Plasma-enhanced direct conversion of CO₂ to CO over oxygen-deficient Mo-doped CeO₂

Plasma-catalytic direct splitting of CO₂ to CO over oxygen-deficient Mo-doped CeO₂ at ambient conditions was achieved. Developing new catalytic technologies involving plasma opens the door to unlocking the potential of using captured CO₂ to make valuable chemicals under mild conditions.

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Plasma-enhanced direct conversion of CO2 to CO over oxygen-deficient Mo-doped CeO2†

Li Wang,†a Xiaomin Du,a Yanhui Yi,†b Hongyang Wang,a Masaud Gul,a Yimin Zhua and Xin Tua†c

Plasma CO2 splitting to CO over oxygen-deficient Mo-doped CeO2 under mild conditions was investigated for the first time, showing ~20 times higher CO2 conversion compared to pure CeO2, which can be attributed to the increased oxygen vacancies (V0) and the formation of Ce3+–V0–Mo on the catalyst surface. Importantly, V0 sites showed excellent catalytic stability.

Converting CO2 to value-added fuels and chemicals has been considered as a promising route in CO2 utilization. Significant efforts have been devoted to the chemical transformation of CO2, including thermal catalysis,1 photocatalysis,2,3 electrocatalysis,4,5 and plasma catalysis.6,7 Direct splitting of CO2 to CO without using any reductant is attractive for CO2 conversion, as CO is an important chemical feedstock for the synthesis of a range of chemicals and fuels. However, this reaction has to overcome a strong thermodynamic barrier (CO2 + 1/2O2 → CO + 1/2O2, ΔH298K = 280 kJ mol−1 = 2.9 eV molecule−1) to break the C=O bond, since CO2 is very stable. Ultrahigh temperatures (2000 K) are often required to activate CO2 (Fig. S1, ESI†).

In recent years, using non-thermal plasmas (NTPs) for the activation of inert molecules with strong chemical bonds (e.g., CO2, CH4 and N2) under mild conditions has attracted significant interest, including CO2 reforming with CH4 to oxygenates,6,9 CO2 hydrogenation to methanol,10 and ammonia synthesis.11 NTP is rich in energetic electrons with a typical energy of 1–10 eV, which is sufficient to activate reactants into chemically reactive species, enabling thermodynamically unfavorable reactions (e.g. CO2 splitting) to proceed at ambient conditions.

Up until now, studies on plasma CO2 splitting to CO mainly focused on the optimization of operating parameters,12–16 and only a few catalysts (e.g., Ni/SiO2, NiO/TiO2 and Rh/TiO2) have been evaluated (Table S1, ESI†).17–20 Recently, surface oxygen vacancies (V0) have been suggested to be the active sites in plasma-catalytic CO2 splitting to CO. Mei et al. reported that higher CO2 conversion was achieved when coupling plasma with BaTiO3, which can be explained by the formation of more V0 sites on the surfaces of BaTiO3 compared to TiO2.20 Chen et al. found the V0 on Ni/TiO2 contributed to the enhanced CO2 dissociation.18 In fact, the coupling of catalysts and plasma is a promising strategy to improve CO2 conversion and energy efficiency. However, the knowledge in selection of appropriate catalysts for highly efficient CO2 splitting to CO using NTP was still very limited until now.

Herein, CO2 splitting to CO over M-doped CeO2 catalysts (M = Fe, Co, Ni, Cu, Cr, V, Mn or Mo) has been carried out in a dielectric barrier discharge (DBD) reactor (Fig. S2–S5, ESI†). CeO2 not only serves as a support to anchor and disperse the metal oxide particles but also generates V0 active sites through the interaction with metal oxides. Significant differences were observed among the M-doped CeO2 catalysts in terms of CO2 conversion, and the Mo-doped CeO2 exhibited the best activity in CO2 conversion (Fig. S3, ESI†). Therefore, Mo-doped CeO2 has been selected for further studies.

Comprehensive catalyst characterization was carried out to understand the physicochemical properties of Mo-doped CeO2. As shown in Fig. 1, the X-ray diffraction (XRD) pattern of CeO2 exhibits characteristic peaks of a cubic fluorite phase (JCPDS, 34-0394). For Mo-doped CeO2, small peaks of z-MoO3 (JCPDS, 05-0508) and Mo3O12 (JCPDS, 05-0337) are observed, revealing the coexistence of Mo(IV) and Mo(V) species. Notably, the characteristic peaks of CeO2 downshift compared to pure CeO2, which suggests that Mo doping leads to the expansion of the CeO2 unit cell. Usually, inserting Mo ions into CeO2 induces shrinkage of the CeO2 unit cell since the radius of Mo ions is much smaller than that of Ce ions, resulting in upshifting of CeO2 peaks, rather than downshifting. Thus, Mo ions do not insert into the CeO2 unit cell, and there might be other reasons responsible for this downshift. X-ray photoelectron spectroscopy
(XPS) was employed to analyze surface properties of Mo-doped CeO₂. The deconvoluted Ce 3d XPS spectra are presented in Fig. 2(a). The peaks labeled as \( v, v', v'' \) and \( u, u', u'' \) are assigned to \( 3d_{5/2} \) and \( 3d_{3/2} \) electrons of Ce⁴⁺, respectively, while the peaks of \( v', u' \) and \( v'' \) correspond to \( 3d_{5/2} \) and \( 3d_{3/2} \) electrons of Ce³⁺, respectively.²¹ Clearly, Ce³⁺ exists in CeO₂ and Mo-doped CeO₂, suggesting the formation of VO in both samples. More importantly, the proportion of Ce³⁺ in Mo-doped CeO₂ is 40.2%, higher than that in CeO₂ (30.0%) (Fig. S6 and S7, ESI†). This finding suggests that Mo doping induces partial transformation of Ce⁴⁺ to Ce³⁺ and creates more VO on Mo-doped CeO₂. As reconfirmed by the O 1s XPS spectra in Fig. 2(b) and Fig. S6 (ESI†), a higher surface VO (30.4%) is achieved in the Mo-doped CeO₂ in comparison to pure CeO₂ (21.0%). Furthermore, the transformation of Ce⁴⁺ to Ce³⁺ leads to the expansion of the CeO₂ unit cell since the ion radius of Ce³⁺ (1.23 Å) is higher than that of Ce⁴⁺ (0.97 Å),²² which explains the reason for the downshifting of CeO₂ peaks in Fig. 1. More interestingly, the binding energies of Ce 3d shift significantly towards higher values after Mo doping, revealing that the electron density of the surface CeO₂ species is lower in Mo-doped CeO₂ compared with pure CeO₂, which might be induced by the electron transfer from Ce to Mo, due to the higher electronegativity of Mo. These results suggest different properties of VO sites in the form of Ce⁴⁺–VO in CeO₂ and Ce³⁺–VO–Mo in Mo-doped CeO₂, as well as the strong interaction between Mo and CeO₂, which agrees with the results of H₂-temperature programmed reduction (H₂-TPR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. S8–S11, ESI†). Fig. 2(c) shows the deconvoluted Mo 3d spectra, in which the Mo-doped CeO₂ sample exhibits typical doublet peaks of Mo⁶⁺ with an energy gap of ca. 3.1 eV, indicating the formation of MoO₃ in Mo-doped CeO₂.²³ The two smaller peaks observed, however, are identified to be \( 3d_{3/2} \) and \( 3d_{5/2} \) electrons of Mo(V), demonstrating the formation of the non-stoichiometric MoO₃/C₁ₓ,²³ which is consistent with the Mo₄O₁₁ species confirmed by the XRD analysis (Fig. 1). Fig. 2(d) shows the Raman spectra of CeO₂ and Mo-doped CeO₂. For pure CeO₂, the intense band at 465 cm⁻¹ is well-indexed to the typical F₂g modes of a cubic CeO₂ fluorite structure, and the weak bands at 262, 597 and 1171 cm⁻¹ are assigned to VO, reconfirming the XPS results in Fig. 2(a and b).²³ For Mo-doped CeO₂, the emerging Raman bands at 673, 824 and 997 cm⁻¹ are assigned to MoO₃ crystallites.²⁴ However, the band at 955 cm⁻¹ is associated with Mo suboxides (MoO₃/C₁ₓ).²⁴,²⁵ These results indicate that the valence state of Mo in suboxides is Mo⁵⁺. Moreover, the presence of Mo⁵⁺ and Ce³⁺ indicates that more VO sites are created through the strong interaction between Mo and CeO₂, as well as the calcining atmosphere with deficient oxygen and rich energetic Ar species, which agrees with the results reported by Chen et al.¹⁸

Fig. 3 shows the effect of different operating conditions on CO₂ conversion. Clearly, no reaction occurred without plasma (catalyst only, 400 °C). The conversion of CO₂ was 3.8% in the plasma reaction without a catalyst (plasma only). In the plasma reaction coupled with pure CeO₂, the CO₂ conversion dropped to 1.2%, which suggests that pure CeO₂ is unfavorable for CO₂ splitting to CO despite CeO₂ being O-deficient. Using Mo-doped
CeO₂ instead of CeO₂₂, however, results in a significant increase of CO₂ conversion by a factor of 9 at 400 °C. In addition, the Mo-doped CeO₂ showed stable CO₂ conversion for at least 10 h (Fig. S12, ESI†). Interestingly, the reaction performance can be further improved by using a lower reaction temperature (30 °C) and an additive gas (Ar or N₂). This promotional effect was more pronounced when adding N₂. The highest CO₂ conversion of 23.2% and energy efficiency of 14.3% were achieved in the plasma splitting of CO₂ with N₂ addition over Mo-doped CeO₂ at 30 °C (Table S1, ESI†), while the corresponding formation rate of CO and O₂ was 24.9 mmol h⁻¹ and 12.4 mmol h⁻¹, respectively (Table S2, ESI†). The optimal energy efficiency achieved in this study is comparable to that reported in previous works (Table S1, ESI†).

Regarding surface reactions, the improved activity over Mo-doped CeO₂, on one hand, is mainly attributed to the increased formation of V₀ (Fig. 2 and Fig. S6, ESI†), since V₀ serve as adsorption centers for CO₂ dissociative adsorption.¹⁷,²⁶ i.e., CO₂ + V₀ → Oₓ/C + CO. On the other hand, the promoted performance originates from the different properties of V₀ in the forms of Ce⁢³⁺–VO and Ce³⁺–VO–Mo due to strong interaction between Mo and CeO₂ and the higher electronegativity of Mo characterized by XPS, Raman, XRD and H₂-TPR (Fig. 4). Interactions between reactive species in the gas phase

![Fig. 4](image-url) (a) XPS spectra, (b) Raman spectra, (c) XRD patterns, (d) H₂-TPR profiles of Mo-doped CeO₂ before and after reaction.

and the Raman band at ~950 cm⁻¹ in Fig. 4(a and b), respectively. The enhancement effect is more pronounced for the catalyst used at 400 °C. Correspondingly, more V₀ sites were created in the high-temperature reaction (Table S3, ESI†). In addition, the color of the catalyst changed from gray/blue (MoO₃–y) to yellow (MoO₃–x) with x > y after the reaction at 30 °C, while no visible changes were observed on the phase structure of Mo-doped CeO₂ before and after the reaction (30 °C), as shown in Fig. 4(c). These results indicate that some O atoms from CO₂ splitting are adsorbed onto the catalyst, as seen by the slightly increased H₂ consumption in Fig. 4(d). Even so, the V₀ concentration of Mo-doped CeO₂ used at 30 °C remained at a similar level with that of the fresh sample (Table S3, ESI†). These findings suggest that V₀-rich Mo-doped CeO₂ is stable after the plasma reaction, and high-temperature reactions facilitate the formation and recovery of V₀ sites, resulting from accelerating recombinative desorption of adsorbed O atoms.²⁷

In addition to surface reactions, gas-phase reactions also play a crucial role in the plasma-catalytic process. In a pure CO₂ DBD, CO₂ splitting to CO mainly proceeds through the electron impact dissociation of CO₂ (CO₂ + e → CO + O + e), which can be confirmed by plasma chemical kinetic modeling,²⁸ as well as the formation of CO bands and O atomic lines detected by optical emission spectra of CO₂ DBD (Fig. 5(a)). As shown in Fig. 5(a), the presence of strong N₂ (C₃Π→B¹Π, B¹Π→A³Σ⁺) molecular bands and Ar atomic lines suggests the formation of excited nitrogen species (N₂⁎) and metastable Ar species (Ar⁎).²⁹,³⁰ These species create an additional reaction route for CO₂ dissociation (N₂⁎ (or Ar⁎) + CO₂ → CO + O + N₂ (or Ar)), supported by the increased intensity of O atomic lines and CO bands when adding N₂ or Ar, which contributes to the enhanced CO₂ conversion. Furthermore, 150 ppm NOₓ was detected by Fourier transform infrared (FTIR) in the case of N₂ addition (Fig. S13, ESI†), revealing that N₂ can be regarded as an alternative scavenger of O species.¹² The elimination of partial O species can effectively limit the reverse reaction, i.e., O + CO + M → CO₂ + M, and thus enhance the CO₂ conversion. This could explain why adding N₂ has a stronger promotion on the CO₂ conversion compared with Ar.

Interaction between reactive species in the gas phase and catalyst is also crucial in plasma-catalytic reactions.³¹ Compared to plasma only, packing Mo-doped CeO₂ into the
discharge zone decreased the current (Fig. S14, ES†), lowering the contribution of the gas-phase reactions. In this case, the CO₂ conversion, however, was still improved, which might be attributed to the interaction between active species and VO-rich Mo-doped CeO₂, accelerating VO₂ recovery. Therefore, a possible reaction mechanism is proposed in Fig. 5(b). Firstly, CO₂ is activated to species of CO₂⁺, CO₂(v) and O radicals as shown in Fig. 5(a) (step 1). Then, the energetic CO₂-species are adsorbed on the VO sites to decrease their internal energy (step 2). After that, the VO sites have the potential to grasp the O atom of the adsorbed CO₂ molecule, which weakens the C═O bond, producing adsorbed CO and O (step 3). Subsequently, the adsorbed CO desorbs as the final CO product. While the adsorbed O mainly desorbs from VO sites in the form of O₂ through reacting with the active O radicals produced in the gas phase (O_g + O_ads + VO → O_2(g) + VO), i.e., Eley–Rideal (E–R) mechanism. Meanwhile, VO sites recover completing the catalytic cycle (step 4). Using isotope trace analysis, we demonstrated the desorption of N₂ through an E–R reaction in plasma-catalytic NH₃ decomposition. Therefore, the desorption of O₂ through E–R reaction is also expected. Note that, too strong of a CO₂–VO bond makes it easy to split the CO₂ molecule, but the corresponding desorption of adsorbed O is difficult. By contrast, too weak of a CO₂–VO bond means it could be hard to split CO₂, although the adsorbed O can easily desorb from the catalyst surface. Therefore, a catalyst with a proper binding strength between VO sites and CO₂ benefits the conversion of CO₂ and favors the catalytic cycle.

In conclusion, plasma-catalytic CO₂ splitting over M-doped CeO₂ catalysts (M = Fe, Co, Ni, Cu, Cr, V, Mn or Mo) has been investigated. Mo-doped CeO₂ exhibited the best activity; this is attributed to the increased oxygen vacancies created by strong interaction between Mo and CeO₂, as well as the calcining atmosphere being oxygen-deficient and rich in Ar metastable species. Furthermore, oxygen vacancies were stable during the reaction, which is ascribed to the interaction between active O produced in the gas phase and the adsorbed O on the oxygen vacancy site, resulting in desorbing as O₂ molecules and recovering oxygen vacancy sites. These findings suggest that introducing proper doping on CeO₂ offers a potential route to tune properties of oxygen vacancy in CeO₂. Additionally, adding N₂ and Ar into the plasma process enhanced the CO₂ conversion, especially when adding N₂. This promotional effect is mainly attributed to the new reaction routes induced by the presence of metastable species. We found that N₂ can be used as an O scavenger to forward the chemical equilibrium and inhibit the reverse reaction to form CO₂.

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Conflicts of interest
There are no conflicts to declare.

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