

Plasma-catalytic Direct Oxidation of Methane to Methanol over Cu-MOR: Revealing the Zeolite-confined Cu $2+$ Active Sites

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Abstract

Efficient methane conversion to methanol remains a significant challenge in chemical industry. This study investigates the direct oxidation of methane to methanol under mild conditions, employing a synergy of non-thermal plasma and Cu-MOR (Copper-Mordenite) catalysts. Catalytic tests demonstrate that the Cu-MOR IE-3 catalyst (i.e., prepared by three cycles of ion exchange) exhibits superior catalytic performance (with 51% methanol selectivity and 7.9% methane conversion). Conversely, the Cu-MOR catalysts prepared via wetness impregnation tend to over-oxidize CH₄ to CO and CO₂. Through systematic catalyst characterizations (XRD, TPR, UV-Vis, HRTEM, XPS), we elucidate that ion exchange mainly leads to the formation of zeolite-confined Cu²⁺ species, while wetness impregnation predominantly results in CuO particles. Based on the catalytic performance, catalyst characterizations and *in-situ* FTIR spectra, we conclude that zeolite-confined Cu²⁺ species serve as the active sites for plasma-catalytic direct oxidation of methane to methanol.

1. Introduction

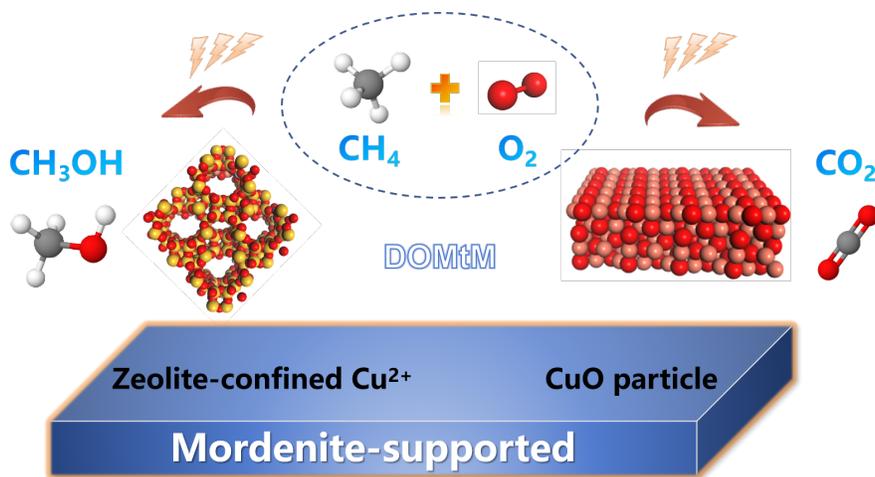
The industrial conversion of methane (CH₄) to methanol (CH₃OH) typically follows an indirect route, involving the initial step of CH₄ steam reforming to generate syngas (CO and H₂) at elevated temperature (above 800 °C). Subsequently, the synthesis of CH₃OH takes place at high pressure (ca. 100 atm) using a Cu-Zn-Al catalyst. Although widely applied on a large scale, this commercial method is unsuitable for small-scale production due to its demanding reaction conditions, intricate operational processes, energy-intensive requirements and high equipment costs.¹ Consequently, there is a growing interest in the direct oxidation of methane to methanol (DOMtM) under mild conditions, offering significant potential for implementation at distributed and small-scale plants.² For over a century, researchers have explored DOMtM through both homogeneous and heterogeneous catalysis. Homogeneous catalysis typically involves the use of fuming sulfuric acid³ or trifluoroacetic acid⁴ as reaction solvents. Complex catalysts featuring Pt, Pd, Au or Hg noble metals as active centers have been employed. In the realm of heterogeneous catalysis, various catalytic materials, including metals⁵ and metal oxides⁶ have been intensely investigated.

Recently, inspired by the binuclear iron and copper active sites observed in natural methane monooxygenase (MMO), researchers have explored iron- and copper-based zeolite catalysts for DOMtM with high selectivity.⁷ Iron-based zeolites exhibit proficient N₂O decomposition ($N_2O + (Fe^{2+})_{\alpha} - (Fe^{3+}-O^{-})_{\alpha} + N_2$) at temperatures below 300 °C, with the α -O species identified as the active component for DOMtM.⁸ Copper-based zeolites show notable catalytic efficacy in DOMtM, especially when O₂ or H₂O is employed as oxidants, positioning Cu-MOR as a highly promising catalytic material for DOMtM.⁹ To overcome the high energy barrier (E_a)

of CH₄ oxidation and to inhibit excessive oxidation of CH₃OH, a multi-step chemical looping approach has been proposed. This method involves catalyst pre-activation of the catalyst with O₂ at high temperatures, followed by a low-temperature reaction with CH₄ to generate adsorbed CH₃OH species. Subsequently, extraction through either solvent or steam leads to the production of CH₃OH. The primary objective of this approach is to safeguard the CH₃OH formed on the catalyst surface from excessive oxidation, thereby achieving a superior CH₃OH selectivity exceeding 90%. However, the intricate multi-step process involves frequent switches in feeding gases and adjustments in temperature, introduces discontinuities in CH₃OH production, diminishes overall reaction efficiency, and entails substantial energy consumption.

Non-thermal plasma (NTP) stands out as a powerful method for activating and converting CH₄ to CH₃OH. Energetic electrons within the NTP effectively activate CH₄ and O₂ molecules, generating reactive radical species (CH_x and O species).^{10,11} Additionally, the low gas temperature in NTP plays a crucial thermodynamic role in CH₃OH production, as excessively high temperatures can lead to CH₃OH decomposition or its reforming with water vapor, producing CO and CO₂. A dielectric barrier discharge (DBD) is one of the most common methods to produce NTP and is widely employed in plasma-assisted DOMtM. Nozaki demonstrated the conversion of CH₄ into oxygenates in a microplasma reactor with a single-pass yield of 5-20% and a selectivity of 70-30%.¹² Furthermore, when employing a Cu/ZnO/Al₂O₃ (CZA) catalyst for DOMtM, oxidized Cu species exhibited higher CH₃OH selectivity compared to copper metal (Cu⁰) species, suggesting that Cu⁺ or Cu²⁺ may serve as active components in plasma-assisted DOMtM.¹³ Subsequently, Chawdhury et al. found that a CuO/γ-Al₂O₃ catalyst enhanced the CH₃OH selectivity, with high Cu loading facilitating formaldehyde (HCHO) generation.¹⁴ Recently, Li et al. reported a strategy to overcome the trade-off relationship between CH₄ conversion and CH₃OH selectivity through co-feeding H₂O vapor with CH₄ and O₂ over a Pt₂/BN-na catalyst.⁹

In summary, Cu-based zeolite catalysts exhibit notable CH₃OH selectivity in thermal catalytic DOMtM, while NTP facilitates DOMtM with impressive CH₄ conversion at low temperatures. Consequently, the synergistic utilization of NTP and Cu-based zeolite catalysts emerges as a promising strategy for DOMtM.



Scheme 1. Diagram of plasma-driven direct oxidation of methane to methanol on Cu-MOR catalysts, aiming to emphasize the active sites of zeolite-confined Cu²⁺ species.

This study presents an investigation into the performance of Cu-MOR catalysts prepared using both wetness impregnation and ion exchange methods in plasma-catalytic DOMtM. The results reveal that ion exchange mainly leads to the formation of zeolite-confined Cu²⁺ species in Cu-MOR, exhibiting excellent catalytic performance (7.9% CH₄ conversion and 51% CH₃OH selectivity), as shown in Scheme 1. In contrast, wetness impregnation predominantly results in the formation of CuO particles in Cu-MOR, hindering the DOMtM

reaction while inducing over-oxidation into CO and CO₂. The correlation of the catalytic performance with catalyst characterization results unequivocally demonstrates that zeolite-confined Cu²⁺ species serve as the active sites for DOMtM, providing valuable information to the advancement of plasma-catalytic systems in the context of DOMtM.

Experimental section

2.1 Catalyst preparation

The Cu-based catalysts were synthesized using both ion exchange and wetness impregnation methods, as illustrated in Supporting Information (SI, section 1, Scheme S1). Commercial MOR zeolite (purchased from Nankai University Catalyst Co., Ltd.) was calcined in a muffle furnace at 400 °C for 5 hours. Cu(CH₃COO)₂·H₂O and Cu(NO₃)₂·3H₂O (provided by Shanghai Aladdin Biotechnology Co.) were used as the copper sources for ion exchange and wetness impregnation, respectively. For the ion exchange method, 10 g MOR zeolite was added to 28 ml Cu(CH₃COO)₂·H₂O solution (0.4 mol_{Cu}/l), stirred, and placed in a 90 °C water bath for 2 hours. Then, the samples were filtered, washed and dried overnight at 100 °C. Subsequently, the dried samples were calcined in a muffle furnace at 540 °C for 5 hours, yielding the ion-exchanged Cu-MOR, designated as Cu-MOR IE-1. To further enhance the Cu loading, various cycles of ion exchange (2, 3, 4, and 5) were used to synthesize Cu-MOR catalysts based on the Cu-MOR IE-1 sample. These samples, prepared through multiple ion exchanges, are denoted as Cu-MOR IE-2, Cu-MOR IE-3, Cu-MOR IE-4 and Cu-MOR IE-5. The wetness impregnation method involved dissolving Cu(NO₃)₂·3H₂O in deionized water, adding MOR zeolite to the solution with calculated loading, and stirring intensively. After aging at room temperature for 12 hours, the samples were dried at 120 °C overnight and calcined in a muffle furnace at 540 °C for 5 hours. Finally, the obtained samples are denoted as X wt.% Cu-MOR (X = 2, 5, 10, 15, and 20) based on different Cu loadings.

2.2 Catalytic tests

The experimental setup is shown in SI, section 2, Scheme S2. Calibrated mass flow controllers were used to control the flow rate of CH₄ and O₂ (both 99.999 % purity), which were mixed well before flowing into the DBD reactor. The DBD reactor, featuring two layers of quartz glass, comprised an inner tube with a 10 mm outer diameter filled with 1.25 g catalyst granules (20-40 mesh). The outer tube had a 30 mm outer diameter, and there was circulated water between both tubes, functioning both as a temperature control for the discharge area and as the grounding electrode. A 2 mm stainless steel rod placed inside the inner tube, was used as the high voltage electrode.

The effective length of the discharge area was fixed at 50 mm. Throughout plasma-assisted DOMtM, the discharge frequency was set at 9.2 kHz. The discharge voltage, current and input power were monitored using a digital oscilloscope (DPO 3012, Tektronix, USA). The gas flow rates before and after reaction were measured by a mass flow controller to account for volume compression or expansion due to the chemical reaction, when determining the CH₄ conversion and product yield/selectivity. Gas products were analyzed using a gas chromatograph (GC-7900, Tianmei, China) with a thermal conductivity detector (TDX-01 column) and a flame ionization detector (alumina-filled column). Liquid products were condensed in a cold trap (a mixture of isopropanol and liquid nitrogen) and subsequently analyzed using a gas chromatograph (GC-2014C, Shimadzu, Japan), GC-MS (5975C, Agilent, USA), and ¹H-NMR (AVANCE III 500, Bruker, Switzerland). Further details on the qualitative and quantitative analysis of products in CH₄/O₂ NTP are provided in SI (section 3), including the formulas of the standard calibrated concentration curves (presented in Table S1). Each catalyst underwent three tests to establish experimental error bars.

To evaluate the reaction performance of the catalysts, the selectivity of reaction products and the CH₄ conversion were calculated using the following equations. Carbon-based selectivity is defined here, excluding H₂O and H₂ from these equations.

The CH₄ conversion was calculated by:

$$X_{\text{CH}_4} (\%) = \frac{\text{moles of CH}_4 \text{ converted}}{\text{moles of initial CH}_4} \times 100 \% (1)$$

In the gaseous products, only CO and CO₂ were collected, and no hydrocarbons (C₂ or higher) were detected. The selectivity of the gaseous products was calculated as:

$$S_{\text{CO}} (\%) = \frac{\text{moles of CO produced}}{\text{moles of CH}_4 \text{ converted}} \times 100 \% (2)$$

$$S_{\text{CO}_2} (\%) = \frac{\text{moles of CO}_2 \text{ produced}}{\text{moles of CH}_4 \text{ converted}} \times 100 \% (3)$$

The selectivity of the liquid products was calculated as follows:

$$\text{Total selectivity of liquid products } (\%) = 100 \% - (S_{\text{CO}} + S_{\text{CO}_2}) (4)$$

The selectivity of every single oxygenates, C_xH_yO_z, can be calculated as:

$$S_{\text{C}_x\text{H}_y\text{O}_z} (\%) = \frac{X \times N_{\text{C}_x\text{H}_y\text{O}_z}}{\sum X_i N_i} \times \text{total selectivity of liquid products} (5)$$

Where $N_{\text{C}_x\text{H}_y\text{O}_z}$ represents the number of moles of various oxygenates in the liquid fraction.

Finally, we defined the energy consumption for CH₃OH formation (kJ/mmol) as:

$$\text{Energy consumption} = \frac{\text{discharge power (J/s)}}{\text{rate of CH}_3\text{OH produced (mol/s)}} \times 10^{-6} (6)$$

2.3 Catalyst characterization and plasma diagnostics

The detailed characterization procedures of X-ray diffraction (XRD), N₂ physisorption, X-ray fluorescence (XRF), H₂-temperature-programmed reduction (H₂-TPR), UV-Visible spectrophotometry (UV-Vis), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), *In-situ* optical emission spectroscopy (OES), and the digital oscilloscope measurements are shown in the SI, section 4.

3 Results and discussion

3.1 Catalytic performance

Figures 1a and b illustrate the comparative catalytic performance of Cu-MOR catalysts prepared via ion exchange and wetness impregnation methods in DOMtM. In Figure 1a, the CH₄ conversion and CH₃OH selectivity of Cu-MOR catalysts demonstrate a volcano trend with increasing ion exchange cycles. Cu-MOR IE-3 exhibits the optimal catalytic performance, achieving 7.9% CH₄ conversion, 51% CH₃OH selectivity, and 72% total selectivity for liquid oxygenates. As shown in Figure 1b, the Cu-MOR catalysts prepared through wetness impregnation reveal a gradual increase in CH₄ conversion but a gradual decrease in CH₃OH selectivity with increasing Cu loading, ranging from 2 wt.% to 20 wt.%. The 2 wt.% Cu-MOR catalyst displays 6.4% CH₄ conversion with 48% CH₃OH selectivity, slightly lower than the results of the Cu-MOR IE-3 catalyst. Conversely, the 20 wt.% Cu-MOR catalyst exhibits 77% CO₂ selectivity, 17% total liquid oxygenates selectivity, and only 12% CH₃OH selectivity. These experimental results suggest that the Cu-MOR IE-3 catalyst demonstrates superior performance in plasma-catalytic DOMtM.

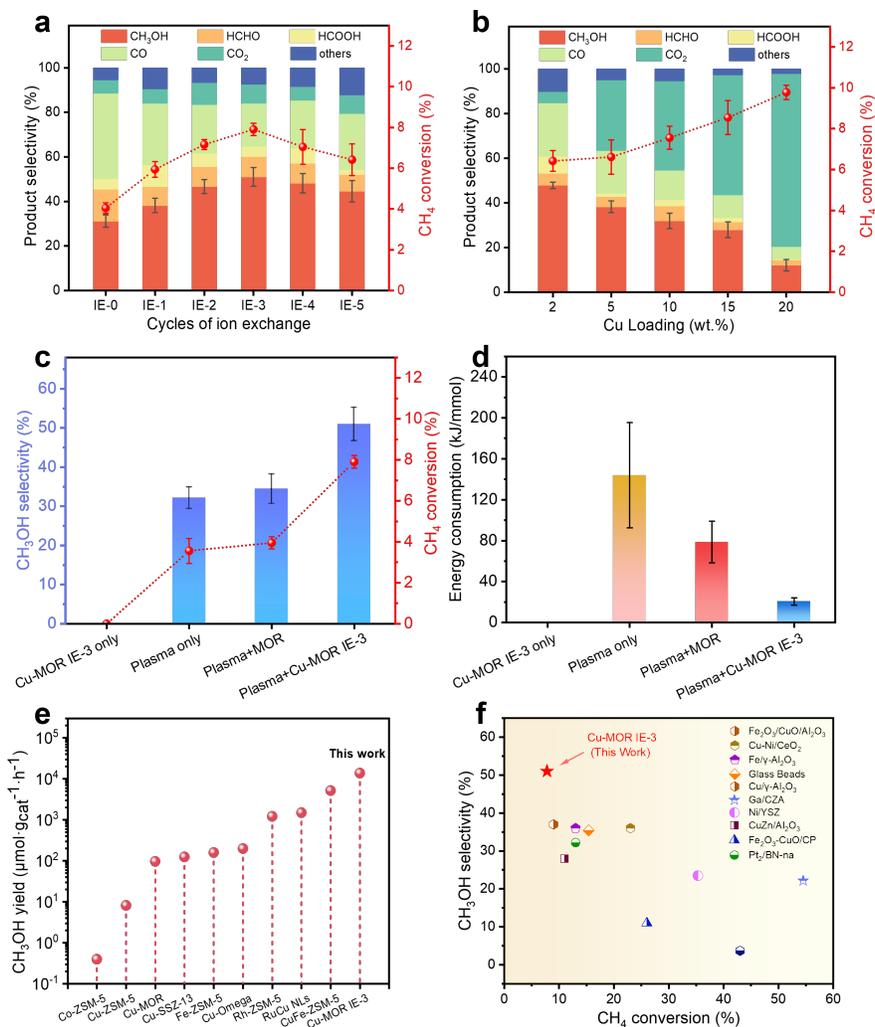


Figure 1. Experimental results of DOMtM. (a) Cu-MOR catalysts prepared by ion exchange, (b) Cu-MOR catalysts prepared by wetness impregnation, (c) Comparison of “only Cu-MOR IE-3 catalyst”, “only plasma”, “plasma + MOR”, and “plasma + Cu-MOR IE-3” for CH₃OH selectivity and CH₄ conversion, and (d) for energy consumption of CH₃OH production, (e) Comparison of this work with literature results for CH₃OH yield (or productivity) by stoichiometric chemical looping using different catalysts, (f) Comparison of this work with literature results of CH₃OH selectivity and CH₄ conversion by CH₄/O₂ plasma using different catalysts. Reaction conditions: 160 ml/min CH₄, 40 ml/min O₂, 20 °C circulating water, 1.25 g catalyst, 25 W input power and 1.178 s residence time.

Figure 1c presents a comparative analysis of the DOMtM reaction outcomes for different modes. In the case of using only a catalyst (Cu-MOR IE-3), the CH₄ conversion is zero, indicating that CH₄ cannot be converted at 20 °C and atmospheric pressure without plasma assistance. For “plasma only” conditions, a CH₄ conversion of 3.6% is achieved with 32% CH₃OH selectivity. Introducing MOR as the packing material for plasma results in a CH₄ conversion and CH₃OH selectivity of 4.0% and 34.5%, respectively, hence similar to the plasma-only results. This suggests that pure MOR zeolite lacks active sites for DOMtM. However, substituting MOR with the Cu-MOR IE-3 catalyst significantly enhances the reaction performance, indicating a synergistic effect between plasma and the copper active sites on Cu-MOR IE-3 catalyst for DOMtM. This enhancement leads to improved CH₄ conversion (7.9%) and CH₃OH selectivity (51%).

Figure 1d depicts the comparison of these modes in terms of energy consumption, which also serves as a crucial indicator for plasma-catalytic DOMtM. The energy consumption for CH₃OH synthesis in the "plasma + Cu-MOR IE-3" system is 20.6 kJ/mmol, which is much lower than that of "plasma only" (143.9 kJ/mmol) and "plasma + MOR" (78.7 kJ/mmol).

Comparison with literature results is presented in Figure 1e and 1f. Figure 1e reveals that the CH₃OH productivity (13877 $\mu\text{mol}\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$) surpasses the best outcomes achieved through stoichiometric chemical looping by an order of magnitude.¹⁵ Additionally, as depicted in Figure 1f, the CH₃OH selectivity exceeds literature results from plasma catalysis using various catalysts, albeit at a lower CH₄ conversion. Notably, a high CH₄ conversion and high CH₃OH selectivity is challenging to achieve simultaneously, as observed by many researchers.¹⁶ Consequently, the CH₃OH yield will always be limited in the DOMtM process.

In summary of the above experimental findings, the catalytic performance of Cu-MOR catalysts prepared via ion exchange generally surpasses that of the catalysts prepared through wetness impregnation. Notably, the Cu-MOR IE-3 catalyst, synthesized via ion exchange, exhibits the highest catalytic performance in plasma-assisted DOMtM. Furthermore, the Cu-MOR catalyst prepared through wetness impregnation, particularly with low loading (2 wt.%), also demonstrates reasonable catalytic performance, although slightly lower than that of Cu-MOR IE-3. It is noteworthy that altering the preparation method (ion exchange vs wetness impregnation), increasing the number of ion exchange cycles, and enhancing the loading of wetness impregnation can lead to the formation of different metal species on zeolites. Consequently, the diverse catalytic performance of the catalysts is closely linked to the variation in copper species present on the Cu-MOR catalysts.

3.2 Characterization of Cu-MOR catalysts

In order to identify the copper species present on the Cu-MOR catalysts, we employed a comprehensive array of techniques for sample characterization, including XRF, XRD, H₂-TPR, UV-Vis, XPS, and HRTEM. The elemental composition of Si, Al, and Cu in the Cu-MOR catalysts was quantified using XRF, and the results are shown in Table S2. The Si/Al ratio of the purchased commercial MOR zeolite is approximately 17, and the Si/Al ratio of the Cu-MOR samples oscillates around this value. The Cu/Al ratio of the Cu-MOR samples increases slowly with increasing number of ion exchanges. Conversely, for the samples prepared via wetness impregnation, the Cu/Al ratio significantly rises with increasing Cu loading. Correlating these findings with the catalytic performance depicted in Figure 1, a volcano-type trend emerges, highlighting an optimal Cu loading range of ca. 2-4 wt%. The effects of Cu loading on the specific surface area and pore volume of MOR zeolite was investigated using N₂-physisorption, and the results are also shown in Table S2. The specific surface area and pore volume of the Cu-MOR samples exhibit a slight decrease with increasing number of ion exchange cycles, primarily attributed to the higher presence of Cu species. Conversely, for the Cu-MOR samples prepared by wetness impregnation, a substantial decrease in specific surface area and pore volume is observed with increasing Cu loading. This drop may be attributed to the presence of CuO particles on the MOR support. The adsorption and desorption curves of MOR and Cu-MOR samples are depicted in Figure S2, illustrating that the MOR support is a typical microporous material with a microporous volume of 0.18 cm³g⁻¹. The grain size and morphology of the MOR support and Cu-MOR IE-3 catalyst were characterized by SEM, as shown in Figure S3. It is evident that the grain size of the MOR zeolite is approximately 250 nm, and both the grain size and morphology of the MOR zeolite remain unchanged after Cu loading.

Figures 2a and 2b present the XRD patterns of the MOR support and Cu-MOR catalysts, synthesized through ion exchange and wetness impregnation methods, respectively. All samples exhibit well-defined diffraction peaks corresponding to MOR zeolite, indicating the preservation of the MOR lattice structure during the preparation process. In Figure 2a, the XRD patterns of Cu-MOR catalysts prepared by ion exchange reveal an absence of characteristic diffraction peaks associated with CuO, Cu₂O, or Cu, suggesting that copper species are highly dispersed on MOR.¹⁷ In contrast, in Figure 2b, the XRD patterns of Cu-MOR catalysts prepared by wetness impregnation display distinct diffraction peaks of CuO (111) and CuO (-111). The intensities of these peaks increase proportionally with higher Cu loadings, indicating the formation of larger CuO particles at elevated Cu loadings.

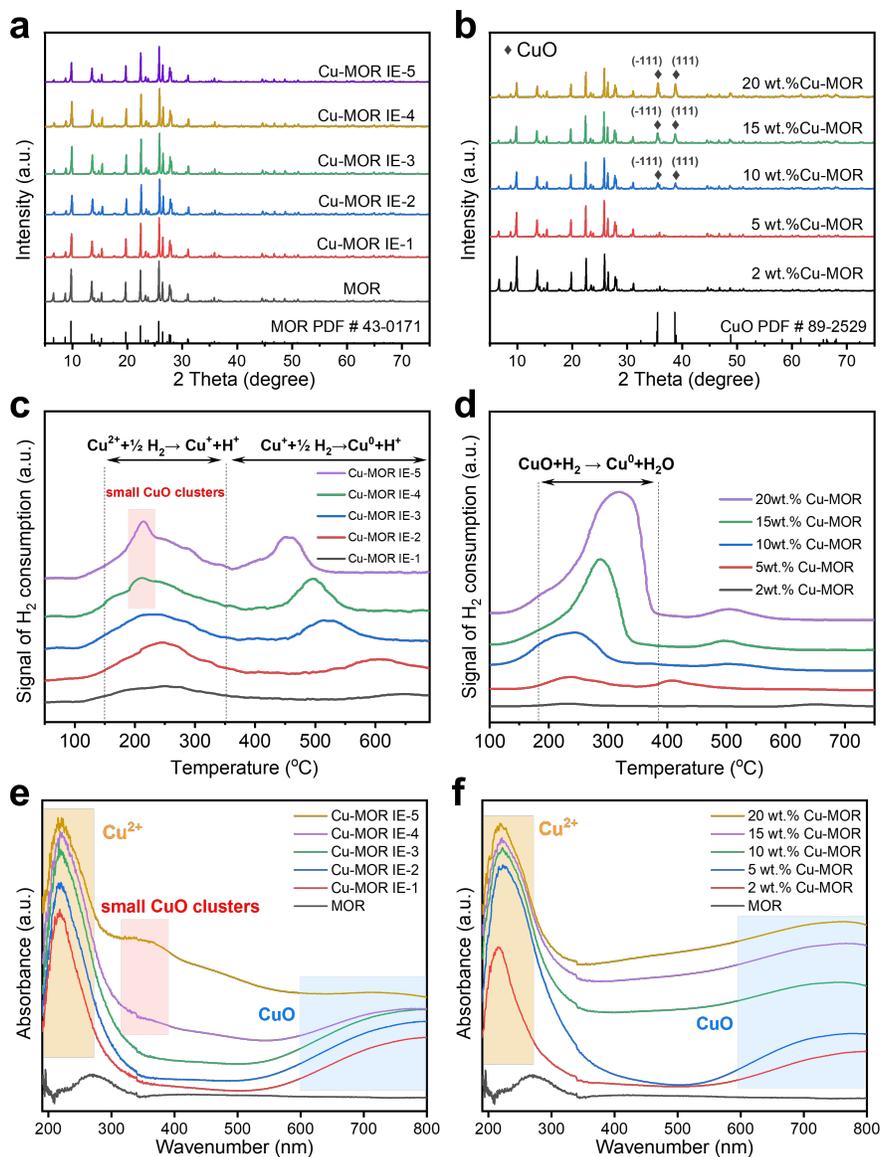


Figure 2. Characterization of Cu-MOR catalysts prepared by ion exchange and wetness impregnation methods. (a, b) XRD patterns; (c, d) H₂-TPR profiles; (e, f) UV-Vis spectra.

In Figure 2d, the Cu-MOR samples prepared by wetness impregnation exhibit a distinct reduction peak in the temperature range of 200-400 °C, indicating a one-step reduction of bulk CuO particles (CuO + H₂ → Cu + H₂O).²⁰ This observation aligns with the predominant presence of copper as CuO particles on the MOR surface, as evidenced by the XRD patterns in Figure 2b. With increasing Cu loading, the intensity of this reduction peak strengthens and shifts toward higher temperatures, suggesting the formation of bigger CuO particles at higher loading. Additionally, a small reduction peak in the high-temperature region, corresponding to the reduction of Cu⁺ to Cu⁰, is observed. This implies that the Cu-MOR samples prepared by wetness impregnation also contain a small amount of zeolite-confined Cu²⁺ species.

The UV-Vis spectra of the Cu-MOR samples prepared by ion exchange and wetness impregnation are presented in Figures 2e and 2f, respectively. The absorption band at 200-300 nm is attributed to the charge transition from the MOR framework coordinated O²⁻ to zeolite-confined Cu²⁺, including mononuclear Cu²⁺,

mono(μ -oxo) di-copper and bis(μ -oxo) di-copper species.²¹ The absorption band within the 300-500 nm range corresponds to the charge transition from coordinated O^{2-} to Cu^{2+} in small CuO clusters, including oligomeric [Cu-O-Cu] species.²² The absorption band within the 600-800 nm range is induced by the d-d transition of Cu^{2+} within an octahedral coordination environment in the bulk CuO particles.²³ As depicted in Figure 2e, with increasing number of ion exchanges, the peak intensities within the 200-300 nm range (corresponding to zeolite-confined Cu^{2+}) and the 600-800 nm range (corresponding to bulk CuO) both gradually increase. Notably, the peak intensities of zeolite-confined Cu^{2+} are significantly higher than those of bulk CuO, indicating a gradual increase in the content of zeolite-confined Cu^{2+} . Furthermore, the absorption band within the 300-500 nm range is clearly observed for the samples of Cu-MOR IE-4 and Cu-MOR IE-5, suggesting that an excessive number of ion exchanges leads to the presence of small CuO clusters, consistent with the H_2 -TPR profiles in Figure 2c.

The UV-Vis spectra of the Cu-MOR samples prepared through wetness impregnation with various loadings are depicted in Figure 2f. In comparison to MOR, the Cu-MOR samples exhibit distinct absorption bands at 200-300 nm and 600-800 nm. Notably, with increasing loading, the intensities of the former peak (200-300 nm) gradually rise (2 and 5 wt.% Cu-MOR) and subsequently stabilize at higher loadings (5, 10, 15 and 20 wt.% Cu-MOR). This observation suggests that the availability of sites on MOR for anchoring zeolite-confined Cu^{2+} species is limited. Conversely, the intensities of the latter peak (600-800 nm) steadily increase with rising loading, indicating the formation of more CuO particles on MOR. This trend aligns with the XRD patterns in Figure 2b and the H_2 -TPR profiles in Figure 2d.

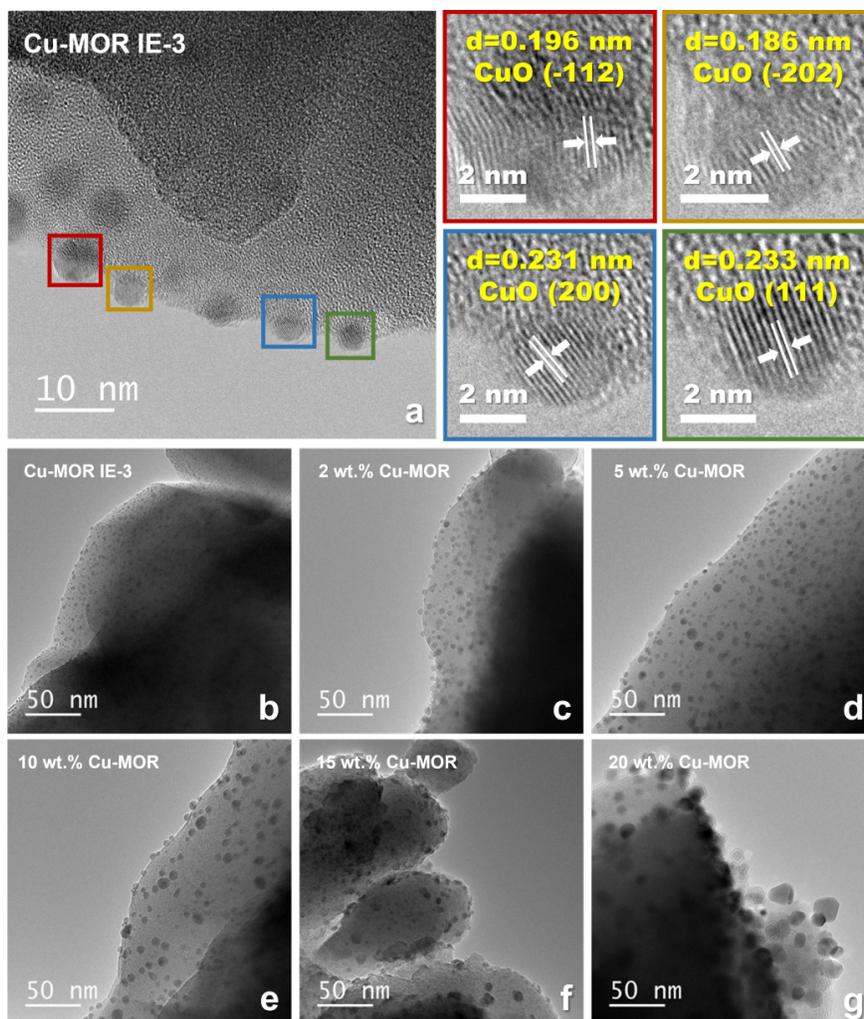


Figure 3. HRTEM images of (a, b) Cu-MOR IE-3 (ion exchange) and (c-g) Cu-MOR prepared through wetness impregnation with various loadings.

Figure 3 presents the HRTEM images of the Cu-MOR IE-3 sample and Cu-MOR samples with various loadings (2, 5, 10, 15 and 20 wt.%). For the Cu-MOR IE-3 sample, the XRD, H_2 -TPR and UV-Vis results demonstrate that most of the copper exists on MOR as zeolite-confined Cu^{2+} species, which may not be readily discerned by HRTEM. Nevertheless, some highly dispersed CuO particles are directly observed. The crystalline spacing of 0.196 nm, 0.186 nm, 0.231 nm, and 0.233 nm corresponds to the (-112), (-202), (200), and (111) crystalline planes of CuO, respectively (Figure 3a). Although the average size of the CuO particles is approximately 3.2 nm (Figure S4), which is not large enough to be detected by XRD, it explains the absence of characteristic diffraction peaks of CuO in Figure 2a.

As depicted in Figures 3(c-g), copper is also highly dispersed on MOR in the Cu-MOR samples prepared through wetness impregnation. However, the size of CuO particles significantly increases with increasing copper loading. The particle size distribution presented in Figure S4 indicates that the average size of the CuO particles on Cu-MOR samples with 2, 5, 10, 15 and 20 wt.% loadings is estimated to be around 4.7, 5.2, 6.8, 8.6, and 13.3 nm, respectively. Hence, it is evident that larger CuO particles are formed on Cu-MOR samples with higher loading, consistent with the findings from XRD, H_2 -TPR, and UV-Vis analyses.

However, small CuO clusters, including [Cu-O-Cu] oligomers, are detected in the Cu-MOR IE-4 and Cu-MOR IE-5 samples. Our catalytic tests highlight that Cu-MOR IE-3 exhibits superior catalytic performance, while Cu-MOR IE-4 and Cu-MOR IE-5 show diminished CH₄ conversion and CH₃OH selectivity (Figure 1a). These findings suggest that zeolite-confined Cu²⁺ species promote CH₄ conversion to CH₃OH, whereas small CuO clusters, including [Cu-O-Cu] oligomers, are less favorable for DOMtM.

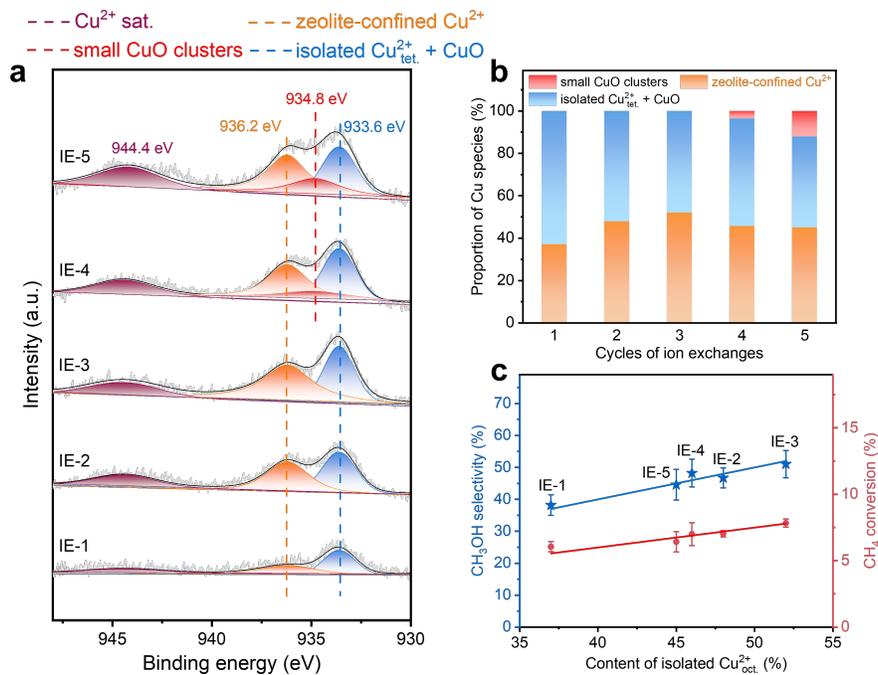


Figure 4. XPS of the Cu-MOR catalysts. (a) Cu 2p_{3/2} spectra; (b) Proportion of highly dispersed Cu²⁺ and CuO species on Cu-MOR surface; (c) Relationship between highly dispersed Cu²⁺ content and reaction performance. The standard charge was calibrated by C 1 s binding energy of 284.8 eV.

The above catalyst characterization results indicate that CuO particles dominate the composition of Cu-MOR catalysts prepared through wetness impregnation. The size of CuO particles gradually increases with higher loading, even though a limited quantity of zeolite-confined Cu²⁺ is also present. Our catalytic tests (Figure 1b) reveal that the CH₄ conversion gradually increases, but the CH₃OH selectivity decreases with rising Cu loading from 2 to 20 wt.%. Additionally, the CO₂ selectivity dramatically increases with higher Cu loading. These outcomes reaffirm that CuO particles facilitate the oxidation of CH₄ to CO₂, while zeolite-confined Cu²⁺ species promote CH₃OH production. In summary, both small CuO clusters (including [Cu-O-Cu] oligomers) and bulk CuO particles are unfavorable for CH₄ conversion to CH₃OH. Therefore, we can conclude that the active sites on Cu-MOR catalysts for the selective oxidation of CH₄ to CH₃OH, driven by CH₄/O₂ plasma, are the zeolite-confined Cu²⁺ species.

To elucidate the active sites of zeolite-confined Cu²⁺ species, XPS analysis was employed to characterize the Cu-MOR catalysts prepared through ion exchange. Figure 4a shows the Cu 2p_{3/2} spectra, in which we observe four peaks, corresponding to a binding energy of 944.4, 936.2, 934.8 and 933.6 eV. The peak at 944.4 eV is attributed to the satellite peak of Cu²⁺ species, confirming the presence of divalent Cu species (CuO and Cu²⁺) on the Cu-MOR catalysts. Generally, the Cu 2p_{3/2} peaks at ca. 933.6 and 936.2 eV correspond to zeolite-confined Cu²⁺ species with tetrahedral and octahedral coordination, respectively.²⁴ The binding energy of CuO nanoparticles is within the range of 933.5–934.5 eV. Therefore, the peak at 933.6 eV could be assigned to both zeolite-confined Cu²⁺ species with tetrahedral coordination and CuO nanoparticles, while the peak at 936.2 eV should be attributed to zeolite-confined Cu²⁺ species with octahedral coordination,

such as mono(μ -oxo) di-copper and bis(μ -oxo) di-copper species. The peak at 934.8 eV is assigned to small CuO clusters, including [Cu-O-Cu] oligomers.²⁵

In Figure 4b, the relative contents of different copper species are presented for the Cu-MOR samples prepared with a different number of ion exchanges. The Cu-MOR IE-3 catalyst exhibits the highest abundance of zeolite-confined Cu^{2+} species with octahedral coordination. Conversely, Cu-MOR IE-4 and IE-5 show the presence of small CuO clusters (including [Cu-O-Cu] oligomers), consistent with the H_2 -TPR results (Figure 2c) and UV-Vis spectra (Figure 2e). Notably, Figure 4c illustrates a linear increase in CH_3OH selectivity and CH_4 conversion with the zeolite-confined Cu^{2+} species having octahedral coordination. Cu-MOR IE-3, with the most abundant zeolite-confined $\text{Cu}^{2+}_{\text{oct}}$ species, exhibits the highest CH_3OH selectivity and CH_4 conversion. Conversely, Cu-MOR IE-4 and IE-5, showing the presence of small CuO clusters with decreased zeolite-confined $\text{Cu}^{2+}_{\text{oct}}$ species, exhibit reduced CH_4 conversion and CH_3OH selectivity. These findings further underscore that zeolite-confined Cu^{2+} species with octahedral coordination, including mono(μ -oxo) di-copper and bis(μ -oxo) di-copper species, serve as the active sites for plasma-catalytic DOMtM.

3.3 Plasma diagnosis

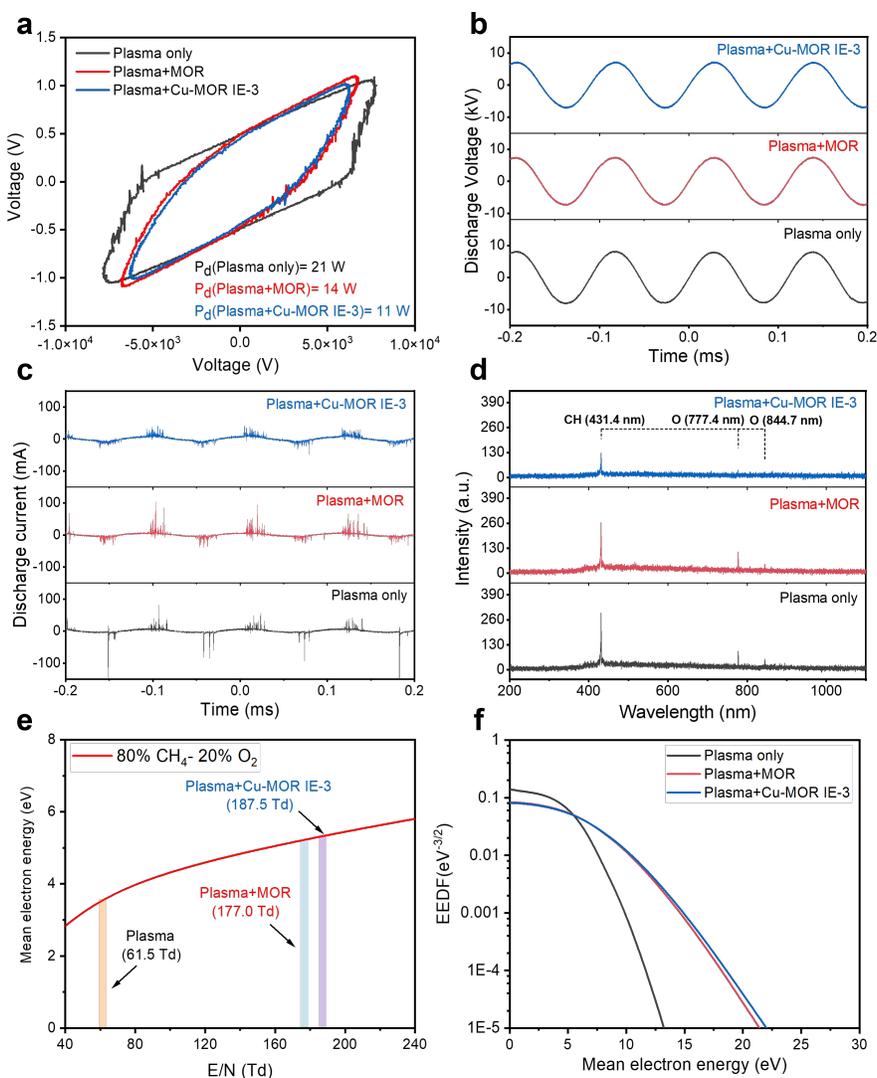


Figure 5. Plasma diagnostics for “plasma only”, “plasma+MOR” and “plasma+Cu-MOR IE-3” at the same conditions as in Figure 1. (a) Lissajous curves; (b) Discharge voltage; (c) Discharge current; (d) *In-situ* OES results; (e) Calculated mean electron energy as a function of reduced electric field (E/N); (f) Electron energy distribution function (EEDF).

The Lissajous curves depicting the CH₄/O₂ plasma are presented in Figure 5a. Notably, variations in equivalent capacitance result in distinct discharge powers when employing different packing materials. The discharge power for “plasma only”, “plasma + MOR”, and “plasma + Cu-MOR” is 21 W, 14 W, and 11 W, respectively. The corresponding discharge voltage and current as a function of time are shown in Figures 5b and 5c. It is evident that the packing material exhibits virtually no influence on the discharge voltage, but it does affect the discharge current. Indeed, the “plasma + Cu-MOR” yields lower current peaks but a higher number of pulses. Filamentary discharges facilitate the generation of reactive species, a localized electric field and surface charge accumulation at the catalyst surface and pores, thereby influencing the reactivity of the potential reactions.^{26,27} The influence of current and voltage amplitudes on the catalytic performance is not significant in this work, indicating that the catalyst rather than the gas-phase is the main reaction area.

Figure 5d shows the optical emission spectra (OES) of the CH₄/O₂ plasmas. OES lines of CH (431.4 nm, A²Δ-X²Π) and O (777.4 nm, 3s⁵S⁰-3p⁵P and 844.7 nm, 3s³S⁰-3p³P) are detected, indicating the presence of a significant amount of CH and O radicals in the CH₄/O₂ plasmas.¹⁰ Notably, the intensities of the above lines attributed to CH and O species vary with different reaction conditions. Compared with the “plasma only”, the OES intensity significantly weakens after packing the CH₄/O₂ plasma with Cu-MOR catalyst. This phenomenon is attributed to the light shielding effect of the catalyst particles or the adsorption of active species by the catalyst sites.^{28,29}

The mean electron energy (MEE) and the electron energy distribution function (EEDF) for the CH₄/O₂ plasma were calculated using Bolsig+, as shown in Figure 5e and f. The MEE in both packing systems is significantly higher than in the “plasma only” system, indicating the enhanced reactivity of the plasma after packing (Figure 5e). This higher reactivity is attributed to the catalyst packing, which increases the E/N values. However, the MEE for MOR support and Cu/MOR catalyst are quite close, primarily determined by their differences in relative dielectric constants. Similar trends are observed in Figure 5f, where high-energy electrons are more likely to be generated in the packing systems. Consequently, the catalyst packing systems are more likely to improve the production of reactive species through electron impact dissociation, excitation, and ionization of the feedstock molecules, as well as their further reactions. The reactive species in the plasma could facilitate catalytic reactions over the MOR surface.³⁰ The computational details for calculating the MEE and EEDF are provided in the Supporting Information (section 5.4).

3.4 *In-situ* detection of surface species

Figure 6 illustrates the surface species of Cu-MOR IE-3 and the 20 wt.% Cu/MOR catalysts, monitored during plasma-catalytic DOMtM using *in-situ* Fourier Transform Infrared (FTIR) spectroscopy. (*In-situ* DRIFTS reaction cell shown in Figure S5) Following plasma activation, the peaks corresponding to surface CH₃O* species are readily observed at 1054, 2910, and 2940 cm⁻¹, serving as key intermediates in the process of CH₃OH formation.³¹ It is noteworthy that CH₃O* is formed through combination of CH₃* (arising from CH₄ dissociation) and O (via O₂ dissociation), consistent with the OES results in Figure 5d. In addition, the peaks of DOMtM by-products are observed between 2400-1700 cm⁻¹, including CO₂ (2347 cm⁻¹), CO (2170 and 2115 cm⁻¹), aldehyde, and carboxylic acid products (1780 and 1750 cm⁻¹).^{32,33} In Figure 6a, Cu/MOR IE-3 exhibits significantly higher FTIR intensity for adsorbed CH₃O* and for CH₃OH (1015 and 1030 cm⁻¹) compared to the 20 wt.% Cu/MOR catalyst (Figure 6b).³⁴ This emphasizes the crucial involvement of exchanged Cu²⁺ in plasma-catalytic DOMtM. Conversely, the 20 wt.% Cu/MOR catalyst obtained through wetness impregnation shows higher FTIR intensity of by-products (CO₂, CO, -C=O, and -COOH). Notably, in the case of 20 wt.% Cu/MOR, a new absorption band of HCOO* at 1585 cm⁻¹ indicates the over-oxidation of CH₄ to CO₂.²⁸ Based on the above characterizations and *in-situ* FTIR results, we can again conclude that zeolite-confined Cu²⁺ species with octahedral coordination, including mono(μ-oxo) di-copper and bis(μ-oxo) di-copper species, are the active sites for plasma-catalytic DOMtM over Cu/MOR catalysts.

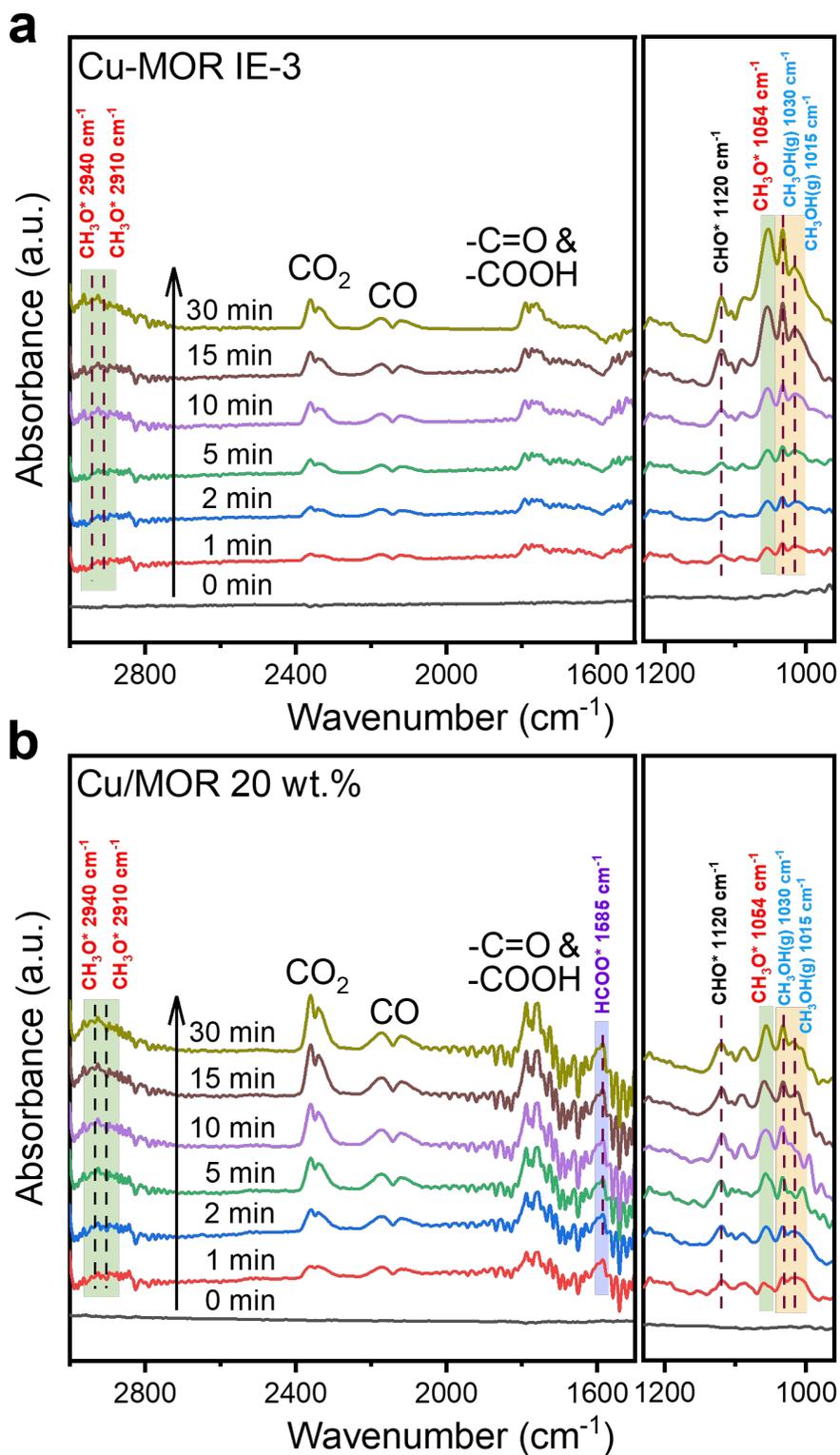


Figure 6 . *In-situ* FTIR spectra of surface species on the (a) Cu-MOR IE-3 and (b) 20 wt.% Cu/MOR during plasma-catalytic DOMtM. 20 °C circulating water, discharge power 24 W, $\text{CH}_4/\text{O}_2 = 4/1$, flow rate

= 200 mL/min.

4 Conclusion

We investigated the catalytic performance of Cu-MOR catalysts, prepared by ion-exchange and wetness impregnation, for plasma-catalytic DOMtM in CH₄/O₂ plasma. The Cu-MOR IE-3 catalyst, synthesized through ion-exchange, demonstrates the most favorable catalytic outcomes, with 7.9% CH₄ conversion and 51% CH₃OH selectivity. Conversely, the Cu-MOR catalysts prepared by wetness impregnation exhibit tendencies towards over-oxidation of CH₄ to CO and CO₂, particularly for the catalysts with higher loadings. The combination of our catalyst characterizations reveals that ion exchange predominantly leads to the formation of zeolite-confined Cu²⁺ species within Cu-MOR, whereas wetness impregnation primarily yields CuO particles. Specifically, zeolite-confined Cu²⁺ species function as the active sites for plasma-catalytic DOMtM, while the presence of CuO clusters and particles proves detrimental to DOMtM. Instead facilitating over-oxidation reactions leading to CO and CO₂ production. Finally, the surface species on the catalyst, detected by *in-situ* FTIR, further corroborate the pivotal role of zeolite-confined Cu²⁺ species in plasma-catalytic DOMtM.

ASSOCIATED CONTENT

Supporting Information . The supporting information is available free of charge via the Internet at XX.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Data availability and reproducibility statement

The data that support the findings of this study are available from the corresponding supplementary material files. The numerical data from Figures 2a-f, 4a-c, 5a-f, 6a-b, S1a-d and S2a-b are available as a .zip file in the Supplementary Material. And the numerical data from Figures 1a-d are tabulated in the Supporting Information. Error bars (where shown) in Figures 1a-d show the spread of data observed in at least triplicate measurements, where independent samples were tested for each measurement. Experimental data shown without error bars are from individual experimental measurements.

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