Supporting Information of

Plasma-chemical promotion of catalysis for CH$_4$ dry reforming: unveiling plasma-enabled reaction mechanisms

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S1. The effect of Helium on plasma chemistry

Practically, helium must be avoided for economic reason. The role of helium is “diluent gas” (or called “balance gas”) in plasma-assisted DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) experiment. The diluent gas is necessary in IR experiment to dilute the reaction gases. Otherwise, the high concentration of reaction gases will lead an uncontrollable signal saturation of IR spectra [1], which is not favor for in situ measurement. Another technical reason is that helium can decrease the applied voltage significantly which minimizes electromagnetic noise during plasma-DRIFTS experiment. There are some similar plasma-IR studies with diluent gas, e.g., helium [2], and argon [1, 3, 4].

The important gas phase plasma chemistry is the secondary reactions induced by metastable helium. Because the excitation threshold of metastable helium is high (19.84 eV), Penning ionization of CO$_2$ (or CH$_4$), stepwise ionization of metastable helium, and the charge transfer of He$^+$ ions with CO$_2$ (or CH$_4$) become significant besides electron impact inelastic collision [5, 6]. Although electron density increases by metastable helium, it does not produce vibrationally excited species.

Yuan et al performed numerical simulation of atmospheric pressure homogeneous helium discharge with a trace N$_2$ [6]. The largest electric field was formed in the plasma sheath, showing 4 kV/cm which corresponds to the reduced electric field of 20 Td at 600 Torr and 300 K [6]. The mean electron energy in the plasma sheath is as high as 3 eV and it would be around 1 eV in the bulk region. In the case of DBD (dielectric barrier discharge), streamer breakdown occurs which would create larger electric field than homogeneous glow-like discharge. Ramakers et al studied discharge behavior of helium and argon DBD with a trace CO$_2$ (5 vol%) [7]. The gas breakdown voltage decreases remarkably due to the contribution of metastable species. Moreover, CO$_2$ conversion behavior in Ar and He is essentially unchanged, indicating that mean electron energy is smaller than 5 eV. In overall, helium would increase electron number density
via metastable species, but mean electron energy and thus electron collision kinetics would not change to a large extent.

**S2. Ex situ CO$_2$-temperature programmed desorption**

Ex situ CO$_2$-TPD (temperature programmed desorption) was performed in a quartz tube reactor, a temperature controllable furnace and a quadruple mass spectrometer (QMS, Prisma-100; Pfeiffer Vacuum GmbH), which are depicted in Figure S1 [8, 9]. The catalyst pellet of Ni/Al$_2$O$_3$ or La-Ni/Al$_2$O$_3$ (ca. 11 g) was pretreated by H$_2$/Ar flow (100/1000 mL/min) at 600 °C for 60 min. CO$_2$-TPD was carried out based on two control groups at 500 °C with 500 cm$^3$/min CO$_2$ flow: plasma CO$_2$ treatment ($SEI = 2.7$ eV/molecule) and thermal CO$_2$ treatment. After 60 min of thermal/plasma CO$_2$ treatment, a rapid cooling program was carried out with a rate of ca. 50 °C/min in an argon atmosphere to avoid surface species desorption during rapid cooling. After the catalyst temperature reached 25 °C, the CO$_2$-TPD started with 1000 cm$^3$/min Ar at a heating rate of 10 °C/min. Figure S2 shows the CO$_2$-TPD patterns of the Ni/Al$_2$O$_3$ catalyst, where peaks I’ and III’ are assigned to carbonate desorption over the interface between Ni and Al$_2$O$_3$.

Figure S1. Experimental setup for CO$_2$-TPD [8, 9].
Figure S2. CO$_2$-TPD patterns of Ni/Al$_2$O$_3$ after 500 °C treatment: (a) thermally activated CO$_2$, (b) plasma-activated CO$_2$. CO$_2$ flow rate was 500 mL/min at 10 kPa. Heating rate was 10 °C/min.

S3. Summary of DRIFTS peaks

Table S1 Carbonate structure over the La-Ni/Al$_2$O$_3$ catalyst and vibration assignments of the DRIFTS peaks

<table>
<thead>
<tr>
<th>Species</th>
<th>Monodentate carbonate</th>
<th>Bidentate carbonate</th>
<th>Polydentate carbonate</th>
<th>Bridged carbonate</th>
<th>Bicarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schematic structure*</td>
<td>O ═ O</td>
<td>O ═ O</td>
<td>O – M</td>
<td>O</td>
<td>O – O – O ─ O – H</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Vibration mode and wavenumber (cm$^{-1}$)</td>
<td>$\nu_{as}$ OCO at 1425 cm$^{-1}$</td>
<td>$\nu_{as}$ OCO at 1560 cm$^{-1}$</td>
<td>$\nu_{as}$ CO$_3$ at 1500 cm$^{-1}$</td>
<td>$\nu$ C=O at 1720 cm$^{-1}$</td>
<td>$\nu_{as}$ OCO at 1655 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\nu_{s}$ OCO, at 1345 cm$^{-1}$</td>
<td>$\nu_{s}$ OCO, at 1290 cm$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>[10-12]</td>
<td>[10]</td>
<td>[13, 14]</td>
<td>[14, 15]</td>
<td>[12, 13, 16-19]</td>
</tr>
</tbody>
</table>

*M represents the coordination metal, lanthanum in this study
**S4. CH$_4$/CO$_2$ activation over La-Ni/Al$_2$O$_3$ at 200 °C**

CH$_4$ was introduced with CO$_2$ over the carbonate containing La-Ni/Al$_2$O$_3$. In spectrum (a) in Figure S3, the gas phase CH$_4$ was detected as the peaks at 1304 cm$^{-1}$ and 3015 cm$^{-1}$. The product CO (g), the intermediate species CH$_x^*$ (in the range of 2800 to 3000 cm$^{-1}$ [20, 21]) and CH$_3$O$^*$ (1750 cm$^{-1}$ [22-24]) were not detected, illustrating that CH$_4$ dehydrogenation did not occur at 200 °C. In spectrum (b), plasma was employed. The peak at 1560 cm$^{-1}$ (bidentate carbonate) was enhanced slightly by plasma. However, the missing CH$_x^*$ ($x$=1-3), CH$_3$O$^*$ and CO (g) imply that plasma at 200 °C is difficult to induce CH$_4$ chemisorption and dehydrogenation. Besides, the intensity of bidentate carbonate peak at 1560 cm$^{-1}$ was enhanced with plasma-on (spectrum (b)) refers to the scale bar (red color), which corresponds with the results in section 3.1.1.

![Figure S3. DRIFTS spectra for CO$_2$/CH$_4$/He (8.3 vol%, 120 mL/min) activation over La-Ni/Al$_2$O$_3$ at 200 °C: (a) plasma-off; (b) plasma-on.](image)

**S5. Oxidation-reduction behavior of La-Ni/Al$_2$O$_3$**

Our previous work confirmed the oxidation-reduction behavior of Ni catalysts by Raman spectroscopy and optical microscopy [13]. The oxidation-reduction behavior enables a change in the transparency of dielectric materials. The absorbance spectra are obtained by the following equation (Beer’s law) based on the transmittance spectra in the background measurement.

$$A (ν) = 2 – \log (%T (ν))$$

Here, $A$ and %$T$ represent the absorbance and percent transmittance, respectively. $ν$ represents the wavenumber (cm$^{-1}$). The absorbance spectra of La-Ni/Al$_2$O$_3$ (thermal H$_2$ reduced sample) and La-NiO/Al$_2$O$_3$ (thermal CO$_2$ oxidized sample) are shown in Figure S4 (a) and (b),
respectively. The spectrum (a) of the reduced sample shows an increase in the profile compared with that of the oxidized sample in the range of 1500–4000 cm$^{-1}$, as well as 600–800 cm$^{-1}$, indicating that the absorbance of the infrared signal increases in the case of the H$_2$-reduced sample (i.e., La-Ni/Al$_2$O$_3$). It should be noted that a strong absorbance band is observed in the range of 800–1500 cm$^{-1}$, which is subtracted as background.

Figure S4. Absorbance spectrum of (a) La-Ni/Al$_2$O$_3$ and (b) La-NiO/Al$_2$O$_3$ under He flow (100 mL/min) at 600 °C.

In Figure S5, the spectrum recorded at 1 min shows carbonate species (1200-1600 cm$^{-1}$). Ni nanocrystals were simultaneously oxidized by thermal CO$_2$ to NiO. When the H$_2$ flowed to the DRIFTS cell from 5 min to 15 min instead of CO$_2$, the baseline lifted upwards, which was attributed to NiO reduction by H$_2$. Carbonates (between 1200 and 1600 cm$^{-1}$) were consumed at 5 min and gradually disappeared after 10 min. A weak OH$^+$ band (3700 cm$^{-1}$) was detected at 5 min in the inset figure. This indicates that OH$^+$ species are the intermediate product when surface hydrogen reacts with carbonates [25] because the decomposition of H$_2$ easily forms adsorbed H species on Ni [26-28]. The bands of gas phase H$_2$O (1250 to 2000 cm$^{-1}$ and 3500 to 4000 cm$^{-1}$) were not clearly detectable, suggesting that H$_2$O may not be produced via the reduction of NiO or carbonates. After 15 min, CO$_2$ was introduced instead of H$_2$, and then the baseline “turned back” to oxidized conditions at 30 min with carbonate peaks, which was similar to the spectrum at 1 min.
Figure S5. DRIFT spectra of oxidation-reduction behavior on La-Ni/Al$_2$O$_3$ at 600 °C: 1 min: oxidized catalyst with CO$_2$/He (9 vol.%, 110 mL/min) treatment; 5-15 min: reduced catalyst with H$_2$/He (9 vol.%, 110 mL/min) treatment; 30 min: reoxidized catalyst with CO$_2$/He (9 vol.%, 110 mL/min) treatment.

References


[5] W. Ning, D. Dai, Y. Zhang, Y. Han, L. Li, Effects of trace of nitrogen on the helium atmospheric pressure


[22] V. Locharf, FT-IR study of methanol, formaldehyde and methyl formate adsorption on the surface of Mo/Sn


