

# Stability of Metal-Organic Frameworks in non-thermal Atmospheric Plasma

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**Abstract:** The stability of nine metal-organic frameworks (MOFs) in direct contact with non-thermal atmospheric plasma has been thoroughly tested at several temperatures and prolonged times. These MOFs have been carefully selected to test the effect of the MOF morphology and the selection of the metal centers and organic linkers on their stability. The set of stable MOFs have been identified as potential candidates for catalyst development.

## 1. Introduction and Methods

The utilization of non-thermal atmospheric plasma (NAP) to supplement the existing chemical industry by using access renewable resources allows for the potential utilization of less heat resilient catalysts like metal-organic frameworks (MOFs). MOFs are a relatively new class of porous crystalline materials combining metal centers connected by organic linkers and offer large flexibility regarding their composition, porosity and large surface area and they are studied to be used for example in CO<sub>2</sub> capture or conversion [1]. Several works utilizing MOFs in the plasma catalysis processes have been published recently [2-4] indicating that MOFs are compatible with reactive plasmas. However, the MOF stability in NAP has not yet been studied in a systematic way.

Therefore, a dielectric barrier discharge (DBD) reactor has been developed to enable the characterization of the MOF interaction with dielectric barrier discharge in H<sub>2</sub>/N<sub>2</sub> or H<sub>2</sub>/CO<sub>2</sub> gas mixtures. The plasma has been operated with 10-15 kV<sub>pp</sub> at 21 kHz and can be externally heated up to 200 °C. The used system is designed with a large contact area between plasma and MOF and without a necessity to bind the material to pellets. The gas exhaust is analyzed by means of mass spectrometry and the adsorbed power is monitored by high voltage and current probes. A transparent high voltage electrode (indium tin oxide) enables to monitor the plasma operation during the treatment. Nine MOFs have been treated by plasma:

<b>ZIF 8</b>	[Zn(C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>2</sub> ],
<b>ZIF 67</b>	[Co(C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>2</sub> ],
<b>MAF 5</b>	[Zn(C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> ) <sub>2</sub> ],
<b>MAF 6</b>	[Zn(C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> ) <sub>2</sub> ],
<b>ZIF-7</b>	[Zn(C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>2</sub> ] · 1 DMF,
<b>ZIF 71</b>	[Zn(C <sub>3</sub> HCl <sub>2</sub> N <sub>2</sub> ) <sub>2</sub> ],
<b>CAU 10</b>	[Al(OH)(m-H <sub>2</sub> BDC)] · n H <sub>2</sub> O,
<b>CAU 24</b>	[M <sub>6</sub> O <sub>4</sub> (OH) <sub>8</sub> (H <sub>2</sub> O) <sub>4</sub> (TCPB) <sub>2</sub> ], M = Ce/Zr,
<b>UiO 66</b>	[Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (p-BDC) <sub>6</sub> ] · n H <sub>2</sub> O.

Their stability has been studied by performing powder X-ray diffraction (XRD), sorption measurements, IR absorption spectroscopy and elemental analysis before and after the treatment.

Additionally, another DBD reactor was also developed with accessible optical axis through the treated material to allow for in situ x-ray analysis of material within the plasma. The plasma operates with H<sub>2</sub> gas combined with Ar or CO<sub>2</sub>. This design was employed during the beam-time of CH-7281 at BM-23 at the European Synchrotron Radiation Facility (ESRF) to treat clusters and MOFs containing cerium. The chemical stability of these compounds was analyzed using in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).

## 2. Results, Discussion and conclusion

The performed analysis allowed to identify four stable MOFs (ZIF 8, ZIF 67, MAF 5 and MAF 6) under all conditions and temperatures studied. The collected data are still being analyzed at the moment, but no structural changes have been observed by these MOFs and the release of possible decomposition products (particularly CH<sub>4</sub>) is observed only briefly after plasma ignition. No catalytic activity has been observed, which is an expected result, because the used MOFs were not decorated with catalytically active centers. The modification of the linkers to introduce the catalytic reactivity into the system is planned in the next step.

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