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Adsorption of nitric oxide in metal-organic frameworks: Low temperature IR and EPR spectroscopic evaluation of the role of open metal sites

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ABSTRACT

The metal-organic framework materials M-MIL-100 (M = Al, Fe) and M-CPO-27 (M = Co, Ni) have been studied with respect to the adsorption of nitric oxide employing low-temperature ESR and IR spectroscopy. Exposure of the previously desolvated Ni (II) and Co (II) sites in CPO-27 leads to the formation of metal nitrosyl complexes that are stable up to temperatures of 393 K. A weaker bond is formed between the iron metal centers in the Fe-MIL-100 type materials and the nitric oxide molecule. Using in-situ DRIFT and EPR spectroscopy at low temperatures, the formation of Co-, Ni- and Fe–NO adducts is evident from the respective spectra, while specifically strong interactions are absent in Al-MIL-100 and Al/Cr-Mil-53.

1. Introduction

Nitric oxide (NO) is a biological signaling molecule in the human organism despite its high toxicity as a gas [1]. The possible use of NO in biomedical applications, employing for example its anti-thrombotic or anti-inflammatory properties, depends on the availability of an applicable storage material [2,3]. A suitable material for NO storage should have a high adsorption capacity and should interact strongly enough with the gas in order to store it in a stable fashion, but at the same time should allow to release the gas under predefined conditions [4].

Different materials, including zeolites, polymers and functionalized silica nanoparticles have been tested as potential NO storage and release materials [5–11]. A common drawback of the majority of those materials is the delivery of side products, which can be carcinogenic or pro–inflammatory [4].

Metal-organic frameworks (MOFs) represent a class of porous solids which are constructed from inorganic metals (or metal clusters) connected by organic linker molecules [12]. MOFs are especially suitable for gas storage applications because of their low density and large specific surface area [12–15]. Possible pathways for storing NO in metal-organic frameworks are physical adsorption or the formation of covalent bonds with the organic linker via the formation of a diazeniumdiolate species [16]. For the second pathway, an accessible secondary amine function is required. If coordinatively unsaturated metal sites (CUS) are present such as Cu^{2+} in HKUST-1 [17] or Ni^{2+} or Co^{2+} in CPO-27 [4], coordinative bonding of guest molecules (e.g. NO) to such open metal sites increases the storage capability of the material [4]. The release of the stored NO can be triggered by exposure to a competitive adsorbent such as water [4]. Considering possible medical applications of MOF-containing devices, the testing of their toxicity and biological activity is an increasingly important topic in recent research [18–20].

In this contribution, we report the spectroscopic properties of NO adsorbed in M-MIL-100 (M = Al, Fe), M-CPO-27 (M = Co, Ni) and Al/Cr-MIL-53 type metal-organic frameworks [21–23]. It has been reported that the adsorption capacity of M-CPO-27 (M = Co, Ni) is more than six times higher than M-MIL-53(M = Al, Cr) [24]. This difference has been attributed to the presence of coordinatively unsaturated metal sites (CUS) in the former material [4,24]. In addition, M-MIL-100 (M = Al, Fe) was studied since Horcajada et al. [18,25] reported that Fe-MIL-100 also shows a good uptake for NO.

Spectroscopic methods have been employed only in a few cases to monitor NO adsorption in MOF materials [26,27]. In particular

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infrared spectroscopy (IR) has given detailed insight into the adsorption behavior of NO onto Ni-CPO-27 [26]. The position and intensity of the signal in the infrared spectrum between 1710 and 1966 cm^{-1} [28], which are assigned to coordinated NO, can yield information on the type of interaction between the NO molecule and the storage material [29,30] as well as information about the relative amount of coordinated NO [26].

The NO molecule is accessible to EPR investigations since it possesses one unpaired electron in an antibonding π^* molecular orbital (MO) [31]. For free NO in the gas phase the $^2\Pi_{1/2}$ ground state is diamagnetic whereas the lowest rotational level of the first excited $^2\Pi_{3/2}$ state of free NO is paramagnetic [31,32]. The corresponding total angular momentum quantum number is $J = 3/2$. This state is responsible for the nine line EPR pattern of NO gas at $g = 0.777$ that can be observed at low pressures [33,34]. Higher rotational states such as $^2\Pi_{3/2}$ with $J > 3/2$ are also EPR active but cannot be observed at X-band frequencies [35] due to their small g-values [36].

The presence of an external electric field gradient with less than axial symmetry can quench the orbital angular momentum [35], e.g. when NO is adsorbed at a surface site and its ground state becomes paramagnetic. Then the two fold degeneracy of the π^* orbital is lifted into the π_x^* orbital and the energetically lower lying π_y^* orbital occupied by the unpaired electron. The NO molecule with an electron spin $S = 1/2$ shows an EPR signal with orthorhombic g-tensor. Its principle values in x-, y- and z-direction are near the free electron g-value $g \approx 2$ but always slightly smaller and hold the relations $g_{xx} > g_{yy} > g_{zz}$ [36–38]. All g-values but especially g_{zz} are sensitive to the strength of the electric field gradient at the adsorption site [35]. A ^{14}N hyperfine interaction of about $A_{yy} = 90$ MHz is only observed along the y axis of the g-tensor.

Especially paramagnetic NO adsorption complexes can be studied with EPR spectroscopy, e.g. NO complexes with sodium cations and aluminum defect centers in zeolites [39,40]. In particular the temperature dependences of the EPR signal intensities of these complexes have reflected the adsorption behavior of NO, whereas the analysis of the corresponding low temperature EPR signals has given insight into the nature of the NO adsorption complex. In addition, the EPR signal of the $^2\Pi_{3/2}$ state of gaseous NO has been employed to monitor the desorption of NO from various zeolites [40,41].

In the present work, infrared spectroscopy in the diffuse reflectance (DRIFTS) mode and EPR are employed to investigate the adsorption of NO in the MOF materials under study. The IR signals of NO as well as the EPR signals of gaseous NO and some NO adsorption complexes have been measured at different temperatures. A large advantage of IR spectroscopy is that it can in principle observe all adsorbed NO species, whereas EPR detects only paramagnetic NO species on a much slower time scale. But in contrast to IR spectroscopy, desorbed NO gas is detectable in very small amounts over a large temperature range by EPR. Furthermore IR data of paramagnetic NO adsorption species which can be obtained for temperatures $T > 173$ K are nicely complemented by EPR experiments at lower temperatures down to $T = 5$ K. In this way a detailed insight into the microscopic nature and strength of NO adsorption in the concerned MOF materials has been obtained taking advantage of the characteristics of both spectroscopic methods.

2. Experimental section

2.1. Synthesis of Al-MIL-100

1.363 g (3.633 mmol) of $Al(NO_3)_3 \cdot 9H_2O$ and 0.614 g (2.434 mmol) of trimethyl 1,3,5-benzenetricarboxylate (Me_3BTC) were dissolved in 17.5 ml of water. Then 0.302 g (4.793 mmol) of nitric acid (60 wt.-%) were added and the mixture was transferred to a Teflon-lined stainless steel autoclave (V = 125 ml). The autoclave was placed in an oven at a temperature of 303 K, which was increased to 483 K at a rate of 3 K/min and subsequently held at this temperature for three days. After the thermal treatment, the light yellow solid was recovered by filtration and washed with 200 ml of water. For further purification the obtained solid was extracted with hot ethanol for 16 h [42].

2.2. Synthesis of Fe-MIL-100

For the synthesis of Fe-MIL-100 a procedure without hydrofluoric acid was selected. 6.262 g (15.501 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ and 2.216 g (10.546 mmol) of benzenetricarboxylic acid (BTC) were filled into a Parr Teflon-liner and 90 ml of water were added.

After 5.44 g (86.272 mmol) of nitric acid (60 wt.-%) were added, the mixture was homogenized for 2 h and transferred to a stainless steel autoclave (V = 125 ml). The reaction temperature of 433 K was held for 24 h after heating from the initial oven temperature of 303 K with a rate of 2 K/min. After cooling to room temperature an orange solid is obtained by filtration and washed with 500 ml of water. For further purification the obtained Fe-MIL-100 was extracted with hot ethanol for 16 h [43].

2.3. Synthesis of CPO-27 type materials

The syntheses of Co-CPO-27 and Ni-CPO-27 were carried out according to our previously published procedure [44].

2.4. Synthesis of Al/Cr-MIL-53

8.495 g (22.645 mmol) of $Al(NO_3)_3 \cdot 9H_2O$ and 0.190 g (0.474 mmol) of $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in 33 ml of water. Then, 5.891 g (34.621 mmol) of terephthalic acid were added, the mixture was homogenized by stirring for ca. 20 min and transferred to a Teflon-lined stainless steel autoclave (125 ml). After thermal treatment at 493 K for 72 h, the slightly purple solid was recovered by filtration, washed three times with 50 ml of water each and briefly dried at 393 K for 1 h. The obtained solid was subject to calcination in air at 603 K for 72 h (heating rate ca. 100 K/h). The overall procedure resembles the one given by Loiseau et al. [23] except for the substitution of 2 mol-% aluminum by chromium.

2.5. Characterization

The crystallinity and phase purity of the synthesized materials were investigated on a PANalytical X'Pert Pro powder diffractometer (Cu Kα radiation) (Fig. S1). Nitrogen sorption measurements were carried out on a Micromeritics ASAP 2010 instrument at 77 K after activation of the materials in vacuum ($p \approx 10^{-3}$ mbar) at different temperatures as summarized in Table 1.

Infrared spectra were recorded on a JASCO 4100 IR spectrometer equipped with a Pike DiffusIR low temperature chamber with a potassium bromide window. For every spectrum 64 scans with a resolution of 4 cm^{-1} were recorded. The intensities of the infrared peaks of the synthesized metal-organic frameworks in a diffuse reflectance setup would be too high to observe changes in the spectra upon exposure to gaseous nitric oxide. Thus, the pure materials were diluted with calcium fluoride (CaF_2) yielding expedient intensities. It has been proven experimentally that only weakly physisorbed NO is formed after adsorption on CaF_2 (see supporting information, Fig. S2).