

SO₂ and NH₃ Gas Adsorption on a Ternary ZnO/CuO/CuCl₂ Impregnated Activated Carbon Evaluated Using Combinatorial Methods

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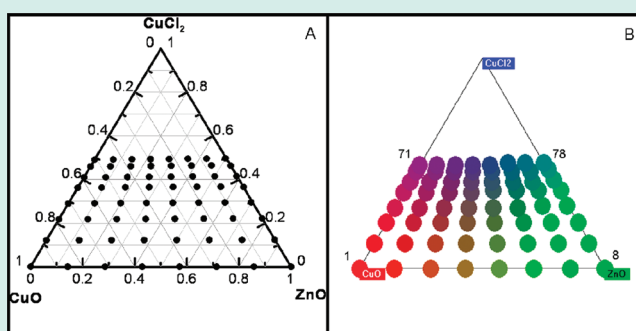
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Supporting Information

ABSTRACT: Ternary libraries of 64 ZnO/CuO/CuCl₂ impregnated activated carbon samples were prepared on untreated or HNO₃-treated carbon and evaluated for their SO₂ and NH₃ gas adsorption properties gravimetrically using a combinatorial method. CuCl₂ is shown to be a viable substitute for HNO₃ and some compositions of ternary ZnO/CuO/CuCl₂ impregnated carbon samples prepared on untreated carbon provided comparable SO₂ and NH₃ gas removal capacities to the materials prepared on HNO₃-treated carbon. Through combinatorial methods, it was determined that the use of HNO₃ in this multigas adsorbent formulation can be avoided.

KEYWORDS: high throughput methods, combinatorial materials science, solutions handling robot, multigas adsorbents, respirator carbons, toxic gas adsorbent materials, gas adsorption capacity, ternary ZnO/CuO/CuCl₂ impregnated activated carbon, HNO₃ treatment



1. INTRODUCTION

Multigas carbon materials are granulated activated carbons (GC) impregnated with either metal salts or metal oxides. These materials can filter a wide selection of toxic gases such as sulfur dioxide (SO₂), ammonia (NH₃), hydrogen cyanide, (HCN) and cyanogen (NCCN). Unimpregnated GC, also known as virgin GC, adsorbs volatile organic vapors well in its intricate networks of channels and pores. Virgin GC is a poor adsorbent for low molecular weight, highly polar gases such as HCN, SO₂, and NH₃. With impregnant addition, these gases are chemically retained through the formation of metal salts or metal complexes.¹

In the development of multigas carbon adsorbent materials, it has been established that a good metal or metal oxide distribution on the surface of the carbon, preferably with nanosized particulates, is necessary for good and efficient gas removal. A correlation between the number of surface functional groups and enhanced impregnant distribution has been established.² HNO₃ acts as an oxidizing agent that increases the amount of acidic (i.e., -COOH groups) and other oxygen-containing functional groups on the surface of the carbon.²

The changes in the surface functional groups on the carbon brought about by HNO₃-treatment result in the formation of highly dispersed particles of the impregnants after the impregnation process.² In addition, these changes were observed to help elevate the NH₃ adsorption capacity of the

materials.² A disadvantage of using HNO₃ as a carbon surface modifier for the reduction of impregnant particle size is the overall reduction in humidified organic vapor (OV) capacity.³ However, it was observed that without HNO₃ treatment, the agglomeration of metal impregnants was enhanced and the adsorption capacities of the materials for both NH₃ and SO₂ gases were reduced.²

A library consisting of 64 different combinations of both the ZnO and the CuO impregnants deposited on HNO₃-treated carbon was reported to have good SO₂ and NH₃ adsorption performance.⁴ Transition metal chlorides such as CuCl₂ and ZnCl₂ have been reported to be effective in removing NH₃ gas.^{5,6} No reports have been made on the gas adsorption properties of ternary mixtures of the ZnO/CuO/CuCl₂ impregnated activated carbon (IAC) system; therefore, this study should provide information on the advantages of the co-impregnation with CuCl₂. It is also possible to determine whether or not the HNO₃-treatment step is necessary in this formulation. In addition, mixing the three components could produce other mixed-metal and/or mixed-valent (Cu¹⁺ and/or Cu²⁺) phases that may have enhanced gas adsorption properties.

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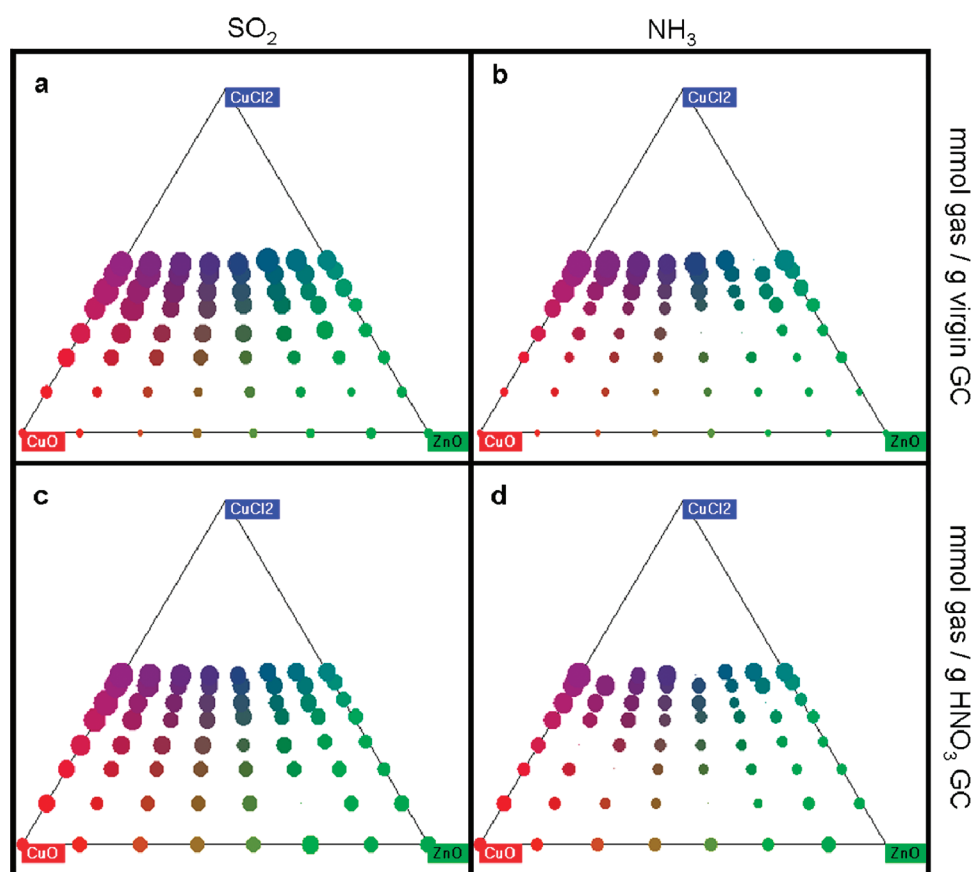


Figure 1. Overview of the gas adsorption capacities (in mmol gas/g AC) relative to the composition of each material prepared on different types of carbon bases. The size of the circles is proportional to the gas sorption performance. For the ternary samples prepared on virgin GC, the SO_2 capacity, panel (A), and the NH_3 capacity, panel (B), are shown on the top half portion of the diagram. For the samples prepared on HNO_3 -treated GC, the SO_2 capacity, panel (C), and the NH_3 capacity, panel (D), of the samples prepared are shown on the bottom half of the diagram. The scale for SO_2 capacities in panels A and C is from 0 to 1.5 mmol $\text{SO}_2/\text{g AC}$. The NH_3 capacity scale in panels B and D is from 0 to 3.5 mmol $\text{NH}_3/\text{g AC}$.

Combinatorial methods⁴ were employed to evaluate the performance of these ternary $\text{ZnO}/\text{CuO}/\text{CuCl}_2$ IAC materials in comparison to the performance of an identical ternary $\text{ZnO}/\text{CuO}/\text{CuCl}_2$ IAC library prepared on HNO_3 -treated GC. These methods were found to work effectively for determining the adsorption capacities of known ZnCl_2 , K_2CO_3 , and CuO IACs.⁴ This comparison should determine if HNO_3 -treatment can be omitted for samples that contain enough CuCl_2 and therefore produce adsorbents with an equivalent SO_2 and NH_3 gas capacity and an improved humid OV adsorption capacity.

2. EXPERIMENTAL PROCEDURES

The combinatorial method was employed to prepare and study IAC materials.⁴ Arrays of 64 samples with varying compositions were prepared by dispensing incremental amounts of each of the 3 solution components ($\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, and CuCl_2) on approximately 10 mg samples of either activated carbon or HNO_3 -treated activated carbon held in microvials. The solutions were dispensed over the grains of the carbon using a solutions handling robot (combi robot) and were decomposed to the desired active phases by employing several heating steps. The gas adsorption properties of the impregnated carbon materials were determined gravimetrically after a 4 h exposure to the toxic gas. Software developed in-house was used to visualize the gas adsorption properties in relation to the ternary composition of the impregnants.⁷ The active impregnant phases were determined by powder X-ray diffraction

(XRD). A detailed description of the methodology can be found in the Supporting Information section.

3. RESULTS AND DISCUSSION

The addition of several impregnants allows a single IAC to effectively remove different toxic gases.^{8–10} In some cases, putting these impregnants together results in compatible adsorption of several toxic gases. For example, SO_2 , NH_3 , and HCN gases are adsorbed well onto carbon impregnated with CuO ^{7,11,12} or combinations of both ZnO and CuO ⁴ when prepared on HNO_3 -treated GCs. It is also common to observe the loss of adsorption of the material for one or more types of gases when several reactive species are incorporated in an adsorbent. Therefore, the combinatorial method was found suitable for the preparation of multigas adsorbents because it allowed for the quick evaluation of the prepared adsorbent materials.⁴

Earlier studies on the HNO_3 -treatment of carbon show the enhanced the distribution of the impregnants leading to a monolayer of impregnant or nanometer sized impregnant grains within the carbon micropores.^{2,7,13} The increase in the number of surface oxide groups after HNO_3 -treatment enhances water adsorption and causes a reduction in humid OV capacity which is not desired.^{3,14–19} The combinatorial method was used to determine whether HNO_3 -treatment could be replaced by an alternative method that did not negatively impact gas adsorption.

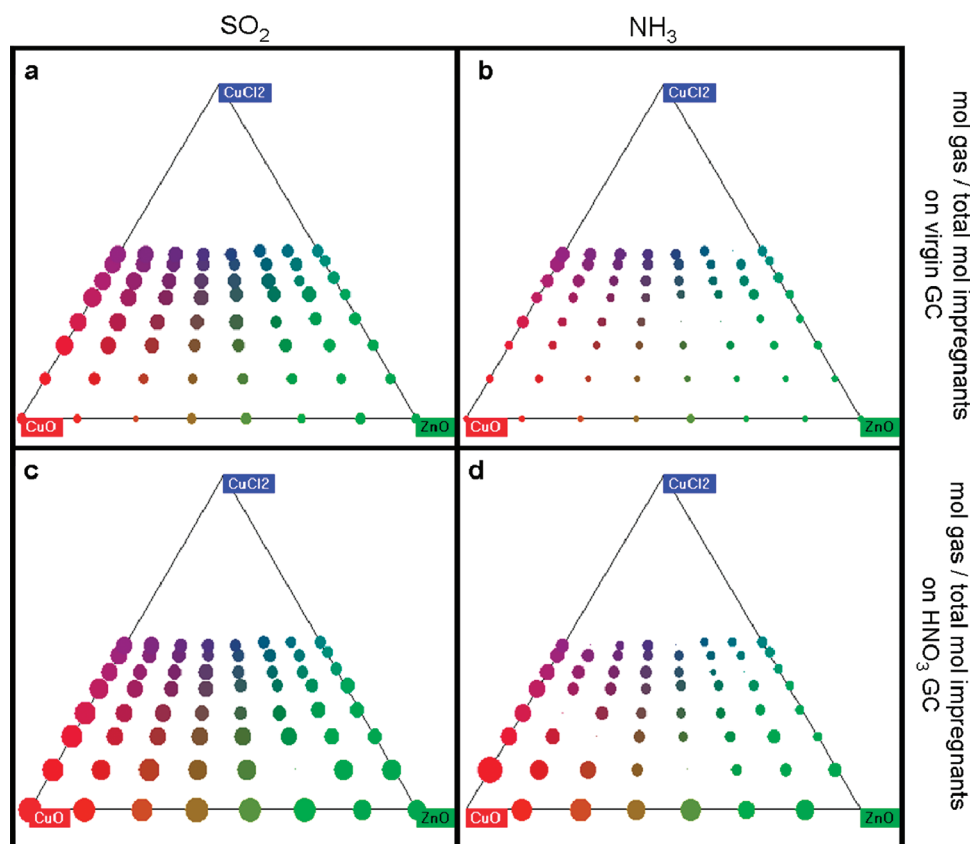
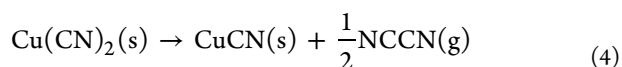
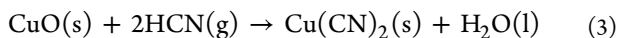
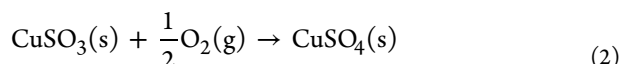
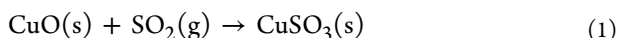
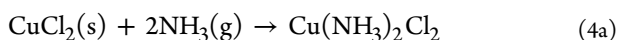


Figure 2. Overview of the stoichiometric ratio of reaction (SRR) relative to the composition of each material prepared on different types of carbon base. The size of the circles is proportional to the gas sorption performance. For the ternary samples prepared on virgin GC, the SO_2 SRR in panel (A) and NH_3 SRR in panel (B) are shown on the top half portion of the diagram. For the samples prepared on HNO_3 -treated GC, the SO_2 SRR in panel (C) and the NH_3 SRR in panel (D) of the samples prepared are shown on the bottom half of the diagram. The scale for SO_2 SRRs in panels A and C is from 0 to 1 while the NH_3 SRR scale in panels B and D is from 0 to 2.5.

The selection of impregnants used was made based on their adsorption of SO_2 , NH_3 , HCN , and NCCN gases. SO_2 is chemically adsorbed onto CuO IACs presumably via the formation of copper sulfate (CuSO_4) from CuO following the reaction described in eqs 1 and 2.^{2,4,7} CuO also functions to remove HCN and NCCN from gas streams to form copper cyanide ($\text{Cu}(\text{CN})_2$) following the reaction in eq 3.²⁰ $\text{Cu}(\text{CN})_2$ is relatively unstable and decomposes to form an equally toxic NCCN gas as shown in eq 4.²⁰



Aside from enhancing impregnant distribution, HNO_3 addition also increases the adsorption capacity for NH_3 .²¹ Using copper(II) chloride (CuCl_2) presents a good alternative to HNO_3 -treatment since it has been reported to effectively chemically adsorb NH_3 gas through the formation of a copper ammonia complex as shown in eq 4.⁵



The addition of CuCl_2 in the formulation of the multigas adsorbents enables the use of untreated carbon which is believed to improve the humid OV capacity of these materials while still maintaining good NH_3 adsorption.

$\text{Zn}(\text{NO}_3)_2$ decomposes to ZnO after heating the IACs to 200 °C.⁴ This species has been found to effectively adsorb SO_2 gas and is now observed to perform well in NH_3 adsorption.⁴ The inclusion of ZnO in the preparation of the multigas adsorbents should give an additional boost in the adsorption capacity of the material for both SO_2 and NH_3 and should compensate for the removal of HNO_3 in the formulation. In addition, novel mixed-metal or mixed valent phases of impregnants may be produced from the combination of the three components that may also show good gas adsorption properties.

A library consisting of 64 samples containing ZnO and/or CuO was prepared on both the HNO_3 -treated and virgin GC substrates. CuCl_2 was added sequentially across the library to study its impact. The compositions of the library were selected so that all samples contained ZnO and/or CuO which have been shown to adsorb SO_2 .⁴

3.1. SO_2 and NH_3 Adsorption of the Prepared ZnO , CuO , and CuCl_2 IACs. The IAC samples were prepared on two types of carbon bases, virgin and HNO_3 -treated GC, and were exposed to either SO_2 or NH_3 for 4 h. A comparison of the gas adsorption properties of the IACs prepared on different carbon substrates should determine whether HNO_3 -treatment can be avoided without sacrificing gas adsorption performance for example, retention of good SO_2 adsorption without fully

Table 1. Summary of Powder XRD Results Obtained from Representative Samples of Unexposed and Exposed Ternary ZnO/CuO/CuCl₂ IACs Prepared on Virgin GC

vial no.	composition (mmol/g GC)				phases identified in samples using powder XRD		
	CuO	ZnO	CuCl ₂	total	unexposed samples	SO ₂ exposed	NH ₃ exposed
1	1.2	0	0	1.2	CuO with disordered C	CuO with disordered C	CuO and Cu ₂ O with disordered C
4	0.7	0.5	0	1.2	CuO with disordered C	CuO with disordered C	CuO with disordered C
8	0	1.2	0	1.2	ZnO with disordered C	ZnO with disordered C	ZnO with disordered C
41	1.2	0	0.7	1.9	CuO, Cu ₂ Cl(OH) ₃ with disordered C	CuO with disordered C	CuO and Cu ₂ O with disordered C
44	0.7	0.5	0.7	1.9	CuO with disordered C	CuO with disordered C	CuO, ZnO with disordered C
48	0	1.2	0.7	1.9	ZnO with disordered C	disordered C	ZnO with disordered C
71	1.2	0	1.2	2.4	Cu ₂ Cl(OH) ₃ with disordered C	disordered C	disordered C
74	0.7	0.5	1.2	2.4	CuO, Cu ₂ Cl(OH) ₃ with disordered C	disordered C	CuO with disordered C
78	0	1.2	1.2	2.4	ZnO, Cu ₂ Cl(OH) ₃ with disordered C	disordered C	disordered C

dispersed impregnants, and increased NH₃ adsorption with CuCl₂ addition. The plots shown in Figure 1 give an indication of the materials' gas adsorption performance.

The SO₂ capacities in Figures 1A and 1C were plotted on a scale of 0 to 1 mmol SO₂/g GC. The NH₃ capacities in Figures 1B and 1D were plotted on a scale of 0 to 3.5 mmol NH₃/g GC. Data points shown at the base of each of the ternary plots represent samples that were impregnated with copper and/or zinc oxides as in (CuO)_(1-x)ZnO_(x). The sizes of each of the data points along the base of each plot are about the same showing the approximate equivalence of ZnO and CuO impregnants on GC for SO₂ or NH₃ adsorption. Figure 1 shows that the adsorption capacities for the toxic gases of all the samples prepared on either virgin GC or HNO₃-treated GC dramatically improved with the addition of CuCl₂. Figure 1 also shows that the samples prepared on virgin GC which contained high amounts CuCl₂ adsorbed about the same amount of gas as the samples with similar compositions prepared on HNO₃-treated GC. At low concentrations of CuCl₂, the gas adsorption of the samples prepared on HNO₃-treated carbon was observed to be higher than that of the corresponding samples prepared on untreated carbon. The highly dispersed nature of the impregnants at low concentrations of CuCl₂ enabled the HNO₃-treated materials to perform better than the corresponding untreated samples.

Figure 2 shows the stoichiometric ratio of reaction (SRR) of the samples for both gases. Small values of SRR were measured for samples with no CuCl₂ prepared on virgin GC. Such samples perform poorly as gas adsorbents compared to similar samples prepared on HNO₃-treated GC. Figure 2 shows that increasing the CuCl₂ content of the materials dramatically improved the gas adsorption ability of the samples prepared on virgin GC. The addition of CuCl₂ decreased the SRR of the materials prepared on HNO₃-treated GC. However, materials having high CuCl₂ content on virgin GC performed about the same as materials made on HNO₃-treated GC with similar compositions, suggesting that for samples containing higher concentrations of CuCl₂, HNO₃-treatment can be omitted in the formulation and still provide high SO₂ and NH₃ adsorption.

3.2. Powder XRD of the ZnO, CuO, and CuCl₂ IACs.

Representative samples were chosen and analyzed by powder XRD. The compositions and the corresponding sample number of the samples chosen are listed in Table 1. Unexposed samples prepared on HNO₃-treated GC representing samples in Figures 1 and 2 were also analyzed by powder XRD.

Figure 3 shows the XRD patterns obtained for corresponding unexposed samples prepared on HNO₃-treated GC (in red). These patterns did not show any diffraction peaks, indicating

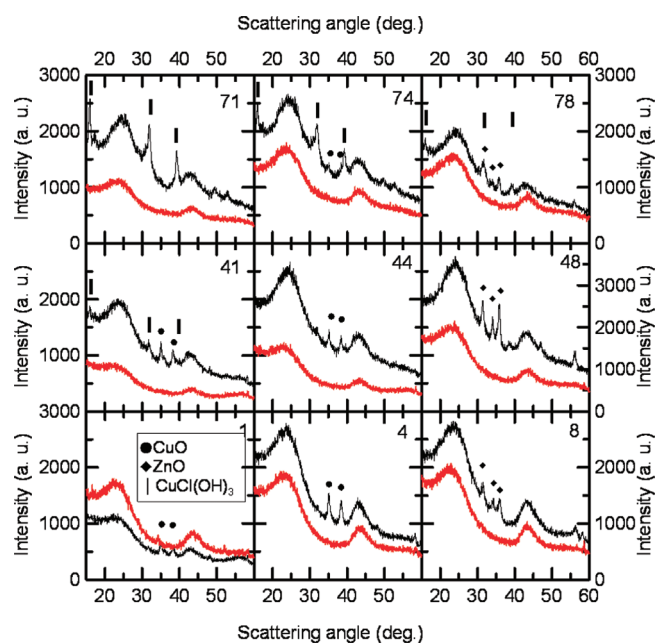


Figure 3. Powder XRD patterns obtained for unexposed samples labeled 1, 4, 8, 41, 44, 48, 71, 74, and 78. ZnO and CuO phases were observed. An additional Cu₂Cl(OH)₃ phase was observed for samples with a high CuCl₂ content. The diffraction pattern for corresponding samples prepared on HNO₃-treated GC is also shown (in red).

that the impregnants in these samples are fully dispersed and is consistent with the literature.²²

Figure 3 also shows the diffraction patterns obtained for the representative samples prepared on virgin GC in the array (in black). The presence of diffraction peaks in these graphs indicated that the addition of CuCl₂ did not enhance the formation of fully dispersed impregnants on the surface of the carbon. The XRD patterns of unexposed samples 1, 4, and 8, which contained no CuCl₂, are consistent with the presence of only CuO and ZnO with broad humps at $2\theta = 26.4$ and $2\theta = 42.2$ associated with the activated carbon support.^{23–25} ZnO has strong diffraction peaks at $2\theta = 31.8$, $2\theta = 34.4$, and $2\theta = 36.3^\circ$, and CuO has strong diffraction peaks at $2\theta = 35.6$ and $2\theta = 38.8^\circ$, all of which are distinct from the amorphous carbon humps.^{24,25} The presence of the metal oxide phases was expected and were previously observed with all metal nitrate impregnated GCs after heat treatment.² Corresponding samples prepared on HNO₃-treated GC show no diffraction peaks which suggests high impregnant distribution on the surface which explains the higher gas adsorption observed

compared with samples prepared on virgin GC (refer to the bottom row data points in Figure 1.)

Samples 41, 44, and 48 contained about 0.37 mol ratio of CuCl_2 or 0.7 mmol $\text{CuCl}_2/\text{g AC}$ as indicated in Table 1. Overall, these samples showed increased gas adsorption relative to the samples that did not contain CuCl_2 . Samples prepared on HNO_3 -treated GC show better gas adsorption than samples prepared on virgin GC. Again, this is due to the presence of metal oxide crystallites on the samples made on virgin GC with the exception of sample 41. The SO_2 gas adsorption appeared to be slightly higher for sample 41 prepared on virgin GC. The diffraction patterns obtained from these samples help explain why.

Figure 4 shows an expanded view of the diffraction occurring between 25 to 45 degrees. Figure 4 clearly shows $\text{Cu}_2\text{Cl}(\text{OH})_3$

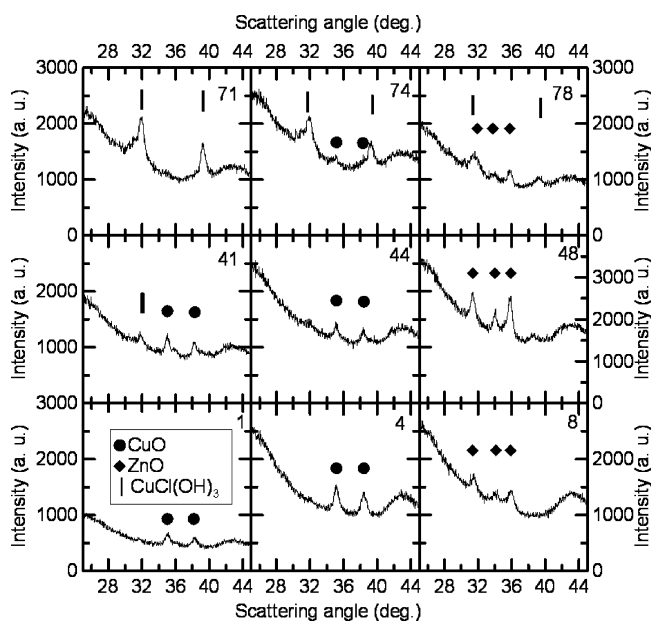


Figure 4. Expanded view of the XRD patterns of the unexposed samples shown in Figure 3 which highlights the diffraction peaks occurring in the region between 25 and 45 degrees.

is observed in sample 41, which contained no ZnO. $\text{Cu}_2\text{Cl}(\text{OH})_3$ has intense diffraction peaks occurring at $2\theta = 16.3$, $2\theta = 32.5$ and $2\theta = 39.9^\circ$.²⁶ Figure 4 also shows that only the metal oxide phases were observed in samples 44 and 48. This indicates that the presence of small crystallites of $\text{Cu}_2\text{Cl}(\text{OH})_3$ influenced the SO_2 gas adsorption of the material.

Figure 4 also shows that more $\text{Cu}_2\text{Cl}(\text{OH})_3$ was observed in samples impregnated with more CuCl_2 ; samples 71 and 74, which also were impregnated with $\text{Cu}(\text{NO}_3)_2$. Very little, if any, CuO was observed in these samples. This suggests that $\text{Cu}_2\text{Cl}(\text{OH})_3$ was formed from a reaction that occurs between CuCl_2 and CuO in the presence of moisture.²⁷ Sample 78, which only contained CuCl_2 and ZnO still shows some evidence for $\text{Cu}_2\text{Cl}(\text{OH})_3$. The presence of this $\text{Cu}_2\text{Cl}(\text{OH})_3$ in samples that did not contain CuO as in vial 78 suggests that a different formation mechanism may be involved. Comparable gas adsorption properties were observed in samples prepared in either virgin GC or HNO_3 -treated GC where $\text{Cu}_2\text{Cl}(\text{OH})_3$ phase was observed on the diffraction pattern. The presence of $\text{Cu}_2\text{Cl}(\text{OH})_3$ may influence the SO_2 adsorption behavior of the impregnated material through reaction with SO_2 in the

presence of moisture to form $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ and possibly $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$.²⁸ However, this is speculation, and any understanding will require further studies. A summary of the observed diffraction peaks and the composition of each sample is given in Table 1.

The diffraction patterns with the view of the scattering angle range between 25 and 45 degrees for SO_2 and NH_3 -exposed samples are shown in Figures 5 and 6, respectively. For the gas

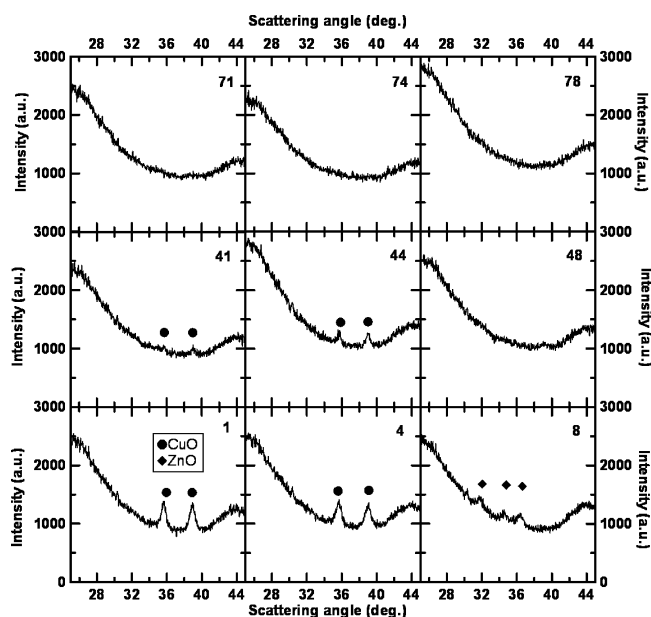


Figure 5. Expanded view of the XRD patterns of the SO_2 exposed samples labeled 1, 4, 8, 41, 44, 48, 71, 74, and 78 which highlights the diffraction peaks occurring in the region between 25 and 45 degrees where only ZnO and CuO phases were observed.

exposed samples, the pattern outside the range indicated in Figures 5 and 6 was identical to that shown in Figure 3. No other XRD peaks were observed outside the specified ranges.

A comparison of the diffraction patterns for unexposed samples with either of the diffraction patterns for the SO_2 -exposed (Figure 5) or NH_3 -exposed (Figure 6) samples indicates that the $\text{Cu}_2\text{Cl}(\text{OH})_3$ phase was consumed after gas exposure. Similarly, the metal oxide diffraction peaks in Figure 5 appeared to lower in intensity with increasing CuCl_2 content for the samples exposed to SO_2 . This may indicate that more metal oxides were consumed by the chemisorption of SO_2 as more CuCl_2 was added. This is in contrast to the metal oxide diffraction peaks obtained for the NH_3 -exposed samples shown in Figure 6 which do not appear to decrease with an increase in the amount of CuCl_2 content. These results are not surprising considering that the metal oxides are expected to chemisorb SO_2 and CuCl_2 is expected to chemisorb NH_3 . XRD peaks from Cu_2O were observed in some of the NH_3 exposed samples.

Recall that the calculated SRRs of the samples with high CuCl_2 content prepared on virgin GC were about same as the samples prepared on HNO_3 -treated GC. Therefore, similar gas adsorption capacities can be achieved despite the differences in impregnant distribution when $\text{Cu}_2\text{Cl}(\text{OH})_3$ is present. Comparison of the gas adsorption properties of the materials from the two combinatorial libraries suggest that HNO_3 -treatment may be omitted from the formulation of multigas adsorbents. Representative samples prepared on virgin GC will

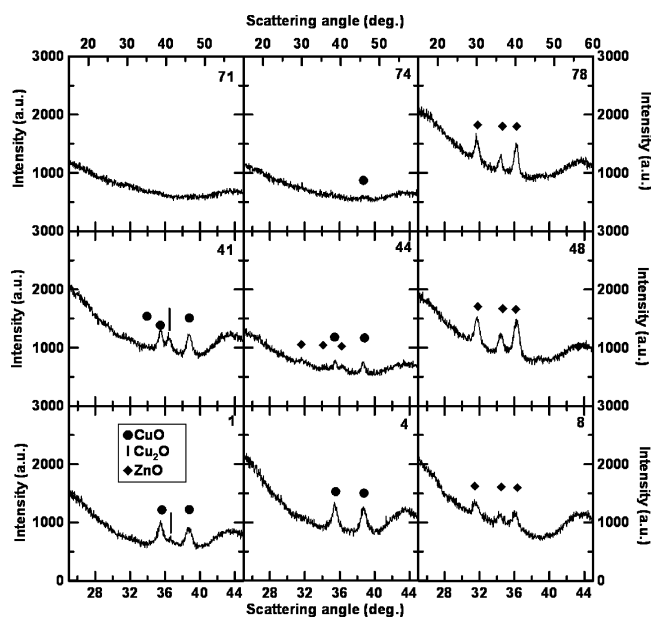


Figure 6. Expanded view of the XRD patterns of the NH_3 exposed samples labeled 1, 4, 8, 41, 44, 48, 71, 74, and 78 which highlights the diffraction peaks occurring in the region between 25 and 45 degrees. ZnO and CuO phases were observed. The presence of the $\text{Cu}_2\text{Cl}(\text{OH})_3$ phase was not observed for samples that were impregnated with CuCl_2 in these NH_3 exposed samples; however, the presence of the Cu_2O diffraction peak was observed in some samples.

be evaluated for HCN/NCCN and humid OV gas adsorption properties.

4. CONCLUSION AND FUTURE WORK

The combinatorial screening method worked well in screening and comparing the gas adsorption properties of 64 samples with varying mole fractions of ZnO, CuO, and CuCl_2 impregnants prepared on different base carbons. The initial screening of the ZnO, CuO, and CuCl_2 IACs showed promising results. The SO_2 and NH_3 gas adsorption capacities were observed to increase with increased amounts of CuCl_2 in the impregnant when prepared on untreated carbon. The samples that contained high amounts of CuCl_2 performed similarly to the impregnated carbon samples prepared on HNO_3 -treated GC with the same composition. Powder XRD also revealed the presence of $\text{Cu}_2\text{Cl}(\text{OH})_3$ in the samples impregnated with high amounts of CuCl_2 which is the likely cause of the improved SO_2 gas adsorption capacity of the materials prepared on virgin GC when compared with materials impregnated only with the metal oxides. Therefore, for the ternary ZnO/CuO/ CuCl_2 IACs, CuCl_2 co-impregnation can be used instead of HNO_3 -treatment to prepare materials with acceptable SO_2 and NH_3 adsorption characteristics. These ternary samples will be evaluated for HCN/NCCN and humid OV adsorption and will be the subject of a separate work.

■ ASSOCIATED CONTENT

Supporting Information

Detailed description of the combinatorial and screening method, dispense procedures, heat treatment, and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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