



Non-thermal plasma-assisted catalytic CO₂ conversion over Zn-TCPP 2D catalyst

Marek Wiśniewski¹ · Artur P. Terzyk¹

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Abstract

There is still a growing interest in CO₂ conversion into useful compounds. Plasma technology is a highly promising alternative due to its non-equilibrium nature, crucial for CO₂ dissociation processes. In this study we present, the non-thermal plasma-assisted catalytic CO₂ reduction to CO on 2D Zn-containing paddle wheel structures based on TCPP. The catalytic efficiency of this MOF material is shown to be high. The experimental data from HRTEM, adsorption and FTIR analyses lead to the simplified model mechanism of this process.

Keywords CO₂ adsorption · CO₂ reduction · Non-thermal plasma · 2D-materials · Zn-TCPP

1 Introduction

Increasing concerns about CO₂ emission issues call for the development of new clean sustainable technologies. Therefore, CO₂ splitting has attracted a great attention over the past years within the fields of environmental sciences (Snoeckx and Bogaerts 2017; Bennett et al. 2017). The technologies using solar derived systems and/or cold plasma, without requirement for high pressures and/or temperatures, powering the conversion of CO₂ to chemical fuels are nowadays of decisive importance to address energy and environmental demands. (Shi et al. 2019; Alliati et al. 2018).

The significant drawback in CO₂ conversion is the fact that, it is a highly stable molecule with $\Delta G^\circ = -394$ kJ/mol. Its dissociation is strongly endothermic ($\Delta H^\circ = +280$ kJ/mol) (Alliati et al. 2018) causing that high conversions in splitting reaction are not easy to achieve. Many research efforts have aimed to overcome these difficulties, among which plasma processing, and especially, plasma-assisted catalytic processes are presented as a promising alternative approaches thanks to their non-equilibrium nature. However, the design and synthesis of suitable materials able to

effectively remove CO₂ from a gas stream is still a great challenge (Snoeckx and Bogaerts 2017).

The favorable catalysts for CO₂ effective splitting need to meet the following requirements: (i) excellent CO₂ adsorption ability at broad temperature range; (ii) high thermal stability; (iii) sufficient ability for O* scavenging; (iv) low reactivity, especially in oxidizing environment. These supplies are extensively fulfilled by two-dimensional (2D) Zn-containing paddle wheel structures based on TCPP (tetrakis(4-carboxyphenyl)porphyrin).

These semiconductor materials have been extensively investigated and applied in photocatalytic processes, including water splitting and CO₂ reduction as a heterogeneous photocatalyst under visible light (Amayuelas et al. 2017). For example, some porphyrin-containing MOFs structures have been applied in photocatalysis (Amayuelas et al. 2017), photovoltaic systems (Spoerke et al. 2017; Aziz et al. 2017) and for photoelectron transfer (Ishihara and Tian 2018). Moreover, their photocytotoxic activity have found application in photodynamic therapy (Buzek et al. 2017; Kan et al. 2018). In some photocatalytic processes they are used for reduction of nitroaromatic compounds (Deenadayalan et al. 2016) or photocatalytic hydrogen production (Leng et al. 2018).

In catalysis, due to excellent thermal stability of Zn-TCPP, the material have found application in many useful reactions as: oxygen reduction (Jahan et al. 2012), for catechol (Castro et al. 2019), alkylbenzenes (Zhang et al. 2016) or water oxidation, (Usov et al. 2016; Dai et al. 2016; Paille

✉ Marek Wiśniewski
marekw@umk.pl

¹ Faculty of Chemistry, Physicochemistry of Carbon Materials Research Group, Nicolaus Copernicus University in Toruń, Gagarin Street 7, 87-100, Toruń, Poland

et al. 2018). They also have found application in photocatalytic conversion of CO_2 (Liang et al. 2018) as well as in electrochemical reduction of CO_2 to CO (Hod et al. 2015; Dong et al. 2018). However, to the best of our knowledge, they were never have been examined in plasma-assisted CO_2 reduction.

There are number of studies on the downstream analysis of the exhaust from non-thermal plasma (NTP) but the in-situ studies, with IR spectroscopy, of the plasma glow on the catalyst surface is only a relatively recent phenomenon (Rivallan et al. 2012; Rodrigues et al. 2016; Stere et al. 2015; Jia et al. 2016). It is crucial, that the identities of the reactive species on and near the catalysts surface are revealed and thus shed some light to the mechanism of the overall process.

The aim of the work reported in this paper was to assess the efficacy of a combination of infrared reflectance and transmission spectroscopy to the study of CO_2 conversion under non-thermal plasma/catalyst interface as well as testing the ability of Zn-TCPP catalyst in the process.

2 Experimental

2.1 ZnTCPP synthesis

The synthesis of ZnTCPP was performed using similar procedure to described in (Wiśniewski et al. 2019). Briefly, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (POCh, 0.250 g) and TCPP (tetrakis(4-carboxyphenyl)porphyrin), TCI chemicals, 0.079 g) in a solvent mixture of DMF (N,N-Dimethylformamide, ACROS Organics™)/EtOH (POCh) 99.8% (15 ml/7.5 ml) were placed in a 30 ml screw-capped glass vial and mixed by about 15 min, until total dissolution of both reagents. Then the vial was placed into oven at 80 °C for 24 h. Purple with glitter precipitate was then obtained by filtration on nylon membrane filters (pore size 0.45 μm). The product was washed with 5 ml mixture of DEF (N N-Diethylformamide) and EtOH (2:1), and 3 times with 10 ml EtOH 96%. The solid was then evacuated at 50 °C and in vacuum for 24 h.

2.2 Materials characterisation

The full characteristic of ZnTCPP including: elemental and thermogravimetric analysis, SEM, PXRD was presented recently (Wiśniewski et al. 2019). The results are consistent with the results presented in the literature (Zhao et al. 2015) and correspond to a 2D chemical structure.

Additionally, material was characterized with scanning electron microscopy (SEM), using a Quanta 3D FEG

(EHT = 30 kV) instrument and HRTEM to show its 2D structure.

2.3 CO_2 adsorption–desorption measurements

Carbon dioxide adsorption–desorption measurements were performed at the temperature of 25 °C using a typical gravimetric adsorption apparatus equipped with the Baratron pressure transducers (MKS Instruments, Germany). Before the measurements sample was thermally desorbed (at 200 °C) under high vacuum (10^{-3} Torr) until a constant mass was obtained (usually after 3 days).

2.4 In-situ DRIFT investigations

CO_2 adsorption was performed under isobaric conditions ($p(\text{CO}_2) = 25$ hPa by flowing CO_2/He 2.5% gas mixture) changing the temperature of the process up and down from 25 to 250 °C, with a period of 1 h at each temperature (period of 25 °C) in order to assure that the equilibrium was achieved. A Praying Mantis in situ cell from Harrick Scientific Corporation was used as reactor for the infrared (IR) spectroscopic DRIFT studies (Fig. 1). The construction of this cell enables the thermal treatment of the powdered sample up to 600 °C in any controlled atmosphere or in a vacuum. The IR spectra for the samples were recorded (using Nicollet S10) at adsorption temperature, i.e. without cooling down to the room temperature. Spectral changes accompanying CO_2 adsorption were established by comparing IR spectra of the same sample recorded in a vacuum and those recorded under a defined adsorption temperature.

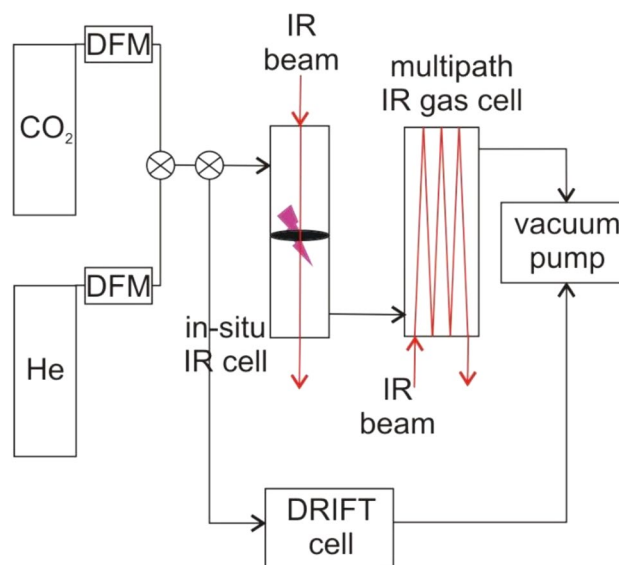


Fig. 1 Scheme of in-situ plasma-assisted catalytic CO_2 conversion system

The respective gas phase was the background for each spectrum. This simple operation enables observation of spectral changes of surface, without perturbation from the gas phase. Once the equilibrium was reached, the band at ca. 2340 cm^{-1} was integrated (I). Experimental results were presented as I/I_{max} , where I_{max} is the band of maximum intensity taken at the lowest temperature. Thus the I/I_{max} value represents the experimental value of relative adsorption.

2.5 In-situ plasma-assisted catalytic CO_2 conversion investigations

The in-situ FTIR studies were carried out in a vacuum cell, described previously (Zawadzki and Wiśniewski 2007, 2002; Wiśniewski 2014), plugged into the vacuum line (Fig. 1). The pressure of CO_2 was constant, and equal 0.38 Torr. The application of this technique makes it possible to determine in what extent physical or chemical adsorption occurs. Moreover, we can easily determine the absence or presence of any surface oxygen compounds formed by chemisorption. We can also, based on the spectra of tested material, check in what extent a material changes its structure during the process and in what extent a sample is affected by possible impurities. The construction of the in-situ FTIR cell enables the thermal treatment of the film sample up to 1200 K in any controlled atmosphere or in a vacuum. The spectra were recorded using the Mattson Genesis II FTIR spectrophotometer. Spectral changes accompanying the tested process were investigated. The respective gas phase was a background for each sample spectrum, enabling the observation of spectral changes of a sample surface only, i.e. without perturbation from the gas phase. A period of at least 0.5 h (monitoring continuously) at each power was held in order to be sure that the equilibrium was achieved.

The gases (CO_2 and CO) were analyzed quantitatively with using a multiple-pass gas cell (with the pathlength of 2 m) attached on-line to the flow system (Fig. 1).

3 Results and discussion

3.1 Material characterisation

The results from the SEM and HRTEM structure determination studies are presented in Fig. 2. Based on these results it can be concluded that ZnTCPP are built mainly of wafers/layers. Their square-shaped sheets visible in both SEM as well as HRTEM pictures are the reflection of organic part of the MOF. Interestingly HRTEM results reveal the square units with distance of 1.2 nm which is in perfect agreement with theoretical predictions. Moreover, porphyrin angles are extended to the micro-scale and observed as a flat sheets with right angles.

These results confirm our previous observations (Wiśniewski et al. 2019) and mean that Zn-TCPP forms 2D material with the distance between particular sheets ca. 0.5 nm based on XRD measurements.

Four nitrogen atoms as well as aromatic units in each porphyrin structure cause that the material is highly thermally stable, even in oxidative atmosphere. Thermogravimetric measurements show its stability up to ca. $400\text{ }^\circ\text{C}$ in air (Wiśniewski et al. 2019). Additionally, these 4 N-atoms are the main reason of its Lewis-base properties, causing that CO_2 molecules should adsorb strongly.

To examine this idea adsorption isotherms were measured at temperature range of $25\text{--}100\text{ }^\circ\text{C}$. In parallel, DRIFT investigations were performed to discover the adsorption mechanism. The experimental adsorption data for pure CO_2 are shown in Fig. 3. As in the case of “ordinary” microporous materials, the adsorption of CO_2 is mainly caused by interactions in very narrow micropores.

The rise in adsorption temperature causes diminish in the adsorbed CO_2 amount, meaning that CO_2 does not chemisorb on the Zn-TCPP surface. The in-situ IR adsorption studies confirm this statement. The observed spectral changes are caused only by physically adsorbed CO_2 .

The presence of adsorbed CO_2 in micropores of Zn-TCPP at slightly higher temperatures, its thermal stability and basic nature make the tested material perfect for CO_2 -plasma treatment. It is well known from the literature (Snoeckx and Bogaerts 2017) that, in non-thermal plasmas the temperature of the electrons is the highest, followed by the temperature of vibrationally excited molecules, while the lowest temperature is shared by the ions and neutral species. The temperature of electrons is in the order of 1 eV (ca. 10 000 K), while the neutral species temperature being initially close to the room temperature can rise slightly due to the collision energy. Moreover, the phenomena generates radicals, ions and vibrationally and electronically excited species not normally present in at room temperature (Aerts et al. 2012; Christensen et al. 2018; Whitehead 2016).

Constructed analytical system (Fig. 1) makes it possible to observe substrates, intermediates as well as products of the plasma-assisted CO_2 conversion due to parallel, in-situ and ex-situ investigations. As the former reveal the presence of the unstable intermediates the latter show stable products enabling quantitative analysis. The results are collected in Fig. 4.

According to the literature (Fridman and Rusanov 1994), almost 97% of the CO_2 , exposed to low temperature plasmas, can be converted into vibrational excitation of the gas feed molecules (CO_2^*). It is confirmed clearly in Fig. 4, observed as a 63 cm^{-1} red-shifting of CO_2 asymmetric stretching vibrations. The CO_2^* molecules relax quite easily, being observed outside the plasma zone as typical CO_2 molecules (2349 cm^{-1}).

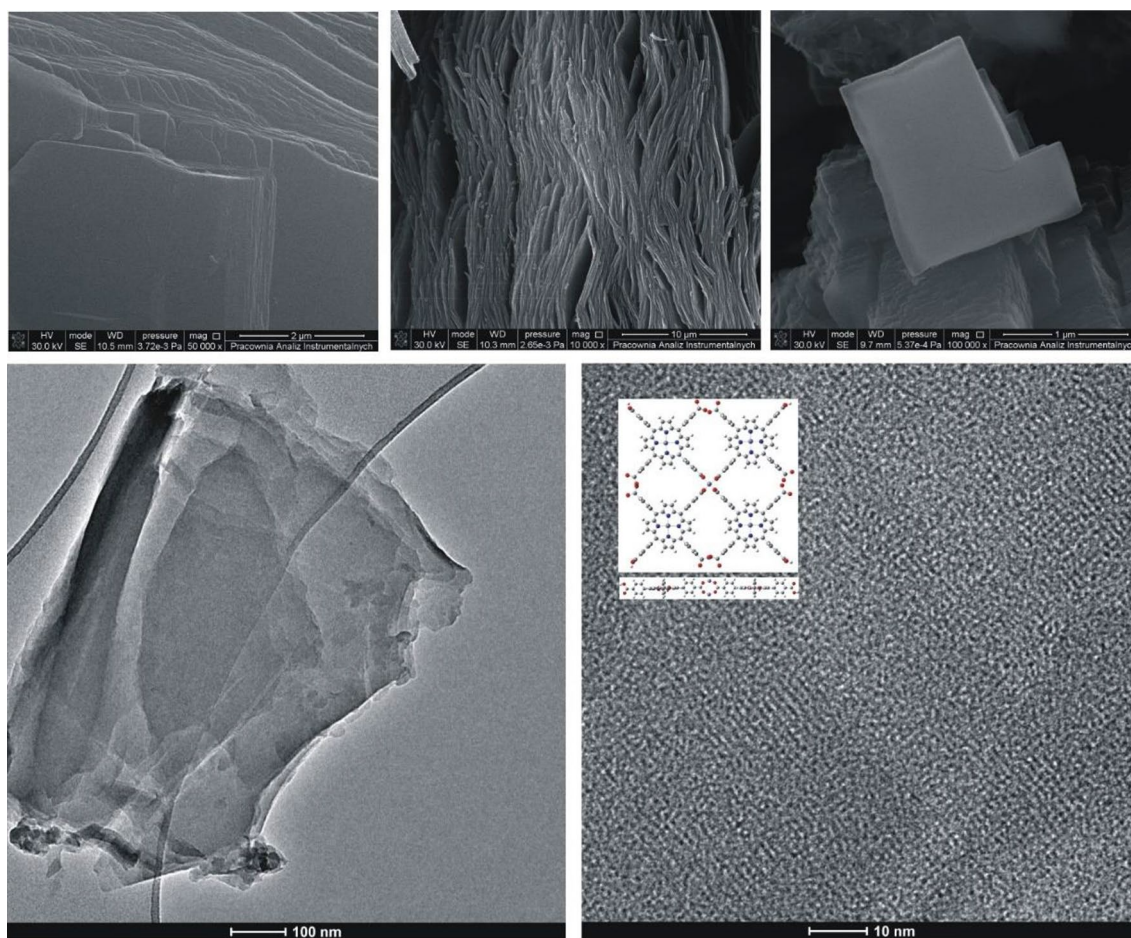


Fig. 2 SEM and HRTEM pictures of ZnTCPP 2D structure. Insets are the theoretical models of observed square-shaped structure sheets

As it was expected, adding a catalyst speed up the chemical processes in a plasma and/or offer alternative mechanistic pathways with lower activation energies. Reactive species are produced and interact with catalyst at temperatures at which most thermally-driven process would be slow and impossible to be observed. Moreover, vibrationally excited molecules cannot have markedly different adsorptive properties. Their acid–base properties should remain constant contrary to the reactivity on the surface of catalysts also being in contact with plasma (Chen et al. 2008) thus it should be possible to enhance targeted reactions and suppress others by controlling the number density of electrons and electron and gas temperatures. That's way, both catalyst addition as well as power increase (Fig. 4) shift the reaction forward, i.e. to CO formation.

The vibrationally excited form of the CO₂ ground electronic state, i.e. CO₂^{*}, is generally accepted as being the intermediate in the plasma-induced reduction of CO₂ to CO and O₂ (Alliati et al. 2018). However, the analysis of Fig. 4 lead to the conclusion that without catalyst the process is

highly inefficient. Thus the in-situ analysis of catalyst surface seem to be reasonable.

As it is shown in Fig. 5, CO₂ adsorption (without plasma) causes formation only physically adsorbed CO₂ species (2336 and 660 cm⁻¹). Contrary, on the Zn-TCPP in CO₂ plasma atmosphere new, interesting surface species appear. Their exact assigned needs further studies, nevertheless the presence of –C=O, –C–O, as well as their intermediates cannot be excluded due to the appearance of the IR bands in the region of 1650–800 cm⁻¹.

The wide band at ca. 2264 cm⁻¹ could be attributed to physically adsorbed CO₂^{*}. The signals at 1605 and 1411 cm⁻¹ most probably are response for the presence of carbonate species in the pores. IR peaks observed at 1107 and 999 cm⁻¹ confirm the existence of –C–O.

Taking into accordance the above, the overall process could be summarized as follows (s denotes the surface active center):



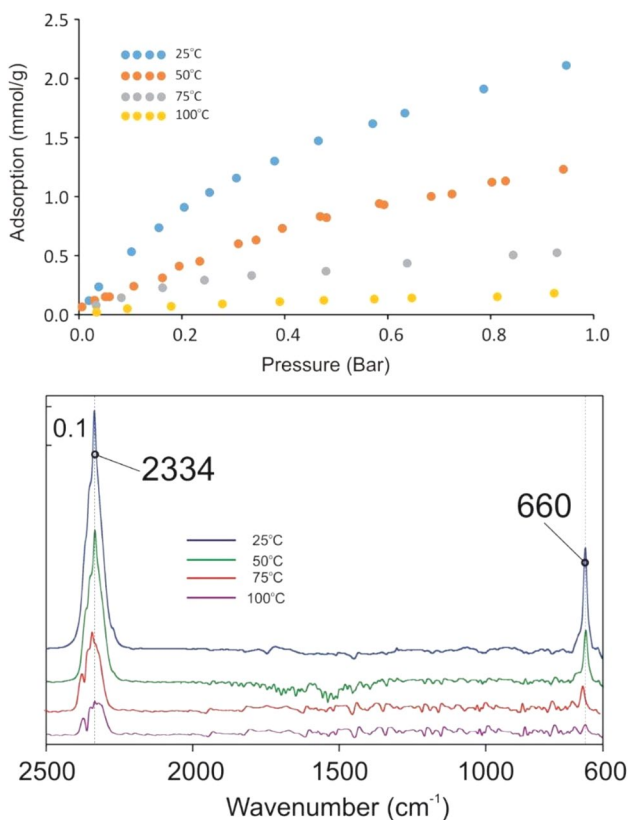
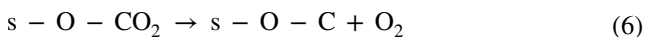
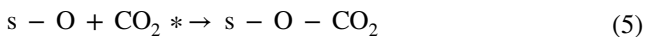
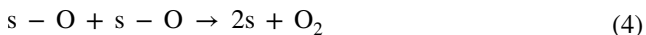


Fig. 3 Upper panel: CO₂ adsorption isotherm on Zn-TCPP; bottom panel: the differential spectra observed after CO₂ adsorption under isobar conditions; both data sets were taken at the temperature range 25–100 °C



Vibrationally excited CO₂ formed in Eq. 1 is observed directly in plasma zone (Fig. 4). Its adsorption on Zn-TCPP surface (Eq. 2) causes the appearance of broad bands below 2300 cm⁻¹ and the decomposition of this surface complex leads to CO liberation (Eq. 3). Formed thus surface oxides s–O can recombine, producing O₂ or adsorb CO₂ creating surface carbonates (Eqs. 4 and 5). Due to the fact that no CO physically adsorbed on the material

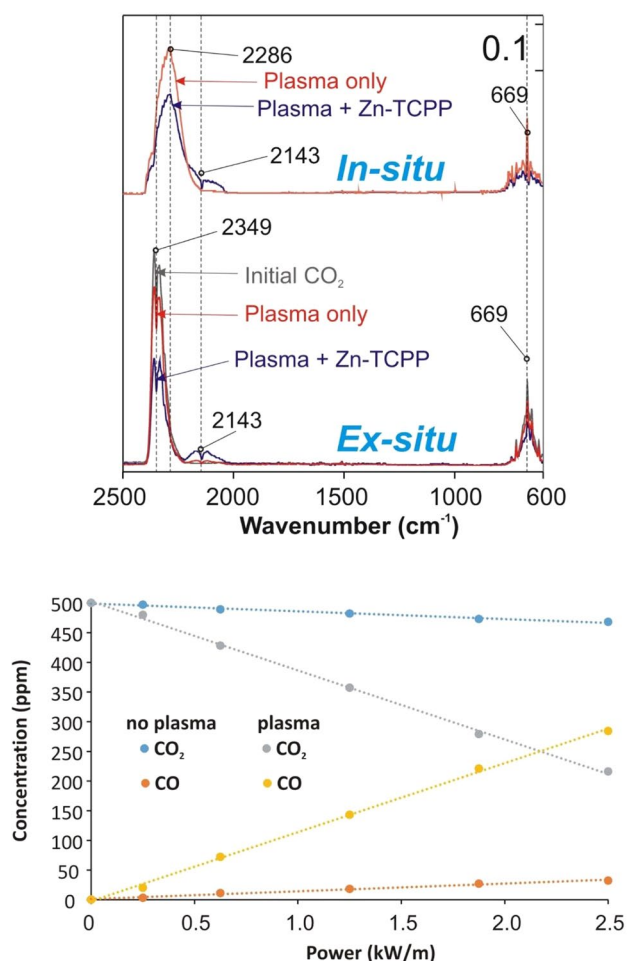


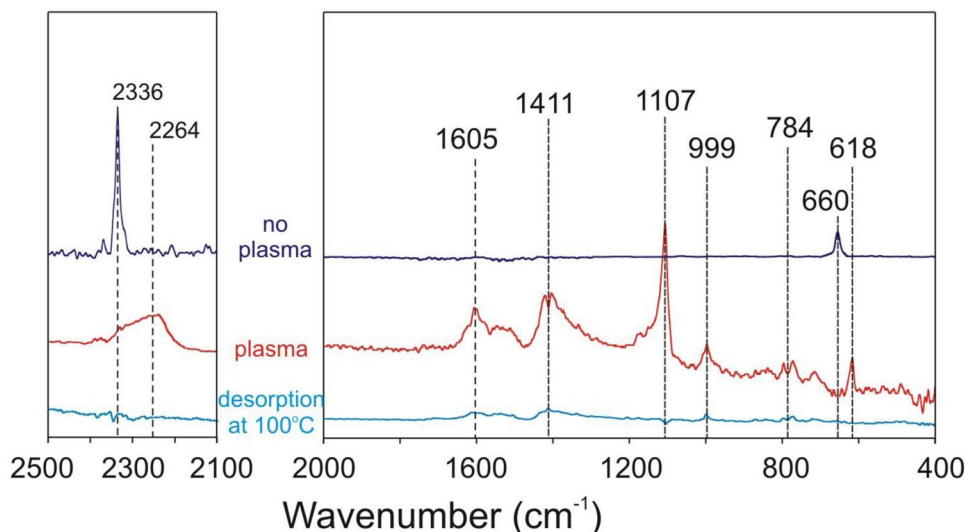
Fig. 4 Upper panel: FTIR spectra of gas phase in-situ i.e. in plasma and ex-situ—stable gas species (see Fig. 1); Bottom panel: quantitative results of plasma-assisted catalytic CO₂ reduction over Zn-TCPP

surface was observed the last process (Eq. 7) should be much faster than the others. The simplified mechanism proposed above, includes that at temperatures as low as 100 °C under high vacuum all formed surface species should be desorbed.

4 Conclusions

Due to a growing interest in CO₂ conversion into useful compounds new solutions are still on the top of the interest. The results presented in this study show that the plasma-assisted catalytic CO₂ reduction to CO on the 2D Zn-containing paddle wheel structures is highly effective. The synthesized catalyst is thermally stable, resistant to oxidative environment, relatively cheap and easy to synthesis. Based on the in situ FTIR studies of the plasma

Fig. 5 The spectral changes of Zn-TCPP surface during CO₂ plasma treatment



assisted catalytic conversion of CO₂ the simplified mechanism of this process is proposed.

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