Ambient Temperature NO Adsorber Derived from Pyrolysis of Co-MOF(ZIF-67)

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ABSTRACT: Co-, Ni-, and Zn-containing MOFs are prepared and then pyrolyzed to generate materials for ambient temperature NO adsorption. Materials containing Co are much more efficient for NO adsorption than those containing Ni and Zn; therefore, Co is identified as the active phase. The best performing material studied here achieves 100% low concentration (10 ppm) NO adsorption for more than 15 h under a weight hourly space velocity of 120 000 mL g−1 h−1. Powder X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared, and Raman spectroscopies, along with scanning electron microscopy and TEM, are used to probe the physicochemical properties of the materials, particularly the Co active phase, and chemistries involved in NO adsorption—desorption. NO adsors on oxygen-covered Co nanoparticle surfaces in the form of nitrates and desorbs as NO at higher temperatures as a result of surface nitrate decomposition. NO storage capacity decreases gradually upon repeated NO adsorption—desorption cycles, likely because of Co3O4 formation during these processes.

1. INTRODUCTION

Nitrogen Oxides (NOx) emitted from automobiles has long been recognized as a major pollutant to the environment and to human health. Over the past decades, three-way catalysis,1,2 NOx storage and reduction,3,4 and selective catalytic reduction5−7 processes have been developed and commercialized to eliminate NOx generated by vehicles. Even though these processes are highly efficient, and certainly responsible for the air quality improvement we have experienced in recent years, none of them can eliminate 100% tailpipe NOx, especially during the so-called “cold-start”.9 As such, in places of poor ventilation, for example, underground transportation tunnels and indoor parking lots, low concentrations of unconverted NOx (up to 10 ppm, mainly as NO) from engine exhausts can accumulate. Air quality in such places is harmful to human health, especially with long periods of exposure. Removal of NOx from these locations in highly economical ways, however, is extremely challenging because of the low NOx concentrations and because of the vast air volumes.

Passing air that contains NOx through basic solutions or precipitation can oxidize low-concentration NO to NO2 at ambient temperatures.10,11 Because of a few restraints, for example, quick nitrate poisoning and low thermal stability, practical applications of these catalysts have not yet been realized. Liu et al.12 reported that CrO3 prepared by ammonia precipitation can oxidize low-concentration NO to NO2 at ambient temperature, and NO2 is then readily adsorbed by an alkaline solution. However, this catalyst does not catalyze NO oxidation with high efficiency. More recently, our group discovered that Cr−X (X = Zr, Co, Fe, Ni) bimetallic oxides synthesized with a sol−gel method are more efficient in catalyzing oxidation of low-concentration NO at ambient temperatures.13,14 These catalysts also display considerable reusability and water resistance. Unfortunately, the high toxicity of chromium oxides may preclude their practical use. Recently, (doped) activated carbon materials have also been found to oxidize NO to NO2 at ambient temperatures. For example, Wang et al.15,16 discovered that activated carbon nanofibers display good efficiency in both oxidizing and trapping low-concentration NO (20 ppm). Particularly, when...
such materials are modified with transition-metal oxides (e.g., MnO₂). NO oxidation capacity can be further enhanced.

An alternative approach is to use solid materials to adsorb (trap) NO directly. In this case, NO oxidation to NO₂ is no longer a prerequisite, even though some of such materials may still catalyze NO oxidation to NO₂ as part of the trapping process. In the past few years, researchers have discovered that Pd-exchanged zeolite materials are efficient passive NOx adsorbers that can be used to trap NOx from diesel engine exhausts during the cold start. However, these materials are likely too costly for use in removing low-concentration NOx from air. For this latter application, desirable materials should have the following features: low cost, low toxicity, high stability, and reusability.

Metal–organic framework (MOF) materials are a new class of porous crystalline materials that have been widely investigated and applied for various applications including the storage of hydrogen and hydrocarbons, gas purification, and sensor techniques, to name a few. Because of their limited thermal stability, these materials are typically not suitable for high-temperature applications. Thanks to their high surface area, tunable porosity, and controllable structures, however, MOFs can be treated by various methods (e.g., pyrolysis) to form thermally stable materials with unique porous nanostructures. In the present study, we seek to synthesize low-cost carbon-supported early transition-metal (oxide) materials by MOF pyrolysis and use them in ambient temperature NOx trapping. Note that even though our target NOx trapping temperature is ambient, regeneration of such materials after use requires elevated temperature treatments. Therefore, high-temperature stability is a requirement for these materials. This study is inspired by the findings described above that activated carbon materials show promise for this application and by the fact that high-temperature treatment of MOFs leads to the formation of materials with high surface areas and specific structures. For example, when the high-temperature treatment is done in the presence of O₂, metal oxides such as Co₃O₄, Mn₂O₃, and bimetal oxides are generated whereas in the absence of O₂ (i.e., pyrolysis), nanoporous carbon materials are generated.

2. EXPERIMENTAL SECTION

2.1. Material Preparation. Co-MOF (ZIF-67) was used as the precursor of the NO adsorber materials. The synthesis of ZIF-67 has been described in detail in recent literature. Important synthesis parameters have been identified as the 2-methylimidazole (C₅H₅N₂) to cobalt ion ratio and the solvent of choice (methanol or deionized water). In the present study, 1.092 g of Co(NO₃)₂·6H₂O (Macklin, 99%) and 1.232 g of 2-methylimidazole (Aladdin, 98%) were first dissolved in 30 mL of methanol (general-reagent, ≥99.5%), and the two solutions were then mixed. The mixture was stirred at 30 °C for 8 h for Co-MOF (ZIF-67) formation. Purple-colored solid ZIF-67 was collected with filtration and washed a few times with methanol. It was then dried at 60 °C in a vacuum oven overnight. Similarly, by using Zn(NO₃)₂·6H₂O (Shanghai Lingfeng Chemical Reagent Co., Ltd, 99%) and Ni(NO₃)₂·6H₂O (Shanghai Lingfeng Chemical Reagent Co., Ltd, 99%) to replace cobalt nitrate, Zn-MOF (ZIF-8) and Ni-MOF were prepared.

Pyrolysis of the MOF materials was carried out by heating the samples placed in a ceramic crucible to target temperatures of 500, 550, and 600 °C at 5 °C/min and maintaining at these temperatures for 1 h, in a flowing nitrogen (Air Liquide, 99.999%) atmosphere. After cooling to ambient temperature in N₂, the samples were ground, pressed, and sieved to 40–60 mesh size in the open air, prior to their use in NO trapping. The materials thus prepared are designed as M-T, where M represents the transition metal and T represents the pyrolysis temperature. For example, Co-600 denotes the material containing Co that is heat-treated at 600 °C.

2.2. NO Adsorption and Desorption Tests. Ambient temperature NO trapping was carried out in a continuous flow quartz reactor (i.d. = 8 mm) and 0.15 g of the sample was used for each test. The reaction temperature was maintained at 25 °C by immersing the reactor in a thermostatic water bath. The reaction feed gas contained 10 ppm NO, 21 vol % O₂, and balance argon. The total gas flow was 300 mL min⁻¹, resulting in a weight hourly space velocity (WHSV) of 120 000 mL g⁻¹ h⁻¹. Before each test, the sample was pretreated at 300 °C for 1 h in argon (200 mL min⁻¹) and then cooled to 25 °C in the same gas. Inlet and outlet NOx (NO and NO₂) concentrations were continuously recorded by an online NOx analyzer (Thermo Fisher 42i-LS).

No removal efficiency is calculated by the following equation

\[
\text{NO removal} (%) = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100\%
\]

where subscripts “inlet” and “outlet” represent the inlet and outlet NO concentrations, respectively. The NO trapping measurement was stopped when inlet and outlet NO concentrations were identical (i.e., adsorption saturation), following which, temperature-programmed desorption (TPD) was performed by heating the sample from 30 to 400 °C in flowing Ar at a ramping rate of 5 °C min⁻¹ and maintaining at 400 °C until no NOx desorption was observable. Samples with the adsorption—desorption cycle described above were tested again for ambient temperature NO adsorption to evaluate their stability and reusability.

2.3. Characterizations. Most of the characterizations described below were conducted on freshly prepared materials stored in air and on materials after desorption of trapped NO. Some measurements were also performed on samples with adsorbed NO to elucidate chemistries involved in NO trapping.

Transient-metal contents (i.e., Co, Ni, and Zn) of the materials were measured using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) apparatus (Varian 710).

Powder X-ray diffraction (XRD) patterns were obtained on an ESCALAB 250Xi focus diffractometer with Cu Kα radiation (40 kV, 100 mA, λ = 1.5406 Å), with 2θ ranging from 10° to 80° at a step size of 0.02°. The grain sizes of the samples were calculated by the Scherrer equation. Crystalline phase identification was made using the JCPDS database.

Specific surface areas were measured with a Micromeritics ASAP 2020 M surface area and pore size analyzer by N₂ adsorption at 77 K. Before the measurements, all samples were pretreated at 80 °C in vacuum for 720 min. The Brunauer—Emmett—Teller (BET) method was adopted for surface area calculations.

Diffuse reflectance infrared Fourier transform spectra were collected on a Nicolet Nexus 6700 spectrometer equipped with a mercury—cadmium—telluride detector and a Harrick diffuse reflectance cell with CaF₂ windows. Ground fine powders were
used for the measurements, with a scanning range of 400–4000 cm\(^{-1}\).

Raman spectra was collected using a Renishaw invia Raman microscope equipped with a CCD detector. The excitation wavelength of laser beam was 514 nm with a power of 1 mW at a resolution of 4 cm\(^{-1}\). Each spectrum was a sum of two scans recorded from 300 to 3000 cm\(^{-1}\).

X-ray photoelectron spectra were collected on a PHI-Quantera SXM spectrometer with Al K\(_\alpha\) (1486.6 eV) radiation. The excitation source was under ultrahigh vacuum (6.7 \(\times\) 10\(^{-8}\) Pa). Binding energies (BE) were calibrated with the adventitious carbon C 1s BE of 284.4 eV. The powder samples were pressed into self-supporting disks and evacuated for 4 h before tests. The X-ray photoelectron spectroscopy (XPS) spectra were deconvoluted and fitted by a Gaussian function with the XPSPEAK 4.1 software.

Field-emission scanning electron microscopy (SEM) images were obtained by a scanning electron microscope (FEI Quanta 200 SEM, FEI Company, Hillsboro, OR) with energy-dispersive X-ray (EDS) analysis function operated at the beam energy of 3 kV. All samples were coated with a thin layer of evaporated gold. Transmission electron microscopy (TEM) images were acquired on a Tecnai G2 F30 S-Twin electron microscope operated at 200 kV. The samples were first dispersed in ethanol and then deposited on copper grids covered with carbon film.

3. RESULTS AND DISCUSSION

3.1. Composition and Pyrolysis Temperature Effects.

Note first that the as-prepared MOF materials do not possess any ambient temperature NO adsorption capacity. However, it is no longer the case after pyrolysis. NO trapping efficiency was first tested on Co-600, Ni-600, and Zn-600 samples, and the results are shown in Figure 1a. These results reveal that Co-600 is significantly more efficient in trapping NO than the other two samples; the former achieves 100% NO trapping efficiency for \(\sim\)6 h. Ni-600 shows some initial NO adsorption capacity but deactivates too rapidly. Zn-600 essentially has no NOx trapping capacity. Such dramatic differences in NOx trapping performance may be a result of differences in metal loadings, surface areas, pore structures, or the nature of the metal-containing species. To obtain information to pinpoint the key causes, metal loadings and surface areas of these materials are presented immediately below. Besides the three samples used for the initial NOx adsorption tests, Co-500 and Co-550 are also included. Table 1 presents the Co, Ni, and Zn contents for all of the samples studied here. In comparing the three M-600 samples, it is readily seen that their metal contents are similar (Ni content is somewhat higher). This immediately demonstrates that the NOx storage capacity difference shown in Figure 1a is irrelevant to metal loading. By comparing the Co-T samples, it is also readily seen that with increasing pyrolysis temperature, the Co content increases. This is because higher temperature causes more complete decomposition of the MOF structure, thus releasing more gaseous products. As indicated from specific surface areas of these materials tabulated in Table 2, such a dramatic difference in NO storage is also irrelevant to their surface areas. These observations lead us to believe that phases containing the transition metals are responsible for NO adsorption; clearly, phases containing Co possess much better NO storage capacity than those containing Ni or Zn. Therefore, Ni- and Zn-containing materials are no longer explored in the rest of the study. More information regarding these samples is nevertheless presented in the Supporting Information (Figures S1 and S3). Next, the ZIF-67 pyrolysis temperature effect was explored. As depicted in Figure 1b, Co-500 shows a remarkable 100% NO trapping duration of \(\sim\)15 h, whereas Co-550 and Co-600 display such durations of \(\sim\)11 and \(\sim\)6 h, respectively. Again, this efficiency difference is irrelevant to material surface areas. As shown in Table 2, Co-550/600 even has a specific surface area higher than that of Co-500, presumably because of extra porosity generated at higher pyrolysis temperatures. However, their NO storage capacities are apparently inferior to the latter.

**Figure 1.** NO removal efficiency for (a) Co-600, Ni-600, and Zn-600, (b) Co-500, Co-550, and Co-600. The reactant feed contains 10 ppm of NO, 21% of O\(_2\), balanced with Ar at a WHSV of 120 000 mL g\(^{-1}\) h\(^{-1}\) and a reaction temperature of 25 °C.

**Table 1.** ICP-AES Results of All the Samples

| sample | Co-500 | Co-550 | Co-600 | Ni-600 | Zn-600 |
|--------|--------|--------|--------|--------|--------|
| metal content (%) | 23 | 25 | 33 | 45 | 31 |

**Table 2.** BET Specific Surface Areas of Co-T (T = 500, 550, and 600), Ni-600, and Zn-600 Samples

| sample | surface area (m\(^2\)/g) | sample | surface area (m\(^2\)/g) |
|--------|--------------------------|--------|--------------------------|
| Co-500 | 242 | Ni-600 | 339 |
| Co-550 | 278 | Zn-600 | 124 |
| Co-600 | 284 | | |
3.2. Morphological and Physicochemical Properties.

X-ray diffractograms of Co-500/550/600 are shown in Figure 2. The three samples exhibit similar diffraction patterns with essentially identical reflection angles suggesting their structural similarity. A metallic cobalt phase with diffraction peaks appearing at 2θ = 44.3, 51.6 and 76.0° is found as the predominant crystalline phase. Therefore, it can be concluded that this metallic Co phase is responsible for NO trapping. By exploiting the Scherrer equation, Co particles are estimated to be 11.5, 13.9, and 21.5 nm, respectively, for the Co-500/550/600 samples. The increase of particle size with increasing pyrolysis temperature is likely due to increased particle sintering at higher temperatures. The fact that NO trapping efficiency decreases with increasing Co particle size further corroborates the statement that Co is the active phase for NO adsorption. Another crystalline phase appears at 2θ = 25.9° for all three samples, which is attributed to graphitic carbon. The intensities of these features are extremely weak, suggesting that large quantities of carbon in these samples are amorphous. To verify this point, Raman spectroscopy was used to probe these samples, and the results are shown in Figure 3. All of the three samples exhibit two strong bands: one at 1590 cm\(^{-1}\) attributed to graphitic carbon and one at 1350 cm\(^{-1}\) assigned to amorphous carbon.

![Figure 2. Powder XRD patterns for Co-500, Co-550, and Co-600.](image)

Intensities of the two bands are comparable for all samples, suggesting, indeed, a highly disordered nature of the carbon matrix. Note also that no Raman scattering is found below 1000 cm\(^{-1}\); this may suggest the absence of cobalt oxides in these samples. For example, CoO\(_4\) possesses five Raman-active modes at 194, 482, 522, 618, and 691 cm\(^{-1}\). However, because these materials have been stored in the open air after pyrolysis, the presence of chemisorbed oxygen or even a surface oxide layer on cobalt is rather anticipated. Therefore, the absence of Co–O scattering may be better rationalized such that the total amount of surface oxygen is below the detection limit of our Raman spectrometer.

SEM was used to study morphologies of the as-synthesized ZIF-67 material and Co-500/550/600 samples. ZIF-67 contains primarily dodecahedral and to a lesser extent cubic primary particles \(\sim 1 \mu m\) in size, as displayed in Figure S2. SEM images of the Co-500/550/600 samples are exhibited in Figure 4 at two magnification levels. As shown in Figure 4A–C, the primary particles largely maintain their morphologies after pyrolysis; however, for Co-600, some level of primary particle aggregation is clearly observed. By comparing images shown in Figure 4D–F collected at higher magnifications, it is readily seen that particle surfaces become more distorted and corrugated following treatment at higher pyrolysis temperatures. EDS analysis was also carried out for Co-500. The following atomic composition was obtained: C (77.5%), N (10.8%), Co (7.8%), and O (3.9%).

To further probe morphological differences of Co-500/550/600, and more importantly, to reveal evolution of the Co particles as a function of pyrolysis temperature, TEM was exploited at a few magnification levels, as Figure 5 shows. Consistent with the SEM results, comparison among Figure 5A–C reveals that the dodecahedral particle shapes are well preserved for Co-500/550, but the particle corners decay considerably for Co-600. For the Co particles (the dark spots in these images), it is readily observed that average particle sizes increase with increasing pyrolysis temperature, consistent with estimations using the Scherrer equation. At higher magnifications, Figure 5D reveals that Co particles are largely uniform in Co-500, measuring \(\sim 10 \mu m\). Again, this is in agreement with estimations via the Scherrer equation. As shown in Figure 5E, Co particle sintering becomes evident at the pyrolysis temperature of 550 °C. At the highest pyrolysis temperature of 600 °C, some carbon nanotubes even develop, likely at the expense of corner decay of the support particles as found in Figure 5C. To study Co particle surface orientations, high-resolution TEM imaging was conducted on selected Co particles. Figure 6 presents the Co particle size distribution obtained from the TEM images (Figure 5), and the average sizes are listed in Table 3, which are 8.9, 10.4, and 17.1 for Co-500, 550, and 600, respectively. This is consistent with the particle sizes calculated from XRD peaks (11.5, 13.9, and 21.5 nm, respectively). For both particles embedded in the carbon matrix (Figure 7A) and the ones located at the external surfaces (Figure 7B), the primary exposed facet is (111) as determined using fast Fourier transform calculations. This result does not suggest that a surface oxide layer is absent on the Co particles. It does suggest, however, that if a surface oxide layer exists, it grows commensurately along the (111) orientation of the Co particles.

On the basis of the characterizations shown above, our Co-T materials can be qualitatively described as Co nanoparticles embedded in a carbon matrix (a small portion of the Co
particles are not embedded and stay on the surface). Elemental analysis from EDS, however, demonstrates that besides Co and C, N and O are also present in these materials. To obtain more details on the nature of the carbon support and the Co active phase, XPS was carried out next. For the sake of brevity, only results for the Co-500 material are presented. Figure 8 depicts C 1s, N 1s, O 1s, and Co 2p XPS spectra for Co-500. As shown in Figure 8a, the C 1s spectrum contains three features with BE of 284.6, 285.7, and 286.6 eV, which are readily assigned to carbon in C–C/C≡C, C–N/C≡N and C–O, respectively.42 Figure 8b displays the N 1s spectrum, where bands at 398.7, 399.4, 400.5, and 401.5 eV are attributed to pyridinic N, Co–N, pyrrolic N, and graphitic N, respectively.43 Note that the N/C atomic ratio in ZIF-67 is 1/2 based on the 2-methylimidazole (C₄H₆N₂) ligand composition. This ratio drops to ~1/8 after pyrolysis at 500 °C (from EDS analysis), suggesting that a majority of imidazole rings are damaged during pyrolysis to release N. The detection of graphitic N and N bonded to Co demonstrates that some of the released N becomes dopant of the Co and graphite phases. However, the presence of pyridinic and pyrrolic N indicates that some fragments of the imidazole rings are maintained during pyrolysis. As exhibited in Figure 8c, the main O 1s band appears at 531.6 eV, which can be assigned to oxygen in C–O.44 The weaker features at ~530 and ~533 eV can be attributed to oxygen in Co–O and C≡O, respectively.45 Oxygen in these bonds likely originates from air. After pyrolysis, Co-500 has been stored in open air during which both the carbon and Co phases have access to oxygen. Finally, the Co 2p XPS spectrum is presented in Figure 8d. Via peak deconvolution, four different Co features are derived. In the 2p₃/2 region, features with BE of 786.3, 781.8, 780.2, and 778.5 eV are attributed to the satellite peak of Co 2p, Co²⁺, Co³⁺, and metallic cobalt, respectively.46,47 It is important to note that the weakness of the Co⁰ feature can indeed only be rationalized by invoking the presence of a surface oxide layer, apparently growing commensurately along the (111) direction as indicated from TEM imaging (Figure 7). Such a surface oxide layer is too thin to have any XRD (Figure 2) and Raman (Figure 3) sensitivity. The co-existence of Co⁰ and

Figure 4. SEM images for Co-500 (A and D), Co-550 (B and E), and Co-600 (C and F).

Figure 5. TEM images for Co-500 (A and D), Co-550 (B and E), and Co-600 (C and F).
Co\(^{3+}\) may indicate that this oxide layer is Co\(_3\)O\(_4\)-like; however, the situation is further complicated by the fact that some Co also coordinates with N as evidenced from the 399.4 eV N 1s XPS feature from Co\(^{-}\)N. Based on XRD, electron microscopy images and XPS analyses shown above, it is not possible to provide further details regarding the Co particle surface structures. Next, NO adsorption and desorption chemistries are described.

### Table 3. Average Particle Size Obtained from TEM Images

| sample  | Co-500 | Co-550 | Co-600 |
|---------|--------|--------|--------|
| average particle size (nm) | 8.9 | 10.4 | 17.1 |

Figure 6. Particle size distribution of Co-500 (a), Co-550 (b), and Co-600 (c).

Co\(^{3+}\) adsorption, the evolution of N 1s band at 406.7 eV and O 1s band at 532.7 eV clearly points to the formation of NO\(_3^-\).\(^{48,49}\) This notion is further corroborated by FTIR measurements, as displayed in Figure S4. After NO adsorption, a sharp IR band appears at 1384 cm\(^{-1}\), which is readily assigned to nitrate species.\(^{13}\) In contrast, C 1s and Co 2p XPS spectra before and after NO adsorption barely display any difference; therefore, the corresponding spectra after NO saturation are only displayed in Figure S5. Quantification of Co species via peak deconvolution, however, does suggest that a small portion of Co\(^{2+}\) (\(~3\sim4\%\) of total XPS detectable Co) is oxidized to Co\(^{3+}\) during NO adsorption (Table 4). Because such quantifications are achieved via peak fitting, a process that may introduce rather large errors, the reliability of this finding awaits proof from further characterizations.

Figure 10 presents NOx TPD following Co-500 saturation with NO at ambient temperature. Although NO\(_2\) evolution is frequently observed upon surface nitrate decomposition, interestingly, NO is the only NOx species that desorbs here. NO desorption occurs in two states: a weak, shoulder peak at \(~130\) °C and a major desorption state at \(~190\) °C. Because no molecular NO adsorption was observed via FTIR (Figure S4), both desorption states are attributed to NO release from surface nitrate decomposition. Following the TPD process, the regenerated Co-500 sample was subjected to XRD, XPS, FTIR, Raman spectroscopic analyses, and TEM imaging to reveal changes of the morphological and physicochemical properties. XRD, FTIR, and TEM reveal little difference between fresh and used samples. The results are displayed in the Supporting Information, that is, Figures S4, S6, and S7. In contrast, XPS and Raman spectroscopic analyses reveal important changes worth detailed discussions as follows.

**Figure 7.** High-resolution TEM images for Co-500 (A and B).

**Figure 6.** Particle size distribution of Co-500 (a), Co-550 (b), and Co-600 (c).

3.3. **Chemistries Involved in NO Storage and Release.**

Note at the onset of this section that during our ambient temperature NO trapping measurements, NO\(_2\) release has never been observed. Therefore, the 2NO + O\(_2\) = 2NO\(_2\) reaction can be safely excluded. The NO adsorption chemistry was first examined with XPS. Figure 9a,b presents the N 1s and O 1s spectra of Co-500 following NO saturation at 25 °C. In comparison to the corresponding spectra prior to NO
As shown in Figure 11, a new Raman band appears at 681 cm\(^{-1}\) after one cycle of NO adsorption−desorption, which can be attributed to Co\(_3\)O\(_4\).\(^{50}\) This notion is further corroborated by XPS analysis. After one cycle of NO adsorption−desorption, both the intensity increase of the O 1s band at \(\sim\)530 eV (Figure 12a, attributed to Co−O) and the intensity decrease of the Co\(^0\) band at 778.5 eV (Figure 12b) suggest Co\(_3\)O\(_4\) formation. Therefore, the Co 2p peak fitting result shown in Table 4 appears to be reliable that during ambient temperature NO adsorption, some Co\(^{2+}\) sites are indeed oxidized to Co\(^{3+}\), leading to stoichiometric Co\(_3\)O\(_4\) formation.

On the basis of the above characterizations, we propose the two following NO adsorption−desorption pathways,

\[
\text{O} + \text{NO} \rightarrow \text{NO}_2
\]

\[
\text{O} - \text{NO} \rightarrow \text{O}_2 + \text{NO}
\]

where * represents coordinatively unsaturated surface Co sites that are capable of NO and O\(_2\) adsorption. In this proposal, pathway (2) represents the primary, reversible NO storage−release mechanism and pathway (3) causes irreversible Co oxidation, which eventually leads to Co\(_3\)O\(_4\) generation.

3.4. Stability and Reuse. Figure 13 presents NO storage results for Co-500 in 5 repeated adsorption−desorption cycles. It is readily seen that NO storage capacity keeps declining during repeated use. For example, 100% NO trapping lasts for

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**Figure 9.** XPS spectra for Co-500 after ambient temperature NO adsorption: (a) N 1s and (b) O 1s.

**Table 4. Percent of Cobalt Valence State from the Curve-Fitted XPS of Co 2p**

| sample       | Co\(^0\) % | Co\(^{2+}\) % | Co\(^{3+}\) % |
|--------------|------------|---------------|---------------|
| Co-500       | 14.2       | 63.8          | 22.0          |
| Co-500-used  | 14.8       | 59.6          | 25.6          |

**Figure 10.** TPD of NO\(_3\) from NO saturated Co-500.

\[
\text{O} - * - \text{O} + \text{NO} \rightleftharpoons * - \text{NO}_3\end{equation}

(2)

\[
* + \text{NO} + \text{O}_2 \rightleftharpoons * - \text{NO}_3\rightarrow \text{O} - * - \text{O} + \text{NO}
\]

(3)
more than 15 h in the first use; however, the duration drops to 11 h in the fifth use. In comparison to NO trapping results shown in Figure 1b, the NO storage capacity for Co-500 after 5 uses is still comparable to that of the fresh Co-550. For the latter material, the lower NO storage capacity as compared to fresh Co-500 is likely due to Co particle sintering (Figure 5). It can be suggested, therefore, that the carbon matrix plays a role of stabilizing the Co particles, particularly the ones that are embedded, during the NO adsorption–desorption cycles. Even so, the deactivation rate found in Figure 13 is likely still too rapid for practical applications. The main cause for deactivation is not clear at this time. Co3O4 formation is a possible one based on XPS results (Figure 12). However, other changes, for example, Co particle sintering and Co surface structural changes can also lead to NO storage performance loss. Even though the Co-500 material at the current stage appears to be not stable enough for practical ambient NO trapping applications, it does own a few desirable features, for example, low cost, low toxicity, and easiness of synthesis to warrant further investigations. We are currently working toward pinpointing the deactivation causes and solutions to their prevention. Furthermore, it is anticipated that both the Co particle size and the matrix composition will play certain roles in stabilizing this type of materials. Work is also planned on using other Co-containing MOFs to generate new NOx trapping materials and to compare with the materials used in the present study.

4. CONCLUSIONS

Pyrolysis of M-MOF (ZIF-67) materials (M = Co, Ni, and Zn) in a nitrogen atmosphere is applied to generate materials for low-concentration NO removal from air at ambient temperature. The nature of the transition metals used to prepare these materials is critical for NO trapping, where materials containing Co are much more efficient than those containing Ni and Zn. Pyrolysis temperature is found to influence NO trapping capacity. The Co-MOF sample pyrolyzed at 500 °C exhibits the best NO trapping efficiency, maintaining 100% low-concentration (10 ppm) NO adsorption efficiency for more than 15 h under a high flow rate of 12 000 mL g⁻¹ h⁻¹. Via XRD, FTIR, Raman, and XPS spectroscopic studies and
SEM and TEM imaging, the active phase for NO adsorption is suggested to be Co nanoparticles with a thin oxide layer embedded in the carbon matrix. NO is found to adsorb in the form of surface nitrates, which decompose to release NO upon thermal treatment. The NO trapping efficiency decreases with repeated NO adsorption–desorption cycles. Co$_3$O$_4$ formation during such cycles is a possible reason for deactivation.

**REFERENCES**

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**Notes**

The authors declare no competing financial interest.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Djerad, S.; Crocoll, M.; Kureti, S.; Tifouti, L.; Weisweiler, W. Effect of Oxygen Concentration on the Nox Reduction by Graphitized Porous Nanofibers. Catal. Today 2013, 201, 109–114.
(2) Yang, M.; Shen, M.; Wang, J.; Jia, J.; Zhao, M.; Wang, J.; Wang, W. Pd-Supported Interaction-Defined Selective Redox Activities in Pt-Doped Al2O3 Model Three-Way Catalysts. J. Phys. Chem. C 2014, 118, 2777–2789.
(3) Li, F.; Forzatti, P.; Nova, I.; Tronconi, E. Nox Storage Activities in Pd-Supported Interaction-Defined Selective Redox Catalysts. Appl. Catal., B 2014, 204, 175–191.
(4) Liu, Z.; Epling, W. S.; Anderson, J. A. Influence of Pt Loading in Aged Nox Storage and Reduction Catalysts. J. Phys. Chem. C 2014, 118, 952–960.
(5) Wang, A.; Arora, P.; Bernin, D.; Kumar, A.; Kamasamudram, K.; Olsson, L. Investigation of the Robust Hydrothermal Stability of Cu/Al2O3 Model Three-Way Catalysts. J. Catal. 2013, 281, 263–282.
(6) Song, J.; et al. Toward Rational Design of Cu/SzS-13 Selective Catalytic Reduction Catalysts: Implications from Atomic-Level Understanding of Hydrothermal Stability. ACS Catal. 2017, 7, 8214–8227.
(7) Wang, A.; Wang, Y.; Walter, E. D.; Washton, N. M.; Guo, Y.; Lu, G.; Peden, C. H.; Gao, F. Ni3Scr on Cu, Fe and Cu+ Fe Exchanged Beta and SzS-13 Catalysts: Hydrothermal Aging and Propylene Poisoning Effects. Catal. Today 2017, 320, 91.
(8) Wang, A.; et al. Unraveling the Mysterious Failure of Cu/Sapo-34 Selective Catalytic Reduction Catalysts. Nat. Commun. 2019, 10, 1137.
(9) Chen, H.-Y.; Mulla, S.; Weigert, E.; Camm, K.; Ballinger, T.; Cox, J.; Blakeman, P. Cold Start Concept (Csc) a Novel Catalyst for Cold Start Emission Control. SAE Int. J. Fuels Lubr. 2013, 6, 372–381.
(10) Shi, Z.; Huang, W.; Hua, Z.; Zhang, L.; Cui, X.; Chen, Y.; Chen, H.; Wei, C.; Wang, Y.; Fan, X.; Yao, H.; He, D.; Shi, J. -Free Synthesis of Mesoporous X–Mn (X = Co, Ni, Zn) Bimetal Oxides and Catalytic Application in the Room Temperature Removal of Low-Concentration No. J. Mater. Chem. A 2013, 1, 10218–10227.
(11) Shi, Z.; Chen, Y.; Huang, W.; Cui, X.; Zhang, L.; Chen, H.; Zhang, G.; Fan, X.; Wang, Y.; Tao, G.; He, D.; Shi, J. Temperature Catalytic Removal of Low-Concentration No over Mesoporous Fe–Mn Binary Oxide Synthesized Using a Template-Free Approach. Appl. Catal., B 2013, 140–141, 42–50.
(12) Liu, S.; Zhang, M.; Huang, Y.; Zhao, K.; Gao, Z.; Wu, M.; Dong, Y.; Wang, T.; Shi, J.; He, D. A Novel Chromic Oxide Catalyst for NO Oxidation at Ambient Temperature. RSC Adv. 2014, 4, 29180–29186.
(13) Wang, A.; Lin, B.; Zhang, H.; Engelhard, M. H.; Guo, Y.; Lu, G.; Peden, C. H.; F.; Gao, F. Ambient Temperature No Oxidation over Cr-Based Amorphous Mixed Oxide Catalysts: Effects from the Second Oxide Component. Catal. Sci. Technol. 2017, 7, 2362–2370.
(14) Wang, A.; Guo, Y.; Gao, F.; Peden, C. H. F. Ambient-Temperature No Oxidation over Amorphous Cro X-Zro 2 Mixed Oxide Catalysts: Significant Promoting Effect of Zro 2. Appl. Catal., B 2017, 202, 706–714.
(15) Wang, M-X.; Huang, Z.-H.; Shen, K.; Kang, F.; Liang, K. Catalytically Oxidation of No into N2O at Room Temperature by Graphitized Porous Nanofibers. Catal. Today 2013, 201, 109–114.
(16) Wang, M.-x.; Guo, Z.-y.; Huang, Z.-h.; Fang, H.-y.; Preparation of Carbon Nanofibers with Controllable Por Structures for Low-Concentration No Removal at Room Temperature. N. Carbon Mater. 2016, 31, 277–286.
(17) Wang, M.; Liu, H.; Huang, Z.-H.; Kang, F. Activated Carbon Fibers Loaded with MnO2 for Removing No at Room Temperature. Chem. Eng. J. 2014, 256, 101–106.
(18) Khivantesv, K.; Jaegers, N. R.; Kovarik, L.; Hanson, J. C.; Tao, F.; Tang, Y.; Zhang, X.; Koleva, I. Z.; Aleksandrov, H. A.; Vayssilov, G. N. Achieving Atomic Dispersion of Highly Loaded Transition Metals in Small-Pore Zeolite SzS-13: A New Class of High-Capacity and High-Efficiency Low Temperature Co and Nox Adsorbers. Angew. Chem. 2018, 130, 17152.
(19) Zheng, Y.; Kovarik, L.; Engelhard, M. H.; Wang, Y.; Wang, Y.; Gao, F.; Szanyi, J. Low-Temperature Pd/Zeolite Passive Nox Adsorbers: Structure, Performance, and Adsorption Chemistry. J. Phys. Chem. C 2017, 121, 15793–15803.
(20) Chen, H.-Y.; Collier, J. E.; Liu, D.; Mantarosie, L.; Durán-Martin, D.; Novák, V.; Rajaram, R.; Thompsett, D. Low Temperature No Storage of Zeolite Supported Pd for Low Temperature Diesel Engine Emission Control. Catal. Lett. 2016, 146, 1706–1711.
(21) Basdogan, Y.; Keskin, S. Simulation and Modelling of Mofs for Hydrogen Storage. CrystEngComm 2015, 17, 261–275.
(22) Kim, H.; Park, J.; Jung, Y. The Binding Nature of Light Hydrocarbons on Fe/Mof-74 for Gas Separation. Phys. Chem. Chem. Phys. 2013, 15, 19644–19650.
(23) Schlichte, K.; Kratzke, T.; Kaskel, S. Improved Synthesis, Thermal Stability and Catalytic Properties of the Metal-Organic Frameworks.
