Plasma-catalytic CO_2 hydrogenation over Fe-Cu-based perovskite catalysts

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Introduction

With the intention of eradicating the serious environmental concern resulting from excessive anthropogenic CO_2 emission, a hybrid dielectric barrier discharge (DBD) plasma-catalysis system was developed for the thermodynamically unfavourable reverse water-gas shift (RWGS) reaction. A variety of $LaMO_3$ (M = Mn, Ni, Fe, Ce, Co) perovskite catalysts were synthesised and assessed. With $LaFeO_3$ exhibiting the best RWGS performance, a series of B-site partial substitution $La_{0.5}Sr_{0.5}Fe_xCu_{1-x}$ (x = 1, 0.9, 0.8) perovskite catalysts were evaluated further. $La_{0.5}Sr_{0.5}Fe_{0.9}Cu_{0.1}O_{3+\delta}$ displayed the greatest potential to promote the selective conversion of CO_2 to CO, and simultaneously inhibited the generation of CH_4. To further investigate the mechanism of plasma-induced surface reactions, a 0D plasma kinetics model was also developed; the results indicate that CHO radicals play a vital role in the plasma-catalytic RWGS process.
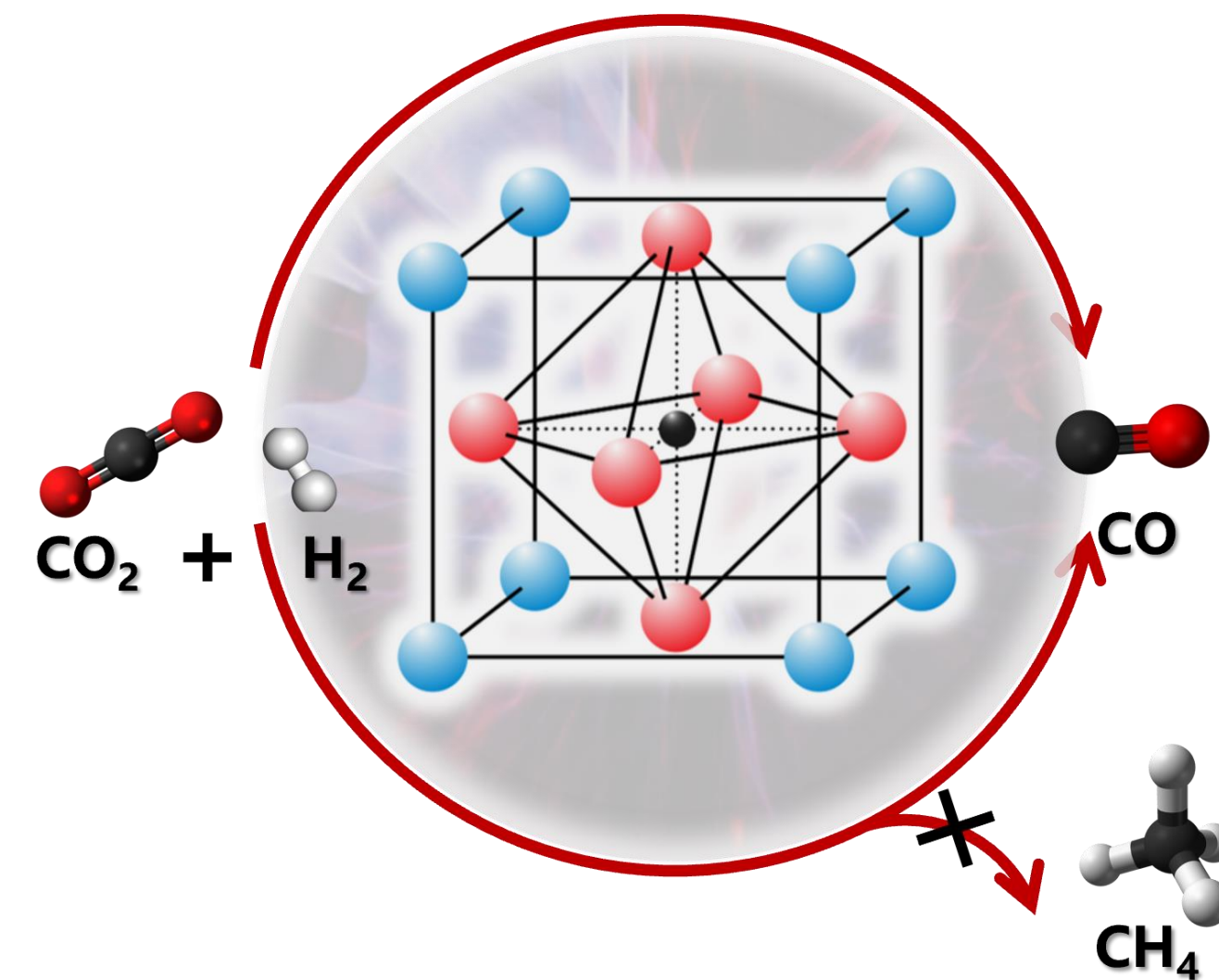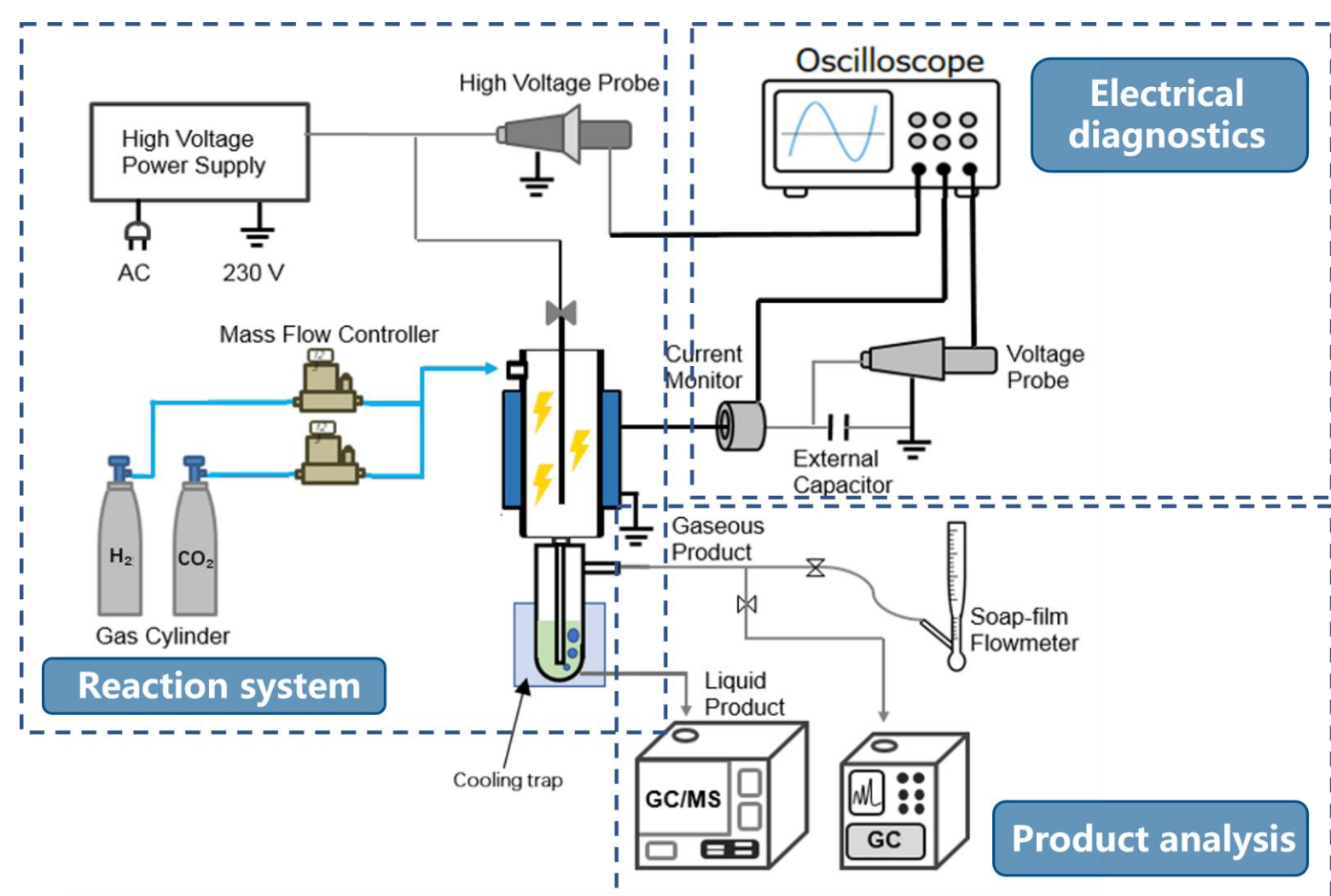

Experimental Setup

Fig. 1 Schematic diagram of the experimental setup.

DBD reactor (cooled)
- Gas gap: 2 mm
- Length: 50 mm
- Electrode: stainless steel

AC Power supply
- Frequency: 9.3 kHz
- Voltage: up to 30 kV

Power/Temperature
- Discharge power: 10 W
- Temperature: ~180 °C

Working gas
- CH_4/H_2= 1:1
- Flow rate: 30 ml/min

Catalysts (1g)
- Sol-gel method
- LaM-perovskite
- LaSrFeCu-perovskite

Experimental Results

Fig. 1 The performance of $LaMO_3$(M = Mn, Ni, Fe, Ce, Co) catalysts: (a) conversion; (b) selectivity; and the performance of $La_{0.5}Sr_{0.5}Fe_xCu_{1-x}O_3$ (x = 1.0, 0.9, 0.8) perovskite catalysts: (c) conversion; (d) selectivity.

- ☐ Coupling plasma with perovskite catalysts significantly enhanced the performance of RWGS reactions in both conversion and selectivity.
- ☐ Among the tested $LaMO_3$ samples, the highest CO2 conversion of 13.7% and CO selectivity of 82.3% are obtained with $LaFeO_3$ catalyst, while $LaNiO_3$ generates more CH_4 than other samples.
- ☐ A modest substitution of Fe by Cu (x = 0.9, LSFC5591) improved the performance, achieving the highest CO_2 conversion of 17.1% and CO selectivity of 96.8%.
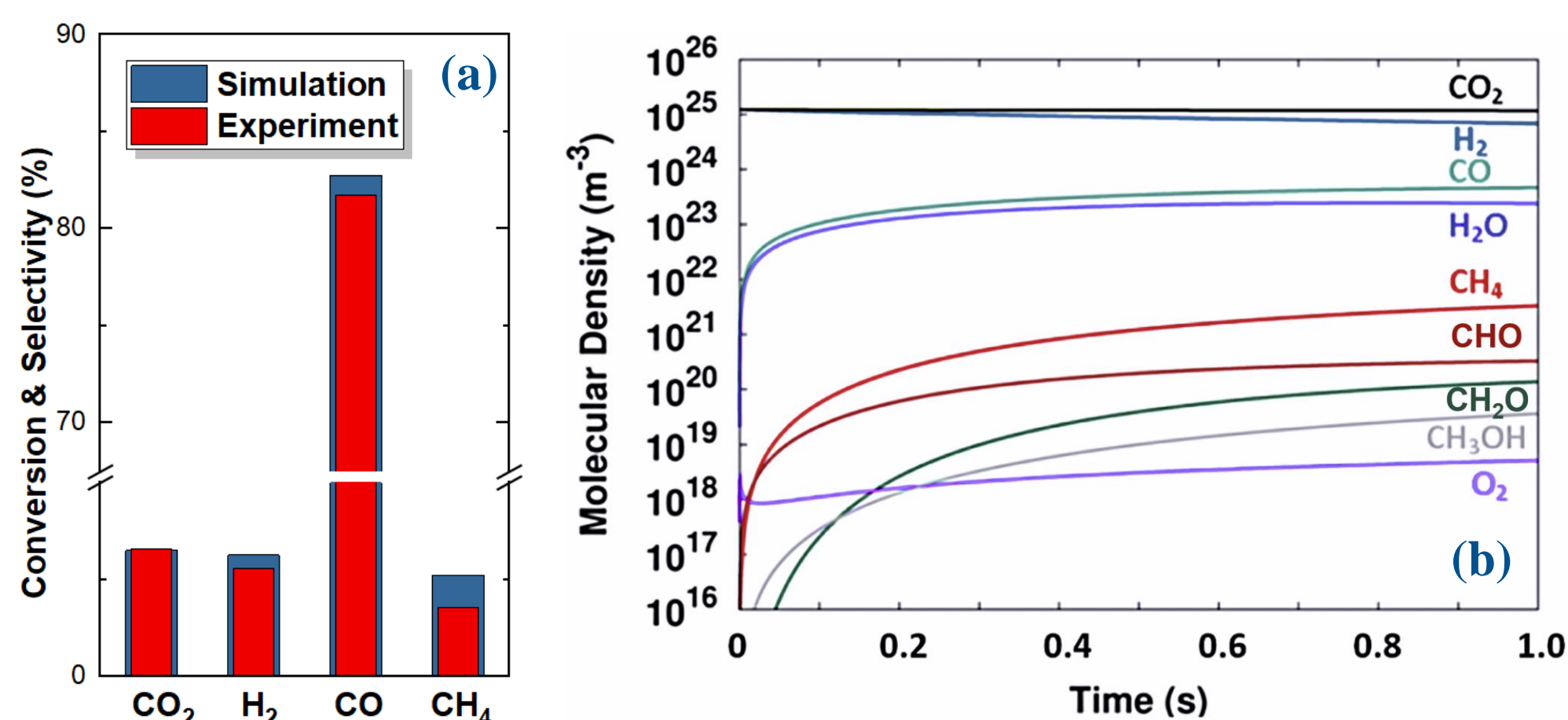
Discussion and Reaction Mechanism

Fig. 2 (a) Comparison of conversion and selectivity obtained by 0D kinetics modelling with experimental data; (b) Averaged densities of the major species as a function of the residence time.

- ☐ A 0D model was developed with ZDPlaskin code, the results showed a reasonable coincidence with the experimental values.
- ☐ CO_2 dissociation predominates the CO generation process; nevertheless, CHO plays a significant part in the contribution and enhances the catalytic surface reactions that create CO.
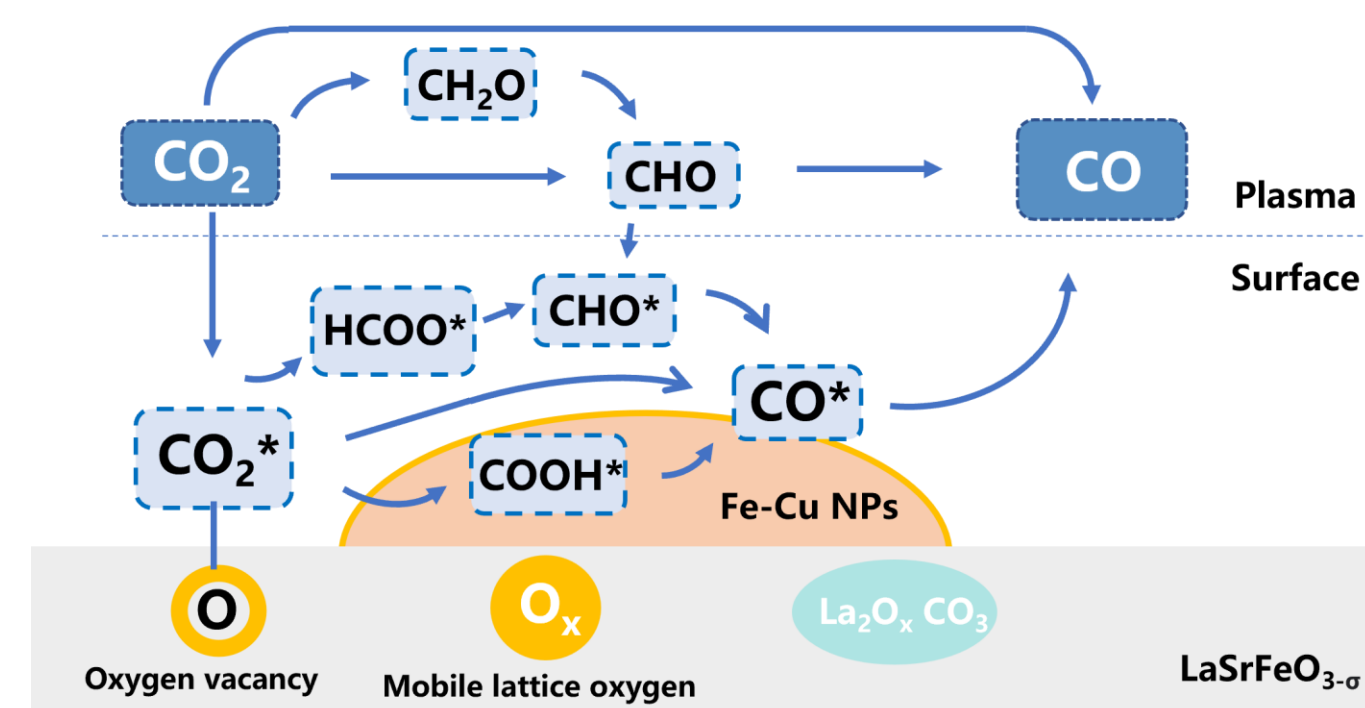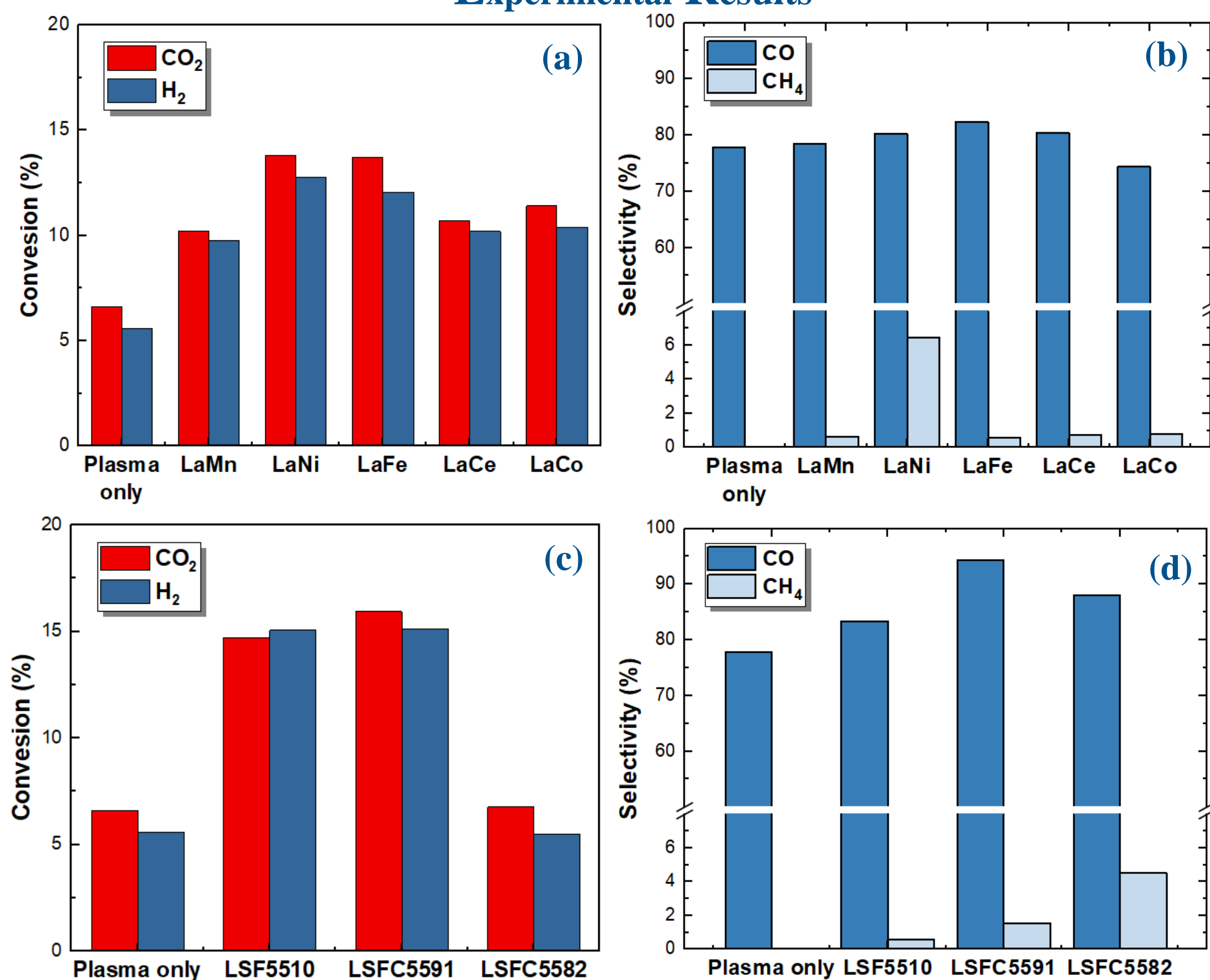

Fig. 3 Schematic diagram of the proposed reaction mechanism of plasma-catalytic RWGS on LSFC5591 catalyst.

- ☐ The catalyst characterisation revealed that higher metal dispersion, smaller particle size, stronger metal-support interaction, and an electronically richer state of Fe were achieved by the formation of Fe-Cu alloy, which facilitated the adsorption and conversion of CO_2.
- ☐ Meanwhile, more oxygen vacancies and higher oxygen mobility were created by the remaining LSFC5591 perovskite structure, which promoted the selective conversion of CO_2 to CO.
- ☐ CHO generated by the plasma enhanced formate mechanism pathway, which led to a higher CO selectivity.

Significance

The above results illustrate the feasibility of employing NTP for the RWGS process under ambient circumstances, and perovskite catalysts may be utilised to modify the product distribution. Due to the formation of uniform Fe-Cu alloys and presence of residual perovskite structures, the B-site partial substitution perovskite catalyst LSFC5591 catalyst shows potential in the selective conversion of CO_2 to CO while suppressing CH_4 formation. Therefore, the perovskite catalysts also illuminate an alternate method for designing plasma-catalysis systems to produce desired compounds.