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Effect of SO_2 on a cordierite honeycomb supported CuO catalyst for NO reduction by NH_3

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Supporting CuO on a Al_2O_3-coated cordierite honeycomb yields a good catalyst (CuO/HC–Al) for selective catalytic reduction (SCR) of NO with NH_3 at 350–500 °C. SO_2 has complex effects on the catalyst's activity. It significantly promotes the SCR activity through conversion of CuO to $CuSO_4$, however, when a certain amount of CuO is converted, it slightly decreases the SCR activity through competitive adsorption with NH_3. This competitive adsorption reduces the amount of NH_3 adsorbed on the catalyst surface, especially on the sites highly active to the SCR. It also prevents transformation of CuO to $CuSO_4$ and as a result, the catalysts subjected to pre-sulfation and *in situ* sulfation show different SCR behaviors.

KEY WORDS: NO; SCR; SO_2; CuO; cordierite honeycomb.

1. Introduction

Nitrogen oxides (NO_x) in flue gas are major air pollutants. The worldwide trend towards the increasingly stringent emission levels has spurred research and development on cost-effective technologies capable of reducing NO_x emission. Among them, selective catalytic reduction (SCR) of NO with NH_3 in the presence of oxygen is proven to be advantageous [1,2], and honeycomb V_2O_5/TiO_2 has been used for this process in industries due to its high activity and low flow resistance [3,4]. However, porous titania in anatase form required in the current practice was reported to be both difficult to prepare and physically weak [5]. A cost-effective honeycomb catalyst with high mechanical strength is needed as an alternative to the current SCR catalyst.

In view of the good SCR activity of CuO/Al_2O_3 [6] and the high mechanical strength and thermal stability of Al_2O_3-coated cordierite honeycomb [7], it is possible that CuO supported on Al_2O_3-coated cordierite may yield a good honeycomb catalyst for NO removal. Since resistance to SO_2 is always a key factor in developing SCR catalyst and many catalysts [8–11] are deactivated by SO_2, the attention of this note focuses on the effect of SO_2 on SCR activity of the novel honeycomb catalyst.

2. Experimental

2.1. Catalyst preparation

The cordierite honeycomb used in this work (marked as HC) is a commercial product with a cell density of 200 cells per square inch (cpsi) and a BET area of 0.7 m^2/g. γ-Al_2O_3 was coated on the cordierite using an aqueous solution containing $Al(NO_3)_3$ and urea. The cordierite bars were immersed into the solution for 4 h, and then removed for drying and calcining. The obtained sample was marked as HC–Al. Weight measurement showed that the amount of Al_2O_3 on HC–Al was about 3.2 wt% and N_2 adsorption showed that it has a BET area of 14 m^2/g. HC and HC–Al were impregnated with 1% $Cu(NO_3)_2$ solution for 2 h at room temperature, then dried and calcined. The resulting samples were marked as CuO/HC and CuO/HC–Al, respectively. Cu loadings, determined by ICP analysis, were 1.16 wt% for these two samples.

2.2. Catalytic activity measurement

Activity measurements were carried out in a fixed-bed reactor of 22 mm in diameter. A monolithic catalyst sample ($\phi 20 \times 30$ mm) was fitted in the reactor and heated to the desired temperature under an Ar stream. At steady state, a gas mixture containing 500 ppm NO, 5.5% O_2, 3% H_2O, 500 ppm NH_3 and balance Ar were introduced into the reactor. In all the runs, the total flow rate was maintained at 440 ml/min, corresponding to a superficial space velocity of 2800 h^{-1}. For experiments involving SO_2, a gas stream of SO_2 in Ar was used in place of Ar to yield a SO_2 concentration of about 1700 ppm. The concentrations of NO, SO_2 and O_2 in the inlet and outlet of the reactor were simultaneously measured on-line by a Flue Gas Analyzer (KM9106, Quintox).

2.3. Temperature programmed reaction (TPR)

Temperature programmed reaction (TPR) experiment was carried out in the same fixed-bed reactor to

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estimate the amount of NH_3 adsorbed on the catalyst. The monolith sample was preheated *in situ* in an Ar stream at 400 °C for 2 h, then cooled to 200 °C in the same stream. The pre-treated sample was exposed to 1000 ppm NH_3/Ar or 1000 ppm NH_3 + 1950 ppm SO_2/Ar at a flow rate of 250 ml/min for 1 h, then purged with Ar for 40 min to remove the physically adsorbed species. The TPR was carried out in 1290 ppm NO/Ar at a heating rate of 10 °C/min from 200 to 550 °C. NO in the effluent was continuously monitored during the whole process. The amount of NH_3 adsorbed can be estimated from the amount of NO consumed.

3. Results and discussion

3.1. *Effect of pre-sulfation*

Figure 1 shows steady state NO conversions of fresh CuO/HC and CuO/HC–Al catalysts (open symbols) at temperatures of 300–450 °C, along with those of a commercial three-way catalyst (marked as Pd–Pt/HC–Al) for comparison. In all the cases, the temperature was controlled stepwise with 50 °C intervals and the reaction was maintained at each temperature for 2 h or more to ensure steady state NO conversions. As can be seen, the fresh CuO/HC shows a NO conversion of about 2% in the whole temperature range and Pd–Pt/HC–Al shows a decreasing NO conversion with increasing reaction temperature, from 55 to −20%. SCR activities of fresh CuO/HC–Al are higher than those of the above two catalysts. Its NO conversion increases from 59 to 70% with increasing temperature from 300 to 350 °C, and then decreases to 63 and 51% with increasing temperature to 400 and 450 °C, respectively. Since NO conversions of greater than 80% may be necessary for industrial application [5], the three fresh catalysts cannot be used for NO removal in the temperature range.

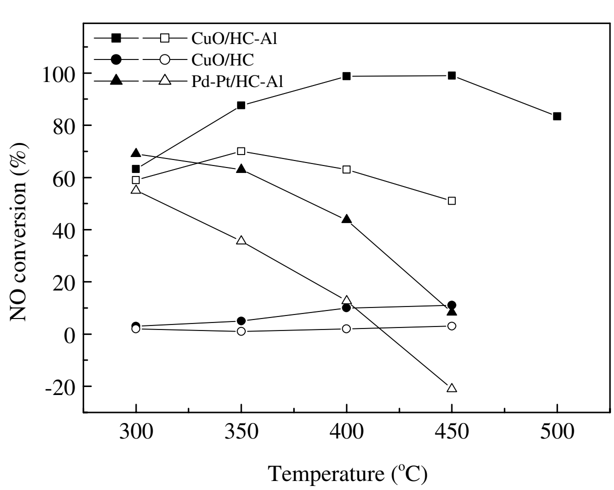

Figure 1. NO conversions of various catalysts at space velocity of 2800 h^{-1}.

It is generally understood that SO_2 improves SCR activities of CuO/Al_2O_3, V_2O_5/AC and V_2O_5/TiO_2 catalysts [12–14]. The above three catalysts, therefore, were subjected to SO_2 treatment, pre-sulfation, which was carried out in a gas stream containing 1700 ppm SO_2, 5.4 vol% O_2 and about 3% H_2O at 400 °C until the outlet SO_2 concentrations were nearly equal to the inlet values. The steady state NO conversions of the sulfated catalysts are also shown in figure 1 (filled symbols). As can be seen, the pre-sulfation improves SCR activities of all the catalysts. However, NO conversions of the sulfated CuO/HC are still very low, not more than 15% in the whole temperature range. The sulfated Pd–Pt/HC–Al, similar to the fresh one, shows a decreasing NO conversion, from 70 to 8%. SCR activities of the sulfated CuO/HC–Al are comparatively higher. Its NO conversion increases from 63 to 99% with increasing reaction temperature from 300 to 450 °C, and then decreases to 83% with a further increase in temperature to 500 °C. These results suggest that the sulfated CuO/HC–Al or $CuSO_4$/HC–Al is very promising for industrial application at temperatures of 350–500 °C. These results also suggest that Al_2O_3 coating is crucial for a high SCR activity and Pd/Pt is not appropriate as the active component of Al_2O_3 substrate for NO reduction with NH_3 at 300–500 °C.

3.2. *Effect of gas phase SO_2*

The above results show that the major role of SO_2 on the CuO/HC–Al catalyst is to convert CuO to $CuSO_4$ to promote the SCR activity. However, SO_2 may play other roles in the SCR reaction. Figure 2 shows NO conversion versus time on stream of the sulfated and fresh CuO/HC–Al in the absence or presence of SO_2 to reflect the dynamic behavior of the SO_2 effect. For clarity, the two catalysts are discussed separately.

To the sulfated CuO/HC–Al (open squares), introduction of 1700 ppm SO_2 into the feed stream, at time on stream of 300 min, results in a finite decrease in NO conversion, from an initial steady state value of 99% to a new steady state value of 93% in a few minutes. This indicates that for the sulfated CuO/HC–Al, SO_2 has a little inhibition effect on SCR of NO with NH_3. Serious or complete deactivation by SO_2 to the SCR reaction was observed on CuO/Al_2O_3 [15], V_2O_5/Al_2O_3 [11, 16] and MnO_X/Al_2O_3 catalysts [10] at temperatures below 300 °C, which were attributed to pore plugging resulted from the formation of ammonium (bi)sulfates [11, 15] or $Al_2(SO_4)_3$ [16] or $MnSO_4$ [10]. However, at 400 °C (figure 2), deposition of ammonium (bi)sulfates is not possible. Furthermore, the formation of $Al_2(SO_4)_3$ is not found in the catalyst because no water-soluble alumina is detected. These suggest that the finite deactivation observed in this work is from other reasons. For better understanding this effect, SO_2 is removed from the gas stream after NO conversion reaches steady state, at time

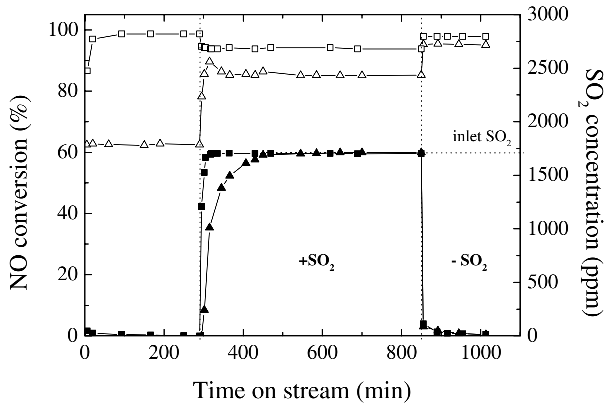

Figure 2. Effect of SO_2 on SCR activity at reaction temperature of 400 °C and GHSV of 2800 h^{-1}.

on stream of 850 min. It is interesting to note that the NO conversion instantly increases to 98% (open squares). The quick finite deactivation in NO conversion upon SO_2 addition and the quick increase in NO conversion upon SO_2 removal from the feed stream suggest that the effect of SO_2 is from the reversible adsorption of SO_2 on the catalyst surface, but not from pore plugging by sulfate salts. The stable NO conversion in the presence of SO_2 may suggest that the amount of SO_2 adsorbed on the catalyst surface is constant and controlled by SO_2 concentration in the gas phase.

The effluent SO_2 concentration of the above experiment is also shown in Figure 2 (solid squares). It is important to note that the outlet SO_2 concentration takes about 30 min to increase to the inlet value of 1700 ppm at a space velocity of 2800 h^{-1}, indicating significant uptake of SO_2. Since the catalyst has been saturated with SO_2 during the pre-sulfation, this SO_2 uptake is likely from adsorption of SO_2 on the catalyst

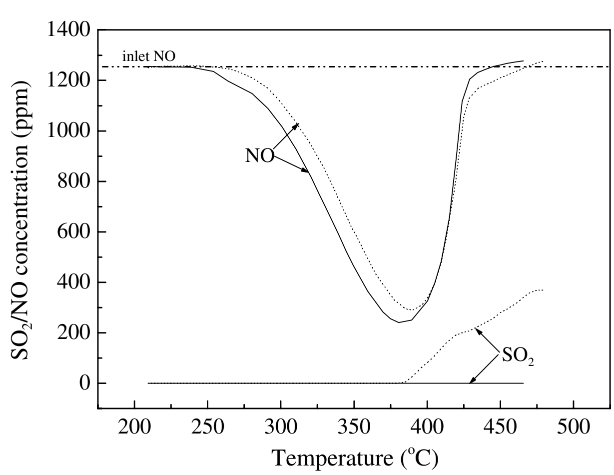

Figure 3. Effluent SO_2 and NO during the TPR over the sulfated CuO/HC–Al catalyst.

surface, as suggested earlier. All these data suggest that this SO_2 adsorption occupies some of the active sites for NH_3 adsorption [17], which results in less amount of NH_3 on the catalyst surface available for the SCR reaction. However, the competitive adsorption of SO_2 and NH_3 is not very significant, although SO_2 concentration (1700 ppm) is far higher than NH_3 concentration (500 ppm) in the feed stream.

To confirm the adsorption of SO_2 and understand the effect of gas phase SO_2 on NH_3 adsorption, TPR is carried out on the sulfated CuO/HC–Al and the results are shown in figure 3. To the catalyst pre-adsorbed with NH_3 in the absence of SO_2, the amount of SO_2 emitted during the TPR is zero (solid line), indicating that no reduction or decomposition of $CuSO_4$ occurs. However, to the catalyst pre-adsorbed with NH_3 in the presence of SO_2, a certain amount of SO_2 is detected during the TPR at temperatures greater than 375 °C (dot line). It is certain that the released SO_2 is from the adsorbed SO_2 because $CuSO_4$ do not decompose or be reduced in this temperature range. In other words, adsorption of SO_2 does take place during the pre-adsorption of NH_3 in the presence of SO_2. The amount of NH_3 adsorbed can be estimated from the amount of NO consumed during the TPR, as indicated by the outlet NO concentration profile. Clearly, the amount of NH_3 adsorbed in the absence of SO_2 is slightly more than that in the presence of SO_2. These observations confirm the above suggestion, i.e. the competitive adsorption of SO_2 and NH_3 results in a decreased amount of NH_3 adsorbed and thus a decreased SCR activity.

In addition to the decrease in NH_3 adsorption in the presence of SO_2, it is interesting to note that the two outlet NO concentration profiles (figure 3) differ only in the low temperature range, at temperatures below 390 °C, but follow a similar pattern in the high temperature range. These phenomena may suggest that some of the SO_2 is adsorbed on the active sites which could adsorb NH_3 and would be the most active for SCR of NO.

The fresh CuO/HC–Al shows a different behavior from the sulfated CuO/HC–Al. The addition of SO_2, at time on stream of about 300 min, significantly promotes SCR activity due to the formation of SO_4^{2-} on the catalyst surface, suggesting *in situ* sulfation. Its NO conversion increases from 63%, before SO_2 addition, to a maximum value of about 89% in the presence of SO_2 (open triangles in Figure 2). However, further increases in reaction time, in the presence of SO_2, results in a slight decrease in NO conversion, from 89% to a steady state, 85%. This finite deactivation of the fresh CuO/HC–Al, similar to that observed on the sulfated CuO/HC–Al, can be attributed to the occurrence of competitive adsorption of NH_3 and SO_2.

It is surprise that in the presence of SO_2, the steady state NO conversion of the fresh CuO/HC–Al, 85%, is lower than that of the sulfated CuO/HC–Al, 93%

(figure 2, between time on stream of 400–850 min), since it was thought that the *in situ* sulfation should have the same effect as the pre-sulfation. The different NO conversions after SO_2 removal from the feed stream, 93% for the fresh CuO/HC–Al and 98% for the sulfated CuO/HC–Al (between time on stream of 850–1015 min), further suggest that there are some differences in surface properties of the two catalysts. ICP analysis shows that $CuSO_4$ content of the used fresh CuO/HC–Al (*in situ* sulfation) is 0.84 wt% while that of the used sulfated CuO/HC–Al is 0.96 wt% (pre-sulfation), which explains the difference in SCR activity.

Clearly, the different $CuSO_4$ contents between the two catalyst samples are related to the sulfation conditions. The pre-sulfation was carried out in the absence of NH_3 and NO, while the P*, in situ* sulfation was in the presence of NH_3 and NO. Since it is generally accepted that NO does not adsorb strongly on the catalyst surface, this suggests that NH_3 should be responsible for the different surface properties. It is likely that NH_3 is adsorbed on some of the CuO sites, which prevents the reaction of $SO_2 + O_2 + CuO$ to form $CuSO_4$.

4. Conclusions

1. CuO supported on Al_2O_3-coated cordierite honeycomb shows high activity for SCR of NO by NH_3 in the presence of 1700 ppm SO_2 at temperatures of 350–500 °C.
2. SO_2 significantly promotes its SCR activity through conversion of CuO to $CuSO_4$.
3. When most of CuO are converted, SO_2 in feed stream will slightly decrease the SCR activity through competitive adsorption with NH_3.
4. The competitive adsorption between SO_2 and NH_3 may prevent transformation of CuO to $CuSO_4$. As a result, the catalysts sulfated in the presence and absence of NH_3 show different SCR activities.
5. These observations suggest that the effect of SO_2 on SCR activity, promotion or deactivation, is related to the catalyst's conditions, i.e. sulfur-contained or not.

Acknowledgments

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