

# Crystallographic Visualization of a Double Water Molecule Addition on a Pt<sub>1</sub>-MOF during the Low-temperature Water-Gas Shift Reaction

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**Abstract:** The low-temperature water-gas shift reaction (WGSR,  $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$ ) is considered a very promising reaction – candidate for fuel cells– despite an efficient and robust catalyst is still desirable. One of the more prominent catalysts for this reaction is based on single Pt atoms (Pt<sub>1</sub>) on different supports, which are supposed to manifold the reaction by the accepted mechanism for the general WGSR, i.e. by addition of one H<sub>2</sub>O molecule to CO, with generation of CO<sub>2</sub> and H<sub>2</sub>. Here we show, experimentally, that not one but two H<sub>2</sub>O molecules are added to CO on the Pt<sub>1</sub> catalyst, as assessed by a combination of reactivity experiments with soluble Pt catalysts, kinetic and spectroscopic measurements, and finally by *in-operando* single crystal X-ray diffraction on a Pt<sub>1</sub>-MOF, to visualize the formation of the hemiacetal intermediate on the solid catalytic site. These results confirm our previous DFT predictions and provide a paradigmatic shift in the assumed mechanism of the WGSR, which may open the debate if two H<sub>2</sub>O molecules are recurrently added during the WGSR, not only for Pt<sub>1</sub> catalysts but also for other metal catalysts.

## Introduction

The development of novel more efficient and less costly methods for hydrogen production is a highly desired objective due to its multiple potential industrial uses<sup>[1]</sup> which, in addition, can play a pivotal role in the decarbonization of today's economy. In particular, the water-gas shift reaction<sup>[1,2]</sup> (WGSR,  $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$ ) has not only emerged –in combination with coal gasification– as an important source of pure hydrogen<sup>[3]</sup> but, in addition, for the removal of carbon monoxide, which can be particularly important in hydrocarbon reforming processes where H<sub>2</sub> is usually contaminated with CO.<sup>[4]</sup> In fact, WGSR participates in industrial processes such as the Fischer–Tropsch process<sup>[5]</sup> (balancing the H<sub>2</sub>/CO ratio) and the synthesis of methanol or ammonia.<sup>[6]</sup> Besides, the low-temperature WGSR is the preferred

reaction in fuel cells,<sup>[7]</sup> where the temperature should not exceed ideally of 200 °C. Despite these remarkable applications and related advances in the last years,<sup>[4,8–15]</sup> the search for optimal catalysts, with easy implementation in industry, still continues.

At present, there is still great controversy regarding the mechanism(s) operating in the low-temperature WGSR, which seems to depend strongly on reaction conditions (temperature being foremost among such conditions) as well as the chosen catalyst, usually metal oxides or a solid supported metal species.<sup>[16]</sup> So far, two possible mechanisms for the WGSR have been proposed: an associative mechanism and a “redox” regenerative one which is probably operative only at high temperatures.<sup>[4]</sup> In any case, none of these mechanisms assume a double addition of H<sub>2</sub>O on CO, neither experimentally or theoretically.<sup>[17]</sup> A total understanding of the mechanism would undoubtedly contribute to the design of more efficient active species capable to outperform industrially used catalysts.

In this context, we recently reported<sup>[18]</sup> the postsynthetic<sup>[19–24]</sup> preparation and structural characterization of well-defined Pt<sub>1</sub><sup>1+</sup> single atom catalysts (SACs) supported, stabilized and homogeneously distributed within the pores of a robust metal-organic framework<sup>[25–30]</sup> (MOF). This hybrid material, with formula  $[\text{Pt}^{2+}_2(\mu\text{-O})(\text{OH})_2(\text{NH}_3)_4]_{0.5}\text{Pt}^{1+}_1@ \text{Na}_3\{\text{Ni}^{2+}_4[\text{Cu}^{2+}_2(\text{Me}_3\text{mpba})_2]_3\} \cdot 79\text{H}_2\text{O}$  (**1**),<sup>[18]</sup> was characterized, in detail, by single crystal X-ray diffraction<sup>[31,32]</sup> and exhibited good catalytic activity for the WGSR at low-temperature. DFT calculations suggested an associative catalytic mechanism where both the coordinated Pt<sub>1</sub><sup>1+</sup> metal and the hydrogen-bonded water molecules cause a double water attack mechanism to CO giving CO<sub>2</sub> with both oxygen atoms coming from water.

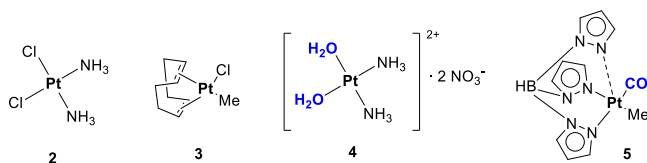
In this contribution, we have explored the catalytic activity of a variety of soluble mononuclear Pt compounds, for the sake of comparison with Pt<sub>1</sub><sup>1+</sup> SACs and aiming at further confirming the proposed associative mechanism at low temperatures. In addition, *in-situ* single crystal X-ray diffraction (SCXRD) using synchrotron radiation on single crystals of MOF **1** in the presence of CO(g)

and H<sub>2</sub>O (g), has allowed us to unveil the crystal structure of a new host-guest adsorbate [Pt<sup>1+</sup><sub>2</sub>(μ-O)(CO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>0.5</sub>·(CO)<sub>2</sub>@Na<sub>4</sub>{Ni<sup>2+</sup><sub>4</sub>[Cu<sup>2+</sup><sub>2</sub>(Me<sub>3</sub>mpba)<sub>2</sub>]<sub>3</sub>}·16H<sub>2</sub>O (**CO@1**) that permits the direct observation of the coordination site for CO as well as the direct attack of two H<sub>2</sub>O molecules to give the corresponding hemiacetal intermediate, ready to collapse into CO<sub>2</sub> and H<sub>2</sub>. One of the H<sub>2</sub>O molecules comes from the MOFs' walls, in accordance with recent findings on the key role of adsorbed OH species in the reverse WGSR.<sup>[33]</sup> The robustness of the MOF **1** crystal is paramount to visualize H<sub>2</sub>O molecules under reaction conditions, a typically difficult task.<sup>[34]</sup> These findings, in combination with isotopic and NMR experiments, strongly suggest that the double H<sub>2</sub>O attack is general for any Pt<sub>1</sub> catalyst, soluble or supported, during the low-temperature WGSR.

## Results and Discussion

### Catalysis

The WGSR has been studied for more than fifty years as an undesired reaction of soluble Pt(0) complexes, since Pt(CO)<sub>n</sub> complexes tend to decompose in the presence of water under certain conditions.<sup>[35,36]</sup> However, it is difficult to find in the literature specific studies regarding soluble cationic Pt complexes as catalysts for the WGSR, perhaps because the most stable and available Pt chloride compounds such as cisplatin PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> early showed no catalytic activity.<sup>[37,38]</sup> Figure 1 shows the structure of the cationic Pt complexes **2-5** used here as catalysts for the WGSR. Cisplatin **2** and complex **3**<sup>[39]</sup> are typical Pt(II) chloride complexes with significantly different solubility in water, the aqueous complex **4**<sup>[40]</sup> is representative of a potential WGSR intermediate with H<sub>2</sub>O, and complex **5**<sup>[41]</sup> is also representative of a potential WGSR intermediate with CO. In particular, stoichiometric amounts of complex **5** have shown to give the WGSR in the presence of water, with the uncoordinated pyrazolyl ligand acting as an anchoring site for the reacting H<sub>2</sub>O molecules, just the role of the walls in MOF **1**.<sup>[41]</sup> However, no catalytic uses in the WGSR have been reported to date, as far as we know.



**Figure 1.** Pt complexes used as catalysts in this work for the low-temperature water-gas shift reaction (WGSR). In bold, the Pt atom; in blue, ligands that act as reactants during the WGSR.

Table 1 shows the catalytic results for the low-temperature WGSR with MOF **1**, with a reported and very active Pt<sub>1</sub>-Na/SiO<sub>2</sub> solid catalyst,<sup>[8,10]</sup> and with complexes **2-5**, H<sub>2</sub>PtCl<sub>4</sub> and commercially available Pt NPs on charcoal (10 wt%). It can be seen that MOF **1** is much more active than any other Pt catalyst tested (entry 1), with an initial turnover frequency (TOF<sub>0</sub>) = 40 h<sup>-1</sup> under the indicated reaction conditions. As expected, Pt chloride compounds, including complexes **2** and **3**, and Pt-C were completely inactive (entries 2-5), however, complexes **4-5** were reasonably active for the reaction, approaching the catalytic

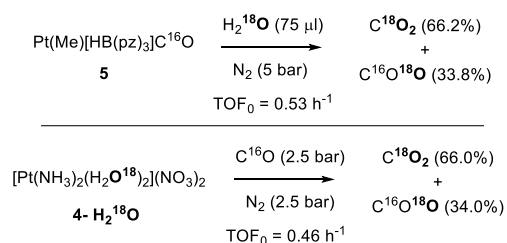
activity of the state-of-the-art solid catalyst Pt<sub>1</sub>-Na/SiO<sub>2</sub> (entries 6-9, see also Figures S1-S3 in the Supporting Information).

**Table 1.** Catalytic results for the low-temperature WGSR with different Pt catalysts. Reaction conditions: 1 mmol CO, 5.5 mmol H<sub>2</sub>O, 0.001 mmol (0.1 mol%) of Pt, 140 °C, total pressure= 5 bar (2.5 bar of N<sub>2</sub>).

Run	Catalyst	P(CO) (bar)	H <sub>2</sub> O (μL)	TOF <sub>0</sub> (h <sup>-1</sup> ) <sup>[a]</sup>
1	MOF <b>1</b>	2.5	100	40.0
2	H <sub>2</sub> Cl <sub>6</sub> Pt	2.5	100	N.D.
3	Pt-C	2.5	100	N.D.
4	PtCl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <b>2</b>	2.5	100	N.D.
5	PtClMe(COD) <b>3</b>	2.5	100	N.D.
6	[Pt(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> <b>4</b>	2.5	100	1.24
7		2.5	0	2.89
8	Pt(Me)[HB(pz) <sub>3</sub> ]CO <b>5</b>	0	100	0.53
9	Pt <sub>1</sub> -Na/SiO <sub>2</sub>	2.5	100	7.2

[a] Measured as mmol of CO<sub>2</sub> generated by mmol of Pt during the linear initial rate: N.D.: non-detected. Results are an average of two different batches.

Complexes **4** and **5** can be used as both catalyst and reagent for the WGSR, to give TOF<sub>0</sub>s= 2.89 and 0.55 h<sup>-1</sup>, respectively (entries 6-8). These results indicate that the activation of CO in the pre-formed aquo Pt complex is feasible, and also the opposite, i.e. the activation of H<sub>2</sub>O in the carbonyl Pt complex, although less efficiently. These results are in good agreement with the previously proposed mechanism for MOF **1**,<sup>[18]</sup> where CO coordinates and activates onto the hydrated Pt<sub>1</sub> site.

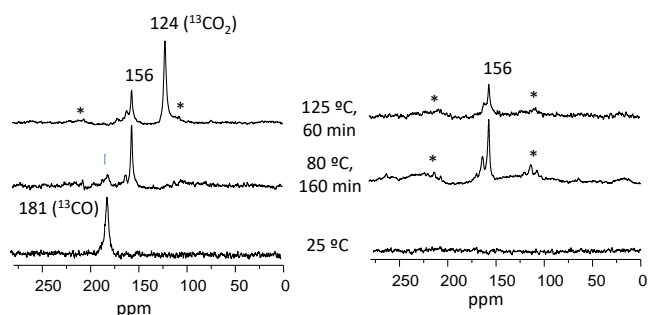


**Figure 2.** Isotopically labelled experiments with stoichiometric amounts of Pt complexes containing one of the reactants for the low-temperature water-gas shift reaction (WGSR).

Figure 2 shows the result for the reaction between the carbonyl complex **5** and H<sub>2</sub><sup>18</sup>O, in the absence of any other water molecule or CO atmosphere. This experiment is designed to assess if one or two H<sub>2</sub>O molecules are coupled to CO on the soluble Pt complex, to give CO<sub>2</sub> with both oxygen atoms coming from water. The results show that C<sup>18</sup>O<sub>2</sub> is formed twice than C<sup>16</sup>O<sup>18</sup>O, the statistical result for a double addition of H<sub>2</sub><sup>18</sup>O (Figure S4). Since the high excess of H<sub>2</sub><sup>18</sup>O may give the isotopically marked product after extensive equilibria, a new experiment was carried out with the isotopically labelled aquo complex [Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O<sup>18</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (**4-H<sub>2</sub><sup>18</sup>O**), and the reaction of **4-H<sub>2</sub><sup>18</sup>O** with CO gives, as shown in Figure 2, the same C<sup>18</sup>O<sub>2</sub> distribution (64.0%) and a similar TOF<sub>0</sub> (0.46 h<sup>-1</sup>) than in excess of water (Figure S5). The similar CO<sub>2</sub> distribution indicates a

double H<sub>2</sub>O addition on CO with the cationic Pt complexes, and the similar initial rate strongly supports that both CO and H<sub>2</sub>O participate in the rate-determining step of the reaction, as occurs with MOF **1**.<sup>[18]</sup>

Figure 3 shows the <sup>13</sup>C magic angle spinning solid-state nuclear magnetic resonance (MAS NMR) of MOF **1** when isotopically labelled <sup>13</sup>CO was co-adsorbed with water (<sup>13</sup>CO:H<sub>2</sub>O 1:2 equivalents respect to Pt) into a sealed rotor and heated.<sup>[18]</sup> It can be seen the appearance a new signal at 156 ppm, which transforms into <sup>13</sup>CO<sub>2</sub> after heating. The shift of this signal fits well with the hemiacetal orthoformate H<sup>13</sup>C(OH)<sub>3</sub> (predicted 140 ppm), and cross polarization (CP) NMR experiments confirm that the <sup>13</sup>C atom bears H atoms at 1–2 bond distance. This result explains the statistical C<sup>18</sup>O<sub>2</sub> distribution found for MOF **1**<sup>[18]</sup> and also above for Pt complexes **4** and **5**, since the hemiacetal intermediate collapses into CO<sub>2</sub> and H<sub>2</sub>O (and also H<sub>2</sub>) with the same probability for the 3 oxygen atoms.

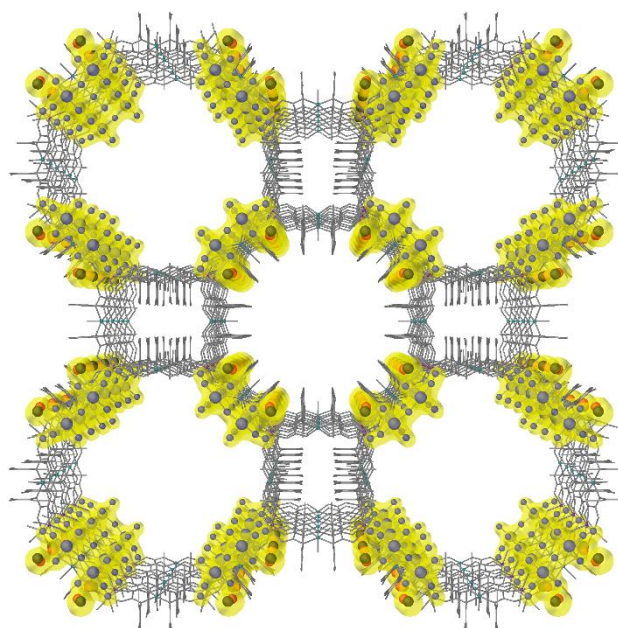


**Figure 3.** <sup>13</sup>C MAS NMR (left) and the corresponding CP-NMR (right) of <sup>13</sup>CO on MOF **1**, co-adsorbed with water (1:2:1 in Pt) and heated at the indicated temperature and time. \* Indicates spinning side bands.

### Crystal Structure of CO@1

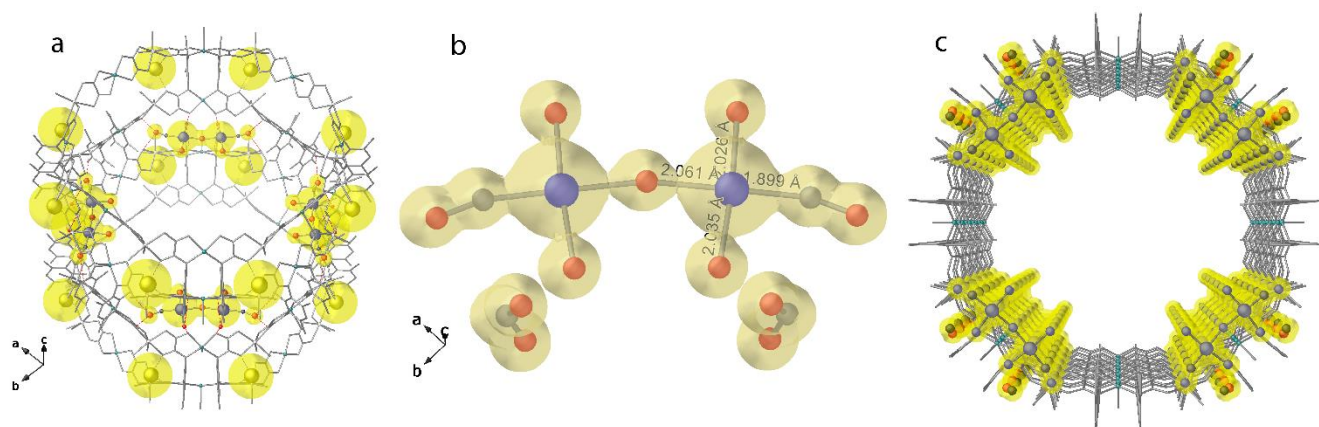
*In-situ* SC-XRD experiments were carried out for MOF **1** at a temperature of 310 K and under the presence of CO/H<sub>2</sub>O mixture, using synchrotron radiation, on single crystal sealed in the gas cell, designed and built at Diamond Light Source, in the I19 beamline (Figure S6).

The sample was sealed in that specially designed cell and the the CO/Ar gas mixture through a heated water bubbler (to generate the CO/H<sub>2</sub>O mixture) was fluxed under a pressure of 1.12 bar for 15 min. The crystal structure of CO@**1** was determined at 310 K. It results isorecticular to **1**, crystallizing in the *P4/mmm* space group of the tetragonal system (Table S1), with the anionic Ni<sup>II</sup><sub>4</sub>Cu<sup>II</sup><sub>6</sub> open-framework structure accommodating Pt-CO adducts and free CO<sub>2</sub> molecules (Figures 4-5, S7-S10) in its hydrophilic and hydrophobic octagonal pores, respectively.



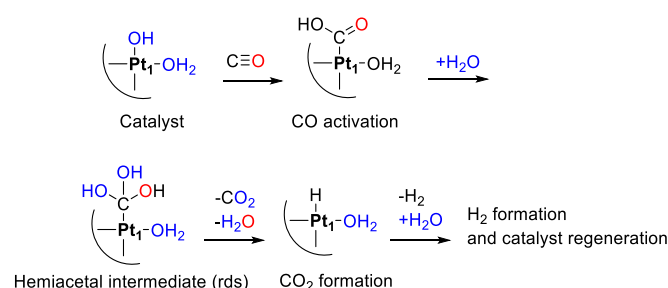
**Figure 4.** Crystal structures, determined by synchrotron X-ray diffraction, of the CO@**1** obtained from the *in-situ* simulation of WGS: Perspective view along *c* crystallographic axis, showing [Pt<sup>1+</sup><sub>2</sub>(μ-O)(CO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] moieties and CO<sub>2</sub> molecules embedded in pores. The heterobimetallic CuNi 3D anionic network is depicted as grey sticks. Pt(I) cations in the pores and carbon atoms of CO molecules are represented by blue spheres whereas oxygen atoms are depicted in red. Surface with Van der Waals radii is used to highlight the generated molecules within MOFs channels. Sodium cation and crystallization water molecules in the pores have been omitted for clarity.

Detailed analysis of SCXRD data indicated that square planar Pt<sup>1+</sup> atoms had been attached by one CO and two H<sub>2</sub>O molecules. Furthermore, the highly hydrophilic environment stabilized an oxo bridge between two approaching complexes giving rise to dimers of formula [Pt<sup>1+</sup><sub>2</sub>(μ-O)(CO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (Figure 5a-b), thus confirming that it is the addition of both CO and two H<sub>2</sub>O promoting the hemiacetal evolution into CO<sub>2</sub>. Noteworthy, CO@**1** crystal structure unveils produced CO<sub>2</sub> molecules as well, within the MOF pores, residing in proximity of Pt intermediate. The crystal structure snapshotted the Pt-CO water adducts perfectly stabilized in hydrophilic pores (Figures 4-5 and S9), whereas CO<sub>2</sub> molecules reside in hydrophobic channels most likely as a direct consequence of the chemical stabilization provided by phenyl rings pointing within MOF pores (Figures 4 and S10-S11). Hydrogen bonds between H<sub>2</sub>O surrounding Pt have a key role to guarantee those active interactions with acceptor oxygen atoms from the walls of the network [CO...O<sub>MOF</sub> of 2.894 and H<sub>2</sub>O...O<sub>MOF</sub> of 3.156(4) Å]. On the contrary the *in-situ* generated CO<sub>2</sub> is stabilized by aromatic rings at a distance of 3.39 Å (Figure S11).



**Figure 5.** Perspective views showing details of **CO@1** crystal structure: a) Single pore side view of hydrogen bonds interactions stabilizing  $[\text{Pt}^{1+}_2(\mu\text{-O})(\text{CO})_2(\text{H}_2\text{O})_4]$  intermediates within hydrophilic pores; b) detailed crystal structure of  $[\text{Pt}^{1+}_2(\mu\text{-O})(\text{CO})_2(\text{H}_2\text{O})_4]$  moieties clarifying CO and  $\text{H}_2\text{O}$  binding sites; c) view down direction of pore's propagation showing (all in blue color) the in-situ generated molecules interacting with MOF's walls.  $\text{Na}^+$  and  $\text{Pt}^+$  in gold and blue ones, respectively. The heterobimetallic CuNi 3D anionic network is depicted as grey sticks. Carbon and oxygen atoms of the in-situ generated molecules, are depicted as grey and red spheres, respectively. Surface has been depicted to highlight Pt-CO water adducts and  $\text{CO}_2$  hosted in pores.

The scope of this experiment design was to unequivocally visualize that two  $\text{H}_2\text{O}$  molecules are coupled to CO on the Pt complex, to give  $\text{CO}_2$ . Looking at the crystal structure of **CO@1** it is evident the geometric organization of the system in which CO molecule activates catalysts with a bind on *cis* arrangement respect to the two active  $\text{H}_2\text{O}$  molecules with optimal geometric requisites for nucleophilic attack. In the square planar Pt environment, the CO molecule is coordinated at a distance of 1.897(9) Å that result shorter than that of Pt-OH<sub>2</sub> bond lengths [2.035(9) and 2.026(9) Å].<sup>[18]</sup>



**Figure 6.** Proposed mechanism of the  $\text{Pt}_1$ -catalyzed low-temperature water-gas shift reaction (WGSR). The main product distribution is colored, although a statistical distribution indeed occurs.

With these results in hand, Figure 6 shows the proposed mechanism for the low-temperature WGSR with  $\text{Pt}_1$  catalysts, either Pt complexes on single atom supported solids. First, CO activation occurs on the  $\text{Pt}_1$  site, with the assistance of a coordinated hydroxyl group. Then, a second  $\text{H}_2\text{O}$  molecule coordinates and attacks the formyl intermediate, to give the corresponding hemiacetal. The formation of this intermediate on the catalytic site is the plausible rate-determining step (rds) of the reaction, not only on the basis of thermodynamic and kinetic parameters,<sup>[6b]</sup> but also suggested by its clear detection by MAS NMR. Then, the hemiacetal easily collapses into  $\text{CO}_2$  in virtue of a favoured  $\beta$ -H elimination to give a gas molecule ( $\text{CO}_2$ ) and to regenerate the catalyst after Pt hydride reaction, to give the

second gas molecule,  $\text{H}_2$ . This mechanism showcases the key role of at least two  $\text{H}_2\text{O}$  molecules, adsorbed and coordinated, to trigger the low-temperature WGSR.

## Conclusion

In summary, in this contribution we have tried to shed light on the mechanisms governing the low-temperature WGSR by using a multi-technique approach that includes catalysts, kinetic and spectroscopic measurements and, last but not least, *in-operando* single crystal X-ray diffraction on a  $\text{Pt}_1$ -MOF under the presence of a  $\text{CO}/\text{H}_2\text{O}$  mixture. SCXRD studies allow to visualize, for the first time, that square planar  $\text{Pt}^{\delta+}$  SACs are simultaneously coordinated by one CO and two  $\text{H}_2\text{O}$  molecules –forming a Pt-CO water adduct perfectly stabilized in the hydrophilic pores of the MOF that suggests the formation of a hemiacetal intermediate– and also the resulting  $\text{CO}_2$  molecules also hosted within the MOF channels. These results, together with the catalytic ones, validate the occurrence of an associative mechanism, with a double  $\text{H}_2\text{O}$  attack, for the low-temperature WGSR with any  $\text{Pt}_1$  catalyst.

## Experimental Section

**Synthesis of  $\text{Pt}_1$ -MOF.** MOF  $[\text{Pt}^{2+}_2(\mu\text{-O})(\text{OH})_2(\text{NH}_3)_4]_{0.5}\text{Pt}^{1+}_1@ \text{Na}_3\{\text{Ni}^{2+}_4[\text{Cu}^{2+}_2(\text{Me}_3\text{mpba})_2\}_3\} \cdot 79\text{H}_2\text{O}$  (**1**) was prepared and characterised as reported earlier.<sup>[18]</sup>

**Synthesis of platinum complexes.** The syntheses of PtCIME(COD) (**3**),  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]^{2+}$  (**4**) and  $\text{Pt}(\text{Me})[\text{HB}(\text{pz})_3]\text{CO}$  (**5**) are thoroughly described in the Supporting Information.

**General catalytic reaction procedure.** The corresponding Pt catalyst (0.001 mmol) was placed in a 6.5 mL glass vial equipped with a valve and a manometer, and Milli-Q water (100  $\mu\text{L}$ , 5.5 equiv.) was added. The vial was closed, purged three times with 5 bar of nitrogen and pressurized with 2.5 bar of CO (1 mmol) and 2.5 bar of nitrogen to a final pressure of 5 bar; the reaction mixture was heated to 140 °C. Samples of the reaction mixture were drawn using a Hamilton SampleLock gas syringe and the

reaction products were analyzed with an Agilent micro GC (Mosiieve 5A column using argon as carrier gas). Experiments were repeated twice.

**Reaction procedure with complex 5 and isotopically labelled  $\text{H}_2^{18}\text{O}$ .** Complex **5** (1.7 mg, 0.73 mg of Pt) and 100  $\mu\text{L}$  of labeled water ( $\text{H}_2^{18}\text{O}$ ) were added to a 6.5 mL glass vial equipped with a valve and a manometer. The vial was closed, purged three times with 5 bar of nitrogen and pressurized with 5 bar of nitrogen (reagent  $\text{CO}$  is obtained from the catalyst); the reaction mixture was heated to 140 ° C. Samples of the reaction mixture were drawn and analyzed as above.

**Reaction procedure with complex 4 or isotopically labelled complex 4- $\text{H}_2^{18}\text{O}$  as a reactant.** Complex **4** or 4- $\text{H}_2^{18}\text{O}$  (1.2 mg, 0.6 mg of Pt) was placed in a 6.5 mL glass vial equipped with a valve and a manometer. The vial was closed (the water is obtained from the complex) and purged three times with 5 bar of nitrogen and pressurized with 2.5 bar of  $\text{CO}$  (1 mmol) and 2.5 bar of nitrogen to a final pressure of 5 bar; the reaction mixture was heated to 140 ° C. Samples of the reaction mixture were drawn and analyzed as above.

**X-ray crystallographic details.** The crystallographic studies on single-crystal X-ray on **1** were carried out at beamline I19 of Diamond Light Source. A crystal of **1** with 0.05 x 0.04 x 0.04 mm as dimensions was selected and mounted on a MITIGEN holder in glue, then the sample pin was inserted in the glass capillary, sealed in the cell and placed on the goniometer system under a controlled temperature at 310 K. The gas loading was precisely controlled and measured on single crystal sealed in the gas cell, to perform *in-situ* gas-dosing experiments. Without activation of the crystal (considering water is part of the gases mixture) data were acquired, measuring on **1** under the presence of the  $\text{CO}/\text{H}_2\text{O}$  mixture, under a pressure of 1.12 bar for 15 min. Once measurements were performed, the gas was exhausted from main rig and sample lines. Then, vacuum was applied on all the lines to remove any residue of previously measured toxic gas and all the rig and gas lines refilled with inert gas. Diffraction data for **1** were collected on using synchrotron radiation at I19 beamline of the Diamond Light Source at  $\lambda = 0.6889 \text{ \AA}$ . Crystal data: Tetragonal, space group  $P4/mmm$ ,  $T = 310(2)$ ,  $Z = 4$ ;  $\text{C}_{81}\text{H}_{96}\text{Cu}_6\text{N}_{12}\text{Na}_4\text{Ni}_4\text{O}_{60}\text{Pt}$ ,  $a = 35.893(2) \text{ \AA}$ ,  $c = 15.1253(10) \text{ \AA}$ ,  $V = 19487(3) \text{ \AA}^3$ . Further details can be found in the Supplementary Information and Table S1. CCDC 2031954 contain the supplementary crystallographic data for **CO@1** reported in this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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## Conflict of Interest

The authors declare no conflict of interest.

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