Preparation and Performance of Binary Copper-Cobalt Based Catalyst Used for Low Temperature Selective Catalytic Reduction of NO\textsubscript{X}

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Abstract. Low-temperature urea-SCR technology is a new type of low temperature denitration technology, which could achieve the removal of NO\textsubscript{X} in low temperature (50–100°C) flue gas, and avoid the ammonia escape problem of traditional NH\textsubscript{3}-SCR technology. In this paper, a series of binary Cu-Co based composite catalysts with different Cu-Co loading ratios (0.1: 0.9–0.9: 0.1) were prepared at calcination temperatures of 300–600°C, and their preparation parameters were optimized. The experimental results showed that when the calcination temperature was 500°C and the Cu-Co loading ratio was 0.9: 0.1, the Cu-Co-based binary catalyst had the highest low-temperature denitration performance. Finally, the XRD analysis of the phase composition for the Cu\textsubscript{0.9}Co\textsubscript{0.1}/NUAC catalyst was carried out in this paper.

1. Introduction

Nitrogen oxides (NO\textsubscript{X}) are one of the main sources of air pollution. NO\textsubscript{X}, mainly composed of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}), is an important factor in the formation of photochemical smog and acid rain. At the same time, NO\textsubscript{X} are also the main pollutant causing environmental problems such as greenhouse effect, acid rain and ozone layer destruction, which will cause great harm to human, environment and ecology [1–3]. Therefore, reducing NO\textsubscript{X} emissions is one of the important considerations in process production, especially in the thermal power industry and the steel industry.

At present, the commonly used flue gas denitration technologies include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). [4] SCR technology uses the reducing agent to selectively react with NO\textsubscript{X} in flue gas, thereby achieving the purpose of purifying NO\textsubscript{X} in flue gas. Compared with SNCR technology, SCR technology has the advantages of high denitration efficiency. Currently, the NH\textsubscript{3}-SCR technology using NH\textsubscript{3} as a reducing agent has been successfully applied to the flue gas in the thermal power industry, but the reaction temperature window of this technology (350–450°C) is high [5–7], which is not suitable for low-temperature sintering flue gas in the steel industry (50–100°C). Moreover, urea can also be used as the reducing agent for SCR technology. Compared with NH\textsubscript{3}, urea has the advantages of easy storage and large reduction amount. However, for the traditional urea SCR technology, the reducing agent is urea solution, which is decomposed into NH\textsubscript{3} at high temperature and reacts with NO\textsubscript{X} in flue gas. Therefore, the essence of traditional urea SCR technology is still NH\textsubscript{3}-SCR technology, which is not suitable for low
temperature sintering flue gas. Seker et al have researched the Pt and Au catalysts supported on Al$_2$O$_3$ [8]. Both Pt and Au are precious metals, which is not conducive to industrial applications.

Low-temperature urea-SCR technology is a new type of low-temperature denitration technology, which can realize the removal of NO$_X$ from low-temperature (50–100°C) flue gas. Aiming at low-temperature urea-SCR technology, Shoreham [9] and Lu [10] et al studied catalysts for removing NO from air at room temperature. Liu et al [11, 12] studied activated carbon supported unary catalysts used in low temperature flue gas at 50–100°C. According to our current research, in this paper, a series of binary Cu-Co based composite catalysts containing different Cu-Co loading ratios (0.1: 0.9–0.9: 0.1) were prepared at the calcination temperature of 300–600°C, and their preparation parameters were determined. In addition, the microstructure of the carrier and the phase composition of the catalyst were also studied.

2. Experimental part

2.1. Preparation of catalyst

Firstly, the nutshell activated carbon (NUAC) was pretreated in a tube furnace and baked at 200 °C for 4 hours in N$_2$ atmosphere to fully remove the water absorbed on the activated carbon surface and easy to decomposable impurities; then, the activated carbon was added to concentrated nitric acid, stirred at room temperature for 3 hours. The pickled activated carbon was repeatedly washed to neutral (pH=6–7) by a large amount of deionized water, filtered and dried in a drying box at 110°C for 12 hours. Finally, the 100-200 mesh activated carbon particles were selected as the carrier of the catalyst by grinding.

Active metal oxides (CuO$_X$ and CoO$_X$) were loaded on NUAC carrier by ultrasonic-assisted equal volume impregnation method. The NUAC carrier was impregnated in metal nitrate precursor solution, vibrated by ultrasonic for 2 h, then placed at room temperature for 12 h, and finally dried at 90°C for 12 h. The sample was calcined in N$_2$ atmosphere for 3 h at specified calcination temperatures (300, 400, 500 and 600°C). Then, urea was loaded on the catalyst by equal volume impregnation method, and the mixture containing urea solution and catalyst was placed at room temperature for 12 h, and then the mixture was dried at 50°C for 5 h to obtain the final sample. In the above preparation process, the total amount of supported active metal oxides is controlled to 12 wt%, and the amount of urea supported is controlled to 6 wt% by weight. The CuO$_X$/CoO$_X$ loading ratio of the Cu-Co based binary catalyst includes 0.1: 0.9–0.9: 0.1, which is uniformly named Cu$_x$Co$_{(1-x)}$/NUAC (x ranges from 0.1–0.9).
2.2. Evaluation of catalyst activity

The catalyst evaluation system used in this research is shown in Figure 1. The simulated flue gas used in the experiment is made up of 550 ppm NO, 16% O₂ and N₂. The total gas flow is 10,000 mL/h, the air flow rate is 5000 mL/(h·g) with the 50 – 100°C reaction temperature. The concentration of NOₓ in the flue gas at the end of the reactor is measured by a flue gas analyser. The performance evaluation index of the catalyst used in the low-temperature urea-SCR technology is the average NOₓ conversion within 5 h:

\[ \text{NO}_{x} \text{ Conversion} = \frac{c(\text{NO}_{x \text{ in}}) - c(\text{NO}_{x \text{ out}})}{c(\text{NO}_{x \text{ in}})} \times 100\% \]

In the formula, NOₓ contains NO and NO₂; c(\text{NO}_{x \text{ in}}) is the concentration of NOₓ in the inlet gas, ppm; c(\text{NO}_{x \text{ out}}) is the concentration of NOₓ in the gas at the reactor outlet, ppm.

2.3. Characterization method of catalyst

In order to obtain the micro-surface morphology of the NUAC carrier, the micro-surface morphology and structure of NUAC carrier were analysed by field emission scanning electron microscope (Zeiss Ultra Plus). The phase composition of NUAC carrier and catalyst were analysed by X-ray diffract meter (XRD-7000). In this study, the specific surface area and pore structure parameters of the carrier and catalyst were studied by Nova1200e automatic physical adsorption instrument.
3. Experimental results and discussion

3.1. Low-temperature denitration activity of pure urea

Figure 2. The NO\textsubscript{$X$} breakthrough curve of pure urea dispersed on quartz wool

In order to investigate the reaction of pure urea with NO\textsubscript{$X$} at low temperature in the absence of a catalyst, this section studies the denitration ability of 0.12g urea powder under experimental atmosphere (10000 mL/h, 550 ppm NO, 16% O\textsubscript{2}, N\textsubscript{2}). For the purpose of preventing the urea powder from falling out of the reactor, the urea powder was supported on inert quartz cotton in the experiment. Figure 2 records the NO\textsubscript{$X$} penetration curve of pure urea in the experimental atmosphere in the absence of a catalyst at 50°C. From the NO\textsubscript{$X$} concentration change curve, it can be seen that when the reactor containing pure urea passes the experimental gas mixture, the presence of NO\textsubscript{$X$} is immediately detected in the gas at the outlet; in addition, the NO\textsubscript{$X$} concentration at the outlet of the reactor continues to increase and quickly reaches the concentration at the entrance (550 ppm), and the corresponding NO\textsubscript{$X$} removal rate is reduced to 0. It indicates that in the absence of a catalyst, pure urea does not have the ability to denitrate at low temperatures, which also illustrates the necessity of the catalyst in low-temperature urea-SCR technology.

3.2. Comparison of unary/binary catalysts

Figure 3 shows the low-temperature denitration activity at 50°C of the unary catalyst and the binary composite catalyst prepared at a calcination temperature of 400°C. The comparison of the NO\textsubscript{$X$} concentration at the outlet of the reactor shown in Figure 3 and Figure 2 proved the necessity of the presence of the catalyst in the low-temperature urea-SCR process. It can be seen from Figure 3 that during the low-temperature denitration process, the NO\textsubscript{$X$} concentration at the outlet of both the unary and the binary composite catalyst increase slowly with the progress of the reaction; Comparing the average NO\textsubscript{$X$} conversion of the unary catalyst and the Cu-Co based binary composite catalyst in Figure 3, it was found that when the total active metal oxide loading was the same (12 wt%), the low temperature denitration performance of the binary composite catalyst was higher than that of the unary catalyst, which indicated that there was a catalytic synergism among different active metal oxides at the binary catalyst.
3.3. Effect of preparation parameters on Cu-Co based binary Catalyst

In the process of optimizing the preparation parameters of Cu-Co based binary catalysts, this study examined different calcination temperatures (300°C, 400°C, 500°C, and 600°C) and the effect of different Cu-Co loading ratio (0.1: 0.9–0.9: 0.1) on the low-temperature denitration activity of Cu-Co based binary catalysts were investigated. The experimental results are shown in Figure 4.

Figure 4 indicates the low-temperature urea-SCR denitration activity of binary Cu-Co/NUAC composite catalysts prepared at different calcination temperatures at 50°C. According to the NOx conversion data of each catalyst in the figure, it could be known that the low-temperature catalytic activity of the binary Cu-Co based composite catalyst was greatly affected by the calcination temperature; as shown in the figure, at the same Cu-Co loading ratio, the low-temperature denitration activity of each catalyst shows a trend of rise first and then decrease with the increase of calcination temperature. However, the optimal calcination temperature of catalysts with different Cu-Co loading ratios is different. When the Cu-Co loading ratio was in the range of 0.1: 0.9–0.5: 0.5 (i.e. \( \leq 0.5: 0.5 \)), the binary Cu-Co/NUAC composite catalyst calcined at 400°C had the highest catalytic activity; when the Cu-Co loading ratio is in the range of 0.7: 0.3–0.9: 0.1 (i.e. \( > 0.5: 0.5 \)), the optimum calcination temperature of each binary Cu-Co/NUAC composite catalyst was 500°C. It could be known from Figure 4 that too high or too low calcination temperature was not conducive to the low-temperature catalytic activity of the Cu-Co-based catalyst, and the optimal calcination temperature of the catalyst depended on the range of its Cu-Co loading ratio.
3.4. Surface morphology of the carrier

Figure 5 shows the microscopic surface topography of the NUAC carrier photographed by scanning electron microscope (SEM). It could be seen from the figure that the NUAC carrier had a well-developed pore structure, which provided a large specific surface area for the carrier, which was conducive to the uniform loading of active metal oxides and urea.

3.5. Phase combination analysis of catalyst

Figure 6 shows the XRD patterns of NUAC carrier, unary catalyst and binary Cu$_{0.9}$Co$_{0.1}$/NUAC (prepared at 500°C) composite catalyst. It could be seen from the figure that the XRD pattern of the
activated carbon carrier of the shell had only two dispersion peaks of the activated carbon; Compared the XRD patterns of the carrier and the catalyst, it was obvious that when the surface of the carrier was loaded with active metal oxides (CuO, CoO), the XRD spectrum of the carrier did not change except for adding some crystal characteristic peaks of metal oxides, which indicated that the phase composition of the carrier would not be changed during the preparation of the catalyst; Compared with the XRD patterns of the unary Cu/Co-based catalyst and the binary Cu_{0.9}Co_{0.1}/NUAC composite catalyst, it was known that the presence of Co element inhibited the formation of crystalline Cu_{2}O; For the Cu_{0.9}Co_{0.1}/NUAC catalyst, the XRD patterns contained a large number of Cu crystal peaks, weak CuO and CoO crystal peaks.

Figure 6. The XRD patterns of Cu/Co based unary catalysts and binary composite catalyst

4. Conclusion

Low-temperature urea-SCR technology is a new type of low-temperature denitration technology, which can realize the removal of NO\textsubscript{x} in low temperature (50–100°C) flue gas without the problem of ammonia escape. In this paper, a series of binary Cu-Co based composite catalysts were prepared and their preparation parameters were optimized. There are two optimal regions for the preparation parameters of Cu-Co-based composite catalysts: the calcination temperature of 400°C at lower Cu-Co loading ratio (≤0.5: 0.5) and the calcination temperature at 500°C of higher Cu-Co loading ratio (>0.5: 0.5). When the calcination temperature is 500°C and the Cu-Co loading ratio is 0.9: 0.1, the Cu-Co based binary catalyst has the highest denitration performance. The active metal oxides on the surface of the Cu_{0.9}Co_{0.1}/NUAC catalyst contained the crystalline Cu, CuO and CoO.

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