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Mechanistic studies on the conversion of NO gas on urea-iron and copper metal organic frameworks at low temperature conditions: *in situ* infrared spectroscopy and Monte Carlo investigations

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ABSTRACT

Nitrogen oxides (NO_x) emissions from high temperature combustion processes under fuel-lean conditions continue to be a challenge for the energy industry. Selective catalytic reduction (SCR) has been possible with metal oxides and zeolites. There is still the need to identify catalytic materials that are efficient in reducing NO_x to environmentally benign nitrogen gas at temperatures lower than 200 °C. Metal-organic frameworks (MOFs) emerged as a class of highly porous materials with unique physical and chemical properties. This study is motivated by the lack of systematic investigations on SCR using MOFs under industrially-relevant conditions. Here, we investigate the extent of NO conversion with two commercially-available MOFs; Basolite F300 (Fe-BTC) and HKUST-1 (Cu-BTC), mixed with solid urea as a source for the reductant, ammonia gas. For comparison, experiments were also conducted using cobalt ferrite (CoFe₂O₄) as a non-porous counterpart to relate its reactivity to those obtained from MOFs. Fourier-transform infrared spectroscopy (FTIR) was utilized to identify gas and surface species the temperature range 115 - 180°C. Computational analysis was performed using Monte Carlo (MC) simulations to quantify adsorption energies of different surface species. The results show that the rate of ammonia production from the *in situ* solid urea decomposition was higher using CoFe₂O₄ than Fe-BTC and Cu-BTC, and that there is very limited conversion of NO on the mixed solid urea-MOF systems due to site blocking. The main conclusions from this study is that MOFs have limited abilities in converting NO under low temperature conditions, and that surface regeneration requires additional experimental steps.

KEYWORDS: Metal organic frameworks, NO_x reduction, Selective Catalytic Reduction, DRIFTS, Monte Carlo Simulations

1. INTRODUCTION

Emission of nitrogen oxides (NO_x , $x=1, 2$) from automobiles and stationary sources has been a major cause of atmospheric environment pollution in the last few decades.¹ In particular, nitric oxide (NO) in the troposphere is known to cause serious environmental and human health impacts due to its role in the production of photochemical smog, acid rain, and fine particulate formation.²⁻⁴ Hence, government regulations were devised in order to mandate controlling measures for NO_x emissions especially that originating from mobile engines or industrial sources such as fossil fuel power stations and oil and gas production and processing.⁵ While NO_x emissions control is classified into three categories: pre-combustion treatment, combustion modification and post-combustion treatment, the first two control steps result in only reducing NO_x levels by less than 50%.⁶ In recent years, more advances were made in the development of technologies associated with post-combustion treatment of NO_x to control and reduce their emission levels.⁷ Selective catalytic reduction (SCR) processes are recognized as effective routes to remove NO_x from the air.⁸⁻¹⁰ In these routes, flue gas containing NO_x is introduced to a reducing agent in the presence of a suitable catalyst at moderate temperature (200 °C -300 °C). An example of such reducing agents is ammonia (NH_3), which has been reported as one of the most efficient, highly selective and cost-effective components of SCR-based technologies for NO_x emission control.³ The reactions that occur during the NH_3 -SCR of NO_x are shown in equations (1) and (2):

Given that the catalyst plays the crucial role in the NH_3 -SCR process, recent studies were focused on the improvement of the catalyst structure and operating conditions in order to boost their efficiency.¹¹

While ammonia has been extensively used as a reducing agent for the SCR reduction of NO_x , urea has recently emerged as a more convenient option in terms of toxicity and hazard control.¹² Mina *et al.*¹³ studied the simultaneous effect of adding manganese oxide (Mn_2O_3) and cobalt oxide (Co_3O_4) along with the use of urea-SCR. The data showed that urea-SCR had a greater impact on de NO_x processes rather than the nano-additives. Several types of catalysts were employed for NO_x elimination. Table S1 lists the recently studied catalysts in the NO SCR reaction highlighting their performance. In general, these catalysts are efficient over considerably high operational temperature (300 - 400 °C). However, they can be deactivated during the application process through several ways such as poisoning, fouling, thermal degradation, and vapor compound formation. Moreover, surface reactions can happen at the gas/solid interface as well as solid/solid reactions between the catalyst support and the promoter, which can deactivate them as well.¹⁴ All in all, the disadvantages listed in Table S1 were the driving force behind replacing such precious metallic catalysts with efficient and safer catalysts in the industrial arena.

As an emerging class of highly ordered porous crystalline materials, metal organic frameworks (MOFs) are regarded as the latest addition to the list of SCR catalysts after zeolites for the reduction of NO_2 .^{15–20} A good example for this class is MIL-100(Fe) MOF, which contains iron(III) metal centers connected to 3 units of 1,3,5-benzenetricarboxylate units in a 3D crystalline network resulting in a surface area of $\sim 2000 \text{ m}^2\text{g}^{-1}$. The authors²¹ found a 100% NO_x conversion efficiency at 240–300 °C, which got reduced to 87% upon adding SO_2 and water vapor. The NO_x conversion percentage was noticed to be almost 55% at 180 °C.

The following mechanism was proposed for the formation of N₂ gas from the reaction of surface ammonium ion (NH₄⁺) with NO₂ or coordinated amide (–NH₂) with NO:

Based on the above, MOFs can be regarded as a powerful candidate for NO_x SCR studies, yet such studies necessitate the need for MOFs that passed bench scale synthesis, and can be utilized in low temperature range that matches the industrial conditions.

Among the commercially-available MOFs are Fe-BTC and its copper-based analogue Cu-BTC (BTC = benzene-1,3,5- tricarboxylate), sold under the names of Basolite F300 and HKUST-1, respectively.²² While both Basolite F300 and MIL-100Fe have the same chemical formula and both are Fe-BTC based, Basolite F300 has a semi-crystalline structure and is commercially-available that makes it convenient for industrial use. Basolite F300 has been used in various applications as a catalyst for the synthesis of multi-walled carbon nanotubes (MWCNTs)^{23,24}, gas separation²⁵, and CO₂ capture.²⁶ In addition, it exhibits catalytic capabilities in Lewis acid reactions and oxidation reactions such as ring opening of epoxides, acetalization of aldehydes, methylation of amines, aldol condensation, aerobic oxidation of thiophenol to diphenyldisulfide, and benzylic oxidation by tert-buthylhydroperoxide.²³ Fe-BTC displays biocompatibility features that lowers toxicity concerns for the environment.²⁷

Cu-BTC is one of the most well-characterized and extensively studied MOFs. Li *et al.*²⁸ reported a conversion efficiency of NO close to 100% with ammonia in the range of 220-300 °C. It was found that high NO adsorption capacity, tunable structure, and abundant unsaturated copper sites marked this kind of MOFs as an efficient and promising denitration catalyst at such

temperature range. Recently, Wang *et al.*²⁹ proposed the MOFs-NTP (non-thermal plasma) synergistic method for the denitration process and obtained an ultra-efficient deNO_x performance without any reducing additives. They prepared Cu-BTC by a simple microwave digestion and then combined it with DBD reactor for NTP generation to test the denitration efficiency. The results showed that the new method achieved 98% NO removal efficiency at ambient temperature. Although plasma assisted techniques for the flue gas treatment have shown good progress, yet the industrial applicability of plasma-based techniques is questionable.³⁰ Another recent study conducted by Zhao *et al.*,³¹ showed deNO_x effect using Ce-modified Cu-BTC catalysts in presence of CO at low temperature by *in situ* DRIFTS. The results demonstrated that the adsorption modes of NO on the catalysts form the following species; monodentate nitrites, chelating bidentate nitrates, bridging bidentate nitrates, trans- N₂O₂²⁻ and NO⁻ species (Scheme S1), whereas the adsorption forms of CO form hydrogen carbonate, carbonate and carbonyl species (Scheme S2). They concluded that the amalgamation of Ce(III) enhanced the catalytic performance of CO-SCR reaction and improved the adsorption abilities of NO_x.

Spinel ferrites are a special class of iron-based oxides with the general formula (MFe₂O₄), where M = Ni, Cu, Co, Mn or Zn. They have recently attracted attention as promising catalysts due to their high stability, robust magnetic and mechanical properties.³² Cobalt ferrite (CoFe₂O₄) has inverse spinel structure and is regarded as a widely used catalyst for many organic reactions due to its added advantage of reusability and recovery.³³ Li *et al.*³⁴ have utilized cobalt ferrite as a catalyst for the NO_x conversion, where they loaded CoFe₂O₄ into graphene (GE) and N-doped graphene (N-GE) as carriers to improve its performance. The results showed that CoFe₂O₄/N-GE has sustained a conversion percentage of 95% at a lower temperature of 200-300 °C because the nitrogen doping allowed a better distribution of the active material with an optimum loading of

4%, and the presence of pyridinic nitrogen as active reducing sites which activate the surface more than $\text{CoFe}_2\text{O}_4/\text{GE}$.³⁴

The above studies highlight the need for molecular level investigations into the reactivity of the commercially-available MOFs for their applicability under industrial conditions. Hence, the objective of this study is to systematically investigate the extent of NO reduction when the temperature does not exceed 200 °C and solid urea is mixed with the MOF as an *in situ* source of ammonia in a dry environment. Two commercially available MOFs were selected for this study, namely Basolite F300 (Fe-BTC) and HKUST-1 (Cu-BTC). Solid urea was mechanically mixed with these MOFs as an *in situ* source of ammonia gas for the reduction step in the reaction. The performance of these MOFs was compared to that of cobalt ferrite (CoFe_2O_4) metal oxide nanoparticles as a non-porous analogue. These experiments were designed to identify, monitor and account for local surface changes and generated gases to calculate ammonia generation rate and NO conversion percentage. To monitor surface species, diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used. The surface studies were complemented with gas phase identification using transmission infrared spectroscopy. Theoretical calculations using Monte Carlo simulations were done to aid in the interpretation of experimental data.

2. EXPERIMENTAL METHODS

2.1. Chemicals.

All chemicals were used as received without further purification: Fe-BTC and Cu-BTC from Sigma-Aldrich (Basolite F300 Cat. No. 690872, and HKUST-1 Cat. No. 688614); Cobalt Iron nano-powder from US research Nanomaterials Inc. (CoFe_2O_4 , 99.9%, CAS# 12052-28-7); NO (g) from Praxair ([NO] = 500 ppm in N_2 gas); urea (Crystalline powder, BDH, CAS: 57-13-

6). Synthetic micronized diamond powder from Lands Superabrasives (6 μm , LST600T). The surface of the diamond powder was cleaned several times with ethanol and water mixtures (50/50%, v/v%) and finally with water using suction filtration. The cleaned diamond powder was oven-dried overnight and used in selected experiments to enhance the scattering efficiency of nanoparticles.

2.2. Characterization experiments.

Thermogravimetric analysis (TGA) was completed on a Q50 V20.8 Build 34 instrument. For Fe-BTC, nitrogen gas was flowed at 40 and 60 mL min^{-1} for balance and sample, respectively. For the Cu-BTC, the TGA analysis was completed on a Q50 V20.13 Build 39 instrument, where gas flow was 40 and 60 mL min^{-1} air and nitrogen gas for balance and sample, respectively. The sample was thermally equilibrated at 25 $^{\circ}\text{C}$, followed by ramping the temperature at a rate of 10 $^{\circ}\text{C min}^{-1}$ to 800 $^{\circ}\text{C}$. Brunauer-Emmett-Teller (BET) surface area and pore size distribution analysis was conducted using a Nova 2200e multi-gas surface area analyzer (Quantachrome Instruments) and N_2 as a gaseous adsorbate. The MOF samples were outgassed at 115 $^{\circ}\text{C}$ under vacuum for 20 hr prior to the start of the analysis. The CoFe_2O_4 sample was outgassed at 150 $^{\circ}\text{C}$ under vacuum for 20 h prior to the start of the analysis.

2.3. DRIFTS experiments.

DRIFTS spectra were collected using a praying mantis diffuse reflectance accessory (Harrick, DRK-4N18) equipped with a stainless-steel high temperature reaction chamber treated with a special SilcoSteelCR coating (HVC, cup 6 by 3 mm, dome cover with two Ge windows and one quartz viewing window). A total mass of 0.23 g filled the sample cup of the HVC reaction

chamber. The gas handling system described in Figure S1 was used to introduce NO vapor and dry/humid air into the reaction chamber using carrier air from a purge gas generator (Parker/Balston Analytical Gas Systems Purge Gas Generator 75-52, less 1 ppm CO₂ and H₂O). The maximum air flow in these experiments after mixing was maintained at 350 standard cubic centimeters per minute (sccm). The DRIFTS accessory was installed into a Nicolet 8700 FTIR spectrometer (Thermo Instruments) equipped with a purge gas generator and a liquid N₂ cooled MCT detector as outlined in Figure S1a. Each experiment started by preparing a fresh sample containing 8% (wt/wt) urea in Fe-BTC, Cu-BTC, or CoFe₂O₄. Mechanical mixing of these chemicals was achieved using a wig-L-bug (no ball) for 1 min or manually until the sample became completely homogeneous. Efficient and reproducible packing of the sample was obtained using a 4 kg weight for 10 min. For DRIFTS experiments conducted under dry conditions, the sample was prepared and kept under dry air flow (350 MFC) at 115 °C for about 12 h prior to flowing NO gas. A single beam spectrum was first collected, and then NO gas was introduced. All spectra were collected by averaging 100 scans at 8 cm⁻¹ resolution. The relative humidity (RH) of the air was measured by a humidity sensor (Vaisala HUMICAP HM70, ±2% RH uncertainty) located at the exit of the DRIFTS reaction chamber. Experiments were repeated 2-3 times, each on a freshly-prepared sample unless noted otherwise.

2.4. Gas phase experiments.

Gas-phase experiments were performed using a similar setup to the DRIFTS experiments. However, during such experiments, the DRIFTS reaction chamber was replaced by a Gas Flow Cell (GFC) into the spectrometer to observe gas phase products as depicted in Figure S1b. The reaction chamber was placed before the FTIR spectrometer, connected with a thermocouple to

monitor the temperature of the reaction chamber. The sample preparation and reaction conditions were maintained according to the same followed procedures in DRIFTS experiments. Using the peak area or peak height of each gas phase species, molar absorptivity (ϵ) in units of $\text{ppm}^{-1}\text{cm}^{-2}$ was calculated as listed in Table S2 by applying Beer's law to quantify the concentration of each gas produced in our experiments. Experiments were repeated 2-3 times, each on a freshly-prepared sample unless noted otherwise.

2.5. Computational details.

Simulations of the adsorption of identified species from the DRIFTS spectra on the surface of a given MOF and metal oxide were done using Monte Carlo (MC) computational methods. BIOVIA materials studio software with the embedded adsorption locator module was employed to perform the MC simulations.³⁵ The crystal structures of all used catalysts, Fe-BTC, Cu-BTC, and CoFe_2O_4 , were obtained from the crystallography open database (COD). Fe-BTC (Basolite F300) is considered a semi-crystalline form of the crystalline analogue MIL-100(Fe). It was previously reported that the proposed structure of Basolite F300 is very close to that of MIL-100(Fe) since both are iron 1,3,5-benzenetricarboxylates³⁸ and was previously employed as a representative for Fe-BTC.³⁹ In this study, the unit cell of MIL-100(Fe) (COD ID: 7102029) was used to model the crystal of Fe-BTC (Basolite F300). The surface of the crystal was cleaved along the (220) as a major surface plane of this crystal⁴⁰. The dimension of the 3D box is $79.9 \times 56.4 \times 58.3 \text{ \AA}$, which consisted of a (3×3) supercell with a 50 $\text{\AA}$ vacuum slab. The surface of Cu-BTC (HKUST-1) (COD ID: 2300380) was constructed by cleaving the crystal along the (222) plane, which represents the main exposed surface of the crystal.^{36,37} A 3D emulated box of $55.8 \times 55.8 \times 57.5 \text{ \AA}$ dimensions were constructed using a supercell of (3×3) and a vacuum slab of 50 $\text{\AA}$ under

periodic boundary conditions. Similar conditions were applied to model the crystal of cobalt ferrite (COD ID: 5910063), where the (311) plane was firstly cleaved as the main exposed surface plane⁴¹, then a supercell of (3×3) was built with a vacuum slap of 50 Å to finally create the 3d box of 52.2 × 30.67 × 17.7 Å.

In order to correlate the results from the DRIFTS with gas phase analysis, the identified species of interest were computationally tested to calculate the adsorption energies (E_{ads}) on a given material. First, the adsorbed molecules under evaluation were geometrically-optimized using the forcite module with COMPASS forcefield. Monte Carlo simulations were executed through the adsorption locator module using simulated annealing algorithm, where the adsorbed species were loaded on the cleaved surface, then a state of minimum energy was determined. All simulations were executed at a final temperature of 453 K to mimic the employed final experimental temperature of 180 °C.

3. RESULTS AND DISCUSSION

3.1. Materials Characterization

Table 1 shows the results of the BET surface area analysis for Fe-BTC, Cu-BTC and CoFe₂O₄. All the samples exhibited high surface area, except CoFe₂O₄ nanoparticles since they are non-porous. Higher surface area may enhance the adsorption capacity of the samples.⁴² BET surface areas were measured using multipoint BET analysis. The external surface areas were obtained using the *t*-method and the pore volume and size were calculated using Barrett, Joyner, and Halenda (BJH) method. The BET surface area for Fe-BTC used here is 771(40) m² g⁻¹, which is close to 685 m² g⁻¹ reported elsewhere.⁴⁴ For comparison, the reported BET surface area value for MIL-100(Fe) varied from 2350 to 1435 m² g⁻¹ according to the synthesis approach.⁴³ It is likely

that lab scale samples had higher surface area than those produced at the industrial scale because of the difference in the scalable synthesis protocol such as reaction time and the extensive purification process.^{23,44}

Table 1: Values of BET surface area and pore size analysis

Material	BET surface area ¹ (m ² g ⁻¹)	External surface area ² (m ² g ⁻¹)	Pore volume ³ (cm ³ g ⁻¹)	Pore size ³ (radius, Å)
Fe-BTC	771(40)	125(6)	7(1)×10 ⁻²	15(1)
Cu-BTC	1380(70)	98(5)	9(1)×10 ⁻²	19(1)
CoFe ₂ O ₄	43(2)	-	-	-

Notes: ¹ multipoint BET, ² t-method, ³ BJH method. Numbers in parenthesis are $\pm \sigma$.

Thermal gravimetric analysis (TGA) was also conducted in order to measure the thermal stability for the MOFs used here at the temperature range of operation (115-180°C). Figure S2 shows the TGA curves for both Fe-BTC and Cu-BTC. The first mass loss step for Cu-BTC and Fe-BTC occurs nearly below 100 °C due to the chemisorbed and physisorbed water molecules inside the structure.^{45,46} The second weight loss step occurs at nearly 380 °C and 320 °C for both Fe-BTC and Cu-BTC, respectively, and is due to the removal of the organic linker and annihilation of the MOF structure.⁴⁷ The temperature values of the second step confirms the need to work with the MOFs below that temperature while thermally-stable.

In the case of urea, it has been reported from the TGA analysis that urea has three stages of mass loss: the first one occurs between 133 -190°C, where urea starts to decompose and biuret forms, the second one occurs between 190 -240°C, which marks the decomposition of biuret, and the third stage occurs between 240 -330°C, which denotes a lower mass loss region, where ammelide and ammeline forms until their final decomposition at 415°C.⁴⁸ It was noted that major production of NH₃ was achieved at nearly 185 °C, which was identified by both a differential

scanning calorimetry (DSC) endothermic maximum, a corresponding MS ion intensity maximum, and vibrational modes of ammonia using FTIR spectroscopy.⁴⁹

3.2. Thermal decomposition of urea: effect of humidity and presence of a catalyst

To clearly understand and facilitate the analysis of *in situ* reactions between NO(g) and M-BTC/urea (M = Fe and Cu), control experiments were performed in the absence of NO(g). In these experiments, urea is the source of NH₃(g), which will be acting as a reducing agent in the conversion of NO(g) in the M-BTC/urea system. Earlier, aqueous or anhydrous ammonia had mostly been used as a reducing agent for SCR as NH₃-SCR. However, recently urea-SCR was implemented as a more convenient option for industrial applications.⁴⁸ This is mainly because aqueous or anhydrous ammonia is a hazardous chemical. Therefore, transportation, storage and handling of NH₃(aq) require a high level of safety and environmental regulation. On the other hand, urea is non-toxic, safe and easy to carry.

Figure 1 shows the concentration of NH₃(g) as a function of time and humidity in the control experiments of thermal decomposition of M-BTC/urea (M = Fe and Cu) mixture. In Figure 1a, Fe-BTC/8% urea was heated to 115 °C for 19 min under dry condition. Then, the temperature was increased to 180 °C and kept for another 40 min. There was no evidence of gas phase NH₃ at 115 °C. However, when the temperature increased to 180 °C, the amount of NH₃(g) went to the maximum (91 ppm) within 10 min. As time passed, the concentration of NH₃(g) went down. The Fe-BTC/8% urea mixture was again heated with the same temperature profile, but this time was under humid conditions (RH = 14%). The amount of NH₃(g) went to the maximum (115 ppm) within 10 min, as evident from the kinetic curve (Figure 1a). As the time progressed, the concentration of NH₃(g) went down. The maximum amount of NH₃(g) produced was 115 ppm,

1.

which was higher than the dry conditions (91 ppm). It was evident that the humid conditions enhanced the production of $\text{NH}_3(\text{g})$ relative to dry conditions.

Figure 1. Kinetic curves for the concentration of ammonia gas, $[\text{NH}_3(\text{g})]$, for the thermal decomposition of (a) Fe-BTC/8%urea and (b) Cu-BTC/8%urea mixtures as a function of time and temperature under dry ($\text{RH} < 1\%$) and humid ($\text{RH} = 14\%$) conditions.

Similarly, Cu-BTC/ 8% urea was heated at 115 °C for 19 min under dry ($\text{RH} < 1\%$) and humid ($\text{RH} = 14\%$) conditions. Then, the temperature was increased to 180 °C and kept for another 40 min. The kinetic curves (Figure 1b) show that the amount of $\text{NH}_3(\text{g})$ produced (63 ppm) under humid conditions, is higher than the dry conditions (18 ppm).

The proposed mechanism for the thermal decomposition of urea is presented in the following equations:⁴⁸

Equation 7 highlights that the presence of water was deemed necessary for the complete decomposition of urea to ammonia and CO_2 . In addition, equation 7 is the slow reaction due to the high stability of HNCO in the gas phase, and water catalyzed its decomposition.⁵⁰

To examine the effect of porosity on $\text{NH}_3(\text{g})$ production, the production rate of $\text{NH}_3(\text{g})$ from urea mixed with M-BTC ($\text{M} = \text{Fe}$ and Cu) was compared with that of diamond powder as a non-porous and unreactive material to replace the MOFs (Figure S3). The produced amount of $\text{NH}_3(\text{g})$ reached a maximum at ~ 1380 ppm. On the other hand, Figure S4 shows the results of urea decomposition mixed with CoFe_2O_4 nanoparticles as a non-porous and reactive material under dry conditions. The maximum level of $\text{NH}_3(\text{g})$ in the $\text{CoFe}_2\text{O}_4/8\%$ urea mixtures was ~ 245 ppm. Comparing these results in Figure 1 versus Figures S3 and S4, it could be concluded that the rate of $\text{NH}_3(\text{g})$ production in the case of the MOFs used here follows this order: diamond powder/urea > $\text{CoFe}_2\text{O}_4/\text{urea}$ > Fe-BTC/urea > Cu-BTC/urea.

3.3. Reaction of $\text{NO}(\text{g})$ with M-BTC/ 8%urea ($\text{M} = \text{Fe}$ and Cu): Gas phase studies

In situ reactions of $\text{NO}(\text{g})$ with M-BTC/ 8%urea were carried out to examine the reduction performance of the MOFs used here. In these experiments, the M-BTC/ 8% urea sample mixture was kept under dry air flow overnight at 115°C . The purpose of this step was to remove any loosely bonded species from the surface and the pores of the active materials, particularly water and volatile organic compounds. This temperature was below the melting point of urea at 133°C . Then, a dry flow of $\text{NO}(\text{g})$ was introduced. All spectra were referenced to the spectrum obtained after the overnight flow of dry air over the sample at 115°C . No evidence of gas phase product appeared at 115°C .

Figure 2 shows the spectra of the gas phase for the reaction between NO(g) and M-BTC/8%urea as a function of time and temperature under dry conditions (RH<1%).

Figure 2: Gas phase spectra collected for (a) Fe-BTC / 8% urea and (b) Cu-BTC / 8% urea samples while flowing NO(g) at 115 and 180 °C. See text for assignment of observed peaks.

When the temperature was increased to 180 °C, several peaks appeared. The detected gas phase species signals were $\delta(\text{NH}_3(\text{g}))$: 930, 964, 1034 cm⁻¹, $\nu(\text{NO}(\text{g}))$: 1874 cm⁻¹, $\nu(\text{HNCO}(\text{g}))$: 2269 cm⁻¹, and $\nu(\text{CO}_2(\text{g}))$: 2350 cm⁻¹.^{51–53} In the case of Cu-BTC, an extra band was observed

corresponding to $\nu(\text{NO}_2(\text{g}))$: 1614 cm^{-1} .^{54,55} This may be attributed to the oxidizing ability of Cu for $\text{NO}(\text{g})$ in Cu-BTC, which is responsible for the presence of NO_2 species in the gas phase spectra.⁵⁶ The peak heights assigned to $\text{NH}_3(\text{g})$ in Figure 2 were converted to concentration as mentioned in the experimental section to generate kinetic curves for $[\text{NH}_3(\text{g})]$ as shown in Figure 3.

Figure 3. Kinetic curves for $[\text{NH}_3(\text{g})]$ for the reaction of $\text{NO}(\text{g})$ [$\sim 300\text{ ppm}$] with (a) Fe-BTC/8%urea and (b) Cu-BTC/8%urea mixtures as a function of time and temperature under dry ($\text{RH} < 1\%$) and humid ($\text{RH} = 14\%$) conditions.

Similar experiment was performed under humid conditions to estimate the effect of dry over humid conditions that affect amount of $\text{NH}_3(\text{g})$ produced and consequently the reaction rate of $\text{NO}(\text{g})$ with M-BTC ($\text{M} = \text{Fe}, \text{Cu}$) / 8%urea mixture. The generated amount of $\text{NH}_3(\text{g})$ with

NO(g) flow under humid conditions was 70 ppm, which is slightly lower than that obtained under dry conditions (80 ppm) as shown in Figure 3a.

The kinetic curve in Figure 3b shows that the maximum amount of $\text{NH}_3(\text{g})$ produced (45 ppm) under humid conditions was higher than that under dry conditions (38 ppm) for the Cu-BTC/8% urea mixture. The data from both humid and dry conditions and in absence and presence of NO for M-BTC (M= Fe, Cu) are listed in Table 2.

Table 2. list of the maximum produced value of $\text{NH}_3(\text{g})$ in ppm, in terms of both the presence or absence of NO and the effect of humidity for M-BTC. The numbers in parenthesis represent $\pm 1\sigma$.

M-BTC, M =		Maximum $\text{NH}_3(\text{g})$ (ppm)	
		Dry conditions	Humid conditions
Fe	Absence of NO	91(23)	115(29)
	Presence of NO	80(20)	70(18)
Cu	Absence of NO	18(4)	63(16)
	Presence of NO	38(10)	45(11)

Upon inspecting the data in Table 2, it becomes clear that the maximum amount of $\text{NH}_3(\text{g})$ produced in the presence of NO(g) was lower than that in the absence of NO(g) under dry and humid conditions for both M-BTC. These results suggest consumption of $\text{NH}_3(\text{g})$ by NO(g) in the reduction reaction. This trend is more obvious in case of humid than dry conditions. An exception was noticed for Cu-BTC where the amount of produced $\text{NH}_3(\text{g})$ in presence of NO (38 ppm) was higher than that in the absence of NO (18 ppm). One possible explanation for this observation is that NO competes for the same sites on Cu-BTC as $\text{NH}_3(\text{g})$ without reacting with each other. The oxidizing ability of Cu-BTC for NO(g) ^{56,57} was evident by the presence of $\text{NO}_2(\text{g})$ in the gas phase spectrum in Section 3.1 and later explained in the DRIFTS results in Section 3.4.

Figure 4 shows the gas phase data for NO as a function of time and temperature under dry conditions with and without urea. The data for Fe-BTC sample (Figure 4a) show an instant decrease in the $[\text{NO}(\text{g})]$ $\sim 10\%$ in the absence of urea upon increasing the temperature to 180°C compared to a $\sim 40\%$ instant decrease in the presence of 8% urea. The enhancement in the conversion rate of $\text{NO}(\text{g})$ in presence of urea ($\sim 40\%$) can be attributed to a surface reaction that consumes NO at first then partially blocks the surface which may reduce its performance.

Figure 4. Kinetic curves for $[\text{NO}(\text{g})]$ for the reaction of $\text{NO}(\text{g})$ [~ 300 ppm] with (a) Fe-BTC and (b) Cu-BTC as a function of time and temperature under dry ($\text{RH} < 1\%$) conditions.

As for Cu-BTC, although it had a higher surface area than Fe-BTC, no $\text{NO}(\text{g})$ uptake was observed under dry conditions in the absence and presence of urea upon increasing the temperature 180°C (Figure 4b). Figure S5 show results from similar studies using CoFe_2O_4 , where a relatively small

decrease was observed likely due to the limited surface reaction compared with Fe-BTC. To have more mechanistic insights on the different surface reactions of each of material when mixed with urea, DRIFTS studies were conducted to investigate surface species.

3.4 Reaction of NO(g) with M-BTC/ 8% (M=Fe, Cu): DRIFTS studies

DRIFTS studies were carried out using M-BTC (M=Fe, Cu) MOFs and CoFe_2O_4 nanoparticles in order to monitor surface species *in situ* and better understand the reaction mechanism. These experiments were designed to thermally treat the solid materials at 115 °C under a flow of dry air before introducing a flow of NO(g) and then observe the changes to surface species over time with heating to 180 °C. Spectra recorded during these experiments were obtained by referencing to the background spectrum collected at 115 °C. Table 3 lists the frequencies and assignment of all identified peaks in Figures 5-7 for the materials used here.

Table 3. Summary of the assignment of DRIFTS bands observed for *in situ* reactions in Figures 5-7.

Material (with and without urea)	Wavenumber (cm^{-1})	Assignment
Fe-BTC	1635	$\delta_a(\text{N-H})$, asymmetric bending of surface NH_3
	2163	$\nu(\text{N-N})$, stretching band of surface N_2O
	2170	$\nu_a(\text{NCO})$, asymmetric stretch for OCN^- .
	2200	$\nu_a(\text{NCO})$, asymmetric stretch for HNCO
	2350	$\nu_a(\text{O=C=O})$, asymmetric stretching for $\text{CO}_2(\text{g})$
Cu-BTC	1386	ν_3 stretching monodentate nitrite
	1450	ν_3 stretching chelating bidentate nitrate
	1651	ν_3 stretching bridging bidentate nitrate
	1882	$\nu(\text{NO}^-)$, nitrosyl stretching band
	2156	$\nu_a(\text{NCO})$, asymmetric stretching for OCN^- .
	2206	$\nu_a(\text{NCO})$, asymmetric stretching for HNCO
CoFe_2O_4	1228	$\delta_s(\text{N-H})$, symmetric bending of NH_3 at the metal Lewis acid sites
	1472	$\delta(\text{N-H})$, bending for NH_4^+

1670	$\delta_a(\text{N-H})$, asymmetric bending of surface NH_3
2156	$\nu_a(\text{N-N})$, stretching band of surface N_2O
2170	$\nu_a(\text{NCO})$, asymmetric stretch of OCN^-
2200	$\nu_a(\text{NCO})$, asymmetric stretch of HNCO

Figure 5 shows the DRIFTS absorbance spectra using Fe-BTC samples. Upon flowing $\text{NO}(\text{g})$, the spectra in Figure 5a show an increase in the peak at 2163 cm^{-1} with time due to the accumulation of surface N_2O , which limited the production of NH_3 and hence limited the reduction of NO . The peak at 2350 cm^{-1} was assigned to gas phase CO_2 , which decreased in intensity with the increase in temperature from 115 to 180°C .⁷³ In Figure 5b, a peak at 2241 cm^{-1} was observed and assigned to $\nu_{\text{as}}(\text{NCO})$ of surface HNCO from urea decomposition. In addition, the peak at 2170 cm^{-1} corresponding to $\nu_{\text{as}}(\text{OCN})$ of adsorbed cyanate ion (OCN^-). This species was formed due to a reaction between the adsorbed HNCO(ads) and generated $\text{NH}_3(\text{g})$ according to the following reaction:^{59,64}

The strong affinity of HNCO to the MOF surface could be explained by the presence of C, O, N in its structure that act as Lewis bases. Moreover, both Figures 5a and 5b show an extra peak at 1635 cm^{-1} assigned to adsorbed NH_3 when urea was present. This feature is absent in samples containing no urea as shown in Figure 5c and 6d. These findings highlight the limited ability of Fe-BTC to generate $\text{NH}_3(\text{g})$ from urea *in situ*, likely due to the high adsorption affinity of HNCO(g) and the generation of surface N_2O which blocked the surface-active centers. Quantification of adsorption energies of these gases on Fe-BTC is presented in Section 3.2.

Figure 5. DRIFTS absorbance of spectra recorded for Fe-BTC/8% urea (a) with NO flow (~ 300 ppm) and (b) no NO flow as a function of time as temperature was increasing from 115 to 180 °C. For (a), the times are (from bottom to top): 4, 5, 6, 8, 12, 16, 20 and 28 min. For (b), the times are (from bottom to top): 4.6, 6.3, 7.9, 20 and 30 min. In (c), spectra are shown for Fe-BTC with no NO flow under dry conditions as a function of time as the sample was heated from 115 °C to 180 °C. The times are (from bottom to top): 10, 20, 30, 40, 50 and 60 min. In (d), a spectrum for Fe-BTC only is shown after heating for 60 min to 180 °C from 115 °C. See Table 3 for assignment of peaks.

Moreover, Figure 6 shows the DIRFITS absorbance spectra collected when Cu-BTC was used. Upon flowing NO(g), the spectra in Figure 6a show a broadening for peak at 2206 cm^{-1} , which may be attributed to the stabilization of the adsorbed HNCO on Cu-BTC active sites. Adsorbed HNCO limited the production of $\text{NH}_3(\text{g})$ needed for the reduction of NO.⁷⁴ Interestingly, the peaks at 1882, 1651, 1450 and 1386 cm^{-1} were present in the spectra collected in the presence of either NO or urea. These bands correspond to a number of surface nitrogen species depicted in Scheme S1: nitrosyl (NO^-) stretching band, ν_3 for bridging bidentate nitrate, chelating bidentate nitrate, and monodentate nitro bands, respectively.^{75–78} All these species were typically present on the surface of Cu due to the oxidizing ability of Cu during SCR reactions that produced these species in the presence of NH_3 , NO, or a mixture of both, and contributed to the deactivation of the surface.^{56,57,79} This data agree with those obtained from gas phase studies with regard to the lower amount of NH_3 production and the presence of NO_2 in the gas phase spectra. The peak at 2206 cm^{-1} in Figure 6b corresponds to the NCO asymmetric stretch for adsorbed HNCO that formed from urea decomposition. Also, the peak at 2156 cm^{-1} is assigned to $\nu_{\text{as}}(\text{OCN})$ for adsorbed OCN^- .

Figure 6. DRIFTS absorbance of spectra recorded for Cu-BTC/8% urea (a) with NO flow (~ 300 ppm). The times are (from bottom to top): 4, 5, 6, 8, 12, 16, 20 and 28 min. For (b) no NO flow as a function of time as temperature was increasing from 115 to 180 °C. The times are (from bottom to top): 4.6, 6.3, 7.9, 20 and 30 min. In (c) spectra are shown for Cu-BTC with no NO flow under dry conditions as a function of time as the sample was heated to 180 °C from 115 °C. The times are (from bottom to top): 1, 4, 9, 18, and 28 min. In (d), a spectrum for Cu-BTC only is shown after heating for 60 min to 180 °C from 115 °C. See Table 3 for assignment of peaks.

Figure 7 shows the DRIFTS spectra when CoFe_2O_4 was used as the material for $\text{NO}(\text{g})$ reduction. Figure 7a shows the effect of $\text{NO}(\text{g})$ on surface species upon heating from 115 to 180 °C, where the intensity of the negative peak at 1670 cm^{-1} decreased with time. This feature is assigned to $\delta_s(\text{N-H})$ of surface NH_3 , and its decreasing intensity with time indicates a reaction between $\text{NO}(\text{g})$ and NH_3 .

Figure 7. DRIFTS absorbance of spectra recorded for $\text{CoFe}_2\text{O}_4/4\%$ urea (a) with NO flow (~ 300 ppm) and (b) no NO flow as a function of time as temperature was increased from 115 to 180 °C. For (a) and (b), the times are (from bottom to top): 10, 20, 30, 40, 50, and 60 min. In (c), a spectrum for CoFe_2O_4 only is shown after heating for 60 min to 180 °C from 115 °C. See Table 3 for assignment of peaks.

In addition, a new peak at 2156 cm^{-1} formed, which corresponds to $\nu(\text{N-N})^{69,70}$ in surface N_2O (ads), which strongly adsorbed to the surface according to reaction (9):^{71,72}

These findings highlight the superiority of CoFe_2O_4 in catalysing the decomposition of urea and increasing NH_3 production. These findings also agree with the data obtained from the gas phase analysis discussed above.

Figure 7b shows negative peaks at 2200 cm^{-1} assigned to $\nu_{\text{as}}(\text{NCO})$ in HNCO from the decomposition of urea to form ammonia.⁵⁸ A neighboring negative peaks at 2170 cm^{-1} is assigned to $\nu_{\text{as}}(\text{OCN})$ in surface OCN^- species.^{59–63} A negative peak was also noticed at 1472 cm^{-1} , which may be attributed to the decomposition of adsorbed $\text{NH}_4^+(\text{ads})$ as shown in equation (8).^{56,65–67} Furthermore, a negative peak at 1660 cm^{-1} was noticed due to the $\delta_{\text{a}}(\text{N-H})$ of desorbed NH_3 and a negative peak at 1228 cm^{-1} assigned $\delta_{\text{s}}(\text{N-H})$ at the metal Lewis acid sites.^{65,68} Since the DRIFTS studies have highlighted the presence of a number of surface nitrogen species, the following section aims to quantify the adsorption energies of these species on the materials studied here.

3.5 Monte Carlo simulations (MC) for the adsorption of DRIFTS identified species over the surface of the catalyst.

Monte Carlo (MC) simulations were completed for the adsorption of the following species on the materials studied here: ammonia (NH_3), ammonium (NH_4^+), isocyanate (HNCO), nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O). The goal of these simulations was to quantify the adsorption energies of these species to aid in the interpretation of the experimental data presented above. Figure 8 shows images of the surfaces of Fe-BTC (220), Cu-BTC (222) and CoFe_2O_4 (311) in the presence of the above surface nitrogen species to highlight their coordination environment and binding sites.

	Fe-BTC (220)	Cu-BTC (222)	CoFe ₂ O ₄ (311)
HCNO			
NH3			
NH4+

Figure 8. Visualization for the MC simulations for HNCO, NH₃, NH₄⁺, NO, N₂O molecules over the surfaces of Fe-BTC (220), Cu-BTC (221) and CoFe₂O₄ (311).

The bonding between the adsorbed species and the catalyst of 3.5 Å long or lower are in Figure 8. The calculated adsorption energy ($-E_{\text{ads}}$) values for the adsorbed species are listed in Table 4. Adsorption energies of HNCO species were generally higher than those for NH_3 , which explain the dominance of HNCO(ads) over gaseous species, HNCO(g). The adsorption energy of HNCO(ads) on CoFe_2O_4 is the lowest compared to the MOF surfaces, which explains enhanced NH_3 production over its surface per reaction (7) above. This conclusion is in line with the DRIFTS data shown in Section 3.4, where the negative peaks assigned to HNCO decomposition peaks are more visible than those in the case of Fe-BTC and Cu-BTC. The adsorption energy data for NH_4^+ were the highest in the case of CoFe_2O_4 highlighting higher affinity for bonding to Co, which is absent from the MOF surfaces used here. All the calculated adsorption energies for the NO molecule were nearly similar and lower compared to those for HNCO(ads) or NH_4^+ (ads) molecules. This result can explain why there was no interaction between the materials and NO(g) flow in the absence of urea. Nitrous oxide (N_2O) was found to have a very high adsorption energy on the surfaces of Fe-BTC, Cu-BTC and CoFe_2O_4 as listed in Table 4. These values illustrate the high affinity of all the used materials towards the adsorption of N_2O that formed on the surface upon flowing NO(g) as discussed above in the DRIFTS spectra. These strongly bonded surface species may have contributed to the deactivation of the surface by blocking the active centers especially for Fe-BTC and Cu-BTC. This finding may also be confirmed by the current ongoing research that utilizes MOFs as a highly promising material for the capture and removal of N_2O gas due to their higher adsorption affinities.^{80–82} In summary, the theoretical MC calculations are aligned with the analysis of the experimental DRIFTS spectra of surface species.

Table 4. Calculated $-E_{\text{ads}}$ values using Monte Carlo simulations for the adsorption of different species over Fe-BT, Cu-BTC and CoFe_2O_4

Species	$-E_{\text{ads}}$ Fe-BTC (220), kcal/mol	$-E_{\text{ads}}$ Cu-BTC (222), kcal/mol	$-E_{\text{ads}}$ CoFe_2O_4 (311), kcal/mol
HNCO	438	342	296
NH_3	163	187	118
NH_4^+	500	369	749
NO	176	176	174
N_2O	5.826×10^3	5.824×10^3	5.821×10^3

CONCLUSIONS AND SIGNIFICANCE

Solid urea was utilized as a source of ammonia where it was mechanically mixed with Basolite F300 and HKUST-1 as an industrial user-friendly alternative to ammonia gas. The data showed that simple mixing of urea with MOF and metal oxides have promoted surface reactions that yielded undesirable surface species such as N_2O in case of Fe-BTC, and NO_2 and NO_3^- in case of Cu-BTC. Although NH_3 was produced from such reactions, the presence of these strongly bonded species blocked surface-active centers, reduced production rate of NH_3 , and consequently further reduction of NO gas.

The mechanistic insights presented in our studies highlight the limitations associated with using MOFs for the reduction of $\text{NO}(\text{g})$ under desirable industrially-relevant conditions aiming to use lower reaction temperatures (below 200°C) and a safe source of ammonia gas. Future research could investigate the extent of NO_x reduction as a function of NO to NO_2 ratio, effect of solar radiation on catalyzing surface reduction reactions of nitrogen species below 200°C to ensure site regeneration, and effect of separating urea from the potential catalytic materials to ensure a steady supply of ammonia at the optimum temperature for urea decomposition, which might not be the same temperature for optimum surface reduction reactions and would also limit the undesirable surface reactions in mixed solid systems.

Supplementary data

Supplementary data are available with the article at <https://doi.org/XXX>

Notes

The authors declare no competing financial interest.

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Graphical abstract