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Capture of nitrogen dioxide and conversion to nitric acid in a porous metal-organic framework

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Air pollution by nitrogen oxides, NO_x , is a major problem, and new capture and abatement technologies are urgently required. Here we report a metal-organic framework (MFM-520: MFM = Manchester Framework Material) that can efficiently confine dimers of NO_2 , resulting in a high adsorption capacity of 4.2mmol/g (298K, 0.01bar) with full reversibility and no loss of capacity over 125 cycles. Treatment of NO_2 @MFM-520 with water in air leads to quantitative conversion of the captured NO_2 into HNO_3 , an important feedstock for fertilizer production, and fully regenerates MFM-520. The confinement of N_2O_4 inside nano-pores has been established at a molecular level, and dynamic breakthrough experiments using both dry and humid NO_2 gas streams verify the excellent stability and selectivity of MFM-520, and confirm its potential for precious-metal-free deNO_x technologies.

Anthropogenic nitrogen oxides (NO_x) are major air pollutants causing serious environmental problems and millions of premature deaths¹⁻⁴. As the most prevalent form of NO_x , NO_2 contributes to the formation of photochemical smog, the destruction of stratospheric ozone and the rise of global warming³. The development of NO_2 abatement technologies is therefore important, and selective catalytic reduction (SCR) with NH_3 at elevated temperatures (up to 600 °C) represents the most mature technology in operation⁵⁻⁷. However, SCR relies critically on the use of toxic chemicals and often precious metal catalysts, and moreover is incapable of complete NO_x elimination. Emissions of NO_x from post-SCR exhaust gas can be as high as 1000-2000 ppm, 5,000-10,000 times those emission limits set by World Health Organisation (WHO)⁸, thus posing significant health risks⁴. Rapid deactivation of SCR catalysts in the presence of trace SO_2 , water, alkali and heavy metals place further restrictions on their long-term

applications^{6,9}. Complete removal of trace NO₂ from exhaust gas requires the capture system to possess not only long-term stability against highly corrosive and reactive NO₂, but also high selectivity over N₂, CO₂ and SO₂. Ideally it would also be possible to convert the captured NO₂ into profitable chemicals, such as nitric acid, millions of tons of which are manufactured each year *via* the energy-intensive Ostwald process¹⁰. This poses additional challenges for the capture medium, requiring system reversibility and material regeneration.

Capture of gases by physisorption within porous materials by exploitation of supramolecular host-guest interactions is a promising approach that can in principle offer high reversibility and low-cost sorbent regeneration. Silica¹¹, carbons¹², zeolites¹³ and organic porous materials¹⁴ have been screened, but none is fully reversible to adsorption of NO₂ due to the reactive and oxidative nature of this substrate. As emerging solid sorbents for a wide spectrum of gases and vapours, metal-organic frameworks (MOFs)^{15, 16} and their composites¹⁷⁻²² have been investigated for the breakthrough separation of NO₂ at 1000-2000 ppm concentrations. Satisfactory dynamic adsorption capacity was achieved in some cases, but the lack of structural stability, particularly under humid NO₂ streams, remains a problem. Recently, MFM-300(Al) was demonstrated as a robust NO₂ sorbent that survives in adsorption/desorption cycles with no loss of crystallinity¹⁷. However, although it achieves a high NO₂ uptake at atmospheric pressure, MFM-300(Al) shows low adsorption capacity with moderate selectivities at low pressures (<0.01 bar), restricting its application in practical processes. Here, we show that MFM-520 overcomes this problem and, in addition, enables facile and quantitative conversion of NO₂ into HNO₃ under ambient conditions. MFM-520 shows very high isothermal NO₂ uptake at low pressure (<0.01 bar) and can achieve complete clean-up of low concentration NO₂ from gas mixtures under flow conditions, even in the presence of moisture and SO₂. The binding

domains in MFM-520 have been determined at crystallographic resolution, showing that each bowtie-shaped pore precisely confines two NO₂ molecules to form an unusually stable N₂O₄ with a short N-N bond: this dimerisation can be followed by electron paramagnetic resonance (EPR) spectroscopy. MFM-520 remains completely intact even when soaked in acid solution, allowing quantitative generation of nitric acid simply by washing the NO₂-saturated material with water in air.

Results

Structure of MFM-520. MFM-520, [Zn₂(L)]·solv, adopts a three-dimensional open framework structure, comprising five-coordinated Zn(II) centers bridged by 4,4-bipyridyl-3,3',5,5'-tetracarboxylate (L⁴⁻) ligands (Fig. 1a)²³. The framework is sustained through two modes of metal-ligand linkages. The Zn(II) binds to the N(pyridyl)-donor along the crystallographic *c* axis, and four bridging carboxylates propagate the structure along the diagonals of the *ab* plane, defining a 4⁴6⁶ topology (Fig. 1b). Desolvated MFM-520 exhibits unique bowtie-shaped pores with dimensions of 6.6 x 4.0 Å² and a BET surface area of 313 m² g⁻¹. It shows excellent chemical, hydrothermal, and structural stability, and notably is entirely stable to treatment with boiling water for one month or with nitric acid.

Gas adsorption in MFM-520. Isothermal adsorption of NO₂ in MFM-520 (298-333 K, up to 1.0 bar; Fig. 2a) reveals record-breaking uptakes of 1.3 and 4.2 mmol g⁻¹ at 0.001 and 0.01 bar, respectively, at 298 K. For comparison, NO₂ uptakes in MFM-300(Al) under the same conditions are 0.1 and 1.4 mmol g⁻¹, respectively¹⁷. This notably high uptake by MFM-520 at very low pressure is accompanied by fast adsorption kinetics, typically within minutes (Supplementary Fig. 21), particularly promising for practical applications in efficient clean-up of high gas-flows containing trace NO₂. The strong adsorption is

also evidenced by the small effect of temperature upon uptake (4.52 and 4.41 mmol g⁻¹ at 298 and 333 K, respectively). At 298 K and 1.0 bar, the excess single-component gas adsorption uptakes for NO₂, SO₂, CO₂, CH₄, CO, H₂, O₂ and N₂ in MFM-520 are 4.53, 3.39, 2.14, 0.71, 0.36, 0.22, 0.19 and 0.18 mmol g⁻¹, respectively (Fig. 2b). The preferential adsorption of NO₂ is most pronounced at 318 K, the temperature of automobile exhaust, because in contrast to NO₂ (4.42 mmol g⁻¹ at 1.0 bar) the uptakes for all other gases decrease notably (Supplementary Figs. 3 and 4). The isosteric heat of adsorption (Q_{st}) for NO₂ in MFM-520 is 65 kJ mol⁻¹ and shows little variation as a function of surface coverage (Fig. 2c). The entropy of adsorption (ΔS) decreases steadily with increasing loading, indicating ordering of the captured NO₂ within MFM-520.

Analysis of pure-component isotherms *via* ideal adsorbed solution theory (IAST)²⁴ affords adsorption selectivities for equimolar mixtures of NO₂/X (X = CO₂, SO₂, O₂, CO, N₂), and for 1:99 mixture of NO₂/N₂, at 298 K and 1.0 bar (Fig. 3d, Supplementary Figs. 13-16). The IAST selectivity for equimolar NO₂/CO₂ and NO₂/N₂ are 675 and >24,000, respectively. These selectivities increase further for 1:99 mixtures and are significantly higher than those for MFM-300(Al)¹⁷, consistent with the gas adsorption isotherm data. To confirm the high selectivity towards NO₂ under more realistic concentrations,¹⁸ a fixed-bed packed with MFM-520 was tested by dynamic breakthrough experiments with a variety of NO₂-containing gas mixtures at 298 K and 1.0 bar. Highly selective adsorption of NO₂ was achieved with 2500 ppm NO₂ in N₂ under both dry and humid (1.5% H₂O) conditions (Fig. 2g). The NO₂ concentration at the outlet was reduced to below 100 ppb until breakthrough; this compares with the WHO emission target of 200 ppb.⁸ The presence of water only showed a small adverse effect upon the retention of NO₂ due to competing adsorption, and more impressively, the crystallinity and structural integrity of MFM-520 was fully retained. Most sorbent

materials studied to date are unstable under such conditions,^{11,12,14,19-22} clearly demonstrating the unusual chemical stability of MFM-520 towards NO₂. Breakthrough experiments using gas mixtures of NO₂/CO₂ (CO₂ 15% and NO₂ 4200 ppm diluted in He) and NO₂/SO₂ (NO₂ 2500 ppm and SO₂ 2500 ppm diluted in He) were also carried out to test the performance of MFM-520 in the presence of competitive gases (Figs. 2h, 2i), and excellent separations were achieved in both cases.

The interaction between NO₂ and MFM-520. We sought to establish the reasons for the effectiveness of MFM-520 to capture NO₂ and conducted *in situ* single crystal X-ray diffraction studies on NO₂@MFM-520 at varying loadings and temperatures (273-373 K). All datasets enabled direct observation of NO₂ within the pores, and no restrictions on the bond lengths or angles were applied to either guest or host at the final stage of refinement (typical R₁ = 5-6%; Supplementary Table 4). Importantly, all of the adsorbed NO₂ molecules dimerise in MFM-520 to form N₂O₄ [NO₂ occupancy at 298 K = 0.93(1), N-O = 1.39(3) Å, N-N = 1.46(7) Å, <ONO = 102(3)°, <ONN = 129(2)°], with each pore having the size and shape to host precisely one N₂O₄. The oxygen atoms of the adsorbed N₂O₄ interact primarily with the adjacent aromatic -CH groups of L⁴⁺ *via* hydrogen bonding *via* sixteen O(δ-)⋯H(δ+) interactions [2.74(8), 3.74(5) Å] *per* N₂O₄. Furthermore, the N₂O₄ molecules interact with the carboxylate O-atoms *via* eight dipole interactions [N(δ+)⋯O(δ-) = 3.68(4) Å] (Fig. 3d). Interestingly, the N-N bond length of 1.46(7) Å in the captured N₂O₄ is notably shorter than in solid N₂O₄ [typical values ranging 1.71(2) to 1.75(2) Å]²⁵, suggesting the formation of a strong N-N bond for confined N₂O₄. The confined N₂O₄ molecules lie in the crystal *ab* planes (Supplementary Fig. 10; Supplementary Table 3), and in contrast to the [NO₂·N₂O₄]_∞ extended chains observed in MFM-300(Al)·(NO₂)₂(N₂O₄)₂¹⁷, the “one-pore-for-one-N₂O₄” packing in MFM-520 affords adsorption independent of

neighbouring molecules. Hence, the thermodynamic host-guest equilibrium can be reached rapidly, leading to optimal adsorption kinetics. No notable structural change was observed on cooling the NO₂-loaded sample to 273 K except for a small variation in NO₂ occupancy (Supplementary Fig. 9). In contrast, on heating, the occupancy of NO₂ decreases to 0.88, 0.78, 0.56 and 0.29 at 313, 333, 353 and 373 K, respectively. The N-N distance reduces as the occupancy decreases, with no changes in N-O distance, (Supplementary Figs. 7 and 8, Supplementary Table 3) indicating some dissociation to monomeric NO₂. Significantly, no loss of crystallinity of the NO₂@MFM-520 was observed even at 373 K. Upon heating briefly under vacuum, all adsorbed NO₂ can be removed and the structure of MFM-520 is retained. These results reveal that the combination of multiple cooperative supramolecular interactions formed within an optimal pore environment of NO₂@MFM-520 leads directly to excellent adsorption reversibility, selectivity and stability.

Inelastic neutron scattering (INS) enabled the visualisation of vibrational dynamics for NO₂@MFM-520 with a focus on the -CH groups involved in the supramolecular contacts. Six major changes in the INS spectra were observed on adsorption of NO₂ (Fig. 4a). Changes are observed for peaks I-III in the low energy region (<80 meV) and IV-VI in the high energy region (110-150 meV) corresponding to deformational modes of the pyridine ring and -CH wagging/scissoring modes, respectively. These changes support the direct interaction between adsorbed N₂O₄ and the soft -CH groups, consistent with the crystallographic data. INS spectra of regenerated MFM-520 confirm the full retention of vibrational dynamics (Supplementary Fig. 12).

NO₂ is paramagnetic with one unpaired electron, while N₂O₄ is diamagnetic. Thus EPR spectroscopy can be used as a sensitive probe of the monomer-dimer equilibrium in the pores of MFM-520. NO₂@MFM-520 is EPR

silent at 200 K, consistent with full dimerization of NO₂. On warming, an isotropic spectrum with ¹⁴N hyperfine coupling of 152 MHz is observed. This is characteristic of NO₂ that can rotate or diffuse in the lattice on the EPR timescale²⁶ as N₂O₄ dissociates (Fig. 4b). This temperature dependence is reversible and confirms that the degree of dissociation of N₂O₄ within the pores is very low compared to the equilibrium for the free gas (Fig. 4d). The suppression of N₂O₄ dissociation in liquid vs. gas phase is well-known^{27, 28}, and confinement of NO₂ in MFM-520 thus mimics the condensed phase process and makes dimerisation of NO₂ more favorable thermodynamically. A van't Hoff analysis of the EPR data gives the enthalpy change for dissociation $\Delta H = 58 \text{ kJ mol}^{-1}$, very close to the gas phase value²⁷. Hence, the major driving force for dimerisation of NO₂ in MFM-520 is enthalpic with the formation of multiple host-guest interactions and N-N bond formation, which overcome the significant decrease in ΔS on dimerisation.

Discussion

We have investigated the recovery and conversion of captured NO₂ from MFM-520. Saturated NO₂@MFM-520 (0.1 g) was soaked in water (5mL) under stirring in air for 10 min, and the pH value of the system stabilised at 1.06, indicating the complete release of the captured NO₂ to form a 0.09 M solution of nitric acid. No gaseous NO₂ was detected during this process and more importantly, the recovered MFM-520 sample was fully regenerated under heating and reused with no loss of subsequent NO₂ uptake capacity or of HNO₃ production over ten consecutive cycles. Thus, this process integrates the clean-up and capture of NO₂ from exhaust gas with its conversion to HNO₃, and avoids the energetic industrial process for synthesis of HNO₃ by oxidation of ammonia (Fig. 5)¹⁰.

Powerful drivers exist for the development of improved technologies that might replace SCR-processes in mitigation of NO_x emissions. MFM-520 integrates

high materials stability with adsorption selectivity, capacity and reversibility for NO₂ capture under conditions relevant to exhaust gas clean-up. MFM-520 can be readily regenerated post-NO₂ adsorption under conventional pressure-swing conditions, and no loss of adsorption capacity of NO₂ or changes in the structure of MFM-520 was observed after 125 cycles of NO₂ sorption-desorption (Fig. 2f). MFM-520 also functions under wet conditions and can be used to convert NO₂ to HNO₃ with water in air with full recovery of the host. In-depth studies using complementary techniques and modelling reveal up to 24-fold weak, additive supramolecular interactions that drive the preferred binding, confinement and dimerisation of NO₂ in MFM-520, leading to both optimal selectivity and reversibility based upon an “easy-on/easy-off” system.

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Methods

NO₂ safety: All systems involved in the supply, delivery and measurement of NO₂ were rigorously leak tested and used only within range of a NO₂ detection system with a sensitivity of 0.1 ppm. All gases exhausted from experimental apparatus was diluted with a flow of N₂ and fed into fume hood extracts.

Gas adsorption isotherms and breakthrough experiment: Measurements of NO₂ adsorption isotherms (0-1 bar) were performed using a Xemis gravimetric adsorption apparatus (Hiden Isochema, Warrington, UK) equipped with a clean ultrahigh vacuum system. The pressure in the system is accurately regulated by mass flow controllers. Research grade NO₂ and He were purchased from AIRLIQUIDE or BOC and used as received. In a typical gas adsorption experiment, 50-100 mg of MFM-520-solvate was loaded into the Xemis, and degassed at 393 K and high dynamic vacuum (10^{-10} bar) for 1 day to give desolvated MFM-520.

***In situ* synchrotron X-ray single crystal diffraction and structure determinations:** *In situ* synchrotron X-ray single crystal diffraction data were collected at beamline 11.3.1 at the Advanced Light Source using a monochromatic radiation [$\lambda = 0.7749(1)$ Å]. A single crystal of MFM-520 was placed in a capillary gas handling cell and evacuated *in situ* under dynamic vacuum with a hot stream of N₂ (393 K) flowing over the capillary for 4 h. The single crystal diffraction data of desolvated MFM-520 was collected at 298 K. NO₂ was loaded into MFM-520 at 1 bar and 298 K, and diffraction data collected at 273-373 K. The gas cell was then connected to vacuum and heated to 393 K, and data for regenerated MFM-520 were collected.

Structure solution was achieved by direct methods and least squares refinements. All non-hydrogen atoms of the desolvated structures were refined anisotropically, and hydrogen atoms were modelled using a riding model. In the NO₂-loaded structures, analysis of the Fourier difference maps reveals the

location of the adsorbed NO₂ molecules, the atoms of which were refined isotropically. The occupancies for all NO₂ molecules were refined globally using free variables. No restriction on the bond length/angle to either guest or host was applied at the final stage of refinement.

Electron Paramagnetic Resonance Experiments: CW EPR measurements were carried out at X-band (ca. 9.5 GHz) on a Bruker EMX spectrometer equipped with temperature control system. A modulation amplitude of 0.4 mT was used with microwave power of ~ 2.0 mW after testing for saturation of spectral lines.

Variable temperature EPR intensity measurements.

For variable temperature EPR intensity data (Fig. 4d), spectra were measured through an entire temperature loop, heating from 300 to 400 K and then cooling from 400 to 300 K, equilibrating for 10 minutes at each temperature. Identical spectrometer settings were used throughout. The second integrals of the measured first derivative spectra were obtained, and these second integrals (*i.e.* the areas under the EPR absorption spectra) are directly proportional to the amount of NO₂ present. In order to obtain the relative amount of NO₂ at each temperature, the second integrals of the first derivative spectrum were divided by the value at 300 K (*i.e.*, at 300K the value is 1). Prior to this, a correction was applied to account for any small Boltzmann population changes with temperature, determined by performing equivalent measurements on a standard sample of TEMPO free-radical trapped in a different MOF [MFM-300(Al)] .

The equilibrium constant for dissociation of N₂O₄ into 2NO₂ can be expressed in terms of the fraction (α) of N₂O₄ that dissociates, giving (1- α) N₂O₄ and 2 α NO₂ ²⁹:

$$K_x = 4\alpha^2/(1-\alpha^2)$$

under the conditions that $\alpha \ll 1$, and K_x is thus proportional to α^2 . Since the EPR intensity is proportional to α , the equilibrium constant is proportional to the

square of the EPR intensity. A van't Hoff plot of the log of the square of the EPR intensity (referenced to 300 K, see above) vs. $1/T$ is linear (Supplementary Fig. 22a) indicating that the enthalpy (ΔH) and entropy (ΔS) changes of dissociation do not vary significantly in the temperature range. Fitting this line gives $\Delta H = 58$ kJ mol^{-1} .

Note that between 300 and 400 K, the EPR intensity of NO_2 -loaded MFM-520 increases by a factor of 20. Under equivalent conditions, the intensity of a gas phase sample changes by a factor of about only 2 (Fig. 4d, Supplementary Fig. 21). This, and the shapes of the curves, shows that the degree of dissociation of N_2O_4 is much greater in the gas phase than in the MOF. The data for NO_2 in the gas phase (empty tube flushed with NO_2) is consistent with literature: at 1 atm pressure, N_2O_4 is almost completely dissociated at 400 K in the gas phase³⁰.

Supplementary Information is available in the online version of the paper.

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Author Contributions JL: syntheses, characterisation of MOF samples, measurements of adsorption isotherms. JL and XH: measurements and analysis of breakthrough data. SY, XZ, JL, SJT and LM: collection and analysis of *in situ* synchrotron X-ray diffraction data. YC, LLD and AJRC: collection and analysis of MD modelling and neutron scattering data. JL, XH, AMS, FT and EJLM: collection and analysis of EPR data. MS and SY: overall direction of project and preparation of the manuscript.

Author Information The crystal structure of MFM-520·N₂O₄ is available free of charge from the Cambridge Crystallographic Data Centre under reference number CCDC 1556634-1556642. Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to M.S. (M.Schroder@manchester.ac.uk) and S.Y. (Sihai.Yang@manchester.ac.uk).

Competing financial interests. The authors declare no competing financial interests.

Data availability. All relevant data are available from the authors, and/or are included with the manuscript. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 1556634 (Bare MOF, 298 K), 1556635 (NO₂-loaded MOF, 273 K), 1556636 (NO₂-loaded MOF, 283 K), 1556637 (NO₂-loaded

MOF, 298 K), 1556638 (NO₂-loaded MOF, 313 K), 1556639 (NO₂-loaded MOF, 333 K), 1556640 (NO₂-loaded MOF, 353 K), 1556641 (NO₂-loaded MOF, 373K) and 1556642 (Regenerated MOF, 393 K). Copies of the data can be obtained free of charge *via* <https://www.ccdc.cam.ac.uk/structures/>. All other data supporting the findings of this study are available within the Article and its Supplementary Information, or from the corresponding author upon reasonable request.

List of Figure Captions

Fig. 1. Views of ligand (a) and MFM-520 framework structure (b).

Fig. 2. Views of adsorption, selectivity, separation and stability data. (a) NO₂ adsorption isotherms in MFM-520 (red 298 K, blue 303 K, olive 308 K, violet 313 K, green 318 K, magenta 323 K and black 333 K); inset: low-pressure isotherms on a logarithmic scale. (b) Single-component gas adsorption isotherms of NO₂ (black), SO₂ (navy), CO₂ (blue), N₂ (red), CO (cyan), H₂ (purple) and O₂ (green) in MFM-520 at 298 K (desorption of CH₄, O₂, H₂ and CO follow the sorption profile but are omitted for clarity). (c) Variation of isosteric heat of adsorption (Q_{st}) and entropy (ΔS) for NO₂ uptake in MFM-520. (d) Comparison of IAST selectivities for equimolar mixtures of NO₂/SO₂, NO₂/CO₂ and NO₂/N₂ at 0.1-1.0 bar for MFM-520 at 298K. (e) PXRD patterns of MFM-520; a: simulated, b: as-synthesised, c: MFM-520 after NO₂ sorption of 125 cycles, d: MFM-520 after soaking in boiling water for 1 month, e: filtered MFM-520 after NO₂ uptake and HNO₃ synthesis. (f) Comparison of NO₂ adsorption capacity in MFM-520 for 125 cycles. (g) Dimensionless breakthrough plots for gas mixtures (N₂ black, dry NO₂ red 2500 ppm and wet NO₂ wet blue 2500 ppm). (h) Dimensionless breakthrough plots for gas mixtures (CO₂ black 15% and NO₂ red 4200 ppm diluted in helium). (i) Dimensionless breakthrough plots for gas mixtures (SO₂ black 2500 ppm and NO₂ red 2500 ppm diluted in helium).

Fig. 3. Views of crystal structures. Views of the crystal structure of MFM-520•N₂O₄ along the *a* (a) and *c* (c) axes. (b) The confinement of N₂O₄ in the bowtie-shaped pores (shown in grey) of MFM-520 along *c* axis (the framework of the MOF is omitted for clarity). (d) View of the 24-fold interaction between N₂O₄ and MFM-520. (e) View of the intermolecular interaction between adsorbed N₂O₄

in MFM-520. (f) View of the intermolecular interaction in solid N_2O_4 ²². Dashed lines in (e) and (f) refer to O•••O distances. (C grey, O red, N blue, H white and Zn sea green).

Fig. 4. Spectroscopic data. (a) Comparison of the difference plots for experimental and DFT-calculated INS spectra of bare and NO_2 -loaded MFM-520. No scale factor was used for the DFT calculations. (b) Comparison of X-band EPR spectra of NO_2 -loaded MFM-520 and an NO_2 -flushed empty quartz tube at 298 K. (c) Temperature dependence of X-band EPR spectrum of NO_2 -loaded MFM-520 between 200-360 K. (d) Changes of second integrals (*i.e.* intensity) of EPR spectra of NO_2 -loaded MFM-520 (relative to that at 300 K) as a function of temperature (a control experiment using an NO_2 -flushed empty quartz tube is shown for comparison).

Fig. 5. Schematic representation of the continuous clean-up and conversion of exhaust NO_2 to HNO_3 using MFM-520. (O red, N blue and H white).