

# In Situ Modification of CuO–Fe<sub>2</sub>O<sub>3</sub> by Nonthermal Plasma: Insights into the CO<sub>2</sub>-to-CH<sub>3</sub>OH Hydrogenation Reaction

Nitesh Joshi and Sivachandiran Loganathan\*

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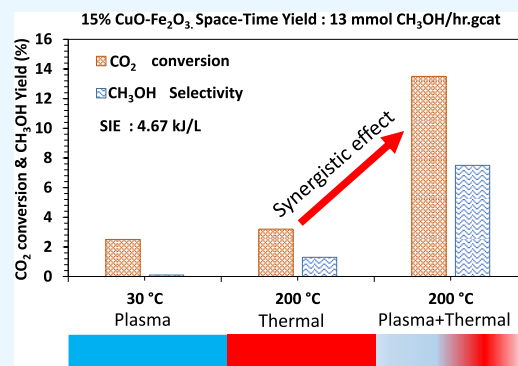


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**ABSTRACT:** The hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH on the binary mixed metal oxides of CuO–Fe<sub>2</sub>O<sub>3</sub> under nonthermal plasma discharge has been reported in this study. The catalysts are synthesized using the sol–gel route and characterized by XRD, FTIR, SEM, and XPS techniques. The impact of CuO mixing with Fe<sub>2</sub>O<sub>3</sub> on CO<sub>2</sub> conversion and CH<sub>3</sub>OH yield has been investigated. Herein, we have compared two distinct techniques, namely thermal and plasma catalytic processes. The overall outcome shows that the CO<sub>2</sub> conversion and CH<sub>3</sub>OH production increase with an increase in CuO mixing with Fe<sub>2</sub>O<sub>3</sub>. The synthesized catalyst does not show significant CO<sub>2</sub> conversion and CH<sub>3</sub>OH formation in the thermal catalytic process (100–250 °C). Interestingly, when plasma discharge is combined with thermal heating, CO<sub>2</sub> conversion and CH<sub>3</sub>OH production significantly improve. The plasma discharges in the CO<sub>2</sub>/H<sub>2</sub> gas stream, at low temperatures (<200 °C), reduce Cu<sup>+2</sup> to Cu<sup>+1</sup> and Fe<sup>+3</sup> to Fe<sup>+2</sup>, which could probably enhance the CO<sub>2</sub> conversion and CH<sub>3</sub>OH production. Among the catalysts prepared, 15% CuO–Fe<sub>2</sub>O<sub>3</sub> exhibited the best catalytic activity with 13.2% CO<sub>2</sub> conversion, 7.3% CH<sub>3</sub>OH yield, and a space–time yield of 13 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub><sup>−1</sup> with 4.67 kJ/L of specific input energy (SIE). The CH<sub>3</sub>OH space–time yield is 2.9-fold higher than that of the commercial catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, which is operated at 30 °C with 45.45 kJ/L SIE.



## INTRODUCTION

The CO<sub>2</sub> levels are rising globally and have reached above 400 ppm.<sup>1</sup> The capture and conversion of CO<sub>2</sub> as the feedstock for the synthesis of value-added chemicals and fuels is an exciting approach to combat the surge in CO<sub>2</sub> levels in the atmosphere. CO<sub>2</sub> can be converted to various products like urea,<sup>2</sup> polymers,<sup>3</sup> oxygenates such as CH<sub>3</sub>OH,<sup>4</sup> C<sub>2</sub>H<sub>5</sub>OH,<sup>5</sup> CH<sub>4</sub>,<sup>6</sup> and synthesis gas,<sup>7</sup> and more importantly, gasoline fractions.<sup>8</sup> There are several technologies for CO<sub>2</sub> conversion, such as photochemical, biochemical, catalysis, electrochemical, plasma catalysis, and solar thermochemical systems.<sup>9–14</sup> As CO<sub>2</sub> is a stable molecule, most of the products obtained from CO<sub>2</sub> are synthesized at high operating pressures and temperatures. Therefore, there is a need to develop technologies that could produce value-added products from CO<sub>2</sub> using economically viable procedures under ambient conditions.

Nonthermal plasma (NTP)-based processes are proven effective for CO<sub>2</sub> conversion to value-added chemicals under ambient conditions.<sup>15,16</sup> The NTP has attracted great interest owing to facilitating thermodynamically unfavorable chemical reactions (such as CO<sub>2</sub> activation) at low temperatures. Although significant efforts have been made to improve the process performance (high CO<sub>2</sub> conversion with better energy efficiency),<sup>9,17–21</sup> product separation is a significant disadvantage from an industrial perspective.

The NTP catalysis is interesting as it operates at a completely different mechanism of electron impact dissociation and, thus, consumes lower energy as compared to thermal catalysis.<sup>22</sup> In thermal catalysis, the vibrational excitation of molecules is a key step that requires higher energy and, thus, affects the overall energy efficiency.<sup>6</sup> Several types of plasma discharges are reported for CO<sub>2</sub> conversion, like glow discharges, corona discharges, radio frequency discharges, microwave discharges, gliding arc discharges, micro-hollow cathode discharges, and DBDs (dielectric barrier discharges).<sup>23–27</sup> Interestingly, except DBD, all other plasmas yield CO as the main product. Remarkably, DBD is also proven to produce oxygenates, namely CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH, and other products with the aid of catalysts.<sup>20,28</sup>

CH<sub>3</sub>OH is a liquid at room temperature, unlike other high energy density gases like liquefied petroleum gas (LPG), CH<sub>4</sub>, and dimethyl ether (DME). Therefore, it does not require any sophisticated storage units. Thus, CH<sub>3</sub>OH is widely used as a

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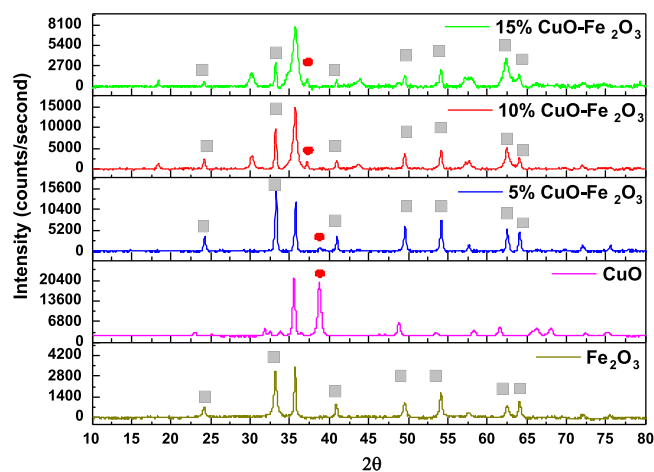
raw material for preparing gasoline, used as fuel blends, and for generating energy. CH<sub>3</sub>OH is produced via various methods like direct CO<sub>2</sub> conversion to CH<sub>3</sub>OH over a heterogeneous catalyst,<sup>29,30</sup> steam reforming<sup>31</sup> and dry reforming of CH<sub>4</sub> with CO<sub>2</sub>,<sup>32</sup> and hydrogenation of CO.<sup>33</sup> With the said and referred, the need of the century is to convert CO<sub>2</sub> to CH<sub>3</sub>OH at atmospheric pressure and temperature compared to industry standards. Using plasma, researchers have tried CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH at atmospheric pressure using 96 kJ/L of specific input energy (SIE) at 50 °C (3H<sub>2</sub>:CO<sub>2</sub>) but could obtain only 0.2% CH<sub>3</sub>OH selectivity.<sup>34</sup> Moreover, the increase in reaction temperature has reduced the CH<sub>3</sub>OH yield to <0.1%. With the incorporation of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA) (with 8 bar, 100 °C, and 60 kJ/L of SIE), CH<sub>3</sub>OH selectivity was increased to 7–10%, with 12% CO<sub>2</sub> conversion, which corresponds to 0.84–1.2% of CH<sub>3</sub>OH yield.<sup>35</sup>

CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst-coupled high-frequency plasma (9 kHz, SIE = 15 kJ/L) exhibited about 11.3% CH<sub>3</sub>OH yield with 21.2% CO<sub>2</sub> conversion.<sup>16</sup> Our previous study demonstrated that a 5 wt % CuO–Fe<sub>2</sub>O<sub>3</sub>/QW-packed plasma DBD reactor with 1.2 kJ/L of SIE at 200 °C exhibited 16% CO<sub>2</sub> conversion and 5.2% CH<sub>3</sub>OH yield.<sup>4</sup> In another study, 10 wt % NiO–Fe<sub>2</sub>O<sub>3</sub> showed about 6.2% CO<sub>2</sub> conversion and 6% CH<sub>3</sub>OH yield with 2.4 kJ/L of SIE at 200 °C.<sup>36</sup> On investigation, the Co<sub>x</sub>O<sub>x</sub>/MgO catalytic system reached 33% CO<sub>2</sub> conversion and 10.2% CH<sub>3</sub>OH yield using 15 kJ/L of SIE.<sup>37</sup> More recently, Han et al.<sup>38</sup> carried out highly selective CO<sub>2</sub> conversion to CH<sub>3</sub>OH. The authors have used CuZnO–ZrO<sub>2</sub> catalyst modified by glow discharge plasma. The modified catalyst, under thermal catalysis (250 °C and 20 bar), exhibited 14.2% CO<sub>2</sub> conversion and CH<sub>3</sub>OH yield and selectivity of 11.3 and 78.2%, respectively.

It is well proven that Cu-based catalysts are active toward CO<sub>2</sub> to oxygenate synthesis. In this study, we have investigated the role of mixed oxides CuO–Fe<sub>2</sub>O<sub>3</sub> on CO<sub>2</sub> conversion and CH<sub>3</sub>OH production under DBD plasma. The synthesized catalysts were systematically characterized by XRD, XPS, SEM, BET surface area analysis, and the basicity of the catalysts (via CO<sub>2</sub>-TPD studies). The synergistic effect between plasma discharge and thermal catalysis has been explored. The influence of plasma input energy on CO<sub>2</sub> conversion and product distribution was also investigated.

## RESULTS AND DISCUSSION

**Catalyst Characterization.** The powder XRD patterns of pure CuO and the binary mixed metal oxides of CuO–Fe<sub>2</sub>O<sub>3</sub> catalysts are presented in Figure 1. CuO exhibits two intense peaks at  $2\theta$  values of 35.5° and 38.5°, which are attributed to the (–002) and (111) planes according to the ICDD database reference number 00-001-1117. In the binary mixed oxides, the characteristic peak at 38.5° was used to calculate the crystallite size of CuO. The peak centered at 35.6° was used to calculate the Fe<sub>2</sub>O<sub>3</sub> crystallite size. It was observed that the resultant peak from CuO for mixed metal oxides was very small due to the low mixing amount. With an increase in mixing from 5 to 15%, the characteristic peak at 38.5° shifted to a lower  $2\theta$  value. This could be due to the possible intercalation of CuO with the Fe<sub>2</sub>O<sub>3</sub> lattice. In addition, with 15% CuO–Fe<sub>2</sub>O<sub>3</sub> mixing, the diffraction pattern matches the CuFeO<sub>2</sub> spinel structure (ICDD database number 00-021-0290) and CuFe<sub>2</sub>O<sub>4</sub> structure. This is due to the start of the spinel (normal and inverse spinels) formation when the metal ion ratio reaches close to the 1:2 ratio. Thus, in 15% CuO–Fe<sub>2</sub>O<sub>3</sub> binary mixed



**Figure 1.** XRD diffraction patterns of CuO and CuO–Fe<sub>2</sub>O<sub>3</sub> binary mixed catalysts.

metal oxide, there could be a mixture of spinels and individual metal oxides, as the perfect ratio of metals for spinel formation is not achieved.

Table 1 represents the physicochemical characteristics of the catalyst. The Scherrer equation was used to calculate the

**Table 1.** Physicochemical Characterization of the Catalysts

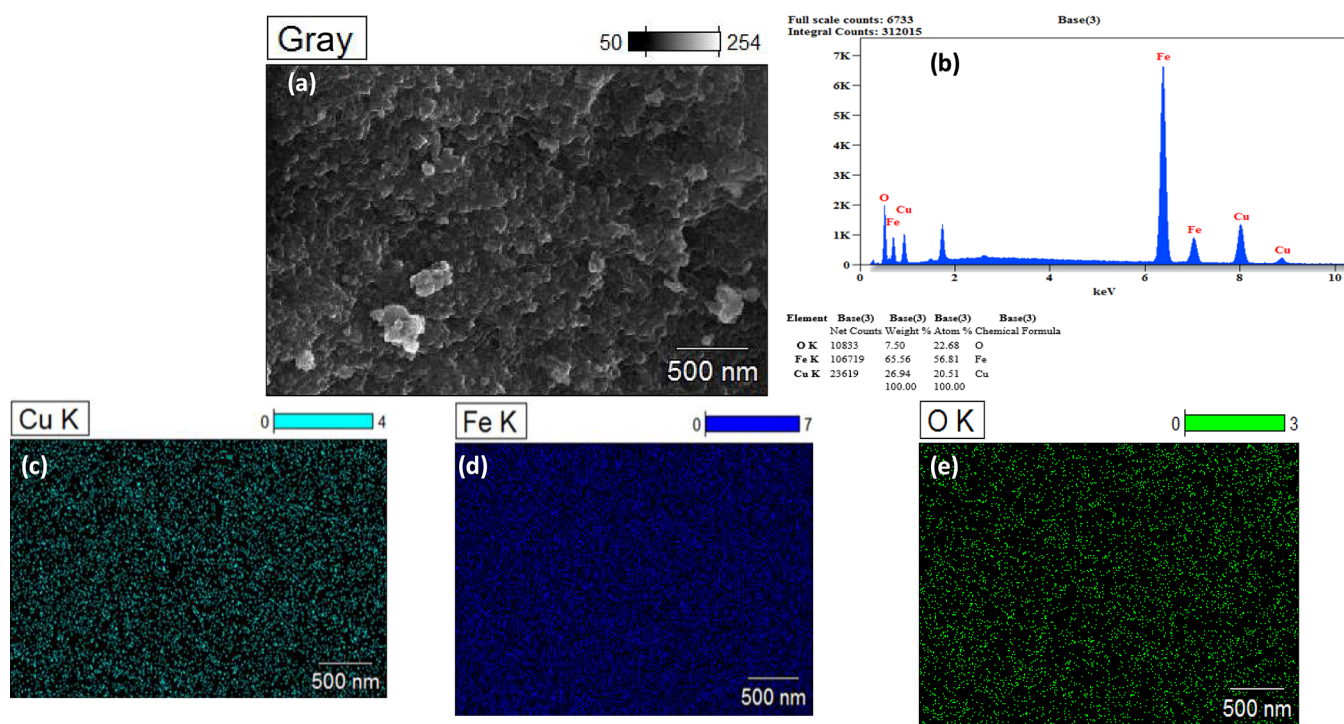
catalyst	crystallite size (nm) <sup>a</sup>		metal loading (%) <sup>b</sup>	BET surface area (m <sup>2</sup> /g) <sup>c</sup>
	CuO	Fe <sub>2</sub> O <sub>3</sub>		
Fe <sub>2</sub> O <sub>3</sub>		32		NA
CuO	31			NA
5% CuO–Fe <sub>2</sub> O <sub>3</sub>	11.6	20.9	6.4	6.0
10% CuO–Fe <sub>2</sub> O <sub>3</sub>	36.8	30.5	12.4	24.1
15% CuO–Fe <sub>2</sub> O <sub>3</sub>	25.8	35.7	20.5	28.5

<sup>a</sup>Using the Scherrer equation. <sup>b</sup>Using the EDX measurement. <sup>c</sup>Using the BET method.

crystallite size of the pure and mixed metal oxides. The crystallite size of CuO was 31 nm; however, when 5% CuO was mixed with Fe<sub>2</sub>O<sub>3</sub>, the crystallite size was reduced threefold (11 nm) under similar synthesis conditions. The smaller crystallite size indicates that the CuO crystals are not agglomerated and could be uniformly dispersed on the Fe<sub>2</sub>O<sub>3</sub> surface. With an increase in CuO mixing, the crystallite size of CuO increases. This infers that above 5% CuO–Fe<sub>2</sub>O<sub>3</sub> mixing, the CuO particles start to adhere to each other. However, the Fe<sub>2</sub>O<sub>3</sub> crystallite size has not been significantly affected by CuO mixing, as seen in Table 1.

The HRSEM and EDX analyses for 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalyst are presented in Figure 2. The elemental mapping of 5 and 10% CuO–Fe<sub>2</sub>O<sub>3</sub> catalysts is reported in Supporting Information (Figures S1 and S2). The HRSEM images revealed that the particles are spherical and uniformly distributed. The EDX analysis showed that the CuO content in the catalyst was slightly higher than the estimated composition, but it serves our motto. The elemental dispersion is studied via elemental mapping, and all the elements are uniformly distributed and not aggregated, even with high percentages of CuO mixing with Fe<sub>2</sub>O<sub>3</sub>.

The total surface area measured for 5% CuO–Fe<sub>2</sub>O<sub>3</sub> was 6 m<sup>2</sup>/g (Table 1). The increase in CuO mixing to 10 and 15% increased the surface area to 24 and 28 m<sup>2</sup>/g, respectively.



**Figure 2.** (a) HRSEM image of 15% CuO–Fe<sub>2</sub>O<sub>3</sub>, (b) EDX compositional details, (c) elemental mapping profile for Cu, (d) elemental mapping profile for Fe, (e) and elemental mapping profile for oxygen.

When CuO was mixed with Fe<sub>2</sub>O<sub>3</sub>, the total surface area was increased. An increase in the surface area could be correlated to the formation of a new mixed oxide structure. This aligns with the CuFe<sub>2</sub>O<sub>4</sub> phase observed in XRD (Figure 1). The detailed pore size distribution and N<sub>2</sub> adsorption–desorption profile are reported in Supporting Information (Figures S3–S5).

**Evaluating the Distribution of Basic Sites on the Catalyst.** The CO<sub>2</sub> adsorption capacity of the fresh catalyst is determined, and the description of CO<sub>2</sub> adsorption experiments is reported in Supporting Information (Figure S6). The CO<sub>2</sub> adsorption capacity of pure CuO and Fe<sub>2</sub>O<sub>3</sub> was 141 and 19.4 μmol/g, respectively (Table 2). It was noted that 5% of

**Table 2. Quantification of the Basic Sites on the Catalyst Surface**

catalyst	CO <sub>2</sub> adsorption (μmol/g)	total basic sites (μmol/g)
Fe <sub>2</sub> O <sub>3</sub>	19.4	17.9
5% CuO–Fe <sub>2</sub> O <sub>3</sub>	49.2	48.6
10% CuO–Fe <sub>2</sub> O <sub>3</sub>	50.9	44.9
15% CuO–Fe <sub>2</sub> O <sub>3</sub>	86.8	78.2
CuO	141.2	137.4

CuO mixing increased the CO<sub>2</sub> adsorption capacity to 49.5 μmol/g, which is 2.5 times higher than that of fresh Fe<sub>2</sub>O<sub>3</sub>. However, when CuO mixing increased to 10%, no significant difference in the CO<sub>2</sub> adsorption capacity was observed (50.9 μmol/g). For 15% CuO–Fe<sub>2</sub>O<sub>3</sub>, the CO<sub>2</sub> adsorption capacity was 86.8 μmol/g. The increase in surface area with the increasing CuO mixing could be attributed to the new porous sites formed, which increases the CO<sub>2</sub> adsorption capacity and eventually could facilitate the CO<sub>2</sub> conversion into CH<sub>3</sub>OH.

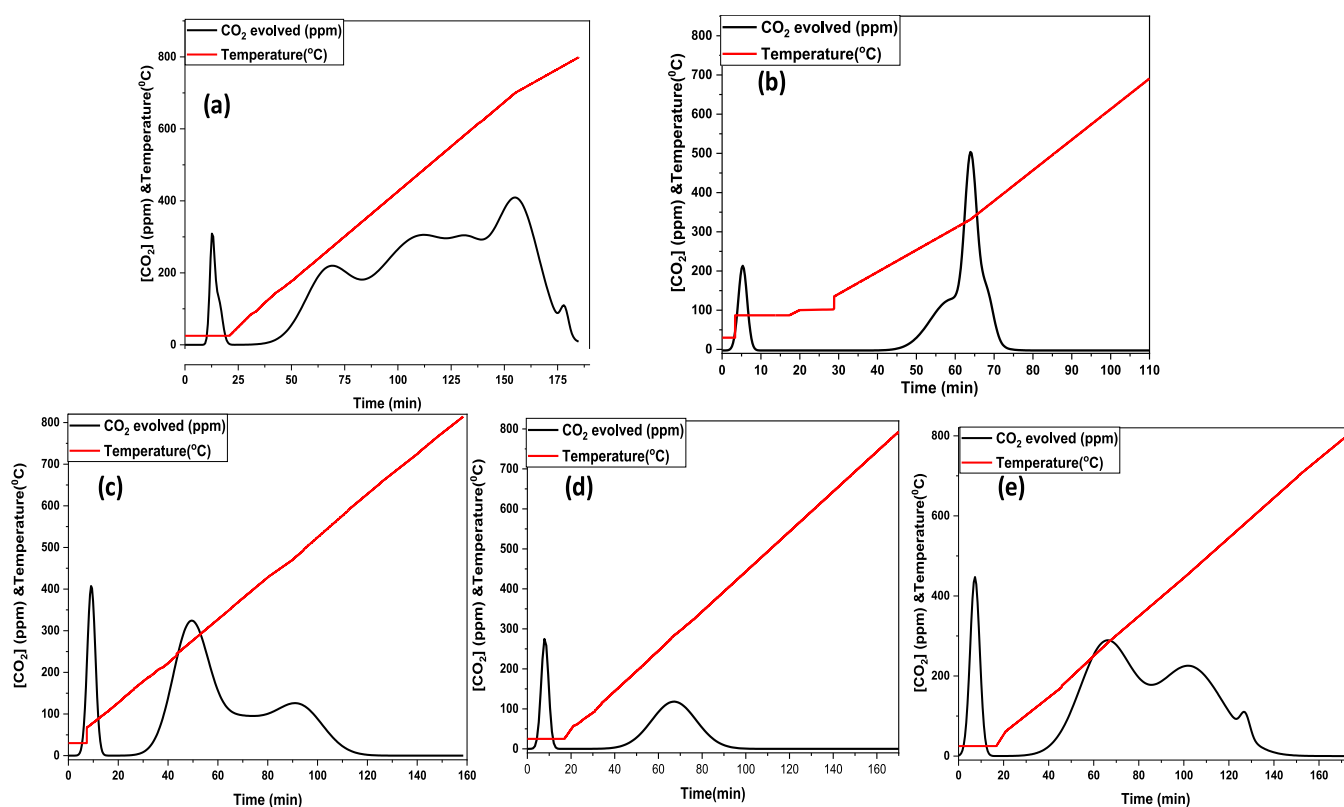
The basic sites on the catalyst surface are quantified by the CO<sub>2</sub>-TPD (temperature-programmed desorption) technique.

According to the CO<sub>2</sub> desorption temperature, basic sites can be classified into three types: weak sites, medium sites, and strong sites. It is well established that the Lewis basic sites largely control the CO<sub>2</sub> adsorption and subsequent conversion to other products.<sup>39</sup> The weakly adsorbed CO<sub>2</sub> desorbs at temperatures between 25 and 100 °C, moderately adsorbed CO<sub>2</sub> used to desorb temperatures between 100 and 350 °C, and strongly adsorbed CO<sub>2</sub> desorbs between 350 and 800 °C.<sup>40–42</sup> The amount of desorbed CO<sub>2</sub> is directly related to the number of basic sites available on the catalyst surface. It was observed that (Figure 3) pure CuO exhibited a mixture of strong and weak sites favoring CO<sub>2</sub> adsorption. However, on Fe<sub>2</sub>O<sub>3</sub>, there are a mixture of mild and weak sites for CO<sub>2</sub> adsorption. The strongly adsorbed CO<sub>2</sub> needed high temperature to desorb from the surface. For the Fe<sub>2</sub>O<sub>3</sub> catalyst, CO<sub>2</sub> desorption was initiated at 300 °C. In the case of mixed metal oxides, the adsorbed CO<sub>2</sub> molecules are very weak and mild in interaction with the catalyst.

The Lewis and Brønsted basic sites on the catalyst surface are mapped by carrying out CO<sub>2</sub> TPD measurements. The area under the peaks is calculated and added to derive the total basic sites on the catalyst surface. In the synthesized fresh catalyst, Fe<sub>2</sub>O<sub>3</sub> possesses 17.9 μmol/g of total basic sites, whereas CuO exhibits a 7.6-fold higher distribution of basic sites on the catalyst surface compared to the Fe<sub>2</sub>O<sub>3</sub> catalyst. The mixed metal oxides synthesized show the intermediate distribution of basic sites which increases with an increase in CuO mixing with Fe<sub>2</sub>O<sub>3</sub>.

**Effect of Catalyst Packing on Plasma Discharge Characteristics.** Table 3 presents the plasma discharge characteristics of empty, QW (quartz wool), and catalyst sandwiched in QW-DBD reactors. The details of the calculation are presented in Supporting Information (Figure S7). The gas-burning voltage is the minimum voltage which will suffice to decompose a gas molecule. Upon the application





**Figure 3.** CO<sub>2</sub>-TPD profiles of synthesized catalysts: (a) CuO, (b) Fe<sub>2</sub>O<sub>3</sub>, (c) 5% CuO–Fe<sub>2</sub>O<sub>3</sub>, (d) 10% CuO–Fe<sub>2</sub>O<sub>3</sub>, and (e) 15% CuO–Fe<sub>2</sub>O<sub>3</sub>.

**Table 3.** Plasma Discharge Characteristics of the DBD Reactor

	temperature (°C)	applied voltage (kV)	burning voltage (kV)	breakdown voltage (kV)	effective capacitance (nC)	$Q_{pk-pk}$ (μC)	dQ (nC)	$Q_d$ (μC)
empty	30	16	0.83	0.52	0.48	24.0	11.5	89.4
	200	16	0.48	0.40	0.53	24.0	8.87	59.8
QW	30	16	0.84	0.47	0.44	22.0	13.8	93.7
	200	16	0.63	0.15	0.70	25.1	12.6	59.4
15% CuO–Fe <sub>2</sub> O <sub>3</sub>	30	16	1.73	0.41	0.60	26.3	13.2	89.6
	200	16	1.61	0.40	0.78	34.4	17.2	55.3

of external thermal heat, the burning voltage is significantly decreased. Similarly, the breakdown voltage, the minimum energy required to cause ionization, is reduced with external heat. This could be due to the additional energy gained by molecules by external heat, which increases their energy population in the excited states. Thus, they were ionized/decomposed easily. The effective capacitance (reactor capacitance) is, as given in eq 1, equal to dielectric capacitance for a fully packed system.<sup>43</sup> For the empty and QW-packed reactors, the effective capacitance does not vary much, which could be due to the similar total dielectric constant of the reactor and packing material. However, for the 15% CuO–Fe<sub>2</sub>O<sub>3</sub> packed reactor, the effective capacitance increases from 0.60 (30 °C) to 0.78 (200 °C); this could be attributed to the additional capacitance from the catalyst.

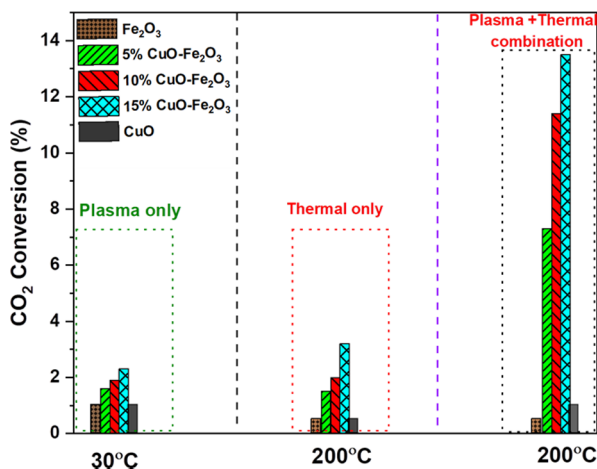
The external heating decreases the burning voltage and increases the effective capacitance, for all the three configurations investigated, owing to the increase in dielectric constant. As the charge accumulation increases with temperature, the charge injection per cycle ( $Q_{pk-pk}$ ) and half-cycle ( $dQ$ ) are also increased. The frequency of the charge-discharge cycle is also increased with external heating. This

could be correlated to the improved charge accumulation on the dielectric materials.

$$\frac{1}{C_{\text{Reactor}}} = \frac{1}{C_{\text{Dielectric}}} + \frac{1}{C_{\text{Gas}}} \quad (1)$$

**Catalytic Conversion of CO<sub>2</sub>.** For the catalytic conversion of CO<sub>2</sub> to CH<sub>3</sub>OH, all the reactions are carried out at atmospheric pressure, with the feed of CO<sub>2</sub> and H<sub>2</sub> in 1:3 ratio in a total feed flow rate of 100 mL/min. The CO<sub>2</sub> conversion was carried out in a QW-packed reactor under ambient conditions (30 °C and 1 atm), but significant CO<sub>2</sub> conversions (<2%) are not attained for all the studied catalysts despite having a good amount of CO<sub>2</sub> adsorption capacity (Table 2). The energy supplied in plasma discharges is insufficient to activate the strongly adsorbed CO<sub>2</sub> on the binary mixed metal oxide catalyst of the CuO–Fe<sub>2</sub>O<sub>3</sub> surface. This is in line with the observation seen from CO<sub>2</sub>-TPD experiments reported in Figure 3 and Supporting Information (Figure S8a,b). Under similar operating conditions, thermal catalysis was performed at 200 °C, and CO<sub>2</sub> conversion was slightly improved (>4%). CO<sub>2</sub> molecules are strongly adsorbed on these catalysts and do not desorb from the catalyst surface even at 200 °C (Figure 3).

To understand the influence of SIE on CO<sub>2</sub> conversion, the plasma input energy was varied from 0.43 to 4.67 kJ/L (0–18.2 kV) under ambient conditions (30 °C and 1 atm), and the corresponding CO<sub>2</sub> conversion is provided in Supporting Information (Figure S8a). CH<sub>3</sub>OH and CO were the main products quantified at the reactor outlet. The detailed product yields, that is, CH<sub>3</sub>OH and CO, are reported in Supporting Information (Figures S9a and 10a). The conditions, which yielded the best results, are presented in Figures 4 and 5a,b.



**Figure 4.** CO<sub>2</sub> conversion as a function of operating parameters for various catalysts. Plasma operating conditions are 18 kV, 50 Hz frequency, and feed flow rate: 100 mL/min SIE 4.67 kJ/L.

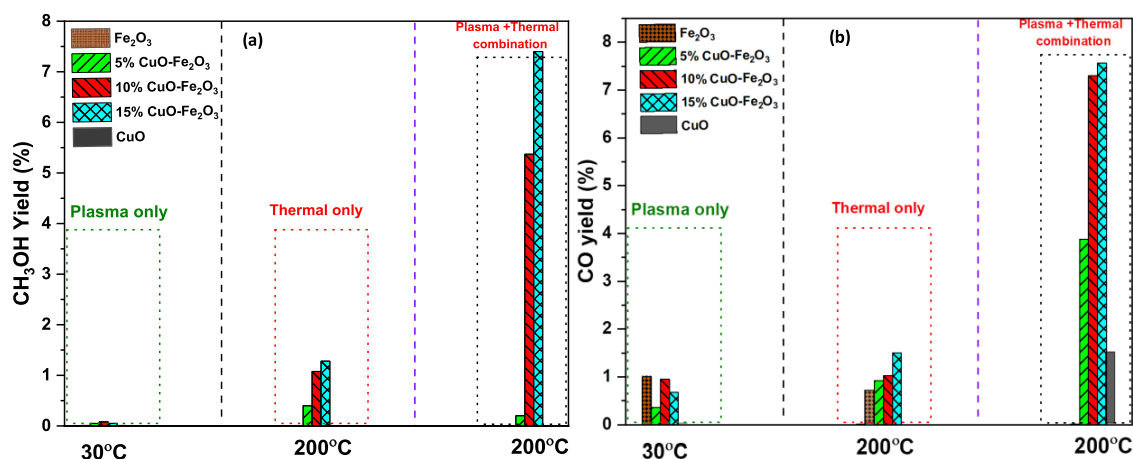
The results in Figure 4 are with 7.7 W input power (corresponding to an SIE of 4.67 kJ/L and 18.2 kV of the applied voltage). The CO<sub>2</sub> conversion in plasma catalysis under ambient conditions is 1.7, 1.9, and 2.3% for 5, 10, and 15% of the binary mixed metal oxide of CuO–Fe<sub>2</sub>O<sub>3</sub> at 4.67 kJ/L of SIE, respectively. Similarly, the CH<sub>3</sub>OH yield of <0.1% is obtained for all the catalysts, as seen in Figure 5a. The plasma catalysis shows very low conversion as the catalyst does not reach its optimum catalysis temperature to achieve the best performance. To evaluate the role of the catalyst bed temperature, it is varied from room temperature to 250 °C, which is provided in Supporting Information (Figures S8b, S9b and S10b). When the catalyst bed temperature is 200 °C, the CH<sub>3</sub>OH yield and selectivity are at peak compared to other

temperatures, as increasing the catalyst bed temperature increases the CO<sub>2</sub> conversion, but CH<sub>3</sub>OH production is reduced due to other product formation.

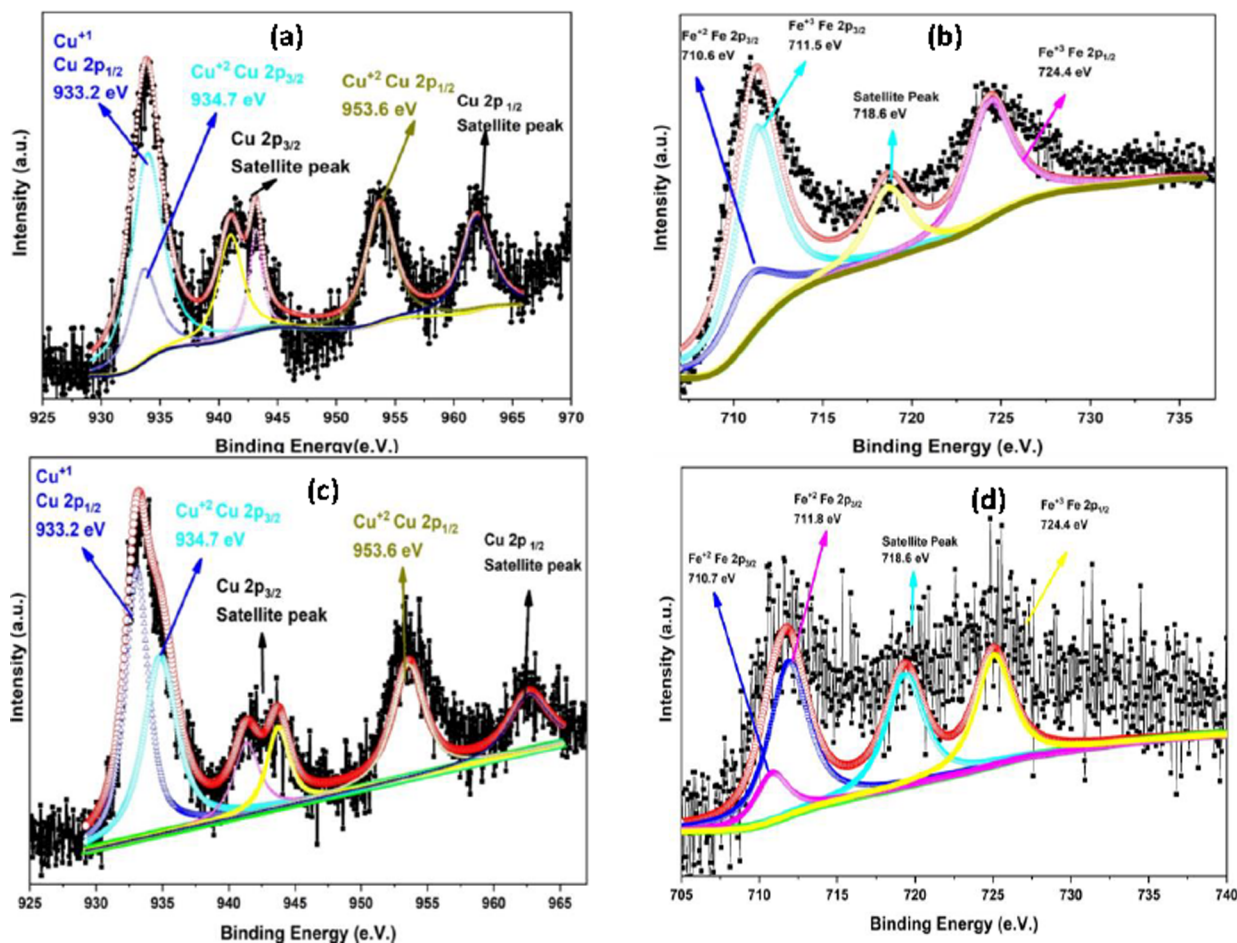
As can be seen from Figure 4, in thermal catalysis at 200 °C, the CO<sub>2</sub> conversion was 1.5, 2 and 3.2% for 5, 10, and 15% of CuO–Fe<sub>2</sub>O<sub>3</sub>, respectively. With the coupling of plasma and thermal heating, the CO<sub>2</sub> conversion is increased to 5.5, 10.9, and 13.5% for 5, 10, and 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalyst, respectively. In the absence of thermal heating, that is, in plasma catalysis alone, at 30 °C, the CO<sub>2</sub> conversion was 1.7, 1.9, and 2.3% for 5, 10, and 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalyst, respectively. In the coupled study (plasma + thermal heating), the influence of SIE on CO<sub>2</sub> conversion and product distribution is evaluated and provided in Supporting Information (Figures S8c, S9c and S10c). A synergistic effect between plasma discharge and thermal heating is observed for all catalysts investigated in this study.

Figure 5a shows the CH<sub>3</sub>OH yield as a function of different operating conditions. The synergistic effect of plasma with thermal heating significantly increased the CH<sub>3</sub>OH yield. In plasma catalysis alone, the CH<sub>3</sub>OH yield was <0.1%. The rise in the catalyst bed temperature from 30 to 200 °C raises the CH<sub>3</sub>OH yield to 1.3% for the 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalyst. The CH<sub>3</sub>OH yield was five- and sixfold higher than that of thermal and plasma catalysis alone. A maximum of 7.4% CH<sub>3</sub>OH yield was obtained for 15% CuO–Fe<sub>2</sub>O<sub>3</sub>; nevertheless, 5.3 and 0.1% CH<sub>3</sub>OH yield were obtained for 10 and 5% CuO–Fe<sub>2</sub>O<sub>3</sub> catalysts, respectively. Thus, it can be concluded that the amount of CuO mixing is beneficial for CH<sub>3</sub>OH production and CO<sub>2</sub> activation.

Figure 5b depicts the CO yield quantified at the reactor outlet. CO is produced via the following proposed pathway: (i) CO<sub>2</sub> dissociation induced by electron impact and then dissociation; (ii) reverse water gas shift reaction (RWGS); (iii) partial decomposition of intermediates/products produced during the hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH. For the catalyst, as shown in Figure 5b, the CO yield increases with an increase in CuO mixing. It is observed that in mixed metal oxides, with an increase in CuO mixing, the CH<sub>3</sub>OH as well as CO yield increases. In plasma and thermal catalysis reactions, the CO yield is <1%, which is further increased to 4% in coupled mode. A synergistic effect is observed when plasma and thermal heating is combined for CO<sub>2</sub> conversion and methanol production. This synergistic effect could be



**Figure 5.** (a) CH<sub>3</sub>OH yield as a function of plasma operating parameters. (b) CO yield as a function of plasma operating parameters.



**Figure 6.** XPS spectra for 15% CuO–Fe<sub>2</sub>O<sub>3</sub> before and after the reaction: (a) high resolution XPS for Cu 2p before the reaction, (b) high-resolution XPS for Fe 2p before the reaction, (c) high-resolution XPS for Cu 2p after the reaction, and (d) high-resolution XPS for Fe 2p after the reaction.

correlated to the new crystallite structure, that is, spinel and inverse spinel structure formation, under a reductive plasma atmosphere. Further catalyst surface analysis is needed to support this hypothesis.

The obtained products are in gas phase and need to be separated to make the process efficient. CH<sub>3</sub>OH and H<sub>2</sub>O could be separated using cooling traps maintained below  $-70$  °C.

#### Catalyst Modification Induced by Plasma Discharge.

The XRD diffraction patterns for the synthesized catalyst and spent catalyst are presented in Supporting Information (Figure S11). It is evidenced that the characteristic peaks for Fe<sub>2</sub>O<sub>3</sub> at 33° diminished completely after the plasma-catalytic reaction. This infers that the combined plasma and thermal heating changed the catalyst composition.

The 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalyst yielded the highest CH<sub>3</sub>OH yield, and it is further characterized by XPS before (fresh) and after the reaction (used). As can be seen in Figure 6a, the catalyst before the reaction shows the presence of Cu in two oxidation states, namely Cu<sup>+1</sup> (Cu 2p<sub>3/2</sub> peak at 933.2 eV) and Cu<sup>+2</sup> (934.7 eV).<sup>44,45</sup> The XPS measurements confirm the presence of CuFeO<sub>2</sub> and CuFe<sub>2</sub>O<sub>4</sub> in the catalyst. In this structure, Cu<sup>+2</sup> occupies tetrahedral voids, and Fe<sup>+3</sup> occupies octahedral voids. As reported in Figure 6b, the fresh catalyst exhibits the mixed oxidation states of Fe (+3 and +2). The peak centered at 711.5 eV that resulted from Fe 2p<sub>3/2</sub> is

indicative of the Fe<sup>+3</sup> oxidation state, and the peak centered at 710.6 eV is indicative of the Fe<sup>+2</sup> oxidation state.<sup>46–49</sup> Therefore, it could be proposed that CuFe<sub>2</sub>O<sub>2</sub> and CuFe<sub>2</sub>O<sub>4</sub> are formed after plasma treatment.

Figure 6c shows that the redox couple (Cu<sup>+2</sup>/Cu<sup>+1</sup>) equilibrium is shifted in the spent catalyst. As CO<sub>2</sub> hydrogenation is carried out in a reductive atmosphere, it could be expected that CuO, where Cu exists in a +2 state, undergoes reduction to a mixture of +2 and +1 oxidation states. Interestingly, after plasma treatment, the ratio of the [Cu<sup>+2</sup>]/[Cu<sup>+1</sup>] redox couple is lowered. The plasma ignition facilitates the reduction process and thus is expected to increase the catalytic activity as the Cu<sup>+1</sup> state is more active toward CO<sub>2</sub> hydrogenation than Cu<sup>+2</sup>.<sup>43,50–58</sup> This could be due to the fact that Cu<sup>+1</sup> sites are important for CO adsorption in the hydrogenation reactions of CO<sub>2</sub> to CH<sub>3</sub>OH.<sup>55</sup> More importantly, Cu<sup>+1</sup> provides stability for intermediates such as carbonates (CO<sub>3</sub><sup>2-</sup>), formates (HCOO<sup>-</sup>), and methoxy adsorbates (H<sub>3</sub>CO<sup>-</sup>) which are formed during CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH due to their higher heats of adsorption.<sup>55</sup>

A similar effect of partial reduction was also seen for the [Fe<sup>+3</sup>]/[Fe<sup>+2</sup>] redox couple. As seen from Figure 6d, the spent catalyst shows a lowering in the ratio of the [Fe<sup>+3</sup>]/[Fe<sup>+2</sup>] redox couple, which infers the partial reduction of Fe<sup>+3</sup> to Fe<sup>+2</sup>.<sup>59</sup>



Table 4. CH<sub>3</sub>OH Production and Energy Efficiency for Various Catalysts and Experimental Conditions

catalysts	input power (W)	operating conditions (°C, atm)	Feed flow rate (mL/min)	CO <sub>2</sub> conversion (%)	CH <sub>3</sub> OH space time yield (mmol/h g <sub>cat</sub> )	ref
Cu/γ-Al <sub>2</sub> O <sub>3</sub>	10.0	25, 1	40.0	21.2	0.3	16
CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	500.0	200, 8	250.0	11.0	NA	35
Pd/In <sub>2</sub> O <sub>3</sub>	30.0	25, 1	40.0	24.9	4.5	65
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	30.0		40.0	25.6	4.4	
In <sub>2</sub> O <sub>3</sub>	30.0		40.0	13.1	1.6	
5% CuO/Fe <sub>2</sub> O <sub>3</sub> /QW	2.0	200, 1	100.0	16.7	9.3	4
10% NiO–Fe <sub>2</sub> O <sub>3</sub>	7.2		100.0	6.2	11.9	36
15% Co <sub>x</sub> O <sub>y</sub> /MgO	10.0	25, 1	28.0	33.0	5.0	37
5% CuO–Fe <sub>2</sub> O <sub>3</sub>	7.7	200, 1	100.0	7.3	2.06	this work
10% CuO–Fe <sub>2</sub> O <sub>3</sub>	7.7		100.0	10.9	6.2	
15% CuO–Fe <sub>2</sub> O <sub>3</sub>	7.7		100.0	18.2	13.0	

**CO<sub>2</sub> Activation Reaction Mechanism.** In plasma-only conditions, the ignition of plasma with a CO<sub>2</sub>/H<sub>2</sub> mixture leads to the dissociation of CO<sub>2</sub> and H<sub>2</sub>. CO<sub>2</sub> could be dissociated (electron impact dissociation or via electron impact vibrational excitation) to produce CO. Similarly, H<sub>2</sub> is dissociated by electron impact dissociation to produce hydrogen radicals. Further, several other reactions among radicals could produce formaldehyde (CH<sub>2</sub>O). CH<sub>2</sub>O hydrogenated to CH<sub>3</sub>OH<sup>16,60,61</sup> along with H<sub>2</sub>O as a byproduct.<sup>3</sup>

The heterogeneous catalyst surface in the discharge zone stimulates the adsorption–desorption process, especially the radical and gaseous species in the gas phase undergo recombination and/or quenching phenomena. Plasma-created radicals in the boundary layer near the catalyst surfaces can be adsorbed directly, and this will likely require much lower energy.<sup>62–64</sup> CO formed in the plasma gas-phase reactions can be directly adsorbed onto the catalyst surface, which is unique in the plasma-catalytic CO<sub>2</sub> hydrogenation process.

In the coupled mode, that is, plasma catalysis with thermal heating, enhancement in the reactor performance is observed. It could be stated that the population distribution of CO<sub>2</sub> molecules in the vibrationally excited state was much higher than that of a plasma catalyst or plasma-only condition carried out at room temperature. Both electron impact dissociation and electron impact vibrational excitation could contribute to CO<sub>2</sub> dissociation. Furthermore, the additional energy supplied in heat increases the reaction rate as the adsorbed species are vibrationally active.

**Comparing the CH<sub>3</sub>OH Production Efficiency with the Literature.** Table 4 shows the CH<sub>3</sub>OH space–time yield given as mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub> for various catalyst-packed reactors. The CH<sub>3</sub>OH yield is normalized with the feed flow rate, the concentration of CO<sub>2</sub>, and grams of catalyst used in the study. The CH<sub>3</sub>OH production from CO<sub>2</sub> is an exothermic process; thus, Wang et al.<sup>16</sup> have used water as a ground electrode in the DBD reactor to remove the heat produced in the reaction. The removal of heat, one of the products of CO<sub>2</sub> hydrogenation, could drive the reaction forward. Using this setup, 21.2% CO<sub>2</sub> conversion with 11.2% CH<sub>3</sub>OH yield was achieved. The CH<sub>3</sub>OH space–time yield for the process was 0.3 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub>. Men et al.<sup>65</sup> harnessed the oxygen vacancies on the Pd/In<sub>2</sub>O<sub>3</sub> catalyst surface, and 8.9% of CH<sub>3</sub>OH yield with 24.5% CO<sub>2</sub> conversion was achieved. The corresponding CH<sub>3</sub>OH space–time yield was 4.5 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub>, whereas the commercial CH<sub>3</sub>OH synthesis catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, under similar conditions, delivered a CH<sub>3</sub>OH space–time yield of 4.4 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub>. In our previous

work, we achieved 16.7% CO<sub>2</sub> conversion with 4.4% CH<sub>3</sub>OH yield using 5% CuO–Fe<sub>2</sub>O<sub>3</sub> loaded on QW. The CH<sub>3</sub>OH space–time yield of 9.3 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub> was attained.<sup>4</sup> In another study, 6.6% CO<sub>2</sub> conversion with 6% CH<sub>3</sub>OH yield was obtained with a 10% NiO–Fe<sub>2</sub>O<sub>3</sub> catalyst, and the corresponding CH<sub>3</sub>OH space–time yield was 11.9 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub>.<sup>36</sup> In the current study, with an increase in CuO mixing, the CO<sub>2</sub> conversion and CH<sub>3</sub>OH yield increased. The CH<sub>3</sub>OH space–time yields for 5, 10, and 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalysts are 2.7, 6.2, and 13 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub> respectively. The obtained CH<sub>3</sub>OH space–time yield is 2.9-fold higher than that of the commercial catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> operated at 30 °C with 45.6 kJ/L (about 10-fold high energy) SIE.

## CONCLUSIONS

In this work, we have successfully shown that CO<sub>2</sub> could be converted to CH<sub>3</sub>OH over CuO–Fe<sub>2</sub>O<sub>3</sub> binary mixed metal oxides. It is observed that an increase in CuO mixing with Fe<sub>2</sub>O<sub>3</sub> leads to the formation of mixed spinel and inverse spinel, namely CuFeO<sub>2</sub> and CuFe<sub>2</sub>O<sub>4</sub>, which is confirmed by XRD and XPS studies. The catalysts exhibited poor performance for CO<sub>2</sub> conversion and CH<sub>3</sub>OH production in plasma catalysis and thermal catalysis alone due to insufficient energy. However, when the plasma discharge and external thermal heating are combined, significant enhancement in CO<sub>2</sub> conversion and CH<sub>3</sub>OH production is observed. The detailed investigation of catalysts, before and after the reaction, reveals that plasma in combination with heating leads to a partial reduction of Cu<sup>+2</sup> to Cu<sup>+1</sup> and Fe<sup>+3</sup> to Fe<sup>+2</sup>. These in situ changes lead to enhancement in CO<sub>2</sub> conversion and CH<sub>3</sub>OH production. The 15% CuO–Fe<sub>2</sub>O<sub>3</sub> catalyst is the best catalyst with 13 mmol<sub>CH<sub>3</sub>OH</sub>/h g<sub>cat</sub> CH<sub>3</sub>OH space–time yield, which is about 2.9-fold higher than the values reported in the literature. The energy efficiency could be further improved by packing the catalyst in a different mode in the reactor and optimizing the experimental conditions.

## EXPERIMENTAL SECTION

**Catalyst Synthesis.** The sol–gel process was used to synthesize the catalysts, and the detailed procedure is reported elsewhere.<sup>4</sup> In brief, various amounts of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were combined with Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and dissolved in 50 mL of ethanol. 10% of NH<sub>4</sub>OH solution was added at the rate of 1 mL/min to complete the precipitation (pH = 12), and the sol was aged overnight at 85 °C. The excess NH<sub>4</sub>OH residue was washed with distilled water and then centrifuged at 7000 rpm

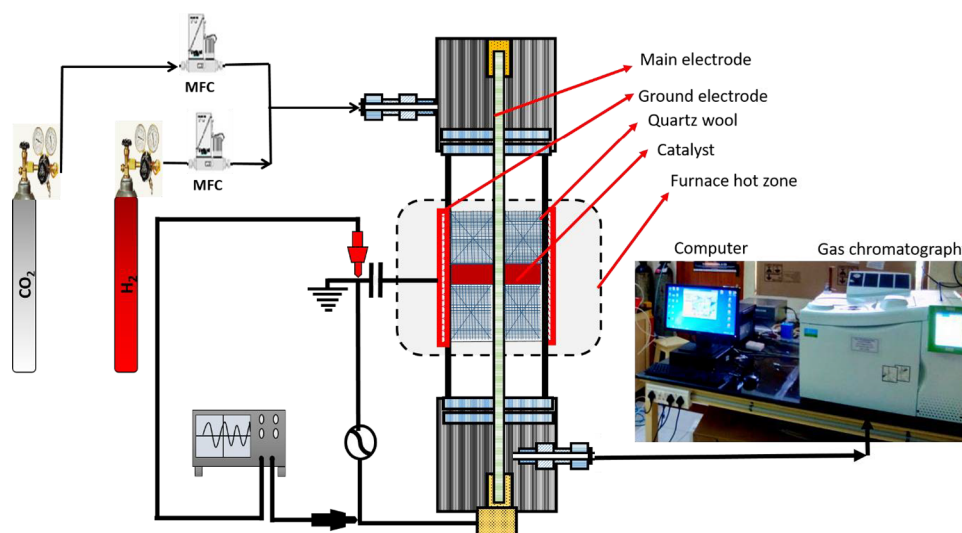


Figure 7. General schematic of the experimental setup. (Photograph courtesy of Nitesh Joshi.)

for 10 min. The washed sol was dried at 100 °C for 6 h and then calcined at 600 °C for 6 h.

**Instrumentation Technique.** The XRD results are collected using a PANalytical X'pert3 equipment [Cu K $\alpha$  1.54 Å, 40 kV, 40 mA]. The nanoscale pictures generated by a high-resolution field emission electron microscope (FESEM, Quanta 200) and a high-resolution transmission electron microscope (HRTEM JEOL, Japan) were used to study the catalyst surface morphology. PHI Versaprobe III was used for the X-ray photoelectron spectroscopy (XPS) study to provide further information on the catalyst's elemental composition and oxidation state. The catalysts' total surface area (BET) was evaluated using an Autosorb iQ Station at 77 K by N<sub>2</sub> physisorption. The catalysts were degassed for 3 h before the analysis in a He atmosphere at 150 °C. CO<sub>2</sub> adsorption and CO<sub>2</sub> TPD were carried out using a homemade setup, as shown in Supporting Information (Figure S5). The CO<sub>2</sub> sensor (model: CM-0121, 100% CO<sub>2</sub> sensor) COZIR 100% was used to monitor the CO<sub>2</sub> concentration.

**CO<sub>2</sub> Adsorption–Desorption Experiments.** The CO<sub>2</sub> adsorption–desorption experiments were carried out using the setup shown in Figure S5. A mixture of 10% CO<sub>2</sub> + 90% N<sub>2</sub> was first passed through a bypass (without a reactor) to validate the mixture concentration; later, the mixture was passed through the reactor, which housed a catalyst (0.3 g). After reaching the CO<sub>2</sub> adsorption/desorption equilibrium, at room temperature, the streamflow was switched to pure N<sub>2</sub> to remove the weakly adsorbed CO<sub>2</sub> from the catalyst surface. For estimating the concentration of basic sites on the catalyst surface, the catalyst bed temperature was linearly increased to 800 °C (monitored with an external thermocouple) with a ramp of 5 °C/min, and the temporal evolution of CO<sub>2</sub> desorption was monitored using a CO<sub>2</sub> sensor. A more detailed experimental procedure is reported elsewhere.<sup>66</sup>

**Plasma Reactor and the Experimental Setup.** The general schematic for the experimental system is illustrated in Figure 7. The coaxial tubular reactor is made up of a 600 mm long quartz tube with a 25 mm outer diameter (OD), a 3 mm wall thickness, and a 19 mm inner diameter (ID). A stainless steel rod was housed in a quartz tube, which served as an inner electrode and resulted in a 3.5 mm discharge gap. A 100 mm stain steel mesh was wrapped around the quartz tube and acted

as a ground electrode, resulting in a 17.4 cm<sup>3</sup> discharge volume and a gas residence time of 10.4 s<sup>-1</sup>. A step-up transformer provided by the Jayanti transformer was used to generate the plasma discharge (Chennai, India). The transformer runs at a constant frequency of 50 Hz, and the applied voltage could be adjusted between 0 and 40 kV (peak to peak). As shown in Figure 7, two high voltage probes (HV) with a 1:100 attenuation were used to measure the applied and discharge voltages. The HV probes were connected to an oscilloscope (Keysight, 70 MHz 2 Ga/s) which monitored the input signal from the probes. The Lissajous technique is used to compute the power dissipated in the reactor.<sup>67,68</sup>

**Gas-Phase Characterization/Quantification.** For all the experiments, the CO<sub>2</sub>-to-H<sub>2</sub> mixing ratio was set as 1:3, and the total flow was also fixed at 100 mL/min using precalibrated KOFOLOC mass flow meters, as shown in Figure 7. Before and after the experiment, the gaseous products at the reactor outlet were analyzed using online gas chromatography. The reactor outlet was connected to the gas-sampling loop (2 mL). The TCD detector connected to the ShinCarbon ST column (mesh size of 100/120, length of 2 m, and an inner diameter of 1/11th inch) are employed for eluting the reactants and the products) was used for product identification and quantification.

The reaction output, such as CO<sub>2</sub> conversion, product selectivity, yield, and energy efficiency, were calculated using the following equations.

$$\text{Conversion of CO}_2 (\%) = \frac{[\text{CO}_{2(\text{in})} - \text{CO}_{2(\text{out})}]}{[\text{CO}_{2(\text{in})}]} \times 100 \quad (2)$$

$$\text{Selectivity of CO } (\%) = \frac{[\text{CO}]}{[\text{CO}_{2(\text{in})} - \text{CO}_{2(\text{out})}]} \times 100 \quad (3)$$

$$\text{Selectivity of CH}_4 (\%) = \frac{[\text{CH}_4]}{[\text{CO}_{2(\text{in})} - \text{CO}_{2(\text{out})}]} \times 100 \quad (4)$$

$$\text{Selectivity of CH}_3\text{OH} (\%) = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}_{2(\text{in})} - \text{CO}_{2(\text{out})}]} \times 100 \quad (5)$$



$$\begin{aligned} & \text{Yield (CH}_3\text{OH}(\%), \text{CO}(\%), \text{CH}_4(\%)) \\ &= \frac{[(S_{\text{CH}_3\text{OH}(\%)} S_{\text{CO}(\%)} S_{\text{CH}_4(\%)} \times X_{\text{CO}_2}(\%)]}{100} \end{aligned} \quad (6)$$

$$\begin{aligned} & \text{CH}_3\text{OH Space Time Yield (mmol h}^{-1} \text{ g cat}^{-1}) \\ &= \frac{F_{\text{CO}_2\text{in}} \times S_{\text{CH}_3\text{OH}} \times X_{\text{CO}_2}}{W_{\text{cat}}} \times 1000 \end{aligned} \quad (7)$$

$S_{\text{CH}_3\text{OH}}$  and  $X_{\text{CO}_2}$  are the selectivity of  $\text{CH}_3\text{OH}$  and conversion of  $\text{CO}_2$ , respectively.  $F_{\text{CO}_2\text{in}}$  is the molar flow rate of  $\text{CO}_2$ , and  $W_{\text{cat}}$  is the weight of the catalyst.

**Experimental Procedure.** For all the experiments, that is, plasma, thermal, and plasma + thermal combination, about  $0.5 \pm 0.05$  g of metal oxide was placed in the center of the quartz tube in sandwich mode using quartz wool (3.7 g). Before each experiment, the catalyst was pretreated at  $300^\circ\text{C}$  for 1 h under 100 mL/min of zero air. Then, the reactor was cooled down to room temperature, and the mixture of  $\text{H}_2:\text{CO}_2$  (3:1) was sent to the reactor inlet. The blank concentrations of  $\text{CO}_2$  and  $\text{H}_2$  were obtained after reaching the adsorption–desorption equilibrium at the reactor downstream.

For thermal catalysis, the catalyst bed temperature was linearly varied from 100 to  $250^\circ\text{C}$ . The online sampling was carried out after reaching the steady state (60 min of the thermal catalytic process). For each set temperature, a minimum of three samples were analyzed to ensure reproducibility, and a minimum of three experiments were performed to reduce the error percentage.

For the plasma + thermal catalytic process, the plasma discharge was ignited after reaching the thermal catalytic steady state (about 60 min of the thermal catalytic process) with the set temperature. The online sampling is performed after 10 min of continuous plasma treatment. Notably, during the plasma treatment, the furnace was switched off to avoid electrical perturbation. It is observed that the temperature difference, before and after plasma treatment, was less than  $\pm 10^\circ\text{C}$ .

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c00915>.

HRSEM, EDAX, elemental distribution,  $\text{N}_2$  adsorption–desorption isotherms,  $\text{CO}_2$  adsorption,  $\text{CO}_2$ -TPD, evaluation of electrical parameters of plasma,  $\text{CO}_2$  conversion and product distribution in plasma catalysis, thermal catalysis, and both combined (plasma catalysis + thermal heating), and XRD diffraction data of the fresh and spent catalysts (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Sivachandiran Loganathan – Laboratory of Plasma Chemistry and Physics (LPCP), Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Chennai 603203, India; Plasma Research Laboratory, Department of Chemical and Biomolecular Engineering, and Center for Air and Aquatic Resources Engineering & Science, Clarkson University, Potsdam, New York 13699, United States; [orcid.org/](https://orcid.org/)

0000-0001-7375-0134; Email: [sloganat@clarkson.edu](mailto:sloganat@clarkson.edu), [sivachal@srmist.edu.in](mailto:sivachal@srmist.edu.in)

### Author

Nitesh Joshi – Laboratory of Plasma Chemistry and Physics (LPCP), Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Chennai 603203, India; Present Address: School of Chemical Sciences, Goa University, Taleigao Plateau, 403206 Goa, India; [orcid.org/0000-0002-3985-6565](https://orcid.org/0000-0002-3985-6565)

Complete contact information is available at:

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### Notes

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