Effect of SO\textsubscript{2} on a cordierite honeycomb supported CuO catalyst for NO reduction by NH\textsubscript{3}

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Supporting CuO on an Al\textsubscript{2}O\textsubscript{3}-coated cordierite honeycomb yields a good catalyst (CuO/HC–Al) for selective catalytic reduction (SCR) of NO with NH\textsubscript{3} at 350–500 °C. SO\textsubscript{2} has complex effects on the catalyst’s activity. It significantly promotes the SCR activity through conversion of CuO to CuSO\textsubscript{4}, however, when a certain amount of CuO is converted, it slightly decreases the SCR activity through competitive adsorption with NH\textsubscript{3}. This competitive adsorption reduces the amount of NH\textsubscript{3} adsorbed on the catalyst surface, especially on the sites highly active to the SCR. It also prevents transformation of CuO to CuSO\textsubscript{4} and as a result, the catalysts subjected to pre-sulfation and \textit{in situ} sulfation show different SCR behaviors.

**KEY WORDS:** NO; SCR; SO\textsubscript{2}; CuO; cordierite honeycomb.

1. Introduction

Nitrogen oxides (NO\textsubscript{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\textsubscript{x} emission. Among them, selective catalytic reduction (SCR) of NO with NH\textsubscript{3} in the presence of oxygen is proven to be advantageous [1,2], and honeycomb \(\text{V}_2\text{O}_5/\text{TiO}_2\) 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\textsubscript{2}O\textsubscript{3} [6] and the high mechanical strength and thermal stability of Al\textsubscript{2}O\textsubscript{3}-coated cordierite honeycomb [7], it is possible that CuO supported on Al\textsubscript{2}O\textsubscript{3}-coated cordierite may yield a good honeycomb catalyst for NO removal. Since resistance to SO\textsubscript{2} is always a key factor in developing SCR catalyst and many catalysts [8–11] are deactivated by SO\textsubscript{2}, the attention of this note focuses on the effect of SO\textsubscript{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\textsuperscript{2}/g. \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} was coated on the cordierite using an aqueous solution containing Al(NO\textsubscript{3})\textsubscript{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\textsubscript{2}O\textsubscript{3} on HC–Al was about 3.2 wt\% and N\textsubscript{2} adsorption showed that it has a BET area of 14 m\textsuperscript{2}/g. HC and HC–Al were impregnated with 1\% Cu(NO\textsubscript{3})\textsubscript{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 (\(\Phi20 \times 30\) 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\textsubscript{2}, 3\% H\textsubscript{2}O, 500 ppm NH\textsubscript{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\textsuperscript{-1}. For experiments involving SO\textsubscript{2}, a gas stream of SO\textsubscript{2} in Ar was used in place of Ar to yield a SO\textsubscript{2} concentration of about 1700 ppm. The concentrations of NO, SO\textsubscript{2} and O\textsubscript{2} in the inlet and outlet of the reactor were simultaneously measured online 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
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 50 °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.

It is generally understood that SO$_2$ improves SCR activities of CuO/Al$_2$O$_3$, V$_2$O$_5$/AC and V$_2$O$_5$/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$_2$O 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$_2$O$_3$ coating is crucial for a high SCR activity and Pd/Pt is not appropriate as the active component of Al$_2$O$_3$ 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$_2$O$_3$ [15], V$_2$O$_5$/Al$_2$O$_3$ [11, 16] and MnO$_3$/Al$_2$O$_3$ catalysts [10] at temperatures below 300 °C, which were attributed to pore plugging resulting 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.