Low-temperature Selective Catalytic Reduction of NO with NH₃ over CuOₓ/CNTs Catalyst

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Abstract. The metal oxide catalyst was prepared by loading CuOₓ on carbon nanotubes (CNTs) with impregnation method. The catalyst was characterized by BET, TEM and XPS, and the catalytic activity of the catalyst for selective catalytic reduction (SCR) of NO was investigated. The results showed that the species of active components loaded on the catalyst was given priority to with CuO. The NO conversion was improved with temperature increase under the range of 150 to 300°C. The oxygen content had an outstanding influence on the NO conversion of catalysts at lower concentration range. Once the oxygen content was enhanced over 5%, there was no significant increase. Increasing of mole ratio of NH₃/NO could increase the NO conversion. When mole ratio of NH₃/NO was continued to exceed 1.1, the NO conversion decreased. With the increasing of space velocity, the NO conversion was decreased under the reaction conditions.

1. Introduction
NOₓ is one of the most predominant pollutants. It has become important to reduce the emission of nitrogen oxides from both stationary and mobile combustion technologies in order to keep the health of humans and protect environment. Among various NOₓ emission control techniques, selective catalytic reduction (SCR) of NO with NH₃ in the presence of excess oxygen has been proven to be the most effective which is widely used. It has been proved that the catalyst being prepared through supported metallic oxides are with good catalytic performance. Various metal oxide based catalysts have been shown to possess some potential for low temperature application, including Fe₂O₃, CuO, Co₂O₃, Mn₂O₃, CeO₂, V₂O₅, etc.. Due to the carbon material with excellent surface properties, the carbon-supported catalysts have the very good performance. Among the reported catalysts, metal oxides supported on carbon materials (activated carbon, activated coke, activated carbon fiber) have shown very high activity. As a novel carbon material, carbon nanotubes (CNTs) have attracted much attention due to their unique electric, mechanical and structural characteristics. It has been widely studied in fields of high strength carbon fiber materials[1], hydrogen storage materials [2-4], new catalytic materials [4-8], etc. With the tunable pore structure and surface properties and the large specific surface area, CNTs have been regarded as the perfect supporting materials for catalysts. Meanwhile, due to one-dimensional tubular structure of CNTs, catalytic materials with specific properties can be prepared in the cavity of tubular. So as a new catalytic material, CNTs have caused attention of many researchers [9-12]. Fe/CNTs, Mn-FeOₓ/ CNTs, Fe₂O₃/CeO₂ catalysts have been investigated the catalytic performance for the selective catalytic reduction of NO with NH₃[13-16]. Cu is one of the typically studied transition metals in SCR catalysts. Also, copper oxides are found to be
active in medium temperature SCR of NO. The reduction of Cu$^{2+}$ to Cu$^{+}$ is a possible reason for catalyst deactivation at low temperatures [17].

Therefore, it can be an issue deserved intensive study to make use of CNTs to develop low temperature de-NOx catalyst. This research prepared CuO$_x$/CNTs catalyst through supported copper oxide on the CNTs after purification. We have investigated copper oxide supported on the CNTs catalysts as low-temperature SCR catalysts.

2. Materials and methods

2.1. Catalyst preparation

The raw CNTs were purified by means of immersion in a 65% of HNO$_3$ solution and refluxed at boiling point for 4 to 6 h. Then the sample was washed with distilled water till pH 6 to 7, and dried at 110 °C for 12 h. The supported CuO$_x$/CNTs catalysts were prepared by impregnation method. The CNTs after purification was impregnated in different concentrations of cupric nitrate solution at room temperature for 24 h, then dried at 110 °C for 12 h. And after grind, the CNTs were calcified at 500 °C nitrogen atmosphere for 5 h.

2.2. Catalyst characterization

The specific surface area and pore volume of the CNTs and CuO$_x$/CNTs catalysts were analyzed by an TRISTAR II 3020M which can be determined through N$_2$ absorption method. The pore volume was calculated using the BET method. A JEM-1200EX transmission electron microscope was used for TEM which acceleration voltage is 120 kv and magnification is 0~200000. XPS analysis was carried out by making use of AXIS Ultra-type X-ray photoelectron spectroscopy (England Kratos).

2.3. Catalytic activity tests

The catalytic activity tests were carried out in a fixed bed reactor made of stainless steel in the 150 to 300°C range. The gas composition was 450 ppm NO, 500 ppm NH$_3$, 5% O$_2$ balanced by N$_2$. The total flow rate was 500 ml•min$^{-1}$. The experimental apparatus of evaluation of the catalytic activity tests included sections of gas configuration, catalytic reaction and flue gas analysis, which was shown in Figure 1.

![Experimental apparatus for activity tests](image_url)

Figure 1. Experimental apparatus for activity tests

NO concentrations in the inlet and outlet gases were measured by flue gas analyzer (KM940, Kane). The NO conversion was calculated from the NO concentration at the inlet and outlet of the reactor. Before starting the activity measurements, the CuO$_x$/CNTs catalysts were degasified under N$_2$ flow at 120°C for 1 h. Afterwards, the activity tests were performed under isothermal conditions. Steady-state the NO conversion was observed when the NO concentration at the outlet of the reactor became steady, several hours after the reaction started.
3. Results and discussion

3.1. Catalyst characterization

The surface area, pore volume and pore size (inner diameters) of the CNTs after purification and CuOx/CNTs catalyst were listed in Table 1. The surface area, pore volume, and mean pore size of catalyst slightly decreased about 34% compared with the data of CNTs after purification, which illustrated that the metallic oxide was loaded on the surface of carrier after impregnation and calcification. Due to the block of pore by metallic oxide, the surface area, pore volume, and mean pore size all decreased. It can be proposed that the active component was already loaded on the surface of CNTs.

| Samples           | \(S_{\text{BET}} / \text{m}^2 \, \text{g}^{-1}\) | \(S_{\text{meso}} / \text{m}^2 \, \text{g}^{-1}\) | Pore volume / \(\text{cm}^3 \, \text{g}^{-1}\) | Mean pore size / nm |
|-------------------|---------------------------------|---------------------------------|---------------------------------|---------------------|
| CNTs after purification | 145.1517                        | 123.4085                        | 0.776334                       | 23.7064             |
| CuOx /CNTs catalyst | 96.2612                         | 84.0927                         | 0.482603                       | 16.3087             |

Figure 2. TEM image of carbon nanotubes: (a) after oxidized by nitrate acid; (b) 20% CuOx/CNTs

Figure 2 showed the TEM image of CNTs-after purification and CuOx/CNTs catalyst, in which the HNO₃ treatment made most of the carbon nanotubes open (Figure 2a), which leads to an increase of the surface areas. For CuOx/CNTs catalyst, CuOx particles were located on the wall of the tubes (Figure 2b). The metal oxide particles loaded on the CNTs was evenly on the surface of the carrier. Future researches should be worthy to be carried out to reveal the effect between the catalyst activity and the metal oxide particle dispersion.
Figure 3. XPS spectra of the CuOx/CNTs: (a) CuOx/CNTs, (b) Cu (2p), (c) O(1s)

Figure 3 illustrated the surface element concentration of CuOx/CNTs catalyst by XPS spectra, in which (a), (b), and (c) were separately CuOx/CNTs catalyst spectra, Cu(2p) spectra and O(1s) spectra. The catalyst XPS spectra showed three obvious peaks, the peak of 934 eV was the absorption peak of cuprum; the binding energy in the middle peak was 530 eV, which was the absorption peak of oxygen; peak with the biggest binding energy was 284 eV, which was the absorption peak of carbon. The surface element concentrations of CuOx/CNTs catalyst sample measured by XPS were 90.44% of C, 5.9% of O, 3.3% of Cu. It can be seen from Figure 3b that the biggest absorption peak was 934 eV corresponded to CuO. Therefore, the combination form of metallic oxide was given priority to with CuO.

3.2. SCR activity of CuOx/CNTs catalyst

Figure 4. Effect of reaction temperature on the activity of CuOx/CNTs

Figure 4 presented the NO conversion of CuOx/CNTs catalyst at different temperature. The result indicated that all catalysts reached to the highest NO conversion rate when in temperature of 300°C. The NO conversion of catalyst prepared with different impregnation concentrations increased rapidly with the rise of temperature under the temperature range of 150 to 300°C. During the process of the SCR, rising temperature would lead to the reaction rate of the NO conversion increased. The consumption of NH3 was mainly for NO reduction reaction, and NO conversion rate increased rapidly. After that, continue to rise the reaction temperature, NO reaction would be restricted for the occurrence of NH3 oxidation reaction because rising temperature made the NH3 oxidation reaction easily occurred.
Figure 5. Effect of O₂ concentration on NO removal over CuOₓ/CNTs

Figure 5 showed the effect of oxygen content on SCR activity of CuOₓ/CNTs catalyst. The result showed that the NO conversion increased with increasing of oxygen content at each reaction temperature. With increasing oxygen content from 1% to 5%, the NO conversion increases rapidly. At 300°C the NO conversion increased rapidly from 39% to 87%. However, no obvious change was observed when the O₂ concentration exceeded 5%. The NO conversion remained stable basically. This indicated that O₂ played a significant promoting role in the SCR reaction. Gas phase oxygen and adsorbed oxygen species achieved a balanced state when the O₂ concentration reached 5%.

Figure 6. Effect of n(NH₃)/n(NO) on NO removal over CuOₓ/CNTs

Figure 6 illustrated the influence of NH₃/NO mole ratio on NO reduction at different temperatures (150 to 300°C). The result showed that the NO conversion increased with increasing of NH₃/NO mole ratio in the range of ratios from 0.7 to 1.1. When the NH₃/NO mole ratio continued to exceed 1.1, the NO conversion decreased. For NH₃/NO mole ratio <1.1, increasing of NH₃/NO mole ratio could increase the unit mass of NH₃ adsorption quantity on the catalyst. So the SCR reaction rate was accelerated. But excessive NH₃ cannot be adsorbed on catalyst. NH₃ was reacted with NO, which could lead to the decease of the NO conversion.
Figure 7. Effect of space velocity on NO removal over CuOx/CNTs

Figure 7 presented the effect of space velocity on the NO conversion at different temperatures (150 to 300°C). The NO conversion all tended to decrease with the increase of space velocity under all the experimental temperatures. However, when reaction happened in 150°C, the NO conversion decreased rapidly with the increase of space velocity. While the NO conversion remained unchanged and then decreased slowly under the temperature range of 150 to 300°C. Which illustrated that higher reaction temperature can weaken the effect of space velocity on the NO conversion. Furthermore, the NO conversion rose constantly with the rising of temperature under each space velocity. The higher the space velocity was, the shorter time the reactant gas stayed on catalyst. At a high space velocity, the decrease in the NO conversion may result from insufficient contact time between the reactants and the catalyst or from insufficient amounts of active sites to react.

4. Conclusions

The CNTs after purification was impregnated in different concentrations of cupric nitrate solution. The metallic oxide was loaded on the surface of CNTs after impregnation and calcification. Due to the block of pore by metallic oxide, the surface area, pore volume, and mean pore size all decreased. The metal oxide particles loaded on the CNTs was evenly on the surface of the carrier. Future researches should be worthy to be carried out to reveal the effect between the catalyst activity and the metal oxide particle dispersion.

During the SCR reaction process of CuOx/CNTs catalyst, rising temperature would lead to the reaction rate of the NO conversion increased. Continue to rise the reaction temperature, NH3 oxidation reaction would happen, the reduction reaction of NO would be restrained, the NO conversion rate started to slow down. O2 played a significant promoting role in the SCR reaction. The NO conversion increased with increasing of oxygen content at each reaction temperature. The oxygen content caused a prominent affect on catalyst at lower oxygen content. Once the O2 concentration exceeded 5%, the NO conversion remained stable basically. For NH3/NO mole ratio<1.1, increasing of NH3/NO mole ratio could increase the unit mass of NH3 adsorption quantity on the catalyst. The NO conversion increased. When the NH3/NO mole ratio continued to exceed 1.1, the NO conversion decreased. The NO conversion all tended to decrease with the increase of space velocity under all the experimental temperatures. Higher reaction temperature can weaken the effect of space velocity on the NO conversion. The higher the space velocity was, the shorter time the reactant gas stayed on catalyst.

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