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The beneficial effect of SO_2 on platinum migration and NO oxidation over Pt containing monolith catalysts

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In this work we investigated NO oxidation over Pt/Al_2O_3. The NO oxidation activity was slowly decreasing during the whole 36 h of experiment and we propose that this is due to formation of platinum oxides, which we detected in an earlier study using XPS. Further, it was not possible to remove these oxides at 250 °C, but some of them could be regenerated in Ar only at 400 °C. However, the NO oxidation activity was completely regained after the introduction of a reducing agent, in this case propene at 400 °C for 30 min. We also investigated the effect of long time exposure of SO_2. The catalyst was exposed to 630 ppm NO+8% O_2 for 30 min, which was followed by 22 h of 630 ppm NO+8% O_2 + 30 ppm SO_2. The NO oxidation activity decreased when introducing SO_2. However, after about 3 h of SO_2 the concentration of NO_2 starts to increase from 30 ppm to 140 ppm after 22 h of SO_2 exposure. The Pt dispersion before the long time SO_2 exposure was 12%, but after this experiment only 3.5%. Thus, it is clear that SO_2 exposure at this low temperature (250 °C) causes a large Pt migration and sintering. Earlier studies have shown that it is beneficial with large Pt particles for NO oxidation. This is due to either that the reaction is structure sensitive or that smaller particles more easily form platinum oxides, which are less active. This can explain the increased NO oxidation during the SO_2 exposure. In addition, we conducted two temperature ramps with NO + O_2, where one was done prior to the SO_2 experiment and one after. We observed a dramatical increase in NO oxidation after the long SO_2 exposure experiment. For example the NO_2 production increased from 27% to 92% at 200 °C. The long SO_2 experiment and the two ramps were repeated on a corresponding catalyst, but the SO_2 exposure was done at an even lower temperature (200 °C). We observed the same phenomenon also at this temperature, with a very large increase in NO_2 production after the long time SO_2 experiment. Thus, SO_2 greatly enhances the Pt migration and sintering and large effects are observed already at 200 °C.

1. Introduction

It is important to reduce the emissions of CO_2, since it is a greenhouse gas. Diesel and lean burn gasoline engines reduces the fuel consumption and thereby the CO_2 emissions. However, the conventional three-way catalyst cannot reduce the nitrogen oxides (NO_x) in oxygen excess. There are mainly three techniques that are proposed for reducing NO_x in lean atmosphere (oxygen excess): (i) Urea selective catalytic reduction of NO_x (urea SCR), where the urea thermally decomposes to for NH_3 which selectively reacts with NO_x using vanadia [1] or zeolite based catalysts [2,3]. (ii) Hydrocarbon (HC) SCR, where extra HC is injected in order to reduce the NO_x [4] (iii) NO_x storage, where the gas is altered between lean and rich (fuel excess) conditions. During the lean periods the NO_x is stored on the catalyst and during the rich periods the NO_x is released and reduced. For urea/NH_3 SCR it has been observed that about 50% NO and 50% NO_2 gives the highest NO_x conversion [3,5]. It is therefore possible to add an oxidation catalyst (typically Pt based) prior to the SCR catalyst in order to oxidize the NO to NO_2. In addition, an oxidation catalyst to produce NO_2 is very beneficial for soot regeneration from the particulate filter, since the regeneration rate is much higher with NO_2 compared with O_2 [6]. Further, in the NO_x storage concept the NO oxidation step over the noble metal is crucial in order to store the NO_x. Thus, the NO oxidation to NO_2 over platinum catalysts is important for many different areas.

NO oxidation has been investigated previously over supported platinum catalyst, both using experiments [7–11] and kinetic modeling [9,12–15]. Further, it has been observed that SO_2 [7], NO_2 [12], H_2O [10,16], C_3H_6 [10] and dodecane [10] decrease the activity and CO [17] and O_2 [18] increases the NO oxidation. In addition, it is observed that the NO oxidation rate is increased when decreasing the Pt dispersion [9,19]. Further, it is also observed using X-Ray Photo electron Spectroscopy (XPS) [20–22],

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X-ray absorption spectroscopy EXAFS [23] and XANES [24] that platinum oxides can be formed. The increase in activity for NO oxidation when increasing the Pt particle size can be either that the reaction is structure sensitive or that the smaller Pt particles more easily forms Pt oxides which has lower activity. We observed that the NO_2 dissociation rate and also NO oxidation rate decreased with time and suggested that the reason was the formation of platinum oxides [10,11]. Fridell et al. [25] observed that SO_2 increased the platinum migration at 400 °C using XPS on a flat model $Pt/BaCO_3$ sample. They also observe a decreased NO_x storage due to the formation of stable barium sulphates. However, there are no studies that investigate the long time NO oxidation activity and the promoting effect of SO_2 on the Pt sintering at temperatures below 400 °C, which is the objective with this work. Further, there are no studies that investigate the NO oxidation activity change due to long term SO_2 exposure and also the promoting effect of SO_2 on platinum migration on supported catalysts, which we do in this study.

2. Experimental

2.1. Catalyst preparation

Three Pt/Al_2O_3 catalysts were prepared using 400 cpsi ceramic monoliths. The samples were 15 mm long and had a diameter of 22 mm. The cordierite monoliths were initially pretreated at 600 °C for 30 min. The alumina washcoat was added by immersing the monoliths repeated times in a solution, containing γ-Al_2O_3 and bohemite (AlOOH) solved in distilled water. The catalysts were then calcined for 2 h at 600 °C. The Pt was added using $Pt(NO_3)_2$. The catalysts were then dried over night at 95 °C and after that calcined at 400 °C for 3 h. In order to stabilize the catalysts they were degreened before used the first time with 2% H_2/Ar for 30 min at 400 °C. This was followed by 10 min of Ar only and heating the catalysts to 650 °C and staying at this temperature for 45 min. The total flow in the pre-treatment was 3700 ml/min, except for the hydrogen exposure which was done using 3000 ml/min. Details about the three samples are shown in Table 1.

2.2. Catalyst characterization

The BET surface area was measured for catalyst C2, using a Micromeritics ASAP 2010 instrument. The measurement was conducted both before and after the long time exposure to SO_2 and the results are found in Table 1. The Pt dispersion was also measured prior and after the long time SO_2 exposure on catalyst C2 (see Table 1) using CO Temperature programmed desorption experiments (TPD). The catalyst was placed in a quartz tube with one thermocouple inside and one about 1 cm in front of it. Mass flow controllers were used to control the gas flow through the reactor and a mass spectrometer (Balzer QME 125) was used to measure the gas phase concentrations. The catalyst was pretreated at 400 °C first with 1% O_2/Ar to remove possible hydrocarbon residues and then with 1% H_2/Ar to reduce the platinum surface. The catalyst was then cooled to ≈5 °C in Ar and the catalyst was exposed to 2000 ppm CO for 10 min. This was followed by flushing the catalyst for 20 min and after that conducting a temperature ramp, with the speed of 40 °C/min up to 500 °C. The total flow during the temperature ramp was 50 ml/min.

2.3. Flow reactor measurements

The flow reactor consists of a quartz tube where the catalyst is placed. There is one thermocouple placed inside the catalyst and one about 1 cm in front of the catalyst. Mass flow controllers regulate the gas flow through the reactor. Ar is used as inert balance and the pressure is 1 atm. The total gas flow in this study was 3700 ml/min. A chemiluminescense detector (CLD 700) was used to measure the NO and NO_2 concentrations and an IR gas analyser (UNOR 610, Maihak) were used to measure the SO_2 concentration.

The catalysts degreening procedure before the first experiment is described in Section 2.1. The Pt/Al_2O_3 catalyst C1 was used for several NO oxidation/NO_2 dissociation experiments. Before the measurement shown in this study the catalyst was pretreated at 400 °C for 10 min with 0.1% H_2/Ar, followed by 10 min Ar and decreasing the temperature to 250 °C. This was followed by exposing the catalyst to 630 ppm NO and 8% O_2 for 36 h. During the last 5 h of the experiment the gas temperature was fluctuating ±2–6 °C, which caused a small variation in the conversion. Different regeneration strategies were than investigated with subsequent activity check at 250 °C and the catalyst was exposed to: (i) 10 min Ar at 250 °C, 10 min 630 ppm NO + 8% O_2 at 250 °C (ii) 30 min Ar at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C (iii) 10 min 550 ppm C_3H_6 at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C (iv) 10 min 0.1% H_2 at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C and (v) 30 min 1% H_2 at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C.

The BET surface area and Pt dispersion (see Section 2.2) on the Pt/Al_2O_3 catalyst C2 was measured after the degreening process (see Section 2.1). This was followed by NO oxidation experiment: (i): 1% H_2/Ar at 400 °C for 30 min (pretreatment) (ii) 10 min Ar and cool to about 40 °C (iii) 630 ppm NO + 8% O_2/Ar for 35 at min at about 40 °C (iv) temperature ramp with a rate of 5 °C/min up to 400 °C and staying for 5 min at 400 °C using 630 ppm NO + 8% O_2/Ar. This was followed by a long NO oxidation experiment in the presence of SO_2 according to: (i) 1% H_2/Ar at 400 °C for 30 min (pretreatment) (ii) 10 min Ar and cool to 250 °C (iii) 630 ppm NO + 8% O_2 in Ar for 30 min at 250 °C (iv) 630 ppm NO + 8% O_2 + 30 ppm SO_2 in Ar for 22 h at 250 °C (v) 630 ppm NO + 8% O_2 in Ar for 30 min at 250 °C and (vi) Ar for 10 min at 250 °C. After this experiment one NO oxidation experiment was conducted again (procedure described above). Finally, CO TPD experiment was used to measure the Pt dispersion and BET measurement for detecting the surface area.

The Pt/Al_2O_3 catalyst C3 was degreened according to Section 2.1. This was followed by a NO oxidation experiment (procedure described above). After this experiment a long NO oxidation experiment with SO_2 was conducted. The experiment is described in detail above and the only difference for this catalyst was that the experiment was conducted at 200 °C. Finally, one NO oxidation experiment was performed again (procedure according to above).

Table 1
Wash-coat weight, Pt amount, Pt dispersion and BET surface are for the three Pt/Al_2O_3 catalysts used.

Catalyst nr	Wash-coat weight (mg)	Amount Pt (%)	Pt dispersion (%)	BET surface (m^2/g)
C1	487	2.0	–	–
C2	489	2.1	12 (Before SO_2 exposure) 3.5 (After SO_2 exposure)	159 (Before SO_2 exposure) 147 (After SO_2 exposure)
C3	499	2.0	–	–

3. Results and discussion

The NO oxidation was investigated using a Pt/Al_2O_3 catalyst (C1) and exposing it to 630 ppm NO + 8% O_2 for 22 h. The result of this experiment is shown in Fig. 1. Initially the NO_2 production is about 420 ppm, but in the end part of the experiment only 215 ppm NO_2 is formed. The deactivation is quite rapid during the first 10 h, but deactivation is still present in the end of the 36 h experiment. We have observed NO oxidation deactivation in an earlier study, where the catalyst was exposed to NO and oxygen for 3 h [11] and on the basis of XPS measurements we suggested the reason to be formation of platinum oxides. Platinum oxides have been observed in several studies using XPS [20,22], EXAFS [23] and XANES [24]. Interestingly, the deactivation is still observed after 36 h (Fig. 1).

We further investigated the regeneration of these platinum oxides using different conditions and the results are presented in Fig. 2. After each regeneration strategy the catalyst activity was checked at 250 °C using NO + O_2. First the catalyst was exposed to Ar only for 10 min (denoted A in Fig. 2), but the catalyst did not regain any activity. This was followed by 30 min Ar at 400 °C (denoted B) and now the catalyst regained some of its initial activity, however, it was still severely deactivated. Then propene was introduced for 10 min at 400 °C, and in the following activity experiment the catalyst regained the NO oxidation activity. In the final two regenerations the catalyst was exposed to 0.1% H_2 for 10 min or 1% H_2 for 30 min at 400 °C, respectively (denoted D and E in Fig. 2). The initial activity does not increase further after the hydrogen pre-treatment compared with the propene exposure but the deactivation slope might have decreased some.

The effect of SO_2 on NO oxidation was investigated. The Pt/Al_2O_3 catalyst C2 was exposed to 630 ppm NO + 8% O_2 for 23 h and after 30 min 30 ppm SO_2 was added to the gas mixture. The results are displayed in Fig. 3. During the first 30 min the NO_2 concentration drops from 330 ppm to 270 ppm and as described above we suggest that this is due to platinum oxides. When introducing SO_2 the activity drops significantly and after about 1 h of SO_2 exposure the NO_2 level is quite constant at 30 ppm. Interestingly, after about 3 h of SO_2 exposure the activity slowly starts to increase. This increase continues throughout the whole last 19 h of the SO_2 exposure, but with a lower rate in the later parts. The NO_2 level increases from 30 ppm to almost 140 ppm. This experiment has been repeated on two other Pt/Al_2O_3 catalysts (not shown here) in order to ensure that the process was repeatable.

In order to further gain information about the activity increase during the SO_2 exposure experiment we conducted one temperature ramp with NO + O_2 before the long SO_2 exposure experiment and one NO + O_2 ramp experiment after. The results from these two ramps (denoted Ramp 1 and Ramp 2, respectively) are shown in Fig. 4. It is evident that there is a dramatical increase in NO oxidation activity after the long time SO_2 exposure. We propose that the reason is that the Pt particles are sintered in the presence of SO_2. It has been observed experimentally that larger Pt particles have higher NO oxidation activity [9–11,19]. In order to verify this, we measured the dispersion of the platinum before the first temperature ramp and also after Ramp 2 and the dispersion had decreased from 12% to 3.5%. In addition, BET experiments showed that there had been a small decrease in the total surface area from 159 m^2/g washcoat to 147 m^2/g washcoat after the experiment. To conclude, the addition of SO_2 makes the platinum very mobile and sintering was observed already at 250 °C. The decreased platinum dispersion increased the NO oxidation activity.

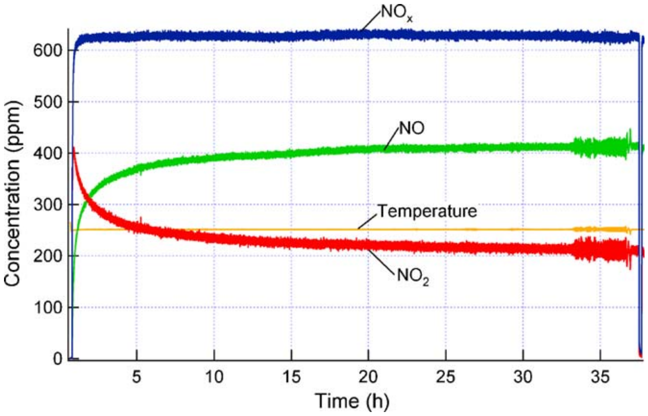

Fig. 1. NO oxidation over a Pt/Al_2O_3 catalyst (C1) at 250 °C during exposure of 600 ppm NO and 8% O_2 in Ar for 36 h.

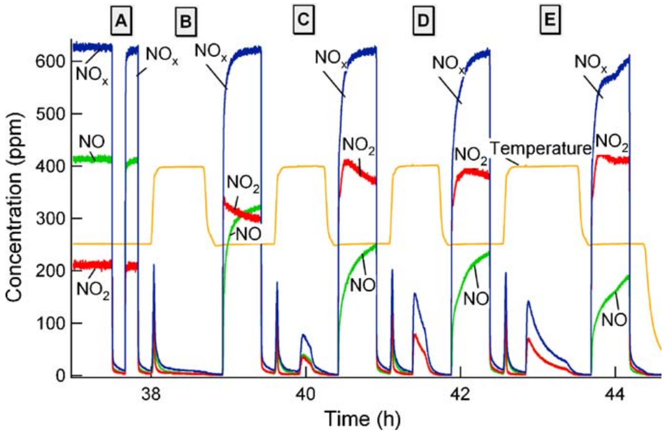

Fig. 2. NO oxidation over a Pt/Al_2O_3 catalyst (C1) after a long-time exposure and treatment with (A) 10 min Ar at 250 °C, 10 min 630 ppm NO + 8% O_2 at 250 °C, (B) 30 min Ar at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C, (C) 10 min 550 ppm C_3H_6 at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C, (D) 10 min 0.1% H_2 at 400 °C, 30 min 630 ppm NO + 8% O_2 at 250 °C and (E) 30 min 1% H_2 at 400°, 30 min 630 ppm NO + 8% O_2 at 250 °C.

In order to investigate the temperature for the sintering, the same long SO_2 exposure experiment as shown in Fig. 3 is repeated at a lower temperature (200 °C). The results from this experiment are shown in Fig. 5. During the first 30 min with only NO + O_2 the NO_2 concentration is decreasing in the same way as was observed at 250 °C and we suggest that the reason is formation of platinum oxides. Further, the NO_2 concentration drops when adding SO_2 to the feed gas mixture. During the 22 h NO + O_2 + SO_2 exposure a

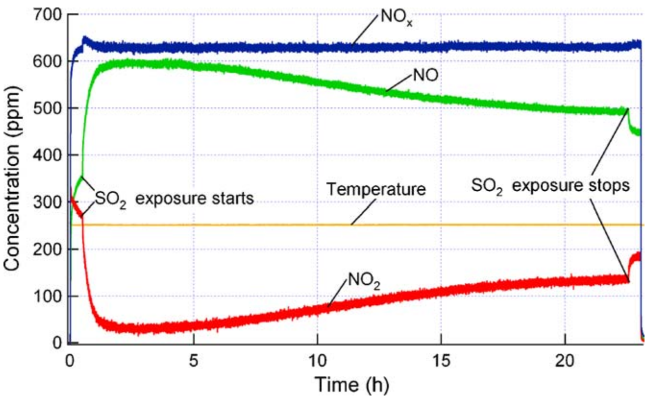

Fig. 3. NO oxidation experiment over a Pt/Al_2O_3 catalyst (C2) at 250 °C. The catalyst was exposed to 630 ppm NO and 8% O_2 for 23 h and after 30 min was 30 ppm SO_2 added and after 22.5 the SO_2 exposure was stopped.

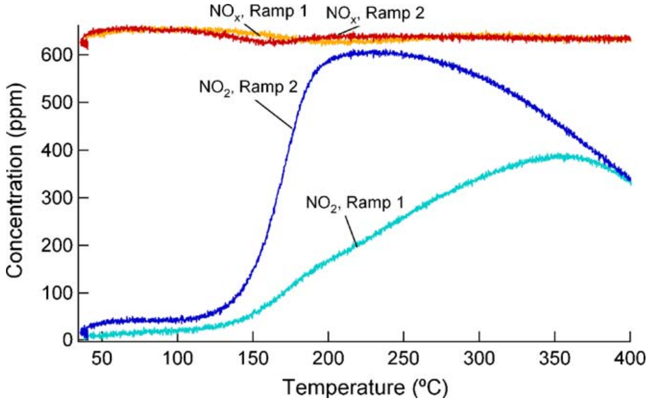

Fig. 4. Temperature ramp (5 °C/min up to 400 °C) with 630 ppm NO and 8% O_2, using a Pt/Al_2O_3 catalyst (C2). Ramp 1 was conducted before the long SO_2 exposure experiment shown in Fig. 3 and Ramp 2 after the SO_2 experiment.

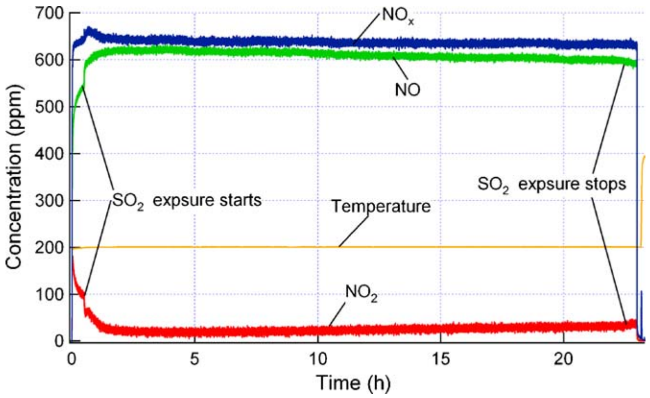

Fig. 5. NO oxidation experiment over a Pt/Al_2O_3 catalyst (C3) at 200 °C. The catalyst was exposed to 630 ppm NO and 8% O_2 for 23 h and after 30 min was 30 ppm SO_2 added and after 22.5 the SO_2 exposure was stopped.

very slow increase in NO_2 concentration is observed. In order to investigate if the platinum sintering induced by SO_2 also occurs at 200 °C, we conducted one temperature ramp with NO + O_2 before the long SO_2 exposure experiment and one ramp after. The results from these two ramps are shown in Fig. 6. It is clear that the NO_2 production is dramatically increased also after SO_2 exposure at 200 °C. Thus, the presence of SO_2 increases the sintering rate enormous already at 200–250 °C, which is very beneficial for the NO oxidation activity.

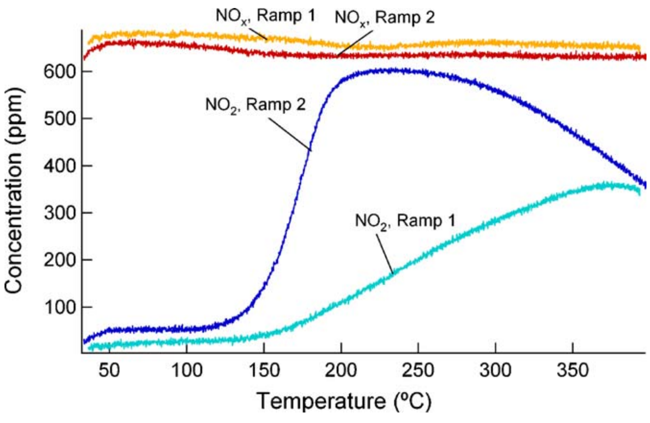

Fig. 6. Temperature ramp (5 °C/min up to 400 °C) with 630 ppm NO and 8% O_2, over a Pt/Al_2O_3 catalyst (C3). Ramp 1 was conducted before the long SO_2 exposure experiment shown in Fig. 5 and Ramp 2 after the SO_2 experiment.

4. Conclusions

In this work the NO oxidation over Pt catalysts is investigated. We chose to use Pt/Al_2O_3 samples in order to increase the fundamental knowledge about the NO oxidation and sintering of Pt when supported on alumina. We observed a decrease in NO_2 production during the whole 22 h experiment and we suggest that the decrease is due to the formation of stable platinum oxides. The deactivation rate was highest during the first 10 h, but still visible after 22 h, which indicates that platinum oxide formation is a quite slow process. In addition, the regeneration of the formed platinum oxides was investigated using five different regeneration strategies, with an NO oxidation activity check at 250 °C after each regeneration. We did not regain any activity with only Ar for 10 min at 250 °C. However, the activity was increased after increasing the temperature to 400 °C, but it was far from the initial activity. Thus, some of the oxygen on platinum is possible to remove in inert atmosphere, but a significant part of the platinum oxides are very stable. After introduction of propene at 400 °C, the NO oxidation activity at 250 °C was back to its original state. This was also followed by two hydrogen regeneration, but no extra activity was observed. However, it seemed that the deactivation rate for platinum oxides was decreased somewhat after regeneration with hydrogen.

We also investigated the effect of long-term exposure of SO_2 at low temperatures. One Pt/Al_2O_3 catalyst was exposed to 630 ppm NO + 8% O_2 for 30 min, which was followed by 22 h of 630 ppm NO + 8% O_2 + 30 ppm SO_2. Initially, the NO oxidation activity decreased when introducing SO_2. However, after about 3 h of SO_2 the NO_2 production slowly increases from 30 ppm to 140 ppm after the 22 h of SO_2. We measured the dispersion before and after this experiment and observed a decrease from 12% to 3.5%. We therefore suggest that the reason for the slow activity increase when adding SO_2 is a slow platinum sintering. It is known that larger platinum particles are more active for NO oxidation. This is due to either that the reaction is structure sensitive or that smaller particles more easily form platinum oxides, which are less active. During sintering the number of sites will decrease, which is also observed by the dispersion measurements. However, the larger Pt particles have so much larger activity that the total conversion increases even though the number of sites decreases. Since the temperature during the sulphur exposure is only 250 °C, the introduction of SO_2 greatly enhances platinum migration. We also conducted two temperature ramps with NO + O_2, one before and one after the long time SO_2 exposure experiment and observed a very large increase in NO_2 production after sulphur exposure. For example the NO_2 production increased from 27% to 92% at 200 °C. In order to further investigate the low temperature platinum migration in the presence of SO_2 the experiment set (NO oxidation ramp, long time SO2 exposure experiment, NO oxidation ramp) described above was repeated on a corresponding Pt/Al_2O_3 catalyst, with the only difference that the long term SO_2 exposure was conducted at 200 °C. Interestingly, similar increase in NO oxidation activity was found, which suggests that platinum migration is even important at 200 °C, which is a very low temperature for platinum migration.

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