Highly Porous Carbon Xerogels Doped with Cuprous Chloride for Effective CO Adsorption

Qiong Zhu, Xiaodong Wang,* Dong Chen, Xueling Wu, Chen Zhang, Wenbing Zou,* and Jun Shen*

School of Physics Science and Engineering & Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, Tongji University, Shanghai 200092, P. R. China

ABSTRACT: Carbon monoxide (CO) has long been recognized as a metabolic waste and toxic gas and is also the most common asphyxiating poison that seriously endangers human health. Thus, an adsorption material with high CO adsorption capability is urgently needed. In this study, carbon xerogels (CXs) doped with CuCl were prepared via a sol–gel method and a facile soaking process. The CuCl-doped CXs show the highest CO adsorption capacity of 12.04 cc/g, which is much higher than those of the undoped CXs and activated carbon. Such a high adsorption capacity of the CuCl-doped CXs is not only because of their high porosity but also because of the chemical adsorption induced by CuCl. Moreover, these CuCl-doped CXs exhibit high desorption rate (∼79%), which is beneficial for repeatability.

1. INTRODUCTION

Carbon monoxide (CO) is a widely distributed pollutant in the atmosphere, which is easily produced due to the incomplete combustion of carbonaceous substances in coal stoves, gas water heaters, automobile engine, and cigarettes.1–4 In many cases, CO is generally not easy to draw people’s attention because of its colorless and odorless properties and causes many hazards.5,6 The acute CO poisoning is one of the most common causes of death due to accidental poisoning. It is reported that at least 15 200 individuals need to seek medical advice for CO poisoning every year in the United States.7 Therefore, scientists have started to study innovative materials that could adsorb CO. However, widely studied CO adsorption materials show unsatisfactory adsorption performance. These CO adsorbents like activated carbon (AC),12–14 zeolites,15 molecular sieves,16–17 metal oxides,18 and metal–organic frameworks19 still need to be improved. Among them, a Y-type molecular sieve needs to be heated at a certain temperature for the effective adsorption of CO. Moreover, molecular sieves are particularly susceptible to moisture and can only be used for temperature swing adsorption due to the high energy consumption and complicated operating steps. This is disadvantageous to the realization of pressure swing adsorption. The activated alumina calcined by aluminum hydroxide shows the unique properties such as high specific surface area (SSA), abundant pores, high thermal stability, and strong acid resistance, but its dispersion and adsorption capacity are relatively poor. Activated carbon, as a kind of porous material, has shown great application in gas adsorption due to the high specific surface area; however, the surface nature of activated carbon is easily affected by the hydrophobic and lipophilic properties of the surface and it is chemically unstable. Therefore, exploring an absorbent with high specific surface area and stable structural properties to enhance the ability to absorb CO is worthy and meaningful. To date, the methods for enhancing the adsorption performance of adsorbents can be divided into two categories: regulating the pore size and pore volume of the adsorbent and doping some metals (such as Cu, Ag, Pt, Fe, Pd, etc.) to introduce some active sites onto the surface of the adsorbent for the adsorption of CO.

Carbon aerogels, as a type of nanocarbon material first synthesized in 1989 by Pekala,20 have many unique advantages including high porosity, high specific surface area, strong structural controllability, and a wide range of density variation.21–24 Based on these advantages, the carbon aerogels can be used as a good absorbent to absorb CO gas. However, the adsorption of CO with carbon aerogels is a physical process. Physical adsorption is a weak adsorption process carried out by van der Waals force. The adsorption speed is fast, and the adsorption equilibrium can be reached instantaneously. Unfortunately, the adsorption capacity of physical adsorption is limited and relatively low, which cannot meet the demands for the absorption of CO in the practical application. Chemical adsorption is a strong adsorption process in which a chemical reaction occurs between the adsorbent and the adsorbate because of the action of the chemical bonding. The adsorption capacity of chemical adsorption is much higher than that of physical adsorption. Therefore, the introduction of chemical adsorption in adsorbents can further enhance the CO adsorption performance of the adsorbent materials. Transition metal ions including Cu¹, Ag¹, and Ni¹ can react with CO to generate the complexes; this reaction is a chemical adsorption process.
and more stable than physical adsorption. According to the reported research results, Cu⁺ has a better adsorption performance than Ag⁺ and Ni⁺. Therefore, the introduction of Cu⁺ into the carbon aerogels is expected to enhance the adsorption performance.25,26

In this work, we used resorcinol (R) and formaldehyde (F) as raw materials and sodium carbonate anhydrous as a catalyst to prepare the CuCl-doped carbon xerogels (CXs) by a sol–gel method and a facile soaking process. When used to adsorb CO, the CXs doped with CuCl show a better adsorption performance than undoped CXs and active carbon. Appropriate doping contents of CuCl can achieve the highest CO adsorption capacity. The enhanced adsorption performance of CXs doped with CuCl can be attributed to the high specific surface area and introduced CuCl that generates complex adsorption.

2. EXPERIMENTAL SECTION

2.1. Materials. Resorcinol (≥99.5%, AR), formaldehyde aqueous solution (37–40%, AR), sodium carbonate anhydrous (≥99.8%, AR), alcohol (≥99.7%, AR), hydrochloric acid (36–38%, AR), and cuprous chloride (≥97%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of CuCl-Doped Carbon Xerogels (CXs). The synthetic pathway of CuCl-doped CXs mainly involved six components: resorcinol (R), formaldehyde (F) aqueous solution, sodium carbonate anhydrous, alcohol, hydrochloric acid, and cuprous chloride. The molar ratio of R and F is set to 1:2. The fabrication process is divided into two steps, as shown in Figure 1. Step 1 involves the synthesis of CXs monoliths. A certain amount of R was dissolved into the deionized water to make R aqueous solution. The F aqueous solution and sodium carbonate were then added to R aqueous solution successively with stirring for 2 h. After stirring, wet resorcinol–formaldehyde (RF) gels were obtained. The wet RF gels were aged in an oven at 30 °C for 1 day, 50 °C for 1 day, and 90 °C for 3 days, respectively. The aged RF gels were then washed in alcohol solution for a week at room temperature. After washing, the gels were stored in a beaker and dried at 50 °C for a week under atmospheric pressure. Finally, the CXs were obtained by carbonization of RF xerogels at 1000 °C for 4 h under the protection of a N₂ atmosphere. Step 2 involves the synthesis of CuCl-doped CXs monoliths. First, certain amounts of CuCl and HCl were mixed with water to obtain CuCl–HCl solution. Second, the CXs were immersed in CuCl–HCl solution and the solution was kept in an oven at 50 °C for 12 h to evaporate the solvent; this process needs to be repeated three times. At length, the CuCl-doped CXs were acquired after heating at 50 °C for 48 h under ambient pressure drying.

To simply distinguish CuCl-doped CXs prepared with various contents of CuCl, all samples were denoted “CX–CuCl-x”, where CX is the abbreviation of CXs and x represents the mass ratio of CuCl and CX.

2.3. Characterization. The morphology of the samples was observed using scanning electron microscopy (SEM, Philips-XL30FEG) and transmission electron microscopy (TEM, JEM2-100F).

The N₂ adsorption–desorption isotherms of the samples were measured at 77 K by a N₂ adsorption–desorption analyzer (TriStar 3000). The specific surface areas (SSAs) were calculated by the Brunauer–Emmett–Teller method. The compositions of the samples were characterized by X-ray diffraction (XRD, D8 ADVANCE), energy-dispersive X-ray spectroscopy (EDS, Philips-XL30FEG), mapping (Philips-XL30FEG), and X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi). The CO adsorption–desorption capacities of active carbon, CXs, and CuCl-doped CXs were evaluated by a gas sorption analyzer (ASAP2460). The FTIR spectra of doped and undoped CXs before and after CO adsorption and desorption were determined by Fourier transform infrared spectrometry (FTIR, TENSOR 27).

3. RESULTS AND DISCUSSION

3.1. Macroscopic and Microscopic Structure of CXs and CuCl-Doped CXs. The macrostructure of samples CX and CX–CuCl-2.5 was shown in Figure 2. The ambient pressure-dried CX shows a black and unbroken monolith shape. After doping, the CX still retains a good integrity, as displayed in Figure 2b, which indicates that the macrostructures of sample CXs show no obvious changes after the soaking process.

The microstructures of CXs and CuCl-doped CXs were characterized by SEM and TEM, as shown in Figure 3. It is obviously observed from Figure 3a–c that CXs and CuCl-doped CXs are composed of carbon nanoparticle interconnected aggregates. Compared to the sample CX, both CX–CuCl-1 and CX–CuCl-2.5 have less pores and a more continuous network structure, which is ascribed to the interference of CuCl in the soaking process. The preservation of the unique microstructure for samples CA–CuCl-1 and CA–CuCl-2.5 will facilitate the adsorption of CO. The combination between CAs and CuCl does not affect the microstructure of CuCl-doped carbon aerogels.
As displayed in TEM images (Figure 3d–f), the doped and undoped CXs display a three-dimensional network structure. The solid phase is composed of interconnected carbon nanoparticles with particle size ranging from 15 to 30 nm. After doping with CuCl, the CXs still retain a continuous and homogeneous network structure. The above analysis demonstrates that samples CX, CX−CuCl-1, and CX−CuCl-2.5 possess a porous, cross-linked, and uniform network structure, which is beneficial for CO adsorption.

3.2. Pore Structure of CXs and CuCl-Doped CXs.

Figure 4 shows the N₂ adsorption–desorption isotherms and the corresponding pore size distributions of samples CX, CX−CuCl-1, and CX−CuCl-2.5. As shown in Figure 4a–c, all of the isotherms of the doped and undoped CXs exhibit a type IV isotherm with an H3-type hysteresis loop, which illustrates the characteristics of mesoporous materials, whereas these prepared samples possess micropores under low pressure. The detailed pore structure parameters are presented in Table 1. After the doping of CuCl, the specific surface areas of CX−CuCl-1 and CX−CuCl-2.5 decrease from 441 to 108 and 97 m²/g, respectively. As shown in Figure 4d–f, the mesopore (2–50 nm) and micropore (<2 nm) size distributions of samples were calculated using the NLDFT method. In the range of mesopores, the curves of samples CX, CX−CuCl-1, and CX−CuCl-2.5 show no significant difference, which indicates that the undoped and doped CXs have a similar mesoporous structure. However, the CX has a higher micropore size distribution peak compared to those of doped CXs. These results illustrate that CuCl-doped CXs possess less

| sample        | specific surface area (SSA) (m²/g) | microporous SSA (m²/g) | average pore size (nm) | density (g/cm³) |
|---------------|-----------------------------------|------------------------|------------------------|----------------|
| CX            | 441                               | 362                    | 2.45                   | 0.33           |
| CX−CuCl-0.5   | 133                               | 32                     | 8.98                   | 0.35           |
| CX−CuCl-1     | 108                               | 28                     | 11.09                  | 0.42           |
| CX−CuCl-2.5   | 97                                | 13                     | 22.46                  | 0.50           |
| CX−CuCl-3.5   | 95                                | 9                      | 23.59                  | 0.58           |
| activated carbon | 82                                   | 7                      | 23.76                  |                |
micropores, which is ascribed to the filling of partial mesopores of CXs in the soaking process. Moreover, the CXs doped with CuCl (CX−CuCl-1 and CX−CuCl-2.5) have a much smaller microporous specific surface area (28 and 13 m²/g, respectively), which confirms to the result of pore size distribution. As presented in Table 1, the bulk density of the doped CXs is larger compared to that of undoped CXs and the bulk density of CuCl-doped CXs rises with the increasing content of CuCl. Although the increase of the content of CuCl is helpful for CO adsorption, the number of micropores decreases and the microstructure of samples gets denser compared to that of pure CXs, which can also be confirmed by the SEM and TEM images in Figure 3. Thus, the introduction of only appropriate contents of CuCl into the CXs can give better CO adsorption capacity to the doped CXs. The combination between the high porosity of CX and strong CO adsorption capacity of CuCl is extremely essential and valuable.

3.3. Composition Characterization of CuCl-Doped CXs. The EDS results of CX−CuCl-1 and CX−CuCl-2.5 are presented in Figure 5a,b. It is obviously observed that the C, Cu, and Cl elements play a dominant role in samples CX−CuCl-1 and CX−CuCl-2.5 and no other elements appear. The weight percent (wt %) of the Cu and Cl elements increase from 9.63 and 13.89 to 13.52 and 17.13, respectively, which is in accordance with the change of the bulk density of doped CXs, as shown in Table 1. To further characterize the dispersion of CuCl in CXs, the EDS mapping of CX−CuCl-2.5 was performed, as shown in Figure 5c. The elements of Cu and Cl almost completely cover the C element, revealing that the CuCl components are homogeneously wrapped on the surface of CXs. Moreover, the mapping trajectories of sample CX−CuCl-2.5 are consistent with those of C and Cl elements, which also indicate that the CuCl was uniformly dispersed in CXs.

The crystal structures of CX, CX−CuCl-1, and CA−CuCl-2.5 were further characterized by XRD. According to the XRD results, the pure CX exhibits two distinct peaks at 2θ = 24 and 44°, corresponding to the {002} and {101} planes (Figure 6a). These two typical peaks demonstrate that the CX is an amorphous and short-range ordered carbon material. The interlayer spacing calculated from the 2θ value (24°) at the peak position of CX was d₀₀₂ = 0.368 nm, which is larger than that of the graphite (d₀₀₂ = 0.335 nm), revealing that there is a graphitized microcrystalline structure in CX. After doping with CuCl, new peaks at 30.9, 33, 50.5, and 57° appear, which correspond to the diffraction peaks of CuCl. These peaks strengthen with the increase of the content of CuCl. To further confirm the existence of Cuo, the Cu 2p XPS spectra of CX−CuCl-2.5 were characterized and are shown in Figure 6b. It is clearly seen that there are two types of copper ions (Cuo and Cu²⁺) in the sample CX−CuCl-2.5. The peaks at 932.60 and 952.45 eV correspond to Cuo species, whereas the bands at 934.75 and 954.65 eV are associated with Cu²⁺ species. The area ratios of Cuo and Cu²⁺ in the Cu 2p₃/₂ and Cu 2p₁/₂ XPS spectra are 1.14 and 0.96, respectively. The existence of Cuo species in CuCl-doped CXs makes the CuCl-doped samples to have excellent characteristic of CO adsorption.

3.4. CO Adsorption−Desorption Performance of CuCl-Doped CXs. Before the CO adsorption and desorption measurement, the samples were degassed at 200 °C. The adsorption−desorption isotherms represent the relationship between adsorption−desorption capacity and the relative pressure. The CO adsorption−desorption isotherms of CuCl-doped CXs, CX, and activated carbon (AC) are shown in Figure 6. As presented in Figure 7a, the CO adsorption capacity of CuCl-doped CXs first increases and then reduces with the increasing content of CuCl. This is due to that the excess CuCl fills the pores of CX, which causes the reduction of specific surface area of doped CXs (see Table 1). It makes
the physical adsorption capacity to drop considerably. Therefore, a desirable combination between CO physical adsorption and chemical adsorption induced by CuCl can only be obtained in an appropriate CuCl doping. The optimal sample (CX–CuCl-2.5) can reach a highest CO adsorption capacity of 12.04 cc/g, which is about 150 and 280% that of the pure CXs (8.19 cc/g) and AC (4.27 cc/g), respectively.

As shown in Figure 7b, from the desorption isotherms of samples, we can clearly see that although the desorption rate of the CuCl-doped CXs (∼79%) is not as high as that of CX (∼88%) and AC (∼90%), it is enough to meet the repeatability that is required in the practical application. In general, the desorption rate of CuCl-doped CXs decreases with the increase of the CuCl content due to more complexes formed by the reaction between Cu⁺ and CO. However, the CuCl-doped CXs still retain a high desorption rate because of the small addition of CuCl. The CO gas adsorption reported in the literature and industry focuses on the interaction of CO molecules and Cu⁺. Here, Cu−C bonds are formed after the interaction of the CuCl-doped CXs and CO molecules. The introduction of Cu⁺ into CX can improve the CO adsorption capacity considerably and hardly affect the desorption capacity of samples. The high CO adsorption capacity of CuCl-doped CXs benefits from the combination of physical and chemical adsorption, whereas CXs and AC can only depend on physical adsorption.

FTIR spectra of samples CX and CX–CuCl-2.5 before and after adsorption of CO are shown in Figure 8. It can be observed that the spectra of CX and CX–CuCl-2.5 are very similar, revealing that they feature a similar chemical structure that is formed after the adsorption of CO. The broad peak at 3440 cm⁻¹ is ascribed to the stretching vibration of hydroxyl (−OH). The existence of −OH may be due to the adsorbed water on the surface of samples. The absorption peaks at around 2903 and 2962 cm⁻¹ are assigned to the stretching vibrations of −CH₃ and −CH₂, respectively, whereas the band at around 1369 cm⁻¹ is attributed to the scissor vibration of −CH₂ and flexural vibration of −CH₃. The band at 1620 cm⁻¹ is due to the stretching vibration of aromatic rings. The absorption peak of methylene-ether (CH₂−O−CH₂) is observed at 1094 cm⁻¹. The cross-linked CH₂−O−CH₂ bond is formed between aromatic rings because of polycondensation. These results illustrate that the chemical groups of CX and CX–CuCl-2.5 before the adsorption of CO are consistent with those after the adsorption of CO, indicating the stability of the CXs.

4. CONCLUSIONS

In summary, we prepared the CXs doped with different amounts of CuCl by a sol−gel method combined with a facile soaking process. The pore structure and morphology characterization reveals that the introduction of CuCl does not destroy the network structure of the CXs, and there is no obvious clustering of CuCl in the framework of CXs. CO adsorption performance of CXs doped with different amounts of CuCl was measured. The sample CX–CuCl-2.5 shows the highest CO adsorption capacity of 12.04 cc/g, which is about 150 and 280% that of the pure CXs (8.19 cc/g) and activated carbon (4.27 cc/g), respectively. These results demonstrate that the CO adsorption of CuCl-doped CXs is the dual effect of physical adsorption and chemical adsorption. In addition, these CuCl-doped CXs exhibit high desorption rate (∼79%), which will make them a good candidate for the effective solution of “CO pollution” in this field.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: xiaodong_wang@tongji.edu.cn (X.W.).
*E-mail: shenjun67@tongji.edu.cn (J.S.).

ORCID
Xiaodong Wang: 0000-0003-1942-4236
Wenbing Zou: 0000-0002-6278-6163

Notes
The authors declare no competing financial interest.

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