Nonthermal plasma (NTP) activated metal–organic frameworks (MOFs) catalyst for catalytic CO₂ hydrogenation

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Abstract
A systematic study of Ni supported on metal–organic frameworks (MOFs) catalyst (i.e., 15Ni/UiO-66) for catalytic CO₂ hydrogenation under nonthermal plasma (NTP) conditions was presented. The catalyst outperformed other catalysts based on conventional supports such as ZrO₂, representing highest CO₂ conversion and CH₄ selectivity at about 85 and 99%, respectively. We found that the turnover frequency of the NTP catalysis system (1.8 ± 0.02 s⁻¹) has a nearly two-fold improvement compared with the thermal catalysis (1.0 ± 0.06 s⁻¹). After 20 hr test, XPS and HRTEM characterizations confirmed the stability of the 15Ni/UiO-66 catalyst in the NTP-activated catalysis. The activation barrier for the NTP-activated catalysis was calculated as ~32 kJ mol⁻¹, being lower than the activation energy of the thermal catalysis (~70 kJ mol⁻¹). In situ DRIFTS characterization confirmed the formation of multiple carbonates and formates on catalyst surface activated by NTP, surpassing the control catalysts (e.g., 15Ni/α-Al₂O₃ and 15Ni/ZrO₂).

1 | INTRODUCTION

Valorization of carbon dioxide (CO₂) by catalytic hydrogenation based on the power-to-gas (P2G) concept is a promising technique that can not only convert the renewable energy to high energy density fuels (e.g., CH₄), but also reduce the anthropogenic CO₂ emissions.¹² P2G process involves the conversion of electricity into synthetic natural gas (SNG), typically consisting of two steps: (a) hydrogen (H₂) production by water electrolysis (using the electricity generated from renewable sources such as wind) and (b) hydrogenation of CO₂ (captured from various industrial sources such as biogas and flue gas) into CH₄.³ As a proof of concept, a production of SNG (ca., 1,000 tons per year) has been achieved by the e-gas plant of Audi Motor Company located in Werlte (Germany) through utilizing the concentrated CO₂ from a nearby biogas plant and renewable hydrogen.² Indeed, CO₂ methanation is the crucial reaction to determine the effectiveness and efficiency of P2G processes.⁴ Catalytic CO₂ methanation (i.e., Sabatier reaction, Equation 1) is thermodynamically favorable (ΔG°₂⁹⁸K = −113.5 kJ mol⁻¹), however, it suffers from kinetic limitations due to the high stability of CO₂ molecule.⁵,⁶ Normally, high temperatures between 200 and 450 °C are required to enable the activation and transformation of CO₂, depending on the catalyst and operating conditions employed.⁷⁻⁹ The reaction is highly exothermic (Equation 1), being prone to form...
local hotspots which leads to the catalyst sintering and deactivation. Generally, conventional catalysts such as the supported nickel (Ni) catalysts present low activity at temperatures below 300°C with low CO₂ conversions which cannot match the corresponding thermodynamic equilibrium value.¹⁰ Additionally, at temperatures higher than 320°C, the reverse water gas shift (WGS) reaction can occur and, therefore, inevitably produce by-products such as CO.¹¹ Therefore, to overcome the limitations and issues experienced by the conventional thermal catalysis, either new catalytic systems or highly active and stable catalysts are needed to activate CO₂ molecule efficiently at relatively lower temperatures (e.g., <300°C).

\[
\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}, \Delta H_{\text{298}}^\circ = -165 \text{kJmol}^{-1} \quad (1)
\]

Nonthermal plasma (NTP) is a promising alternative to the conventional thermal system for activating catalysts at comparatively low temperatures (<200°C), enabling various challenging reactions.¹²,¹³ Specifically, NTP activation has been demonstrated as an efficient technique for promoting WGS and CH₄ oxidation, without an external heat source.¹⁴⁻¹⁶ Recently, catalytic CO₂ hydrogenation was also enabled by NTP at low temperatures of <150°C.¹⁷⁻¹⁸ For instance, hydrogenation of CO₂ to CH₄ over Ni-Ce₀.₅Zrₙ₋₁O₂ catalyst was activated by NTP with high CO₂ conversion (ca., 80%) and CH₄ selectivity (ca., 100%) at low temperatures (<100°C).¹⁷,¹⁸ Conversely, for the Ni-Ce₀.₅Zrₙ₋₁O₂ catalyst under thermal conditions, much higher temperatures (>425°C) are needed to progress the reaction with appreciable rates (i.e., CO₂ conversion of >80%).¹⁹

The development of new heterogeneous catalysts is another strategy to enhance catalytic CO₂ hydrogenation. Generally, high surface area and porous supports are beneficial to disperse heterogeneous metal catalysts.²⁰ Zirconium (Zr)-based metal–organic frameworks (MOFs), that is, UiO-66, present unique features such as large surface area (1,000 m² g⁻¹) and good thermal stability (decomposition temperature above 400°C due to the high oxidation state of Zr).²¹⁻²³ Additionally, surface hydroxyl groups on the hexanuclear Zr clusters are also beneficial to stabilize transition metals, making UiO-66 ideal as the support for developing robust heterogeneous catalysts.²⁴⁻²⁶ To date, many metals (e.g., Ru, Pd, and Ni) have been successfully anchored on/into UiO-66 for various catalytic reactions and shown satisfactory catalytic performance.²⁷⁻²⁹ For example, Lippi et al. recently presented a highly active and stable Ru/UiO-66 catalyst for catalyzing CO₂ hydrogenation under thermal conditions (at 330°C), with CO₂ conversion of 96% and CH₄ selectivity of 99%.²⁴

Although the limited stability of MOFs has been deemed to be a major issue of these materials,²⁵ NTP activation has been recently shown to alleviate the issue, even under challenging reaction conditions, for example, in the presence of water.²⁶⁻²⁷

Herein, we present a NTP-activated catalytic system of CO₂ hydrogenation over Ni supported on Zr terephthalate UiO-66 MOF (Ni/UiO-66). Systematic and comparative studies of activity and stability were performed to facilitate the catalyst development for NTP system. The structural stability of Ni/UiO-66 catalysts and UiO-66 MOF under both NTP and thermal conditions (<20 hr time-on-stream, TOS) was examined carefully using ex situ characterization techniques (e.g., X-ray photoelectron spectra (XPS), high-resolution transmission electron microscopy (HRTEM) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Kinetic studies were also performed to understand the combined effect of the NTP-catalyst system compared to the thermal system. Finally, comparative in situ DRIFTS studies (using Ni catalysts supported on conventional Al₂O₃ and ZrO₂ supports as the control) under NTP and thermal conditions were carried out to understand the surface reaction mechanisms.

2 | EXPERIMENTAL SECTION

2.1 | Chemicals and materials
Zirconium chloride (ZrCl₄, 99.5%) was purchased from Alfa Aesar. Benzene-1,4-dicarboxylic acid (terephthalic acid, 98%), N,N-dimethylformamide (DMF, 99.9%) and nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98.5%) were purchased from Sigma-Aldrich. Acetic acid (100%) and methanol (100%) were purchased from Merck. α-Al₂O₃ and ZrO₂ as the conventional catalyst support were also purchased from Sigma-Aldrich. All chemicals and materials were used as received without any further purification.

2.2 | Catalysts preparation
Ni/UiO-66 catalysts were prepared according to the method reported elsewhere.²² UiO-66 MOF was prepared firstly. In a typical procedure of synthesis UiO-66, 334 mg ZrCl₄ and 250 mg terephthalic acid were firstly dissolved in the 50 mL DMF and stirred at ca. 600 rpm for 1 hr followed by the addition of 7 ml acetic acid. Then the mixture was accommodated in a Teflon-lined autoclave (4744 General Acid Digestion Vessel, 45 ml, Parr Instrument), and placed in a convection oven at 120°C for 24 hr. After the synthesis, UiO-66 crystals were collected by centrifugation at 6,000 rpm and washed using DMF at least three times. The as-synthesized UiO-66 was immersed in methanol for 24 hr and dried under vacuum for 12 hr at 50°C for desolvation. Subsequently, Ni/UiO-66 catalysts were prepared by a conventional incipient wetness impregnation method (with variation of the theoretical Ni loading of 5, 10, and 15 wt%, respectively). Specifically, UiO-66 MOF was impregnated with the Ni(NO₃)₂ aqueous solution for 12 hr and dried at 80°C. Then the resulting solids were calcined in a tube furnace at 250°C under N₂ for 5 hr with a ramp of 5°C min⁻¹. The catalyst was named according to the theoretical Ni wt% loading, that is, xNi/UiO-66 (x = 5, 10, 15, and 20, respectively). Reference supported Ni catalysts were prepared using conventional supports as well, that is, Ni/ZrO₂ and Ni/α-Al₂O₃ catalysts (with the nominal Ni weight content of 15 wt%). The metal loading was measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) which can be found in Table S1.

2.3 | Characterization of materials
Catalysts were comprehensively characterized to understand their physical and chemical properties using X-ray diffraction (XRD), infrared (IR) spectroscopy, XPS, HRTEM, ICP-OES, hydrogen (H₂) chemisorption, scanning electron microscopy (SEM), nitrogen (N₂) physisorption analysis, hydrogen temperature programmed reduction
(H₂-TPR), and CO₂/CO temperature programmed desorption (CO₂-and CO-TPD). The relevant technical details of characterization were presented in Supporting Information.

2.4 | Catalysts evaluation for catalytic CO₂ hydrogenation under NTP conditions

The NTP-assisted CO₂ hydrogenation over Ni/UiO-66 catalysts was carried out in a continuous-flow dielectric barrier discharge (DBD) plasma reactor (fixed-bed configuration) at atmospheric pressure without an external heat source (Figure 1). The DBD plasma reactor consists of a cylindrical quartz reactor (6 mm O.D. × 4 mm I.D.), a stainless steel rod (1 mm O.D., which is used as the ground electrode and placed along the axis of quartz cylinder) and an aluminium foil sheet (acting as a high voltage electrode) which is wrapped around the outer surface of the quartz reactor. The discharge length and gap of the DBD reactor were 10 and 1.5 mm, respectively. In a typical experiment, 100 mg of the as-synthesized catalyst (pelletized with particle size of about 250–425 μm) was packed in the discharge zone between ground electrode and quartz reactor body. Prior to reaction, the catalyst was reduced using plasma with pure H₂ as the discharge gas (flow rate = 50 ml [STP] min⁻¹). The applied peak voltage was varied (i.e., 5.5, 6.0, and 6.5 kV with constant frequency at 20.3 kHz) to study its effect on the catalysts during the pretreatment. For comparison, the 15Ni/UiO-66 catalyst was also reduced thermally at 250 °C (for 5 hr) under H₂. During reaction, a mixture of H₂ and CO₂ with a specific molar composition of H₂:CO₂ = 4 was introduced into the DBD reactor via two mass flow controllers (Bronkhorst®, F-201CV-500-RAD-11-V), and the weight hourly space velocity (WHSV) was 30,000 ml (STP) gcat⁻¹ hr⁻¹. An alternating current (AC) high voltage power supply (Info Unlimited, U.S., PVM500-2500) with a peak voltage of up to 40 kV and a variable frequency of 20–70 kHz was employed to generate the plasma. During the reaction, the applied peak voltage was adjusted from 6.0 to 7.5 kV, while keeping the frequency constant at 20.3 kHz. The applied peak voltage was measured using a digital oscilloscope (TBS1102B) with a high voltage probe (P6015A). The outlet gases for the reactor was measured by a gas chromatograph (GC, PerkinElmer, Clarus® 590) equipped with an Elite-Carbon molecular sieve packed column (N9303926), methaniser, thermal conductivity detector (TCD), and flame ionization detector (FID). Specifically, for each sampling point, several samples were collected via an automated six-way vale containing a sample loop until at least three consecutive measurements were in the range of ~5% error. Condensable vapors (e.g., water) generated from the reaction was condensed from the outlet stream in a water trap cooled by an ice bath. The dry gas flow rate was also measured using a bubble-flow meter in order to determine the CO₂ conversion and selectivity to CH₄ and CO. Control experiments of NTP-assisted gas phase reaction (i.e., empty reactor without a catalyst) and the thermally activated reaction over the 15Ni/UiO-66 catalyst were also performed for comparison. CO₂ (XCO₂) conversion, selectivity towards CH₄ (SCCH₄) and CO (SCO), as well as turnover frequency (TOF) were determined accordingly to evaluate the catalytic performance, these are detailed in Supporting Information.

2.5 | In situ DRIFTS characterization of catalytic CO₂ hydrogenation

To understand the surface reactions under the NTP condition, in situ DRIFTS characterization of the catalytic system under thermal and NTP conditions was performed. The hybrid NTP-DRIFTS setup is described elsewhere. For in situ NTP-DRIFTS analysis, the catalyst was loaded into an IR flow cell and pretreated in a 10% H₂/Ar flow under plasma (applied peak voltage: 5.0 kV, frequency: 23 kHz) for 30 min. The gas mixture (4 vol.% CO₂/16 vol.% H₂ diluted in Argon, Ar) at 75 ml min⁻¹ was then introduced into the cell to enable the reaction. For the transient experiments, a constant applied peak voltage of 5.0 kV (at a frequency of 23 kHz) was applied to the power electrode in order to avoid arcing. DRIFTS spectra were recorded at every ~56 s with a resolution of 4 cm⁻¹ and analyzed with the OPUS software. The procedure for in situ thermal DRIFTS was detailed elsewhere.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of catalysts and their performances in NTP-assisted catalytic CO₂ hydrogenation

Comprehensive characterization data of all catalysts are presented in SI with detailed analysis (as shown in Figures S1–S4, S7, S8, Tables S1–S3). Figure 2 shows the comparison of relevant catalytic results of the different systems, that is, catalyst-free, with the UIO-66, 15Ni/ZrO₂, 15Ni/α-Al₂O₃, and Ni/UiO-66 packing, respectively. The
catalyst-free NTP system along with that with the UiO-66 and 15Ni/ZrO2 packing showed relatively low CO2 conversions (ca., 5–10%) and no selectivity to CH4 (Figure 1a,b), while CO was found to be the main product (Figure 1c) due to the NTP-induced CO2 dissociation.27,28 Conversely, the system using 15Ni/α-Al2O3 and Ni/UiO-66 packing showed significant improvements regarding CO2 conversion. However, the Ni/UiO-66 catalyst outperformed the 15Ni/α-Al2O3 catalyst concerning both CO2 conversion and selectivity to CH4, suggesting a promoting effect by UiO-66 (as the support to promote the dispersion of Ni phase).23 This is confirmed by the findings of H2 pulse chemisorption analysis (Table S2), which showed significantly higher Ni dispersion in the Ni/UiO-66 catalysts (e.g., about 1.17% for 5Ni/UiO-66) than that of 15Ni/α-Al2O3 (ca., 0.3%). An increase in Ni loading was found to be beneficial to the selective conversion of CO2 into CH4, as shown in Figure 2a. For example, at 6.0 kV, 15Ni/UiO-66 catalyst demonstrated the highest CO2 conversion of ca. 80% and the lowest selectivity to CO (<1.5%). However, as shown in Figure S5, the 20Ni/UiO-66 catalyst presented a relatively poor catalytic activity, which could be the result of the segregation of Ni particles to the surface due to the overloading of Ni.29 Hence, the 15Ni/UiO-66 catalyst was selected for further investigation in this work.

Under the thermal condition, at least 200°C was needed to activate CO2 over the 15Ni/UiO-66 catalyst, as evidenced by the light-off curve in Figure 3a. At 350°C, the CO2 conversion was about 75%, which is ~15% lower than the corresponding theoretical thermodynamic equilibrium conversion (red dashed line, calculated using Aspen Plus 8.0). At least 300°C was required to enable the high selectivity to CH4 (ca., 95%), as evidenced by the result in Figure 3b. Additionally, based on the results from the kinetic study (as shown in Tables S5 and S6), the TOF values of the catalyst under both NTP and thermal conditions were calculated, and the results are presented in Figure 3c. Specifically, at an applied voltage of 6.0 kV, the specific reaction rate (i.e., TOF) of the NTP-catalysis system was calculated to be 1.8 ± 0.02 s⁻¹ (using the CO2 conversion of 8.1 ± 0.07%), surpassing that of the thermal system at 240°C (i.e., TOF value of 1.0 ± 0.06 s⁻¹ which was calculated using the CO2 conversion of 4.7 ± 0.06%).

The activity of the 15Ni/UiO-66 catalyst for catalytic CO2 hydrogenation as a function of TOS was evaluated under both NTP (20 hr, at 6.5 kV) and thermal conditions (70 hr, at 380°C). The longevity test under the NTP condition was relatively short compared to the thermal case in order to protect the power supply. Under the thermal condition, as shown in Figure 4, the deterioration of the catalytic performance was evident as a function of TOS, even over the initial 20 hr TOS (i.e., ~5% reduction in CO2 conversion). Conversely, under the NTP condition, the catalyst showed comparably stable CO2 conversion and CH4 selectivity over the 20 hr TOS. Specifically, under the NTP conditions, energetic electrons (induced by electric field) collide with bulk gas molecules and subsequently lead to the breaking of the molecular bonds and creation of highly reactive species such as ions and free radicals. However, NTP does not create a significant temperature rise in the bulk gas due to the relatively low electron mass (i.e., <10⁻²⁰ kg).30 Hence, the bulk gas temperature in NTP catalytic system remains close to the ambient (<100°C),31 explaining the reason behind the improved stability of the NTP system (within 20 hr TOS) compared with the thermal one.

Post reaction XPS analysis of the used catalysts (from the stability tests) shows that the NTP activation maintains the chemical nature of the MOF support to a large extent, as compared to the reaction under thermal activation. Figure 5 shows the comparison of XPS spectra for the as-synthesized and used 15Ni/UiO-66 catalysts, respectively. In comparison with the as-synthesized 15Ni/UiO-66 catalyst, significant changes were recorded regarding the binding energies (B.E.) of Ni2p,

![Image](https://example.com/image.png)
C1s, O1s, and Zr3d for the catalyst used under the thermal condition. In comparison, the changes measured for the used catalyst from the NTP-catalysis are less significant. Figure 5a shows the main peak of Ni2p3/2 of the as-synthesized catalyst with B.E. = 856.7 eV, corresponding to the isolated pseudo-tetrahedral Ni (II) species.32 After the NTP-catalysis, a new peak with the B.E. = ~853 eV (corresponding to the reduced nickel, Ni0) was identified in Ni 2p3/2 region of the used catalyst (Figure 7b), indicating partial reduction of Ni (II) species under the NTP condition. The XPS spectra for the C1s and Zr3d regions in Figure 5a,b are comparable, indicating that the plasma did not alter the UiO-66 structure significantly. Deconvolution of the XPS spectra for O1s shows that the presence of additional peaks with the B.E. of 531 and 530 eV in the used catalysts from NTP-catalysis, in addition to the primary one located at ~531.5 eV in the fresh catalyst (corresponding to the carboxylate species in UiO-66).33 This might be due to the NTP-induced decomposition of the Ni precursor, leading to the formation of carboxylate and hydroxylated species (Zr[OH]Zr) in UiO-66.33

Conversely, the used catalyst from the thermal catalysis shows significant differences in the XPS spectra for Ni/UiO-66 catalyst, confirming the substantial change in the chemical state of both the catalyst and MOF support due to the extended exposure at 380°C (which is necessary to enable the catalysis). For example, by comparing C1s spectra of the fresh and used catalyst (from the NTP-activated
reaction), the peaks at 284.6 and 288.6 eV (corresponding to the C–C and C=O species in the organic linker of UiO-66, that is, benzene-1,4-dicarboxylic acid) are similar, whereas new peaks located at ca. 285.5 and 287.5 eV (which could be assigned to Zr–O–C) were found in the used catalyst from the thermal system. The deconvolution of O1s spectrum of the used catalyst from the thermal system resulted in new peaks representing C–O and O–Zr4+. Additionally, in comparison with the fresh and used catalyst (from the NTP-catalysis), the Zr3d spectrum of the used catalyst under thermally activation shows new peaks located at ~182, 187, and 189 eV, which could be attributed to the Zr–C, Zr–O, and Zr–O–C bonds, respectively. Overall, the XPS results suggest the decomposition of the 15Ni/UiO-66 catalyst under the thermal condition.

HRTEM analysis also confirmed the effect of NTP and thermal activation on the 15Ni/UiO-66 catalyst, as shown in Figure 6. The UiO-66 MOF exhibits the characteristic octahedral morphology (Figure 6a,b). After the Ni dispersion, the as-synthesized catalyst (as shown in Figure 6c,d) retains the octahedral morphology. Specifically, Ni particle sizes are determined by counting different particles for multiple TEM images taken in different sample regions. Additionally, Ni nanoparticles were formed nonuniformly on the support with large Ni particles possibly on the external surfaces of UiO-66 crystals (with the average particle size of 12 ± 2.6 nm). After the NTP-activated catalysis, as shown in Figure 6e,f, the MOF support was largely intact. Interestingly, the dispersion of Ni particles was improved significantly due to the NTP activation, showing the presence of highly dispersed small Ni particles at 4 ± 0.5 nm. In contrast, the decomposition of the MOF support, as shown in Figure 6g,h, was caused by the conventional thermal activation of the catalysis. Additionally, metal sintering was also observed after the thermal catalysis, leading to the presence of relatively large Ni particle sizes of 13 ± 1.4 nm in the used catalyst.
3.2 | Kinetic study of catalytic CO₂ hydrogenation over 15Ni/UiO-66 catalyst: Thermal activation versus NTP activation

NTP-activation sustained the activity of the 15Ni/UiO-66 catalyst for catalytic CO₂ hydrogenation by maintaining the function of the MOF support and enabling an improved Ni catalyst dispersion, being superior to thermal activation. In order to gain the mechanistic understanding of the two systems, kinetic studies were performed to compare their apparent activation energies (Eₐ). Figure 7a shows that the thermal catalysis exhibits a typical Arrhenius behavior which allows the calculation of Eₐ, thermal as ~70 kJ mol⁻¹, being comparable to the previous reported value (i.e., ~69 kJ mol⁻¹).²³ For NTP-catalysis, the method developed by Hicks et al.²⁶ was employed in this study to determine the apparent activation energy (Eₐ, NTP, or the energy barrier) for CO₂ hydrogenation under the NTP conditions. Previous research has shown that the NTP-activated catalysis presents the non-Arrhenius behavior likely due to the complex interactions between plasma and catalyst surface.²⁶ Under the thermal conditions, reactant molecules (i.e., H₂ and CO₂) must firstly adsorb on the catalyst surface, and subsequently, the surface reaction between the surface dissociated H and adsorbed CO₂ proceeds via the Langmuir-Hinshelwood mechanism.¹³ Therefore, the input energy of thermal system (i.e., heat) is
the key factor to enable the dissociation of reactants and the following surface reaction. Therefore, the activation energy of thermal catalytic system was determined according to the Arrhenius law as a function of temperature. Conversely, unlike the catalysis under the thermal conditions, in an NTP-catalyst system, NTP-created vibrationally-excited CO2 and dissociated H species could interact readily with the Ni active sites, leading to a reduced energy barrier (i.e., the dissociation of molecules on the catalyst surface might not be necessary). Therefore, under the NTP conditions, both the residence time of the total feed gases and the density of high-energy electron (which is determined by the input plasma power) are the key parameters in determining the apparent activation energy of NTP catalysis system.36 Accordingly, a modified Arrhenius expression, which depends on the plasma power and total feed flow rate, was developed to extract the kinetic parameters such as the energy barrier from the NTP-activated catalysis (exemplified by dry reforming of CH4 with CO2 over Ni catalysts supported on γ-Al2O3).36 As shown in Figure 7b, the linear fit of the plot of the reaction rate of NTP-catalysis (ln (NTP-cat)) against the inverse DBD discharge power (1/powerDBD) was performed, giving $E_A, NTP = \sim 32 \text{ kJ mol}^{-1}$, which is 55% lower than the counterpart of the thermal catalysis. Additionally, the reaction rate of the NTP-catalysis can be improved significantly by increasing the specific input energy (SIE), indicating that the generation of vibrationally-excited gas species (CO2 and H2) could be improved by NTP activation with higher input energy. This phenomenon is in line with the finding reported by Kim et al.36

### 3.3 | In situ DRIFTS characterization of catalytic CO2 hydrogenation

The comparatively easy activation of CO2 over the 15Ni/UiO-66 catalyst by NTP was also confirmed by in situ DRIFTS study of the NTP and thermal systems. As shown in Figure 8, under the thermal activation, the 15Ni/UiO-66 catalyst was inactive at relatively low temperatures of <150°C with the insignificant change of the surface species. By increasing the temperature above 150°C, the intensity of the gas phase CO2 IR band (at 2,340 cm$^{-1}$, as shown by the shaded region) decreased gradually, suggesting the conversion of CO2 over the catalyst. Additionally, multiple surface species with IR signals at 1,000–2,000 cm$^{-1}$ were observed by increasing the reaction temperature, which could be attributed to surface carbonates37-39 (possibly due to both the surface reactions and the decomposition of UiO-66 support according to the XPS analysis). It can be concluded that, under the thermal conditions, CO2 hydrogenation over the catalyst requires high reaction temperatures above 200°C to overcome the activation barrier, matching well with the catalytic data presented in Figure 3. More importantly, the DRIFTS spectra further confirmed that the thermal activation can possibly destroy the MOFs structure at high temperatures, which is consistent with the XPS and HRTEM results.

In situ DRIFTS study of the NTP-activated CO2 hydrogenation was coupled with mass spectrometry (MS). Under the plasma-off conditions at ambient temperature, MS profiles confirm that the 15Ni/UiO-66 catalyst was not active for CO2 conversion (Figure 9b) under the plasma-off condition. The relevant DRIFTS presents a wide IR band located at 1,500–1,800 cm$^{-1}$, which may be attributed to the
OH vibrational stretching of water molecules and also the hydroxyl groups adsorbed on the surface of Ni and/or Zr nodes of UiO-66. With the ignition of NTP, both the DRIFTS and MS showed the simultaneous activation of the catalysis. Specifically, the MS profiles in Figure 9b show the emerging of the line at m/z = 16, confirming the production of CH$_4$ in the NTP-catalysis system. Furthermore, under NTP, the following changes of the gas-phase and surface species as a function of time were observed: (a) the significant reduction of IR band intensity of the gas-phase CO$_2$ (at 2,340 cm$^{-1}$); (b) the disappearance of hydroxyl IR bands located at 1,500–1,800 cm$^{-1}$; (c) the progressive increase of the IR band intensity at 1,561, 1,433, and 1,292 cm$^{-1}$ (possibly the surface carbonate and formate species, shaded by the blue squares). Comparative in situ DRIFTS of the catalysis over the reference 15Ni/$\alpha$-Al$_2$O$_3$ and 15Ni/ZrO$_2$ catalysts under the NTP conditions was also performed, and the results are presented in Figures S10 and S11. Neither the gas phase CO$_2$ nor the surface species IR bands were changed appreciably under the NTP conditions. These results suggest that the 15Ni/UiO-66 catalyst is much more active for catalytic CO$_2$ hydrogenation in comparison with the control catalysts supported on $\alpha$-Al$_2$O$_3$ and ZrO$_2$, in good agreement with the activity data shown in Figure 2.

Based on the in situ DRIFTS study under NTP conditions, two possible reaction pathways could co-exist in the NTP-activated CO$_2$ hydrogenation system over 15Ni/UiO-66 catalyst. Typically, the plasma-activated and vibrationally excited CO$_2$ species readily adsorbed on the surface of Ni sites, and probably also interacted with hydroxyl groups adsorbed on the surface of Zr nodes of UiO-66, generating surface carbonate species. Subsequently, these species can react with surface-dissociated H to form formates, which can be finally hydrogenated into CH$_4$ molecules. Additionally, the dissociated H species in the gas phase induced by plasma may also react with surface carbonate species directly from gas phase to form formates species, progressing CO$_2$ conversion.

4 | CONCLUSIONS

The limited thermal stability of MOFs-based catalysts greatly hinders their practical applications under the conventional thermal conditions, especially catalysis which requires high-temperature activation. Experimental results revealed that the NTP activation is indeed an ideal technique to enable heterogeneous catalysis over MOFs-based catalysts (e.g., 15Ni/UiO-66) for catalytic CO$_2$ hydrogenation under mild conditions. NTP-catalysis showed high catalytic activity with TOF = 1.8 ± 0.02 s$^{-1}$ compared to the thermal system (TOF = 1.0 ± 0.06 s$^{-1}$). Additionally, the longevity tests revealed that the NTP-catalysis was stable for at least 20 hr on stream, while the deterioration of the catalytic performance was measured under the thermal condition at 380°C (i.e., CO$_2$ conversion decreased by ca. 5% after 20 hr TOS). Also, the postreaction characterization (e.g., XPS, HRTEM) of the catalyst and in situ DRIFTS showed significant changes in the state of the catalyst after the thermal activation. Kinetic study showed that the NTP activation reduced the apparent activation energy of the catalytic CO$_2$ hydrogenation compared to the thermal activation (by ~55%). The vibrationally and electronically excited gas species (e.g., CO$_2$ and H$_2$), and radicals induced by plasma discharge under the NTP conditions could readily interact with catalyst surface and adsorbed species, leading to a relatively low energy barrier required to activate CO$_2$ hydrogenation, which was confirmed by in situ DRIFTS characterization of the NTP-catalysis. Comparative in situ DRIFTS characterization of surface species on different catalysts showed that the 15Ni/UiO-66 catalyst is much more active under the NTP conditions than the control of Ni/$\alpha$-Al$_2$O$_3$ and Ni/ZrO$_2$.

The improved fundamental understanding of the NTP-catalysis systems (exemplified by CO$_2$ hydrogenation over the Ni/UiO-66 catalyst) is beneficial to enable the rational design of effective catalysts for NTP conditions and also the initial preliminary design, configuration and operation of NTP reactors for potential practical usages.
However, the practical application of NTP-catalysis is still challenging, especially at large-scales. Therefore, future multi-/inter-disciplinary efforts (involving physics and engineering) are needed to enable the development of stable yet durable NTP reactors/processes to be developed for the practical scenarios.

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NOTATION

Symbols

\( E_{a, \text{thermal}}, \text{kJ mol}^{-1} \) activation energy of the thermal catalysis

\( E_{a, \text{NTP}}, \text{kJ mol}^{-1} \) energy barrier of the NTP catalysis

\( r_{\text{thermal-cat}}, \text{mol s}^{-1} \text{g}^{-1} \) reaction rate of thermal catalytic system

\( r_{\text{NTP-cat}}, \text{mol s}^{-1} \text{g}^{-1} \) reaction rate of NTP catalytic system

\( \text{power}_{\text{DBD}}, \text{W} \) DBD discharge power

SIE, J ml\(^{-1}\) specific input energy

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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