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RESEARCH NOTE

Promoting Effect of SO_2 on Activated Carbon-Supported Vanadia Catalyst for NO Reduction by NH_3 at Low Temperatures

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The effect of SO_2 on the V_2O_5/AC catalyst for the NO reduction with NH_3 at low temperatures (150–250°C) is studied using a transient method. The results show that the presence of SO_2 in the reaction stream can significantly promote catalytic activity, which is largely conditioned by V_2O_5 loading and reaction temperature. Lower V_2O_5 loading and higher reaction temperature are favorable. Higher V_2O_5 loading causes heavy deactivation of the catalyst. The reason for the behavior of the catalyst is also studied and discussed. The promoting role of SO_2 seems to result from the sulfate species formed and deposited on the carbon surface, which increase the surface acidity and hence the activity of the catalyst.

Selective catalytic reduction (SCR) of NO with NH_3 has been well proven and employed in the removal of NO_x from stationary sources (1). However, current catalysts, such as V_2O_5/TiO_2 or $V_2O_5–WO_3/TiO_2$, must be operated at above 350°C to avoid catalyst deactivation by SO_2 (1). A low-temperature SCR process is believed to have low energy consumption and to be economical for retrofitting into an existing system for flue gas cleaning (2, 3). The key to the low-temperature SCR process is to develop a catalyst which resists SO_2 poisoning. We recently reported a carbon-supported vanadium oxide (V_2O_5/AC) catalyst for the SCR reaction. Interestingly, it not only shows high catalytic activity but can be greatly promoted by SO_2 in the reaction gas (4). In this note, the effect of SO_2 on the SCR activity of the V_2O_5/AC catalyst is studied in detail using a transient method, and the influences of V_2O_5 loading and reaction temperature on the effect are also examined.

The support, activated carbon (AC), was prepared from a commercial coal-derived semicoke through steam activation at about 900°C and subsequent preoxidation with concentrated HNO_3 at 60°C for 1 h. The resulting AC has a BET surface area of 560 m^2/g. V_2O_5/AC catalysts were prepared by pore volume impregnation of the AC with an aqueous solution of ammonium metavanadate in oxalic acid. The V_2O_5 loadings in the catalysts were determined by the concentration of ammonium metavanadate used in the impregnation. After the impregnation, the catalysts were dried at 50°C overnight and then at 120°C for 5 h, followed by calcination in an Ar stream at 500°C for 8 h and by preoxidation in air at 250°C for 5 h.

The experiments were carried out in a fixed bed quartz reactor at reaction temperatures of 150–250°C. The catalysts were initially subjected for 4 h to a reaction mixture containing 500 ppm NO, 560 ppm NH_3, 3.3 vol% O_2, and the balance Ar at a space velocity of 90,000 h^{-1} to allow steady-state NO conversion to be reached. A SO_2-containing Ar stream was then fed into the reactor to replace the same volume of Ar and hence to maintain the initial concentrations of NO, NH_3, and O_2 unchanged and yield a SO_2 concentration of 400 ppm. The concentrations of NO, NO_2, SO_2, and O_2 at the inlet and the outlet of the reactor were simultaneously monitored by an online flue gas analyzer (KM9006 Quintox, Kane International Limited) equipped with NO, NO_2, SO_2, and O_2 sensors. During some experiments, N_2O was also monitored by gas chromatography, which showed very little N_2O, corresponding to an NO conversion of 2–5%. In addition, to understand possible oxidation of the AC by the excess oxygen, after 12- to 35-h runs in the SCR reaction, the V_2O_5/AC catalysts were weighted. The catalyst loss greatly depends on the V_2O_5 loading. Almost no loss was observed for the catalysts with lower V_2O_5 loading (<5 wt%), but there is weighable loss for the catalysts with higher V_2O_5 loading (>5 wt%).

Figure 1 shows the effect of SO_2 on the activities of the V_2O_5/AC catalysts with different V_2O_5 loadings at 250°C. In the absence of SO_2, the activity of the AC (with 0 wt% V_2O_5 loading) is very low and sharply decreases with reaction time. The V_2O_5/AC catalysts, however, show obvious high and stable activities under the same conditions. The NO conversion initially increases, from 59 to 80%, with increasing V_2O_5 loading, from 1 to 5 wt%, and maintains at about 80% for the V_2O_5 loadings of 5–13 wt% and

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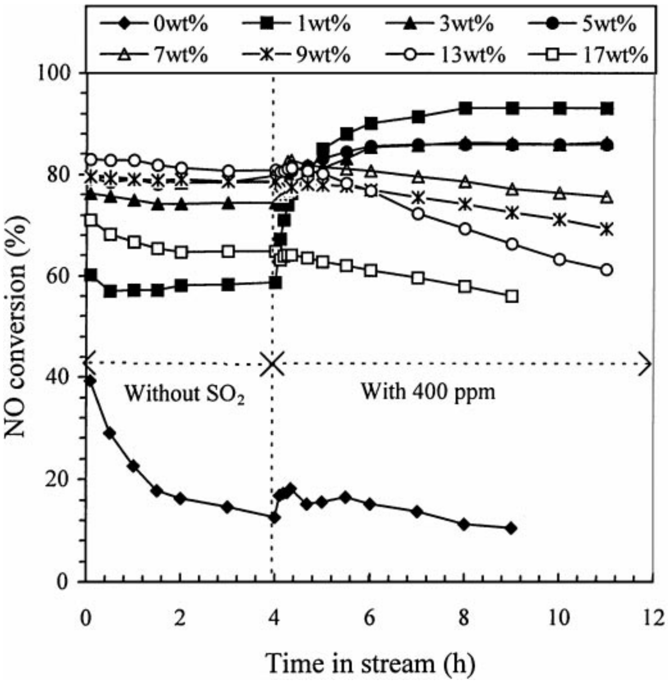

FIG. 1. Effect of SO_2 on the activities of V_2O_5/AC catalysts with V_2O_5 loadings of 0–17 wt%. Reaction conditions: 500 ppm NO, 560 ppm NH_3, 3.3 vol% O_2, 400 ppm SO_2 (when used), balance Ar, WHSV of 90,000 h, reaction temperature of 250°C.

then drops to about 65% at V_2O_5 loading of 17 wt%. The addition of SO_2 into the feed results in different response in activity for these catalysts. For the AC, the presence of SO_2 increases NO conversion initially but does not alter the decreasing pattern of the activity. For the V_2O_5/AC catalysts with V_2O_5 loadings of 1–5 wt%, the presence of SO_2 increases the activities and results in steady-state NO conversions in 4 h. The most pronounced change was found for the 1 wt% V_2O_5/AC catalyst; its SCR activity increased from 59% without SO_2 to 93% with SO_2. For the 7 wt% V_2O_5/AC catalyst, the NO conversion increases in the first 20 min after SO_2 addition but then gradually decreases with reaction time. For the catalysts with V_2O_5 loadings of 9–17 wt%, the presence of SO_2 gradually reduces the activities and stabilities. As a conclusion, in the presence of SO_2, NO conversion on the V_2O_5/AC catalyst almost monotonically decreases with increasing V_2O_5 loading. These results clearly indicate that V_2O_5 loading is crucial for the effect of SO_2 on the V_2O_5/AC catalyst. At lower V_2O_5 loadings SO_2 plays a promoting role, but at higher V_2O_5 loadings it acts as a poison.

Figure 2 shows the effect of SO_2 on the activity of 1 wt% V_2O_5/AC catalyst at temperatures of 150–250°C. In the absence or presence of SO_2, the catalytic activity constantly increases with increasing reaction temperature within the range employed, and upon addition of SO_2 into the feed the catalytic activity constantly increases. However, more interestingly, there is a large difference in the subsequent behavior of the catalyst at different temperatures. After SO_2 introduction, deactivation of the catalyst starts in 20 min at 150°C but 4 h at 180°C. At and above 200°C, deactivation is not observed within the reaction times used, and the promoting effect of SO_2 can be sustained. In fact, as a test the 1 wt% V_2O_5/AC catalyst was subjected to a SCR reaction of more than 260 h at 250°C and showed no sign of deactivation (4). These observations show that as the V_2O_5 loading increases the reaction temperature is also crucial for the effect of SO_2.

To understand the reason for the promoting role of SO_2 on the V_2O_5/AC catalyst, a special experiment, consisting of six consecutive parts as shown in Fig. 3, was carried out using the 1 wt% V_2O_5/AC catalyst at 220°C. The experimental procedure and the conditions of parts I and II are similar to those in Fig. 2. In this experiment the outlet SO_2 concentration was also monitored. As the NO conversion increases from 43% to a steady-state value of 84% upon introduction of SO_2 in part II, SO_2 concentration simultaneously increases following the same pattern. The removal of SO_2 from the feed, as shown in part III, does not cause any decline in NO conversion but exhibits a slight increase. A heating treatment of the catalyst in Ar at 350°C for 1 h (part IV) was performed, during which a considerable amount of SO_2 was detected. After the reactor was cooled to the original temperature of 220°C and the reaction gas was refed under

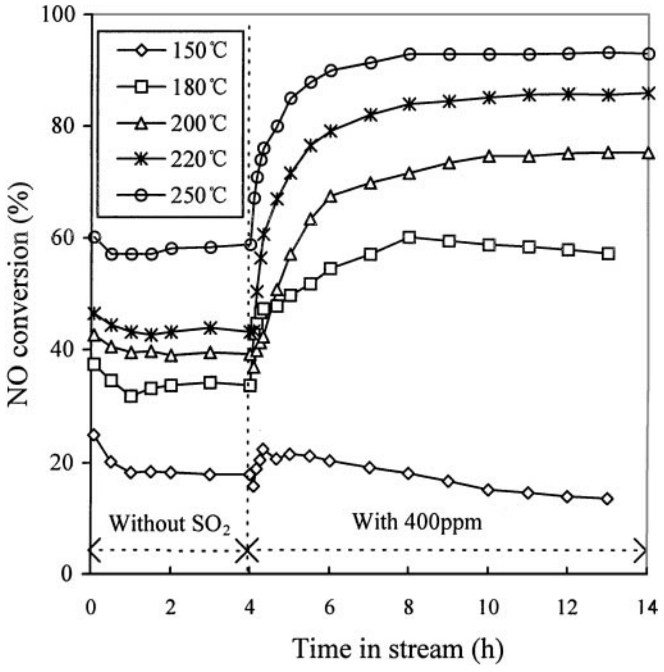

FIG. 2. Effect of SO_2 on the activity of 1 wt% V_2O_5/AC catalyst at temperatures of 150–250°C. Reaction conditions: 500 ppm NO, 560 ppm NH_3, 3.3 vol% O_2, 400 ppm SO_2 (when used), balance Ar, WHSV of 90,000 h^{-1}.

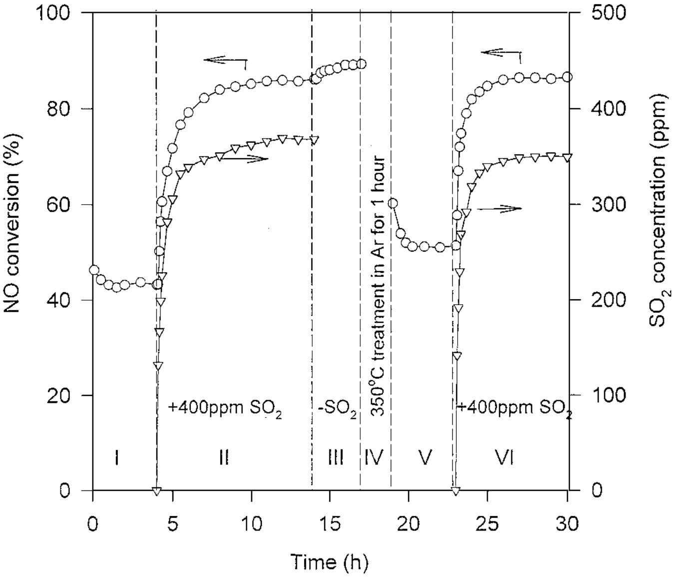

FIG. 3. Effect of SO_2 on the activity off 1 wt% V_2O_5/AC catalyst at 220°C. Reaction conditions: 500 ppm NO, 560 ppm NH_3, 3.3 vol% O_2, 400 ppm SO_2 (when used), balance Ar, WHSV of 90,000 h^{-1}. (I) NO–NH_3–O_2 reaction; (II) adding SO_2 into feed gas; (III) removal of SO_2 from feed gas; (IV) treating the catalyst at 350°C in Ar (300 ml/min) for 1 h and cooling to 220°C; (V) and (VI) the same as (I) and (II), respectively.

the same conditions in part I, the NO conversion reached a steady-state value of 50% (part V), which is much lower than that in part III and is just slightly higher than that in part I. A reintroduction of SO_2 in the feed (part VI), as expected, increased the NO conversion again and to result in a value (in steady state) the same as that in part II. These results clearly indicate that the promoting effect of SO_2 is not from the gas phase SO_2 but from some sulfur-containing species formed and deposited on the catalyst surface.

A similar promoting effect of SO_2 was also found on the V_2O_5/TiO_2 (5, 6) and TiO_2 (7) catalysts for the SCR reaction at temperatures above 350°C and was attributed to the formation of a stable sulfate species on the TiO_2 surface. Chen and Yang also suggested that the sulfated TiO_2 showed a solid superacid property which increased the catalyst surface acidity (7). In the present study, the dependence of the effect of SO_2 on the V_2O_5 loading (see Fig. 1) suggests that the effect is somehow associated with the carbon surface uncovered by the vanadium species. However, the support AC itself shows very low and unstable activity in the presence of SO_2. This indicates that the promoting effect of SO_2 on the V_2O_5/AC catalyst may result from a coordinated mechanism involving both activated carbon and vanadium species. After a SCR reaction of 30 h in the presence of SO_2 at 250°C, the 5 wt% V_2O_5/AC catalyst was studied by FT-IR spectra and EXAFS, which showed respectively that sulfate species exist on the catalyst surface and the V^{5+} species is the dominant vanadium species. These two observations are in good agreement because, as is well known, V_2O_5 is a very active catalyst for the SO_2 oxidation. The temperature-programmed desorption of $SO_2 + O_2$ showed that the V_2O_5/AC catalysts can adsorb a considerable amount of SO_2, while the AC or V_2O_5 does not. Therefore, the coordinated mechanisms of the vanadium species and the activated carbon may follow a path where the former acts as a “opening” through which SO_2 is oxidized into SO_3; the latter acts as a “container” to store the formed SO_3, which may be more easily adsorbed than SO_2 on the activated carbon surface and, in the presence of H_2O formed during the SCR reaction, may thereafter be transformed into sulfate species. Consistent with the previous observation that treatment with sulfate acid (or salt) greatly increases the NH_3 adsorption ability of activated carbon (8), the sulfate species formed may increase the surface acidity of the V_2O_5/AC catalyst and hence its activity.

On the other hand, it is known that sulfate species can react with ammonia and form NH_4HSO_4 and/or $(NH_4)_2S_2O_7$ on the catalyst surface (1). As previously reported, although the deactivation of the V_2O_5/TiO_2 catalyst is due to the deposition of As_2O_3 and alkali salts at higher temperatures (>350°C), at lower temperatures (<300°C) the catalyst deactivation due to the ammonium salts becomes heavy (1). For the present V_2O_5/AC catalyst, the formation of the ammonium salts may be the reason for the gradual deactivation at temperatures below 180°C (Fig. 2). At higher temperatures (>200°C) they may decompose and/or react with NO and hence the steady-state reaction may result. Concerning this, some valuable evidence was obtained recently. Through a deliberate deposition of NH_4HSO_4, we found that NH_4HSO_4 deposited on V_2O_5/AC catalyst is much easier to decompose and react with NO than that deposited on V_2O_5/TiO_2 catalyst (9). Similar experiments were also performed for the V_2O_5/AC catalysts with different V_2O_5 loadings and showed that the decomposition temperature of deposited NH_4HSO_4 greatly increases with increased V_2O_5 loading and that V_2O_5 plays a negative role in NH_4HSO_4 decomposition. This can provide an explanation for the promoting effect by SO_2 being decreased with increasing V_2O_5 loading (Fig. 1). At higher V_2O_5 loading, the deposited ammonium salts may act as poisons to offset the promoting role of SO_2. In addition, for the AC no promoting role of SO_2 being observed may be due to its weak catalytic ability for SO_2 oxidation and thus to no sulfate species depositing on it. This is supported by the result of the $SO_2 + O_2$ TPD experiment for the AC, which showed no detectable SO_2 (or SO_3) desorption (9).

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