Role of Defects and Metal Coordination on Adsorption of Acid Gases in MOFs and Metal Oxides: An In Situ IR Spectroscopic Study

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ABSTRACT

Metal-organic frameworks (MOFs) often display promising performance in ideal, one- or two-component systems; however, industrial adsorption and catalytic applications are almost always in the presence of acid gases that degrade the adsorbent or catalyst. Therefore, it is necessary to understand the interaction of acid gases with MOFs to drive future material design. Acid gas adsorption has been widely investigated on metal oxides, while few fundamental studies exist for MOFs. Therefore, MOF-derived oxides were prepared to give insight into adsorbed species on MOFs by connecting to the understanding that exists for adsorbed species on metal oxides. These MOF-derived oxides retain the overall morphology of the parent MOF, allowing direct comparison of the effect of morphology and the metal coordination environment on adsorbed species and acid gas stability of MOF, MOF-derived oxide, and traditionally synthesized metal oxide. A cerium-based MOF with open-metal sites, CeBTC, and the Ti-based MIL-125 were chosen to prepare MOF-derived oxides. IR studies show that adsorbed species during SO₂ and CO₂ adsorption on the MOF materials could be directly correlated to species observed on the MOF-derived and traditional oxides. In addition, the adsorbed species on the MOF-derived oxides differed from traditional oxides due to their different morphology and retained porosity. SEM and TEM images taken before and after CO₂/SO₂ adsorption experiments revealed degradation of all materials giving visual insight into the degradation mechanism after acid gas exposure. This study advances the understanding of acid gas adsorption on MOFs by correlation of adsorbed species with MOF-derived and traditional metal oxides.

KEYWORDS

Metal-organic framework; ceria; titania; acid gas; MOF derived-oxide

1. INTRODUCTION

Developing gas adsorption systems and catalytic applications for a wide range of industries has garnered much research attention in the field of porous materials.[1-9] Often, materials that are designed with promising capabilities for applications such as CO₂ capture are unable to retain their performance in the presence of harsh acid gases that exist in many industrial applications.[10] To advance the development of industrially viable porous materials, a better understanding of the effects of these acid gases is required. Metal-organic frameworks (MOFs) have emerged as a promising class of materials for acid gas separations and catalysis.[5, 8, 11, 12] MOFs are characterized by metal clusters and organic linkers, large surface areas, and tunable chemical properties that make them excellent candidates for these applications. Recent work has also identified MOFs as excellent templates for producing MOF-derived unique, porous, structured metal oxides[13-18] that may offer improved acid gas separation and catalytic properties in comparison to their MOF or traditionally synthesized oxide (oxide) counterparts. Furthermore, these MOF-derived oxides can be used to study adsorbed species on MOFs by creating a bridge to the fundamental understanding of adsorbed species on metal oxides, which have been widely studied using IR[19-25], Raman[26, 27], and TPD[28] techniques. CeO₂, for example, is widely used as a catalyst in the automotive industry,[29-32] and several studies have investigated the reduction in catalytic performance CeO₂-based catalysts can suffer upon exposure to even low concentrations of SO₂ present in exhaust gases.[33-37] TiO₂ is also widely used in catalysis[38-40] and photocatalysis,[41] and the effect of exposure to various acid gases has been studied.[42-44] In conjunction with these studies, a MOF-derived CeO₂ or TiO₂ will allow the investigation of adsorbed species and effects of acid gas exposure with those observed for a parent cerium or titanium-based MOF. Therefore, these fundamental studies on metal oxides serve as an excellent basis for investigating the effect of acid gases on MOFs using MOF-derived oxides.

In this work, adsorption of acid gases, including CO₂ and SO₂, on several classes of materials was investigated using in situ IR spectroscopy coupled with mass spectrometric techniques. Adsorbed species were examined for each MOF-derived oxide and compared with an oxide as well as the parent MOF to gain insight into the similarities in these species across morphologies and coordination environments. Two sets of samples were

chosen for comparison, a cerium series: CeBTC, a cerium-based MOF, CeO₂-d derived from CeBTC, and CeO₂ wires, prepared and studied in previous studies,[45] and a titanium series: MIL-125, a titanium-based MOF that has shown promising acid gas removal properties,[46, 47] TiO₂-d derived from MIL-125, and a bulk mixed-phase TiO₂. In addition to IR spectroscopic studies, the effect of acid gas exposure was also explored through SEM and TEM imaging before and after acid gas exposure, as well as structure analysis via XRD before and after in situ measurements. Water adsorption experiments were coupled with SEM and TEM imaging to investigate material stability and the similarity of the degradation mechanism during water and acid gas exposure. It is expected that exposure to SO₂ would result in a decrease in the intensity/amount of adsorbed CO₂ species for all samples and also the nature of adsorbed species for the MOF-derived oxide samples due to retention of SO₂ species at potential adsorption sites and the degradation and loss of those sites. In addition, the visual degradation observed with SEM and TEM for MOF and MOF-derived oxide samples after exposure to SO₂ or H₂O gave insight into the degradation mechanism of these samples.

2. EXPERIMENTAL

Synthesis of CeBTC. The synthesis of CeBTC was performed using a similar procedure to that reported previously by Mu, et al.[48] Ce(NO₃)₃·6H₂O (9.6 mmol) and 1,3,5 benzene tricarboxylic acid (BTC) (8 mmol) were added to 30 mL of *n,n*-dimethylformamide (DMF) in a 60 mL scintillation vial. The vials were heated in an isothermal oven at 120 °C for 24 hours. The resultant beige product was rinsed with DMF three times followed by one methanol wash.

Synthesis of MIL-125. The synthesis of MIL-125 was performed by adding benzene dicarboxylic acid (BDC) (2.75 mmol) to a mixture of DMF (6.5 mL) and methanol (6.5 mL). Acetic acid (22.5 mmol, 1.4 mL) was added to the mixture before the addition of titanium isopropoxide (0.75 mmol, 0.22 mL) to prevent the titanium precursor from hydrolyzing when added to the solution. The solution was placed in a 60 mL scintillation vial and heated in an isothermal oven at 110 °C for 24 hours. The resultant white product was rinsed with DMF three times followed by methanol one time.

Synthesis of MOF-derived oxides. Porous anatase TiO₂ and porous CeO₂ were prepared using the method described in a previous study for preparation of porous TiO₂ from MIL-125.[15] MIL-125 or CeBTC was placed in a ceramic crucible and calcined at 350 °C for 6 hours in air. The resulting oxide was recovered and stored in a desiccator until the materials were characterized.

TiO₂ Bulk. Bulk mixed-phase TiO₂ was obtained from City Chemical (T7346-500GM) and used as received with no further purification or treatment.

CeO₂ wires. The preparation of CeO₂ wires has been described in detail elsewhere.[45] The morphology of CeO₂ was controlled by varying the pH, temperature and duration of the reaction. Ce(NO₃)₃·6H₂O and NaOH were used as precursors for CeO₂ wires. The light yellow precipitate was centrifuged after the hydrothermal synthesis, and washed with deionized water and ethanol three times. The Na impurities were removed by base-acid wash, which was discussed in detail in previous work. The base-acid washed products were dried in vacuum overnight and then calcined at 400 °C in air for 4 hours.

Powder X-ray diffraction. Powder X-ray diffraction patterns were recorded on an X'Pert X-ray PANalytical diffractometer with an X'accelerator module using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature, with a step size of 0.02° in two theta (2 θ).

N₂ physisorption. Nitrogen physisorption isotherms were measured at 77 K for samples activated at 473 K for 12 h under vacuum using the Quadrasorb system from Quantachrome instruments. Nitrogen adsorption analysis was performed on all resulting products, and surface areas for the MOFs were determined by applying BET theory over a range of data points applicable to microporous materials.[49] N₂ isotherms showed typical Type I behavior as per the IUPAC classification.

In situ IR and Raman spectroscopy. The MOF-derived and oxide materials were pretreated at 300 °C at the rate of 10 °C/min and held for 1 hr in He flow at 50 cm³/min. The MOF materials were activated ex situ under vacuum at 150 °C for MIL-125 and 250 °C for CeBTC. MIL-125 was pretreated at 150 °C to avoid degradation

of the sample, and CeBTC was pretreated at 300 °C at the rate of 10 °C/min and held for 1 hr in He flow at 50 cm³/min. The in situ spectroscopic studies consist of three cycles in succession on the same sample, two CO₂ cycles, one before and one after an SO₂ cycle. Each cycle consisted of the following steps (i) adsorption, (ii) He purge, and (iii) temperature programmed desorption (TPD). During the first step of the first and third cycles, CO₂ adsorption, the material was exposed to 2% CO₂/He flow at 50 cm³/min for 15 min at 25 °C. During the first step of the second cycle, SO₂ adsorption, the material was exposed to 15 ppm SO₂/He flow at 50 cm³/min for 15 min at 25 °C. During the second step of each cycle, the He Purge, the residual gas was purged by He flow at 50 cm³/min for 10 min at 25 °C. For the final step of each cycle temperature programmed desorption was performed, during which the material was heated to 300 °C at the rate of 10 °C/min; the temperature of the material was held at 300 °C for 30 min, followed by cooling the material to 25 °C at the rate of 10 °C/min. For MIL-125 the temperature chosen for TPD matched that of its activation, 150 °C, instead of 300 °C used for all other samples to prevent degradation of the material during heating.

IR spectra were collected continuously through the entire measurement cycle using a Thermo Nicolet Nexus 670 spectrometer in Diffuse Reflectance mode (DRIFTs), the outlet gases from the DRIFTs cell (Pike Technologies HC-900) were analyzed using a quadrupole mass spectrometer (Omnistar GSD-301 O₂, Pfeiffer Vacuum). Absorbance spectra during SO₂ adsorption were calculated as $Abs = -\log(I/I_o)$, where I is the single beam spectrum during adsorption and I_o is the single beam spectrum before adsorption.

The Raman measurements were performed with a catalytic Raman reactor (Linkam CCR1000) using in-house built multiple-wavelengths Raman system[50] that includes laser excitations at $\lambda=325$ and 532 nm. Raman scattering was collected using fiber optics connected directly to the spectrograph stage of the triple Raman spectrometer (Princeton Instruments Acton Trivista 555). Samples pretreatment and SO₂ adsorption were carried out similarly as in the IR studies.

Scanning Electron Microscopy. Samples were imaged on a Zeiss Ultra60 FE-SEM instrument with a high-efficiency in-lens SE detector at a working distance of 7-8 mm and accelerating voltage of 5 kV. The samples

were sonicated for 10 s in methanol and then dispersed on a flat Al sample holder with two-sided adhesive conductive carbon tape. Prior to SEM observations, samples were coated with carbon for 30 s at 4.4 V using a Cressington 108A Carbon Coater to exclude the charging effect. Several images were captured for each sample with varying levels of magnifications.

Transmission Electron Microscopy. TEM images were obtained using a Hitachi HT7700 operated at 120keV. The samples were deposited on a lacy carbon copper grid by suspending less than 1 mg of material in methanol and dropcasting the suspension on the grid.

Water Vapor and CO₂ Adsorption. A 3Flex Surface Characterization Analyzer from Micromeritics was used to collect water vapor isotherms at 22 °C for all samples. Isotherms were collected after in situ IR experiments with fresh, unexposed sample. Prior to water adsorption measurements, CeBTC was activated in a Smart VacPrep degasser at 300 °C for 12 hours under dynamic vacuum, MIL-125 was activated at 175 °C for 12 hours under dynamic vacuum, and all metal oxides were activated at 150 °C for 12 hours under dynamic vacuum. All water vapor isotherms were measured to $P/P_0 = 0.95$ to avoid water condensation.

CO₂ isotherms were collected on MIL-125, TiO₂-d, and CeBTC on fresh sample as well as samples after in situ IR experiments. Prior to adsorption measurements, CeBTC was activated in a Smart VacPrep degasser at 300 °C for 12 hours under dynamic vacuum, MIL-125 was activated at 150 °C for 12 hours under dynamic vacuum, and TiO₂-d was activated at 150 °C for 12 hours under dynamic vacuum. All isotherms were measured with $P_0 = 760$ mmHg.

3. RESULTS AND DISCUSSION

3.1 Characterization of pristine materials

Powder X-ray diffraction (PXRD) was used to verify the structures of the MOFs and the oxides. Fig. A1 shows that the as-synthesized patterns for CeBTC and MIL-125 match the simulated patterns generated from

literature.[51, 52] The MOF-derived CeO₂, and CeO₂ wires match the simulated ceria pattern (JCPDS Card No. 34-394), confirming the MOF-derived oxide possesses the same crystal structure as the CeO₂ wires, albeit a different morphology. Derived TiO₂ is synthesized in the anatase phase (JCPDS Card No. 21-1272), while the bulk TiO₂ is present as a mixture of rutile (JCPDS Card No. 88-1175) and anatase phases. In addition, elemental analysis was performed on the derived oxide materials to verify that all carbonaceous material had been removed. Less than 0.5 wt.% carbon remained for each sample, 0.44 for CeO₂-d and 0.39 for TiO₂-d, indicating complete removal of the organic linkers during preparation.

After confirming the crystalline structure of all materials, N₂ physisorption was performed on each sample to determine the surface area and also elucidate the retained porosity of the MOF-derived oxides, which is a key feature of MOF-templated oxides in literature.[14] The MOF BET surface areas, shown in Table 1, were similar to those found in literature; 1392 m²/g for MIL-125 and 752 m²/g for CeBTC.[51, 52] After preparation through calcination of MIL-125, TiO₂-d possesses mesopores with sizes ranging between 2-4 nm, while bulk TiO₂ displays a distribution of micro, meso and macropores as seen in the pore size distribution shown in Fig. A2. The mesopores present in the TiO₂-d are the result of various degrees of connectivity arising during calcination between the 1.25 nm pores present in MIL-125. CeO₂-d shows a larger abundance of micropores than CeO₂ wires, due to a degree of retained pore structure from the CeBTC parent material, though both show a distribution of macro, meso, and micropores. The TiO₂-d and CeO₂-d displayed markedly higher surface areas, 133 and 138 m²/g, than the traditionally prepared oxides, 49 and 107 m²/g, respectively. It is important to note that both of the MOF-derived oxides possess a large number of particle defects, such as cracks and voids, leading to an increase in surface area, which will be investigated further with SEM in a later section. These porous MOF-derived oxides will not only provide the basis for understanding acid gas adsorption on MOFs, but also insight into the effect of morphology and defects on material stability in MOFs and MOF-derived oxides.

3.2 Structure of SO_x species from SO₂ adsorption

Fig. 1 shows the IR spectra during SO₂ adsorption on CeBTC, CeO₂-d, and CeO₂ wires at room temperature as a function of time. SO₂ adsorption on ceria is well-studied and the IR spectra shown in Fig. 1(c) for the CeO₂ wires exhibits characteristic peaks at 1424, 1340, 1233, 1194, 1064, 1018, and 897 cm⁻¹ indicating the formation of surface sulfates[20, 21, 37, 53-58] while peaks at 1018 and 989 cm⁻¹ indicating the formation of surface sulfites [59, 60] during SO₂ adsorption. The broad IR band at 1064 cm⁻¹ appearing upon the start of SO₂ adsorption also indicates the presence of surface sulfate species.[58] In addition, the spectra also exhibit characteristic negative peaks at 1398, 1289, and 1218 cm⁻¹ indicating the perturbation of previously adsorbed surface carbonates [61-63] by adsorbed SO₂. It is interesting to note that there is no increase in MS intensity to indicated CO₂ evolving during SO₂ adsorption, suggesting that few carbonates are displaced completely from the surface and rather the majority remain bound to the surface. This hypothesis is supported by the release of CO₂ during SO₂ TPD shown in Fig. A3, where these strongly bound species are not evolved until temperatures above 150 °C, with a maximum intensity observed at 225 °C. These remnant carbonate species are likely explained by the high number of defects present in the material. To characterize the abundance of these defect sites, the ratio of the defects (600 cm⁻¹) to the bulk (465 cm⁻¹) in the Raman spectra shown in Fig. A4 was calculated in Table A1.[45] The ratio of defects to bulk for CeO₂ wires drops 6.7% after exposure to SO₂, suggesting the continued presence of SO_x species occupying defect sites.

The preparation method for CeO₂-d is hypothesized to produce a material that possesses a large number of defects in addition to the porosity retained from CeBTC. The defect ratio (see Table A1) calculated for freshly prepared CeO₂-d from Raman spectrum is quite similar to that calculated for the CeO₂ wires; however, after SO₂ exposure the ratio drops 33.9%, indicating a large loss of oxygen vacancies, likely due to a large number of SO_x species occupying these sites. Comparison of the IR spectra on CeO₂ wires with the spectra on CeO₂-d shown in Fig. 1(b) shows a similar multitude of peaks at 1424, 1340, 1233, 1194, 1110, 898, and 849 cm⁻¹ indicating the formation of surface sulfates, and the peak at 980 cm⁻¹ indicating the formation of surface sulfites during SO₂ adsorption.[20, 21, 37, 53-58, 64] The surface sulfate peaks at 1110 and 849 cm⁻¹ are not observed

for the CeO₂ wires, and the 1110 cm⁻¹ peak can be attributed to adsorption on an exposed (100) face as seen in our ongoing studies. In addition to these unique sulfate species, a difference is observed in the intensity of the negative peaks characteristic of the disturbed carbonates (1398, 1289, and 1218 cm⁻¹); these features are much more intense for CeO₂-d. The increase in intensity suggests the carbonate species are in higher abundance on CeO₂-d than on CeO₂ wires, which is supported by the higher intensity of CO₂ observed during SO₂ TPD for CeO₂-d shown in Fig. A3 and calculated in Table A2.

SO₂ adsorption on CeBTC has not previously been investigated; however, the species observed over the CeO₂-d allow the assignment of the species observed for the MOF. The IR spectra shown in Fig. 1(a) on CeBTC during SO₂ adsorption exhibited a characteristic peak at 1166 cm⁻¹ indicating the presence of physisorbed species, similar to that observed during SO₂ adsorption over MOFs.[65] Peaks observed at 1027 and 983 cm⁻¹ can be correlated with bands indicating the formation of similar surface sulfite species occurring at the location of oxygen vacancies seen on CeO₂ wires. CeBTC possesses trivalent cerium atoms and the uncoordinated metal sites closely resemble cerium at sites with an oxygen vacancy; therefore, it can be determined that the formation of the observed sulfite species on CeBTC is occurring at the coordinatively-unsaturated metal sites. The peaks exhibited at 891 and 853 cm⁻¹ mirror those seen on CeO₂-d characteristic of the formation of surface sulfates species. The formation of these sulfates likely occurs between the oxygens connecting the tricarboxylate ligands and cerium atoms, as seen in other MOFs.[65] In addition, it is hypothesized that the observed sulfate species may form polynuclear species with the sulfites adsorbed on the open metal sites. No peaks characteristic of perturbation of adsorbed carbonates are observed on CeBTC during SO₂ adsorption. In a study of co-adsorption of CO₂ and SO₂ on another open-metal site MOF, Tan et al. discovered that the replacement of adsorbed CO₂ by SO₂ is slow,[66] which supports the lack of peaks characteristic of disturbed carbonates during the short time the sample is exposed to low concentration SO₂. Monitoring of the CO₂ evolved during SO₂ TPD indicates a significant release of CO₂ as the temperature rises above 250 °C. A temperature of 300 °C has been identified as the necessary temperature to fully expose the open metal sites present in CeBTC;[48] therefore, these carbonate

species remained adsorbed throughout the previous TPD and their bonds with the open metal sites have been slightly weakened by adsorbed SO₂, allowing their displacement during SO₂ TPD.

As expected, comparison of the amount and maximum desorption temperature of SO₂ evolved during TPD (Fig. A5) for the three cerium containing samples reveals CeBTC adsorbs the largest amount of SO₂ due to its high surface area, with continual release of physisorbed SO₂ (indicated by the IR band at 1166 cm⁻¹) beginning at 30 °C. A peak in intensity is observed at 275 °C for CeBTC, correlated with the previously mentioned temperature required during activation to remove adsorbed species from open metal sites. A similar peak at 280 °C has been observed on CeO₂ rods in current work,[67] correlated with the release of sulfite species adsorbed at oxygen vacancies. Therefore, these similar peaks observed during TPD further support the hypothesis that the surface sulfite species observed at 1027 and 983 cm⁻¹ for CeBTC occur at open metal sites mirroring the oxygen vacancies present in CeO₂ wires. CeO₂-d and CeO₂ wires both exhibit a maximum in intensity at 65 °C, with CeO₂-d exhibiting a slightly higher amount of evolved SO₂, as calculated in Table A2. The lack of a second maximum similar to that observed for CeBTC leads to the hypothesis that species remaining after the primary CO₂ adsorption stage of the experiment occupy the most strongly adsorbing sites in the oxide materials, which is further supported by the release of CO₂ at temperatures greater than 150 °C for both oxide materials, shown in Fig. A3.

Fig. 2 shows the IR spectra during SO₂ adsorption on MIL-125, TiO₂-d, and TiO₂ bulk at room temperature as a function of time. All samples exhibit weak interactions with SO₂, in agreement with previous studies demonstrating TiO₂ has weak interactions with SO₂ in comparison to other metal oxides.[68] TiO₂-d and TiO₂ bulk exhibit an intense characteristic peak at 1628 cm⁻¹, which, combined with a significant increase in intensity of the negative peak between 3800-3600 cm⁻¹, indicates the reaction of SO₂ with surface hydroxyl groups to form adsorbed H₂O.[42] Both TiO₂ materials also exhibit characteristic peaks at 1380 and 1033 cm⁻¹ indicating the formation of surface sulfate and sulfite species, respectively, on the anatase phase of titania.[56] In addition to these similar peaks, TiO₂-d exhibits a peak at 1133 cm⁻¹ also characteristic of adsorbed surface sulfite species on anatase titania.[56] This feature is lost in the background of the spectra of TiO₂ bulk due to the mixture of

anatase and rutile phases. While the IR spectra for both TiO₂ samples resemble each other, an analysis of the SO₂ TPD (Fig. A5) reveals a difference in the strength of adsorbed species. TiO₂-d exhibits a slow release of SO₂ reaching a maximum at 100 °C, while TiO₂ bulk reaches a maximum at 100 °C and a second maximum at 290 °C, indicating strongly adsorbed SO₂ species. The lack of this second increase in intensity in TiO₂-d is explained by monitoring of CO₂ evolved during SO₂ TPD (Fig. A3). Only TiO₂-d releases CO₂ during SO₂ TPD, with a large amount of CO₂ released at 50 °C, with smaller peaks observed at 220 °C and 290 °C. Carbonate species present from the initial CO₂ adsorption stage likely occupy the strongest adsorbing defect sites in the material, while physisorbed CO₂ displaced by SO₂ adsorption is trapped in the high porosity of the material until TPD is performed.

As with CeBTC, SO₂ adsorption has not been studied on MIL-125; however, the knowledge of adsorbed species on TiO₂-d allows for the assignment of the weak features observed on the metal-organic framework. The formation of surface sulfites, indicated by the characteristic peak at 1023 cm⁻¹, likely occurs at the metal clusters where titanium-bridging oxygen atoms resemble the structure of anatase titania. The characteristic peak indicating an interaction of SO₂ with surface hydroxyls to form adsorbed surface water, at 1628 cm⁻¹, is also observed on MIL-125, a possible assignment given each titanium atom in the metal node possesses a hydroxyl group. However, the corresponding decrease in the region between 3800-3600 cm⁻¹ is not observed. Instead, a steady increase in this region is observed during SO₂ adsorption. This increase is explained by the presence of uncoordinated carboxylates as the material is degraded by reaction with SO₂ leading to the evolution of bands corresponding to the hydroxyl (3700-3600 cm⁻¹) and corresponding carbonyl groups (1715 cm⁻¹) of the uncoordinated carboxylic acid linker. Furthermore, it is hypothesized that the formation of water by interaction of SO₂ with the surface hydroxyls serves to further degrade the material and lead to a drastic loss of surface area, as shown in Table 1.

3.3 Effect of SO₂ exposure on adsorbed species during CO₂ adsorption

In situ IR spectroscopy during CO₂ adsorption was performed before and after in situ IR SO₂ adsorption to evaluate (i) the differences in adsorbed species between materials, and (ii) the effect of SO₂ exposure on adsorbed CO₂ species for each material. Fig. 3 shows the IR spectra during CO₂ adsorption before and after in situ SO₂ experiments on CeBTC, CeO₂-d, and CeO₂ wires at room temperature as a function of time. The IR spectra shown in Fig. 3(b) of CeO₂-d during CO₂ adsorption before SO₂ adsorption exhibited peaks characteristic of bicarbonate, bridged carbonate, bidentate carbonate, and monodentate carbonate species summarized in Table 2.[61-63, 69-72] Ceria wires exhibited similar peaks; however, several peaks differed between the two samples. Notably, CeO₂-d exhibits peaks characteristic of carbonate species at 1237, 1131, 997 cm⁻¹, [63, 72] while the CeO₂ wires exhibit a peak characteristic of bidentate and monodentate carbonates at 1588 cm⁻¹ not observed for CeO₂-d.[61] The difference in observed species is likely due to the retained porosity of CeO₂-d. This hypothesis is further supported by comparison of the IR spectra for both samples after SO₂ experiments. The monodentate carbonate peak that is unique to the CeO₂-d remains, but the unique bicarbonate species are no longer present on the CeO₂-d sample, indicating the loss of these unique adsorption sites either through occupation by adsorbed sulfates or through degradation; a hypothesis supported by the 33.9% reduction in defect sites after SO₂ exposure observed through Raman spectroscopy (Table A1). In addition, the IR spectra on CeO₂-d very closely resembles the spectra on ceria wires after SO₂ experiments, suggesting CeO₂-d has transformed into a material possessing facets and defects very similar to those found on the ceria wires. Further investigation of this hypothesis with SEM and BET is discussed in the following section. The IR spectra shown in Fig. 3(a) of CeBTC during CO₂ adsorption before SO₂ adsorption exhibited characteristic peaks at 1165, 1048, 980 cm⁻¹ similar to those observed on CeO₂-d indicating the formation of bicarbonate and carbonate species during CO₂ adsorption.[61] After exposure to SO₂, CeBTC exhibits a single carbonate peak at 1123 cm⁻¹. [72] The loss of the peaks observed before SO₂ exposure is correlated with the 100% loss of surface area, leaving only surface sites available for adsorption.

Fig. 4 shows the IR spectra during CO₂ adsorption on MIL-125, TiO₂-d, and TiO₂ bulk at room temperature as a function of time both before and after the in situ IR SO₂ experiment. The IR spectra on MIL-125 during CO₂ adsorption exhibits no characteristic adsorption peaks due to the lack of open metal sites. TiO₂-d and TiO₂ bulk exhibit characteristic peaks at 1672 and 1429 cm⁻¹ indicating the formation of mono- and bidentate bicarbonates, respectively, originating from the reaction of CO₂ with residual hydroxyl groups.[23] In addition, TiO₂-d exhibits peaks at 1221 and 1245 cm⁻¹ indicative of monodentate bicarbonates and a peak at 1606 cm⁻¹ that slowly shifts to 1635 cm⁻¹ with increasing surface coverage indicative of bidentate bicarbonates not observed for the TiO₂ bulk sample.[23] These species are likely more intense and able to be observed on TiO₂-d due somewhat to the sample being pure anatase, but more importantly the presence of defects inherited through synthesis from the parent MIL-125. The TiO₂ bulk sample also possesses a band at 1496 cm⁻¹ characteristic of bidentate bicarbonates adsorbed on a rutile phase titania,[73, 74] demonstrating the mixed-phase titania results in the formation of slightly different species than the pure phase TiO₂-d. There is no loss of species observed for TiO₂-d or TiO₂ bulk after exposure to SO₂; however, the intensity of the adsorbed species does decrease 31% and 14%, respectively, after exposure, indicating a loss of adsorption sites after SO₂ exposure. TiO₂-d possesses double the overall intensity of adsorption over TiO₂ bulk, and experiences approximately double the decrease in intensity due to the loss of retained mesoporosity; a loss directly tied to the degradation of the MOF-like particles observed with SEM and discussed in the following section.

3.4 Material stability after SO₂ adsorption

After in situ IR studies, the effect of acid gas exposure was first explored through PXRD analysis. As is known from literature, MOFs are often unstable upon exposure to certain gases and vapors,[10, 75] rapidly losing porosity and crystallinity. Comparison of the PXRD patterns taken before and after IR studies for MIL-125 and CeBTC (Fig. 5) reveals that both materials have not retained their crystallinity and no longer resemble the as-synthesized patterns. The instability of these materials is further confirmed by comparing BET surface areas calculated from N₂ physisorption before and after IR experiments. Both materials experience a drastic loss in

surface area attributed to a degradation and loss of the material structure and porosity, 86% for MIL-125 and 100% for CeBTC, as shown in Table 1.

Analysis of the oxide materials; however, did not mimic the loss of stability observed for the MOF materials. Comparison of the PXRD patterns for all oxides revealed no change between the as-synthesized patterns and those taken before IR experiments. Although there was no observed change in the PXRD patterns after acid gas exposure, analysis of the materials' BET surface area revealed changes did occur for the MOF-derived oxide samples. The surface area of CeO₂ wires and TiO₂ bulk did not change after exposure; however, CeO₂-d and TiO₂-d experience a loss in surface area of 10% and 65%, respectively. The large loss in surface area without a corresponding change in the diffraction pattern indicates a loss of the retained porosity in the MOF-derived oxide particle, as illustrated in Fig. A2, reducing the surface area without greatly affecting the crystal structure.

In order to explore if a visual change to the particles could further confirm this hypothesis, SEM and TEM images were taken of all samples before and after in situ IR experiments. Fig. 6 shows the SEM images of titanium containing samples before and after in situ IR experiments, while Fig. A6-8 contains TEM images for these samples before and after in situ IR experiments. Fig. 6(a) and Fig. A6(a,d) show the characteristic terminated octahedral crystal of MIL-125. TiO₂-d retains this overall particle structure in Fig. 6(b) and Fig. A7(a,d) as seen in literature.[14, 15] While the macroscopic particle morphology is retained, a loss of volume is observed upon preparation of the MOF-derived oxide, as expected. Fig. 6(c) and Fig. A8(a,d) show TiO₂ bulk is composed of small agglomerates. Fig. 6(d-f) are SEM images of the titanium containing samples after in situ IR experiments. It can be observed from comparison of Fig. 6(c,f) that the TiO₂ bulk sample does not undergo any change to the overall particle structure after acid gas exposure, further supporting the hypothesis that the TiO₂ bulk is not degraded by exposure to SO₂. Instead, the 22% reduction in CO₂ capacity (calculated in Table A2) is likely due to retention of strongly bound SO_x species even after desorption and TPD in He. A comparison of the images before and after exposure for MIL-125 yields the observation of the evolution of small agglomerates resembling the morphology of bulk TiO₂ particles. In addition, close inspection of the SEM and TEM images reveals several instances of the creation of cavity defects in the MIL-125 crystal. These cavity defects are

centered on the crystal edges where the surface is the most uncoordinated and allows for the strongest surface adsorption of acid gas molecules. The creation of these defects leads to an increase in uncoordinated sites where SO_2 can strongly adsorb, allowing the degradation to propagate throughout the crystal. Furthermore, the degradation can be observed at different stages of progression in the image. In the upper right hand corner of Fig. 6(d), a crystal can be seen with a cavity defect that has begun at the corner of the particle and propagated along the face, while to the left, a particle is seen that has undergone much more degradation and has formed many more small agglomerates. This degradation and loss of material structure results in a loss in CO_2 adsorption capacity as illustrated by the reduction in quantity adsorbed after IR experiments shown by the isotherms in Fig. A9. It is observed for TiO_2 -d that the retained particle structure has been lost upon exposure to acid gases as the sample is mainly comprised of the agglomerates seen in the bulk TiO_2 sample. However, observation of one of the few remaining particles gives a glimpse into the degradation of the macroscopic particle and it is seen to be identical to the mechanism observed for a MIL-125 crystal. A small cavity defect has formed at the corner of the octahedral particle as well as a small agglomerate as the structured particle dissolves upon exposure. Additional SEM images shown in Fig. A10(a-e) illustrate the almost complete degradation of the TiO_2 -d particles to form small agglomerates after exposure to SO_2 during in situ IR experiments. One important difference to note between the agglomerates observed in the MIL-125 sample after exposure and those in the TiO_2 samples is that those observed in the MOF sample cannot yet be identified, while those in the TiO_2 -d are crystalline TiO_2 . Although visually similar, this difference is supported by the lack of evolution of any reflections characteristic of TiO_2 in the PXRD pattern of MIL-125 after IR experiments. However, these reflections might be low in intensity and hidden by the still relatively intense reflections of degraded MIL-125.

SEM and TEM images of cerium containing samples before and after in situ IR experiments are shown in Fig. 7 and Fig. A11-13, respectively. Fig. 7(a) shows rod shaped crystals characteristic of CeBTC. The CeO_2 -d species is seen to retain this overall particle structure in Fig. 7(b), but as with TiO_2 -d the macroscopic particle structure is retained with a corresponding loss of volume. Fig. 7(c) shows the CeO_2 wires, displaying characteristic small

wire shaped particles. SEM images of the cerium containing samples after in situ IR experiments are shown in Fig. 7(d-f). As with the bulk TiO_2 , comparison of the CeO_2 wires in Fig. 7(c,f) and in the TEM images in Fig. A13 shows that the sample does not undergo any change to the overall particle structure after acid gas exposure, supporting the hypothesis that the synthesized oxides are not degraded by exposure to SO_2 . Instead, the 10.9% reduction in CO_2 adsorption capacity (Table A2) is likely due to retention of SO_x species even after desorption and TPD in He. CeBTC particles after SO_2 exposure in Fig. 7(d) resemble the overall morphology of the original material; however, the particles have agglomerated and have softened edges, suggesting a mechanism for degradation similar to MIL-125, where the most uncoordinated edge sites are attacked by SO_2 during adsorption. Fig. A11(b,e) display the degradation of the CeBTC particle edges, with small fissures forming after SO_2 exposure. CeO_2 -d particles, on the other hand, seem to retain a somewhat rod-like morphology even after acid gas exposure, and only a 2.3% reduction in CO_2 capacity is observed (Table A2) with little to no change in the CO_2 breakthrough time shown in Fig. A14. The retention of this morphology is probable given that rod shaped ceria has been synthesized previously.[61, 70] However, comparison of CeO_2 -d before and after experiment reveals the formation of cracks and fissures in the rod shaped particles and that some of the larger rod shaped particles have broken apart after exposure to form smaller rod shaped particles. This observation is explained by the high number of defects in the MOF-derived oxide allowing numerous sites for SO_2 adsorption and the propagation of already existing cracks to break apart the larger rods and form smaller particles. It is important to note that the degradation of the samples is unlikely solely due to the TPD step during each segment of the experiment. The oxide materials showed less than 2 wt.% loss during TGA as shown in Fig. A15. For the MOF materials, the chosen TPD temperature is well below the known upper stability limit, illustrated by a large wt.% loss in Fig. A15. However, the addition of heat and the presence of adsorbed SO_2 species likely hasten the degradation process. Additional studies are necessary to determine the kinetics of the degradation mechanism and how the addition of heat or additional acid gases will affect the speed of the degradation.

3.5 Effect of water adsorption on material stability

Material stability and degradation in the presence of water vapor has been a widely explored topic within MOF literature.[75] Therefore, in order to explore similarities between degradation observed during acid gas exposure presented in the previous section and that observed during water exposure, each sample was characterized as above after water adsorption isotherms were collected. Water adsorption isotherms for cerium and titanium containing samples are shown in Fig. A16. As expected, the oxide materials do possess the high water adsorption observed for the MOF materials. The discrepancy in adsorbed amount is due to the high porosity of the MOF materials and the ability of water to cluster in the pores. Both MOF materials possess a virtually linear increase in adsorption as the relative water pressure is increased; however, MIL-125 desorbs the majority of the water adsorbed during the experiment while CeBTC possesses a much larger hysteresis and retains 17 mmol/g of water after desorption. As CeBTC possesses open metal sites, water is strongly adsorbed and will not desorb during evacuation without heating.

SEM and TEM images of both cerium and titanium containing samples after water adsorption experiments are shown in Fig. A17 and Fig. A6-12 (c,f), respectively. Fig. A17(a) and Fig. A11(c,f) show that the rod shaped crystals of CeBTC become softened after water adsorption; however, the change in morphology is not as drastic as observed after SO₂ exposure. N₂ physisorption and PXRD analysis after water adsorption revealed a drastic loss of surface area, 93%, and a reduction in the intensity of reflections during diffraction experiments supporting the similar effects of water exposure and SO₂ exposure for CeBTC. The CeO₂-d sample shown in Fig. A17(b) possesses numerous cracks and fissures in particles as well as a corresponding loss of surface area attributed to a loss of porosity after water exposure (Table 1); however, as with the CeBTC sample, the degree to which degradation has occurred is seemingly less than with SO₂ as there is much less formation of smaller rod shaped particles. CeO₂ wires continue to maintain their morphology after water exposure, confirming the particles are stable after water exposure due to their preparation via hydrothermal treatment.

MIL-125 after water adsorption is shown in Fig. A17(d) and Fig. A6(c,f). The crystals do not display the cavities seen in the sample after SO₂ exposure, but instead a roughening and etching of the crystal surface is observed. This observation suggests that, similar to the CeBTC crystals, the degradation of the MIL-125 particles is proceeding at a much slower rate upon exposure to water over the day long isotherm run than that observed after 15 minutes of 15 ppm SO₂ exposure. This hypothesis is further supported by PXRD and BET analysis, where some crystallinity is retained (Fig. A18, A19) and a less drastic loss of surface area is observed (Table 1). The TiO₂-d species; however, does possess the cavities seen to evolve after exposure to SO₂ as well as the corresponding decrease in surface area, 133 to 51 m²/g, suggesting the degradation mechanism proceeds through the same pathway for both SO₂ and H₂O adsorption for the derived titania sample. Furthermore, the majority of TiO₂-d has transformed from the octahedral shaped particles to the small agglomerates observed for the bulk TiO₂. As was expected, the bulk TiO₂ did not undergo any change in morphology, surface area, or diffraction pattern after water adsorption experiments.

4. CONCLUSIONS

In conclusion, we have investigated the effect of acid gas adsorption on a set of cerium and titanium MOFs, MOF-derived oxides, and oxides with IR spectroscopy, SEM, and TEM imaging. MOF-derived oxides were studied to create a link between the morphology of the parent MOF and the composition of the oxide, and gain insight into adsorbed species and possible degradation mechanisms. Adsorbed species on both parent MOFs could be directly correlated with observed adsorbed species on the MOF-derived oxide material. The retained porosity and inherent defects of CeO₂-d changed the nature of species adsorbed, as well as enhanced the overall strength of adsorption of both SO₂ and CO₂. Although neither TiO₂-d nor the bulk TiO₂ strongly adsorbed SO_x species, an increase in overall adsorption of the acid gases studied was observed for TiO₂-d, explained by the retained porosity during formation of the MOF-derived oxide. Insight into the degradation mechanism was developed through SEM and TEM imaging of samples before and after acid gas exposure. For MIL-125 and TiO₂-d samples, exposure to SO₂ or H₂O resulted in the formation of cavity defects on the particle edge. It is hypothesized that the formation of these defects is due to the porous nature of the samples, the attack and

degradation of the material begins at an uncoordinated edge and quickly propagates through the particle as the acid gas is able to penetrate into the particle. For CeBTC and CeO₂-d samples, similar exposure resulted in a softening of particle edges, and for the MOF-derived oxide the breaking of particles into smaller particles along pre-existing cracks and fissures.

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Table 1. BET surface areas for samples as-synthesized, after in situ IR experiments (Post IR), and after water adsorption experiments (Post H₂O).

Material	SA _{BET} (m ² /g)	SA _{BET} (m ² /g)	SA _{BET} (m ² /g)
		Post IR	Post H ₂ O
CeBTC	752	0	52
CeO ₂ -d	138	124	117
CeO ₂ wires	107	104	108
MIL-125(Ti)	1392	190	398
TiO ₂ -d	133	47	51
TiO ₂ bulk	49	54	47

Table 2: Assignment of IR bands observed upon room temperature CO₂ and SO₂ adsorption on cerium and titanium containing samples.

Species	Band Assignment
sulfates	1424, 1380, 1340, 1233, 1194, 1133, 1110, 1064, 1033 1018, 897, 849
sulfites	1133, 1018, 989
physisorbed SO ₂	1166
Species	Band Assignment
bicarbonates	1674, 1606, 1496, 1429, 1245, 1221, 1215, 1025, 980
carbonates	1588, 1402, 1284, 1237, 1165, 1131, 1025, 997

Fig. 1. IR spectra during 15 minutes of SO_2 adsorption on CeBTC, $\text{CeO}_2\text{-d}$, and CeO_2 wires at 25°C .

Fig. 2. IR spectra during 15 minutes of SO_2 adsorption on MIL-125, TiO_2 -d, and TiO_2 bulk at 25 °C.

Fig. 3. IR spectra during 15 minutes of CO₂ adsorption on (a,d) CeBTC, (b,e) CeO₂-d, and (c,f) CeO₂ wires on pristine sample (a-c) and after in situ SO₂ exposure (d-f) at 25 °C.

Fig. 4. IR spectra during different time intervals of CO₂ adsorption on MIL-125, TiO₂-d, and TiO₂ bulk on pristine sample (top) and after in situ SO₂ exposure (bottom) at 25 °C.

Fig. 5. PXRd patterns of (top) CeBTC as-synthesized, CeBTC after SO₂ exposure, CeO₂-d as-synthesized, CeO₂-d after SO₂ exposure, CeO₂ wire as-synthesized, CeO₂ wires after SO₂ exposure, and (bottom) MIL-125 as-synthesized, MIL-125 after SO₂ exposure, TiO₂-d as-synthesized, TiO₂-d after SO₂ exposure, TiO₂ bulk, TiO₂ bulk after SO₂ exposure.

Fig. 6. SEM images of (a) MIL-125, (b) TiO₂-d, (c) TiO₂ bulk before IR experiments, and (d) MIL-125, (e) TiO₂-d, (f) TiO₂ bulk after IR experiments.

Fig. 7. SEM images of (a) CeBTC, (b) CeO₂-d, (c) CeO₂ wires before IR experiments, and (d) CeBTC, (e) CeO₂-d, (f) CeO₂ wires after IR experiments.

Graphical Abstract