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Effect of different potassium species on the deactivation of V_2O_5-WO_3/TiO_2 SCR catalyst: Comparison of K_2SO_4, KCl and K_2O

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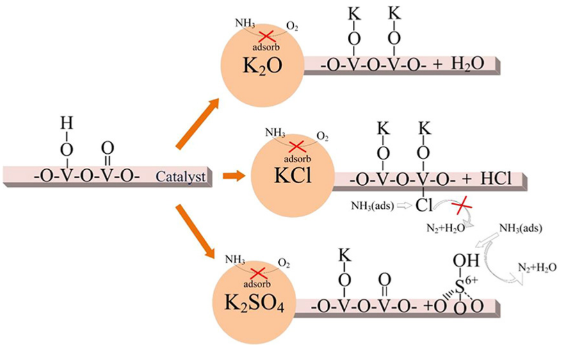
HIGHLIGHTS

- Deactivation mechanisms of three potassium species on V_2O_5-WO_3/TiO_2 catalyst are compared.
- Deactivation rate of potassium-poisoned catalysts follows KCl > K_2O > K_2SO_4.
- The introduction of SO_4^{2-} creates new sites and contributes to catalyst acidity.
- Cl^- provides new ammonia adsorption sites but is useless for NO reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of different potassium species, including K_2O, KCl and K_2SO_4, on the deactivation of V_2O_5-WO_3/TiO_2 catalysts were measured in the research. Potassium species were supplied by impregnating catalyst with corresponding KNO_3, KCl and K_2SO_4 aqueous solution. Catalytic activity was also measured and the physical and chemical properties of fresh and poisoned catalysts were characterized by XRD, N_2 physisorption, NH_3-TPD, H_2-TPR, XPS and NH_3-DRIFTS. Deactivation could be observed in the potassium-containing catalysts and the deactivation rate follows KCl > K_2O > K_2SO_4. The surface chemisorbed oxygen was also reduced and the downward trend was in good accordance with the SCR activity. In addition, both the amount and stability of the Brønsted and Lewis acid sites dropped after potassium introduction, and the reducibility of surface active species decreased. The introduction of SO_4^{2-} created new Brønsted acid sites and performed advantages to ammonia adsorption and NO reduction. Cl^- could react with vanadia active sites to form -O-V-Cl bond, which provided some new ammonia adsorption sites, but these newly generated sites could not revitalize the adsorbed ammonia and were helpless to catalytic activity promotion. Besides, KCl presented the maximum impact on catalyst reducibility was another contribution to its largest activity decline. Finally, the probable poisoning mechanisms of different potassium species over V_2O_5-WO_3/TiO_2 catalysts were proposed.

1. Introduction

Combustion of most fuels results in the emission of nitrogen oxide (NO_x), which causes serious threat to the environment because it would create issues of acid rain and photochemical smog [1–3]. Selective catalytic reduction (SCR) of NO_x with NH_3 has been proven as one of

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the most effective technologies for NO_x removal in the fuels-fired flue gas. Catalysts system, containing 0.5–3.0 wt% V_2O_5, 5–10 wt% WO_3 (or MoO_3) and TiO_2 as the support, is the most widely applied on commercial for decades [4–7]. Vanadium is the active component and tungsten is the promoter that stabilizes the anatase titania, favors the spreading of vanadia on the catalyst surface and increases catalyst acidity. However, several issues concerning deactivation of the SCR catalysts are emergency to be considered. The catalyst unit usually works before flue gas purification equipment to satisfy temperature requirement. Therefore, large amount of fly ash and alkali (alkaline earth) metals in the flue gas would deactivate the catalyst [8–10].

Research have shown that alkali oxides and salts are the major components to deactivate SCR activity and the effect of alkali metals on V_2O_5-based catalysts has been widely studied [11–23]. Previous studies generally concluded that alkalis in the main group IA (K and Na) exhibit greater poisoning extent than that in the main group IIA (Ca and Mg). The deactivation of V_2O_5-WO_3/TiO_2 catalysts is usually caused by the neutralization of the BrØnsted acid sites, the decrease of surface chemisorption oxygen and the reduced reducibility of vanadium species. The way and state K^+ is added to the catalyst also have an influence on its effect. Lei et al. [17] compared the deactivation of V_2O_5-WO_3/TiO_2 catalysts by KCl via three methods, wet impregnation, solid diffusion and vapor deposition. They found that the deactivation rate follows the order of vapor deposition ≫ solid diffusion > wet impregnation. Larsson et al. [23] compared the wet impregnation and the aerosol injection, they reported that the poisoning effect of wet impregnation was more serious than that of the aerosol injection. But Klimczak et al. [19] found that the wet impregnation and aerosol deposition of alkali metals caused the same deactivation behavior. However, in view of these studies, researchers primarily focused on comparison of different alkalis species [12,16,18–20] and different poisoning methods [17,19,23], or studies on single alkali metal [11,14,21,22]. Therefore, it was difficult to make a comparison or conclusion from these results due to the total different materials, preparation methods and properties characterizations.

Based on this, the single alkali metal, potassium, was selected as the object in our research. Three main kinds of potassium species, K_2O, KCl and K_2SO_4, were selected to be loaded on the catalysts. Wet impregnation method was used to deactivate catalyst due to the solubility of potassium in water-containing flue gas. The obtained poisoned catalysts were then characterized by the same measurements. It aimed at comparing the effect of different potassium species on the deactivation of V_2O_5-WO_3/TiO_2 catalysts at the same level and distinguishing their differences on the poisoning mechanism.

2. Experimental

2.1. Catalyst preparation

The fresh V_2O_5-WO_3/TiO_2 catalyst with 1 wt% V_2O_5 and 5 wt% WO_3 was prepared by impregnation method. The ammonium metavanadate (NH_4VO_3) and ammonium paratungstate [$(NH_4)_{10}(W_{12}O_{41})\cdot 5H_2O$] were mixed in the oxalic solution of desired proportions, and commercial TiO_2 (P25) was used as the precursor to obtain the slurry. The slurry was then stirred for 6 h, dried at 110 °C for 12 h and calcined at 500 °C for 5 h in air. The fresh catalyst (denoted as 1 V) was then grinded and sieved within 40–60 meshes for evaluation.

The poisoned catalysts were prepared by wet impregnation with K_2SO_4, K_2O (KNO_3 was used as the precursor) and KCl solution, respectively. The potassium loadings were 0.5 wt%, 1.0 wt% and 2.0 wt% (denoted as KS*x* for K_2SO_4, KN*x* for K_2O, and KC*x* for KCl, where *x* is the molar K/V ratio), corresponding to molar K/V ratios of 0.6, 1.2 and 2.4 respectively. The potassium-induced catalysts were then stirred for 6 h, dried at 110 °C for 12 h and calcined at 500 °C for 5 h in air. The samples with 1.0 wt% potassium loading were selected to do the characterization afterwards.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were determined by Rigaku D/max-2500/PC diffractometer, operating at 40 kV and 40 mA using CuKα radiation.

The BET surface area, pore size and pore volume of the samples were measured by N_2 physisorption at 77 K using Micromeritics ASAP 2010 instrument.

Temperature-programmed desorption of NH_3 (NH_3-TPD) and temperature-programmed reduction of H_2 (H_2-TPR) experiments were conducted on a chemisorption analyzer (AutoChem II2920, Micromeritics Instrument). In a typical NH_3-TPD experiment, 100 mg sample was pretreated in He (50 ml/min) for 1 h at 400 °C and then cooled down to 100 °C. Prior to temperature program desorption, the sample was exposed to gas mixture of 5% NH_3 in He (50 ml/min) for 1 h and then purged in He until the TCD signal was stabilized. Finally, the sample was heated up to 400 °C (10 °C/min) under a flow of helium (50 ml/min) to record the NH_3 TCD signal. For H_2-TPR experiment, 100 mg of sample was placed in one arm of a U-shaped quartz tube. It was carried out under 5% H_2 in Ar (50 ml/min) from 50 °C to 900 °C at a rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) profiles were acquired with a Thermo-Scientific system at room temperature using Al Kα radiation (1484.6 eV). The binding energy was referenced to the C 1 s line at 284.6 eV and peak deconvolution was performed using the Thermo Avantage v5.973 software.

Diffuse reflectance infrared Fourier transform spectroscopy of NH_3 (NH_3-DRIFTS) was recorded on a Thermo Scientific Nicolet 6700 spectrometer, which was equipped with a Harrick IR cell and an MCT detector cooled by liquid N_2. Prior to the experiment, catalysts were firstly purged at 350 °C for 1 h under N_2 gas (total flow rate 100 ml/min), and the background spectrum at desired temperature was collected NH_3 was adsorbed at 50 °C with 500 ppm NH_3/N_2 flow for 1 h, and then flushed in N_2 for 1 h. Before scanning, samples were kept for 30 min at the desired temperature and the DRIFT spectra were collected by accumulating 64 scans at a resolution of 4 cm^{-1}.

2.3. Catalyst activity measurements

SCR activity measurements were conducted in the fixed-bed reactor containing 200 mg of catalysts (40–60 meshes). The feed gas mixture contained 500 ppm NO, 500 ppm NH_3, 4% O_2, and N_2 as the balance gas. The total gas flow rate was 500 ml/min. The outlet gas concentrations (NO, NO_x and O_2) were monitored by flue gas analyzer (MRU, Germany OPTIMA7), and the measurement was performed between 200 and 500 °C in intervals of 50 °C. Each data acquisition was preceded by equilibration for 20 min. The catalytic activities were evaluated by NO_x conversion (%) according to the following equation:

$$NO_x\,\text{conversion}(\%) = \frac{[NOx]inlet - [NOx]outlet}{[NOx]inlet} \times 100\% \tag{1}$$

3. Results and discussion

3.1. Catalytic activity

Fig. 1 presents the catalytic activity of fresh and K^+-poisoned catalysts with different potassium species and contents. The results show that fresh catalyst performs the best NO reduction efficiency that keeps above 90% in the temperature range of 200–450 °C. Introducing potassium deactivates the catalysts and the activity sequence follows the order of 1V > KS > KN > KC. The catalytic activity declines with increasing potassium contents and promotes with temperature elevating. When the K/V molar ratio is 0.6, K_2O and K_2SO_4 perform negligible effect on NO reduction from 300 °C to 450 °C but presents severe deactivation below 300 °C. When the K/V molar ratio increases to 1.2,