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Sequential high temperature reduction, low temperature hydrolysis for the regeneration of sulfated NO_x trap catalysts

Do Heui Kim *, Ja Hun Kwak, Xianqin Wang [1],
Janos Szanyi, Charles H.F. Peden

Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354, United States

Abstract

We describe a new method that minimizes irreversible Pt sintering during the desulfation of sulfated $Pt/BaO/Al_2O_3$ lean NO_x trap (LNT) catalysts. While it is known that the addition of H_2O to H_2 promotes desulfation, we find that the significant and irreversible Pt sintering arising from the presence of water is unavoidable. Control of precious metal sintering is considered to be one of the critical issues in the development of durable LNT catalysts. The new method described here is a sequential desulfation process: the first step is to reduce the sulfates with hydrogen only at higher temperatures to form BaS, followed by a treatment of the thus reduced sample with water at low to moderate temperatures to convert BaS to BaO and H_2S. The data showed that Pt sintering was significantly inhibited due to the absence of H_2O during the desulfation at high temperatures, and also demonstrates the similar NO_x uptake with the desulfated sample cooperatively with H_2 and H_2O. This study clearly revealed both positive and negative roles for water in desulfation processes and these factors must be considered when optimizing LNT operation.

Keywords: NO_x storage; $Pt/BaO/Al_2O_3$; Desulfation; Pt sintering; H_2O effect

1. Introduction

The lean NO_x trap (LNT) technology, also known as NO_x adsorber and NO_x storage/reduction, is considered one of the promising solutions to reduce NO_x emissions from lean burn gasoline and diesel engines [1,2]. Typically, a LNT catalyst, which consists of a precious metal (e.g., Pt), a storage material (alkali and/or alkaline earth oxides, e.g., BaO), and a high surface area support material (usually γ-Al_2O_3), operates under transient conditions. During the lean cycle, NO is oxidized to NO_2 over Pt sites and the NO_2 reacts with $BaO/Ba(OH)_2/BaCO_3$ species to be stored as $Ba(NO_3)_2$, which is subsequently reduced to N_2 by reductants during a short rich cycle.

Although there has been significant progress in the development of high performance NO_x storage catalysts, the stability of the material against SO_2 poisoning remains a critical issue. The precious metal component of the catalyst that converts NO to NO_2 is also effective in the oxidation of SO_2 to SO_3. Thus, the LNT catalyst is poisoned by SO_2 due to the higher affinity of barium oxide to react with SO_3 than NO_2, as the $BaSO_4$ formed is thermodynamically more stable than $Ba(NO_3)_2$ [3]. The conversion of BaO into $BaSO_4$ results in a decrease in the number of available sites for NO_x adsorption, leading to deactivation of the catalysts. Even low concentrations of SO_2 gradually reduce the ability of the catalyst to store NO_x. The regeneration process to desulfate the catalysts requires high temperatures (e.g., 600 °C or higher) and a reducing gas (e.g., H_2). During this process, sulfate species are transformed to sulfides, and the primary S-containing species desorbing is H_2S [4]. Several research groups have reported [5–7] that water plays a key role in promoting the desulfation process, enhancing the production of H_2S when a reductant is introduced together with water.

Water, however, has also been shown to have a negative effect on the catalytic performance as it facilitates the deactivation of the catalyst via the promotion of Pt sintering [8]. In addition, our group has clearly demonstrated that the NO_x uptake efficiency is adversely affected by the growth of platinum particles arising from thermal aging [9]. Hence, Pt sintering is detrimental to the performance of these LNT

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* Corresponding author. Tel.: +1 509 371 6489; fax: +1 509 376 5106.
E-mail address: do.kim@pnl.gov (D.H. Kim).

[1] Present address: Deptartment of Chemical Engineering, New Jersey Institute of Technology, New York, NJ 07102. Tel.: +1 509 371 6489; fax: +1 509 371 6242.

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catalysts. Even more important is the irreversible nature of this deactivation process since the sintered Pt particles cannot be re-dispersed. To explore ways to prevent such sintering, we studied a desulfation process in which H_2 and H_2O are separately introduced in two sequential steps: desulfation with H_2 only at high temperatures (up to 800 °C), followed by H_2O treatment at lower temperatures (maximum of 300 °C). The first step is expected to transform the sulfate species into sulfides and even desorb some of the sulfur as H_2S, while minimizing the Pt sintering. In the second step, the thus formed BaS reacts with H_2O in a hydrolysis reaction to form BaO and additional H_2S. The catalyst desulfated by this two-step process showed very similar NO_x uptake properties as the one that was desulfated in $H_2 + H_2O$; however, the sintering of the Pt particles was almost completely inhibited. The high Pt dispersion retained after desulfation should positively affect the long-term stability of the catalyst.

2. Experimental

Pt–BaO(20)/Al_2O_3 samples were prepared by using a conventional impregnation method, as described in our previous publication [10]. The samples were calcined at 500 °C for 2 h in flowing air, resulting in 2 wt% Pt and 20 wt% BaO supported on an ~200 m^2/gm γ-Al_2O_3.

The sulfation/desulfation studies were performed in a fixed bed quartz reactor following procedures as illustrated in Fig. 1. Sulfations were carried out by treating 0.3 g of catalyst at 500 °C with 10% O_2 for 2 h, followed by exposure to 50 ppm SO_2 and 10% O_2 balanced with He at 300 °C for 6.5 h. Since we did not observe any breakthrough of SO_2 within the detection limit of 5 ppm SO_2 during sulfation period with a mass spectrometer (MKS, Minilab), it is assumed that all sulfur species are taken up by the samples. Thus, the total amount of SO_2 exposed is 0.24 mmol, which is smaller than the amount of Ba (0.39 mmol) in the sample.

After completing the sulfation process and without exposing the sample to the ambient air, H_2 temperature programmed reaction (H_2 TPRX) either with or without H_2O was performed. The temperature was ramped from 20 °C (without H_2O) or 160 °C (with 10% H_2O) to 800 °C under the 10% H_2 in He flow at a rate of 8 °C/min. For the case of the sequential process, 10% H_2O in He was subsequently applied to the sample at 300 °C, a temperature that was obtained after completing the H_2 TPRX up to 800 °C. A mass spectrometer was used to observe the evolution of H_2S during these processes. The samples with simultaneous exposure to H_2/H_2O, and the sequential process of exposure to H_2 TPRX followed by H_2O are designated as PtBaAl_H_2/H_2O and PtBaAl_$H_2 \rightarrow H_2O$, respectively.

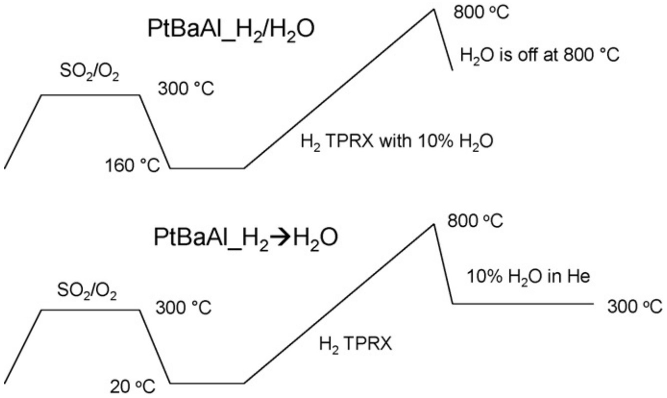

Fig. 1. The two regeneration protocols used here to desulfate the sulfated Pt–BaO(20)/Al_2O_3 samples.

The NO_x uptake measurements were carried out in the same reactor as the sulfation/desulfation experiments, with detailed reaction conditions described elsewhere [10]. NO_x uptakes are defined as the ratio of the amount of NO_x stored to the amount of inlet NO_x (200 ppm) during the lean cycle for 30 min, prior to a rich cycle of 1 min, measured at 300 °C.

TEM images were collected for PtBaAl_H_2/H_2O and PtBaAl_$H_2 \rightarrow H_2O$ samples. The TEM specimens were prepared by dusting the powder particles onto a carbon film-coated 200 mesh copper TEM grid. TEM analysis was carried out on a JEOL JEM 2010 microscope.

X-ray photoelectron spectroscopy (XPS) experiments were carried out for PtBaAl_H_2/H_2O and PtBaAl_$H_2 \rightarrow H_2O$ samples in the analysis chamber of a Physical Electronics Instruments Quantum 2000, using Al Kα X-rays and a pass energy of 71 eV. The position and intensity of the Al 2s peak at 119.2 eV were used as references.

3. Results and discussion

Fig. 2 shows the H_2 TPRX spectra obtained during temperature ramping with H_2 (dotted red trace) and H_2/H_2O (solid black trace) for the sulfated Pt–Ba(20)/Al_2O_3 samples. Note that the H_2S signal from the mass spectrometer fluctuated significantly for the case of H_2 TPRX with water, most likely due to the condensation of water along the gas lines which are kept at room temperature. H_2S evolution, resulting from the

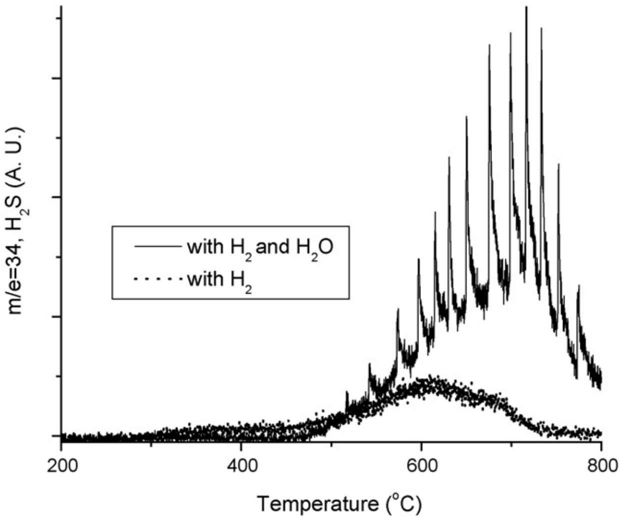

Fig. 2. H_2 TPRX spectra obtained during the two desulfation procedures (i.e., with and without water). The cooperative and sequential treatments are indicated by the solid and dotted line, respectively.

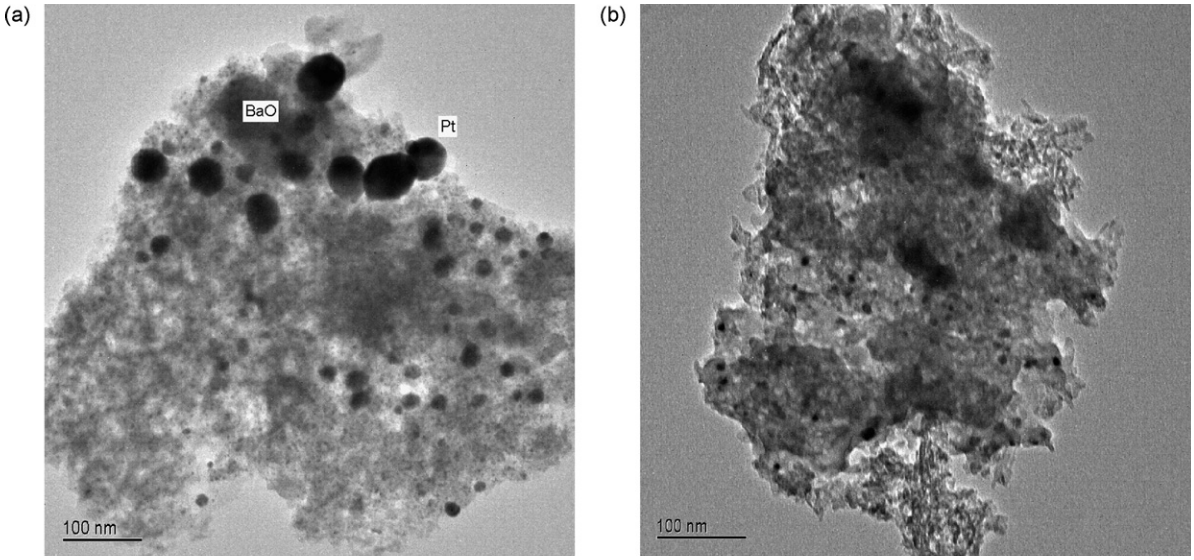

Fig. 3. TEM images of PtBaAl_H_2/H_2O (a) and PtBaAl_$H_2 \rightarrow H_2O$ (b) samples.

reaction between sulfate and hydrogen and the subsequent hydrolysis reaction between BaS and H_2O as described in reactions (1) and (2), was observed in both H_2 TPRX spectra.

$$BaSO_4 + 4H_2 \rightarrow BaS + 4H_2O \quad (1)$$

$$BaS + H_2O \rightarrow BaO + H_2S \quad (2)$$

For the case of regeneration with hydrogen only, the amount of H_2S evolved is about four times less than that observed with H_2/H_2O, and the peak maximum is located at 600 °C. On the basis of our prior time-resolved X-ray diffraction (TR-XRD) results [4], $BaSO_4$ is transformed into a BaS phase just above 550 °C, with the BaS continuing to grow up to 800 °C, concurrent with the generation of H_2S during the temperature ramping. The lesser amount of H_2S evolution observed in the H_2-only process is due to the limited availability of H_2O (only a small amount of water, formed during sulfate reduction, can participate in the subsequent hydrolysis of BaS). On the other hand, regeneration with H_2/H_2O gives rise to a larger amount of H_2S peaked at higher temperature, i.e., 700 °C. In the presence of water, the hydrolysis reaction (2) becomes facile since a sufficient amount of water is available to hydrolyze the BaS formed in the reduction portion of the desulfation process. Therefore, the effect of H_2O on H_2S evolution becomes significant above 550 °C, where BaS begins to form, leading to the formation of additional H_2S from reaction (2) between BaS and H_2O at temperatures higher than 550 °C.

In summary, water is quite effective in removing residual sulfur species on the LNT catalyst samples via its reaction with barium sulfide. The process restores the NO_x storage capacity of the LNT system, in agreement with findings of other researchers [5–7] who reported the promotional effect of H_2O during desulfation processes.

One of the critical issues for maintaining LNT performance, as we have already mentioned above, is the sintering of metallic Pt particles during high temperature (up to 800 °C) desulfation. In other work, Graham et al. [11] reported that the average Pt particle size in Pt/Al_2O_3 samples ranges from 2 to 6 nm after treatment in a H_2 flow up to 950 °C. In addition, we [9] have shown that the average Pt particle size does not exceed 10 nm after a model Pt–Ba/Al_2O_3 catalyst is treated in H_2 flow up to 900 °C (note that the sample is different from that in the current study). However, as the TEM image in panel (a) of Fig. 3 clearly demonstrates, Pt particle sizes increased to about 10–30 nm (some Pt clusters are even over 50 nm) during H_2 TPRX up to 800 °C in the presence of 10% H_2O. Note also the virtual absence of Pt particles smaller than 10 nm in this catalyst. These results are in good agreement with those of Barbier and Duprez [8] that revealed accelerated sintering of platinum particles in the presence of H_2O under both oxidizing or reducing conditions at temperatures higher than 550 °C. They concluded that steam apparently increased the rate constant of the Pt sintering reaction [8].

Meanwhile, a prior study published by our group [9] clearly demonstrates the inverse relationship between Pt particle size and NO_x storage performance. In this study, we used the results of a combined TR-XRD and NO_x uptake study to establish a direct correlation between catalyst performance and Pt particle size as a function of sample aging temperature and time. The relationship suggests that retention of Pt particle size during regeneration processes at high temperatures is crucial to maintaining high NO_x storage/reduction performance. In fact, the sintering of Pt particles has a negative effect on the desulfation process as well since they provide the active sites for activating the reductant, H_2, before it can react with the sulfur-containing species (i.e., barium sulfate).

According to the protocol described in Fig. 1, we separated the simultaneous reduction/hydrolysis process into two sequential steps: H_2 treatment to transform $BaSO_4$ to BaS (reduction, reaction (1)), followed by subsequent H_2O treatment at lower temperature (hydrolysis, reaction (2)). This desulfation approach was expected to minimize Pt sintering which occurs extensively at high temperatures in the presence of H_2O. After reduction in H_2 only up to 800 °C in the TPRX

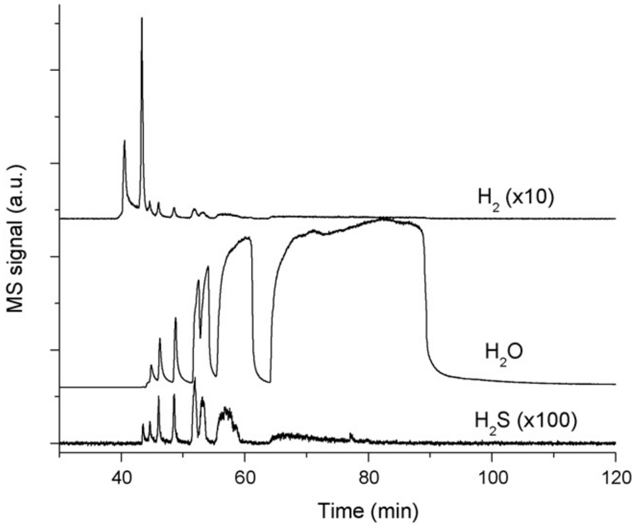

Fig. 4. Gases (H_2, H_2O and H_2S) evolved during H_2O treatment at 300 °C, subsequent to an H_2-only TPRX up to 800 °C.

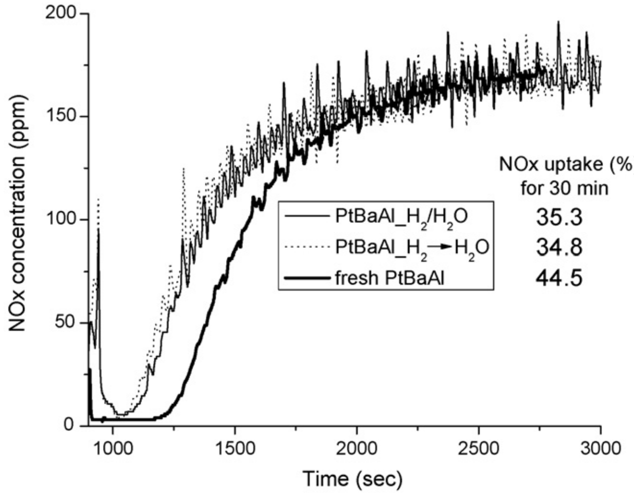

Fig. 5. NO_x uptake profiles of fresh PtBaAl, PtBaAl_$H_2 \rightarrow H_2O$ and PtBaAl_H_2/H_2O samples measured at 300 °C.

experiment, the sample was cooled to 300 °C, and then exposed to a 10% H_2O in He flow (this water concentration is typical in diesel engine exhausts).

Fig. 4 shows mass spectra data of gases (H_2O, H_2S and H_2) evolved during H_2O treatment of the H_2-reduced sample at 300 °C. Initially, hydrogen is formed just before H_2O breakthrough via a process (perhaps artifactual) we do not understand at present. As water appears in the effluent, H_2S evolution is also observed. It is important to note that the possibility of reaction (1) between the H_2 evolved and the residual sulfate species can be excluded since 300 °C is too low of a temperature to generate H_2S even if the H_2 concentration was significantly higher than present in these experiments. Therefore, H_2S formed under the conditions used here is explicitly generated via reaction (2) between BaS and H_2O. Estimating the total amount of H_2S evolved in this sequential reduction–hydrolysis process reveals that it is only about half of that measured in the regeneration process carried out with simultaneous H_2/H_2O flow. The amounts of residual sulfur were also estimated for these two samples with XPS by integrating the S 2p region normalized with the Al 2s region. Consistent with the H_2S evolution results during H_2 TPRX, the relative surface concentration of S/Al on the PtBaAl_$H_2 \rightarrow H_2O$ sample by XPS (2.36%) was found to be about 20% larger than that over the PtBaAl_H_2/H_2O catalyst (1.97%). These results suggest a relatively poorer effectiveness of sulfur removal from these sulfated catalysts using the two-step approach. On the other hand, considering the changes in the average size of the Pt clusters, the sequential treatment resulted in significantly lower Pt particle size increases, as shown in Fig. 3(b). This TEM image clearly demonstrates that the average Pt particle size was between 5 and 10 nm when the sequential desulfation process was applied, while increasing to 10–30 nm (and even to as high as over 50 nm) in the cooperative desulfation process. These results imply that the subsequent H_2O treatment at 300 °C (following the reduction in H_2 at 800 °C) does not facilitate Pt sintering, only the removal of additional residual sulfur-containing species.

Fig. 5 shows the NO_x uptake profiles of fresh Pt–BaO/Al_2O_3, PtBaAl_$H_2 \rightarrow H_2O$ and PtBaAl_H_2/H_2O at 300 °C for a 30 min lean period where the inlet NO_x (NO) concentration was 200 ppm. Surprisingly, no significant difference, either in the total 30 min NO_x uptake or the region where the full NO_x uptake occurred, was observed for these samples desulfated by the two different methods (i.e., under simultaneous $H_2 + H_2O$ flow at 800 °C, or H_2 reduction at 800 °C followed by hydrolysis with H_2O at 300 °C). Despite the large differences in both the amount of residual S-containing species and the average Pt particle sizes after desulfation by the two protocols, the NO_x storage properties of the two samples are practically identical. This is thought to be due to a relative cancellation of the effects of these two deactivating phenomena in this particular case.

Although the amount of H_2S desorbed during the cooperative desulfation process is larger than that of sequential one under the experimental conditions presented here, a modification of the two-step desulfation protocol may offer a means to improve the desulfation efficiency while maintaining the lack of Pt particle size growth. This can be achieved by optimizing the experimental conditions, in particular H_2O concentration and hydrolysis temperature. Our most recent results [12] suggest that the hydrolysis rate of BaS is significantly enhanced at catalyst temperatures below 120 °C. Therefore, we believe that reacting sulfate to sulfide via reduction in H_2 at high temperatures, and the subsequent hydrolysis of the BaS to BaO in H_2O at low temperatures (<100 °C), will yield optimum desulfation conditions that result in high levels of sulfur removal (low residual sulfur content). At the same time, this process can ensure the retention of high dispersion levels of Pt particles (small extent of sintering). Both issues are critical for the development of efficient LNT systems: low residual sulfur to preserve high NO_x storage capacity, and high Pt dispersions to retain high efficiencies of the precious metal for NO oxidation and NO_x reduction reactions. Another possible strategy to enhance LNT durability from the findings presented here would be to develop a material specifically designed to stabilize Pt particle size in the presence of H_2O at elevated temperatures.

4. Conclusions

Desulfation processes of model LNT catalysts are shown to be primarily composed of two elementary reactions, including $BaSO_4$ reduction to BaS by H_2, and BaS conversion to BaO and H_2S by reaction with H_2O. The second process is regarded as a key factor for promoting irreversible Pt sintering behavior. The idea presented in this contribution is the separation of these two reactions. We reduced $BaSO_4$ to BaS first at high temperatures with H_2 only, and then performed a reaction with water at much lower temperatures (e.g., 300 °C). The second reaction is known to occur even at room temperature with a sufficient amount of water. By using this sequential desulfation process, we can significantly decrease the levels of Pt sintering. The NO_x uptake results showed similar NO_x uptake performance for catalysts desulfated cooperatively with H_2 and H_2O or sequentially. Our study confirms two important roles of water in desulfation processes, which act on the performance of LNT catalysts in opposite ways. Hence, these findings should be useful for the development of more durable LNT catalysts.

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