SELECTIVE CATALYTIC REDUCTION OF NO WITH UREA SUPPORTED ON PITCH-BASED SPHERICAL ACTIVATED CARBON AT LOW TEMPERATURES

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Introduction

The control of NO_x emissions becomes a worldwide concern because NO_x can cause serious environmental problems [1]. Recently, Shirahama et al. [2,3] proved that urea supported on activated carbon fibers (ACFs) could efficiently reduce NO to N_2 at 30 ^oC in the presence of O_2. The possible reaction steps were proposed as follows:

$$NO+0.5O_2 \rightarrow NO_2 \quad (1)$$

$$NO_2+NO+(NH_2)_2CO \rightarrow 2N_2+CO_2+2H_2O \quad (2)$$

Here some potential problems in the urea-supported ACFs system, such as the poor mechanical properties and unstable bed resistance of ACFs, should be taken into consideration in industrial applications.

Pitch-based spherical activated carbon (PSAC) with high mechanical strength, smooth surface, uniform spherical shape, large surface area and easily controlled pore size distribution is expected to serve as one of the most promising catalysts or catalyst supports. In this paper, the reactivity of NO with urea supported on PSAC was studied. The research focused on the influence of reaction temperature and space velocity on low-temperature NO_x removal efficiency.

Experimental

A commercial PSAC supplied by Shanghai Heda Carbon Company was used in this work. Its properties were summarized in Table 1. Urea was supported onto PSAC by pore volume impregnation using an aqueous solution of urea. After impregnation, the obtained sample was kept at room temperature for 24 h, and then was vacuum-dried at 60 ^oC for 24 h. The urea loading was controlled at 8 wt.%.

Table 1. Physical Properties of PSAC.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)
PSAC	1182	0.47	0.41

Nitrogen adsorption-desorption isotherms of PSAC were measured at 77 K using a Micromeritics ASAP 2020M analyzer to determine the texture properties. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method. The total pore volume and micropore volume were calculated according to the density functional theory (DFT).

The reactivity of NO with urea supported on PSAC was measured in a vertical fixed-bed glass reactor with an internal diameter of 10 mm. The feed gas consisted of 500 ppmv NO, 21 vol% O_2, and balance N_2. In all tests, the total flow rate was maintained at 100 ml/min. The reaction temperature was controlled from 30 to 90 ^oC, and the space velocity was in the range of 2000~12000 h^{-1}. The concentrations of NO, NO_2 and NO_x were continually measured by an ECO PHYSICS CLD62 chemiluminescence NO/NO_x analyzer with a minimum detectable concentration of 0.5 ppmv. NO_x conversion during selective catalytic reduction (SCR) reaction tests was defined by the following equation:

$$NO_x \text{ conversion} = (C_{NO,in}-C_{NOx,out})/C_{NO,in}\times 100\% \quad (3)$$

Results and Discussion

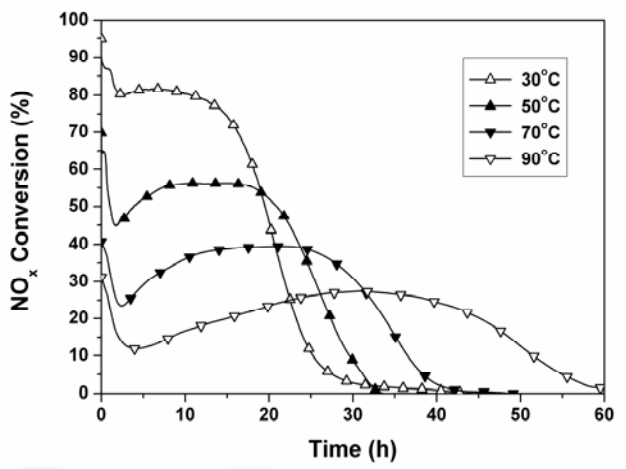

Fig. 1 Effect of reaction temperature on NO_x conversion over PSAC with 8 wt.% urea loading. Reaction conditions: 500 ppmv NO, 21 vol% O_2, balance N_2, space velocity = 6000 h^{-1}.

Fig. 1 shows the effect of reaction temperature on NO_x conversion over PSAC with 8 wt.% urea loading. It is clear to see that the SCR activity decreased with increasing reaction temperature. The initial and steady-state NO_x conversions were 90% and 82% at 30 ^oC, 65% and 56% at 50 ^oC, 41% and 39% at 70 ^oC, and 31% and 27% at 90 ^oC, respectively. Generally, a high reaction temperature benefits the activation of reactants and the desorption of products, but inhibits the adsorption of reactants on the surface of catalysts. Therefore, the data found in this work suggested that the NO removal process over urea-supported PSAC was controlled by the adsorption of NO. Similar results were previously reported. Zhang et al. [4] investigated NO adsorption and oxidation on activated carbons at temperatures below 100 ^oC, and found that both the NO adsorption capacity and the reaction rate of NO oxidation to NO_2 decreased with increasing temperature. Mochida et al. [5] observed that in NH_3-SCR over pitch-based ACFs in the low temperature window of 25~70 ^oC, NO

adsorption was mainly dependent on the reaction temperature, and the increased reaction temperature was unfavorable for NO adsorption and oxidation. They concluded that the decrease in NH_3-SCR activity with increasing reaction temperature was attributed to poor NO adsorption. Thus, high urea-SCR activity achieved at 30 ^oC in the present research was due to high NO adsorption on PSAC. On the basis of the above data, the optimum reaction temperature for NO removal over PSAC with 8 wt.% urea loading was 30 ^oC.

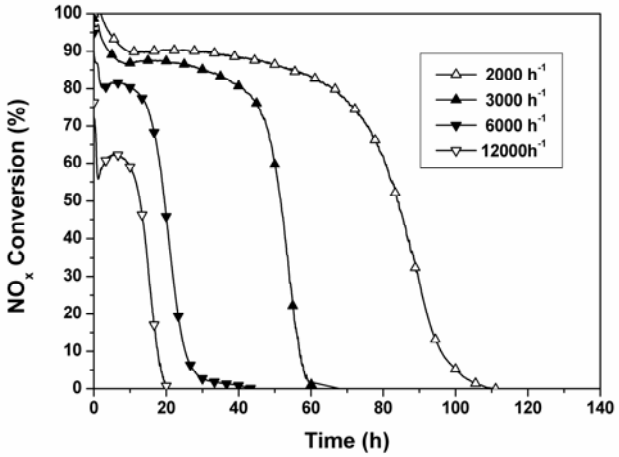

Fig. 2 Effect of space velocity on NO_x conversion over PSAC with 8 wt.% urea loading. Reaction conditions: 500 ppmv NO, 21 vol% O_2, balance N_2, urea loading = 8 wt.%, reaction temperature = 30 ^oC.

Fig. 2 shows the effect of space velocity on NO_x conversion over PSAC with 8 wt.% urea loading at 30 ^oC. The NO_x conversion in the whole time span decreased with increasing space velocity. The initial and steady-state NO_x conversions decreased from 100% and 90% at 2000 h^{-1} to 72% and 62% at 12000 h^{-1}. The NO_x removal period was also shortened with increasing space velocity, from 111 h at 2000 h^{-1} to 20 h at 12000 h^{-1}. These results showed that in the studied range, the space velocity markedly affected the SCR activity. At a low space velocity, reactants and PSAC had sufficient contact time and the micropore availability was increased in PSAC, which resulted in the increase in urea-SCR activity.

Conclusions

In this paper, urea supported on PSAC was studied for low-temperature SCR of NO. Reaction temperature and space velocity had potent impacts on the SCR activity of urea-supported PSAC. Low reaction temperature was favorable for NO adsorption and thus had a positive effect. Low space velocity also contributed to high SCR activity. More than 85% NO_x conversion for 55 h could be achieved over PSAC with 8 wt.% urea loading at 30 ^oC under the condition of 500 ppmv NO, 21 vol% O_2 and a space velocity of 2000 h^{-1}.

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