Study on the poisoning effect of non-vanadium catalysts by potassium

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Abstract. The poisoning effect of catalyst by alkali metals is one of the problems in the selective catalytic reduction (SCR) of NO by NH\textsubscript{3}. Serious deactivation by alkali poisoning have been proved to take place in the commercial vanadium catalyst. Recently, non-vanadium catalysts such as copper oxides, manganese oxides, chromium oxides and cerium oxides have attracted special attentions in SCR application. However, their tolerance in the presence of alkali metals is still doubtful. In this paper, copper oxides, manganese oxides, chromium oxides and cerium oxides supported on TiO\textsubscript{2} nanoparticle was prepared by impregnating method. Potassium nitrate was chosen as the precursor of poisoner. Catalytic activities of these catalysts were evaluated before and after the addition of potassium. Some characterization methods including X-ray diffraction and temperature programmed desorption was utilized to reveal the main reason of alkali deactivation.

1. Introduction

Nitrogen oxides (NO\textsubscript{x}) have important contributions to atmospheric pollutions and secondary pollutions such as photochemical smog, haze and atmospheric acid deposition. Their participation in the regional atmospheric compound pollutions became especially underscored in recent years. The reduction of NO\textsubscript{x} emissions has become the inevitable choice of improving atmospheric environment.

Among various kinds of NO\textsubscript{x} control technology, selective catalytic reduction (SCR) method with the highest deNO\textsubscript{x} efficiency has been used successfully in power plants, and may have good prospects in the flue gas purification of industrial boilers, cement kiln, glass furnace and so on. Catalyst is an important component of SCR system, and its longevity is the key factor affecting the economy of SCR system. The catalyst system V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5}-MoO\textsubscript{3}/TiO\textsubscript{2} is world widely used for removing NO\textsubscript{x} from stationary sources. In the meantime, the existing problems including toxicity of vanadium pentoxide, relatively high operation temperature and N\textsubscript{2}O formation become huge concerns \cite{1-3}. Therefore, non-vanadium SCR catalysts have been a hotspot of research.

Cu, Mn, Cr, Ce and other transition metal based materials have been proved to have good SCR activity\cite{4-6}. However, there are few studies focusing on the alkali poisoning effect of these non-vanadium catalysts. Previous works have shown that vanadium based catalyst suffered serious deactivation by alkali metals. Herein, Cu-, Mn-, Cr-, and Ce-based catalyst were loaded respectively on nanoparticle TiO\textsubscript{2}, and then potassium was added with the same molar ratio. Under the same test condition, the SCR activities were investigated on these samples with or without potassium. The
tolerance to potassium was compared. Moreover, some characterization methods were utilized to reveal the main reason of alkali deactivation and the difference of tolerance.

2. Experimental

2.1. Catalyst preparation

The introduction of metal oxides into TiO_{2} nanoparticle (P25) was carried out by impregnating P25 into the solution of copper nitrate, manganese nitrate, chromium nitrate or cerium nitrate and stirred for several hours. Then the mixed solution was dried at 80 °C for 12 h and calcined at 450 °C for 3 h. The loading amount of metal was controlled with M/Ti (M=Cu, Mn, Cr, Ce) molar ration at 1:19. The as-prepared catalysts were denoted as Cu/P25, Mn/P25, Cr/P25 and Ce/P25.

2.2. Introduction of potassium

The introduction of potassium nitrate into Cu/P25, Mn/P25, Cr/P25 and Ce/P25 was also carried out by impregnating method. The loading amount of potassium was controlled with active metal molar ration at 1:1. The as-prepared catalysts were denoted as Cu/P25-K, Mn/P25-K, Cr/P25-K and Ce/P25-K.

2.3. SCR activity tests and measurements

SCR test were performed under atmospheric pressure at 110 °C-470 °C in a fixed-bed reactor with 0.5 g catalysts. The gas composition was: 600 ppm NO, 600 ppm NH\textsubscript{3}, 3% O\textsubscript{2}, balanced N\textsubscript{2}. The gas hourly space velocity (GHSV) for this system was about 100,000 h\textsuperscript{-1}. NO, NO\textsubscript{2} and O\textsubscript{2} concentration were monitored by a flue gas analyser (KM9106, Quintox Kane International Limited).

NOx conversion is calculated as:

\[
\text{NOx conversion }\% = \left(\frac{[\text{NOx}]_{\text{in}} - [\text{NOx}]_{\text{out}}}{[\text{NOx}]_{\text{in}}}\right) \times 100 \%
\]

where [NOx]=[NO] + [NO\textsubscript{2}], and the subscripts “in” and “out” refer to the inlet and outlet concentration of NOx, respectively.

2.4. Catalyst characterization

X-ray diffraction (XRD) analysis was performed with Cu K\alpha radiation (model D/max RA, Rigaku Co, Japan). Brunauer-Emmett-Teller (BET) specific surface area (SBET) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P\textsubscript{0}) range from 0.05 to 0.30. Pore size distributions were calculated by employing the Barrett-Joyner-Halenda (BJH) model. Temperature programmed desorption (TPD) were carried out using a TP-5080 setup. Samples of 50 mg was placed in the middle of quartz tube and held in position with silica wool. Prior to TPD experiments, samples were purified in N\textsubscript{2} at 350 °C for 1h and then saturated with 4 % NH\textsubscript{3}/N\textsubscript{2} or 4 % NO/N\textsubscript{2} at room temperature. Desorption was conducted by heating the samples in He from 100 °C to 600 °C (heating rate: 10 °C/min).

3. Results and discussion

3.1. SCR performance

The NOx conversion in NH\textsubscript{3}-SCR of Cu/P25, Mn/P25, Cr/P25 and Ce/P25 was shown in Fig. 1(a). The highest NOx conversion of 83%, 81%, 87% and 76% at 340-400 °C under a space velocity of 100,000 h\textsuperscript{-1} could be observed on Cu/P25, Mn/P25, Cr/P25 and Ce/P25, respectively. This meant all of these catalysts have good SCR activity before the addition of potassium.
Figure 1. Variation of NOx conversion with reaction temperature over catalysts before and after potassium loading.

Figure 1(b) shows the NO conversion of the four catalysts with potassium loading. Quite different performances could be observed. Cr/P25-K and Ce/P25-K were deactivated thoroughly. NOx conversions were lower than 20% in the whole tested temperature range. The NO conversion of Cr/P25-K was negative above 390 °C, which might be due to some generated NO by the oxidation of ammonia. Comparatively speaking, Mn/P25-K was not fully deactivated. NO conversion still remained at 34% at 350 °C. Unlike the other three catalysts, Cu/P25-K was only deactivated slightly. A high NO conversion of 67% at 350 °C could be observed.

3.2. X-ray diffraction
XRD was utilized to clarify the crystal phases of Cu/P25, Cu/P25-K, Mn/P25, Mn/P25-K, Cr/P25, Cr/P25-K, Ce/P25 and Ce/P25-K. As depicted in Fig. 2, all these catalysts showed a mixing structure of anatase (PDF-#21-1272, 25.28°, 37.80°, 48.05°, 53.89°, 55.06° and 62.69°) and rutile (PDF-#21-1276, 27.45°, 36.09° and 54.32°). Table 1 shows the crystal parameters of the [101] face of anatase. After poisoning, a variety of diffraction peaks were increased, and the titanium dioxide was particularly obvious. After Ce/P25 poisoning, CeO2 was further transformed from amorphous phase into crystal phase. As such, the oxidation-reduction performance of CeO2 was depressed to a certain extent and the deNOx activity was reduced. In the case of Cu/P25, Mn/P25, Cr/P25, the active species were not detected before and after the poisoning, and it was highly dispersed on the surface of supports.

| Sample   | FWHM | Peak area | Peak height | Grain size calculated by [101] face (nm) |
|----------|------|-----------|-------------|----------------------------------------|
| Cu/P25   | 0.376| 12651     | 583         | 22.5                                   |
| Cu/P25-K | 0.369| 21454     | 1006        | 22.9                                   |
| Mn/P25   | 0.381| 18918     | 860         | 22.1                                   |
| Mn/P25-K | 0.375| 21326     | 985         | 22.5                                   |
| Cr/P25   | 0.374| 14103     | 653         | 22.6                                   |
| Cr/P25-K | 0.394| 20921     | 920         | 21.4                                   |
| Ce/P25   | 0.404| 10506     | 451         | 20.8                                   |
| Ce/P25-K | 0.403| 21370     | 918         | 20.8                                   |
3.3. Physical characterizations (BET)

The physical characterizations of the samples are shown in Table 2, the specific surface area of Mn/P25, Cr/P25 and Ce/P25 decreased after the addition of potassium, whereas that of Cu/P25 increased slightly. XRD results showed that the active species of Cu/P25-K still highly dispersed on the surface of the support, so the increase of surface area would further promote the dispersion of active substances on the surface of the support. The decrease of the specific surface area of Mn/P25-K is one of the reasons that the SCR activity is lower than Cu/P25-K.

| Catalysts | BET (m$^3$.g$^{-1}$) | Pore volume (cm$^3$.g$^{-1}$) | aperture(m$^3$.g$^{-1}$) |
|-----------|----------------------|-------------------------------|---------------------------|
| Cu/P25    | 46.5                 | 10.4                          | 28.9                      |
| Mn/P25    | 49.4                 | 10.5                          | 31.3                      |
| Cr/P25    | 49.3                 | 10.4                          | 25.7                      |
| Ce/P25    | 51.0                 | 10.4                          | 28.4                      |
| Cu/P25-K  | 47.8                 | 10.4                          | 29.7                      |
| Mn/P25-K  | 47.6                 | 10.4                          | 30.8                      |
| Cr/P25-K  | 48.4                 | 10.4                          | 27.2                      |
| Ce/P25-K  | 46.0                 | 10.4                          | 28.3                      |

3.4. Temperature programmed desorption

In the SCR reaction, the content and strength of surface acidic sites on the catalysts directly determines the ability of NH$_3$ to adsorb and participate in chemical reactions on the surface[7]. In order to investigate the effect of K doping on the acidity of non-vanadium catalysts, the experiment of NH$_3$-TPD was carried out. As depicted in Fig.3, Cu/P25, Mn/P25, Cr/P25 and Ce/P25 catalysts have two obvious desorption peaks at 100-400 °C, which corresponds to NH$_3$ adsorbed on the weak acid sites of the catalyst. Compared with the results after potassium loading, Mn/P25-K and Cr/P25-K had no obvious
peaks of desorption peak, indicating that K significantly reduced their surface acid sites. Cu/P25-K and Ce/P25-K have a desorption peak at 100-350 °C.

Figure 3. NH3-TPD profiles of the catalyst samples.

4. Conclusions
The Cu/P25, Mn/P25, Cr/P25 and Ce/P25 catalysts were deactivated more or less by the loading of potassium. Comparatively, Cu/P25 showed stronger tolerance to potassium and Ce/P25 showed the most serious deactivation. A high NO conversion of 67% at 350 °C could be observed on Cu/P25-K. According to the results of XRD, BET and NH3-TPD, the change of crystal morphology and the decrease of specific surface area were the main factors that led to the deactivation of Ce/P25-K. Cu/P25-K has more surface acidity and better dispersion of the active species, which were the key reasons for its good SCR activity.

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