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# Selective CO Adsorption by CuCl-FeCl<sub>2</sub>@USY Adsorbents with Good Antioxidant Ability

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> Abstract. Separation and purification of CO from industrial tail gas is an important way to achieve resource recycling, with important economic and social benefits. The adsorption separation of CO technology has the advantages of simple process, high degree of automation, convenient operation, and low energy consumption, Cu(I) based adsorbents are commonly used as CO adsorbents due to the  $\pi$  complexation interaction with CO molecules, however, they are prone to oxidative deactivation. In this study, the reductive metal salts were loaded onto the Cu(I) based adsorbents in order to further improve their antioxidant capacity. A series of reduced metal salt doped Cu(I) based adsorbents were prepared using CuCl<sub>2</sub> as precursor, activated carbon as reducing agent and reduced metal salts as antioxidants and the prepared adsorbents were characterized by SEM, XRD and N<sub>2</sub> adsorption/desorption tests. The results show that the reduced metal salt FeCl<sub>2</sub> doped Cu(I) based adsorbent exhibits a better antioxidant performance, and the adsorption of CO remains 55% of the original amount after placing it in the atmosphere for 12 h. Moreover, the adsorbent shows high CO adsorption capacity and adsorption selectivity as well as good cycling stability.

Keywords. CuCl-FeCl<sub>2</sub>@USY, CO, π complexation adsorption, anti-oxidation

## 1. Introduction

Carbon monoxide (CO) is an important chemical raw material and can be synthesized into a variety of chemical products, such as acetic acid, phosgene and methyl formate [1]. CO mainly comes from natural gas reforming gas, water gas, semi-water gas, and a variety of industrial waste gas also contains CO, such as coke oven gas, calcium carbide furnace tail gas and yellow phosphorus tail gas [2]. The recovery of CO from these industrial waste gases is not only used as an important source of carbon chemistry, but also can alleviate exhaust pollutants in industrial production. However, CO usually coexists with other substances, so in order to obtain high purity CO, it is necessary to purify and separate industrial waste gases. Compared with traditional separation methods, adsorption separation method has the advantages of low energy consumption and simple operation, and is considered a promising method for the CO separation [3].

The adsorption capacity of  $\pi$ -complexation adsorbents for CO is stronger than that of traditional physical adsorbents, while the  $\pi$ -complexation bond can be easily broken

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at high temperature or low pressure, so as to facilitate the recovery of adsorbents. Currently, Cu(I) based  $\pi$ -complexation adsorbents are widely used for the CO separation. Initially, monovalent copper salts were directly introduced into porous materials to prepare Cu(I) based adsorbents. However, due to the easy oxidation and deactivation of Cu<sup>+</sup> ions in the air, the operating conditions were harsh [4]. Subsequently, divalent copper salts were used as precursors to prepare Cu(I) based adsorbents, and the reducing gas CO or H<sub>2</sub> was used to reduce Cu<sup>2+</sup> ions to Cu<sup>+</sup> ions. However, CO and H<sub>2</sub> have strong reducing ability, and making it difficult to accurately control the degree of reduction [5]. Therefore, it is a great urgency to develop a more gentle and safe reduction method to achieve the reduction of Cu<sup>2+</sup> ions to prepare Cu(I) based adsorbents.

In addition, due to the problem of susceptibility to oxidation of Cu(I) based adsorbents, the reducing metal ions have a higher oxidation potential than  $Cu^+$  ions, which can protect the Cu(I) ions active sites. Therefore, in this work, a series of reduced metal salts doped modified CuCl loaded adsorbents were prepared using CuCl<sub>2</sub> as the precursor, ultra-stable Y-type molecular sieve (USY) as the carrier, activated carbon as the reducing agent, and reduced metal salt as the antioxidants. The adsorbents were characterized using XRD, SEM and N<sub>2</sub> adsorption/desorption tests, and the effects of the type and amount of reducing metal salts on the CO adsorption performance and oxidation resistance of the adsorbents were systematically studied. In addition, the CO adsorption selectivity and reusability of the adsorbent were also investigated.

## 2. Experimental

## 2.1. Preparation of Reduced Metal Salts Doped Modified CuCl Loaded Adsorbents

In this work, a series of reducing metal salts doped CuCl loaded USY adsorbents were prepared by impregnation method using CuCl<sub>2</sub> as precursor, USY as support, activated carbon as reducing agent, and reducing metal salts as antioxidants. As an example, the reduced metal salt FeCl<sub>2</sub> doped CuCl loaded adsorbent was prepared: USY (5 g) and activated carbon (0.8 g) were weighed and placed in a mixed solution containing FeCl<sub>2</sub> (1.0 g) and CuCl<sub>2</sub> (25 mmol), and the obtained sample was treated with activated reduction in N<sub>2</sub> atmosphere at 523 K for 4 h, and the final CuCl-FeCl<sub>2</sub> loaded adsorbent was obtained, which was named as CuCl-FeCl<sub>2</sub>(x)@USY. In addition, according to the above steps, FeCl<sub>2</sub> was replaced with NiCl<sub>2</sub>, MnCl<sub>2</sub>, SnCl<sub>2</sub>, obtaining CuCl-NiCl<sub>2</sub> loaded adsorbent, respectively, and named as CuCl-NiCl<sub>2</sub>(x)@USY, CuCl-MnCl<sub>2</sub>(x)@USY and CuCl-SnCl<sub>2</sub>(x)@USY, respectively, where x represents the amount of reducing metal salts (g).

#### 2.2. Adsorption Measurements

The CO,  $CO_2$  and  $N_2$  adsorption isotherms were obtained from a static volumetric adsorption capacity measuring device, and the detailed operation and calculation processes have been reported in our previous works [6].

#### 3. Results and Discussion

## 3.1. Adsorption of CO by Reducing Metal Salts Doped Modified CuCl Loaded Adsorbents

Figure 1 shows the CO adsorption capacity of CuCl-FeCl<sub>2</sub>(1.0)@USY, CuCl-NiCl<sub>2</sub>(1.0)@USY, CuCl-MnCl<sub>2</sub>(1.0)@USY and CuCl-SnCl<sub>2</sub>(1.0)@USY before and after exposure to air for 12 h. As can be seen from figure 1, all four reducing metal salts doped CuCl based adsorbents exhibits high CO adsorption capacity. After being placed in the atmosphere for 12 h, the CO adsorption capacity of the adsorbents was reduced due to the partial oxidation of the active component CuCl. Among the four adsorbents, the adsorption capacity of CuCl-FeCl<sub>2</sub>(1.0)@USY was significantly better than that of the other adsorbents, and 55% of the original adsorption capacity was still maintained after being placed in the atmosphere for 12 h, indicating that the introduction of the reducing metal salt FeCl<sub>2</sub> could effectively inhibit the oxidation of CuCl. Therefore, in this paper, the adsorbent CuCl-FeCl<sub>2</sub>@USY was selected to further investigate its CO adsorption performance.



Figure 1. Adsorption equilibrium isotherms of CO at 303 K for adsorbents doped with different reducing metal salts before and after 12 h of exposure to air.

Figure 2 shows the adsorption isotherms of CO on adsorbents CuCl-FeCl<sub>2</sub>(0.8)@USY, CuCl-FeCl<sub>2</sub>(1.0)@USY, and CuCl-FeCl<sub>2</sub>(1.2)@USY at 303 K. As can be seen from figure 2, the CO adsorption capacity of the adsorbent increases first and then decreases with the increase of FeCl<sub>2</sub> loading, indicating that the adsorption performance of the adsorbents can be improved by increasing the FeCl<sub>2</sub> loading within a certain range. However, due to the limited loading capacity of the carrier USY, too much FeCl<sub>2</sub> will block the pores and affect the adsorption of CuCl. The above results show that when the loading amount of FeCl<sub>2</sub> is 1.0 g, CuCl-FeCl<sub>2</sub>(1.0)@USY exhibits a better adsorption performance for CO.



Figure 2. CO adsorption equilibrium isotherms on adsorbents with different FeCl<sub>2</sub> loadings at 303 K.

#### 3.2. Characterizations of CuCl-FeCl<sub>2</sub>@USY Samples

Figure 3 shows the SEM images of (a) USY support and (b) CuCl-FeCl<sub>2</sub>(1.0)@USY. As can be seen from figure 3(a), the USY support used in this work is composed of particles with a particle size of 400-500 nm, and the surface of the particles is rough, resulting in a large specific surface area of the USY carrier, which is conducive to the loading of active components. As can be seen in figure 3(b), the surface morphology of CuCl-FeCl<sub>2</sub>(1.0)@USY is not significantly different from that of the USY carrier, which suggests that CuCl and FeCl<sub>2</sub> have been highly dispersed in the pores of the USY carrier.



Figure 3. SEM images of (a) USY support and (b) CuCl-FeCl<sub>2</sub>(1.0)@USY adsorbent.

Figure 4 shows the XRD patterns of USY carrier and  $CuCl_2$ -FeCl<sub>2</sub>(1.0)@USY before and after activation. As shown in figure 4,  $CuCl_2$ -FeCl<sub>2</sub>(1.0)@USY before and after activation showed the same diffraction peaks as USY support, which indicates that the structure of USY is not destroyed during the impregnation and activation process. For the sample  $CuCl_2$ -FeCl<sub>2</sub>(1.0)@USY, diffraction peaks of  $CuCl_2$  and FeCl<sub>2</sub> were detected. For the adsorbent CuCl-FeCl<sub>2</sub>(1.0)@USY, only the diffraction peaks of USY were observed and no diffraction peaks of  $CuCl_2$  and FeCl<sub>2</sub> were detected, indicating that  $CuCl_2$  and FeCl<sub>2</sub> have been highly dispersed on the surface of the USY carrier during the activation treatment of the sample and  $CuCl_2$  has been completely reduced to CuCl.



Figure 4. XRD patterns of USY support and CuCl<sub>2</sub>-FeCl<sub>2</sub>(1.0)@USY before and after activation.

Figure 5 shows the equilibrium isotherms of  $N_2$  adsorption/desorption on USY support and CuCl-FeCl<sub>2</sub>@USY samples with different FeCl<sub>2</sub> loadings at 77 K. As shown in figure 5, the adsorption capacity of  $N_2$  on support USY is relatively high, and after loading CuCl and FeCl<sub>2</sub>, the  $N_2$  adsorption gradually decrease with the increase in FeCl<sub>2</sub> loading. In addition, hysteresis loops can be clearly observed in the  $N_2$ 

adsorption/desorption isotherm of USY, which suggests that the USY carrier contains a mesoporous structure, which is conducive to the loading of the active components.



Figure 5. Equilibrium isotherms of  $N_2$  adsorption/desorption at 77 K for USY support and CuCl-FeCl<sub>2</sub>@USY samples with different FeCl<sub>2</sub> loadings.

#### 3.3. Adsorption Selectivity

Figure 6(a) shows the adsorption equilibrium isotherms of CuCl-FeCl<sub>2</sub>(1.0)@USY for single component CO, CO<sub>2</sub> and N<sub>2</sub> at 303 K. As can be seen from figure 6(a), the adsorption capacity of CuCl-FeCl<sub>2</sub>(1.0)@USY for CO are significantly higher than that for CO<sub>2</sub> and N<sub>2</sub>, which is due to strong  $\pi$ -complexation interaction formed between the adsorbent and CO, while the adsorbent is weakly physisorbed with CO<sub>2</sub> and N<sub>2</sub>. In addition, based on the single-component adsorption equilibrium isotherms of CO, CO<sub>2</sub> and N<sub>2</sub>, the adsorption selectivity of the adsorbent for the equimolar binary gas mixtures of CO/CO<sub>2</sub> and CO/N<sub>2</sub> was calculated by using the ideal adsorbent solution theory (IAST) [7], and the results are shown in figure 6(b). The adsorbent has high selectivity for CO, which indicates that the prepared CuCl-FeCl<sub>2</sub>(1.0)@USY can effectively separate and recover CO from the mixture containing CO<sub>2</sub> and N<sub>2</sub>.



Figure 6. (a) Adsorption equilibrium isotherms of CO,  $CO_2$  and  $N_2$  by CuCl-FeCl<sub>2</sub>(1.0)@USY at 303 K, (b) adsorption selectivity of CuCl-FeCl<sub>2</sub>(1.0)@USY for CO/CO<sub>2</sub> and CO/N<sub>2</sub> systems at 303 K.

## 3.4. Cyclic Stability

In this section, five CO adsorption/desorption tests were conducted on the same adsorbent to investigate the cyclic stability of the adsorbent CuCl-FeCl<sub>2</sub>(1.0)@USY, and the results are shown in figure 7. The adsorption capacity of the adsorbent for CO does not change significantly during the five adsorption/desorption cycling operations,

which indicates that the prepared CuCl-FeCl<sub>2</sub>(1.0)@USY has a good cycling stability, and it can be used repeatedly for CO adsorption and desorption operations.



Figure 7. Cyclic adsorption capacity of CuCl-FeCl<sub>2</sub>(1.0)@USY for CO at 303 K and 500 kPa.

#### 3.5. Isosteric Adsorption Heat of CO on CuCl-FeCl<sub>2</sub>(1.0)@USY Adsorbent

Figure 8(a) shows the adsorption isotherm of CO by CuCl-FeCl<sub>2</sub>(1.0)@USY at different temperatures. As shown in figure 8(a), the adsorption capacity of the adsorbent for CO decreases with increasing temperature, which indicates that the adsorption process is exothermic. In addition, based on the adsorption equilibrium isotherms at different temperatures, the isosteric adsorption heat of CO on the adsorbent was calculated by the Clausius-Clapeyron equation [8], and the results are shown in figure 8(b). The adsorption heat of CuCl-FeCl<sub>2</sub>(1.0)@USY for CO decreases with increasing CO adsorption amount, indicating the energy heterogeneity of the USY support surfaces. The initial adsorption calorific value is 75 kJ/mol, indicating that the  $\pi$  complex interaction between CuCl-FeCl<sub>2</sub>(1.0)@USY and CO is between physical and chemical adsorption, and thus the adsorbent has a good CO adsorption capacity and adsorption selectivity.



**Figure 8.** (a) CO adsorption equilibrium isotherm of CuCl-FeCl<sub>2</sub>(1.0)@USY adsorbent at different temperatures, (b) the isothermal adsorption heat of CuCl-FeCl<sub>2</sub>(1.0)@USY adsorbent for CO adsorption.

#### 4. Conclusion

In this work, a series of CuCl loaded USY adsorbents doped with the reducing metal salts were prepared using USY as support,  $CuCl_2$  as precursor, activated carbon as activating reducing agent, and reducing metal salts as antioxidants. Activated reduction in a N<sub>2</sub> atmosphere at 523 K for 4 h resulted in the complete reduction of  $CuCl_2$  to CuCl, and CuCl and FeCl<sub>2</sub> were highly dispersed in the pores of the USY. CuCl-

FeCl<sub>2</sub>(1.0)@USY shows better antioxidant capacity, and after being placed in the atmosphere for 12 h, the its adsorption capacity for CO can still maintain the original 55%. In addition, the adsorbent exhibits high CO adsorption capacity, better adsorption selectivity, and good cyclic stability.

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