# Resistance to sulfidation of the catalytic reduction of $NO_x$ over $Ag/Al_2O_3$ by controlling the loadings of Ag and $Ag^+$

Rui Ke [a,*], Qiang Chen [a], Junhua Li [b], Yongqing Zhu [b], Jiming Hao [b]

[a] *Department of Mechanical Engineering, Tsinghua University, Beijing, PR China*
[b] *Department of Environment Science and Engineering, Tsinghua University, Beijing, PR China*

## Abstract

$SO_2$ strongly decreased the catalytic activities of low loading $Ag/Al_2O_3$ below 500 °C in selective catalytic reduction (SCR) of $NO_x$ by propene with or without the assistance of non-thermal plasma (NTP), which was mainly attributed to the competition between $SO_2$ and NO. By controlling the loadings of Ag and $Ag^+$ over alumina, the resistance of $SO_2$ was remarkably enhanced between 400 °C and 500 °C in thermal SCR. In the NTP-assisted SCR, most of the $NO_x$ conversions were also apparently recovered from 250 °C to 500 °C.
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## 1. Introduction

Silver oxide supported on alumina catalysts have raised a lot of interest in reducing $NO_x$ in the presence of excess $O_2$, and have shown high $NO_x$ conversions and hydrothermal stability when using propene or actual diesel fuel as reductant [1]. Moreover, the $NO_x$ reduction can be further enhanced by the assistance of non-thermal plasma [2], which remarkably promotes the activation of the hydrocarbon reductants. However, the $SO_2$ resistance of silver catalysts was unsolved so far both in thermal SCR and NTP-assisted SCR [5,6]. Regarding the effect of sulfidation, it has been found that silver sulfate [3] and alumina sulfate [4] over $Al_2O_3$ has limited influence in $C_3H_6$-SCR. Meunier and Ross [5] suggested that the reduction of ad-$NO_x$ species or $NO_2$ over low loading $Ag/Al_2O_3$ most probably occurred on the alumina. Our recent research on the competitive adsorption of $SO_2$ and NO showed that $SO_2$ had advantage to deprive the alkaline sites that ad-$NO_x$ occupied over alumina.

In order to promote the adsorption of $NO_x$ in the presence of $SO_2$, one way is to provide new kinds of alkaline sites that preferentially bind to $NO_x$. According to the hard–soft acid–base concepts of Ralph Pearson [6], $SO_2$ is a harder acid than NO and has advantage in competition for hard alkaline sites over alumina. However, it is quite on the contrary if soft alkaline sites are presented over the catalyst. It is supposed that ad-$NO_x$ is preferential over soft alkaline sites. Recently, the role of silver in $C_3H_6$-SCR over $Ag/Al_2O_3$ has been extensively clarified [7]. Silver ion $Ag^+$ and metallic silver are considered to be effective in NO reduction and NO oxidation, respectively. In this study, the $SO_2$ effect in thermal SCR and NTP-assisted SCR were investigated. Meanwhile, metallic silver was purposely used as a soft alkaline site for ad-$NO_x$ reduction in cooperation with $Ag^+$ to obtain high $SO_2$ resistance. NTP was used to provide SCR with activated reductants for activity enhancement at low temperature regions.

## 2. Experimental

$Ag/\gamma$-$Al_2O_3$ was prepared by a single step sol–gel method. $AgNO_3$ and $Ag_2SO_4$ were chosen as the precursor of Ag. High loading of $AgNO_3$ was thought to form Ag clusters on alumina support, while $Ag_2SO_4$ should remain undecomposed at the calcine temperature of 550 °C. By appropriately controlling the proportion of $AgNO_3$ and

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* Corresponding author. Tel.: +86 1062794369.
*E-mail address:* reesimon97@mails.tsinghua.edu.cn (R. Ke).

$Ag_2SO_4$, it is tried to control the loadings of Ag and $Ag^+$ over alumina. The final obtained catalysts were sieved to 0.15–0.28 mm for later use. The sulfated $Ag/Al_2O_3$ samples were obtained by pretreating the fresh samples in 100 ppm $SO_2$ and 8% $O_2$ for 24 h at 450 °C. The samples used in this paper were named as (F/S)-AgxN–AgyS, in which F or S means a fresh or sulfated sample while AgxN and AgyS means x-wt% Ag and y-wt% Ag of the sample were from $AgNO_3$ and $Ag_2SO_4$, respectively.

The activity test system is of the PPCR (post plasma catalytic reactor) type. Non-thermal plasma was generated in a cylinder type dielectric barrier discharge (DBD) reactor with sinusoidal 5 kV high voltage of 50 Hz power input. The catalysts were placed in a quartz tube reactor downstream from the plasma reactor with the dosage of 0.25 g. The total flow of the feed gas was 100 mL/min and the space velocity was 14,000 $h^{-1}$. During the activity test, the reaction temperature went from low to high temperature. The data points were obtained in an approximately 'steady' status of the SCR reaction, during which the activities observed did not change. The concentration of $NO_x$ was analyzed by a $NO–NO_2–NO_x$ analyzer (Thermo Electron Model 44).

## 3. Results and discussion

It has been reported that the sulfidation of low loading $Ag/Al_2O_3$ (e.g. 1.2-wt%) causes a permanent loss of activity [5]. Fig. 1 shows the $SO_2$ effects on both thermal SCR and NTP-assisted SCR over 5-wt% $Ag/Al_2O_3$. In thermal SCR without $SO_2$ poisoning, the effective temperature window covered from 400 °C to 550 °C over fresh $Ag/Al_2O_3$ with a $NO_x$ conversion above 60%. This temperature window was extended to from 200 °C to 550 °C in NTP-assisted SCR. After the $Ag/Al_2O_3$ sample was poisoned by $SO_2$ for 24 h, the activities at below 550 °C were obviously lost both in thermal SCR and in NTP-assisted SCR with
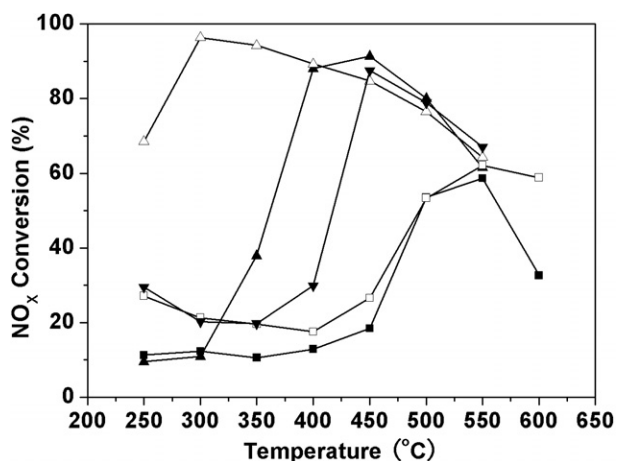
100 ppm $SO_2$ in the feed gas. The assistance of NTP provided an activity enhancement of only 7–20% at below 400 °C under the $SO_2$ poisoning condition which was far lower than that could be achieved under the condition without $SO_2$ poisoning. If $SO_2$ was not present in the feed gas, the sulfidation of 5-wt% $Ag/Al_2O_3$ sample caused mainly the loss of SCR activities below 400 °C while the activities above 400 °C did not apparently decrease.

Fig. 2 shows the variation of intermediate species during the $SO_2$ poisoning process in $C_3H_6$-SCR over 5-wt% $Ag/Al_2O_3$. Typical intermediates including nitrates (1590 $cm^{-1}$, 1550 $cm^{-1}$, 1298 $cm^{-1}$, 1253 $cm^{-1}$), acetate (1560 $cm^{-1}$, 1454 $cm^{-1}$) and enolic species (1637 $cm^{-1}$) [8] in $C_3H_6$-SCR were observed without $SO_2$ in the feed gas. After $SO_2$ was added, obvious sulfate species occurred at 1350 $cm^{-1}$ and 1170 $cm^{-1}$ with the decrease of nitrate species at 1550 $cm^{-1}$, which revealed that the adsorption of $SO_2$ was superior to that of $NO_x$. With the assistance of NTP, the amount of NCO species (2231 $cm^{-1}$) [8] and enolic species apparently increased, which were thought to be essential in SCR reactions, while no promotion effect was found for the nitrate species at 1550 $cm^{-1}$. The evidences above suggested that NTP could not promote the adsorption of $NO_x$ during the $SO_2$ poisoning process, which led to the low activities even in the presence of abundant NCO and enolic species.

In order to improve the resistance to $SO_2$, the loading of $Ag/Al_2O_3$ was purposely increased with different silver precursor. The results were presented in Fig. 3. Pure $Ag_2SO_4$ was found to be ineffective in thermal $C_3H_6$-SCR between 250 °C and 550 °C, which might be attributed to the small surface area of $Ag_2SO_4$. With the assistance of NTP, slight enhancement of $NO_x$ conversions (less than 30%) were achieved which should come from NO oxidation and propene activation by NTP. All the 8-wt% $Ag/Al_2O_3$ samples



Fig. 1. $NO_x$ conversions under the following process: SCR over F-Ag5N (▲), NTP–SCR over F-Ag5N (△), SCR over S-Ag5N in the absence of $SO_2$ (▼), SCR over S-Ag5N exposed to $SO_2$ (■), NTP–SCR over S-Ag5N exposed to $SO_2$ (□). Conditions: NO, 1000 ppm; $C_3H_6$, 1000 ppm; $O_2$, 8%; $SO_2$, 100 ppm; balance gas, $N_2$; GSHV, 14,000 $h^{-1}$.
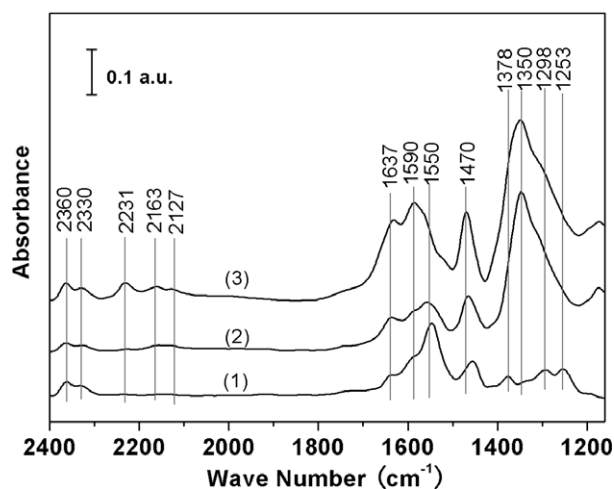


Fig. 2. Dynamic changes of DRIFTS spectra over F-Ag5N at 450 °C during the process of SCR for 40 min (1), adding $SO_2$ into the feed gas and dwelling for 40 min (2), turning on non-thermal plasma for NTP–SCR for 40 min (3). Conditions: NO, 1000 ppm; $C_3H_6$, 1000 ppm; $O_2$, 8%; $SO_2$,100 ppm; balance gas, $N_2$.
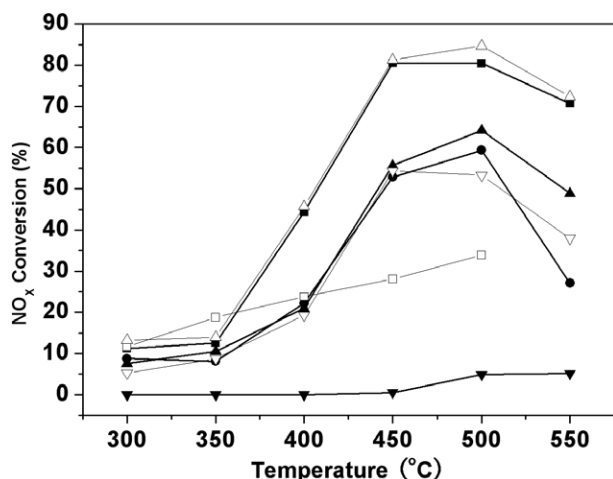
Fig. 3. $NO_x$ conversions in thermal SCR over S-Ag6N–Ag2S ($\triangle$), S-Ag4N–Ag4S ($\blacksquare$), S-Ag2N–Ag6S ($\triangledown$), S-Ag8N ($\bullet$), S-Ag8S ($\blacktriangle$), pure $Ag_2SO_4$ ($\blacktriangledown$) and in NTP-assisted SCR over pure $Ag_2SO_4$ ($\square$). Conditions: NO, 1000 ppm; $C_3H_6$, 1000 ppm; $O_2$, 8%; $SO_2$, 100 ppm; balance gas, $N_2$; GSHV, 14,000 $h^{-1}$.

showed higher resistance to $SO_2$ relative to the 5-wt% Ag/$Al_2O_3$ sample. The S-Ag6N–Ag2S sample whose silver were from both $Ag_2SO_4$ and $AgNO_3$ showed higher $SO_2$ resistance at 400–500 °C among all samples. This promotion effect might be resulted from appropriate proportion of $Ag^+$ and metallic Ag over alumina. It is worth mentioning that silver from $AgNO_3$ are probably easier to conglomerate when calcined at high temperature. The introduction of $Ag_2SO_4$ may enhance the dispersion of $Ag^0$ and prevent the formation of large silver particles. However, large proportion of $Ag_2SO_4$ can decrease the amount of reduced silver sites over alumina, which is also unfavorable for the purpose of $SO_2$ resistance. More detailed characterization on this phenomenon will be presented in other papers.

Fig. 4 shows the comparison of the $NO_x$ conversions in thermal SCR and NTP-assisted SCR over S-Ag4N–Ag4S
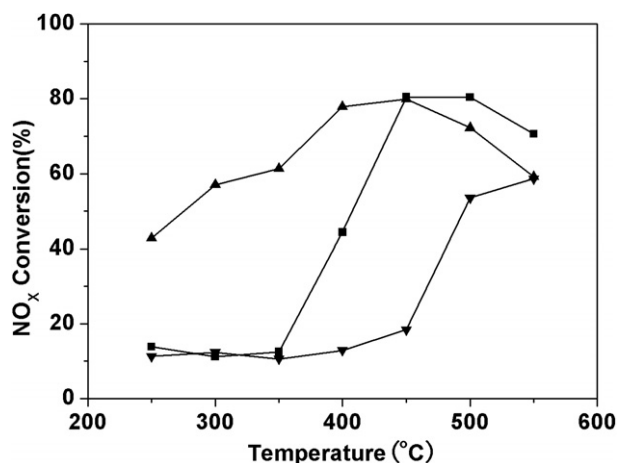
relative to those over S-Ag5N, exposing to $SO_2$. It is seen that the $NO_x$ conversions of S-Ag4N–Ag4S sample were much higher than those of S-Ag5N between 400 °C and 500 °C in thermal $C_3H_6$-SCR. In addition, the $NO_x$ conversions below 400 °C could also be apparently enhanced with the assistance of NTP in the presence of $SO_2$. More than 60% $NO_x$ conversions were achieved in a wide temperature window of 300–550 °C. The assistance of NTP favored the oxidation of NO, the activation of propene and the direct formation of N-containing organics, which were very important over a sulfated Ag/$Al_2O_3$. The maximal $NO_x$ conversion over S-Ag4N–Ag4S was about 10% lower than that over fresh 5-wt% Ag/$Al_2O_3$. This should be resulted from the sulfidation of the alumina support.

The adsorption competition between $SO_2$ and $NO_x$ was observed to be very contrary over sulfated 8-wt% Ag/$Al_2O_3$ relative to sulfated 5-wt% Ag/$Al_2O_3$ (Fig. 5). At the beginning of the SCR over the sulfated 8-wt% Ag/$Al_2O_3$ sample which was just sulfated in 100 ppm $SO_2 + 8\% O_2$ for 24 h, the $NO_x$ conversion was quite low (about 60%). As the reaction continued, it gradually increased with time and finally stabilized at 80%. We speculate that the $Ag^0$ soft alkaline sites were mainly occupied by ad-$SO_x$ after the sulfidation. When NO and $C_3H_6$ was added into the feed gas, the adsorption of $NO_x$ gradually deprived the alkaline sites occupied by ad-$SO_x$ as the SCR reaction continued.

Based on the evidences above and other literature [5,9], an interesting rule could be concluded that the loading and proportion between $Ag^+$ and metallic silver were essential to the adsorption competition between $SO_2$ and $NO_x$. Over the Ag/$Al_2O_3$ samples with very low Ag loadings (e.g. 1.2%), the sulfidation caused a permanent poisoning effect between 400 °C and 550 °C [5]. However, this depended on the presence of $SO_2$ in the reaction mixture over 5-wt% or 2-wt% [9] Ag/$Al_2O_3$, which showed that $SO_2$ was of superiority in the adsorption competition with NO. If it was
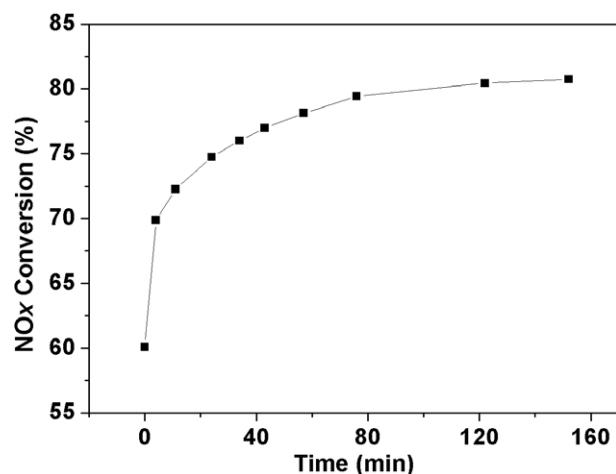


Fig. 4. $NO_x$ conversions over Ag/$Al_2O_3$ samples exposed to $SO_2$ in the following process: SCR over S-Ag5N ($\blacktriangledown$), SCR over F-Ag5N ($\blacksquare$), NTP-assisted SCR over S-Ag4N–Ag4S ($\blacktriangle$). Conditions: NO, 1000 ppm; $C_3H_6$, 1000 ppm; $O_2$, 8%; $SO_2$, 100 ppm; GSHV, 14,000 $h^{-1}$.



Fig. 5. The $NO_x$ conversion in dependence of time over F-Ag4N–Ag4S exposed to $SO_2$ at 450 °C. Conditions: NO, 1000 ppm; $C_3H_6$, 1000 ppm; $O_2$, 8%; $SO_2$, 100 ppm; balance gas, $N_2$; GSHV, 14,000 $h^{-1}$.

over the 8-wt% (or higher Ag loadings) $Ag/Al_2O_3$ samples, the adsorption of $NO_x$ turned to be preponderant and remarkable resistance to $SO_2$ could be obtained. Since the increase of Ag loading over alumina favored the formation of metallic silver, this could be explained that the increase of silver clusters provided more soft alkaline sites and promoted the adsorption of $NO_x$. It has been suggested in many literature that the reactions between N-containing organic species and ad-$NO_x$ should be the final steps of $NO_x$ reduction [5]. Since the oxidation of the N-containing organic species only by $O_2$ often easily leads to the formation of $NO_x$, the proportion between N-containing organic species and ad-$NO_x$ should be quite important for effective $NO_x$ reduction. $Ag^+$ in both $Ag_2O$ and $Ag_2SO_4$ has been found to be effective $C_3H_6$-SCR [9]. It is speculated that $Ag^+$ contributed to the partial oxidation of hydrocarbon reductants and metallic silver might be useful for providing ad-$NO_x$ ($x = 0.5$–3) species.

## 4. Conclusion

Although low loading $Ag/Al_2O_3$ catalysts are effective to reduce $NO_x$ with propene above 400 °C, their activities are strongly suppressed by $SO_2$ in both thermal SCR and NTP-assisted SCR. It was found effective to enhance $SO_2$ resistance by increasing the silver loading and controlling appropriate $Ag/Ag^+$ over alumina. With the assistance of NTP, better performance in low temperature region was also obtained. Metallic silver should be in the role of soft alkaline and preferentially build bonds with NO in the presence of $SO_2$.

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