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Short communication

An efficient novel regeneration method for Ca-poisoning V_2O_5-WO_3/TiO_2 catalyst

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ABSTRACT

Ca poisoning and regeneration on V_2O_5-WO_3/TiO_2 catalysts for selective catalytic reduction of NOx was investigated based on the changes of activity, structure, reducibility, acidity and reaction details. It is found that high contents of CaO can lead to $CaWO_4$ formation and thus passivate bulk tungsten species and surface acid sites of fresh catalyst. Additionally, reactable surface oxygen species and reducibility are also greatly suppressed by CaO species. However, unlike previous regeneration method, HEDP showed exclusive and excellent removal rate of CaO without large active ingredients loss, which had a better prospect of industrial application.

1. Introduction

Selective catalytic reduction with NH_3 (NH_3-SCR) has been widely used as an effective method in the field of controlling stationary source NOx emissions in recent decades [1,2]. Unfortunately, in practice, many kinds of toxic components such as alkali metal, CaO, As_2O_3 and SO_2 under complex flue gas conditions often result in the deactivation and lifetime reduction of catalysts, thus its replacement cycle in practical application is shortened dramatically [3–5]. Since direct landfill not only endangers environment, brings hazard (V, As, Hg, etc.) to human health but also results in huge waste of resources, treatment and disposal of lots of discarded catalysts remains a tricky subject.

Regeneration is a good choice for disposition of deactivated SCR catalysts, because of its low-cost, cycle idea and extended lifetime. Several rejuvenated methods focused on specific poisoning types have been explored and reported recently. For alkali metals deactivation, hot-water washing and electrophoresis treatment were found to efficiently remove K^+ and Na^+ on novel CeO_2-WO_3 and V_2O_5-WO_3/TiO_2 catalysts, respectively [6,7]. Additionally, alkaline $Ca(NO_3)_2$ solution was lately proved as an more effective way than previous H_2O_2 method to reduce the surface arsenic on catalyst surface in our researches [8]. However, to the best of our knowledge, regeneration of Ca-poisoning SCR catalyst has seldom been reported before, which may be linked with multiple factors. On the one hand, Chen et al. found that the degree of the poisoning effect for all the alkali/alkaline-earth metal doped catalysts was shown with the sequence of K > Na > Ca > Mg, and only when the concentration of CaO was larger than 2 wt%, obvious activity loss could be found [9]. Nevertheless, Ca poisoning behavior should actually be more general and serious than alkaline metals for coal-fired stations, since PRB (Powder River Basin) and other kinds of high-calcium content coals are used a great deal to combustion for power generation which makes calcium oxide content in SCR catalyst usually be higher than 2%. On the other hand, unlike alkaline metal, poorer aqueous solubility of CaO leads to its regeneration becoming troublesome. While considering the existence of SO_2, calcium sulphate formation makes it harder to be eliminated. Additionally, it was found that exposing the deactivated catalyst surface to sulphate by SO_2 or H_2SO_4 was a promising way to rejuvenate the initial activity of the catalyst poisoned by multiple contaminants [10]. However, other downsides such as the loss of the active ingredients, body strength reduction and equipment corrosion simultaneously arise under the real environment.

Herein, we developed a novel regenerated method based on 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) liquid under weak acid environment for directional complexing Ca^{2+} and improving dissolution, which showed efficient surface calcium species removal and low cost but a lower loss of active components, which had a better prospect of industrial application.

2. Experimental

Fresh V_2O_5-WO_3/TiO_2 catalysts were prepared by traditional co-precipitation method, while poisoned ones were obtained by impregnation with $Ca(OH)_2$ solutions followed by evaporation, drying and calcination. Poisoned catalysts with 4% CaO mass percentage were selected for reactivation with 1 wt% HEDP solution. Catalysts structures were

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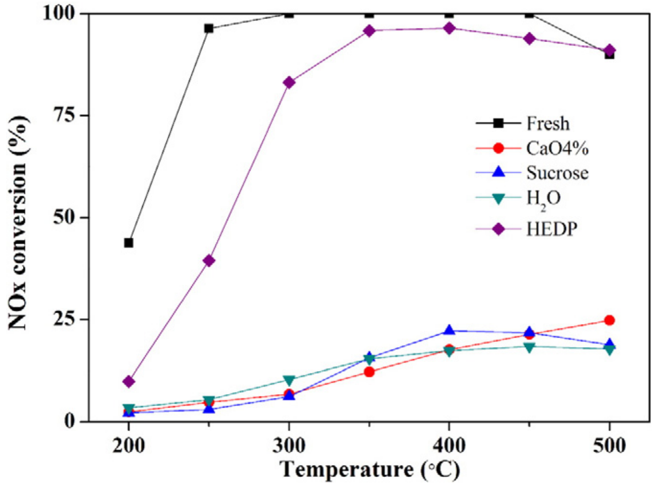

Fig. 1. The SCR performance of fresh, poisoned and regenerated catalysts with a GHSV of 120,000 h^{-1}. (NO = NH_3 = 500 ppm, O_2 = 3%, balanced by N_2).

characterized by XRD, N_2 adsorption-desorption, XPS and Raman spectroscopy. Their adsorption behavior and redox properties were investigated using in situ IR spectroscopy, and TPR techniques, respectively. The detailed experiment methods, activity test and characterization techniques were described in Supporting information.

3. Results and discussion

Fig.1 shows the NOx conversions of the fresh, poisoned and reactivated catalysts from 200 to 500 °C with a GHSV of 120,000 h^{-1}. Poisoned catalyst with 4 wt% CaO content exhibits poor SCR performance for the maximum conversion below 25%. After H_2O and sucrose (classical reagent for improving CaO solubility) washing, hardly obvious conversion changes can be found, indicating that the CaO is powerfully tied by the catalyst surface species and cannot be easily removed. However, the NOx conversion can be significantly recovered up to 96% at 350 °C for HEDP regeneration. Additionally, it is found that the best regeneration effect is gained under weak acid environment (Fig. S1). Therefore, it is a high-efficiency and promising regenerated method for severe Ca-poisoning SCR catalyst.

Fig. 2 shows the XRD patterns (a) and Raman spectra of the fresh, poisoned and regenerated V_2O_5-WO_3/TiO_2 catalysts. The fresh sample shows XRD peaks at 2θ values of 25.33, 37.87, 48.05, 53.92, 52.11, 62.78, 68.77, 70.33 and 75.51°, manifesting the presence of anatase TiO_2. Besides, two small XRD peaks belonging to the crystalline WO_3 are observed at 23.74° and 33.68°, which is due to higher surface densities of tungsten(~4.9 μmol m^2) than the theoretical surface coverage degree (4 μmol m^2). After introduction of the CaO, the $CaWO_4$ phase can be detected by the appearance of several peaks centered at 2θ = 18.71, 29.03, 31.48, 34.45, 47.21 and 58.22°with WO_3 phase disappearing, indicating that CaO can passivate bulk tungsten species rather than incorporating into the anatase phase. For the regenerated sample, neither well-crystallized $CaWO_4$ nor small peaks corresponding to WO_3 can be identified, suggesting that generated $CaWO_4$ species are washed away and highly dispersed WO_3 are recovered after HEDP cleaning. However, according to the final composition detected by ICP technology (Table S1), only less than 35% active ingredients V_2O_5 and WO_3 are lost at the same time, which is obviously better than traditional H_2SO_4 regeneration method.

All the Raman spectra (Fig. 2b) of three samples show three main bands located at 396 cm^{-1} (E_g), 514 cm^{-1} (A_{1g}/B_{1g}) and 635 cm^{-1} (B_{1g}), and a broad band centered at 789 cm^{-1}, which are attributed to four kinds of fundamental active modes and weak second-order texture of anatase structure, respectively [11]. For poisoned catalyst, the appearance of band at around 910 cm^{-1} is indicative of Raman-active modes of $CaWO_4$, in line with XRD results (Fig. 2a). The Raman band in the range of 930–990 cm^{-1} can be assigned to the symmetrical V═O or W═O stretching modes of the two-dimensional surface species [12–14]. This band of fresh sample is shifted towards lower wavenumbers with intensity lessening after CaO poisoning, implying that the W═O vibration frequency decreases for the expended WO_4^- structure arising from the new phase formation, and the peak shifts to higher wavenumbers after regeneration. Therefore, $CaWO_4$ phase formation is the main reason for shifting towards lower wavenumbers.

The surface area and pore volume measurements have also been performed and the results are listed in Table S1. The BET surface areas of three catalysts vary between 78 and 80 m^2 g^{-1}, and the pore volume of the poisoned sample is obviously less than the other. So it can be inferred that CaO deactivation is concerned with not only the modification of the surface WO_3 by interacting with Ca but also channel plugging.

Fig. 3 shows the O 1s (a) and W 4f (b) XPS spectra of the three samples. Two distinct sub-bands located at 529.8–530.3 eV and 531.3–531.8 eV can be ascribed to lattice oxygen O^{2-} (designated as "β") and surface chemisorbed labile oxygen (labeled as "α") [15,16]. The latter also called active O species is beneficial for the NO oxidation to NO_2 in the SCR reaction because of its higher mobility [17]. The

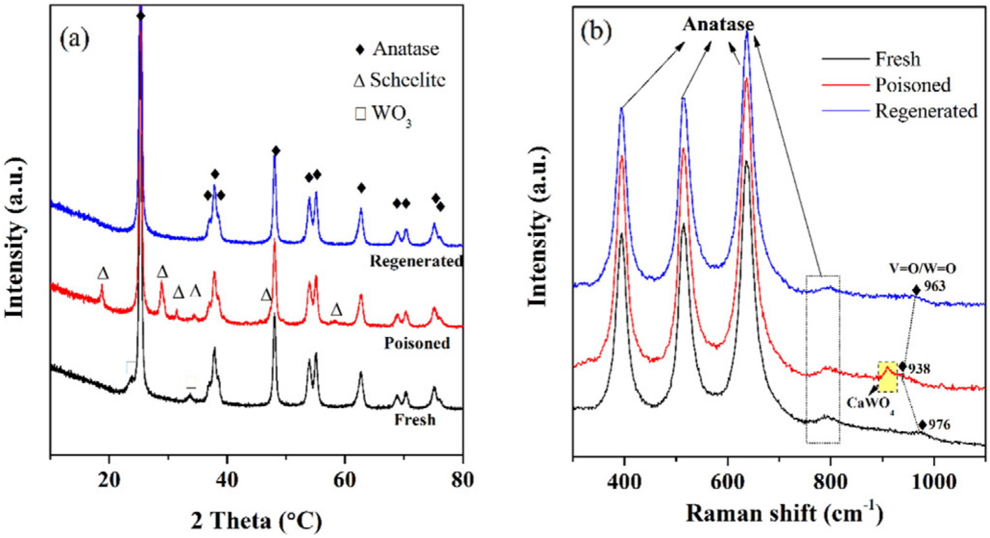

Fig. 2. The XRD curves (a) and Raman spectrum (b) of fresh, poisoned and regenerated catalysts.