1. Introduction

Carbon dioxide (CO$_2$) emissions management and mitigation are one of the global challenges for modern societies due to increasingly severe environmental and social problems associated with Green House Gases. Indeed, conversion of CO$_2$ to value-added products constitutes a natural pathway for CO$_2$ utilization, and it is one of the major endeavors for the global scientific community. Among the various routes, methanol synthesis with the renewable hydrogen and CO$_2$ is regarded as a key process to make possible the liquid sunshine approach while storing renewable energy (Scheme 1). Furthermore, the methanol is a convenient liquid fuel and raw material for other chemicals and fuels as well as hydrogen production, which leads to a methanol and hydrogen economy. So far, one of the challenging problems for the green hydrogen energy is its storage and transportation. The metallic hydrides and metal–organic frameworks have been extensively reported for hydrogen storage, but their limited capacity is still difficult for large-scale application. The methanol as one of high density hydrogen storage materials is facile to transport and also could be reformed to hydrogen at low temperatures (<300 °C). Therefore, it is desirable for design of a robust catalyst toward both of the methanol synthesis and decomposition reactions during use of renewable hydrogen via methanol as a carrier (Scheme 1). In fact, aqueous reforming of CH$_3$OH with amine and the reverse reaction has been reported in the presence of the same homogeneous catalytic...
system based on the same Ru-pincer catalysts. To reduce the catalyst cost and develop a facile separation process, herein, the heterogeneous catalytic system based on the same CuZnSi catalysts is designed.

Nevertheless, considering the inertness of CO₂, the challenges concerning product selectivity, as well as the catalyst deactivation drawbacks during high-temperature reaction, an efficient and robust catalyst becomes a cornerstone for the methanol synthesis and steam reforming. Numerous catalysts, such as classic copper-based, Ni-based, emerging indium- or MoS₂-based and noble metal-based catalysts have been developed for methanol synthesis or steam reforming. However, a bifunctional and efficient heterogeneous catalyst for both of CO₂ hydrogenation synthesis and methanol steam reforming (MSR) reactions has been rarely reported. For example, most of the Ni-based catalysts are active for MSR, but the product of CO₂ hydrogenation over Ni-based catalysts is almost methane instead of methanol. Cu-based catalysts, especially the CuZn-based system with low cost and high activity, are widely studied and used for CO₂ hydrogenation to methanol or its reverse process. However, Cu-based catalysts often show a poor stability due to the Cu sintering, especially under the presence of water vapor. Silica is an interesting support, which possesses high thermal stability, large surface area, variable pore structure, and a sustainale synthesis process. The CuSi-based catalysts have also been extensively used in hydrogenation of carbon—oxygen bonds, for instance, hydrogenation of CO₂[15] and dimethyl oxalate.[16] In the year of 2015, an excellent Cu/SiO₂ catalyst with predominance of Cu⁺ species was reported for CO₂ hydrogenation to methanol with satisfactory performance.[17] Then, the CuZn@SiO₂ and CuIn@SiO₂ catalysts with core–shell structure displayed appealing catalytic stability and high methanol selectivity.[14b,18] In addition, the CuSi-based catalysts have also been reported for the H₂ production by MSR. A Cu/SiO₂ catalyst was reported for MSR with a new reaction pathway including a methyl formate intermediate.[19] Then, the Zn was added to Cu/SiO₂ to reduce the CO selectivity and stabilize the Cu⁺ species during the MSR.[13b]

It has been widely accepted that the catalytic performance of supported catalysts is directly influenced by the textural and structural properties, surface compositions, and metal–support interactions, which are significantly affected by the preparation method. CuZn- and CuSi-based catalysts are conventionally fabricated via co-precipitation and impregnation methods. However, most of these catalysts synthesized by conventional preparation methods are attempted to have low surface area and poor catalytic stability.[17,20a] Recently, several new preparation methods, such as ultrasound-assisted method[20a] and rotary evaporation-assisted deposition–precipitation method, have been applied for the synthesis of CuZn- and CuSi-based catalysts.[20b] For example, the micro-spherical SiO₂ (50–100 μm) supported Cu/ZnO catalysts were prepared by AEM and applied for CO₂ hydrogenation to methanol.[15] In addition, fundamental questions, such as property of the active species, activity and selectivity controlling parameters, key stability factors, etc. and influencing factors for methanol synthesis and steam reforming, have been under intense debate for a long time. To address these quests and circumvent controversies around the process, a simple but effective catalysts design is needed. This is precisely the genesis of this work whose main motivation is to propose an alternative catalysts design for both high performing CO₂ to methanol and MSR.

In this work, three preparation methods, namely, modified Stöber method (StM), sol–gel method (SGM), and AEM, are used to synthesize Cu–ZnO/SiO₂ catalysts. A comparative examination of the resultant three catalysts was performed on CO₂ hydrogenation to reveal fundamental aspect of structure–performance correlation as well as to identify the key factors governing the direct methanol synthesis from CO₂. In addition, the optimized AEM was extended to prepare other methanol synthesis catalysts, whereas CuZnSi-SGM and CuZnSi-AEM catalysts were further used for the MSR. Thus, the carbon cycling investigated in this work may shed some lights for the methanol and hydrogen economy.

2. Results and Discussion

2.1. Textural and Structural Properties

To synthesize the catalysts with different textural and structural properties, three Cu–ZnO/SiO₂ (CuZnSi) catalysts were prepared by different methods (Scheme 2). The tetraethylorthosilicate (TEOS) was directly used in the preparation of CuZnSi-SGM and CuZnSi-StM catalysts, whereas the alkaline silica sol was used for CuZnSi-AEM. In a macroscopic view, three CuZnSi catalysts show different colors (light blue, dark blue, and light
green) in the photographs (Figure S1, Supporting Information). The microcosmic surface morphology and dispersion of metals species were further observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques (Figure S2, Supporting Information, and Figure 1). The SEM images show that the CuZnSi-StM catalyst has a larger spherical structure, whereas the other two samples contain smaller silica spheres (Figure S2, Supporting Information). An irregular morphology showcasing a more pronounced metal particles sintering noticed over the CuZnSi-SGM catalyst. The TEM images show that the silica spheres (diameter: ≈14 nm) are highly dispersed over CuZnSi-AEM catalyst (Figure S3c, Supporting Information, and Figure 1f). This is ascribed to the utilization of spherical silica sol in the synthesis procedure (Figure S3d, Supporting Information) and suggests that the structure of the silica sol was not destroyed during preparation. As the CuZnSi-StM catalyst, it possesses larger silica spheres with an average diameter of ≈265 nm, and the Cu/Zn species is encapsulated within the SiO₂ sphere (Figure 1a,b). From the high resolution transmission electron microscopy (HRTEM) images in Figure 1, the metal nanoparticles (indicated by yellow circles) are clearly visible.
nanoparticles with an average size of \( \approx 5 \) nm could be obviously observed on the edge of silica over CuZnSi-SGM and CuZnSi-AEM catalysts while not in the CuZnSi-StM catalyst. The energy dispersive spectrometer (EDS) elemental mapping of CuZnSi-AEM catalyst also indicates that the Cu and Zn are highly dispersed in SiO\(_2\) support (Figure S4, Supporting Information). It should be noted that the rodlike copper phyllosilicate with typical filandrous structure was not observed over all the calcined samples (Figure S3, Supporting Information). It means that other copper species was formed. In short, it can be observed that the three CuZnSi catalysts have different morphologies, and Cu/Zn species was highly dispersed in different locations on the silica support.

The textual and structural properties of CuZnSi catalysts have been investigated and shown in Table 1. Figure 2a presents that all the isotherms exhibit type IV with an H-type hysteresis loop, indicating that they possessed a mesoporous structure with an average pore diameter from 9.9 to 20.8 nm. The specific pore size distribution curves are shown in Figure 2b. The CuZnSi-StM catalyst exhibits the lowest \( S_{\text{BET}} \), pore diameter, and pore volume. However, the CuZnSi-SGM catalyst prepared by SGM has large pore volume (1.07 \( \text{cm}^3 \text{g}^{-1} \)) and high \( S_{\text{BET}} \) (313 \( \text{m}^2 \text{g}^{-1} \)), suggesting that the SGM is helpful for the formation of pores-rich architecture. It is worth noting that the average pore size of CuZnSi-AEM catalyst (20.8 nm) is the largest. Furthermore, the results of inductively coupled plasma (ICP) tests showed that the three CuZnSi catalysts exhibit similar copper and zinc loadings. The total metal loadings are around 10 wt\% with the Cu/Zn molar ratios around 2.3. Furthermore, the \( \text{N}_2 \) titration was used to determine the \( S_{\text{Cu}} \) and \( D_{\text{Cu}} \). It reveals that the \( S_{\text{Cu}} \) and \( D_{\text{Cu}} \) among CuZnSi catalysts are much different under the similar copper loading. The CuZnSi-AEM catalyst obtains the highest \( S_{\text{Cu}} \) (5.5 \( \text{m}^2 \text{g}^{-1} \)) and \( D_{\text{Cu}} \) (14.2\%), whereas they are only 1.2 \( \text{m}^2 \text{g}^{-1} \) and 2.9\% over CuZnSi-StM catalyst.

### Table 1. Component contents and textural properties of CuZnSi catalysts.

| Samples          | Cu [wt\%] | Zn [wt\%] | \( S_{\text{BET}} \) [\( \text{m}^2 \text{g}^{-1} \)] | \( D_p \) [nm] | \( V_p \) [\( \text{cm}^3 \text{g}^{-1} \)] | \( S_{\text{Cu}} \) [\( \text{m}^2 \text{g}^{-1} \)] | \( D_{\text{Cu}} \) [\%] | \( \text{TOF}^{\alpha} \) [h\(^{-1}\)] |
|------------------|-----------|-----------|----------------------------------|--------------|----------------------------------|----------------------------------|--------------|-----------------|
| CuZnSi-StM       | 6.7       | 3.4       | 24                                | 9.9          | 0.04                             | 1.2                              | 2.9          | 14.4            |
| CuZnSi-SGM       | 8.2       | 3.6       | 313                               | 11.6         | 1.07                             | 2.9                              | 5.5          | 25.5            |
| CuZnSi-AEM       | 6.0       | 2.6       | 144                               | 20.8         | 0.78                             | 5.5                              | 14.2         | 14.8            |

\( ^{\alpha} \text{TOF values were calculated using Cu active sites according to the previously reported formula:} \) \( \text{TOF} = \frac{\text{mole of reactive CO}}{\text{mole of active sites}} \times \text{reaction time} \). Test conditions: \( P = 2.0 \text{ MPa}, T = 240 \text{ °C}, \text{GHSV} = 4000 \text{ mL (g\text{-cat})}^{-1} \), and \( \text{H}_2\text{CO}_2\text{N}_2 \text{g} = 72:24:1 \).

2.2. The Analysis of Metal Species

The X-ray powder diffraction (XRD) patterns of CuZnSi catalysts are shown in Figure 3. It can be seen that the diffraction peaks of CuO were observed at \( 2\theta \) of 35.5\(^\circ\) and 38.9\(^\circ\) over CuZnSi-SGM catalyst. After reduction, the typical diffraction peak of Cu\(_2\)O at \( 2\theta \) of 36.5\(^\circ\) and metallic Cu at \( 2\theta \) of 43.3\(^\circ\), 50.4\(^\circ\), and 74.1\(^\circ\) emerged. Thus, the copper species was exposed well, but to some extent, they were aggregated over CuZnSi-SGM catalyst. On the contrary, the metal species was in an amorphous state or highly dispersed on the silica support, as no obvious diffraction peaks appearing over the CuZnSi-StM and CuZnSi-AEM catalysts. In addition, it should be noticed that the diffraction peaks belonging to ZnO or Zn were also not observed, due to its low loading extent, they were aggregated over CuZnSi-StM catalyst. The IR spectroscopy of the calcined samples was used to analyze the composition, as shown in Figure S5, Supporting Information. The three different CuZnSi catalysts present similar IR spectra. The main stretching bands at \( \approx 1100, 800, \) and 473 \( \text{cm}^{-1} \) belong to the Si-O bonds of amorphous SiO\(_2\) support.[21] The other two peaks at 1645 and 970 \( \text{cm}^{-1} \) are attributed to the OH groups of adsorbed water and Cu-O-Si species, respectively.[22] The characteristic adsorption peak of copper phyllosilicate at around 670 \( \text{cm}^{-1} \) was not observed, indicating

![Figure 2](image-url)  
(a) N\(_2\) adsorption–desorption isotherm curves and b) pore size distributions of CuZnSi catalysts.
the formation of Cu—O—Si species instead of copper phyllosilicate. Thus, the Cu$_2$O in the reduced samples was derived from the reduction of Cu—O—Si species.

### 2.3. Reducibility and Surface Acidity of the Studied Catalysts

H$_2$ temperature-programmed reduction (H$_2$-TPR) tests were performed to study the reducibility property, and the corresponding profiles are presented in Figure 4a. The samples were carried out under identical conditions with the same mass, but the CuZnSi-StM sample showed a much weak reduction peak. This phenomenon further indicates that copper species was encapsulated into silica and, thus, difficult to be reduced.[23] The other two CuZnSi catalysts presented similar reduction peak at around 200 °C due to the reduction of oxidised copper species supported on the silica. Compared with the CuZnSi-SGM catalyst, the reduction peak of CuZnSi-AEM catalyst shifted to higher temperature, indicating high dispersion of metal species and stronger interactions with silica support.

In addition, the surface acidity of the reduced CuZnSi catalysts was determined by the NH$_3$ temperature-programmed desorption (NH$_3$-TPD) tests. They present three distinguishable NH$_3$ desorption peaks in the temperature range of 150–600 °C (Figure 4b), which can be attributed to some Lewis acid sites originated from the cations of Si—O—Cu$^+$ species. The CuZnSi-AEM catalyst only displayed a large desorption peak at around 175 °C, indicating that its surface was dominated by weak acid sites.[24] When changing the preparation method, the CuZnSi-StM and CuZnSi-SGM catalysts presented another desorption peak at around 400 °C, suggesting that their surface exhibited both weak and medium to strong acid sites. The observed differences in acidity suggest different reactant–catalyst interactions, which, in turn, results in a different catalytic behaviour as revealed in the catalytic screening (see Section 2.5).

### 2.4. Surface Composition of the Studied Catalysts

The samples were reduced at 350 °C under the 5%H$_2$–Ar flow and then sent for the X-ray photoelectron spectroscopy (XPS) test under protection of Ar atmosphere. Still, some Cu$^{2+}$ species was detected as illustrated by the weak satellite lines between 940 and 947 eV (Figure 5a), which was probably from the oxidization during the sample preparation. Also, the Zn $2p_{3/2}$ at ~1022.7 eV was attributed to the exposed Zn$^{2+}$ species (Figure 5b).[25] In addition, the content of surface Cu/Zn species over CuZnSi-StM catalyst was much lower than those in the other two CuZnSi catalysts, as the former peaks'...
Intensities were much lower (Figure 5a,b). The specific atomic percentages of Cu, Zn, and Si are summarized in Table 2. Although the bulk metal loading was similar among the CuZnSi catalysts, the surface atomic concentrations were much different, especially the exposed Zn content. CuZnSi-StM exhibits the lowest Zn content (0.44%), whereas the CuZnSi-SGM catalyst exhibited 1.21% of Zn, which is even higher than the Cu content. It should be noted that the bulk Cu content was about 2.3 times of Zn content, and the CuZnSi-AEM catalyst exhibited the highest surface Cu content, which is consistent with the results from N\textsubscript{2}O titration in Table 1. In addition, the Cu LMM X-ray Auger electron spectroscopy (XAES) spectra were obtained to analyze the Cu\textsuperscript{+} and Cu\textsuperscript{0} species (Figure 5c and Table 2). It can be seen that their values of kinetic energy are similar, and the ratios of Cu\textsuperscript{+}/(Cu\textsuperscript{+} + Cu\textsuperscript{0}) present no obvious difference. However, the total exposed Cu metallic surface area is much different.

To further identify the copper species, the in situ Fourier-transform IR (FT-IR) spectra of CO adsorption were applied to analyze the CuZnSi samples. The CuZnSi catalysts present different CO adsorption peaks after purging the Ar for 20 min and the intensity with the following order: CuZnSi-AEM > CuZnSi-SGM > CuZnSi-StM (Figure 6). The CuZnSi samples showed a strong CO adsorption peak at around 2128 cm\textsuperscript{-1} and a weak shoulder peak at around 2098 cm\textsuperscript{-1}, which were attributed to the linear vibration of CO on Cu\textsuperscript{+} sites and metallic Cu\textsuperscript{0}, respectively.\textsuperscript{[26]} We know that CO linearly

Table 2. Surface Cu and Zn species of the reduced CuZnSi catalysts.

| Samples          | Binding energy [eV] | Surface atomic concentration [%] | Kinetic energy [eV] | X\textsubscript{Cu}\textsuperscript{+} \textsuperscript{a} [%] |
|------------------|---------------------|----------------------------------|---------------------|-----------------|
|                  | Cu 2p\textsubscript{3/2} | Zn 2p\textsubscript{3/2} | Cu 2p\textsubscript{3/2} | Zn 2p\textsubscript{3/2} | Si 2p | Cu\textsuperscript{+} | Cu\textsuperscript{0} |
| CuZnSi-StM       | 933.3               | 1022.7                          | 0.95                | 0.44            | 30.01 | 912.7 | 916.0  | 55.7 |
| CuZnSi-SGM       | 933.4               | 1022.6                          | 0.92                | 1.21            | 30.46 | 912.2 | 915.5  | 58.3 |
| CuZnSi-AEM       | 934.4               | 1022.7                          | 1.18                | 0.71            | 30.76 | 912.6 | 915.8  | 57.7 |

\textsuperscript{a}X\textsubscript{Cu}\textsuperscript{+} is the intensity ratio between Cu\textsuperscript{+} and (Cu\textsuperscript{+} + Cu\textsuperscript{0}) tested by Cu LMM Auger spectra.
bonded with a surface Cu$^{+}$ sites has higher thermal stability than gas-phase CO adsorption, Cu$^{2+}$–CO, and Cu$^{0}$–CO species, which were predominantly weak and reversible at room temperature.\[^{[26b]}\] It can be seen that the surfaces of CuZnSi-AEM and CuZnSi-SGM are dominated by Cu$^{+}$ species, whereas the CuZnSi-StM exhibits much Cu$^{0}$ species. Thus, it suggests that the surface of CuZnSi-StM exposed extremely less copper species, whereas CuZnSi-AEM exposed the most copper species, which is consistent with the results of N$_2$O titration in Table 1, the H$_2$-TPR result in Figure 4a, and the XPS result in Figure 5. The copper species over CuZnSi-StM sample was challenging to be reduced, so that the intensities of XPS and in situ FT-IR spectra of CO adsorption profiles were weak. It indicated that most of the copper species was encapsulated into silica support. Based on the previous report and the above-mentioned characterization results,\[^{[27]}\] it demonstrated that the CuZnSi-StM catalyst possessed a core–shell structure.

### 2.5. Catalytic Performance

The catalytic performance of CO$_2$ hydrogenation over CuZnSi catalysts prepared by different methods is shown in Figure 7 and Figure S6, Supporting Information. Figure 7a shows the variation of space-time yield (STY) of methanol, indicating that: 1) CuZnSi-SGM and CuZnSi-AEM catalysts presented high activity, leading to the highest STY of methanol at 280 °C and 2) CuZnSi-StM showed the lowest activity for methanol synthesis, and the STY of methanol was still low even at 300 °C. Figure 7b further demonstrates that the CuZnSi-AEM exhibits the highest specific activity. Thus, the CuZnSi-AEM has been investigated in detail. As shown in Figure 7c and Figure S6, Supporting Information, we observe that the main products were methanol and CO during different reaction temperatures. The Sel$_{\text{CH}_3\text{OH}}$ was decreased, whereas the Sel$_{\text{CO}}$ and Con$_{\text{CO}_2}$ were gradually increased upon rising the reaction temperatures. The methanol selectivity over CuZnSi-AEM catalyst maintains around 10% even under low reaction temperatures and low Con$_{\text{CO}_2}$ (Figure S6d, Supporting Information). Indeed, in the high-temperature window, CO is the dominant end product, and methanol selectivity is low when the temperature is higher than 240 °C for other CuZn-based catalysts. This trend mirrors the competition with the reverse water gas shift (RWGS) reaction, which is an endothermic process favored at high temperature.\[^{[28]}\] The highest Sel$_{\text{CH}_3\text{OH}}$ was about 60% at 220 °C, whereas the highest STY of methanol (48.8 g kg$_{\text{cat}}^{-1}$ h$^{-1}$) was obtained at 280 °C with the Con$_{\text{CO}_2}$ reached up to 16.7% over CuZnSi-AEM catalyst, which was nearly to the equilibrium Con$_{\text{CO}_2}$.

---

**Figure 7.** Catalytic performance of CuZnSi catalysts: a) STY of methanol at different reaction temperatures, b) specific activity at 280 °C, c) the Con$_{\text{CO}_2}$ and product selectivity over the CuZnSi-AEM catalyst via different reaction temperatures, and d) catalytic stability of CuZnSi-AEM at 280 °C. Reaction conditions: $P = 2.0$ MPa and GHSV = 4000 mL (g$_{\text{cat}}$ h)$^{-1}$ for (a–c) and 12 000 mL (g$_{\text{cat}}$ h)$^{-1}$ for (d), H$_2$: CO$_2$: N$_2$ = 72: 24: 1.
In addition, Figure S6c,d, Supporting Information, indicates that the Cu-ZnO-AEM catalyst without silica exhibits higher Sel\textsubscript{CH\textsubscript{3}OH} and lower Con\textsubscript{CO\textsubscript{2}} than the CuZnSi-AEM catalyst at 280 °C. However, the Cu-Si-AEM catalyst without ZnO presents the opposite results, namely, lower Sel\textsubscript{CH\textsubscript{3}OH} and higher Con\textsubscript{CO\textsubscript{2}} than the CuZnSi-AEM catalyst. Docherty and Coperet also demonstrated that the Cu/M@SiO\textsubscript{2} catalysts with Lewis acid sites and alloy-forming phases could boost methanol activity and selectivity than Cu@SiO\textsubscript{2}.\textsuperscript{[29]} These results further demonstrate that the Cu–ZnO\textsubscript{2} interface with a synergy of Cu and ZnO is the key active point of methanol synthesis due to the decreased apparent activation energy for methanol synthesis over Cu–ZnO\textsubscript{2} than pure Cu\textsuperscript{[8b,30]} After a stability test at 280 °C and a gas hour space velocity (GHSV) of 12 000 mL (g\textsubscript{Cu} cat)\textsuperscript{-1}, a mean STY of methanol (113.3 g kg\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}) was obtained for ≈54 h without deactivation (Figure 7d). This is an excellent result, which showcases that CuZnSi-AEM prepared by the AEM exhibits better stability than the CuSi-based catalysts prepared by the impregnation and rotary evaporation-assisted deposition–precipitation method.\textsuperscript{[17,20b]} The TEM image and XRD patterns of the spent CuZnSi-AEM catalyst confirm that the metallic active species preserves high dispersion (Figure S7, Supporting Information), a good indication of its demonstrated stability.

Furthermore, a comparative study of the catalytic performance over CuZnSi catalysts from the reported literature is summarized in Table S1, Supporting Information, providing an idea of the advances of our engineered catalysts compared with CuSi- and CuZn-based systems. Certainly, the catalytic property of CuZnSi catalysts reported here reaches the advanced level from the perspectives of STY\textsubscript{CH\textsubscript{3}OH} based on Cu, which is the highly commendable results for a noble metal-free system. The STY\textsubscript{CH\textsubscript{3}OH} reached up to 1888.3 g kg\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1}, and a specific activity was 282.6 mol\textsubscript{CO} mol\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1} on CuZnSi-AEM, whereas those values were lower than 1000 g kg\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1} and 100 mol\textsubscript{CO} mol\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1} over most of other reported CuSi- and CuZn-based systems. We should also point out that these results are achieved at relatively low pressure (2 MPa), because most of the reported studies use a larger pressure range with the process cost and health and safety implications. Interestingly, with a further increase in the reaction pressure to 5.0 MPa and the GHSV to 24 000 mL (g\textsubscript{Cu} cat)\textsuperscript{-1}, the STY of methanol over CuZnSi-SGM is improved to 212.2 g kg\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1} (2587.8 g kg\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1}), matching the performance of benchmark catalysts for methanol synthesis.

To further unravel the universality of AEM, a series of CuZnX-AEM (X = KIT-6, SBA-15, ZrO\textsubscript{2}, and CeO\textsubscript{2}) catalysts were also synthesized by AEM and applied for CO\textsubscript{2} hydrogenation. The Con\textsubscript{CO\textsubscript{2}} and STY of methanol over the silica supported CuZn catalysts are higher than those of the metal oxides supported CuZn catalysts (Figure S8, Supporting Information), with the CuZnSBA-AEM achieving the highest STY of methanol (133.7 g kg\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}). The TEM images of CuZnSBA-AEM show that the regular channel structure of SBA-15 was not damaged during preparation, and the metal species was highly dispersed around the pores (Figure S9, Supporting Information). Thus, the AEM could be further extended to prepare other silica-based materials, whereas the metal oxides-based systems are not suitable. The reason is probably that Cu(OH)\textsubscript{2} generated along with the evaporation of NH\textsubscript{3} could interact with the silica support to produce copper silica species such as copper phyllosilicate and Cu–O–Si units.\textsuperscript{[8b]} However, Cu(OH)\textsubscript{2} would be further evolved to copper oxide over the metal oxides supported CuZn catalysts prepared by AEM, which is explained by the black mixture after ammonia evaporation, whereas the mixture over the silica supported CuZn catalysts is still blue after ammonia evaporation. The XRD results show that the bulk copper species was generated over the reduced CuZnZr-AEM and CuZnCe-AEM catalysts (Figure S10, Supporting Information).

The CuZnSi-AEM catalyst has been demonstrated to an effective catalyst for CO\textsubscript{2} hyrogenation to methanol. According to the microreversibility principle in catalysis, an obvious quest would be would these advanced materials catalyze the reverse process? In the context of methanol economy, another significant process is how to use the methanol to produce syngas, in particular, hydrogen-rich syngas mixtures. Liquid methanol with high H/C ratio is an ideal hydrogen carrier. Thus, the investigation of CO\textsubscript{2} hydrogenation to methanol and methanol reforming is meaningful for the carbon cycle, hydrogen transportation, and hydrogen refueling station. MSR process is a complex process encompassing not only methanol decomposition reaction but also the water gas shift reaction in the 200–300 °C temperature range. Thus, a careful control on catalysts activity/selectivity/stability for a flexible production of end products remains a challenge for the catalysis community. In this study, the CuZnSi-SGM and CuZnSi-AEM catalysts were further implemented in the MSR reaction, and the results are presented in Table 3. We observe that the CuZnSi-AEM still exhibits a much higher activity and slightly lower CO selectivity than those over the CuZnSi-SGM. The hydrogen generation rate could reach up to 85.7 μmol g\textsuperscript{-1} s\textsuperscript{-1} over the CuZnSi-AEM, which is probably due to the highly dispersed metal species instead of the high S\textsubscript{BET}. The previously reported Cu/ZrO\textsubscript{2} catalysts prepared by three different methods also indicate that the one with higher S\textsubscript{Cu} and D\textsubscript{Cu} presents better MSR performance.\textsuperscript{[12]} To the best of our knowledge, the copper silica-based catalysts synthesized by the AEM have been rarely reported so far. Thus, the CuZnSi-AEM catalyst could be recognized as a suitable candidate for MSR. In other words, combining the results from CO\textsubscript{2} hydrogenation and MSR, we can indicate that our CuZnSi-AEM multicomponent catalyst is a switchable system for MeOH production/MeOH reforming, enabling a close carbon loop and flexibility within the end products.

| Catalyst     | T [°C] | Con\textsubscript{CH\textsubscript{3}OH} [%] | Sel\textsubscript{CO} [%] | H\textsubscript{2} prod. rate [μmol g\textsuperscript{-1} s\textsuperscript{-1}] |
|--------------|--------|---------------------------------|-----------------|-----------------------------------------------|
| CuZnSi-SGM   | 300    | 10.3                            | 5.6             | 11.4                                          |
|              | -      | 280                             | 8.2             | 1.8                                           |
|              |        | 250                             | 6.4             | 0.8                                           |
| CuZnSi-AEM   | 300    | 75.5                            | 3.0             | 85.7                                          |
|              | -      | 280                             | 68.4            | 1.0                                           |
|              |        | 250                             | 43.1            | 0.4                                           |

\textsuperscript{4} Reaction conditions: n\textsubscript{H\textsubscript{2}}/n\textsubscript{CH\textsubscript{3}OH} = 1, weight hourly space velocity (WHHSV) = 4.5 h\textsuperscript{-1}, 0.1 MPa, and 30 mL min\textsuperscript{-1} of N\textsubscript{2}.
2.6. Structure–Performance Relationship

The ternary CuZnAl-based catalysts have been applied for CO/CO₂ hydrogenation to methanol for more than 50 years. Its active sites and influencing factors for methanol synthesis have been widely studied and debated. These key factors include catalyst structure, metal loading, promoter doping, the size of active nanoparticles, Cu⁺ concentration, the synergistic interaction among Cu and ZnO, and so on.

Three preparation techniques, including modified StM, SGM, and AEM, were used to synthesize engineered CuZnSi catalysts for studying the influencing factors. Their structural properties and catalytic performances were much different. First, their total metal loadings were similar. Thus, the influence of metal contents on the catalytic performance was negligible. For CuZnSi-StM catalyst, the use of structural directors of polyvinylpyrrolidone (PVP) and hexadecyl trimethyl ammonium bromide (CTAB) led to a core–shell-structured material with a poor pore structure, low specific surface area, and very less exposed metal species. The copper species was difficult to be reduced from the result of H₂–TPR. As a result, its activity for methanol synthesis was weak, and the STY of methanol was very low during the whole reaction temperatures. This not only proves that the porous channels have significant roles in heat and mass transfer but also demonstrates the exposed active sites for CO₂/H₂ adsorption/activation and conversion. For CuZnSi-SGM catalyst, it has abundant pores and high S_BET, especially the overexposed Cu/Zn species resulting in some bulk CuO and metallic Cu. As a result, its activity for methanol synthesis was commendable, and the turnover frequency (TOF) value (25.5 h⁻¹) based on Cu active sites was the highest (Table 1). When using the silica sol as silica source to prepare CuZnSi-AEM catalyst by AEM, textural properties such as S_BET are enhanced along with achieving the highest Cu dispersion and availability of Cu surface species. As a result, the CuZnSi-AEM possesses the highest STY of methanol. However, the TOF value (14.8 h⁻¹) of CuZnSi-AEM catalyst was about half of that over CuZnSi-SGM catalyst. This is probably due to the CuZnSi-AEM catalyst exhibiting higher surface Cu species but lower concentration of Zn species than those shown by the CuZnSi-SGM catalyst. With the comparison of the catalytic performance of CuSi-AEM and CuZnSi-AEM catalysts, it further indicates that the Cu–ZnO interfaces are deemed as key active sites for methanol synthesis, whereas the overall surface area plays a minor role. In addition, the three catalysts exhibit clearly different proportions of surface exposed Cu⁺ (Table 1 and Figure 6). Hence, we speculate that the exposed Cu⁺ species is also a key factor for the activity to ensure successful design of CuZnSi catalyst for methanol synthesis.

The in situ diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) experiment is used to monitor the intermediates, and the results are presented in Figure S11, Supporting Information. The peaks of formates were observed at 1651 and 1595 cm⁻¹, whereas the peaks of CO were not shown. Based on the above-mentioned discussion and previous literature results, the possible reaction pathway for CO₂ hydrogenation to methanol over CuZnSi-AEM catalyst is associated with the formate (HCOO⁻) intermediate (Scheme 3). In turn, the methanol would be first converted to a methyl formate or formaldehyde intermediate then to formic acid intermediate during the MSR. The synergy of Cu and ZnO at the interface has been highlighted for promoting methanol synthesis via formate intermediates. In this work, the exposed metal species and Cu–ZnO interfaces would significantly influence the adsorption and desorption of CO₂ and its intermediates, as well as the activation of hydrogen. In particular, the exposed Cu⁺ species at the Cu⁺–O–Zn/Cu–O–Si interfaces plays a significant role in stabilizing the HCOO⁻, H₂COO⁻, HCO⁻, and H₂CO species by Cu–O interaction. In addition, the pore structure would affect the mass transfer. The CuZnSi-AEM catalyst exhibited a high Cu dispersion, high content of exposed Cu⁺, and suitable pore structure, thus resulting in high methanol yields as well as high hydrogen production rate.

3. Conclusion

This work provides a comparison of Cu–ZnO/SiO₂ catalysts prepared by different synthesis routes with the target to unravel the critical factors involved in a rational catalyst design. A cost-effective CuZnSi-AEM catalyst with highly dispersed metal species and low metal loading has been found to be an efficient catalyst not only for CO₂ hydrogenation to methanol but also for the MSR, showcasing a proper switchable catalyst system. Furthermore, the AEM could also be extended for other silica-based catalysts. Its economic viability along with its relatively simple upscaling and end products flexibility indicates potential for the transportation and on-site production of renewable hydrogen.

Beyond identifying a suitable catalyst for this process, our work sheds some lights on the key factors influencing methanol synthesis and its steam reforming to hydrogen. The take-home messages are: 1) The specific surface area is not a controlling factor for methanol synthesis and decomposition; and 2) the crucial parameters behind an advanced catalytic performance are optimum pore channels, concentration of exposed Cu⁺ surface species, and availability—dispersion of Cu–ZnO active interfaces with synergetic interactions. As a result, the pure Cu/SiO₂-AEM catalyst without ZnO exhibited higher CO₂ conversion but much
lower methanol selectivity than the Cu–ZnO/SiO$_2$-AEM catalyst over a wide temperature range. Overall, this work provides a strategy to design highly active heterogenous catalysts for CO$_2$ to methanol and methanol to hydrogen by pinpointing the key guiding factors controlling the reaction.

4. Experimental Section

Materials: Chemical reagents were used as received with the following information: Copper nitrate trihydrate (AR), zinc nitrate hexahydrate (AR), ethanol (EOH; AR), N,N-dimethylformamide (DMF; AR), PVP K30 (GR), CTAB (AR), ammonia aqueous solution (25–28% NH$_3$H$_2$O; AR), TEOS (AR), and CeO$_2$ (99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd., whereas alkaline silica sol (30%) was received from Shanghai YUANYE Bio-Technology Co., Ltd. The SBA-15 and KIT-6 powders were received from Nanjing XFNANO Materials Tech Co., Ltd. In addition, the ZrO$_2$ powder was received from Shanghai HANLANE new material Tech Co., Ltd.

Catalyst Preparation: Three Cu–ZnO/SiO$_2$ catalysts were prepared by modified StM, SGM, and AEM, respectively, as shown in Scheme 2 and shown in the following.

CuZnSi-StM Catalyst: The preparation procedures were modified from a previous study. Specifcally, 0.484 g Cu(NO$_3$)$_2$·3H$_2$O, 0.298 g Zn(NO$_3$)$_2$·6H$_2$O, and 3.0 g PVP were dissolved into 200 mL of ethanol to form solution A. Then, solution A was added to a conical flask with 80 mL H$_2$O, 100 mL ETOH, 3.0 g CTAB, and 20 mL NH$_3$H$_2$O (25–28%). TEOS (5.5 g) was added and stirred at room temperature (RT) for 24 h. The resultant solid was recovered by centrifugation and washed by water and ethanol (volume ratio 1:1) for several times. After being dried at 100 °C for 12 h and calcined at 450 °C for 5 h in a muffle furnace with a heating rate of 1 °C min$^{-1}$, the obtained catalyst was named CuZnSi-StM.

CuZnSi-SGM Catalyst: Cu(NO$_3$)$_2$·3H$_2$O (0.484 g) and Zn(NO$_3$)$_2$·6H$_2$O (0.298 g) were dissolved into a mixture solution of water, DMF, and ethanol (60 mL, volume ratio 1:1:1). After reacting with TEOS (5.5 g) at RT for 20 min, the mixture was moved into 100 mL autoclave and reacted at 150 °C for 9 h. The generated sol–gel mixture was washed by water and ethanol (volume ratio 1:1) for several times. The sample was dried at 80 °C for 10 h in a vacuum oven, 100 °C for 12 h in an air oven, and calcined at 450 °C for 5 h in a muffle furnace with a heating rate of 3 °C min$^{-1}$. The obtained catalyst was named CuZnSi-SGM.

CuZnSi-AEM Catalyst: The preparation method was referenced to previous reports from Jiang et al. and Ye et al.$^{[15,17]}$ Cu(NO$_3$)$_2$·3H$_2$O (0.484 g), Zn(NO$_3$)$_2$·6H$_2$O (0.298 g), and urea (1.0 g) were dissolved into 30 mL deionized water and stirred at RT for 10 min. NH$_3$H$_2$O (3 mL) (25–28%) was then added into it to form a copper ammonia complex solution. After stirring at RT for 20 min, 6.337 g colloidal silica (30%) added and stirred for another 20 min. Then, the mixture was transferred to a 50 °C water bath and heated to 80 °C and then kept at 80 °C to evaporate ammonia and deposited the CuZn species on silica. The evaporation process was stopped until the water was nearly evaporated. The precipitate was washed using water for several times, dried at 100 °C for 12 h, and then calcined at 450 °C for 5 h in a muffle furnace with a heating rate of 3 °C min$^{-1}$. The obtained catalyst was named CuZnSi-AEM. The other CuZnX-AEM (X = KIT-6, SBA-15, ZrO$_2$, and CeO$_2$) catalysts were also prepared similarly to CuZnSi-AEM except that the colloidal silica was changed to other corresponding supports. The reference catalysts of Cu–ZnO-AEM and CuSi-AEM were also prepared by the AEM except that without adding silica or Zn(NO$_3$)$_2$·6H$_2$O, respectively.

Catalyst Characterization: The structural properties of the CuZnSi catalysts have been characterized by ICP optical emission spectroscopy, nitrogen sorption, XRD, FT-IR, CO adsorption in situ FT-IR, H$_2$-TPR, NH$_3$-TPD, the TEM, SEM, and XPS. The in situ DRIFTS was used to monitor the possible reaction intermediates. More detailed information about the characterizations is shown in the Supporting Information.

Catalyst Evaluation: The CO$_2$ hydrogenation reaction and MSR reactions were performed in a stainless steel fixed-bed reactor. Prior to the CO$_2$ hydrogenation reaction, the calcined sample (0.6 g, 20–40 meshes; or 0.2 g sample with 0.5 g silica sand) was pre-reduced at 350 °C and 1.0 MPa for 2 h under a flow of hydrogen (40 mL min$^{-1}$). After the reduction, the hydrogen was changed to a mixture of CO$_2$ and H$_2$, and N$_2$ (H$_2$: CO$_2$: N$_2$ = 72: 24: 1), and the GHSV was 4000–12 000 mL (g cat$^{-1}$ h$^{-1}$). The reaction pressure was increased to 2.0 MPa whereas the reaction temperatures varied from 300 to 220 °C with 20 °C per step. The products maintained at 150°C were analyzed by online gas chromatography (SHIMADZU GC-2014) with flame ionization detector (FID) and thermal conductivity detector (TCD). Porapak-S 80/100 and molecular sieve-13X 80/100 packed columns were connected to TCD, whereas Rtx-1 (60 m) and Rt-Q-BOND (30 m) capillary columns were connected to FID. Finally, the CO$_2$ conversion (Con,CO$_2$), main products selectivity (Sel), specific activity (SA$_{cat}$), and STY (g kg$_{cat}$ h$^{-1}$) of methanol were calculated using the following formulas.$^{[38]}$

\[
\text{Con,CO}_2 = \frac{f_{CO}A_{CO} + i(f_{CH,A_{CH}_4} + f_{CH,OH,A_{CH}_OH} + 2f_{CH_2H_4,A_{CH}_2H_4} + 2f_{CH_3,OH,A_{CH}_3OH})}{f_{CO,Ac_0} + f_{CO,A_{CO}} + i(f_{CH_2H_2,A_{CH}_2H_2} + f_{CH_3H_2,A_{CH}_3H_2} + 2f_{CH_4,OH,A_{CH}_4OH})}.
\]

\[
\text{Sel}_{CH_2OH} = \frac{f_{CH_2OH,A_{CH}_2OH}}{f_{CO,Ac_0} + i(f_{CH_2H_2,A_{CH}_2H_2} + f_{CH_3H_2,A_{CH}_3H_2} + 2f_{CH_4,OH,A_{CH}_4OH})}.
\]

\[
\text{Sel}_{CO} = \frac{f_{CO,A_{CO}} + i(f_{CH_2H_2,A_{CH}_2H_2} + f_{CH_3H_2,A_{CH}_3H_2} + 2f_{CH_4,OH,A_{CH}_4OH})}{f_{CO,Ac_0} + i(f_{CH_2H_2,A_{CH}_2H_2} + f_{CH_3H_2,A_{CH}_3H_2} + 2f_{CH_4,OH,A_{CH}_4OH})}
\]
\[ i = \frac{f_{\text{CH}_4}}{f_{\text{FID}}}, \quad \text{TCD}\frac{\text{A}_{\text{CH}_4}}{\text{TCD}} = \frac{\text{A}_{\text{CH}_4}}{\text{FID}} \]

\[ \text{STY}_{\text{CH}_3\text{OH}} = \frac{1000 \times 22.4 \times V\%(\text{CO}_2) \times \text{Conv.-CO}_2}{\text{Select}_{\text{CH}_3\text{OH}}} \times \frac{\text{M}_{\text{CH}_3\text{OH}}}{\text{M}_{\text{CO}_2}} \]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported financially by the China Postdoctoral Science Foundation (No. 2020T130639 and No. 2019M661143), the Natural Science Foundation of Liaoning Province, China (No. 2020-YQ-01), the Liaoning Revitalization Talents Program, China (No. XLYC180707), the National Natural Science Foundation of China (No. 22005296), and the Excellent Research Assistant Funding Project, Chinese Academy of Sciences (CAS). The authors also thank Prof. Qihua Yang and Dr. Jiije Wang from the Dalian Institute of Chemical Physics, CAS, and Mr. Chong-Chong Chen and Dr. Yuan-Yuan Huang from the Fujian Institute of Research on the Structure of Matter, CAS, for supporting this work.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

CO₂ hydrogenation, Cu-based catalysts, hydrogen generation and storage, methanol stream reforming, sustainability

Received: March 25, 2021  
Revised: May 13, 2021  
Published online:

[1] C. F. Shih, T. Zhang, J. Li, C. Bai, Joule 2018, 2, 1925.
[2] R.-P. Ye, J. Ding, W. Gong, M. D. Argyle, Q. Zhong, Y. Wang, C. K. Russell, Z. Xu, A. G. Russell, Q. Li, M. Fan, Y.-G. Yao, Nat. Commun. 2019, 10, 5698.
[3] S. Dang, B. Qin, Y. Yang, H. Wang, J. Cai, Y. Han, S. Li, P. Gao, Y. Sun, Sci. Adv. 2020, 6, eaaz2060.
[4] G. A. Olah, Angew. Chem. Int. Ed. 2005, 44, 2636.
[5] a) S. Sá, H. Silva, L. Brandão, J. M. Sousa, A. Mendes, Appl. Catal. B: Environ. 2010, 99, 43; b) M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, Chem. Rev. 2012, 112, 782.
[6] J. Kothandaraman, S. Kar, R. Sen, A. Goeppert, G. A. Olah, G. K. S. Prakash, J. Am. Chem. Soc. 2017, 139, 2549.
[7] a) Z. Li, Y. Ju, J. Wang, H. Liu, M. Li, S. Miao, C. Li, Joule 2019, 3, 570; b) A. R. Richard, M. Fan, ACS Catal. 2017, 7, 5679.
[8] a) J. Zhong, X. Yang, Z. Wu, B. Liang, Y. Huang, T. Zhang, Chem. Soc. Rev. 2020, 49, 1385; b) S. Kettel, P. J. Ramirez, J. G. Chen, J. A. Rodriguez, P. Liu, Science 2017, 355, 1296.
[9] L. F. Bobadilla, S. Palma, S. Ivanova, M. I. Dominguez, F. Romero-Sarria, M. A. Centeno, J. A. Odriozola, Int. J. Hydrogen Energy. 2013, 38, 7984.
[10] X. Jiang, X. Nie, Y. Gong, C. M. Moran, J. Wang, J. Zhu, H. Chang, X. Guo, K. S. Walton, C. Song, J. Catal. 2020, 383, 283.
[11] J. Hu, L. Yu, J. Deng, Y. Wang, K. Cheng, C. Ma, Q. Zhang, W. Wen, S. Yu, Y. Pan, J. Yang, H. Ma, F. Qi, Y. Wang, Y. Zheng, M. Chen, R. Huang, S. Zhang, Z. Zhao, J. Mao, X. Meng, Q. Ji, G. Hou, X. Han, X. Bao, Y. Wang, D. Deng, Nat. Catal. 2021, 4, 242.
[12] X. Jiang, X. Nie, X. Guo, C. Song, J. G. Chen, Chem. Rev. 2020, 120, 7984.
[13] a) Y. Matsumura, H. Ishibe, J. Catal. 2009, 268, 282; b) B. An, J. Z. Zhang, K. Cheng, P. F. Ji, C. Wang, W. B. Lin, J. Am. Chem. Soc. 2017, 139, 3834.
[14] a) A. Popat, S. B. Hartono, F. Stahr, J. Liu, S. Z. Qiao, G. Qing Max Lu, Nanoscale 2011, 3, 2801-2818; b) H. Y. Yang, P. Gao, C. Zhang, L. S. Zhong, X. P. Li, S. Wang, H. Wang, W. Wei, Y. H. Sun, Catal. Commun. 2016, 84, 56.
[15] Y. Jiang, H. Yang, P. Gao, X. Li, J. Zhang, H. Liu, H. Wang, W. Wei, Y. Sun, J. CO₂ Util. 2018, 26, 642.
[16] R.-P. Ye, L. Lin, L.-C. Wang, D. Ding, Z. Zhou, P. Pan, Z. Xu, J. Liu, H. Addidharma, M. Radosz, M. Fan, Y.-G. Yao, ACS Catal. 2020, 10, 4665.
[17] Z.-Q. Wang, Z.-N. Xu, S.-Y. Peng, M.-J. Zhang, G. Lu, Q.-S. Chen, Y. Chen, G.-C. Guo, ACS Catal. 2015, 5, 4255.
[18] Z. Shi, Q. Tan, D. Wu, AlChE J. 2019, 65, 1047.
[19] T. Takahashi, N. Takezawa, H. Kobayashi, Appl. Catal. 1982, 2, 363.
[20] a) V. D. B. C. Dasireddy, B. Likozar, Renew. Energy 2019, 140, 452; b) K. Chen, J. Yu, B. Liu, C. Si, H. Ban, W. Cai, C. Li, Z. Li, K. Fujimoto, J. Catal. 2019, 372, 163; c) J. Ashok, M. L. Ang, S. Kawi, Catal. Today 2017, 281, 304; d) X. Li, J. Deng, J. Shi, T. Pan, C. G. Yu, H. J. Xu, Y. Fu, Green Chem. 2015, 17, 1038.
[21] R.-P. Ye, L. Lin, C.-Q. Liu, C.-C. Chen, Y.-G. Yao, ChemCatChem 2017, 9, 4587.
[22] A. Yin, X. Guo, W.-L. Dai, K. Fan, J. Phys. Chem. C. 2009, 113, 11003.
[23] R.-P. Ye, L. Lin, C.-C. Chen, J.-X. Yang, F. Li, X. Zhang, D.-J. Li, Y.-Y. Qin, Z. Zhou, Y.-G. Yao, ACS Catal. 2018, 8, 3382.
[24] J. Gao, J. Guo, D. Liang, Z. Hou, J. Fei, X. Zheng, Int. J. Hydrogen Energy 2008, 33, 5494.
[25] C. Zhang, H. Yang, P. Gao, H. Zhu, L. Zhong, H. Wang, W. Wei, Y. Sun, J. CO₂ Util. 2017, 17, 263.
[26] a) A. Chen, X. Yu, Y. Zhou, S. Miao, Y. Li, S. Kuld, J. Sehested, J. Liu, T. Aoki, S. Hong, M. F. Camellone, S. Fabris, J. Ning, C. Jin, C. Yang, A. Nefedov, C. Wöll, Y. Wang, W. Shen, Nat. Catal. 2019, 2, 334; b) Z. He, H. Q. Lin, P. He, Y. Z. Yuan, J. Catal. 2011, 277, 54.
[27] H. Yang, Y. Chen, X. Cui, G. Wang, Y. Cen, T. Deng, W. Yan, J. Gao, S. Zhu, U. Olsbye, J. Wang, W. Fan, Angew. Chem. Int. Ed. 2018, 57, 1836.
[28] N. Nityashree, C. A. H. Price, L. Pastor-Perez, G. V. Manohara, S. Garcia, M. M. Maroto-Valer, T. R. Reina, Appl. Catal. B Environ. 2020, 261, 118241.

[29] S. R. Docherty, C. Coperet, J. Am. Chem. Soc. 2021, 143, 6767.

[30] J. Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, Science 2014, 345, 546.

[31] L. Chen, P. Guo, M. Qiao, S. Yan, H. Li, W. Shen, H. Xu, K. Fan, J. Catal. 2008, 257, 172.

[32] C. Yao, L. Wang, Y. Liu, G. Wu, Y. Cao, W. Dai, H. He, K. Fan, Appl. Catal. A Gen. 2006, 297, 151.

[33] D. Laudenschleger, H. Ruland, M. Muhler, Nat. Commun. 2020, 11, 3898.

[34] A. Karelovic, P. Ruiz, Catal. Sci. Technol. 2015, 5, 869.

[35] a) M. Behrens, F. Studt, I. Kasatkin, S. Kuhl, M. Havecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. L. Kniep, M. Tovar, R. W. Fischer, J. K. Norskov, R. Schlogl, Science 2012, 336, 893; b) S. Kattel, P. Liu, J. G. Chen, J. Am. Chem. Soc. 2017, 139, 9739.

[36] J. Yu, M. Yang, J. Zhang, Q. Ge, A. Zimina, T. Pruessmann, L. Zheng, J.-D. Grunwaldt, J. Sun, ACS Catal. 2020, 10, 14694.

[37] R.-P. Ye, L. Lin, J.-X. Yang, M.-L. Sun, F. Li, B. Li, Y.-G. Yao, J. Catal. 2017, 350, 122.

[38] a) J. Wang, C. Li, Z. Li, C. Tang, Z. Feng, H. An, H. Liu, T. Liu, C. Li, Sci. Adv. 2017, 3, e1701290; b) R. P. Ye, L. Liao, T. R. Reina, J. Liu, D. Chevella, Y. Jin, M. Fan, J. Liu, Fuel 2021, 285, 119151.