

Evaluation of the SO₂ and NH₃ Gas Adsorption Properties of CuO/ZnO/Mn₃O₄ and CuO/ZnO/NiO Ternary Impregnated Activated Carbon Using Combinatorial Materials Science Methods

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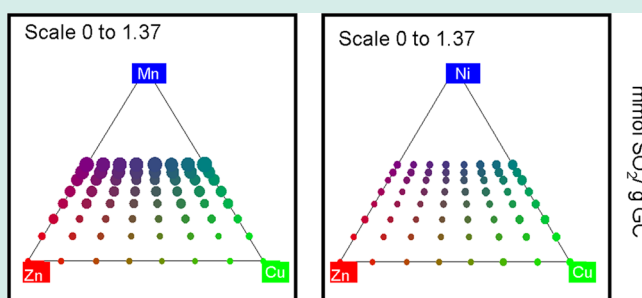
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S Supporting Information

ABSTRACT: Impregnated activated carbons (IAC) are widely used materials for the removal of toxic gases in personal respiratory protection applications. The combinatorial method has been employed to prepare IACs containing different types of metal oxides in various proportions and evaluate their adsorption performance for low molecular weight gases, such as SO₂ and NH₃, under dry conditions. Among the metal oxides used for the study, Mn₃O₄ was found to have the highest capacity for retaining SO₂ gas under dry conditions. NiO and ZnO were found to have similar NH₃ adsorption capacities which are higher than the NH₃ capacities observed for the other metal oxide impregnants used in the study. Although Cu- or Zn-based impregnants and their combinations have been extensively studied and used as gas adsorbents, neither Mn₃O₄ nor NiO have been incorporated in the formulations used. In this study, ternary libraries of IACs with various combinations of CuO/ZnO/Mn₃O₄ and CuO/ZnO/NiO were studied and evaluated for their adsorption of SO₂ and NH₃ gases. Combinations of CuO, ZnO, and Mn₃O₄ were found to have the potential to be multigas adsorbents compared to formulations that contain NiO.

KEYWORDS: ternary impregnated activated carbons, multigas adsorbents, combinatorial evaluation of adsorbents, CuO, ZnO, Mn₃O₄, NiO impregnants



INTRODUCTION

The discovery of new versatile gas adsorbent materials is faced with increasing challenges because of the rising cost of production, a higher number of potentially dangerous gases, as well as new regulations and limitations imposed on the production of air filtration materials. Impregnated activated carbon materials are still the best choice for air filtration adsorbents because of the low cost of production and acceptable performance. However, the structural and functional diversity of carbon-based materials limits the ability to accurately define the exact requirements for developing versatile gas adsorbents.^{1,2}

The type of activated carbon and various treatments of that carbon affect the way impregnants disperse within the activated carbon during imbibing or soaking and affect the way the impregnants decompose at high temperature.³ The overall gas adsorption performance of impregnated activated carbon materials can be easily modified by changes to the chemistry of the impregnants, the impregnant loading, the impregnant composition after heat treatment, the morphology of the impregnant, and the drying conditions. Joseph Hanak introduced the combinatorial approach in the 1970s as a way to prepare and screen numerous materials simultaneously.^{4–6}

The approach enabled the quick determination of a correlation between an observed material property and the material composition and allowed the faster discovery of new materials. Combinatorial materials science (combi) methods were found suitable for the development of impregnated activated carbon (IAC) adsorbent materials for respiratory filters.^{7–9} Parallel preparation and subsequent testing of many compositions of impregnated activated carbon was achieved and a correlation can be made on the observed diffraction patterns and the gas adsorption performance of the material.^{7–10}

CuO and ZnO IACs have been used for the production of broad spectrum gas adsorbents.^{1,2,11} The production of these materials can involve formulations that use aqueous ammonia to dissolve the salts during production.^{11–14} Recent environmental concerns about the use of NH₃ during respirator material production led to formulations using HNO₃ and phosphomolybdic acid (PMA) instead of NH₃. This formulation resulted in an improved adsorption of low molecular weight gases such as SO₂, NH₃, HCN, and

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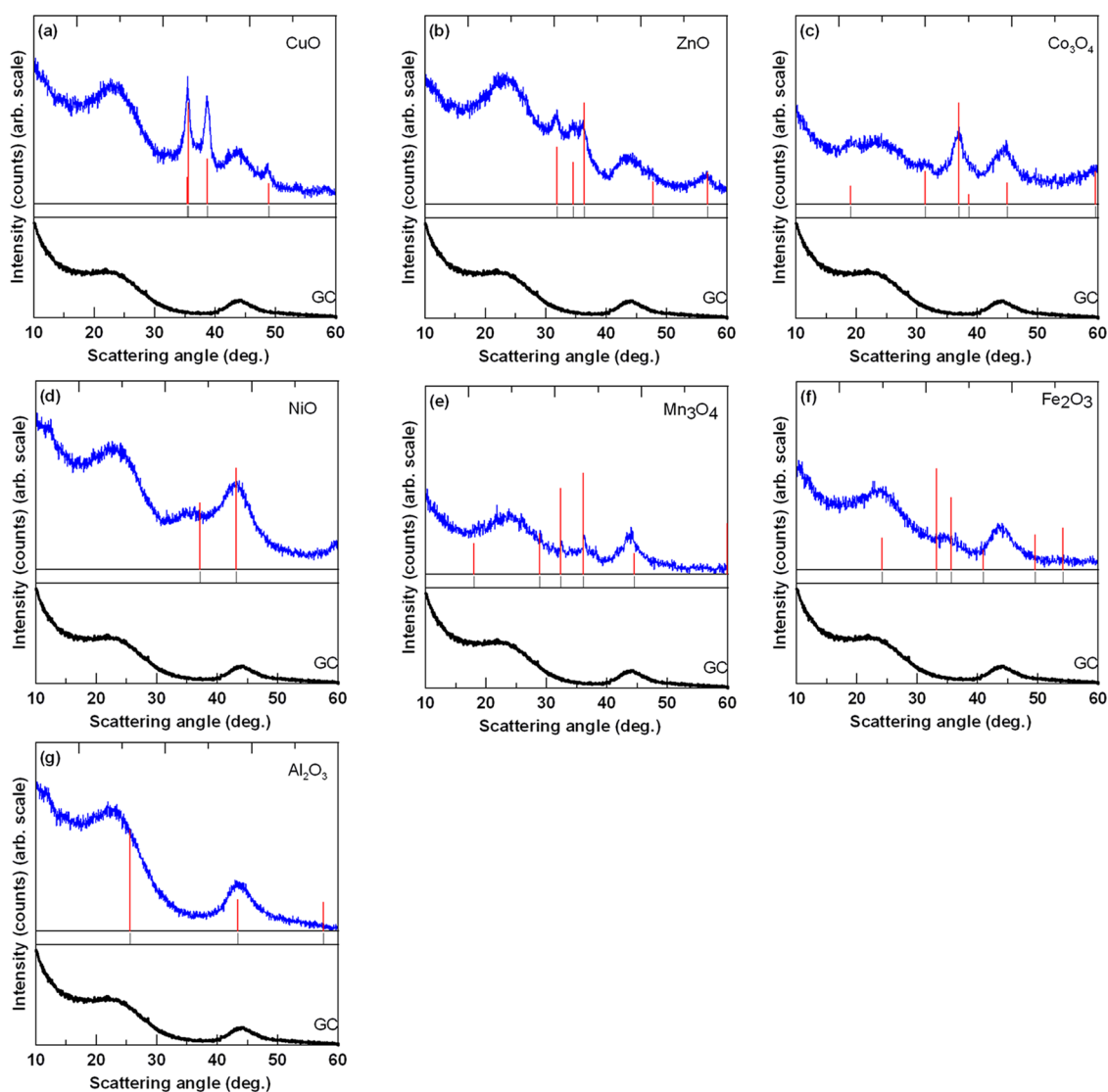


Figure 1. Powder XRD patterns obtained for the thermally decomposed impregnants on activated carbon upon addition of (a) $\text{Cu}(\text{NO}_3)_2$, (b) $\text{Zn}(\text{NO}_3)_2$, (c) $\text{Co}(\text{NO}_3)_2$, (d) $\text{Ni}(\text{NO}_3)_2$, (e) $\text{Mn}(\text{NO}_3)_2$, (f) $\text{Fe}(\text{NO}_3)_3$, and (g) $\text{Al}(\text{NO}_3)_3$ solutions and are shown relative to the pattern obtained for unimpregnated activated carbon (GC). The most intense reflections for each of the reference phases for either CuO, ZnO, Co_3O_4 , NiO, or Mn_3O_4 in each panel have been marked.^{22–26} The labels on each of the plots correspond to the impregnant phases found except for panels f and g, where the materials were presumed to contain well-dispersed Fe_2O_3 and Al_2O_3 .^{27,28}

NCCN.^{3,15–17} However, the observed low humid- C_6H_{12} adsorption associated with HNO_3 treatment may limit the potential use of these formulations for multigas adsorbents. Therefore, formulations that eliminate HNO_3 and PMA coimpregnation or the use of ammonia, while maintaining a reasonable production cost, must be developed.

Previous combinatorial studies of CuO and ZnO IACs showed an equivalent gas adsorption capacity for both SO_2 and NH_3 gases.⁷ The addition of a third component such as CuCl_2 produced ternary impregnated materials that had improved NH_3 adsorption, while retaining SO_2 adsorption.^{8,9} The ternary CuO/ZnO/ CuCl_2 IACs showed good gas adsorption properties despite the lack of monolayer dispersion of the deposited impregnant material indicating that HNO_3 coimpregnation may not always be needed.^{8,9} The study showed that the composition, phases and the morphology of the impregnants related directly to the observed gas adsorption behavior of the material. The combi method considerably improves the rate of discovery of viable multigas adsorbents.

Here, the gas adsorption performance of ternary IACs impregnated with combinations of CuO and ZnO, along with either Mn_3O_4 or NiO was explored. The coimpregnants, Mn_3O_4 or NiO, were chosen based on the studies made on single component metal oxide IACs, which showed that Mn_3O_4 had the highest capacity for retaining SO_2 gas under dry conditions. NiO was chosen because it had similar NH_3 adsorption capacities to ZnO IAC and is higher than the other metal oxide impregnants used in the study. The combination of Mn_3O_4 or NiO with the base impregnants, CuO or ZnO, has never been investigated and may eliminate the need for other coimpregnating materials, such as HNO_3 and PMA.^{18–20}

■ EXPERIMENTAL SECTION

Arrays of 90 samples were prepared and evaluated using the combinatorial method described in ref 7. Typically, 26 of the 90 vials contained control samples, such as unimpregnated carbon (Kuraray GC, 12×35 mesh), Calgon universal respirator

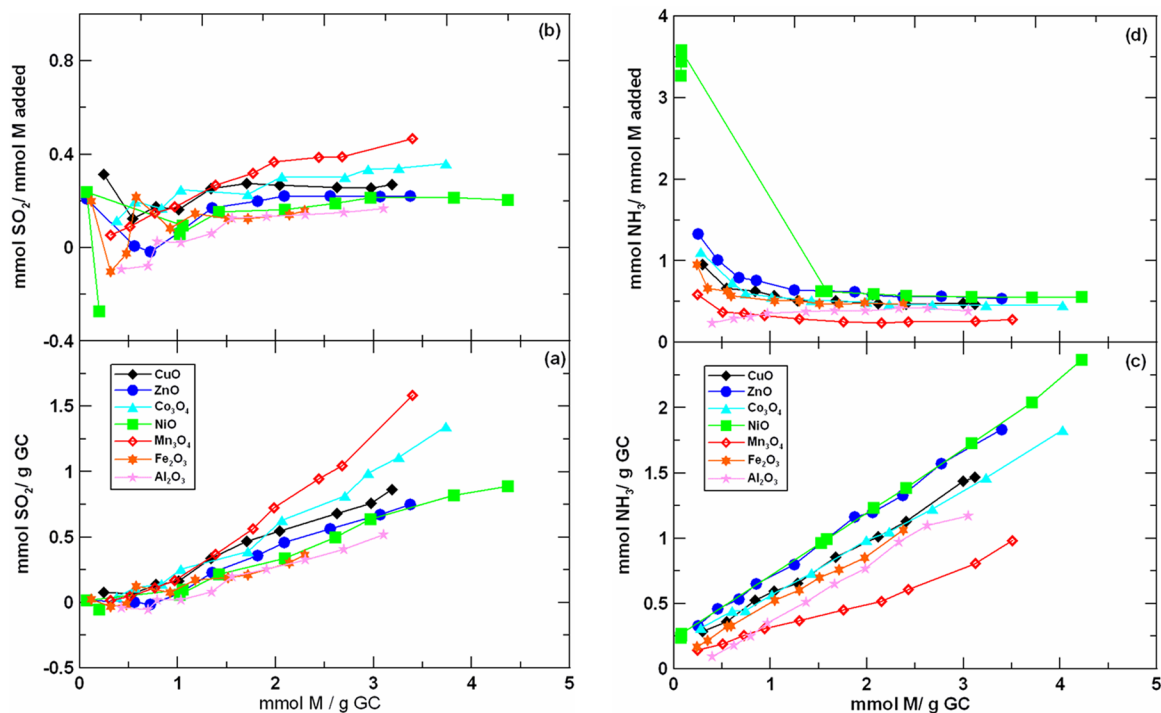


Figure 2. Gas adsorption performance of different metal oxides at various metal loadings (in mmol M/g GC). The panels on the left show the (a) SO₂ gas adsorption capacity and the (b) stoichiometric ratio of reaction (SRR) data with respect to SO₂ for metal oxide impregnated activated carbon. The panels on the right show the (c) NH₃ gas adsorption capacity and the (d) SRR with respect to NH₃.

carbon (URC), and product no. BKV-0425 from 3M Canada Co. The control samples were exposed to toxic gas simultaneously with the combi samples. The combi samples were prepared via the “incipient wetness method” by dispensing the required volume of each impregnating solution using a solutions handling robot, into vials containing about 10.0 ± 1.0 mg of unimpregnated activated carbon. The impregnants were decomposed to the desired phases by performing several heating steps, which also ensured that the samples were adequately dried. For this study, the heating temperature was chosen to be 200 °C under argon gas. To determine the effect of a higher heating temperature on decomposition of the CuO/ZnO/NiO ternary IACs, representative samples were heated at 250 °C under Ar. Under these conditions, the decomposition of the metal nitrates into metal oxides was achieved. Further details are available in the Supporting Information.

Performance evaluations of each combinatorial library were made by exposure of two identical 90-sample arrays to challenge gases (SO₂ or NH₃) under dry conditions (0% relative humidity) and to gravimetrically determine how much gas was adsorbed after 4 h relative to unimpregnated carbon. The gas adsorption capacities were calculated from the difference in the mass of each sample before and after exposure to the challenge gas. The stoichiometric ratio of reaction (SRR) was taken to be ratio between the number of mmoles of gas adsorbed and the total number of mmoles of metal used for impregnation. Software developed in-house was used to visualize and relate the gas adsorption properties to the ternary composition of the impregnants.²¹ Unexposed samples were analyzed by powder X-ray diffraction. A detailed description of the experiment can be found in the Supporting Information section and in ref 7.

RESULTS AND DISCUSSION

Effect of Varying Impregnant Loading and Impregnant Materials on Gas Adsorption. The overall gas adsorption performance of impregnated activated carbon materials can be varied by introducing changes to the choice of impregnants, impregnant loading, impregnant composition, and heating conditions. In this section, the gas adsorption properties of IACs that contain only one type of impregnant are presented to determine the effect of varying the impregnant loading on the SO₂ and NH₃ gas adsorption behavior of the materials. This study also shows how different metal oxide impregnants behave as SO₂ and NH₃ gas adsorbers in comparison to the well-studied Cu and Zn-based impregnants.^{3,7,15–17} Our selections for combinations of different metal oxide precursors were based on the results obtained.

Two identical libraries of seven different metal oxide impregnated activated carbons were prepared and evaluated for variations in gas adsorption (for SO₂ and NH₃) with respect to increasing impregnant loading. The metal oxides were thermally decomposed from nitrate solutions of Cu, Zn, Co, Ni, Mn, Fe, or Al. The impregnant phases present after thermal treatment were identified by powder X-ray diffraction by matching the diffraction peaks observed from each material to the most intense reflections of database patterns. Figure 1 shows the diffraction patterns collected from the samples and are plotted relative to unimpregnated GC. The XRD patterns collected for these samples were matched to the most intense diffraction peaks for the corresponding metal oxides. The analysis of these XRD patterns showed that the single component metal nitrates decomposed to CuO, ZnO, Co₃O₄, NiO, and Mn₃O₄ during thermal treatment in the presence of carbon.^{22–26} Only the amorphous carbon humps were observed for Al(NO₃)₃ and Fe(NO₃)₃ IACs, which were expected to decompose to Al₂O₃ and Fe₂O₃.^{27,28}

The actual % loading was calculated from the mass difference of the samples before impregnation and after thermal decomposition. The theoretical % loading was calculated from the mmol of the impregnant multiplied by the molar mass of the metal oxide assuming full decomposition of the impregnant (see Supporting Information). The observed difference between the actual and the theoretical percent loading for these materials is only between the range of 5% and 7% suggesting that the impregnant phase present is consistent with having Al_2O_3 and Fe_2O_3 as the deposited material. This portion of the study demonstrated that various materials behave differently when thermally decomposed in the presence of activated carbon. This also confirmed that the desired metal oxide phase of the impregnant was generated at 200°C under an inert argon atmosphere.

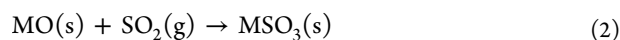
Unimpregnated GC derived from coconut shells can physically adsorb SO_2 but cannot adsorb much NH_3 . The average SO_2 adsorption capacity for 1000 ppm SO_2 in air at ambient temperature and 0% RH recorded for 10.0 ± 1.0 mg of GC is 0.35 ± 0.046 mmol/g GC. The addition of metal oxide impregnants is known to enhance the adsorption of both gases.^{1,2,12,13,29,30} The reported gas capacities for the IACs are the capacities of the impregnated samples minus the capacity of the GC control. In all cases the measured SO_2 and NH_3 gas adsorption capacities of the IAC samples were observed to be higher than the GC controls regardless of the type of impregnant used. Using combinatorial methods, the gas adsorption performance of the various IACs with varying impregnant loadings can be compared.

Figure 2 shows the SO_2 (Figures 2a and b) and NH_3 (Figures 2c and d) gas adsorption properties as the impregnant composition and the loading (in mmol M/g GC where M represents metal atoms added) were varied. Figure 2a and 2c shows the calculated gas adsorption capacities reported as mmoles of gas per gram of GC. Figure 2b and 2d shows the adsorption efficiency reported as the stoichiometric ratio of reaction (SRR) between the moles of gas adsorbed and the total moles of metal atoms in the of impregnants added. Figure 2a shows that for materials impregnated with a single component, the SO_2 capacity increased as the impregnant loading was increased from approximately 0.2 to about 4.5 mmol M/g GC. All metal oxides have equivalent SO_2 gas adsorption capacities with the exception of the oxides of Cu, Mn, and Co. Mn_3O_4 was observed to have the greatest SO_2 capacity followed by Co_3O_4 , both of which showed greater capacities than CuO and ZnO, the typical impregnants used in IACs. The SRR also increased with the loading of Mn and Co oxides (Figure 2b). For the other impregnants, the SRR remained constant when the impregnant loading was 2.0 mmol M/g GC or higher.

SO_2 gas was reported to undergo high temperature oxidative adsorption onto spinel (MgAl_2O_4).^{20,31} Therefore, a possible explanation for the larger SO_2 adsorption capacity observed for Mn_3O_4 and Co_3O_4 IACs is that Mn_3O_4 and Co_3O_4 may react according to the equation given below:



The other metal oxide impregnants that do not have a similar spinel structure would chemisorb following the chemical equation



Theoretically, the SO_2 to metal oxide ratio should have a value close to 1 according to the chemical equations given in eqs 1 and 2. It is possible that the SRRs for Mn_3O_4 and Co_3O_4 IACs are higher and closer to the theoretical value compared to the other metal oxide impregnants because the spinels may have more reactive sites available for SO_2 adsorption.

The SO_2 chemisorption reaction is usually observed from the comparison of the diffraction patterns collected from SO_2 exposed and unexposed IAC samples. For example, diffraction patterns collected for single component CuO showed a significant difference and is shown in Figure 3. Figure 3

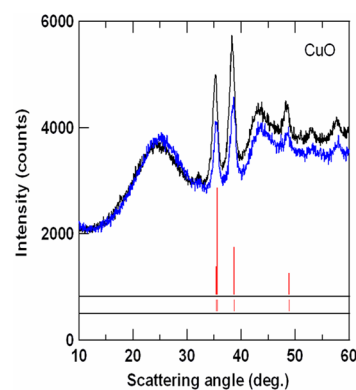


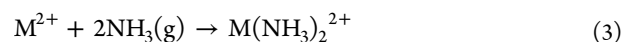
Figure 3. Powder XRD patterns obtained for the single component CuO impregnated activated carbon before (top graphs in black) and after (bottom graphs in blue) exposure to SO_2 . The most intense reflections for the reference phase are marked.

shows a comparison of SO_2 -exposed IAC samples (bottom plot in blue) and the unexposed IAC sample (top plot in black). From these graphs, the intensity of the diffraction peaks for the most intense reflections for CuO decreased in the SO_2 -exposed samples. In addition, it was previously reported that when the SO_2 -exposed CuO and ZnO IAC samples were soaked in water for about 10 days then filtered; the filtrate was found to contain CuSO_4 and ZnSO_4 salts (identified by XRD), which proved that SO_2 was captured by the adsorbent.⁷ Presumably, the sulfites converted to the sulfates according to the reaction



NH_3 adsorption is reported to be enhanced by metal oxide impregnation through either the catalyzed oxidation of NH_3 to form nitrogen gas or through an intermediate metal-ammonia complex formation.^{29,32,33} Figure 2c shows that Ni and Zn oxides have similar NH_3 gas adsorption capacities and were higher compared with the other metal oxides. Mn_3O_4 was observed to have the least capacity for NH_3 gas adsorption. Mn_3O_4 is a thermally stable spinel oxide with Mn occurring in (2+) and (3+) oxidation states.³¹

The increase in the NH_3 adsorption capacity of the IAC materials relative to unimpregnated GC suggests that materials effectively chemisorb NH_3 gas through the formation of metal-ammonia complexes as shown in eq 3.³⁴



The low adsorption capacity of Mn_3O_4 IACs for NH_3 may be due to the inability of Mn^{3+} to form NH_3 complexes.³⁵ This is in contrast with Co_3O_4 , another spinel, wherein Co also occurs in the (2+) and (3+) oxidation states; however, both Co(II) and Co(III) readily form NH_3 complexes.³⁵ The theoretical

SRR according to the reaction given in eq 3 is equal to 2. For most of the metal oxide in the study, the SRR was calculated to be close to 0.5 with the exception of Mn_3O_4 , which is lower because of the reason stated above. Transition metal oxides are basic and could explain why the reactivity of these impregnants with NH_3 is low.³¹

2.2. Effect of the Addition of a Third Component to Cu or Zn-Based Impregnated Activated Carbon. Figure 2 showed that Mn_3O_4 and NiO IACs only adsorb one of the two challenge gases well. Mn_3O_4 is good for SO_2 and NiO is good for NH_3 . The combination of either Mn_3O_4 or NiO with well-known impregnants (CuO and ZnO) may lead to an all-purpose adsorbent thus eliminating the need for other coimpregnating materials, such as HNO_3 and PMA. Figures 3 and 4 show comparative plots of the gas adsorption behavior of

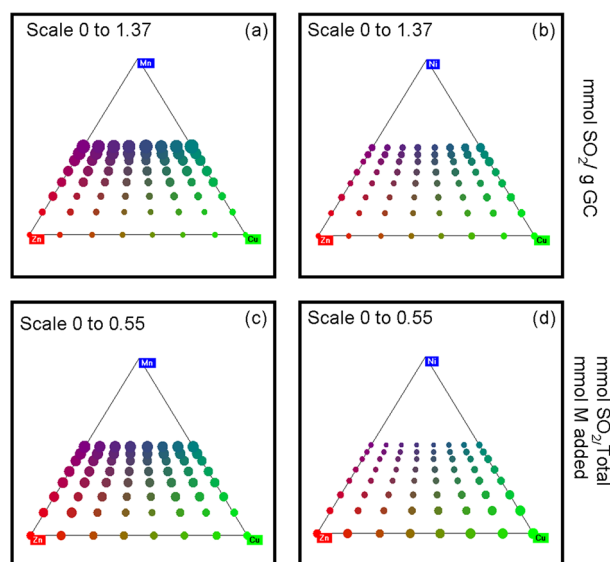


Figure 4. SO_2 gas adsorption performance of the ternary libraries of $\text{CuO}/\text{ZnO}/\text{Mn}_3\text{O}_4$ and $\text{CuO}/\text{ZnO}/\text{NiO}$. Panels a and c are the gas adsorption capacity and the stoichiometric ratio of reaction for the $\text{CuO}/\text{ZnO}/\text{Mn}_3\text{O}_4$ library. Panels b and d are the gas adsorption capacity and the stoichiometric ratio of reaction for the $\text{CuO}/\text{ZnO}/\text{NiO}$ library.

the two ternary libraries of IACs studied as the total impregnant loading was increased from 1.2 mmol/g GC (data points shown at the base of each plot) to 2.4 mmol/g GC (topmost data points on each plot). Figure 5 shows plots that clearly present the impact of the addition of the third impregnant component.

The presence of strong diffraction peaks for most of the IACs suggest that the impregnants may have formed large grains (>5 nm). Previous scanning electron microscopy studies of CuO and ZnO IACs show that the impregnants generally form a dispersed layer of impregnants on the surface of the carbon. However, with an increase in impregnant loading, it was observed that the impregnants start to form larger particles. When this occurs, more intense diffraction peaks for the impregnants were observed.^{3,36} The porosities of CuO and ZnO IACs have also been previously evaluated.³⁶ BET adsorption studies determined that for CuO IACs with a 21% impregnant loading, there was less than a 25% reduction of the micropore volume of the material relative to unimpregnated carbon.³⁶ The determination of porosities and surface activities of the other IACs will be the subject of future work

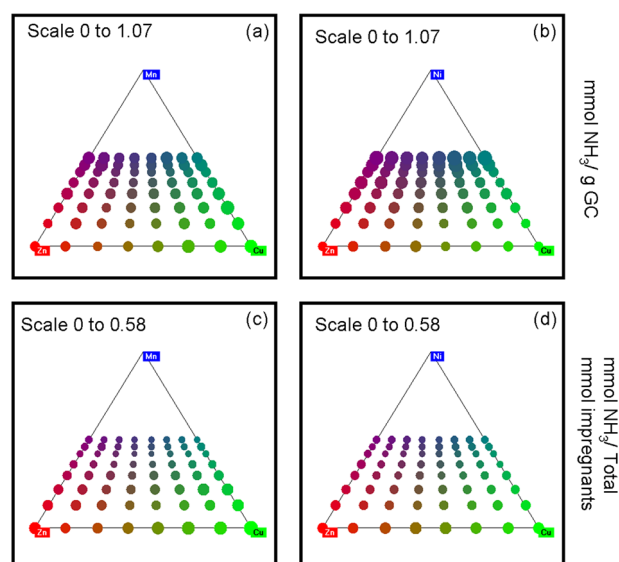


Figure 5. NH_3 gas adsorption performance of the ternary libraries of $\text{CuO}/\text{ZnO}/\text{Mn}_3\text{O}_4$ and $\text{CuO}/\text{ZnO}/\text{NiO}$. Panels a and c are the gas adsorption capacity and the stoichiometric ratio of reaction for the $\text{CuO}/\text{ZnO}/\text{Mn}_3\text{O}_4$ library. Panels b and d are the gas adsorption capacity and the stoichiometric ratio of reaction for the $\text{CuO}/\text{ZnO}/\text{NiO}$ library.

2.2.1. Ternary $\text{CuO}/\text{ZnO}/\text{Mn}_3\text{O}_4$ Impregnated Activated Carbons. A ternary library consisting of 64 IAC samples impregnated with various combinations of CuO , ZnO , and Mn_3O_4 was evaluated. Figures 4 and 5 show the gas adsorption properties of the materials. The diameter of the data points in Figures 4 and 5 is proportional to amount of gas adsorbed. The base of each of the plots corresponds to CuO or ZnO IACs as in $(\text{CuO})_{1-x}(\text{ZnO})_x$. The gas adsorption properties of materials that are impregnated only with Cu and Zn do not change significantly with x in $(\text{CuO})_{1-x}(\text{ZnO})_x$.^{7,8}

Figure 4a shows the SO_2 gas adsorption capacity for $\text{CuO}/\text{ZnO}/\text{Mn}_3\text{O}_4$ IACs. An increase in SO_2 adsorption was observed when the composition of the impregnant changed from 1.2 mmol of $(\text{CuO})_{1-x}(\text{ZnO})_x/\text{g GC}$ and no Mn (represented by the data points at the bottom of the plot) to 2.4 mmol of total impregnant added/g GC with the addition of 50% Mn (represented by the data points at the topmost portion of the graph). Equivalent SO_2 adsorption capacities were observed for all combinations of CuO , ZnO , and Mn_3O_4 IACs with similar impregnant loading and are represented by samples that corresponded to each row of data points. The opposite trend was observed for the NH_3 adsorption properties of these materials. Figure 5a shows that despite the increase in the Mn content of the material (topmost data points), the NH_3 gas adsorption capacity became slightly lower compared to the capacities calculated for $(\text{CuO})_{1-x}(\text{ZnO})_x$ IACs (bottom row of data points).

Figures 4c and 5c show the SRRs of the materials for both gases. Figure 4c shows that the SO_2 /metal ratio increases with the addition of Mn . These materials adsorbed more SO_2 relative to the binary impregnated materials ($(\text{CuO})_{1-x}(\text{ZnO})_x$ IACs). Figure 5c shows a decrease in the ratio between mmol of NH_3 gas adsorbed and the total mmol metal. The ability of these materials to adsorb NH_3 gas is compromised when Mn is added. This trend is not surprising considering that IACs containing only Mn show a decreased ability to adsorb NH_3 (Figure 2c and 2d).

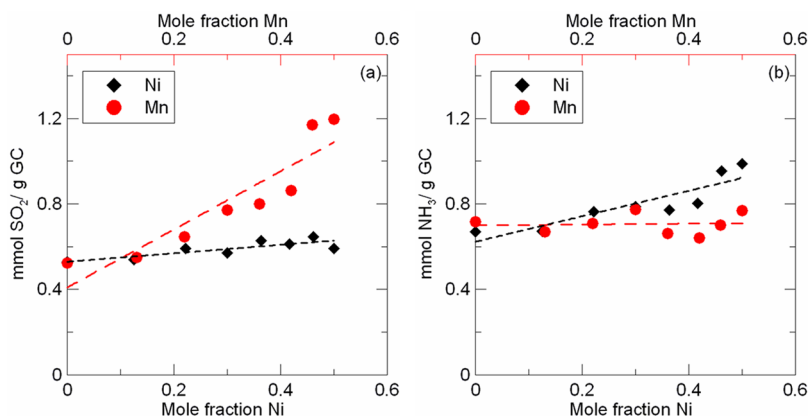


Figure 6. Calculated (a) SO_2 and (b) NH_3 gas adsorption capacities (in mmol gas/g GC) of samples impregnated with similar proportions of CuO to ZnO (0.7 mmol CuO/g AC and 0.5 mmol ZnO/g AC) plotted against the molar fraction of either Mn_3O_4 or NiO added. A best fit line was drawn for each set of data points.

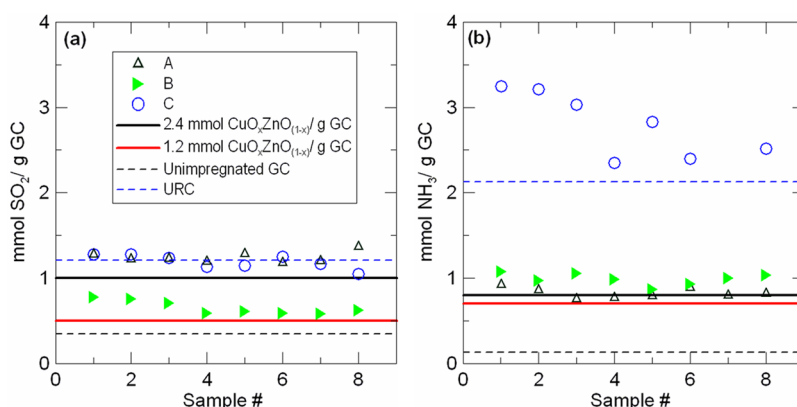


Figure 7. Calculated (a) SO_2 and (b) NH_3 gas adsorption capacities (in mmol gas/g GC) of various impregnated activated carbon samples containing 2.4 mmol M/g GC (Data points labeled A, B, and C). Data points labeled A (black open triangle) correspond to samples containing 1.2 mmol $(\text{CuO})_x(\text{ZnO})_{(1-x)} + 1.2$ mmol Mn/g GC. Data points labeled B (green horizontal triangle) represent materials with 1.2 mmol $(\text{CuO})_x(\text{ZnO})_{(1-x)} + 1.2$ mmol Ni/g GC. These materials were compared to IACs from a previously reported ternary (data points labeled C (blue open circle)) containing 1.2 mmol $(\text{CuO})_x(\text{ZnO})_{(1-x)} + 1.2$ mmol CuCl_2 /g GC.^{8,9} A summary of the compositions for each of the samples labeled 1 to 8 is given in Table 1.

2.2.2. Ternary CuO/ZnO/NiO Impregnated Activated Carbons. IACs with added NiO behaved differently compared to the ternary materials where Mn was added. Figure 4b shows that the SO_2 adsorption of the CuO/ZnO/NiO IACs increased at a slower rate with the addition of Ni than with Mn (compared to Figure 4a). Figure 5b shows only an improvement in NH_3 adsorption of these materials with an increase in Ni content.

Figures 4d and 5d show a decrease in SRR's of the materials containing Ni. Despite the small improvement in gas adsorption of the Ni containing ternaries, the materials do not perform as efficiently as the Mn ternaries in the adsorption of both the SO_2 and NH_3 gases since the SRRs tend to be lower.

Figure 6 shows sections of Figures 4a, 4b, 5a, and 5b to demonstrate the effect of the addition of a third impregnant on the gas adsorption behavior of the materials. Representative samples containing 0.7 mmol CuO + 0.5 mmol ZnO/g GC with the addition of incremental amounts of either Mn (red circle) and Ni (black diamond) were selected. The selected data points show a three-component series of materials and do not necessarily indicate optimum compositions. A best fit line was drawn for each data set to highlight the trend observed.

Figure 6a shows that the slope for the SO_2 adsorption of the Cu/Zn/Mn ternaries is greater than the slope for the Cu/Zn/Ni ternaries proving that Mn addition has a larger impact on SO_2 adsorption. Figure 6b shows a flat best fit line for the data points corresponding to the NH_3 adsorption of CuO/ZnO/ Mn_3O_4 IACs indicating that Mn does not affect NH_3 adsorption in this ternary.

Figure 6 shows that SO_2 adsorption of Cu and Zn based impregnants can be enhanced by Mn additions with small effects in the NH_3 adsorption capacity of the materials demonstrating the compatible nature of the impregnants. By contrast, Figure 6 shows that Ni improves NH_3 adsorption and does not strongly affect SO_2 adsorption.

2.3. Gas Adsorption Behavior of Mn and Ni Ternary Systems Compared to Previously Studied Ternary Systems. Different combinations of impregnants impart differences in the adsorption behavior of the resulting materials. Ideally, the amount of gas adsorbed increases with an increase in impregnant loading for both SO_2 and NH_3 gases regardless of the type and combination of impregnant used, which implies the compatibility of materials used in gas adsorbent formulations.^{7,8} For example, in the studies made on ZnO, CuO, and CuCl_2 combinations, it was determined that these

materials are capable of adsorbing both SO₂ and NH₃ gases and that suitable impregnant materials were used.^{8,9} It was also determined from these studies that ZnO and CuO IACs behave similarly as SO₂ and NH₃ gas adsorbents regardless of their combinations.^{7–9} Therefore, materials containing 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC were used as a starting point for all the combinations in all ternary libraries being investigated. In this section, evaluations of ternary Mn or Ni combinations with a loading of 2.4 mmol impregnant/g GC was performed by comparing the gas adsorption capacities of these materials with the previously reported ternary CuCl₂ combinations with a similar loading. The results were also compared with the standards used in the combinatorial studies and instead of showing several ternary diagrams side by side, portions (top and bottom rows) of the libraries have been picked and combined into two graphs (Figure 7).

Figure 7 shows the data points in the top row of each of the ternary diagrams shown in Figures 4a, 4b, 5a, and 5b. Figure 7 also includes a portion (top row) of the previously reported CuO/ZnO/CuCl₂ ternary library.^{8,9} Figure 7 shows the average gas adsorption capacities of unimpregnated GC (black dashed line) and the benchmark URC material (blue dashed line) used as standards in all of the ternary libraries. An average of the data points in the bottom row of the ternary libraries represent materials containing 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC and are shown in the graphs as a red solid line. The gas adsorption behavior of materials impregnated with 2.4 mmol M/g GC (data points labeled A, B and C in the graphs) were plotted relative to the average gas adsorption capacities of the materials with 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC (in red solid line) to show the effect of doubling the impregnant loading by the addition of a third component that is neither CuO nor ZnO. The results were compared to the average values obtained for materials impregnated with 2.4 mmol (CuO)_x(ZnO)_(1-x)/g GC shown in the graphs as a black solid line.

In the graphs, data points labeled A, B, and C represent IAC materials, wherein a third component (1.2 mmol M/g GC) has been added to materials containing 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC, where M is either Mn (black open triangle), Ni (green horizontal triangle), or CuCl₂ (blue open circle). The composition of each of the 2.4 mmol M/g GC samples in Figure 7 are given in Table 1.

Figure 7a shows the SO₂ capacity of the samples. The graph shows that for materials containing only CuO, ZnO or

(CuO)_x(ZnO)_(1-x), the SO₂ capacity doubled from 0.5 to 1.0 mmol SO₂/g GC when the impregnant loading was doubled from 1.2 to 2.4 mmol/g GC. When the 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC were fortified with an additional 1.2 mmol/g GC of either CuCl₂ (blue open circle)^{8,9} or Mn (black open triangle) the SO₂ capacity more than doubles and even perform as well as the benchmark URC material. The addition of 1.2 mmol Ni/g GC (green horizontal triangle), however, only caused a small increase in the SO₂ capacity relative to the IACs impregnated with only 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC. This means that the addition of Ni does not help improve the materials adsorption for SO₂ gas.

Figure 7b shows the NH₃ adsorption for the same materials. From the graph, materials with 1.2 mmol (CuO)_x(ZnO)_(1-x)/g GC (red solid line) adsorbs about 0.7 mmol NH₃/g GC. Doubling the amount of impregnant to 2.4 mmol (CuO)_x(ZnO)_(1-x)/g GC slightly increased the NH₃ adsorption to 0.8 mmol/g GC. Similar results were obtained with the addition of 1.2 mmol Mn/g GC (black open triangle). Slightly higher values were calculated for IACs impregnated with an additional 1.2 mmol Ni/g GC (green horizontal triangle). The change in the NH₃ gas adsorption capacity brought about by the addition of either Mn or Ni is not quite as significant as the increase in the NH₃ adsorption capacity when 1.2 mmol CuCl₂/g GC was added (blue open circle).^{8,9} In fact, the samples with CuCl₂ outperformed the benchmark URC product. In summary, it was found that it may be more beneficial to use Mn as a coimpregnant with ZnO/CuO IAC compared to Ni and such materials may be a more viable combination in multigas adsorbent formulations.

2.4. Powder XRD Analysis of the Impregnated Activated Carbon Samples. The impregnant phases for representative unexposed samples from the CuO/ZnO/Mn₃O₄ and CuO/ZnO/NiO ternary systems were analyzed by powder XRD and a correlation between the gas adsorption behavior and the impregnant phase present can be made. Figure 8 shows the powder XRD (pXRD) patterns acquired for each of the representative samples. Table 2 shows a summary of the composition of the samples analyzed by pXRD and lists the predominant impregnant phases observed for these samples.

Figure 8 shows samples impregnated with 1.2 mmol/g GC of either CuO, (CuO)_{1-x}(ZnO) or ZnO indicated by the patterns in red (bottom graphs in each panel). Diffraction peaks consistent with the CuO, ZnO, and broad humps at 2θ = 26.4 and 2θ = 42.2 associated with the activated carbon support were observed and were consistent with what was previously observed in section 2.1.^{37–39}

Figure 8 also shows the patterns (top graphs colored black in each panel) acquired for samples impregnated with an additional 1.2 mmol M/g GC of either Mn (panels a–c) or Ni (panels d–f). The predominant diffraction peaks observed for samples with either Mn or Ni were a match to CuO and ZnO as well as the amorphous carbon humps.^{37–39}

In Figure 8 (panels a–c), the absence of Mn₃O₄ diffraction peaks in Mn-containing IACs shown in the patterns drawn in black, may be an indication that the Mn oxides are decomposed into an amorphous Mn₃O₄ or into highly dispersed Mn₃O₄ layer on the surface of the activated carbon. It is likely that the high activity of these materials for SO₂ adsorption is due to highly dispersed nature of the Mn₃O₄ impregnant consistent to what was previously reported in literature.³ The diffraction patterns for materials containing Ni in Figure 8 (panels d–f) do not show diffraction peaks for NiO. However a close inspection

Table 1. Summary of the Composition for Each of the Samples Impregnated with an Additional 1.2 mmol/g GC of Mn or NiO and Compared with Samples with CuCl₂ (from ref 9) Shown in Figure 6

sample	composition (mmol/g GC)			total
	ZnO	CuO	X*	
1	0.00	1.20	1.2	2.4
2	0.20	1.00	1.2	2.4
3	0.35	0.85	1.2	2.4
4	0.50	0.70	1.2	2.4
5	0.70	0.50	1.2	2.4
6	0.85	0.35	1.2	2.4
7	1.00	0.20	1.2	2.4
8	1.20	0.00	1.2	2.4

*Where X is the third component and may either be CuCl₂, Mn, or Ni as shown in Figure 6.

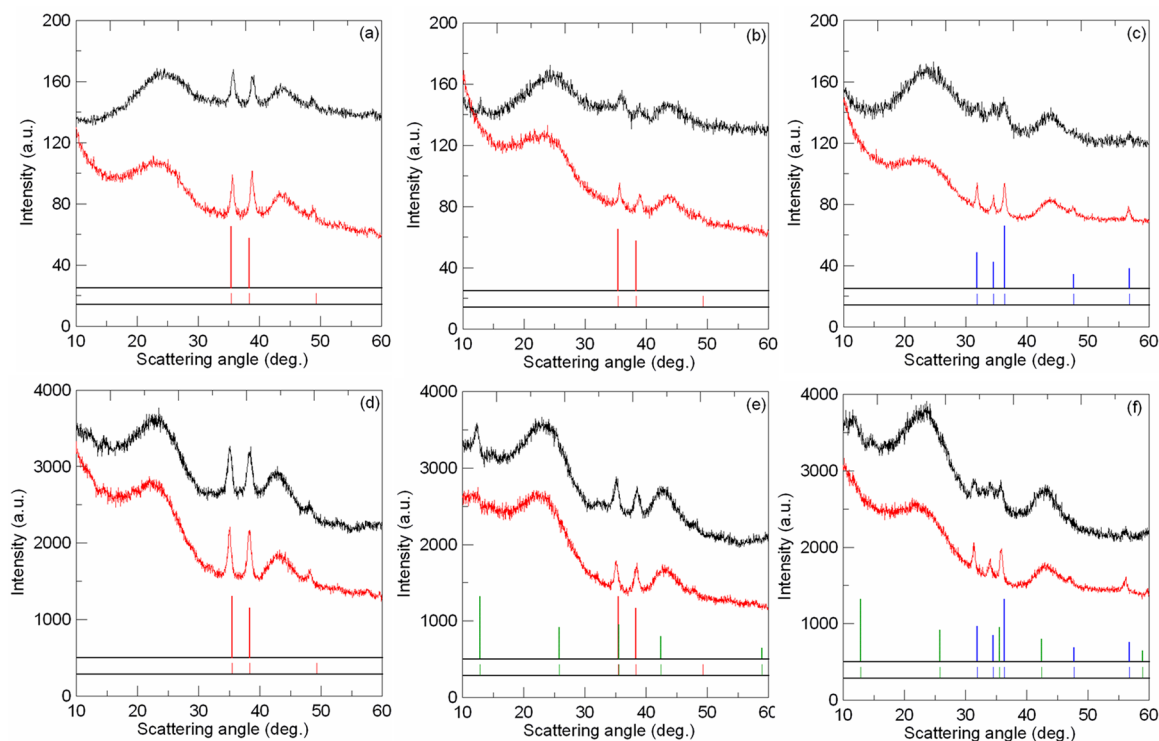


Figure 8. Powder diffraction patterns obtained for representative unexposed samples containing 1.2 mmol impregnant/g GC (plots in red) and similar impregnated samples wherein an additional 1.2 mmol of either Mn or Ni/g GC has been added (plots in black) heated at 200 °C for 2 h, under Ar. The diffraction peaks observed were matched to the most intense reflections for CuO (bar graph in red), ZnO (bar graph in blue), and $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (bar graph in green).^{39,40}

Table 2. Summary of the Composition and the Identified Impregnant Phases from the Representative Combinatorial Samples Shown in Figure 7^a

panel	composition (mmol M/g GC)				total	phases identified in samples using powder XRD
	Zn	Cu	Mn	Ni		
diffraction patterns shown in red (bottom graphs in each panel in Figure 7)						
a, d	0	1.2	0	0	1.2	CuO with disordered C
b, e	0.5	0.7	0	0	1.2	CuO with disordered C
c, f	1.2	0	0	0	1.2	ZnO with disordered C
diffraction patterns shown in black (top graphs in each panel in Figure 7)						
a	0	1.2	1.2	0	2.4	CuO with disordered C
b	0.5	0.7	1.2	0	2.4	CuO with disordered C
c	1.2	0	1.2	0	2.4	ZnO with disordered C
d	0	1.2	0	1.2	2.4	CuO with disordered C
e	0.5	0.7	0	1.2	2.4	CuO, $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ with disordered C
f	1.2	0	0	1.2	2.4	ZnO, $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ with disordered C

^aThe diffraction peaks were matched to the most intense reflections for CuO, ZnO, and $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (refs 38–40).

of the patterns shown in panels e and f reveals a peak at a scattering angle of 12.8° which may be consistent with the most intense diffraction peak associated with the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ phase (bar graph in green).⁴⁰ This is in contrast with what was observed from the diffraction pattern of samples impregnated solely with $\text{Ni}(\text{NO}_3)_2$ (section 2.1), which shows broad humps where diffraction peaks for NiO are expected (Figure 1d). When combined with other impregnants such as Cu or Zn nitrates, the $\text{Ni}(\text{NO}_3)_2$ does not decompose completely to NiO

at 200 °C. The presence of the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ suggested incomplete decomposition to NiO which could explain the observed low SO_2 and NH_3 gas adsorption behavior for the binaries and ternaries containing Ni (Figure 7) and help explain the trends observed in Figures 4–6.

Figure 9 shows XRD patterns for representative CuO/ZnO/NiO ternary samples heated at 250 °C. Heating at a higher temperature promotes the reduction of CuO to form Cu_2O as indicated in the plots drawn in red in panels a and b of Figure 9.^{38,41} The loss of the diffraction peak at a scattering angle of 12.8° associated with $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ for samples impregnated with an additional 1.2 mmol of Ni/g GC (plots drawn in black) confirms that for CuO/ZnO/NiO combinations, heating at 200 °C is not enough for the complete conversion of $\text{Ni}(\text{NO}_3)_2$ to NiO to occur.⁴⁰ However, it is not clear from the diffraction patterns that reflections for NiO are present.⁴² It is likely that NiO may be also fully dispersed on the surface of the carbon. For these ternary combinations, when strong diffraction peaks were observed, the impregnant was assumed to form larger particles on the macropore and mesopore wall surfaces similar to that reported in ref 3. The measurement of the active surface area and porosities for these materials will be the subject of a future work.

CONCLUSION

The addition of a third active component on CuO/ZnO-based impregnated activated carbon through combinatorial methods, improved the gas adsorption performance of these materials for either SO_2 or NH_3 . The addition of Mn in the form of highly dispersed Mn_3O_4 increased the adsorption capacity for SO_2 . The addition of Ni showed only small improvements in the both SO_2 and NH_3 gas adsorption. The combinatorial method

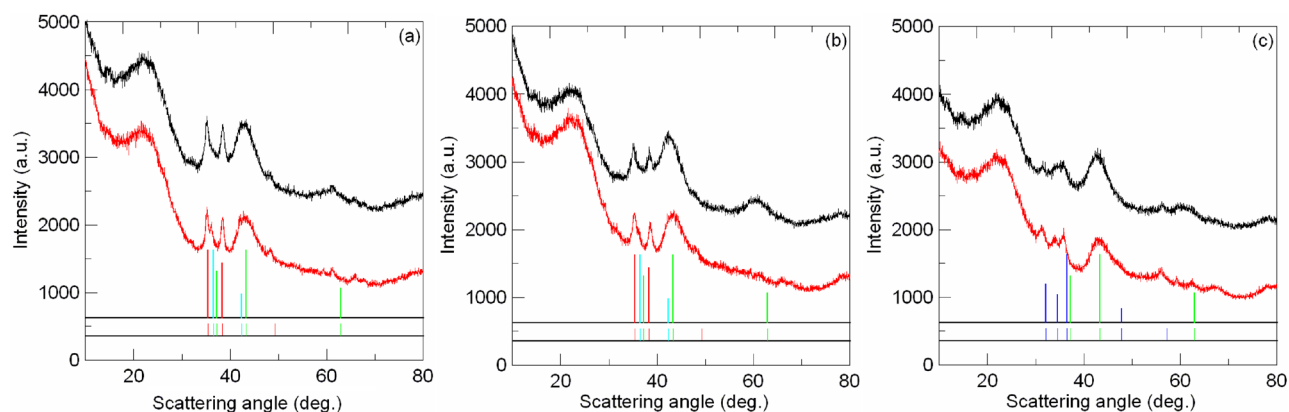


Figure 9. Powder diffraction patterns obtained for representative unexposed samples containing 1.2 mmol impregnant/g GC (bottom plots in red) and similar impregnated samples, wherein an additional 1.2 mmol of Ni/g GC has been added (top plots in black) heated at 250 °C for 2h, under Ar. The diffraction peaks observed were matched to the most intense reflections for CuO (bar graph in red), ZnO (bar graph in blue) and Cu₂O (bar graph in green)^{39–41}. Reflections associated with NiO were not observed.⁴²

allowed a large number of materials to be screened and for correlations between impregnant composition and gas adsorption properties to be developed.

■ ASSOCIATED CONTENT

📄 Supporting Information

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

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Notes

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