Microscopic investigation on the V$_2$O$_5$-WO$_3$/TiO$_2$ denitration catalyst with visible variation in color

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Abstract: Most commercial V$_2$O$_5$-WO$_3$/TiO$_2$ honeycomb SCR denitration catalysts is light yellow and uniform. However, some catalysts have gray cylindrical regions through the center. There is visible variation between samples from normal area and gray area in one catalyst. X-ray photoelectron spectroscopy is conducted to find the correlation between color difference and microscopic performance of V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. The results show that different V oxidation states and W chemical states between two samples result in the color variation. The catalyst sample from gray area possesses less chemisorbed oxygen.

Keywords: NH$_3$-SCR, color variation, valence state.

1. Introduction

The NH$_3$ selective catalytic reduction technique is an effective way for controlling emission of NOx. The commercial V$_2$O$_5$–WO$_3$/TiO$_2$ SCR catalyst has been widely used in thermal power plants and other stationary sources. Most research has mainly focused on the chemical activities of the V$_2$O$_5$-WO$_3$/TiO$_2$ system. Lietti et al reported that the catalyst redox properties control the reactivity of the samples at low temperatures whereas the surface acidity plays an important role in the adsorption and activation of ammonia at high temperature. Few studies are about the correlation between appearance difference in color and microscopic property of commercial V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. It is concerned that whether the service performance of catalysts is influenced by this variation to some degree and which kind of microscopic characteristic and local chemical composition difference results in the variation.

2. Experimental

The catalysts are in honeycomb monolith structure and the main components are V$_2$O$_5$–WO$_3$/TiO$_2$. The catalytic activities were evaluated in the reactor with the dimeter of φ 9.3 mm. The gas hourly space velocity of reaction was 56000 h$^{-1}$. The components of gas stream were: c(NO) = 400 mg/m$^3$, c(SO$_2$) = 1700 mg/m$^3$, O$_2$ = 5.27 vol %, water vapor = 3.00 vol % and n(NH$_3$)/n(NO) = 0.820 with N$_2$ as balance gas. The elemental valence was detected by X-ray photoelectron spectroscopy (XPS) analysis, which was collected on a ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) with monochromatic Al K$_\alpha$ radiation (E = 1486.2 eV).

3. Results and discussion

Fig. 1 shows the photos of two catalysts with different appearance. The tested samples were extracted from yellow color and gray color areas (Fig. 1b) and they are named as S-N and S-G, respectively (Fig. 1c and d). When the molar ratio of NH$_3$ vs NO is 0.820, the NO conversion rate was about 78.6% for the S-G sample, and that of S-N sample is about 80.6% at 370°C.

The influence of surface V, W and O species was investigated by XPS. As shown in Fig. 2a, the V2p$_{3/2}$ spectra in S-G sample are resolved into three peaks at 517.00 eV (orange line), 515.95 eV (blue line) and 515.50 eV (gray line), which are assigned to V2p$_{3/2}$ binding energy values of V$^{5+}$, V$^{4+}$ and V$^{3+}$, respectively. The V2p$_{3/2}$ spectra in S-N sample are resolved into two peaks assigned to V2p$_{3/2}$ binding energy values of V$^{5+}$ at 517.00 eV and V$^{4+}$ at 515.95 eV. The color of vanadium oxides varies with the change in valence of vanadium. V$_2$O$_5$ are brighter yellow, VO$_2$ are darker, almost brown, and V$_2$O$_3$ shows
brown color. The higher ratio of $V^{4+}$ and $V^{3+}$ in S-G sample may contribute to the difference in color between two samples.

![Figure 1](image1)

**Figure 1.** Photos of catalysts: (a) normal catalyst, (b) catalyst with color variation,(c) S-N sample, (d) S-G sample.

The O1s spectra of samples (Fig. 2b) have been resolved into three peaks assigned to lattice oxygen $O^{2-}$ (peak I), hydroxyl groups (peak II) and adsorbed water molecules (peak III), respectively. S-N sample possesses higher intensity of OH oxygen than S-G sample. It is known that surface chemisorbed oxygen is highly active in reactions because of its higher mobility than the lattice oxygen. This could contribute to the higher activity of S-N sample.

W 4f Peaks overlap with Ti 3p peaks in XPS spectra. In S-N sample, two peaks at 35.20 eV and 37.16 eV correspond to W 4f7/2 and W 4f5/2 binding energy of W$^{6+}$ in WO$_3$. The fitted peaks at about 36.26 eV and 38.19 eV of binding energy are assigned to W 4f7/2 and W 4f5/2 peaks of W$^{6+}$ in tungstate formation, which may be attributed to the interaction between W and other elements in the SCR catalyst. The color of WO$_3$ is yellow but other tungsten oxides have different colors. So, different W chemical states also might devote to the color variation between S-N sample and S-G sample to some degree.

![Figure 2](image2)

**Figure 2.** XPS spectra of S-N and S-G samples: (a) V2p, (b) O1s, (c) W4f analyzed by the curve fitting differential method.

4. Conclusions

The samples from normal area and gray area in the whole commercial V$_2$O$_5$-WO$_3$/TiO$_2$ monolithic honeycomb denitration catalyst are different in color and activity. The difference in V oxidation state and W chemical state between S-N sample and S-G sample may result in their color variation. Less chemisorbed oxygen may contribute to the lower activity of S-G sample.

References