbed formate to methoxy.[36] A density functional theory (DFT) calculation suggests that CO₂ hydrogenation to trans-COOH is kinetically more favorable than formate in the presence of water via a unique hydrogen transfer mechanism.[37] Notably, isotope-tracing experiments show that water and water-derived species might serve as reactants to form critical active intermediates or might serve as a "catalyst" for one or more hydrogenation steps in CO₂ hydrogenation.[38] In particular, the conversion of methoxy species to methanol by hydrolysis is believed to be more rapid than by reductive elimination and is considered as a primary pathway to methanol generation.[15] Although substantial evidence verify the crucial role of water in CO₂ hydrogenation, direct evidence for water-assisted step(s) is still missing, and little is known about the effect of water on the methional selectivity.

Here, we provide strong evidence for deeper understanding of the role of water during CO₂ hydrogenation over CZZ catalysts by using *in situ* Fourier transform infrared and transient isotope-tracing experiments. Water is an actual participant in the transformation of intermediates (i.e., methoxy), and a suitable amount of additional water in the system can improve the methanol generation. The enhancement on the water vapor diffusion in catalysts by forming a three-dimensional (3D)-ordered macroporous (3DOM) structure strongly promotes the methanol selectivity without lowering the CO₂ conversion.

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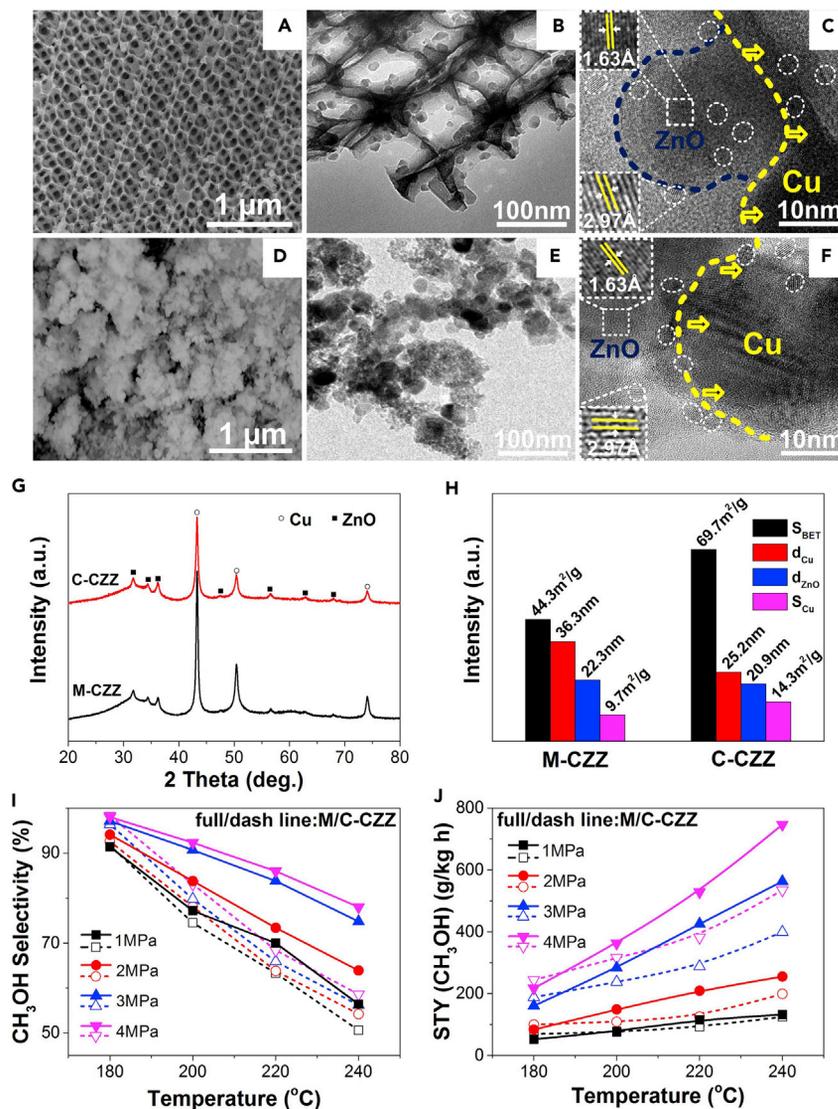https://doi.org/10.1016/j.chempr.2019.10.023

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Figure 1. Structural Characterizations and Catalytic Performance of the M-CZZ and C-CZZ Catalysts

(A) SEM image of M-CZZ. Scale bar, 1 μm.

(B) TEM image of M-CZZ. Scale bar, 100 nm.

(C) HRTEM image of M-CZZ. Scale bar, 10 nm.

(D) SEM image of C-CZZ. Scale bar, 1 μm.

(E) TEM image of C-CZZ. Scale bar, 100 nm.

(F) HRTEM image of C-CZZ. Scale bar, 10 nm.

(G) XRD patterns of M-CZZ and C-CZZ.

(H) S_{BET}, d_{Cu}, d_{ZnO}, and S_{Cu} of M-CZZ and C-CZZ samples.

(I) Methanol selectivity at different temperatures (180°C to 240°C) and different pressures (1–4 MPa) over M-CZZ and C-CZZ.

(J) Space-time yield of methanol at different conditions.

RESULTS AND DISCUSSION

Structural Characterizations and Catalytic Performance

The catalytic performance of the 3DOM Cu-ZnO-ZrO$_2$ (M-CZZ) catalyst, prepared by a colloidal crystal template method, was investigated at different temperatures and pressures, and the results were compared with a conventional sample (C-CZZ) prepared by a co-precipitation method. As shown in Figures 1A and 1B, the SEM

and TEM analyses suggest that the M-CZZ catalyst possesses open and periodic 3D frameworks with an average diameter of 120 ± 10 nm. The additional EDS and TEM measurements (Figure S1 in the Supplemental Information) reveal that the 3DOM framework mainly consists of Cu and that the ZnO particles are well dispersed on the wall of the macroporous. The high-resolution transmission electron microscope (HRTEM) image (Figure 1C) shows that t-ZrO$_2$ nanoparticles (3 ± 1nm), with a fringe spacing of 0.295 nm corresponding to the (011) plane, are highly dispersed on both ZnO particles and Cu framework. Similar distribution patterns of Cu, ZnO, and ZrO$_2$ are also observed on the C-CZZ sample (Figure 1F).

The X-ray diffraction (XRD) patterns (Figure 1G) exhibit that both the samples are characterized by similar diffraction peaks of Cu ($43.3°$, $50.5°$, and $74.1°$) and ZnO ($31.7°$, $34.4°$, and $36.2°$). The diffraction peaks of ZrO$_2$ are barely visible due to the relatively high dispersion and small particle sizes. In particular, the C-CZZ sample shows larger -specific surface area (S$_{BET}$), smaller Cu grain size (d$_{Cu}$), and higher Cu surface area (S$_{Cu}$) than in the M-CZZ sample (see Figure 1H). In addition, the C-CZZ sample also shows a relatively high reducibility in the H$_2$-TPR testing (see Figure S2; Table S1).

Figures 1I and 1J compare the selectivity and yield of methanol for the M-CZZ and C-CZZ samples at different temperatures and pressures, and details (data on conversion, selectivity, and yield) in the catalytic performances of the two samples are presented in Figure S3 and Tables S2–S5. As can be seen, the M-CZZ catalyst shows much higher methanol selectivity and yield than the C-CZZ sample at the corresponding temperatures and pressures. It is also observed that the selectivity of methanol decreases whereas the conversion of CO$_2$ increases as the reaction temperature increases. CO$_2$ hydrogenation to methanol (CO$_2$ + 3H$_2$ → CH$_3$OH + H$_2$O, ΔH_{298} = -49.5 kJ/mol) is an exothermic reaction, and the RWGS reaction (CO$_2$ + H$_2$ → CO + H$_2$O, ΔH_{298} = +41.2 kJ/mol) is an endothermic reaction. Thermodynamically, the increase in reaction temperature would result in the decline in methanol selectivity (see Figure S4). On the other hand, higher pressures facilitate methanol production because of the net reduction of pressure during the CO$_2$ hydrogenation process. The trend for the changes of methanol yield when increasing the temperatures is different from that for the selectivity, as shown in Figure 1J. The methanol yield is significantly enhanced with the initial increase in temperature.

The gaps for the methanol generation (both the selectivity and yield of methanol) among different pressures are much higher for M-CZZ than C-CZZ, indicating that the effect of pressure change on methanol selectivity is stronger for the M-CZZ catalyst (see Figures 1I and 1J). This phenomenon suggests that the formation of the 3DOM structure could significantly improve methanol synthesis, especially at relatively high temperatures and high pressures.

Reaction Pathways

Figures 2A and 2B show the DRIFT spectra of the M-CZZ and C-CZZ catalysts after switching the feed from CO$_2$ to H$_2$ at 220°C and 3.0 MPa. Before this switching, only carbonate species can be detected, and their intensity is similar for the two samples. The peak at $\sim$1,532 cm^{-1} is related to monodentate (m-CO$_3^{2-}$), and the bands at $\sim$1,596 and 1,358 cm^{-1} represent bidentate (b-CO$_3^{2-}$) carbonate species.[39] The strong bands, observed at 1,589, 1,386, and 1,362 cm^{-1} as soon as H$_2$ is introduced in the reactor for 1 min, are assigned to the υ_{as}(OCO), δ(CH), and υ_s(OCO) modes of formate species, respectively.[40] Note that carbonate species disappear very fast with the formation of formate, indicating that formate species should be generated from the reaction of carbonate species with active H species.
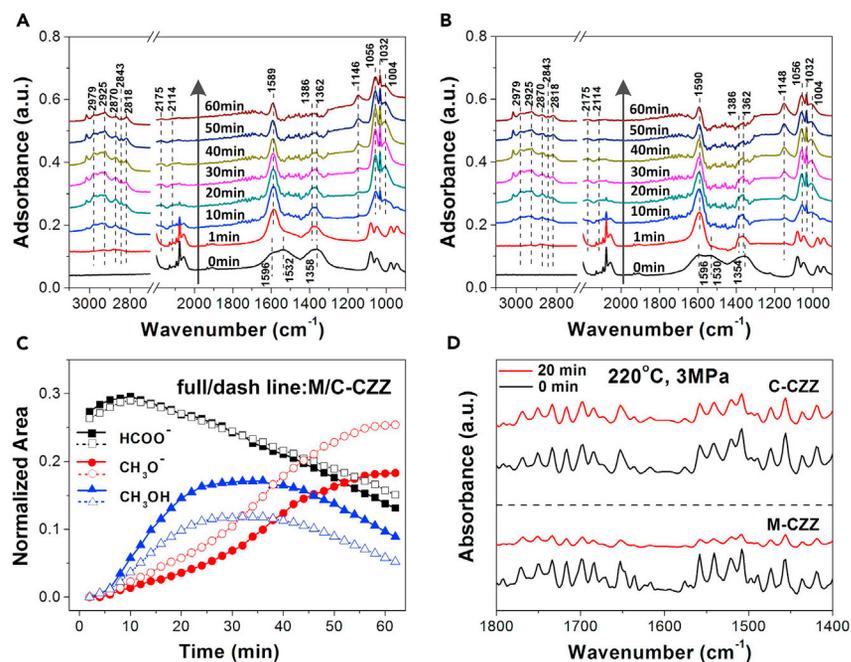
Figure 2. Evolution of Carbon-Containing Intermediates and Methanol over M-CZZ and C-CZZ Catalysts in CO₂ Hydrogenation

(A) *In situ* DRIFT spectra of M-CZZ after switching the feed from CO_2 to H_2 at 220°C and 3.0 MPa. The spectra are referenced to M-CZZ under a He flow at the same conditions.

(B) *In situ* DRIFT spectra of C-CZZ after switching the feed from CO_2 to H_2 at 220°C and 3.0 MPa. The spectra are referenced to C-CZZ under a He flow at the same conditions.

(C) Evolution of the peak areas of generated intermediate species and methanol on catalysts during the DRIFT experiments.

(D) *In situ* DRIFT spectra of M-CZZ and C-CZZ after switching the feed from 2.0 mol % H_2O/He to He for 20 min at 220°C and 3 MPa.

As the reaction proceeds for 10 min, the bands at $\sim$1,146 cm^{-1}, assigned to the methoxy species[40] and the bands at $\sim$2,979, 2,925, 2,870, 2,843, 2,818, 1,056, 1,032, 1,004 cm^{-1}, assigned to the methanol[41] are observed.

Figure 2C shows the concentration changes of formate, methoxy, and methanol species during the reaction. The concentration of formate species on each catalyst slightly increases and then decreases during the reaction. The initial increase in formate can be attributed to the hydrogenation of carbonate species after switching from CO_2 to H_2, and its further decrease should be related to the hydrogenation of formate to methoxy. It is very interesting that, although methoxy continuously accumulates during the reaction, methanol exhibits a volcano-shape variation trend. In general, it is well accepted that methoxy species is the last intermediate for methanol generation from CO or CO_2 hydrogenation.[5,6,8,42] Methanol can be generated from methoxy either by hydrogenation ($CH_3O^* + H^* \rightarrow CH_3OH$) or by hydrolysis reaction ($CH_3O^* + H_2O \rightarrow CH_3OH + OH^*$). In this experiment, the switching of feed gas from CO_2 to H_2 would result in abundant H species on the surface of catalysts, which could continuously convert formate to methoxy and then to methanol. However, the concentration of methoxy continues to increase during this process, even when the methanol intensity starts to decrease. This suggests that the methoxy hydrogenation pathway is very doubtful.

It has been previously suggested that the hydrolysis of methoxy is more favorable than methoxy hydrogenation by thermodynamic calculations.[43–45] To identify

the possibility of hydrolysis reaction of methoxy for methanol formation, we performed experiments with and without introduction of water vapor in the catalytic system, and the results are shown in Figure S5. As shown in Figure S5A, formate and methoxy species are detected after switching the feed gas from CO$_2$ to H$_2$. When the reaction pressure is increased to 3.0 MPa, the formation of methoxy is enhanced, but almost no methanol species (the bands at 1,056 and 1,034 cm^{-1}) are detected (see partial enlargement of the *in situ* DRIFT spectra in Figure S5C). In contrast, upon the introduction of water vapor into the system and increasing the pressure to 3.0 MPa, methanol can be observed (see Figure S5C). This suggests that the hydrolysis of adsorbed methoxy to methanol is feasible.

In the CO$_2$ hydrogenation process, water for methoxy hydrolysis can come from the hydrogenation of formate. Methoxy hydrolysis will result in the formation of OH*, which could react with the activated hydrogen to form additional water. With the consumption of formate, less water can take part in methoxy hydrolysis, resulting the accumulation of methoxy. If this is true, the diffusion of water vapor should be very important for methanol formation. Figure 2D shows the variation of water vapor during switching of the feed from H$_2$O+He to He over different catalysts. It is observed that the vibrational and/or rotational bands in the range of 1,800–1,400 cm^{-1} corresponding to the presence of water vapor[46] are much weaker on M-CZZ than on the C-CZZ sample after the He purge. This observation indicates that the 3DOM structure is beneficial for steam desorption and diffusion, which might enhance the hydrolysis of methoxy and improve the formation of methanol.

As observed in Figure 1I, the M-CZZ catalyst shows a much higher activity than the C-CZZ sample despite its lower specific surface area (S$_{BET}$), bigger Cu particle size (d$_{Cu}$), and smaller Cu surface area (S$_{Cu}$). In addition, both M-CZZ and C-CZZ show almost the same HD signal in the H$_2$-D$_2$ exchange experiment (see Figure S6), suggesting that they possess similar ability for hydrogen dissociation. Simultaneously, the evolution of intermediate species (carbonates, formates, and methoxys) on two catalysts are similar (see Figure S7). In these cases, the high activity of the macroporous CZZ catalyst for methanol generation can only be attributed to enhanced water diffusion within the 3DOM structure. Therefore, as shown in Figure S8, the accumulation of methoxy species because of the inefficiency hydrolysis on the C-CZZ catalyst reduces the formation of methanol.

Role of Water in Methanol Formation

Isotope tracing technique using deuteroxide vapor was performed for further understanding the role of water in methanol formation. As shown in Figure 3A, after introducing D$_2$O vapor (0.95 mol %) into the CO$_2$+H$_2$ flow, the intensity of CH$_3$OH (with a mass number of 32) remains stable, but new MS signals of CH$_3$OD (33 amu) and D$_2$O (20 amu) were detected. When the D$_2$O loading was increased to 2.24 mol % (see Figures 3B and S9), the formation of CH$_3$OD was obviously enhanced, but the generation of CH$_3$OH and H$_2$O was suppressed. It was also noted that the total amount of CH$_3$OH and CH$_3$OD decreased when increasing the D$_2$O concentration to 4.08 mol %. These phenomena indicate that water is involved in methanol formation, and a suitable amount of water in the reaction system can improve the generation of methanol.

To understand how water is involved in the pathway of methanol synthesis, we performed *in situ* DRIFT experiments on the catalyst in different atmospheres with and without loading of water. In the CO$_2$ hydrogenation to methanol via a formate pathway, carbonate, formate, and methoxy are three important intermediates,
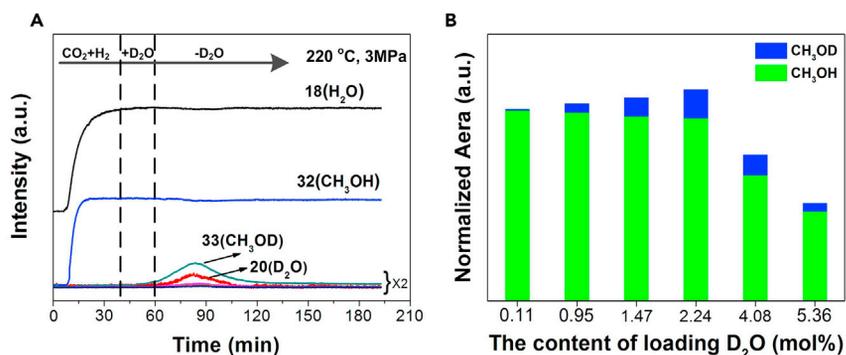
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Figure 3. Effect of D$_2$O Addition on the Formation of Methanol

(A) Mass spectra of the products in CO$_2$ hydrogenation over CZZ catalysts loaded with deuteroxide vapor (0.95 mol %).

(B) Effect of D$_2$O content on the formation of CH$_3$OD and CH$_3$OH during the reaction (on the basis of the normalized peak areas of generated CH$_3$OD and CH$_3$OH in the MS experiment, as shown in Figure S9). Reaction conditions: gas flow rate = 100 mL/min, T = 220°C, CO$_2$:H$_2$ = 1:3, P = 3.0 MPa.

and their conversions are very important for methanol formation. As shown in Figure 4A, in the CO$_2$ atmosphere, carbonate species (1,593, 1,525, 1,354 and 1,079 cm^{-1}) are detected, and their peak intensities remain stable after loading H$_2$O, indicating that the carbonate might not react with H$_2$O. In the CO$_2$+H$_2$ atmosphere (see Figure 4B), both formate species (2,975, 2,878, 1,588, 1,386, and 1,365 cm^{-1}) and methoxy species (2,926, 2,821, 1,145, and 1,043 cm^{-1}) are observed. After introducing H$_2$O, the IR peaks of formate species retain similar intensities, but the peaks of methoxy species disappear. When the loading of H$_2$O is stopped, the methoxy species becomes detectable again, suggesting that water should be involved in methanol formation via reaction with methoxy (i.e., hydrolysis of methoxy).

To further confirm methoxy hydrolysis to methanol, we performed *in situ* DRIFTS experiments on the CZZ catalyst under different environments and reaction pressures, as shown in Figure 4C. By switching the flow gas from CO$_2$+H$_2$ to pure H$_2$ and adjusting the reaction pressure (see the steps 1–3 in Figure 4C), the formate species (2,975, 2,878, 1,588, 1,386, and 1,365 cm^{-1}) on the surface of the catalysts have been mostly converted to methoxy species (2,926, 2,821, 1,145, and 1,043 cm^{-1}), which immediately disappear when water vapor is loaded (see step 4 in Figure 4C). After the water vapor loading is stopped, the methoxy is still absent. In addition, semi-heavy water (HDO) was observed when loading D$_2$O into H$_2$ or H$_2$+CO$_2$ flow at 3 MPa and 220°C in the presence of the CZZ catalyst (Figure S10), indicating that water easily dissociates and reacts with other species on the CZZ catalyst. All the above phenomena suggest that methoxy should be consumed via reaction with water.

However, it is noted that no methanol is detected in this process, which might be due to the low amount of adsorbed methoxy on the surface of the catalysts. To further confirm the hydrolysis of methoxy to methanol, we also performed similar tests with steps 1–3 in Figure 4C in the catalytic activity evaluation device using 1.4 g of catalyst, and then we loaded D$_2$O into the reactor and monitored products using a mass spectrometer. As shown in Figure 4D, signals of 20 amu (D$_2$O) and 33 amu (CH$_3$OD) were detected with the loading of D$_2$O, suggesting that methoxy species react with D$_2$O to form CH$_3$OD, and the continuous consumption of methoxy species leads to the decline of the CH$_3$OD product.
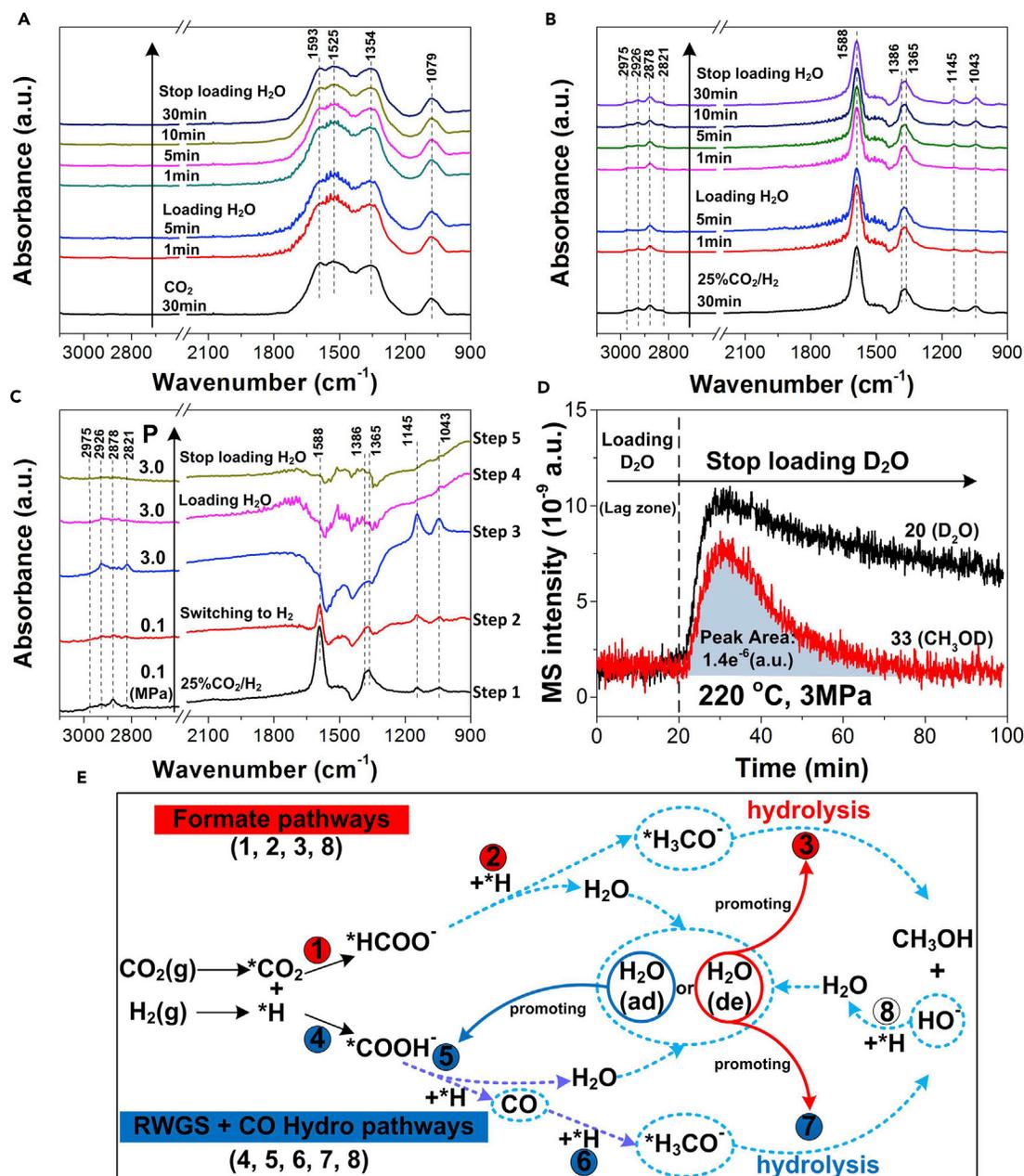
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Figure 4. Confirmation of Methoxy Hydrolysis to Methanol and Possible Reaction Path of CO$_2$ Hydrogenation over CZZ Catalysts

(A) *In situ* DRIFT spectra of water vapor effect on the evolution of intermediate species on CZZ catalysts at 220°C in CO$_2$ at atmospheric pressure.

(B) 25% CO$_2$+H$_2$ at atmospheric pressure with changed reaction gases.

(C) 25% CO$_2$+H$_2$ at different pressures with changed reaction gases.

(D) Mass spectra of deuteroxide vapor loaded after the step 3 in Figure 4C using 1.4 g catalyst.

(E) Possible reaction path of CO$_2$ hydrogenation over CZZ catalysts. The *in situ* DRIFT experiment conditions: gas flow rate = 30 mL/min, T = 220°C, P = atmospheric pressure or 3 MPa. MS experiment conditions: gas flow rate = 100 mL/min, T = 220°C, P = 3 MPa.

In CO$_2$ hydrogenation over Cu-based catalysts, methanol can be produced via two major reaction pathways (Formate pathway and CO-Hydro pathway), and both pathways involve many reaction intermediates.[9] As shown in Figure 4E, formate (*HCOO) is produced by the reaction between adsorbed CO$_2$ and dissociative H, and its further hydrogenation should produce water and methoxy (*CH$_3$O), which is the final intermediate for methanol formation. CO is generated from the RWGS

reaction, which can be a byproduct or be further hydrogenated to methional also via methoxy (*CH$_3$O) as the final intermediate (Figures S11 and S12). As discussed above, methoxy can preferentially react with water (methoxy hydrolysis) rather than with H$_2$ (methoxy hydrogenation) to form methanol over CZZ catalysts, and the facile release of methoxy by hydrolysis should promote the hydrogenation of carbonate and formate species, facilitating the transformation of CO$_2$ to methanol.

The water needed for the hydrolysis reaction might come either from the hydrogenation of formate or from the RWGS reaction. It should be highlighted that Cu-ZnO-ZrO$_2$ catalysts show dual or multiple sites (Cu$^{\delta+}$ and Cu-oxides interfaces and/or ZnO-ZrO$_2$ interface) for CO$_2$ hydrogenation to methanol,[12,47,48] and the active sites for methanol formation and for the conversion of CO$_2$ to CO are also different.[25,49,50] In this case, water (via the hydrogeneration formate and RWGS reaction) might be generated from different sites on the catalysts, which need to release to the methoxy sites for producing methanol by hydrolysis. Therefore, the diffusion efficiency of water should be very important for the formation of methanol.

Methanol synthesis and RWGS reactions can be related to each other via water as a medium. The comparisons of the experimental values of CO$_2$ conversion, equilibrium constants and yields of methanol and CO with the thermodynamic equilibrium values over the M-CZZ and C-CZZ catalysts in various temperatures (180°C–240°C), pressures (1–4 MPa), and space velocity (9,000–18,000 h^{-1}) are performed to clarify kinetics or thermodynamics control for the formation of CO and methanol, and the results are shown in Figures S13–S15. As can be seen, the experimental values of CO$_2$ conversion and equilibrium constants are much lower than the thermodynamic equilibrium ones for either methanol synthesis (MS) or RWGS, regardless of the changes of experimental conditions. In addition, with the presence of water (1–10 vol %), the experimental CO$_2$ conversion and yields of methanol or CO are also much lower than the thermodynamic equilibrium values (Figure S16). These phenomena indicate that under the present experimental conditions (180°C–240°C, 1–4 MPa, and water content lower than 10 vol %), both the formation of CO and methanol are under a kinetically controlled regime.

The steady-state reaction tests with the addition of water in catalytic CO$_2$ hydrogenation are also performed, as shown in Figure S17. Both CO$_2$ conversion and product selectivity are affected by the addition of water. The methanol yield and CO$_2$ conversion for both catalysts increase with increasing the amount of water. However, the addition of water slightly reduces the methanol selectivity, and this trend is more obvious for the C-CZZ catalyst. Figure S18 shows the kinetic study on the effect of water addition on the formation rates of methanol and CO. Both rates linearly rise when the water content increases to 10% over the M-CZZ and C-CZZ catalysts, (see Figures S18A and S18B). In addition, the increase in the formation rate of methanol was because of the addition of water is more obvious over M-CZZ than C-CZZ. These phenomena indicate that the macroporous structure of catalyst might improve the kinetic conditions for selective conversion of CO$_2$ to methanol in the presence of additional water. This should be related to its high ability for the desorption and diffusion of water, which can promote the formation of methanol by enhancing the hydrolysis of methoxy, as discussed previously.

In addition, the reaction pressure also influences the catalytic performance with the presence of additional water (see Figure S19). The improvement of water addition on the CO$_2$ conversion is more obvious at relatively high pressures, whereas it shows weaker effect on the methanol selectivity, especially for the M-CZZ sample. This is likely attributed to that high pressures can improve the diffusion rate of free water

in the bulk of catalysts, and the 3DOM structure might further enhance water diffusion, improving the formation of methanol from hydrolysis. As a result, high reaction pressures enhance the positive role of water for methanol formation.

The effects of hydrophobic property and water diffusion rate of catalysts on the catalytic performance for methanol formation were also investigated. Zeolite-3A, a typical hydrophilic material, was used to tune the hydrophilicity of M-CZZ catalyst. H_2O contact angle (see Figure S20) and H_2O-TPD (see Figure S21) measurements were used to analyze hydrophilicity of catalysts, which revealed that the M-CZZ catalyst with a macrostructure shows much weaker hydrophilicity (better hydrophobic property) than the C-CZZ sample, and the addition of Zeolite-3A further improves the hydrophilicity of catalysts. In addition, the M-CZZ catalyst also showed a much higher water diffusion rate (0.023 versus 0.013 mol/min·g_{cal}, see Figure S22) than the C-CZZ sample. Given that M-CZZ catalyst shows much higher activity and selectivity than the C-CZZ sample, and the presence of Zeolite-3A results in a sharp decrease in the selectivity and yield of methanol (see Figure S23), it is reasonable to conclude that enhancement on the water diffusion and hydrophobic property of catalysts facilitates the formation of methanol from CO_2.

The D_2O isotope experiment (see Figures S25 and S26) is used to further identify the role of adsorbed water in methanol formation. Before loading D_2O, the catalysts are pretreated for producing methoxy on the surface (which is pretreated by the same procedure with the steps 1–3 in Figure 4C). Figure S25C shows that almost no CH_3OD is detected over the Zeolite 3A containing catalyst, and the signal of D_2O is also very weak during the initial 40 min after introducing He to desorb the D_2O adsorbed on the catalyst (which is pretreated in D_2O steam for 20 min). This indicates that the adsorbed D_2O molecules on this catalyst are very stable, and they cannot react with methoxy to form methanol. In contrast, for the M-CZZ catalyst (Figure S25A), both H_2O and CH_3OD are detected in the very early stage of the desorption process of D_2O, and their intensities are much higher than that of the C-CZZ sample (Figure S25B). This suggests that freely desorbed water should be the active species for converting methoxy to methanol.

In summary, the experimental results in the current study have clearly pointed out the crucial role of water for methanol synthesis. Methanol is mainly generated by the hydrolysis of methoxy rather than the reaction of methoxy with the activated H_2 (*H). The water needed for hydrolysis reaction can come either from the hydrogenation of formate or from the side reaction RWGS. Given that water formation (especially from RWGS) and methoxy hydrolysis might take place on different sites of catalysts, the diffusion or spillover of water on the catalyst strongly affects the formation of methanol. Compared with the conversional CZZ catalyst, the 3DOM catalyst with lower specific surface area (S_{BET}), larger Cu grain size (d_{Cu}), and lower Cu surface area (S_{Cu}) shows a much higher selectivity and yield of methanol, which is attributed to the formation of the 3DOM structure that can improve the hydrolysis of methoxy to methanol by enhancing the desorption and diffusion of water vapor. In contrast, addition of hydrophilic Zeolite 3A into the catalyst reduces the selectivity of methanol, and the strongly adsorbed water vapor on catalysts seems to promote CO formation via RWGS.

In general, the selectivity of methanol can be controlled by modifying the surface properties of catalysts[51,52] or by choosing different supports,[53,54] which could hinder the formation of CO or improve the desorption of methanol. The promotion effect of water for methoxy hydrolysis via modifying the microstructure of catalysts provides a new strategy to tune the selectivity of methanol production.

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EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in the Supplemental Information.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2019.10.023.

AUTHOR CONTRIBUTIONS

Y.W. performed the catalyst preparation, characterizations, and catalytic tests. W.G. co-worked with Y.W. to perform high-pressure *in situ* DRIFTS measurements and analysis. Y.Z. contributed to catalyst preparation and TEM characterization. Z.X. helped to perform the thermomechanical analysis. W.N. helped to analyze data of isotopic experiments. K.L., J.G.C., and H.W. designed the study, analyzed the data, and co-wrote the paper. All the authors discussed the results.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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