Petroleum and Coal

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THE EFFECT OF SO_2 ON Cu-SSZ-13 SYNTHESIZED BY SiO_2 AEROSOL IN SELECTIVE CATALYTIC REDUCTION OF NO WITH NH_3

*Hao Fan, Rui Wang**

School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250199, China

Received March 17, 2018; Accepted May 11, 2018

Abstract

Cu-SSZ-13 was successfully synthesized by a one-pot method with silica aerosol acting as the silicon source. The physicochemical properties of obtained samples were characterized by X-ray diffraction, thermogravimetric and differential scanning calorimetry, and NH_3-temperature programmed desorption. The effects of deionized water usage during catalyst preparation on catalyst activity were investigated in detail. Among all catalysts, Cu-SSZ-13-25 possessed best NO conversion up to 85% at 250-450 ºC, and the denitration efficiency at 300 ºC could be stabilized at about 90%. Furthermore, the NH_3-SCR activity of Cu-SSZ-13-25 reduced to 62% in the presence of water vapor and bounced back to 88% with the removal of H_2O (g). The SO_2 in flue gas reduced the desorption rate of ammonia on the catalyst surface, resulting in the activity of Cu-SSZ-13-25 down to 47%.

***Keywords**: Cu-SSZ-13; SiO_2 aerosol; Selective Catalytic Reduction; NH_3-TPD; SO_2 poisoning.*

1. Introduction

NO may cause a series of non-negligible environmental problems such as photochemical smog and acid rain[1-2]. In the previous decade, selective catalytic reduction of NO using NH_3 as a reducing agent (NH_3-SCR) has been a commonly used method to effectively reduce NO emission[3]. At present, V_2O_5/TiO_2 series catalysts are widely used in industrial denitration which can remove 90% NO at 300-400ºC [4]. However, the above-mentioned catalyst is restricted by the volatilization of vanadium in the catalyst at high temperature[5]. Thus, further development of high efficiency and eco-friendly SCR catalyst remains to be a challenge.

Alternatively, the molecular sieve catalysts especially zeolite-supported metal catalysts have obtained a lot of attentions due to their good specific surface area and stable space structure [6]. Song *et al.* [7]analyzed the effect of copper precursors of Cu/ZSM-5 catalysts on the SCR catalytic activity and verified copper nitrate was the optimized one to remove 90% NO_x at 225–405 ºC. Another prominent molecular sieve catalyst is Cu-SSZ-13 because of its regular microporous structure and excellent resistance to hydrothermal aging [8]. Mn-Ce/Cu-SSZ-13 catalyst [9] was synthesized with favorable activity from 125°C to 450 °C up to 90% NO conversion. Nevertheless, the template of Cu-SSZ-13 N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH) and silica sol used as silicon source was expensive leading to high cost in catalyst synthesis [10]. In order to reduce the cost, Xie *et al.* [11] reported a one-pot synthesis method using copper–tetraethylenepentamine (Cu–TEPA) as both template and copper source. This method significantly reduced the synthesis cost which is good for commercialization. However, perfect alternatives to silica sol have not been found. A possible cheaper silicon source is silica aerosol with the advantages of small silicon particles (about 50 nm) and benign dispersion in water.

In this study, a series of Cu-SSZ-13 were synthesized by one-pot method where Cu–TEPA used as template and silica aerosol acting as silicon source. The effects of deionized water usage during catalyst preparation on catalyst activity were investigated in detail. The sample with the best activity was selected to investigate the influence of poisoning caused by water vapor and SO_2 in flue gas. And physicochemical properties of samples were characterized by X-ray diffraction (XRD), Thermogravimetric and differential scanning calorimetry (TG-DSC), and NH_3-temperature programmed desorption (NH_3-TPD).

2. Materials and methods

2.1 Materials

In this work, all reagents and solvents used were A.R. grade without further purification. $CuSO_4·5H_2O$ was purchased from Liqiang (Guangzhou) Chemical Co. Ltd. $NaAlO_2$ were received from the Xiya Reagent Co. Ltd. Tetraethylenepentamine(TEPA) was supplied by Damao (Tianjin) Chemical Co. Ltd. Silica aerosol was produced by Tianjin Kemiou Chemical Reagent Co. Ltd. the NaOH was purchased from Tianjin Guangcheng Chemical Reagent Co. Ltd.

2.2. Catalysts preparation

The Cu–SSZ-13 samples were prepared using the one-pot method. In a typical synthesis, 0.51 g $NaAlO_2$ and 0.5 g NaOH were dissolved in 4.72 g of deionized water by ultrasound for 10 minutes. Then 1.149 g $CuSO_4·5H_2O$ was added to the solution and stirred for 30 minutes. Next, 1.07 g TEPA was dropped into the mixture followed by intense stirring for 1h. Finally, 2.63 g silica aerosol and x g deionized water (x=13, 17, 25, 35, 50) were added and stirred for 3h. The resulting solution was transferred into Teflon-lined autoclaves and heated at a temperature of 140°C for 6d. The product was collected by vacuum filtration, washed by deionized water for several times and dried at 100°C for 12h, named as Cu-SSZ-13-x. Before NH_3-SCR activity tests, 1 g Cu-SSZ-13-x was added into 100 ml NH_4NO_3 solution (1 $mol·L^{-1}$) and stirred for 12h to remove excess copper ions. Then, the samples dried at100°C for 12h and calcinated at 550°C for 8h (heating rate was kept at $5°C·min^{-1}$).

2.3. Catalyst characterization

The XRD pattern of sample is conducted with a Bruker D8 Advanced diffractometer with a Cu target Kα-ray and Nickel filter was utilized to ensure the incoming x-rays are monochromatic. In addition, the scanning angle is from 5 to 50° of 2θ at a scanning rate of 2.8° per minute. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis of obtained samples were carried out with a SDT Q600 Universal V4.1D TA instrument under a flow of N_2 from 100°C to 700°C with a heating rate of $10°C·min^{-1}$. NH_3-TPD was finished by a thermal conductivity detector (TCD) at a heating rate of $8°C·min^{-1}$, and the total carrier gas flow is 100 $ml·min^{-1}$.

2.4. NH_3-SCR activity

The NH_3-SCR activity measurements were carried out in a fixed bed reactor placed in the center of a tubular furnace. The catalyst was positioned in the quartz tube between two layers of quartz wool. The typical reaction conditions were regulated by mass controllers as following: 600 parts per million by volume (ppmv) NO, 700 ppmv NH_3, 6% O_2 and N_2 was the equilibrium gas. In typical conditions, 0.13 g sample was used in each run. The total flow rate was 100 $ml·min^{-1}$ corresponding to a space velocity (GHSV) of 15000 h^{-1}. The NO_x conversion rate can be expressed as $(C_0-C)/C_0\times100\%$, where C_0 stands for the concentration of NO_x in the feed gas and C stands for the concentration of NO_x in the outlet gas.

3. Results and discussion

3.1. Characterizations

XRD pattern of Cu-SSZ-13-25 was shown in Fig. 1, it can obviously find the characteristic peaks of CHA molecular sieves [12] (2θ=9.5°, 12.9°, 16.2°, 20.8°) illustrating that Cu-SSZ-13 was successfully synthesized with silica aerosol. However, the intensity of peaks is weaker than Cu-SSZ-13 synthesized by silica sol. It has been reported that the interaction between the templating agent and inorganic species is the key to the formation of a stable hybrid mesostructured. Different silicon sources have diverse effects on the structure and species of the silicate ions in the crystallization solution [13]. The poor dispersion of silica aerosol in water resulted in a decrease of silicate ions in crystallization solution which is the main reason for the weaker crystallinity of the catalyst.

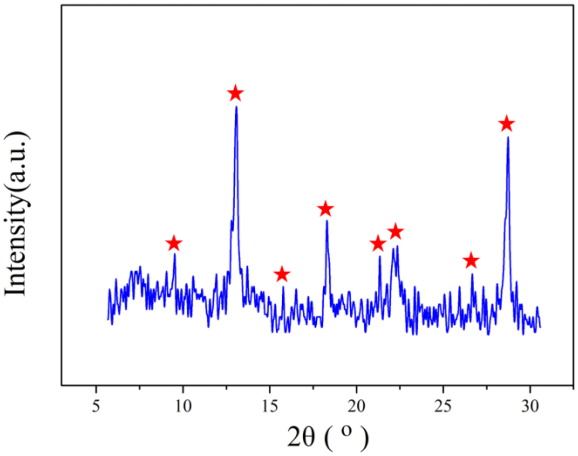

Fig. 1. XRD pattern of Cu-SSZ-13-25 sample

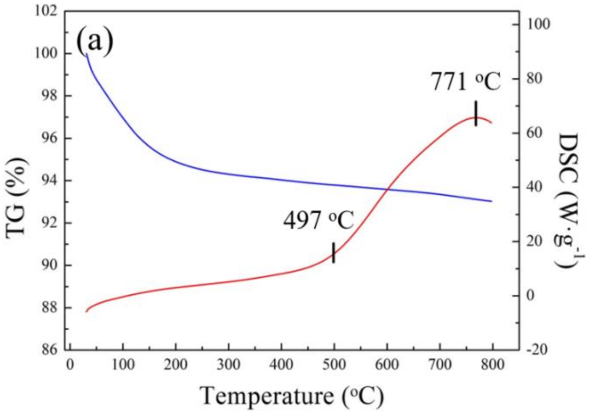

Fig. 2. TGA-DSC curves of Cu-SSZ-13-25 sample

In order to study the thermal stability of the catalyst, TG-DSC analysis of Cu-SSZ-13-25 was done, as shown in Fig. 2. It was obvious that the mass fraction of the sample dropped to 94% at a temperature below 200°C due to moisture evaporation from the sample. Then, the mass fraction went down steadily and slowly indicating that the catalyst had good thermal stability. Furthermore, there are two endothermic peaks located at 497°C and 771°C, which could be attributed to the decomposition of residual TEPA calcination and the oxidation of the Cu species, respectively.

3.2. SCR activity

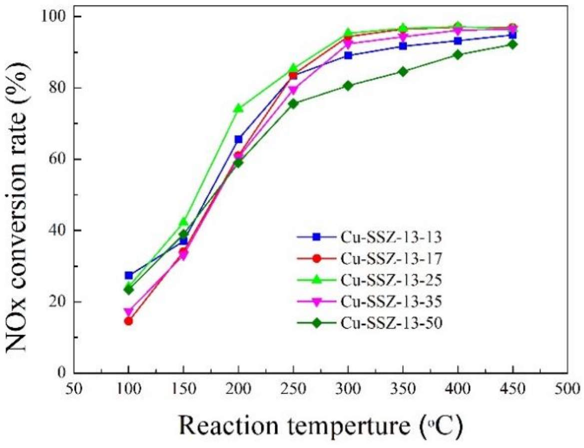

Fig. 3. The effects of deionized water usage during catalyst preparation on catalyst activity

It is undoubted that the amount of deionized water and NaOH used in catalyst preparation has a great influence on the structure and activity of Cu-SSZ-13, and moderate Na^+ content can improve both the low-temperature activity and the hydrothermal stability [14]. Xie *et al.* [15] testified that higher Na^+ contents brought in poorer hydrothermal stability because excess Na^+ ions in the catalysts decreased the stability of Cu species seriously.

In this study, deionized water usage was changed in order to improve the dispersion of silica aerosol in crystallization solution leading to the change of Na^+ concentration. Hence, the effects of deionized water usage during catalyst preparation on catalyst activity was nonnegligible. As shown in Fig. 3, the tendency of the catalytic activity of each sample was similar, among them, Cu-SSZ-13-25 possessed the best NO conversion up to 85% at 250-450°C, and the denitration efficiency at 300°C can be stabilized at about 90%. Comprehensively, Cu-SSZ-13-50 has the lowest catalytic efficiency due to the increase of deionized water usage decreased the Na^+ concentration in the crystallization solution leading to the insufficient crystallinity of sample [15]. In summary, Cu-SSZ-13-25 is the optimal catalyst.

3.3. Effect of SO_2 and water vapor

In the life test, the conversion of NO could be stabilized at 95% in 10 minutes, and there is no significant fluctuation in the test. However, in the presence of water vapor, the activity of Cu-SSZ-13-25 decreased rapidly within half an hour, then stabilized at about 62% after an hour. After removing H_2O(g), the NO conversion recovered to 88% within half an hour, furthermore, as the reaction continues, the activity of the sample is returned to the initial state after two hours.

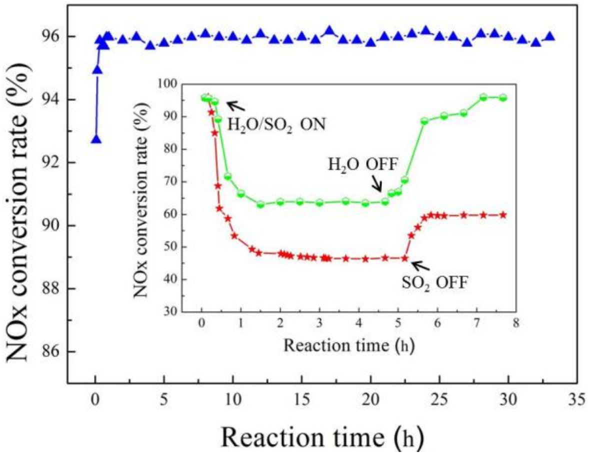

Fig. 4. The life test and the effect of SO_2 and water vapor on the SCR activities of the Cu-SSZ-13-25 catalyst. All Reaction was conducted at 300 °C

In the denitrification reaction with SO_2 in the flue gas, low temperature deactivation is primarily caused by the formation of ammonium sulfate species or competitive adsorption between SO_2 and NO_x. what is more, the formation of metal sulfate species is considered to be a key step in the standard SCR reaction [16]. As shown in Fig. 4, after the introduction of SO_2, the NO conversion was significantly reduced to about 47% after one hour, and then it was basically stable. With the removal of SO_2, the activity of Cu-SSZ-13-25 recovered rapidly to 60%. Therefore, the activity of the catalyst is not sufficient to meet the needs of industrial applications. Further work is needed to improve the resistance to SO_2 of Cu-SSZ-13 synthesized by silica aerosol.

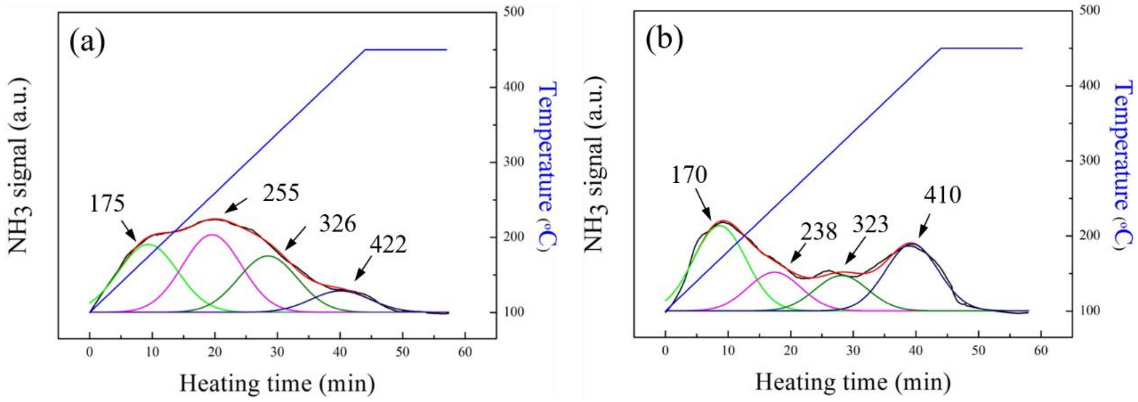

Fig. 5. NH_3-TPD profiles of (a) Cu-SSZ-13-25, (b) Cu-SSZ-13-25 after SO_2 and water vapor poisoning experiment.

NH_3-TPD results (Fig. 5) demonstrated the change of the surface acid amount of Cu-SSZ-13-25 before and after SO_2 and water vapor poisoning experiment. As shown in Fig. 5(a), The peaks position of Cu-SSZ-13-25 was mainly concentrated in the low temperature, where the peak at 175°C was attributed to weak acid sites and peaks at 255°C, and 326°C are assigned to mid-strong acid sites [17]. The peaks position of Cu-SSZ-13-25 after SO_2 and water vapor poisoning experiment did not change significantly, but the peak intensity of mid-strong acid sites obviously reduced, indicating that the poisoning effect of SO_2 was mainly concentrated on the medium-strong acid sites. However, the intensity of the peak at 410 °C was increased, verifying that the active sites were converted to strong acid sites after the introduction of SO_2

in the flue gas, which was more difficult to desorb in NH_3-SCR reaction at 300°C. Therefore, the presence of SO_2 reduced the desorption rate of ammonia on the catalyst surface, resulting in a decrease in the activity of Cu-SSZ-13-25.

4. Conclusions

Cu-SSZ-13-x was successfully synthesized by a one-pot method with silica aerosol acting as the silicon source. However, the crystallinity of Cu-SSZ-13-x is weaker than Cu-SSZ-13 synthesized by silica sol due to the poor dispersion of silica aerosol in water. In all catalysts, Cu-SSZ-13-25 possessed best NO conversion up to 85% at 250-450°C, and the denitration efficiency at 300°C can be stabilized at about 90%. Furthermore, the NH_3-SCR activity of Cu-SSZ-13-25 reduced to 62% in the presence of water vapor and bounced back to 88% with the removal of H_2O. SO_2 reduced the desorption rate of ammonia on the catalyst surface, resulting in the activity of Cu-SSZ-13-25 down to 47%. Further work is needed to improve the resistance to SO_2 of Cu-SSZ-13 synthesized by silica aerosol.

Acknowledgements

This work was financially supported by the Ministry of Education of China under New Century Excellent Talents program (NCET-05-0584), Natural Science Foundation of China (20776080, 20911120088), and Scientific & Technological Development Program of Shandong Province (2008GG10006005).

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To whom correspondence should be addressed: prof. Rui Wang, School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250199, China, ree_wong@hotmail.com