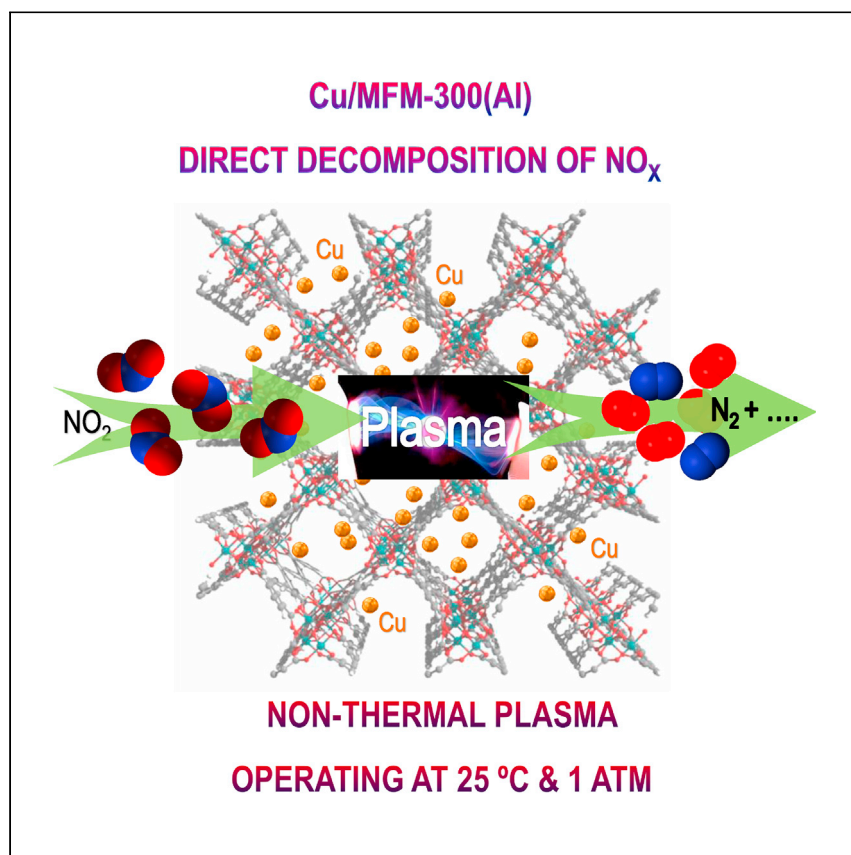


Article

Catalytic decomposition of NO₂ over a copper-decorated metal–organic framework by non-thermal plasma



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HIGHLIGHTS

MOF-based catalyst with plasma-activation to directly convert NO₂

Cu/MFM-300(Al) shows a high NO₂ conversion, N₂ selectivity, and long-term stability

Cu²⁺...NO nitrosylic adducts formed facilitate NO dissociation and N₂ selectivity

Nitrogen oxide causes significant effects on the environment and human health. Xu et al. report, to the best of their knowledge, the first example of nonthermal plasma-activated direct decomposition of NO₂ over stable and efficient metal-organic framework-based catalysts at room temperature and without the use of NH₃ or other reducing agents.

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Article

Catalytic decomposition of NO₂ over a copper-decorated metal–organic framework by non-thermal plasma

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SUMMARY

Efficient catalytic conversion of NO₂ to non-harmful species remains an important target for research. State-of-the-art deNO_x processes are based upon ammonia (NH₃)-assisted selective catalytic reduction (NH₃-SCR) over Cu-exchanged zeolites at elevated temperatures. Here, we describe a highly efficient non-thermal plasma (NTP) deNO_x process catalyzed by a Cu-embedded metal-organic framework, Cu/MFM-300(Al), at room temperature. Under NTP activation at 25°C, Cu/MFM-300(Al) enables direct decomposition of NO₂ into N₂, NO, N₂O, and O₂ without the use of NH₃ or other reducing agents. NO₂ conversion of 96% with a N₂ selectivity of 82% at a turnover frequency of 2.9 h⁻¹ is achieved, comparable to leading NH₃-SCR catalysts that use NH₃ operating at 250°C–550°C. The mechanism for the rate-determining step (NO → N₂) is elucidated by *in operando* diffuse reflectance infrared Fourier transform spectroscopy, and electron paramagnetic resonance spectroscopy confirms the formation of Cu²⁺...NO nitrosylic adducts on Cu/MFM-300(Al), which facilitates NO dissociation and results in the notable N₂ selectivity.

INTRODUCTION

Nitrogen oxide (NO_x) is the cause of significant effects on the environment and human health.^{1–3} Nitrogen dioxide (NO₂) is the most toxic and prevalent form of NO_x in the atmosphere, and its removal and catalytic degradation into non-harmful species (i.e., N₂) are important challenges. A great deal of effort has been devoted to developing catalysts for deNO_x processes, with a focus on NO reduction from exhaust gases. The NH₃-assisted selective catalytic reduction (NH₃-SCR) over Cu-exchanged zeolites is by far the most effective method to reduce NO_x to N₂ and H₂O^{4,5} (Equations 1, 2, and 3). However, this process has several inherent limitations, notably the high operating temperature (typically 250°C–550°C), high running cost of reductants, use of corrosive and toxic NH₃, and the potential release of NH₃ into the atmosphere.^{1,2} In contrast, the catalytic degradation of NO₂ for domestic environments is poorly studied. The development of new efficient catalysts and catalytic processes to enable the direct decomposition of NO₂ at room temperature and without the use of reducing agents (Equation 4) has, therefore, attracted considerable attention.^{6–10}

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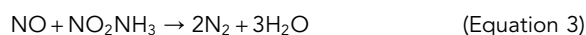
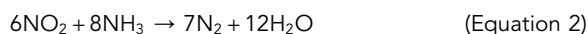
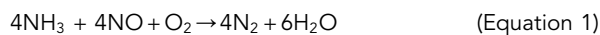
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Porous metal-organic framework (MOF) materials show promise for the highly selective adsorption and separation of NO_2 at room temperature under both dry and humid conditions.^{1,9,11–16} However, the stability and reusability of MOFs for NO_2 adsorption has only been demonstrated in exceptional cases.^{9,11} Due to their high porosity and tailored-to-design pore functionality, MOFs can also be used as heterogeneous catalysts and catalyst supports.^{17,18} For example, embedding metal nanoparticles (MNPs) into MOF pores can overcome the aggregation of MNP and thus improve the catalytic stability.^{17,19,20} Moreover, the synergistic effects between the pore interior of MOFs and MNPs can result in highly desirable product selectivities.²¹ However, the application of MOF-based catalysts in de NO_x processes has been rarely explored,^{22–24} primarily due to the limited stability of MOFs against highly corrosive NO_2 and NH_3 at elevated temperatures.

Non-thermal plasma (NTP) activation can promote de NO_x processes at room temperature by generating highly reactive species, especially vibrationally and electronically excited states of molecules (e.g., N_2 , O_2 , NO), N and O atoms, radicals, and electrons with a typical electron temperature of 10^4 °C.^{8,10,25,26} NTP-promoted de NO_x processes can be readily tuned by balancing the power input, and potentially this enhances the overall energy efficiency by controlling the reaction pathway within a reversible and active heterogeneous catalyst. Recently, NTP activation in MOF-based catalysts has been shown to enhance performance in water-gas shift reactions, with the structure and porosity of the MOF being preserved.¹⁸ NTP-modified $[\text{Cu}_3(\text{BTC})]$ (H_3BTC = benzene-1,3,5-tricarboxylic acid) has been shown to give high catalytic conversion of NO (~98%) owing to the abundant Cu sites generated from the decomposition of the framework.¹⁰ However, the efficient catalytic conversion of NO_2 into N_2 over MOFs remains a highly challenging and important research pipeline.

Here, we report, to the best of our knowledge, the first example of NTP-activated direct decomposition of NO_2 over MOF-based catalysts at room temperature and without the use of NH_3 or other reducing agents. At 25°C and 1.0 bar, 7 wt% Cu-embedded MFM-300(Al) enables a near-quantitative conversion of NO_2 (500 ppm diluted in He) into N_2 , NO , and N_2O with selectivities of 82%, 11%, and 7%, respectively. Cu/MFM-300(Al) also shows excellent catalytic stability and an exceptional turnover frequency (TOF) value of 2.9 h^{-1} . It should be emphasized that theoretical TOF values are quoted in this study, and the determination of the effective TOF is described in [Tables S4](#) and [S5](#). *In operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been applied to study the adsorption and reactivity of NO_2 on Cu/MFM-300(Al) and reveals strong adsorption of the key reaction intermediate NO on the Cu sites, thus promoting its efficient conversion to N_2 . Electron paramagnetic resonance (EPR) spectroscopy confirms the formation of a triplet spin state that is consistent with ferromagnetic interaction between Cu^{2+} and NO .

RESULTS

Synthesis and characterization of MOF-based catalysts

MFM-300(Al) has been selected in this study due to its ultra-high structural stability and reversible adsorption of NO_2 (14.1 mmol g^{-1} at 298 K and 1.0 bar).⁹ MFM-300(Al) has an

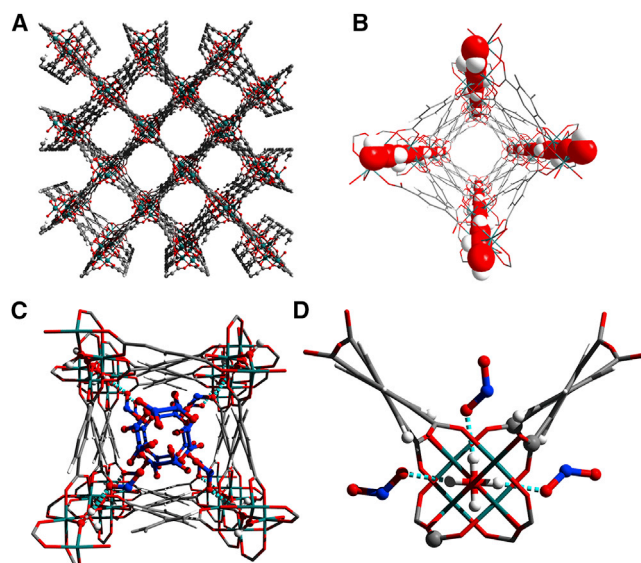


Figure 1. Views of crystal structure of MFM-300(Al) and its adsorption sites for NO₂

(A) View of the 3-dimensional (3D) framework structure of MFM-300(Al).

(B) View of the square-shaped channel comprising the corner-sharing extended octahedral chain of [AlO₄(OH)₂]_∞. The μ₂-(OH) groups are highlighted as a space-filling model and linked to each other in a *cis*-configuration (Al, green; C, gray; O₂, red; H₂, white; N₂, blue).

(C and D) Views of binding sites for adsorbed NO₂ molecules within MFM-300(Al).⁹

open framework with 1-dimensional channels ($\sim 6 \times 6 \text{ \AA}^2$) constructed by [AlO₄(OH)₂]_∞ chains bridged by organic linkers (Figures 1A and 1B).²⁷ The *cis*-configured hydroxyl groups protrude into the square-shaped channels, affording accessible μ₂-OH sites to bind guest species, notably with NO₂ (Figures 1C and 1D). The activity of the MOF as a catalyst support has been evaluated by comparing to the benchmark γ-Al₂O₃ (with mesopores of 25 Å) and ZSM-5 (with a pore size of 6 Å). Both CuO and Cu NPs have been investigated as active sites for the NTP-activated deNO_x reaction to reveal the impact of the oxidation state of Cu on reactivity.

Catalysts based upon CuO/support (support = MFM-300(Al), γ-Al₂O₃, and ZSM-5) were prepared using an incipient wetness impregnation method (see [Supplemental experimental methods](#)) followed by calcination at 250°C in air for 12 h. The corresponding Cu-embedded catalysts were prepared by reducing the CuO-embedded catalysts under a flow of 5% H₂ at 250°C for 12 h. High-resolution synchrotron X-ray powder diffraction confirmed the retention of the crystal structures of all of the catalysts on the loading of CuO and Cu (Figures 2A and 2B), and the loading of MNPs was determined by elemental analysis (Table S1). Transmission electron microscopy (TEM) confirms that there are no changes in the sample morphology on the loading of CuO and Cu (uniform particle size of ~ 1 nm, Figures 2C and 2D), and energy-dispersive X-ray spectroscopy (EDX) mapping shows a homogeneous distribution of the loaded Cu sites (Figure S3). Synchrotron Fourier transform infrared spectroscopy (FTIR) spectra of MFM-300(Al) show a reduction in the intensity of the μ₂-OH stretching band at 3,687 cm⁻¹, coupled with peak broadening and a slight redshift on the loading of CuO and Cu, indicating interactions between the μ₂-OH groups and Cu/CuO NPs (Figure S4).^{20,28–30} N₂ adsorption isotherms at 77 K confirmed that loading of Cu/CuO NPs leads to small reductions in the porosity of all of the catalysts and that the NTP treatment has a negligible impact on the porosity of these materials (Table S2).

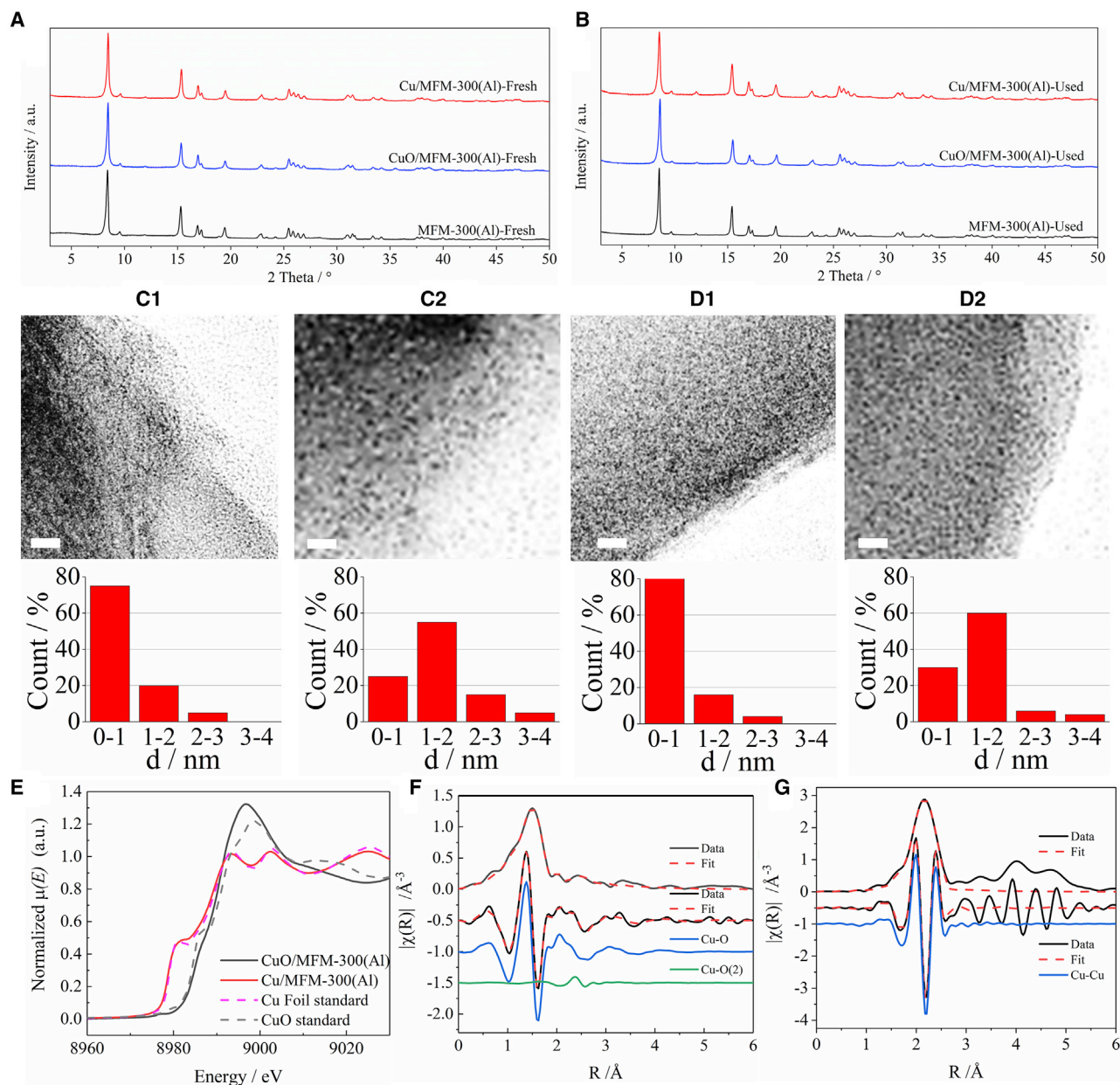


Figure 2. Characterization of catalysts

(A–D) High-resolution synchrotron X-ray powder diffraction (of MFM-300(Al), CuO/MFM-300(Al) and Cu/MFM-300(Al) (A) before (fresh) and (B) after (used) NTP-assisted NO_2 decomposition. TEM micrograph of Cu/MFM-300(Al) (C1) before and (C2) after, and of CuO/MFM-300(Al) (D1) before and (D2) after de NO_2 reaction (scale bars 5 nm). The corresponding particle size distribution graphs are shown underneath the TEM views.

(E) Normalized Cu K-edge XANES spectra of fresh Cu/MFM-300(Al) and CuO/MFM-300(Al) recorded after drying in He at 250°C and standard XANES spectra of a Cu foil and CuO recorded as references.

(F and G) Stacked plots of the magnitude (top) and imaginary (bottom) non-phase corrected Fourier-transformed Cu K-edge EXAFS of (F) CuO/MFM-300(Al) and of (G) Cu/MFM-300(Al) recorded after drying in He at 250°C. These have been plotted with the fit constructed from Cu–O and Cu–Cu scattering paths.

Continuous-wave EPR spectra of desolvated samples of Cu- and CuO-embedded MFM-300(Al) (Figures S5 and S6, Table S6) reveal 2 types of Cu^{2+} sites in both cases: (1) one that is characteristic of a monomeric Cu(II) with a tetragonal coordination environment, manifested in an axial EPR signal with $g_z \gg g_{x,y} > 2$ and a

well-resolved 4-line pattern in the z component due to highly axial hyperfine interactions with the $I = 3/2$ $^{63/65}\text{Cu}$; and (2) one that is characterized by a broad isotropic signal and is typical of small NPs or clusters in which Cu(II) is involved in spin-spin interactions with its neighbors. Larger NPs are usually EPR inactive due to extensive spin-spin interactions that stabilize a non-magnetic spin state.²⁸ Similarly, Cu^+ ($3d^{10}$) is EPR inactive.

To identify further the electronic properties and local coordination environment of the embedded Cu species, we performed the *ex situ* X-ray absorption fine structure (XAFS) spectroscopy of CuO/MFM-300(Al) and Cu/MFM-300(Al) at the Cu K-edge. In the near-edge region (Figure 2E), the X-ray absorption near-edge structure (XANES) spectra of Cu/MFM-300(Al) compares well with the Cu foil reference, and the CuO/MFM-300(Al) appears to be similar to CuO. The Fourier transform of the k^2 weighted extended XAFS (EXAFS) data for CuO/MFM-300(Al) compared to that of a CuO reference material shows (Figure S7, Table S7) much lower intensity of the features at a longer distance, suggesting that these CuO clusters in the MOF are small. A reasonable fit of the data (Figure 2F) was obtained using 2 Cu-O scattering paths at 1.936 ± 0.003 and 2.9 ± 0.2 Å, the distances being consistent with CuO. From the reduced intensity of the μ_2 -OH stretching band at $3,687\text{ cm}^{-1}$ observed in the synchrotron FTIR spectra (Figure S4), the Cu site is likely attached to the framework O_2 centers of MFM-300(Al). Fitting the EXAFS spectra of Cu/MFM-300(Al) using the 1st shell Cu-Cu scattering path provides a good fit to Cu metal (Figure 2G). The coordination number of the 1st shell Cu-Cu path is 11 ± 1 , with a calculated Cu particle size of 3.5 ± 0.5 nm,²⁹ which is consistent with the transmission electron microscopy (TEM) measurements of the Cu particle size. Thus, reduction of CuO/MFM-300(Al) with H_2 generates Cu/MFM-300(Al), in which the Cu^{2+} ions are reduced and slightly sintered to give Cu^0 with an average particle size of 3 nm.

Catalytic reactions

A typical vehicle emission contains 100–1,000 ppm NO_x (mainly NO and NO_2) and 5% O_2 in N_2 .^{1,2} To examine the performance of these catalysts for the direct decomposition of NO_2 , a model gas stream of 500 ppm NO_2 diluted in He was used as the feed for catalysis tests throughout the present study. In the absence of plasma and catalyst, the empty reactor showed negligible conversion of NO_2 at 25°C – 250°C , while the presence of catalysts alone without the plasma at 25°C gives very low conversion of NO_2 (<10%). In contrast, in the absence of a catalyst at 25°C , gas phase NTP gives a NO_2 conversion of 66%, but a low N_2 selectivity of 13% and a high NO selectivity of 81%. These results suggest that NO_2 can be readily dissociated to NO by gas phase NTP, but further reduction of NO to N_2 (the rate-determining step) cannot be achieved by NTP alone, which is consistent with previous reports on the NTP-assisted decomposition of NO_x in which only a small amount of N_2 can be produced via the collision of NO_x with the excited state of He^* in gas phase.^{25,30}

The catalytic activity and product selectivities for NO_2 decomposition have been systematically investigated for all 9 catalysts (namely, bare support, CuO/support and Cu/support; support = MFM-300(Al), $\gamma\text{-Al}_2\text{O}_3$, and ZSM-5) under steady-state plasma conditions: the specific energy input (SEI) was $\sim 0.4\text{ kJ L}^{-1}$ at a frequency of 10 kHz and alternating current (AC) peak-to-peak voltage ($V_{\text{pk-pk}}$), of 13 ± 0.5 kV at 25°C (Figure 3; Table S3). The bare supports of $\gamma\text{-Al}_2\text{O}_3$, ZSM-5, and MFM-300(Al) show enhanced NO_2 conversions (71%, 76%, and 92%, respectively) and N_2 selectivities (15%, 35%, and 46%, respectively), compared with the tests under thermal

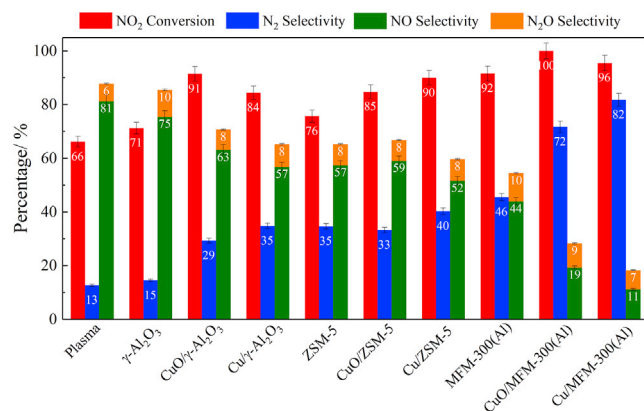


Figure 3. Comparison of results for all of the catalysts in this study

NO₂ conversion and product selectivities over catalysts supported by γ -Al₂O₃, ZSM-5, and MFM-300(Al) under steady-state NTP conditions (0.4 kJ L⁻¹, 13 ± 0.5 kV, 10 kHz, 25°C) using a feed of 500 ppm NO₂ in He. The control experiment without catalyst is labeled “Plasma.” Each data point is an average of 3 consecutive measurements with an error of < ±3% for NO₂ conversion and < ±4% for product selectivity.

conditions (NO₂ conversions <10%). The NO₂ conversions are enhanced by the CuO- and Cu-embedded catalysts. A small improvement in the N₂ selectivity was observed for CuO- or Cu-embedded γ -Al₂O₃ and ZSM-5, with the highest selectivity of 40% achieved in Cu/ZSM-5. More significant increases in N₂ selectivity were achieved with the MFM-300(Al) supported catalysts, in which CuO/MFM-300(Al) showed N₂ selectivity of 72% with a quantitative conversion of NO₂, and Cu/MFM-300(Al) achieved the highest N₂ selectivity of 82% with NO₂ conversion >96% (equivalent to an energy efficiency of 0.06 mmol kJ⁻¹ for the dissociation of NO₂). These observations indicate a synergistic positive effect on N₂ selectivities between the loaded Cu-NPs and the MOF host. More important, Cu/MFM-300(Al) also exhibits a high TOF value of 2.9 h⁻¹ without the use of any reductant, thus outperforming the state-of-the-art Cu-based catalysts for the direct decomposition of NO₂ (Table S4). For example, the CuO/Al₂O₃ catalyst shows a TOF of 0.1 and 2.8 h⁻¹ at 325°C and 520°C, respectively, with N₂ selectivities of ~50%.⁶ Recently, a Cu-embedded ZSM-5 catalyst has been reported to show a TOF value of 1.8 h⁻¹ and a N₂ selectivity of 86% for NTP-activated deNO_x reactions using H₂ as reducing agent at 25°C³¹ (Table S5). It is worth noting that the superior catalytic activity of Cu/MFM-300(Al) is comparable to that of the leading NH₃-SCR catalysts based upon Cu-exchanged SSZ-13 zeolites, which critically rely on the use of NH₃ and operate at 250°C–550°C, with TOF values of 1.9–2.2 h⁻¹ and N₂ selectivities of 85%–100%.³²

Stability tests

It has been widely reported that MNP-embedded catalysts for deNO_x reactions often suffer from rapid deactivation and thus have poor time-on-stream (ToS) stabilities due to the oxidation of active metal sites.^{5,33} We sought to investigate the ToS stability of all three Cu-embedded catalysts in this study. As expected, Cu/γ-Al₂O₃ and Cu/ZSM-5 catalysts show steady deactivation under reaction conditions (Figure 4A) due to the formation of aggregated CuO particles, which has been confirmed by powder X-ray diffraction (PXRD) (Figure S8). In comparison, Cu/MFM-300(Al) exhibits excellent catalytic stability, with a ToS of >200 min, and X-ray photoelectron spectroscopy (XPS) analysis confirms that in fresh Cu/MFM-300(Al) catalyst, 75% of the Cu(II) was reduced to Cu(I) and Cu(0), while 60% of the

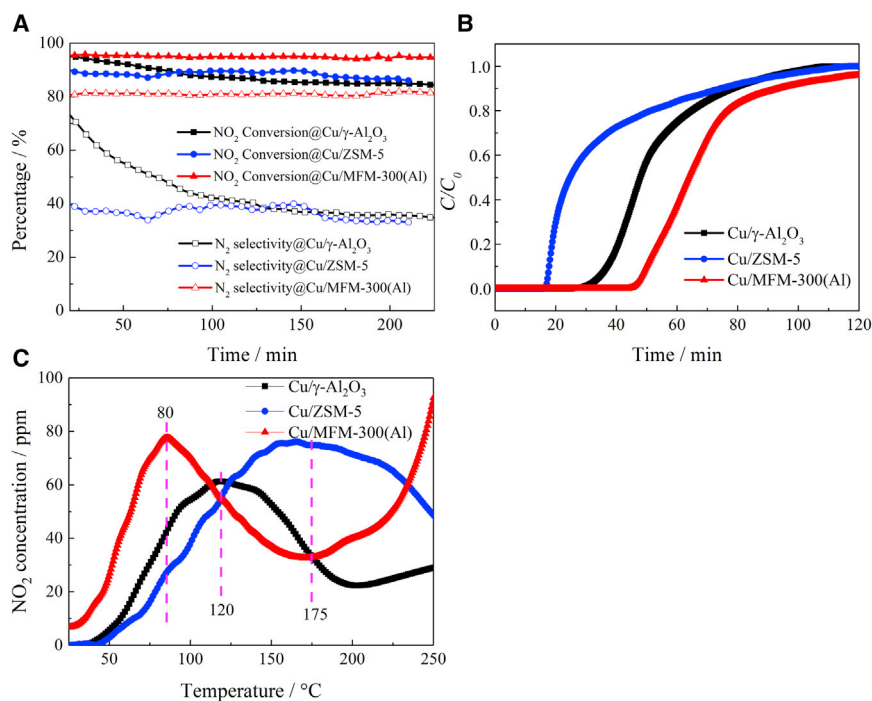


Figure 4. Comparison of the time-on-stream stability, breakthrough capacity, and NO₂-temperature-programmed desorption plots for various catalysts

(A) Comparison of the time-dependent ToS plots for NO₂ conversion and N₂ selectivity over various Cu-embedded catalysts under NTP conditions (0.4 kJ L⁻¹, 10 kHz, 25°C, 500 ppm NO₂ in He and atmospheric pressure).

(B) Dynamic breakthrough experiments for Cu/support catalyst (support = MFM-300(Al), ZSM-5, and γ -Al₂O₃) at 25°C using the same NO₂ gas feed as in catalysis tests.

(C) NO₂-TPD plots of NO₂-saturated Cu/support (support = MFM-300(Al), ZSM-5, and γ -Al₂O₃) catalysts.

Cu species remained in the form of Cu(I) and Cu(0) in used Cu/MFM-300(Al) catalyst (Figure S9). Furthermore, PXRD analysis suggests the full retention of the crystal structure of all MOF-based catalysts after the reaction, and Cu or CuO aggregates of >5 nm^{19,34} are not observed (Figure 2B). High-resolution TEM studies further confirm the negligible aggregation of CuO and Cu NPs within the MOF-based catalysts after the reaction (Figures 2C, 2D, and S3), and this retention of particle size is likely to be the basis for the high catalytic stability of the MFM-300(Al)-based catalysts.

Cu/MFM-300(Al) exhibits good stability in terms of NTP-promoted catalytic activity and structural integrity in the presence of water vapor up to a ToS of 250 min (Figure S10). The conversion of NO₂ (95%) on Cu/MFM-300(Al) was not affected by water vapor, although the selectivity for N₂ decreases from 82% to 61%. These results confirm that Cu-embedded MFM-300(Al) shows high resistance to competitive adsorption and maintains its high activity in the presence of water vapor.

Catalyst-NO₂ surface chemistry

The decomposition of NO₂ to N₂ and O₂ over Cu-based catalysts has been reported as a zero-order reaction, with the adsorption being the rate-determining step.⁶ To gain further insights into the preferential adsorption of NO₂ in these materials, dynamic breakthrough experiments at 25°C using the same NO₂ gas feed were

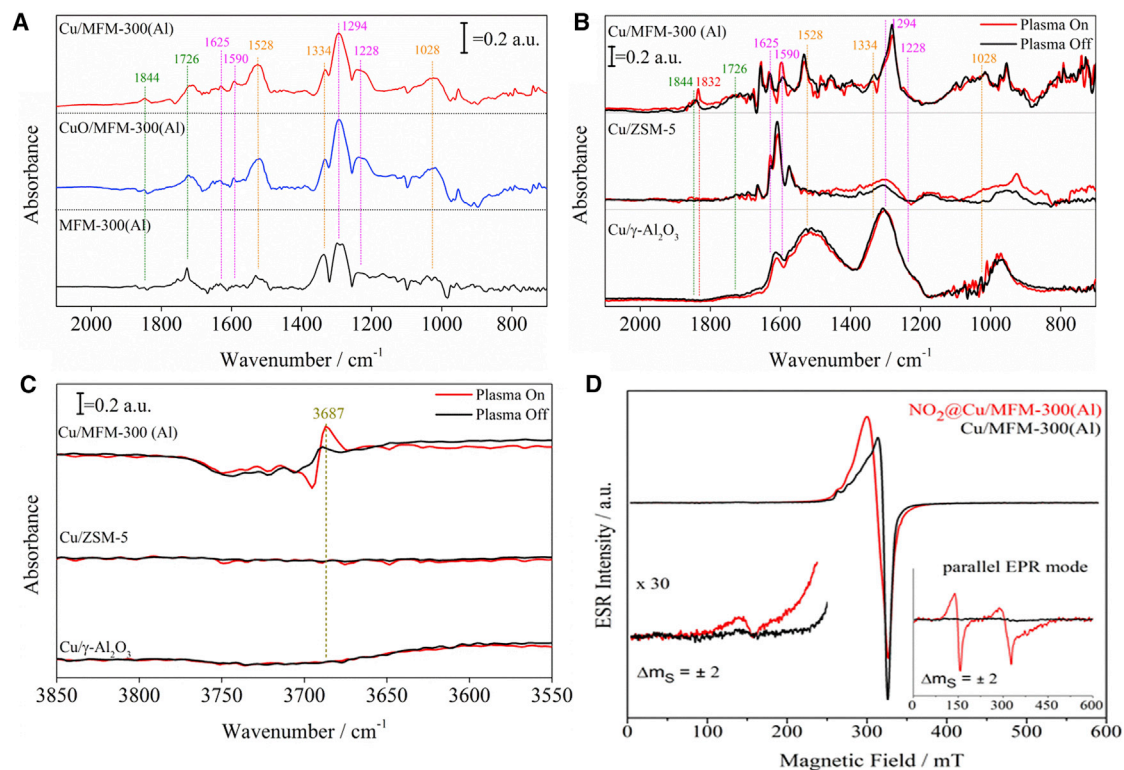


Figure 5. *In situ* and *in operando* DRIFTS spectra of Cu/MFM-300(Al), Cu/ZSM-5, and Cu/ γ -Al₂O₃ as a function of NO₂ adsorption and reactions
 (A) *In situ* DRIFTS spectra of adsorbed NO₂ on MFM-300(Al), CuO/MFM-300(Al), and Cu/MFM-300(Al). The background spectra for bare samples have been removed and gas phase NO₂ was removed using an Ar purge.
 (B and C) *In operando* DRIFTS spectra over Cu/support catalysts (support = MFM-300(Al), ZSM-5, and γ -Al₂O₃) under steady-state NTP conditions (0.2 kJ L⁻¹, 7.5 \pm 0.5 kV, 26 kHz, and 25°C with a NO₂ conversion of \sim 85%) using a feed of 500 ppm NO₂ in He. All DRIFTS spectra were recorded at a resolution of 4 cm⁻¹. The spectrum of bare samples has been subtracted.
 (D) X-band (9.4 GHz) EPR spectra at 5 K of Cu/MFM-300(Al) before (black) and after (red) NO₂ loading. Inset: parallel-mode EPR spectra of the same samples revealing that the half-field forbidden transition ($\Delta m_s = \pm 2$) of the triplet state resulted from Cu-NO interaction.

conducted (Figures 4B and S11). These experiments confirmed that MFM-300(Al)-based materials showed notably higher retention of NO₂ than γ -Al₂O₃- and ZSM-5-based catalysts. Interestingly, embedding CuO and Cu NPs into all three types of supports had a positive impact on NO₂ adsorption, and Cu/MFM-300(Al) showed the strongest retention of NO₂ among all of the studied catalysts. Temperature-programmed desorption (TPD) plots confirm that Cu/MFM-300(Al) released significantly higher amounts of NO₂ than γ -Al₂O₃- and ZSM-5-based catalysts (Figures 4C and S12).

In situ DRIFTS has been used to investigate the adsorption of NO₂ (500 ppm diluted in He) on these catalysts at 25°C (Figures 5A and S13A). The differences in DRIFTS spectra (with the background of bare catalysts and the gas phase NO₂ removed) suggest the formation of various adsorbed nitro/nitrate species on the catalyst surface. In particular, the bands for monodentate and bidentate surface nitro/nitrate species at 1,590–1,500 cm⁻¹, 1,380–1,330 cm⁻¹, and 1,060–980 cm⁻¹ and of bridging nitrates at 1,650–1,600 cm⁻¹ and 1,290–1,210 cm⁻¹ are observed for all of the catalysts studied, which is entirely consistent with previous reports.^{35–40} Interestingly, NO₂-adsorbed Cu/MFM-300(Al) shows new bands at 1,844 and 1,726 cm⁻¹, which can be assigned to the formation of M⁺...NO nitrosylic species^{37,39}; these bands are not observed or are much weaker for γ -Al₂O₃- and ZSM-5-based catalysts

(Figure S13A). This is further confirmed by the DRIFTS spectra using NO as a probe, with peaks at 1,844 cm and 1,726 cm⁻¹ observed on Cu/MFM-300(Al), but not on MFM-300(Al). This observation indicates that Cu/MFM-300(Al) can form unique Cu²⁺⋯NO nitrosylic adducts with NO, thus greatly facilitating its further reduction to N₂ and leading to the observed excellent selectivity for N₂ formation. These results are consistent with the recent reports that MOFs provide an excellent platform to optimize both reaction conversion and product selectivity.^{41,42}

X-band EPR spectroscopy of NO₂-loaded Cu/MFM-300(Al) reveals magnetic coupling between NO and Cu²⁺ (Figures 5D and S14, Table S8). Thus, the EPR spectrum of the NO₂-loaded sample displays a half-field transition at ~175 mT, characteristic of species with S ≥ 1, which is non-observable for bare Cu/MFM-300(Al) and which confirms magneto dipole-dipole interaction between NO_x (S = 1/2) and Cu²⁺ (S = 1/2).⁴³ The spectrum for NO₂-loaded Cu/MFM-300(Al) differs dramatically from that of Cu/MFM-300(Al) in the field range with g-factor values close to 2. A similar spectrum was reported previously for adducts of NO molecule and copper sites.^{44,45} Our tentative simulations support the formation of Cu²⁺⋯NO adducts rather than Cu²⁺⋯NO₂ adducts (Figure S15).

Operando DRIFTS studies on the reaction pathway

The underlying catalyst-substrate interaction has been studied further by *in operando* DRIFTS experiments as a function of plasma on-off over the catalyst and reaction time (Figures 5B, 5C, and S13B). Upon ignition of plasma (0.2 kJ L⁻¹, 7.5 ± 0.5 kV, 26 kHz, and 25°C with a NO₂ conversion of ~85%), the bands of adsorbed nitro/nitrate species reduced rapidly on all of the catalysts, indicating the rapid conversion of these species. The bands at 1,844 cm and 1,726 cm⁻¹ observed on NO₂-adsorbed Cu/MFM-300(Al) also reduced in intensity, indicating the rapid decomposition of M⁺⋯NO nitrosylic complexes and the promoted reduction of NO to N₂. Interestingly, a new peak at 1,832 cm⁻¹ (assigned to gas phase NO) appears upon switching the plasma on and disappears upon switching the plasma off, owing to the gas phase NO₂ dissociation under NTP conditions. More intriguing, a notable change in intensity has been observed for the μ₂-OH stretching mode at 3,687 cm⁻¹ in Cu/MFM-300(Al) as a function of plasma on and off (Figure 5C), indicating the retrieval of accessible μ₂-OH sites from those occupied by NO_x species during the conversion of NO₂. Thus, the catalytic mechanism of NO₂ decomposition over Cu/MFM-300(Al) can be tentatively proposed as a three-step process: (1) NO₂ is reduced directly to NO and a small amount of N₂O in the gas phase by NTP, as confirmed by control experiments; (2) strong adsorption of NO₂ and intermediates to form surface nitro/nitrate/nitrite species on Cu/MFM-300(Al); (3) NTP-assisted surface decomposition of adsorbed NO_x species: the surface nitro/nitrate/nitrite species dissociate under high-energy electrons generated by NTP to yield N₂ and O₂, thus regenerating accessible active sites at the surface. The excellent catalytic performance of Cu/MFM-300(Al) originates from a combination of optimal pore size, synergistic effects between the MOF interior and the embedded Cu NPs, high materials stability, and strong adsorption of NO₂.

DISCUSSION

There are powerful drivers for the development of efficient deNO_x systems that can operate at room temperature and avoid the use of toxic reductants. A new process combining robust MOF-based catalysts and NTP activation has been developed for one-through conversion of NO₂ into N₂ without using any external reducing agent at room temperature. The rigid and robust open structure of MFM-300(Al) offers an

excellent platform to embed uniformly dispersed Cu NPs of diameters of ~ 1 nm using a simple incipient wetness impregnation method. Cu/MFM-300(Al) shows simultaneously high NO_2 conversion and high N_2 selectivity, as well as excellent long-term stability under the NTP activation at 25°C and 1.0 bar. The high catalytic activity of Cu/MFM-300(Al) is attributed to the unique formation of $\text{Cu}^{2+}\cdots\text{NO}$ nitrosyl adducts, which facilitates the dissociation of NO to improve the yield of N_2 . Compared with conventional thermal-based catalysis, NTP activation can effectively preserve the structure and porosity of MOF-based catalysts. Coupled with emerging stable MOFs showing ultra-high and selective NO_2 adsorption, we now seek to design new MOF-based catalysts to drive the future development of efficient reductant-free deNO_x processes to mitigate air pollutants.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Prof. Martin Schröder (m.schroder@manchester.ac.uk).

Materials availability

This study did not generate new unique materials.

Data and code availability

All of the data associated with the study are included in the article and the [supplemental experimental procedures](#). Additional information is available from the lead contact upon reasonable request.

Catalyst preparation

All of the chemicals were obtained from Sigma-Aldrich and used as received. The catalysts were prepared using supports of $\gamma\text{-Al}_2\text{O}_3$, ZSM-5, and MFM-300(Al). $\gamma\text{-Al}_2\text{O}_3$ and ZSM-5 were purchased from Sigma-Aldrich and used as received. MFM-300(Al) was synthesized following our previously reported method.²⁷ The loading of Cu (7 wt%) to the catalyst supports was carried out using the incipient wetness impregnation method. As illustrated in [Figure S1](#), in a typical experiment, a known amount of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ was dissolved in 2 mL deionized water. The solution was then added to 100 mg $\gamma\text{-Al}_2\text{O}_3$, ZSM-5, or MFM-300(Al) and a slurry formed in each case, which was dried in an oven at 80°C for 1 h. The dried sample of $\text{Cu}(\text{NO}_3)_2/\text{support}$ was then oxidized at 250°C (heating ramp: 5°C min^{-1}) for 12 h in air to produce the corresponding CuO/support as catalysts. To prepare the Cu/support catalysts, the CuO/support sample was reduced at 250°C under a 5% H_2 flow (balanced in Ar, 70 mL min^{-1} , heating ramp: 5°C min^{-1}) for 12 h.

Catalyst testing

The catalytic activity and selectivity of NO_2 decomposition over these catalysts have been carried out under both conventional thermal heating and NTP activation conditions ([Figure S2](#)). The gas feed contained 500 ppm NO_2 diluted in a flow He. The total flow of 100 mL min^{-1} at 25°C was controlled by mass flow controllers (MKS Instruments), and the same gas feed was used throughout for catalysis tests in this study. Before the reaction, all of the catalysts were pre-treated with a dry flow of He for 1 h at 80°C to remove moisture. The NO_2/He gas mixture was then passed through a fixed-bed reactor and the catalytic performance of each catalyst tested.

For thermal activation, a reactor of 6 mm outer diameter (OD) quartz tube was used and the catalyst held in place between quartz wool plugs. The reactor was placed in a tube

furnace and the reaction conducted from 25°C to 250°C. For NTP activation, a reactor comprising 2 coaxial quartz tubes of 6 mm OD for the outer tube and a 3-mm OD inner tube were used to give a discharge gap of 0.5 mm. The outer tube was covered by a metal mesh electrode, and a metal wire electrode was placed inside the inner tube. The outer electrode was connected to a high-voltage output and the inner electrode grounded. The catalyst was packed in the discharge region to ensure that the plasma was generated only around the catalyst. The plasma was ignited by an alternating current power source (CPT-2000K, 0–25 kV, 10 kHz). The AC peak-to-peak voltage (V) was measured using a high-voltage probe, and the voltage across an internal capacitor (0.47 μF) placed between an electrode and ground was measured to obtain the charge (Q) generated by the discharge. The electrical parameters were recorded in real-time online using an oscilloscope (Tektronix TDS 2022B), and the discharge power was calculated using the area of the Q-V Lissajous figure, as detailed in our previous work.^{46,47} The discharge power was $\sim 0.6 \pm 0.05$ W and the SEI was ~ 0.4 kJ L⁻¹ at a frequency of 10 kHz and AC peak-to-peak voltage (V_{pk-pk}) $\sim 13 \pm 0.5$ kV. The temperature was controlled by a fan and monitored by an infrared thermometer (IRT670, General Tools & Instruments).

To test the water stability of the catalysts, the Cu/MFM-300(Al) catalyst with MFM-300(Al) as a benchmark were tested in the plasma reaction in the presence of water vapor. Water and NO₂ were introduced to the reactor separately to avoid the pre-reaction of NO₂ and H₂O in the pipeline. The catalysts were treated with 2.8% H₂O vapor in He at 25°C with a flow rate of 100 mL min⁻¹ for 250 min. The activity of the catalyst was then tested in plasma for 250 min under the same operating conditions as above in the absence of water.

Analysis of gaseous products emitted from the reactor was carried out using (1) a Bruker Matrix MG5 FTIR spectrometer (resolution = 0.5 cm⁻¹) for NO_x (NO₂, NO, and N₂O) and (2) a mass spectrometer (Hiden QGA quantitative gas analysis system, Hiden Analytical) for N₂ and O₂. Equations 5, 6, 7, and 8 have been used to calculate the NO₂ conversion (X) and the product selectivity (S). The energy efficiency, EE, for the dissociation of NO₂ is defined by Equation 9. Each data point is an average of 3 consecutive measurements, with an error of $< \pm 3\%$ for NO₂ conversions and $< \pm 4\%$ for product selectivities. The N balance is typically close to within 99% based on the concentration of NO₂, NO, N₂, and N₂O as determined by FTIR and mass spectrometry.

$$X_{NO_2} = \frac{[NO_2]_{inlet} - [NO_2]_{outlet}}{[NO_2]_{inlet}} \times 100\% \quad (\text{Equation 5})$$

$$S_{N_2} = \frac{[NO_2]_{inlet} - [NO_2]_{outlet} - 2[N_2O]_{outlet} - [NO]_{outlet}}{[NO_2]_{inlet} - [NO_2]_{outlet}} \times 100\% \quad (\text{Equation 6})$$

$$S_{N_2O} = \frac{[NO_2]_{inlet} - [NO_2]_{outlet} - 2[N_2]_{outlet} - [NO]_{outlet}}{[NO_2]_{inlet} - [NO_2]_{outlet}} \times 100\% \quad (\text{Equation 7})$$

$$S_{NO} = \frac{[NO_2]_{inlet} - [NO_2]_{outlet} - 2[N_2O]_{outlet} - 2[N_2]_{outlet}}{[NO_2]_{inlet} - [NO_2]_{outlet}} \times 100\% \quad (\text{Equation 8})$$

$$EE(\text{mmol kJ}^{-1}) = \frac{n_{NO_2} \text{ input}(\text{mmol s}^{-1}) - n_{NO_2} \text{ output}(\text{mmol s}^{-1})}{\text{Discharge power (kW)}} \quad (\text{Equation 9})$$

Continuous wave (CW) EPR spectroscopy

EPR spectroscopy has been used to investigate the local environment of the Cu²⁺ ions and their interaction with NO₂. Spectra were recorded at X-band (~ 9.5 GHz) with a Bruker EMX 300 EPR spectrometer equipped with a high-Q resonator and a

liquid He cryostat. Recording of the half-field “forbidden” transitions involved an ER 4116DM dual mode resonator operating at ~ 9.6 GHz in perpendicular mode and at ~ 9.4 GHz for the parallel B_1 pattern. Theoretical modeling of the EPR spectra was performed using the EasySpin software in MATLAB (more details are given in the [supplemental information](#))

Ex situ X-ray absorption spectroscopy

Ex situ X-ray absorption spectroscopy measurements were performed at the Cu K-edge (8,979 eV) on the B18 beamline at the Diamond Light Source (Didcot, UK). Measurements were performed in transmission mode using a quick scanning extended X-ray absorption fine structure (QEXAFS) setup with fast-scanning Si(111) double crystal monochromators for the Cu edge. The data processing was performed using IFEFFIT with the Demeter package (Athena and Artemis). The fitting parameters were $S_0^2 = 0.86$; fit range $3 < k(\text{\AA}^{-2}) < 12.4$, $1 < R(\text{\AA}) < 3$; number of independent points = 11.7. Each sample was preheated from room temperature to 250°C at a rate of 10°Cmin⁻¹ in He to remove water and other adsorbed species, and then transferred into a sealed sample cell inside a glovebox. The metal particle size was calculated based on the previously reported method.²

In situ and in operando DRIFTS analysis

DRIFTS measurements were carried out using a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N₂-cooled detector. The spectra were recorded at a 4 cm⁻¹ resolution, and each spectrum was averaged 128 times. For the IR measurements of the bare samples, the sample was activated at 250°C under Ar (99.999%, BOC Gas) for 4 h to remove adsorbed water from the pores. The spectrum of KBr, thermally dried at 250°C in Ar for 4 h, was used as the background.

In situ DRIFTS measurements of the catalysts as a function of NO₂ adsorption were also conducted. The sample was first activated at 250°C under Ar for 4 h to remove adsorbed water from the pores. The sample temperature was then reduced to room temperature for all of the measurements. The spectrum of the activated sample was used as the background reference for the spectra of NO₂-loaded samples. A stream of 500 ppm NO₂ diluted in Ar with a total flow rate of 50 mL min⁻¹ was introduced to the DRIFTS cell to establish the NO₂ adsorption for each sample. The gas mixture was then switched to pure Ar at a total flow rate of 50 mL min⁻¹ to purge the cell and remove the gas phase NO₂ and weakly adsorbed NO₂ to reveal the strongly bound NO_x species on the catalysts.

In operando DRIFTS measurements of the dissociation of NO₂ over the catalyst under plasma were measured using a Bruker Tensor 70 FTIR spectrometer (resolution = 4 cm⁻¹) with a specifically designed in situ plug flow cell with the plasma generated in the catalyst bed using a modified Spectra Tech Collector II DRIFTS accessory.¹⁷ The catalyst was activated at 120°C under He (99.999%, BOC Gas) for 4 h to remove adsorbed water. The temperature of the sample was then reduced to room temperature, and the spectrum of the desolvated sample at room temperature was used as the background reference for the following reaction. The reaction was performed at 25°C using a stream of 500 ppm NO₂ diluted in He with a total flow rate of 50 mL min⁻¹. The plasma generator was an alternating current power source (PVM500 model), and the electrical parameters were monitored using an oscilloscope (Tektronix TBS1062) that was connected to the reactor through a high-voltage probe (Tektronix, P6015). The applied voltage was 7.5 ± 0.5 kV at a frequency of 26 kHz and a SEI of ~ 0.2 kJ L⁻¹.

Dynamic breakthrough and temperature-programmed desorption of NO₂

Dynamic breakthroughs of NO₂ and NO₂-TPD experiments were performed to determine the NO₂ adsorption capacity and adsorbate-adsorbent strength for each catalyst. In a typical experiment, the powder sample was packed in a fixed-bed reactor equipped with a Bruker Matrix MG5 FTIR spectrometer (resolution = 0.5 cm⁻¹) as the detector. The sample was first activated at 250°C under a dry He flow at 100 mL min⁻¹ (99.999%, BOC Gas) for 20 h. After activation, the temperature of the reactor was decreased to 25°C and a gas mixture of 500 ppm NO₂ diluted in He was introduced to the fixed bed to establish the adsorption of NO₂. The complete breakthrough of NO₂ is observed when the concentration of NO₂ at the outlet is equal to that of the inlet. On saturation, the gas stream was switched to pure He (flow rate = 100 mL min⁻¹) to remove the physical (weakly) adsorbed NO₂ from the sample until a stabilized IR spectrum is obtained. The temperature of the reactor was then increased at a rate of 5°C min⁻¹ under a dry He flow to measure the desorption of strongly adsorbed NO₂. The signals for CO, CO₂, H₂O, and NO_x (N₂O, NO, and NO₂) were monitored by the FTIR spectrometer continuously until desorption was complete.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.xcrp.2021.100349>.

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AUTHOR CONTRIBUTIONS

S.X., materials synthesis and characterization and catalysis tests, including the reactor design. S.X. and X.H., measurements and analysis of the breakthrough data and temperature-programmed desorption data. S.X., T.D.D., and D.-T.N., TEM characterization. S.X., Y.M., S.C., and C.H., DRIFTS experiments. A.W., measurement and analysis of XPS data. S.X. and C.C.T., collection and analysis of synchrotron X-ray diffraction data. S.X., L.L., and M.D.F., collection and analysis of synchrotron infrared data. S.X., E.K.G., and C.R.A.C., measurement and interpretation of the XAFS data. A.S., F.T., and E.J.L.M., measurement and interpretation of the EPR data. S.Y. and M.S., overall design, direction, and development of the project and preparation of the manuscript, with contributions from all of the authors.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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