CO$_2$ Hydrogenation at Atmospheric Pressure and Low Temperature Using Plasma-Enhanced Catalysis over Supported Cobalt Oxide Catalysts

Ronda-Lloret, M.; Wang, Y.; Oulego, P.; Rothenberg, G.; Tu, X.; Shiju, N.R.

DOI
10.1021/acssuschemeng.0c05565

Publication date
2020

Document Version
Final published version

Published in
ACS Sustainable Chemistry and Engineering

License
CC BY-NC-ND

Citation for published version (APA):
CO₂ Hydrogenation at Atmospheric Pressure and Low Temperature Using Plasma-Enhanced Catalysis over Supported Cobalt Oxide Catalysts

Maria Ronda-Lloret,† Yaolin Wang,† Paula Oulego, Gadi Rothenberg, Xin Tu,* and N. Raveendran Shiju*

ABSTRACT: CO₂ is a promising renewable, cheap, and abundant C1 feedstock for producing valuable chemicals, such as CO and methanol. In conventional reactors, because of thermodynamic constraints, converting CO₂ to methanol requires high temperature and pressure, typically 250 °C and 20 bar. Nonthermal plasma is a better option, as it can convert CO₂ at near-ambient temperature and pressure. Adding a catalyst to such plasma setups can enhance conversion and selectivity. However, we know little about the effects of catalysts in such systems. Here, we study CO₂ hydrogenation in a dielectric barrier discharge plasma-catalysis setup under ambient conditions using MgO, γ-Al₂O₃, and a series of Co₃O₄/MgO catalysts. While all three catalyst types enhanced CO₂ conversion, Co₃O₄/MgO gave the best results, converting up to 35% of CO₂ and reaching the highest methanol yield (10%). Control experiments showed that the basic MgO support is more active than the acidic γ-Al₂O₃ and that MgO-supported cobalt oxide catalysts improve the selectivity toward methanol. The methanol yield can be tuned by changing the metal loading. Overall, our study shows the utility of plasma catalysis for CO₂ conversion under mild conditions, with the potential to reduce the energy footprint of CO₂-recycling processes.

KEYWORDS: green chemistry, plasma catalysis, methanol synthesis, cobalt oxide, CO₂ conversion

INTRODUCTION

The increasing amount of CO₂ in the atmosphere is a global problem.1−3 Yet CO₂ is also an important chemical resource that should not be thrown away. Ideally, we should use it as a raw material to make valuable products. This can be done via carbon capture, either from the atmosphere or from industrial flue-gases, followed by a chemical reaction.4−6 Typically, this would involve a catalytic process.

Hydrogenation is a versatile option for CO₂ valorization, provided that renewable hydrogen is used.7−11 One can alter the reaction parameters (CO₂/H₂ ratio, temperature, and pressure) and the catalyst composition to control the product distribution.12 CO₂ can be hydrogenated to carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), ethanol (C₂H₅OH), and lower olefins (C₃−C₅). Of these, methanol is especially interesting, as it is a precursor for formaldehyde, dimethyl ether, gasoline, and olefins.13,14 Methanol is also an efficient energy carrier.15−17 CO₂ hydrogenation to methanol (eq 1) is exothermic and, therefore, favored at low temperatures. This reaction is also favored at high pressures because fewer molecules are produced. However, the high thermodynamic stability of CO₂ (ΔG° = −394.4 kJ mol⁻¹) requires high temperatures for high conversion. The reverse-water gas shift reaction (RWGS, eq 2) is favored at < 200 °C because of its endothermic character. The side product, CO, is itself a useful building block for making a variety of chemicals.12,18 Therefore, CO₂ hydrogenation to methanol is typically performed at 250 °C and 20 bar.14,19

$$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_{\text{298 \degree C}} = -49.5 \text{ kJ mol}^{-1}$$

(1)

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{\text{298 \degree C}} = 41.2 \text{ kJ mol}^{-1}$$

(2)

Yet there is an alternative to thermal catalysis: plasma-enhanced catalysis can be used for converting CO₂ to useful chemicals at near-ambient temperatures and pressures.20−29 In nonthermal plasmas, high-energy electrons (with an average electron temperature of 1−10 eV) collide with stable molecules and activate them, while the bulk gas temperature remains low.30,31 Catalysts can be introduced into these systems to increase the conversion and control the...
selectivity.\textsuperscript{19,32} The most common option in plasma catalysis is the dielectric barrier discharge (DBD), among the different types of plasma discharges. This is because DBD reactors usually run at low temperatures and atmospheric pressure, reducing operating costs and complexity, and allow facile combination with catalysts.\textsuperscript{30,33,34}

Despite the growing research activity in plasma-enhanced catalysis, we still do not fully understand the relationship between the catalyst properties and overall reaction performance.\textsuperscript{35–38} This is because of the variety of the reactions and plasma configurations, which lead to different plasma species and different plasma–catalyst interactions.\textsuperscript{19–42} Here, we study the effect of basic catalysts (MgO and Co$_3$O$_4$/MgO catalysts) on conversion and product selectivity during CO$_2$ hydrogenation. We ran the reaction in a water-cooled DBD plasma-catalysis setup, at 35 °C and ambient pressure. Furthermore, we tested γ-Al$_2$O$_3$ to check if the enhanced adsorption of acidic CO$_2$ on basic supports is also valid under plasma conditions.\textsuperscript{43} We observed that basic materials enhance CO$_2$ conversion, and that the production of methanol is related to the metal loading and the dispersion of metal–support interface sites in Co$_3$O$_4$/MgO catalysts.

**Experimental Section**

**Materials and Instrumentation.** Powder X-ray diffraction (XRD) analyses were carried out on a MiniFlex II diffractometer using Cu Kα radiation (X-ray tube set at 30 kV and 15 mA). The XRD patterns were recorded between 2θ = 20–80° at a speed of 2.5°-min$^{-1}$. A Thermo Scientific Surfer instrument was used to carry out N$_2$ adsorption–desorption analyses at 77 K. The samples were pretreated under vacuum at 200 °C for 6 h. Surface areas were determined with the Brunauer–Emmett–Teller (BET) method, and the mesoporosity was analyzed using the Barrett, Joyner, and Halenda (BJH) method. Hydrogen temperature-programmed reduction (H$_2$-TPR) profiles were obtained using a TPDRO Series 1100 from Thermo Scientific, following the procedure previously reported by Ronda-Llorét et al.\textsuperscript{6} High-resolution transmission electron microscopy (HRTEM) micrographs and transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM–EDS) images were obtained on a JEOL-JEM 2100F microscope running at 200 kV. X-ray photoelectron spectroscopy (XPS) analyses were performed with a SPECS PHOIBOS 100 MCDS hemispherical electron analyzer operating in a constant pass energy. The analysis details were described previously in Matthaiou et al.\textsuperscript{35}

**Procedure for Catalyst Synthesis.** Using Co(NO$_3$)$_2$·6H$_2$O (99%, Acros Organics) as the metal oxide precursor and MgO (Sigma-Aldrich) as the support, we prepared samples containing different percentages of cobalt (5, 10, 15, and 20 wt % on Co metal-basis) by wet impregnation.\textsuperscript{5} After impregnation, the materials were dried at 120 °C for 2 h and then calcined in a muffle furnace at 450 °C for 4 h. Bulk Co$_3$O$_4$ was prepared by mixing Na$_2$CO$_3$, polyethylene glycol, and Co(NO$_3$)$_2$·6H$_2$O in water, as reported earlier.\textsuperscript{5} After stirring for 3 h at room temperature, the precipitate was centrifuged and washed several times with water and ethanol. After drying at 65 °C for 6 h in a vacuum oven, the sample was calcined in air at 300 °C for 3 h.

**Plasma Setup and Plasma-Catalytic Tests.** The plasma-catalytic tests were performed in a coaxial DBD reactor with a 50 mm discharge length and a 1 mm discharge gap (Scheme 1). Circulating water was used as the ground electrode and cooling system (Grant LT Ecocool 150) to keep the reaction temperature at 35 °C. An AC high-voltage power supply (with a peak-to-peak voltage of up to 30 kV) was used to ignite the plasma with a fixed frequency of 9.2 kHz. CO$_2$ and H$_2$ (H$_2$/CO$_2$ = 3:1) were used as reactants with a total flow rate of 28 mL·min$^{-1}$. The catalysts (500 mg) were fully packed in the discharge area, the plasma reaction was run for 1.5 h and the products were then analyzed.

![Scheme 1. Diagram of the Plasma-Catalysis DBD Reactor, Showing the Analysis, Feed, and Cooling Units; Adapted from ACS Catal.\textsuperscript{26,46}](https://doi.org/10.1021/acssuschemeng.0c00565)
The characteristic peaks of Co₃O₄ and CoO are not visible, as they overlap with those of MgO. HRTEM and STEM images of 15% Co₃O₄/MgO show that cobalt oxide nanoparticles are highly dispersed over the support (Figures 1 and 2). The average size of cobalt oxide nanoparticles was 27.7 ± 11.5 nm. Moreover, HRTEM shows lattice fringes with interplanar distances of 0.24 and 0.28–0.29 nm (Figure 1b,c), assigned to the (311) and (220) planes of cobalt oxide nanoparticles, respectively. The selected-area electron diffraction (SAED) pattern shows diffraction rings characteristic of a polycrystalline material, corresponding to the MgO [(220), (200), and (311)] and cobalt oxide nanoparticles (311) planes.

We then used XPS to study the surface composition of the catalysts. The Co 2p spectra of the Co₃O₄/MgO catalysts show the doublet of two spin–orbit components, Co 2p₁/₂ and Co 2p₃/₂ (Figure 3). The relative atomic percentage of Co₃O₄ species is higher than that of CoO species for all fresh catalysts, indicating that the surface of the catalysts mainly contains Co₃O₄ (Table S1). This reveals that Co₃O₄–CoO/MgO interface sites are available on the catalyst surface as active centers for CO₂ hydrogenation. The O 1s, C 1s, and Mg 2s spectra of the 15% Co₃O₄/MgO catalyst, as well as details of the binding energies are included in the Supporting Information (Figure S2 and Tables S2–S5).

The H₂-TPR profiles of the as-prepared materials (Figure S3, bottom profiles) show two regions. The low-temperature region (150–450 °C) is assigned to the reduction of “free” Co₃O₄ (supported cobalt oxide, i.e., interacting weakly with the support, thus not forming a stable compound). This reduction peak contains two or more contributions, corresponding to the Co₃O₄ step wise reduction sequence where Co₃O₄ is reduced to CoO, and CoO is reduced to metallic cobalt at higher temperatures. The reduction of Co₃O₄ species with different interaction with the support can also lead to different contributions in the reduction peak. They are less defined in the 20% Co₃O₄/MgO sample, most likely because the first contribution shifts to a higher temperature. This reflects the presence of larger cobalt oxide particles, which are harder to reduce than smaller ones.

In the high temperature region (500–1000 °C), the 5% Co₃O₄/MgO reduction profile clearly shows a small peak at 500–600 °C, ascribed to the reduction of MgCo₂O₄ species. Above 700 °C, all the samples show the reduction of stable (Co,Mg)O solid solution species. These peaks overlap at higher metal loadings. In some cases, the (Co,Mg)O solid solution is only partially reduced.

The fresh catalysts showed nitrogen adsorption–desorption isotherms (Figure S4) similar to type IV, with a hysteresis feature characteristic of mesoporous materials. The BET surface area and pore volume values increase with the metal loading up to 15% (Table 1). 20% Co₃O₄/MgO catalyst does not follow this trend, indicating the presence of larger cobalt oxide particles that block the pores and decrease the surface.

![STEM-EDS analysis of the fresh 15% Co₃O₄/MgO catalyst. (a) TEM micrograph and its corresponding SAED pattern (inset), showing a set of diffraction rings characteristic of the MgO and Co₃O₄ planes. (b,c) Magnified HRTEM images of 15% Co₃O₄/MgO. The yellow and blue lines mark the lattice fringes of the planes of cobalt oxide nanoparticles.](https://acs.s3-external-1.amazonaws.com/acs/acs000000i0000.pdf)

**Figure 1.** Representative TEM images of 15% Co₃O₄/MgO. (a) TEM micrograph and its corresponding SAED pattern (inset), showing a set of diffraction rings characteristic of the MgO and Co₃O₄ planes. (b,c) Magnified HRTEM images of 15% Co₃O₄/MgO. The yellow and blue lines mark the lattice fringes of the planes of cobalt oxide nanoparticles.

$$\text{energy efficiency (mmol kWh}^{-1} \text{)} = \frac{\text{converted product (mmol h}^{-1}\text{)}}{\text{discharge power (W)}}$$

(10)

**RESULTS AND DISCUSSION**

**Catalyst Synthesis.** We tested MgO and γ-Al₂O₃ as packing materials in the DBD plasma. MgO was also used as support for the cobalt oxide catalysts with different cobalt metal loadings. We also prepared bulk Co₃O₄ by mixing polyethylene glycol and cobalt nitrate hexahydrate in water (see the detailed procedures in the Experimental Section).

**Catalyst Characterization.** The XRD patterns of the fresh Co₃O₄/MgO samples show the characteristic diffraction peaks of MgO at 2θ = 36.9, 42.9, 62.2, 74.6, and 78.6° (Figure S1a). The characteristic peaks of Co₃O₄ and CoO are not visible, as they overlap with those of MgO. HRTEM and STEM–EDS images of 15% Co₃O₄/MgO show that cobalt oxide nanoparticles are highly dispersed over the support (Figures 1 and 2).
HRTEM analysis of this sample confirmed the presence of larger cobalt oxide particles compared to the 15% sample (Figure S5a).

Catalytic Tests. We performed the CO2 hydrogenation reaction in a coaxial DBD reactor, maintained at 35 °C using circulating cooling water. The plasma operated at atmospheric pressure and 10 W. Previous plasma-catalytic CO2 hydrogenation studies show that an excess of hydrogen in the reaction mixture, up to a 4:1 H2/CO2 molar ratio, typically increases the conversion.22,25,58 In addition, two recent studies reported higher methanol yields at a 3:1 H2/CO2 molar ratio.26,27 To favor CO2 conversion and methanol formation, we set the H2/CO2 molar ratio to 3:1.

First, we tested plasma alone (Figure S6), which gave 15% CO2 conversion and 7% H2 conversion (the plasma background reaction). The products were mainly CO (71% selectivity) and methanol (22%), as well as 2% methane and 6% acetic acid (all results are averages of triplicate measurements).

We then tested the effect of different packing materials. MgO and γ-Al2O3 are conventional supports, which are usually inactive in thermal catalysis. However, these materials enhanced the activity when introduced in the DBD plasma chamber even under the mild reaction conditions mentioned above (Figure S6). MgO showed significantly higher conversion values (27% CO2 conversion and 13% H2 conversion) than plasma alone. CO selectivity also increased, from 71% with plasma only to 84% with MgO. Alumina also gave higher CO2 and H2 conversion (17 and 7%, respectively) than plasma alone, and higher CO selectivity (80%).

The changes in conversion and product distribution when placing a packing material in the plasma discharge can be explained by examining the possible reaction pathways. Typically, in a CO2/H2 mixture in DBD plasma (without catalyst), consumption of CO2 predominantly occurs via electron impact dissociation to CO (R1).59,60 The contribution from the electron impact vibrational excitation of CO2 is negligible because of its tendency to react back to ground CO2. Similarly, H2 is consumed by electron impact dissociation to two hydrogen radicals (R2). CO and H+ radicals can start several reactions that lead to formaldehyde CH2O (R3–R9). CH2O is then hydrogenated to methanol (R11 and R12),26,59 while water is also produced (R12 and R13).59

Table 1. BET Surface Area, Cumulative Pore Volume, and Average Pore Diameter (from BJH Analysis) Values Derived from Nitrogen Sorption Isotherms

<table>
<thead>
<tr>
<th>catalyst</th>
<th>(S_{\text{BET}}) (m²·g⁻¹)</th>
<th>pore volume (cm³·g⁻¹)</th>
<th>average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Co3O4/MgO</td>
<td>33</td>
<td>0.2</td>
<td>56</td>
</tr>
<tr>
<td>10% Co3O4/MgO</td>
<td>37</td>
<td>0.4</td>
<td>44</td>
</tr>
<tr>
<td>15% Co3O4/MgO</td>
<td>39</td>
<td>0.6</td>
<td>49</td>
</tr>
<tr>
<td>20% Co3O4/MgO</td>
<td>26</td>
<td>0.3</td>
<td>26</td>
</tr>
</tbody>
</table>

Figure 3. Co 2p XPS spectra of the fresh Co3O4/MgO catalysts.
When combining plasma and a catalyst, previous work found that both plasma-assisted surface reactions and gas-phase reactions contribute to the conversion and selectivity. Gas-phase reactions involve reactions R1 to R11. In addition, CO derived from CO$_2$ dissociation in the gas phase can adsorb on the catalyst surface and react with adsorbed hydrogen to form methanol, as represented in Figure 4a. CO$_2$ can also adsorb on the catalyst surface, as confirmed elsewhere with the detection of carbonates using in situ spectroscopy analysis. Both ground and excited CO$_2$ can be adsorbed, although the contribution of excited CO$_2$ can be neglected because it is prone to quenching on the surface.
Adsorbed CO$_2$ is then hydrogenated to either hydrocarboxyl (HOCO) or formate (HCOO$^-$) species (Figure 4b). The decomposition of HOCO to CO initiates the so-called RWGS (Rohrmann-Wagner gas-water shift) reaction. The formate pathway can also take place, where HCOO$^-$ is hydrogenated in several steps. Both pathways lead to the formation of H$_2$CO, which is hydrogenated to methanol via the methoxy (H$_3$CO) intermediate.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity.

The increase in CO$_2$ conversion and CO selectivity when placing MgO or Al$_2$O$_3$ in the plasma chamber is ascribed to their ability to adsorb CO$_2$ and perform both plasma-assisted surface reactions and gas-phase reactions. MgO shows higher conversion than Al$_2$O$_3$, which is related to their acid-base properties. CO$_2$ is attracted better by the basic sites of solid surfaces because of its acidic property. MgO is significantly more basic than Al$_2$O$_3$ and therefore it has a higher CO$_2$ adsorption capacity. Both materials increase CO selectivity, indicating that they promote the RWGS pathway. These metal oxides do not have a strong affinity to CO and H$_2$/H species, hindering the formation of methanol.

Shifting the selectivity toward methanol requires a stronger binding energy of CO and hydrogen, as well as the participation of a considerable amount of adsorbed hydrogen in the reaction pathway. Cobalt-based catalysts are active in CO$_2$ hydrogenation to ethanol, methane, and larger hydrocarbons. Therefore, we tested the influence of MgO-supported cobalt oxide catalysts with different metal loadings on the reaction performance (Figure 5). Our results show an improved conversion when using Co$_3$O$_4$/MgO catalysts, which is partially ascribed to their ability to promote surface reactions. These catalysts also gave a narrower product distribution. We also observed acetic acid (<1%), ethanol (trace), and methane (<2%).

The 5% Co$_3$O$_4$/MgO catalyst converted 30% of CO$_2$ and 13% of H$_2$, giving 92% selectivity to CO and 6% of methanol. Compared to MgO, it only improved CO$_2$ conversion, thereby increasing CO selectivity. The low amount of cobalt oxide in this catalyst does not shift the product distribution to methanol.

The 10% Co$_3$O$_4$/MgO catalyst showed 31% CO$_2$ conversion and 15% H$_2$ conversion, as well as 76% selectivity to CO and 20% selectivity to methanol. Further increasing the cobalt loading to 15% improved the conversion values to 33% CO$_2$ and 24% H$_2$, and the methanol selectivity to 31%. This catalyst gave the highest methanol yield (>10%). This indicates that catalysts with high metal loading increase the amount of adsorbed CO and hydrogen available for the reaction, facilitating methanol production. Increasing the metal loading to 20% gave 31% CO$_2$ conversion and 9% methanol yield.
From these results, we conclude that the quantity and dispersion of the Co₃O₄/CoO sites play an important role in the activity enhancement and methanol selectivity, in agreement with previous studies. CO₂ conversion and methanol selectivity increase when increasing the metal loading from 5 to 15%. The BET surface area and pore volume also increase when increasing the metal loading up to 15% (see Table 1). This indicates that a good dispersion of the metal oxide nanoparticles on the support favors CO₂ conversion. Higher metal loadings (20%) lead to larger cobalt oxide particles (as confirmed by HRTEM), which block the pores of the support and decrease the catalyst surface area. This reduces the metal oxide dispersion compared to lower metal loadings, inhibiting a further increase on conversion and methanol production.

For comparison, we tested unsupported Co₃O₄ (Figure 5). This gave lower conversion (8% CO₂ and 10% H₂) than the supported Co₃O₄/MgO catalysts, with CO as the main product (98% selectivity). The decrease in methanol formation when using Co₃O₄ emphasizes the importance of metal oxide-support interface sites for methanol synthesis.

Compared to plasma only, the combination of plasma and any tested catalyst improves the energy efficiency of CO production (Figure S7), reaching its maximum when using 10% Co₃O₄/MgO catalyst (509 mmol CO-kWh⁻¹). The energy efficiency of methanol production is improved when a considerable metal loading of cobalt is used (10, 15, and 20% Co₃O₄/MgO catalysts). The optimal methanol energy efficiency was obtained with 15% Co₃O₄/MgO (190.8 mmol MeOH-kWh⁻¹), which is related to the balance between a considerable amount of Co₃O₄/CoO sites and their good dispersion on the support. None of these catalysts were active in thermal activity tests, showing the importance of the plasma-catalytic hybrid approach in activating CO₂ at near-ambient temperatures. In addition, we studied the stability of the 15% Co₃O₄/MgO catalyst under reaction conditions (Figure S8). The catalyst performance was stable up to 4.5 h, with only a slight deactivation at the start of the reaction.

**Plasma and Catalyst Interactions.** We studied the effect of the plasma discharge on the physicochemical properties of the Co₃O₄/MgO catalysts. The XRD patterns of the spent catalysts correspond to those of the fresh catalysts (Figure S1b). HRTEM and STEM images of 15% Co₃O₄/MgO spent catalyst (Figures S8 and S9) discard the sintering of cobalt oxide particles because the average size of cobalt oxide nanoparticles (24.5 ± 7.6 nm) is very similar to the fresh catalyst (27.7 ± 11.5 nm). HRTEM images of spent 20% Co₃O₄/MgO (Figure S5b) do not show a significant change on the particle size neither. In general, the surface area and porosity of the spent catalysts are similar to the fresh ones (Table S7). The 20% sample shows the largest increase in the BET surface area (from 26 to 35 m²·g⁻¹), and the 15% sample shows the largest increase in the pore volume and average pore size. In addition, XPS analysis of all catalysts shows that the I₉⁰/I₉₈ ratio remains unaltered (Table S6), indicating that the
dispersion of cobalt oxide on the support is not affected by the plasma.

XPS and H₂-TPR analyses of the spent catalysts indicate that Co₃O₄ surface species undergoes partial reduction under CO₂/H₂ plasma. For the samples with a cobalt metal loading lower than 20%, the XPS Co 2p peaks corresponding to CoO species increase in intensity, while the ones of Co₃O₄ decrease (Figure 6 and Table S1). The 20% Co₃O₄/MgO catalyst does not show a major reduction after plasma exposure, as the Co₃O₄ and CoO peak intensities remain similar to the fresh catalyst. In the reduction profiles (Figure S3), the first contribution in the low temperature region becomes less intense for the spent 5, 10, and 15% Co₃O₄/MgO catalysts. This contribution corresponds to the easily reducible Co₃O₄ species. There are no major changes in the reduction profile of 20% Co₃O₄/MgO, indicating that this sample contains larger Co₃O₄ particles that are harder to reduce.

We conclude that the catalysts with a cobalt metal loading lower than 20% are significantly reduced from Co₃O₄ to CoO in the hydrogen-rich plasma environment. Nevertheless, we cannot exclude the formation of metallic cobalt because of plasma exposure. Because all spent catalysts were stored in air prior to characterization, we cannot detect metallic cobalt in XPS and H₂-TPR analysis.

We also studied the effect of the catalysts on the plasma discharge properties, which in turn might affect the reaction performance. Figure S10a shows the current signals of the discharge in the presence and absence of packing materials. The intensity and density of the current pulses of the discharge follow the order of 15% Co₃O₄/MgO > plasma alone > MgO > Co₃O₄, which agrees with the order of CO₂ conversion. Packing MgO or Co₃O₄ into the discharge gap weakens the formation of microdischarges compared to plasma alone. The 15% Co₃O₄/MgO catalyst enhances the discharge, as evidenced by the increase in the current pulse, thereby favoring the formation of radicals and vibrationally excited species that can participate in the reaction. 46,75,76 In addition, the Q−V Lissajous plot (Figure S10b) of the plasma with a packing material is very similar to the one of plasma alone, remaining with an elliptical shape. We find that the change in the cobalt loading of the Co₃O₄/MgO catalysts does not affect the discharge, as the electrical signals are almost the same. Thus, we attribute the difference in product selectivity when using packing materials to their properties and to the plasma-enhanced promotion of surface reactions on the metal–support interface sites (see Figure 5 above).

**CONCLUSIONS**

In this study, we show the potential of plasma-enhanced catalysis for CO₂ hydrogenation reactions under ambient conditions. Packing a catalyst in a DBD plasma enhances the conversion and narrows the product distribution of CO₂ hydrogenation. We found that the basicity of the MgO support enhances the conversion of CO₂ compared to more acidic supports (γ-Al₂O₃). Both type of supports promote the production of CO as the main product. When testing the Co₃O₄/MgO catalysts, the quantity and dispersion of metal−support interface sites are important for the activity enhancement and methanol selectivity. Although CO is the main product, the catalysts with higher cobalt metal loadings and a good cobalt oxide dispersion favor methanol production. The most active catalyst was 15 wt % Co₃O₄/MgO, which converted 33% CO₂ and 24% H₂ near room temperature and at atmospheric pressure. This catalyst gave 10% methanol yield, the highest among the tested materials. A further increase in the metal loading leads to larger cobalt oxide particles that block the pores, giving lower CO₂ conversion and less methanol. Finding correlations between catalyst properties and reaction performance remains a challenge in this field. We hope that this study will help in the rational design of materials for plasma-enhanced catalysis applications.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c05565.

XRD patterns of the fresh and spent catalysts; XPS data of the fresh and spent catalysts; temperature-programmed reduction profiles of the fresh and spent catalysts; nitrogen adsorption—desorption isotherms of the fresh catalysts; HRTEM and STEM−EDS images of the spent 15% Co₃O₄/MgO catalyst; HRTEM images of the fresh and spent 20% Co₃O₄/MgO catalyst; plasma-catalytic tests of plasma alone, MgO, and γ-Al₂O₃; energy efficiency values of all catalysts; stability test of the 15% Co₃O₄/MgO catalyst; plasma electrical diagnostics (current signals, Q−V Lissajous plots, and calculated discharge properties) of plasma alone, MgO, 15% Co₃O₄/MgO, and Co₃O₄ (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Xin Tu – Department of Electrical Engineering and Electronics, University of Liverpool, L69 3GJ Liverpool, U.K.; orcid.org/0000-0002-6376-0897; Email: xin.tu@liverpool.ac.uk

N. Raveendran Shiju – Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1090GD Amsterdam, The Netherlands; orcid.org/0000-0001-7943-5864; Email: n.r.shiju@uva.nl

**Authors**

Maria Ronda-Lloret – Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1090GD Amsterdam, The Netherlands

Yaolin Wang – Department of Electrical Engineering and Electronics, University of Liverpool, L69 3GJ Liverpool, U.K.

Paula Oulego – Department of Chemical and Environmental Engineering, University of Oviedo, E-33071 Oviedo, Spain

Gadi Rothenberg – Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1090GD Amsterdam, The Netherlands

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.0c05565

**Author Contributions**

M.R.-L. and Y.W. contributed equally for this article. This article 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.
M.R.-L., G.R., and N.R.S. thank the Netherlands Organization for Scientific Research (NWO) for the grant “Developing novel catalytic materials for converting CO₂, methane and ethane to high-value chemicals in a hybrid plasma-catalytic reactor” (China.15,119). X.T. acknowledges the funding from the Marie Skłodowska-Curie Action (grant number 823745) of the European Union (EU) and Horizon 2020 research and innovation program. Y.W. acknowledges the funding awarded to the EUROPAH Consortium (grant number 722346) and European Union (FEDER) for funding. P.O. acknowledges the technical support provided by the University of Oviedo Scientific and Technical Services.

**REFERENCES**


Selective Hydrogenation of CO$_2$ to Ethanol over Cobalt Catalysts. 


