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Promotion of ceria for decomposition of ammonia bisulfate over V_2O_5-MoO_3/TiO_2 catalyst for selective catalytic reduction

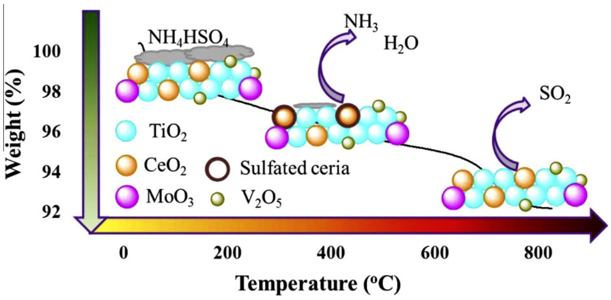
Liyun Song [a], Jingdi Chao [a], Yujiao Fang [a], Hong He [a,b,*], Jian Li [a], Wenge Qiu [a,b], Guizhen Zhang [a,b]

[a] *Key Laboratory of Beijing on Regional Air Pollution Control, Beijing Key Laboratory for Green Catalysis and Separation, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China*
[b] *Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, China*

HIGHLIGHTS

- CeO_2 facilitated the decomposition of ammonia bisulfate over V-Mo/Ce-Ti catalyst.
- Sulfated ceria formed in the decomposition process of ammonia bisulfate over CeO_2.
- S species accumulated for CeO_2 in the catalyst and released at high temperatures.
- Activity of V-Mo/Ce-Ti catalyst covered by ABS could be regenerated by annealing.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonia bisulfate (ABS) that usually generates on the surface of SCR catalysts has strong negative effect on selective catalytic reduction (SCR) process at low temperatures (<220 °C, dew-point temperature of ABS). In this work, the decomposition of ABS over CeO_2 and V_2O_5-MoO_3/CeO_2-TiO_2 catalyst was investigated in detail via TG-MS analysis. The results showed that CeO_2 could facilitate the decomposition of ABS over the V_2O_5-MoO_3/CeO_2-TiO_2 catalyst, on which cerium sulfate species formed by the interaction of CeO_2 and ABS.

1. Introduction

Nitrogen oxides (NO, NO_2, N_2O) emitted from the stationary and mobile sources have been the main pollutants over the past decades. The selective catalytic reduction (SCR) by ammonia is the best developed and the most widely used technology for nitrogen oxide elimination until now due to its superior performance [1]. In this technology, the catalyst plays a key role. WO_3 or MoO_3 modified V_2O_5/TiO_2 catalysts have been used in NO_x emission control as the main catalysts since 1970s. However, this catalyst possesses high SCR activity and SO_2 resistance only in a narrow working temperature window (300–400 °C). As we know, the temperature of the flue gas emitted from industrial heaters or furnaces is usually lower than 300 °C, and the downstream temperature of the particulate collector and flue gas desulfurization is even lower.

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[*] Corresponding author at: Key Laboratory of Beijing on Regional Air Pollution Control, Beijing Key Laboratory for Green Catalysis and Separation, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China.

E-mail address: hehong@bjut.edu.cn (H. He).

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In the recent years, with emission standards being more stringent, the present catalysts were hard to meet the requirement, especially at low temperatures (lower than 300 °C). It requires an additional heat exchanger or heater to increase the working temperature for guaranteeing the $deNO_x$ activity over the traditional SCR catalyst. Meanwhile the operating costs will be increased significantly. In order to cope with this problem, many attempts have been made to develop NH_3-SCR catalysts with high activity in the low-temperature range (160–300 °C). As we know, low-temperature SCR technology can be used to control NO_x emission from industrial boiler and heater, chemical processes, metallurgical industry etc. It was well known that sulfurous fuels, such as coal contained sulfur, were widely used and SO_2 usually existed in the exhaust gas [2]. SO_2 can be oxidized into SO_3 over the surface of SCR catalysts. The SO_3 yielded will react with NH_3 in steam atmosphere to generate ABS and other sulfides or sulfates [3,4]. With extending the running time under temperature below ca. 220 °C (dew-point temperature of ABS), the ABS will be accumulated and covered parts of the active sites on the surface of catalyst, leading the deactivation of SCR catalysts in low-temperature process [5]. In practical applications, the ABS formation has been the primary cause for the deactivation of low-temperature SCR catalyst [6], which is a critical problem in low-temperature SCR technology [7]. Fortunately, ABS can be decomposed as it is heated above 350 °C. Therefore, deactivated SCR catalyst can be *in situ* regenerated as heated at 350 °C, which was confirmed by the $deNO_x$ project of a coking furnace in Zhanjiang located south of China (Baosteel Group) [8]. As we know, the decomposition temperature of ABS can be affected by the chemical composition of SCR catalyst [9]. The energy consumption will be cut off a lot as the decomposition temperature of ABS decreased. So, it is an important issue for us to investigate the decomposition of ABS over SCR catalysts.

During the past several years, the promotion of ceria on the SCR activity over V_2O_5-WO_3/TiO_2 [7,10,11], MnO_x [12,13], and zeolite catalysts [14] have been deeply investigated. Ceria has the unique property that its electrons can easily shift between reduced and oxidized states ($Ce^{3+} \leftrightarrow Ce^{4+}$), which is in favor of variable levels of bulk and surface oxygen vacancies over the catalyst [15]. Chen et al [10] reported that small clusters of cubic CeO_2 could be formed in the V_2O_5-WO_3/TiO_2 catalyst, which could enhance the NO_x adsorption and consumption of NH_4^+ adsorbed over the surface of catalyst in presence of NO and O_2, and then the SCR reaction was accelerated. It was also found that CeO_2 in the SCR catalysts could give an increase of chemisorbed oxygen concentration on the surface and facilitate NO oxidation to NO_2, leading the occurrence of 'fast SCR' process over the catalyst [10,16].

Furthermore, CeO_2 can react with SO_2 to give sulfates and sulfites under oxidizing conditions [17,18]. With this property, CeO_2 was tried to be used as adsorbent of SO_2 in dry desulfurization process. As it used as SCR catalyst for NO_x elimination in the flue gas containing sulfur, the performance and SO_2 resistance [19] will be improved after the sulfation. When ceria is introduced into V_2O_5/TiO_2 catalyst as an active component, the activity and SO_2 resistance of the catalyst [20] will be enhanced. Yang et al [19] also found that the sulfation of SCR catalysts with CeO_2 involved could enhance the $deNO_x$ activity, which was due to the improvement in the adsorption of NH_3 over the catalyst accompanying with an increase in the number of acidity sites.

An investigation on the interaction of sulfate species and ceria is important for us to understand the decomposition behaviors of ABS over the SCR catalysts with CeO_2 involved and develop the low-temperature SCR technology including the *in situ* catalyst regeneration. In this work, the interaction between ABS and CeO_2 as well as the decomposition of ABS over CeO_2 and CeO_2 modified V_2O_5-MoO_3/TiO_2 catalyst were investigated in detail.

2. Experimental

2.1. Catalysts preparation and characterization

All chemicals used were analytical grade without any further pretreatment before used. The CeO_2-TiO_2 and TiO_2 used as support were prepared by sol-gel method [21]. The materials with CeO_2 loading of x% (denoted as xCeTi with $x = 0$, 2, 6 and 10) were obtained in the following method. In a typical procedure for 10CeTi preparation, a mixture solution of acetic acid (19 mL), ethanol (32.3 mL) and cerium nitrate (3.8 g) was dropped slowly into another solution of butyl titanate (56.7 mL) and ethanol (64 mL) under vigorous stirring. Then dilute nitric acid was added into the solution to regulate pH = 1.0. The yellowish gel was obtained after the solution was kept at 40 °C for 3 h and then aged at room temperature for 24 h. Subsequently, the gel was dried at 100 °C overnight to give a xerogel. After being crushed, the xerogel was calcined at 500 °C for 3 h in air, giving 10CeTi solid.

The V_2O_5-MoO_3/CeO_2-TiO_2 catalysts were prepared by an impregnation method. V_2O_5 and MoO_3 were loaded on the supports by impregnation of the CeO_2-TiO_2 powders in a mixture solution of oxalic acid, ammonium metavanadate and ammonium molybdate, then followed by drying at 105 °C for 3–4 h, calcining at 250 °C for 1 h and 450 °C for 3 h in air, giving the V_2O_5-MoO_3/CeO_2-TiO_2 catalysts with the V_2O_5 and MoO_3 loadings of 3 wt% and 6 wt%, respectively (denoted as 3V6MoxCeTi with $x = 2$, 6 and 10). Similarly, the V_2O_5/TiO_2 (denoted as 3VTi), V_2O_5-MoO_3/TiO_2 (denoted as 3V6MoTi) and V_2O_5/CeO_2-TiO_2 (denoted as 3V10CeTi) catalysts were obtained using a similar method.

2.2. Catalyst characterization

The crystal structures of the samples were measured by an X-ray diffractometer (Bruker/AXS D8 Advance) operating at 40 kV and 40 mA using Cu Kα radiation. The samples were scanned from 10° to 80° (2θ) with a step of 0.02°. The patterns were referred to the powder diffraction files–1998 ICDD PDF Database for identification.

In order to get insight of the decomposition behavior of ABS over CeO_2, *in situ* XRD and FT-IR experiments were carried out to capture the possible intermediates in the process. CeO_2-ABS sample was prepared by grinding the CeO_2 and ABS (50 wt% in the mixture). For the *in situ* XRD experiment, patterns of the samples of CeO_2 mixed with ABS were collected at room temperature, 220, 350, and 500 °C, respectively.

The sulfur-containing species measurements of the sample (CeO_2 + ABS) and the mixture annealed at 220, 350 and 500 °C, respectively, were carried on a Fourier transform infrared spectroscope (Nicolet 6700) equipped with a wafer supporting device [22]. Each sample calcined at a certain temperature was blended in KBr with the sample/KBr ratio (w/w) of 1/50, and then was pressed into wafer. All the spectra were collected from 32 scans at 4 cm^{-1} resolution with pure KBr as background.

Raman spectra were collected on a spectrometer (Horiba, JY T64000) under ambient conditions. A laser with a wavelength of 532 nm was used as the excitation source and the power output was about 300 mW.

2.3. Decomposition behavior of ABS over catalysts

Temperature-programmed decomposition of ABS (10 wt%) mixed with CeO_2 and the catalysts was carried out on a thermal gravimetric analyzer (TG, Seiko 6300TG-DTA) coupled with a mass spectrometer (MS, Hiden HPR 20) (TG-MS) [9]. The samples were prepared by grinding the ABS with the catalysts until the mixture