Catalysis Communications 50 (2014) 83–86

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Study on the NO reduction by NH_3 on a SO_4^{2-}/AC catalyst at low temperature

Zhanggen Huang *, Yaqin Hou, Zhenping Zhu, Zhenyu Liu

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

ARTICLE INFO

Article history:
Received 4 December 2013
Received in revised form 19 February 2014
Accepted 6 March 2014
Available online 13 March 2014

Keywords:
SO_4^{2-}/AC catalyst
SO_2
H_2O
Oxygen-containing functional group
Carbon

ABSTRACT

The selective catalytic reduction (SCR) of NO with NH_3 at low temperature over a novel SO_4^{2-}/AC catalyst (activated coke supported sulfate acid) was investigated especially in the presence of SO_2 and H_2O. A higher SCR activity and stability were attributed to the cooperation of the oxygen-containing function group and carbon. SO_2 promoted SCR activity, which was due to the formation of H_2SO_4 on the catalyst surface and adsorbed more NH_3. The capillary condensation of H_2O in the micropores of the catalyst inhibited SCR activity and the reaction of adsorbed NH_3 and NO.

1. Introduction

Selective catalytic reduction (SCR) of NO with NH_3 is the most effective technology for NO_x removal from stationary flue gas. Low-temperature SCR process is preferable because it allows the process with downstream of dust removal equipments and desulfurization devices without flue gas pre-heating [1,2]. Now many catalysts ($MnOx/Al_2O_3$, CuO/AC, CuO/CNTs) show higher SCR activity at low temperature, however, those are easily deactivated in the presence of SO_2 [3–5]. Zhu et al. studied vanadium oxide supported activated coke (V_2O_5/AC) catalysts and showed higher SCR activity in the presence of SO_2 at 180–250 °C due to the formation of SO_4^{2-} [6–8]. But a V_2O_5/AC catalyst is easily deactivated in the presence of H_2O and SO_2 [9], which is because of the excess deposition of ammonium-sulfate salts on the catalyst surface [10], so the V_2O_5/AC catalyst must be used under rigorous conditions, such as, low V_2O_5 loading, lower space velocity and higher reaction temperature [11].

Many studies have indicated that increasing the surface acidity of a catalyst could promote the sulfate species in the presence of SO_2 and H_2O above 350 °C and the catalytic activity was improved [12–14]. SO_4^{2-}/TiO_2, as a super acid catalyst, exhibited a considerable SCR activity above 400 °C [15]. The SO_4^{2-}/AC catalyst may also serve as a super acid catalyst for the SCR reaction of NO with NH_3 at lower temperatures in the presence of SO_2 and H_2O, however, there is no related report in literatures.

In this work, the SO_4^{2-}/AC catalyst was prepared by impregnation of H_2SO_4 on AC, and then the SCR activity and stability of the SO_4^{2-}/AC catalyst were investigated at low temperature, especially in the presence of SO_2 and H_2O.

2. Experimental

2.1. Catalyst preparation

Activated coke (AC) is a commercial coal-derived coke from Shanxi Xinhua Chem. Co. LTD, China. AC was crushed and sieved to collect 30–60 mesh fraction, and then dried at 110 °C for 12 h.

AC supported sulfuric acid (SO_4^{2-}/AC) is prepared by an equivalent volume impregnation using an aqueous solution of H_2SO_4 on AC ($V(H_2SO_4)/m(AC) = 1$ ml:1 g). After the impregnation, the catalyst is dried at 110 °C for 5 h. H_2SO_4 contents on the catalyst is determined by the concentration of H_2SO_4. The catalyst used in this work that contains 1.0 mmol H_2SO_4 is termed as SO_4^{2-}-1.0/AC for the sake of clarity.

2.2. Catalytic activity measurement

The activity of the SO_4^{2-}/AC catalyst is carried out with a fixed bed glass reactor. The tubing of the reactor system is wrapped with heating tapes to prevent the formation and deposition of the ammonium sulfate/bisulfate [16], through the reaction between SO_2 and NH_3 occurring prior to the catalyst bed.

H_2O is introduced into the system through a heated gas-wash bottle containing deionized water by passing Ar, O_2/Ar and NO/Ar. The concentrations of the inlet and outlet NO, SO_2 and O_2 are simultaneously

---

* Corresponding author. Tel./fax: +86 351 4043727.
E-mail address: zghuang@sxicc.ac.cn (Z. Huang).

http://dx.doi.org/10.1016/j.catcom.2014.03.008

measured by an on-line Flue Gas Analyzer (KM9006, Kane-May International Limited).

2.3. Characterization analysis

BET surface area and pore volume of the SO_4^{2-}/AC samples were determined by a micromeritics ASAP 2000 micropore physical adsorption analyzer. Before being measured, all samples are outgassed at 150 °C under 10^{-4} Pa for 3 h. The surface area of the catalyst is measured by nitrogen adsorption at − 196 °C. Contents of the elements C, O and S in the SO_4^{2-}/AC catalyst samples are measured on an element analyzer (Vario EL, Germany).

The FTIR analyses of the SO_4^{2-}/AC catalyst samples were performed on a Bruker Equinox 55 FTIR instrument with KBr optics and a MCT detector. The catalyst samples were mixed with potassium bromide, ground, and pelletized. Thirty-two scans were made and averaged to yield a spectrum with a resolution of 8 cm^{-1} over the spectral range 4000–400 cm^{-1} with 200 scans.

NH_3-TPD was performed in a fixed bed glass reactor the same as in Section 2.2. 1.0 g catalyst was exposed to a stream containing 1500 ppm NH_3 and balance Ar. After the adsorption, the sample was purged with Ar for 30 min to eliminate physically adsorbed NH_3, and then heated to 500 °C at a rate of 10 °C/min in a flow of Ar at 400 ml/min. The outlet gas was monitored on-line by an infrared gas analyzer (JNYQ-I-41C).

NO oxidation and NO_x-TPD were performed on the catalyst samples using Flue Gas Analyzer KM9006 to record the concentration of NO and NO_2. For NO oxidation, the samples were exposed to 600 ppm NO + 5% O_2 + Ar for 2 h at room temperature and then followed by an Ar purge. After the oxidation, the samples were heated to 500 °C at a rate of 10 °C/min in a flow of Ar at 400 ml/min.

3. Results and discussion

3.1. FTIR spectra of the SO_4^{2-}/AC catalyst

AC supported different contents of H_2SO_4 are analyzed by FTIR, and the results are shown in Fig. 1. The bands at 1091 cm^{-1} and 616 cm^{-1} are the vibration of the SO_4^{2-} ions. The SO_4^{2-} ions show two infrared peaks at 1104 cm^{-1} (ν_1) and 613 cm^{-1} (ν_2) on the SO_4^{2-}/TiO_2 catalyst [15]. When SO_4^{2-} is bound to the catalyst surface, the symmetry is lowered to either $C_{3\nu}$ or $C_{2\nu}$ [15]. The band at 1356 cm^{-1} is the vibration of S═O. These FTIR results indicate that only H_2SO_4 is on the surface of the SO_4^{2-}/AC catalyst.

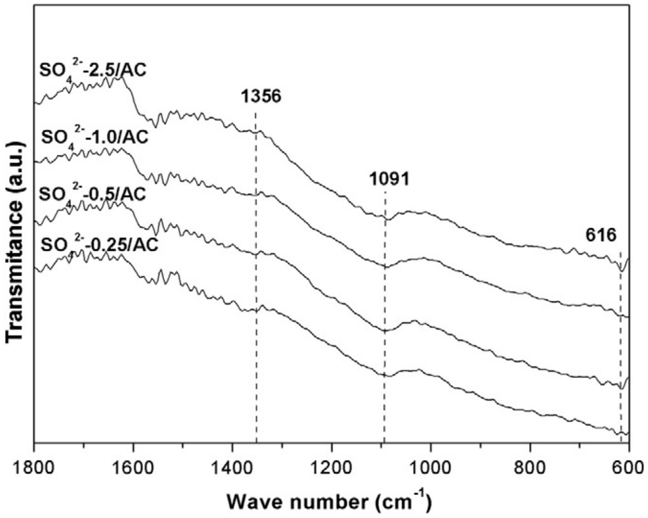

Fig. 1. FTIR spectra of the SO_4^{2-}/AC catalyst with different contents of H_2SO_4 impregnation.

3.2. SCR activity of H_2SO_4 content

Fig. 2 shows the NO conversion and oxygen element content on different H_2SO_4 contents of the SO_4^{2-}/AC catalyst at 250 °C in the presence of SO_2. NO conversion increases from 44% to 97% with increasing H_2SO_4 amount from 0 to 1.0 mmol, maintains at about 97% in the H_2SO_4 range of 1.0–1.5 mmol and then drops to about 95% when H_2SO_4 amount reached 2.5 mmol. In the presence of SO_2 and O_2, the formed SO_3 or H_2SO_4 adsorbs on the AC surface [17] that can increase the catalyst surface acidity and promote NH_3 adsorption. From NH_3-TPD profiles of AC and SO_4^{2-}-1.0/AC, the amount of NH_3 desorbed from AC was 0.018 mmol/g, while from SO_4^{2-}-1.0/AC, it was 0.064 mmol/g.

Fig. 2 also shows the relation of the number of oxygen-containing functional group and NO conversion on the SO_4^{2-}/AC catalyst samples. With the amount of H_2SO_4 impregnation ranges from 0 to 2.5 mmol on AC, the oxygen element content of the SO_4^{2-}/AC catalyst samples linearly increases from 2.2% to 20.29%, which is in agreement with the literature [18–20]. NO conversion increases to 97% when oxygen content is about 15–17%, and it decreases when the oxygen content is above 20%.

Table 1 shows the primary parameters of the SO_4^{2-}/AC catalyst samples. With the H_2SO_4 impregnation, the amount of oxygen and sulfur elements increases, however, the amount of carbon significantly decreases. The decreasing of carbon content may be due to the reaction of H_2SO_4 and carbon on AC, which results in the eroding of the AC surface and the decreasing of surface area.

3.3. Effect of H_2O and SO_2

Fig. 3 shows the effect of SO_2 and H_2O on the SCR activity of the SO_4^{2-}-1.0/AC catalyst sample using a transient response reaction. At the beginning of the SCR reaction, the higher NO conversion may be due to the coexisting of the adsorption of NO and the reaction of NO with NH_3 [18,20]. Teng and Suuberg [21] have found that NO can be reversibly and irreversibly adsorbed on the activated carbon and the reversible adsorption of NO is being on the $(NO)_2$ state at the temperature below 200 °C [21,22]. When SO_2 is introduced, the NO conversion quickly increases and reaches the stable state from 61% to 71%. The result suggests that when more SO_3 or H_2SO_4 adsorbed on the catalyst surface in the presence of SO_2, then more NH_3 are adsorbed. It is necessary to point out that the outlet SO_2 concentration was not detected in the test, indicating that SO_2 is oxidized to SO_3 consumed. Finally, when H_2O is also introduced, NO conversion quickly decreases and then remains stable, which is not similar to the results of the

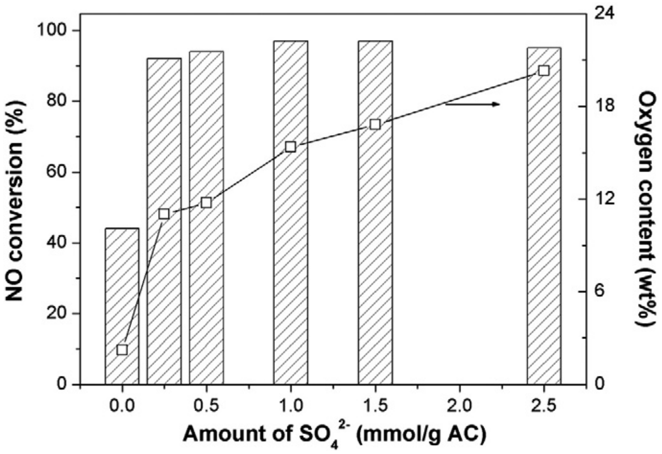

Fig. 2. Activity and oxygen content of the SO_4^{2-}/AC catalyst versus H_2SO_4 impregnation. Reaction conditions: 500 ppm NO, 600 ppm NH_3, 500 ppm SO_2, 3.4% O_2, balance Ar, space velocity of 9000/h, and reaction temperature of 250 °C.