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Low temperature selective catalytic reduction of NO by C_3H_6 over CeO_x loaded on AC treated by HNO_3

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Abstract: The activated carbons from coal were treated by HNO_3 (named as NAC) and used as carriers to load 7% Ce (named as Ce(0.07)/NAC) by impregnation method. The physical and chemical properties were investigated by thermogravimetric-differential thermal analysis (TG-DTA), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), scanning electron microscopy (SEM) and NH_3-temperature programmed desorption (NH_3-TPD) and NO-temperature programmed desorption techniques. The catalytic activities of Ce(0.07)/NAC were evaluated for the low temperature selective catalytic reduction (SCR) of NO with C_3H_6 using temperature-programmed reaction (TP-reaction) in NO, C_3H_6, O_2 and N_2 as a balance. The results showed that the specific surface area of Ce(0.07)/NAC was 850.8 m^2/g and less than NAC, but Ce oxides could be dispersed highly on the activated carbons. Ce oxides could change acid sites and NO adsorption as well as oxygen-containing functional groups of activated carbons, and Ce^{4+} and Ce^{3+} coexisted in catalysts. The conversion of NO with C_3H_6 achieved 70% at 280 °C over Ce(0.07)/NAC, but with the increase of O_2 concentration, heat accumulation and nonselective combustion were exacerbated, which could cause surface ashing and roughness, resulting in a sharp decrease of catalytic activities. The optimum O_2 concentration used in the reaction system was 3% and achieved the high conversion of NO and the widest temperature window. The conversion of NO was closely related to the NO concentrations and [NO]/[C_3H_6] ratios, and the stoichiometric number was just close to 2:1, but the presence of H_2O could affect the denitration efficiency of catalyst.

Keywords: low temperature; activated carbon; cerium oxides; selective catalytic reduction; hydrocarbon; rare earths

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Nitrogen oxides (NO_x) from combustion of fossil fuels are one of the major pollutants in air, which can cause photochemical smog, acid rain, ground level ozone and respiratory problems. Therefore, stringent regulations in the world require the development of efficient $DeNO_x$ technologies. The selective catalytic reduction (SCR) of NO_x to N_2 has drawn more attention. The SCR of NO_x by NH_3 in the presence of O_2 is the most effective and commercial removal technology[1], but there is the difficulty of NH_3 storage and potential hazards of NH_3 leakage to human health. Another efficient way is to remove NO_x from exhaust using hydrocarbon as reducing agent[2]. Iwamoto and coworkers[3] have reported that the Cu exchanged ZSM-5 material is an effective catalyst for the SCR of NO with hydrocarbon.

Many catalysts, including noble metals (such as Pt[4,5], Pd[6], Au[7] and Ag[8]) and transition metals (such as Mn[9], Cu[10] and Fe[11]) are investigated for SCR. Among them, metal-exchanged ZSM-5 has been widely studied due to higher NO removal. However, this catalyst has low thermal stability and can be severely deactivated by H_2O. It is reported that CeO_2 has excellent oxygen storage capacity because it can release and store oxygen according to the transformation between Ce^{4+} and Ce^{3+} [12], and cerium oxide is used as a common promoter in automotive three-way catalysts[13]. The CeO_2 can promote the oxidation of NO to NO_2, which is conducive to the improvement of NO reduction activity[14,15]. Huang et al.[16] have found that the addition of cerium oxide to SCR catalysts can improve low-temperature SCR activities. Zeolite[17], Al_2O_3[6,18], SiO_2[19], TiO_2[20] and carbon materials[21] have been used as catalyst supports. Activated carbon as the support for the low-temperature SCR of NO_x with hydrocarbon will be possible because of its high specific surface area and chemical stability[5]. And, the porosity structure and functional groups on the surface of activated carbon can improve the formation of some intermediates in the reactions[5]. Cu/AC has been used to remove NO_x by Shigemoto et al.[22], but effects of oxygen concentration on the carbon carrier and hydrocarbon re-

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ductant was not involved.

V_2O_5/TiO_2, mixed with WO_3 or MoO_3, as commercial NH_3-SCR catalysts, exhibits high activity and resistance to SO_2 but has a narrow temperature window of 300–400 ºC[23]. This catalyst in SCR unit must be located before the precipitator and desulphurization to be reheated by the flue gas, and a large number of dusts will be deposited on the catalysts. For these reasons, the most importance is to develop low-temperature catalysts with high activities when they are placed downstream of the desulfurizer and the particle removal device at the temperature window of 120–350 ºC[24]. Therefore, it is critical to find the effective active component and suitable support because characteristics of the catalysts depend mainly on these two ingredients. The objective of this paper was to develop an active SCR catalyst for a low temperature SCR of NO with hydrocarbon (C_3H_6). The active component used in preparing catalyst in the present work was CeO_x because it had release/storage oxygen as an oxygen reservoir via redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions[25]. In this work, the SCR of NO by C_3H_6 over a CeO_x/AC was studied in different O_2 concentrations and [NO]/[C_3H_6] ratios. The physical and chemical properties of catalysts were characterized by thermogravimetric-differential thermal analysis (TG-DTA), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), scanning electron microscopy (SEM) and NH_3-temperature-programmed desorption (NH_3-TPD).

1 Experimental

1.1 Catalyst preparation

All chemicals used in this work were of analytical grades. The original activated carbons (named as AC; Henan Tongxing Chemical Co., Ltd., China) were crushed and sieved to 40–60 meshes. The obtained carbon particles were completely immersed in 65% HNO_3 solution at 80 ºC water bath for 2 h. After treatment, the samples were washed with distilled water until washing fluid became neutral, and then dried in a vacuum oven at 110 ºC for 2 h. The carbon supports treated by HNO_3 were denoted as NAC. The precursor used was $Ce(NO_3)_3\cdot 6H_2O$. The supports were impregnated with an appropriate concentration (0.12 g/mL) precursor solution to achieve Ce loading of 7%. After the mixtures were allowed to stand for 24 h, they were dried in a vacuum oven at 110 ºC and calcined at 400 ºC for 2 h in a sealed muffle furnace under N_2 atmosphere. The obtained catalyst was written as Ce(0.07)/NAC.

1.2 Activity evaluation

The activity measurement (Fig. 1) was carried out in a fixed-bed flow micro-reactor (15 mm I.D.). The height of catalyst bed in micro-reactor contained 1 cm, and NO removal was performed by passing a flue gas mixture. A thermocouple was directly immersed into the catalyst bed and connected to a programmable temperature controller to monitor the reaction temperature. The flue gas mixture contained NO, C_3H_6, O_2 and N_2 as a balance. The concentration of the gas before and after reactor was monitored on-line by a five-component analyzer FGA-4100 (Analysis Instrument Co., Ltd., Fushan, China). The conversion of NO or C_3H_6 is calculated by formulas as follows:

$$\text{NO coversion (\%)} = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{inlet}}} \times 100\% \quad (1)$$

$$C_3H_6 \text{ coversion (\%)} = \frac{[C_3H_6]_{\text{inlet}} - [C_3H_6]_{\text{out}}}{[C_3H_6]_{\text{inlet}}} \times 100\% \quad (2)$$

The generation of CO_2 or CO was directly detected by the five-component analyzer.

1.3 Catalyst characterization

The catalyst stability was studied by TG-DTA technique on a Beijing Hengjiu HCT-2 apparatus. The catalysts were heated from room temperature to 650 °C at a

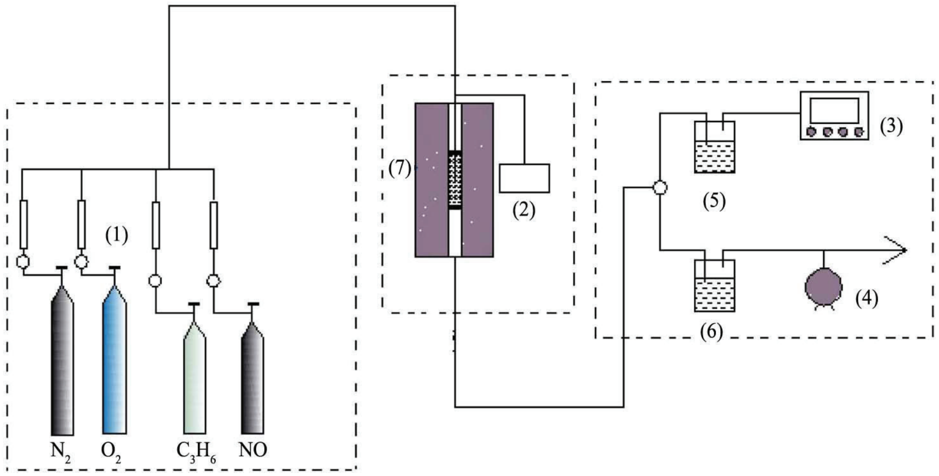

Fig. 1 Evaluation device of catalysts

(1) Mass controller; (2) Temperature controller; (3) Five gas analyzer; (5) Wet flow-meter; (6) Protection bottles; (7) Tube furnace