

## Article

# Adsorption and Oxidation Investigations over Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst: A Microcalorimetric Study

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**Abstract:** The differential adsorption heats of oxygen and NO, as well as catalytic oxidation behavior during NO oxidation and NO<sub>2</sub> dissociation reactions over supported Pt-catalysts, were investigated by microcalorimetric measurements. The average heat of adsorption ( $\Delta H$ ) of oxygen ranged from 310 kJ/mol at 200 °C to 289 kJ/mol at 400 °C. Over this temperature range formation of platinum oxides and coverage dependence caused variations in the apparent heat of adsorption. NO heat of adsorption from 50 to 150 °C was near constant with an average value of 202 kJ/mol over the temperature range.

**Keywords:** microcalorimetry; adsorption heat; Pt/Al<sub>2</sub>O<sub>3</sub>; NO; NO<sub>2</sub> oxidation; Pt dispersion

## 1. Introduction

There are stringent requirements on vehicle emissions and their environmental impact is an important issue. Vehicle NO<sub>x</sub> emission after-treatment technologies (NO<sub>x</sub> storage-reduction, selective catalytic reduction) play a significant role on the reduction of vehicle emissions [1,2]. Furthermore, diesel oxidation catalysts (DOC) are important for meeting the emission standards of CO and hydrocarbons and, additionally, the DOC converts nitric oxide to nitrogen dioxide, which is important for the downstream catalytic processes. Extensive research has been undertaken on the noble metals (e.g., Pt) supported on high surface area materials (e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) to improve their activity during various oxidation reactions (e.g., CO, NO) [3–6], which are important for the DOC functionality. Platinum was found to be very active, but when it is exposed to oxygen at high temperatures for long periods of time it can sinter, involving migration of oxide species [7]. The formation of platinum oxide is also induced by NO<sub>2</sub> and its ability to develop a high oxygen surface coverage on the Pt (111) surface due to its coordinative flexibility [8]. Based on the reduction temperatures from TPR (temperature programmed reduction) experiments, four different platinum oxide species (surface platinum oxide, PtO, PtO<sub>2</sub>, and PtAl<sub>2</sub>O<sub>4</sub>) have been reported by Yeh's group [9–11] and their formation depends on the oxidation temperatures. By using a simultaneous TG-DSC technique, Wang and Yeh [10] observed that oxygen adsorbs at ambient or lower temperature, while above 27 °C the platinum surface is reconstructed for extensive accommodation of oxygen. In addition, a stable surface layer of platinum oxides is formed at about 477 °C. Advanced studies on the adsorption of NO on stepped Pt surfaces using density functional theory (DFT), reflection absorption infrared spectroscopy (RAIRS), fast X-ray photoelectron spectroscopy (XPS), and other techniques were reported [12–14], concluding that above –23 °C, NO adsorbs both molecularly and dissociatively, while NO adsorption was found to be only dissociative at about 100 °C [13].

Heat-flow microcalorimetry gives the opportunity of directly exploring the strength of surface chemical bonds, the coverage of adsorbates involving the interaction between adsorbates and solid catalytic surfaces, and the heats of adsorption [15,16]. The studies of heats of adsorption for NO and oxygen on a Pt (110) surface using microcalorimetric measurements has been described by Wartnaby *et al.* [17], concluding that the adsorption heat shows a strong coverage dependence, with an initial heat of adsorption of 335 kJ/mol for O<sub>2</sub> Pt(110) at 27 °C. Furthermore, Brown *et al.* [18] found an initial heat of adsorption of oxygen for Pt(110) of  $316 \pm 34$  kJ/mol, which is in good agreement with the study by Wartnaby *et al.* [17]. Moreover, Fiorin *et al.* [19] reported heats of adsorption of NO on Pt (111) and Pt (211) of 182 kJ/mol and 192 kJ/mol, respectively, whereas Wartnaby *et al.* [17] reported a slightly lower heat of adsorption of NO on Pt (110) of 160 kJ/mol.

Pt supported on alumina plays a significant role as a DOC catalyst in exhaust after treatment systems. The formation of Pt oxides and so called “structure sensitivity” of Pt also influences its performance. A comprehensive evaluation of adsorption heats of NO and oxygen on Pt supported on alumina should contribute to a deeper understanding for its application in the automotive sector and can be used as a base for kinetic modelling. There are some studies in the literature that describe the heat of adsorption of O<sub>2</sub> and NO on single-crystal platinum surfaces. However, there are, to our knowledge, no studies available where heat of adsorption of NO and O<sub>2</sub> is measured on supported platinum particles on alumina at atmospheric pressure, which is the objective of the present study. This is done by performing temperature-programmed desorption experiments (O<sub>2</sub> TPD, NO TPD), at different temperatures. Furthermore, the activity of the catalyst for NO oxidation and NO<sub>2</sub> dissociation was examined.

## 2. Results and Discussion

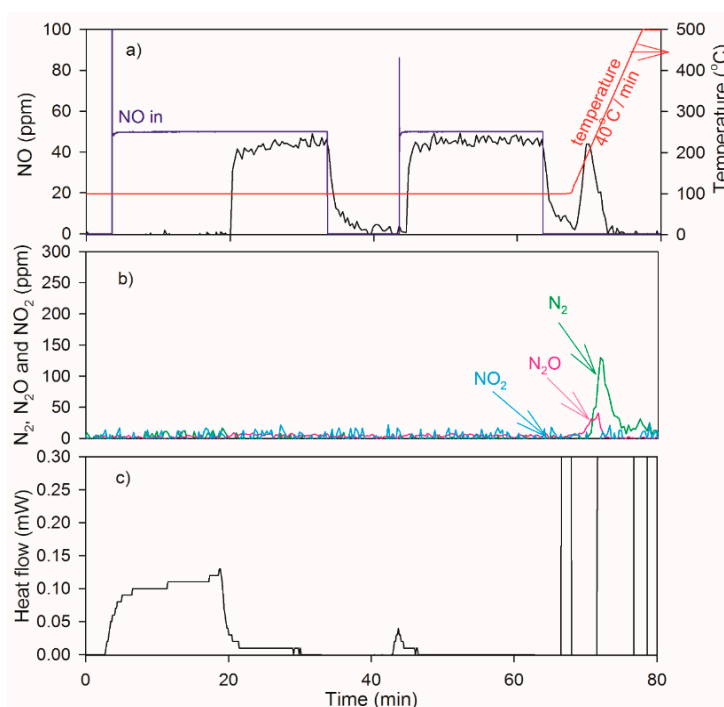
### 2.1. Pt Dispersion

The Pt surface dispersion was determined by analyzing the results from a N<sub>2</sub>O dissociation experiment using 200 ppm N<sub>2</sub>O at 100 °C for 1 h. The total amount of N<sub>2</sub> produced during the N<sub>2</sub>O dissociation was  $1.12 \times 10^{-5}$  mol/g<sub>cat</sub>, which results in a dispersion of 12%, when assuming that the number of formed N<sub>2</sub> molecules is equal to the number of surface metal sites, since N<sub>2</sub>O dissociation results in the formation of an O atom on Pt and N<sub>2</sub> in the gas phase. The evolution of N<sub>2</sub> and N<sub>2</sub>O were qualitatively the same as that reported earlier [20].

### 2.2. Heat of Adsorption during NO TPD Experiments

A calorimeter combined with an MS for gas phase analysis was used to measure both the amount of gas adsorbed during gas dosing and the heat developed during adsorption of a given amount of adsorbate. The dynamic profile of measured NO during the NO TPD experiment with 50 ppm NO feed at 100 °C (chosen as an example) is depicted in Figure 1a. Prior to the experiment, the catalyst was pre-treated with 2% H<sub>2</sub> at 500 °C for 20 min and, thereafter, cooled in Ar, in order to clean the noble metal surface. The resulting amounts of N<sub>2</sub>, NO<sub>2</sub>, and N<sub>2</sub>O formed during the TPD are also shown in Figure 1b. NO was adsorbed on the Pt surface at a constant temperature (100 °C), 16 min of total uptake was observed and, thereafter, a breakthrough of NO was seen due to saturation of the catalytic surface with NO. A small release of NO from the catalyst was observed when the NO feed was switched off and the catalyst was exposed to Ar only at 100 °C for 10 min, but then an approximately equal amount re-adsorbed when the catalyst was re-exposed to 100 ppm NO. Moreover, rapid desorption of NO was observed during the linear increase of the temperature (heating rate of 40 °C/min up to 500 °C) in Ar. In addition to NO desorption (see Figure 1a), N<sub>2</sub>O and N<sub>2</sub> are produced during the NO TPD (see Figure 1b). Both N<sub>2</sub>O and N<sub>2</sub> are desorbed at higher temperature compared to NO (Figure 1a). These features are also clearly seen when comparing the desorption peaks for NO TPD at 50 °C, 100 °C, and 150 °C (see Figure 2). The desorption peaks have their maximum in the range of 170–252 °C for NO, 263–267 °C for N<sub>2</sub>O, and 280–285 °C for N<sub>2</sub>. Thus, first NO is desorbing, which is followed by a small N<sub>2</sub>O production and, finally, N<sub>2</sub> is observed. Relatively high amounts of N<sub>2</sub> were desorbed for all three NO TPD experiments (Figure 2b), which is related to the dissociation

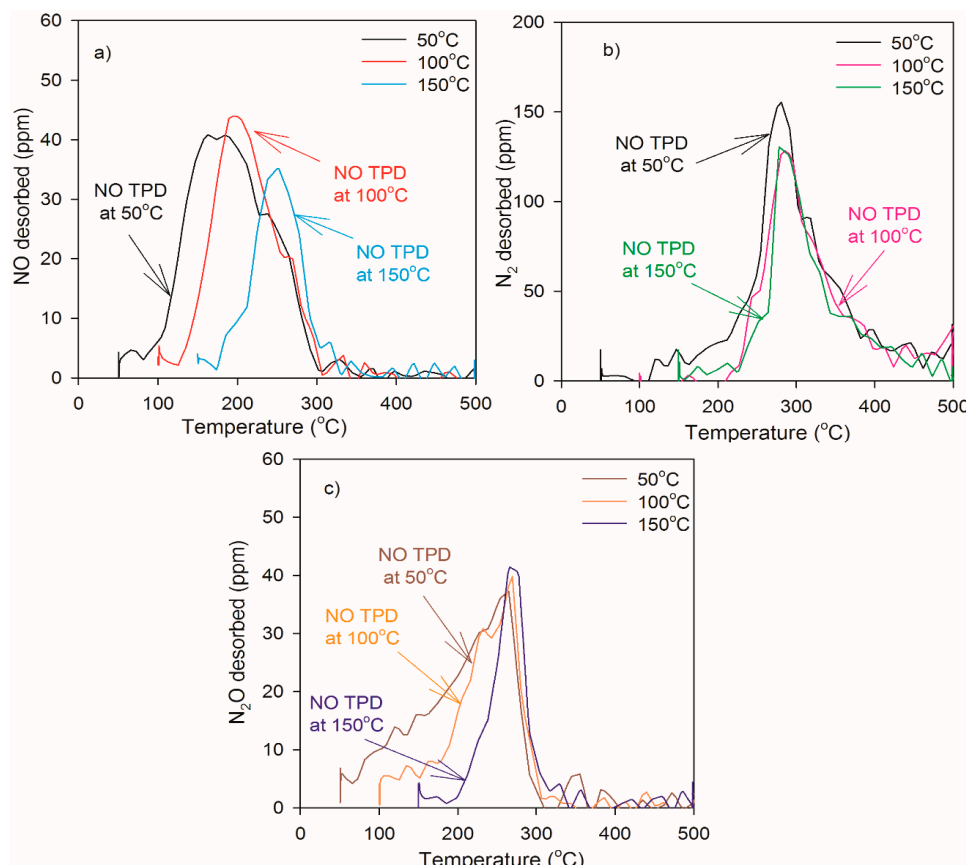
of the adsorbed NO on the catalyst surface. A nitrogen balance resulted in that  $0.83 \mu\text{mol}$  NO was stored during the first storage phase, which corresponded to a coverage of 68% on Pt. During the desorption phase after the second pulse  $0.096 \mu\text{mol}$  was desorbed. In addition, some loosely bound NO was desorbing after the first pulse, but this is re-adsorbed in the second pulse and was, therefore, not considered in the molar balance. Moreover,  $0.32 \mu\text{mol}$   $\text{N}_2$  was formed and  $0.076 \mu\text{mol}$   $\text{N}_2\text{O}$  was formed during the desorption, which results in  $0.93 \mu\text{mol}$  nitrogen atoms and this is similar to the stored amount ( $0.83 \mu\text{mol}$ ). The small difference is likely due to the accuracy of the MS measurement at these very low concentrations. For the oxygen balance, a small amount of oxygen was produced ( $0.008 \mu\text{mol}$ ), in addition to the oxygen atoms present in the desorbed NO and  $\text{N}_2\text{O}$ . However, this results in a deficiency of  $0.65 \mu\text{mol}$  of oxygen atoms and the reason for that is likely that oxygen is very stable on Pt and a large part of it does not desorb during the ramp up to  $500^\circ\text{C}$ . The oxygen coverage remaining is 53% (considering 12% Pt dispersion).



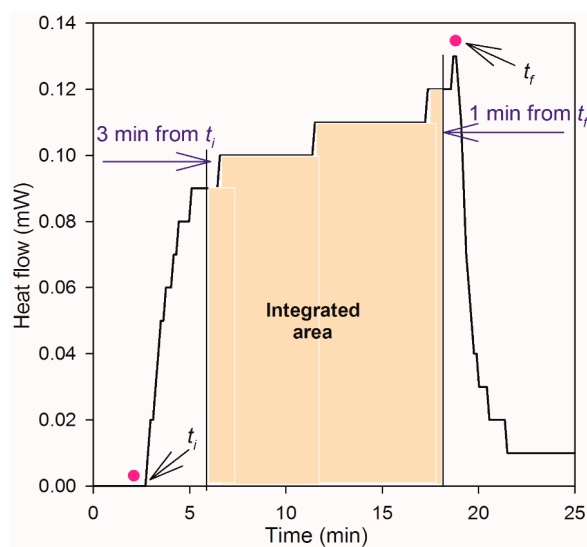
**Figure 1.** (a). NO concentration and temperature as function of the time, (b) resulting  $\text{N}_2$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$  concentrations, (c) corresponding heat flow during NO TPD at  $100^\circ\text{C}$  for 2 wt. % Pt/ $\text{Al}_2\text{O}_3$ . Experimental details are described in Section 3.

The heat flow signal from the TPD experiment as a function of time is presented in Figure 1c. Heat flow was immediately observed when the sample was exposed to 50 ppm NO with a maximum exotherm of 0.13 mW. After being exposed to NO, the catalyst was flushed with Ar and a small heat flow was observed corresponding to the amount of NO, which is re-adsorbed during the second NO readsoption. Figure 3 shows the enlarged heat flow measured during the first 30 min of the first NO exposure (see Figure 1). The details used for the calculation of the adsorption heat are schematically shown in Figure 3. The initial time ( $t_i$ ) is taken into account when the catalyst is exposed to 50 ppm NO, while  $t_f$  represents the highest point of heat flow, just before the catalyst becomes saturated and heat flow decreases. During the first few minutes the heat flow rapidly increased and the data in this region are highly influenced by the transient response behavior of the calorimeter. Therefore, the middle region of the heat signal is used to determine the heat of adsorption. More specifically, we chose 3 min after  $t_i$  and 1 min before  $t_f$  for the measurement time interval. During this time interval there was total uptake of the adsorbate and the heat flow, since it varied slightly, was integrated to

calculate the heat of adsorption. The heat signal varied only about 0.03 mW during the measurement time interval. This indicates that the gas flows through the catalyst bed in a near plug flow manner, first saturating the front of the bed with adsorbate and, thereafter, the adsorption front moves through the catalyst bed [21].

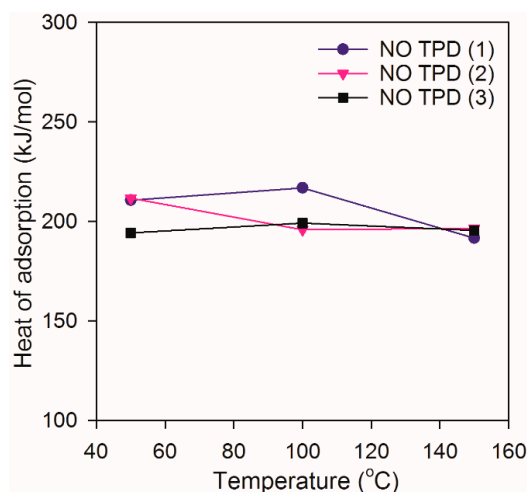


**Figure 2.** Desorbed (a) NO, (b) N<sub>2</sub>, and (c) N<sub>2</sub>O during temperature ramp from 100 °C to 500 °C for NO TPD experiments at adsorption temperatures of 50 °C, 100 °C, and 150 °C for 2 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>. Experimental details are described in Section 3.



**Figure 3.** Details for the integrated area of adsorption heat during the first 30 min of the first NO exposure for NO TPD at 100 °C for 2 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

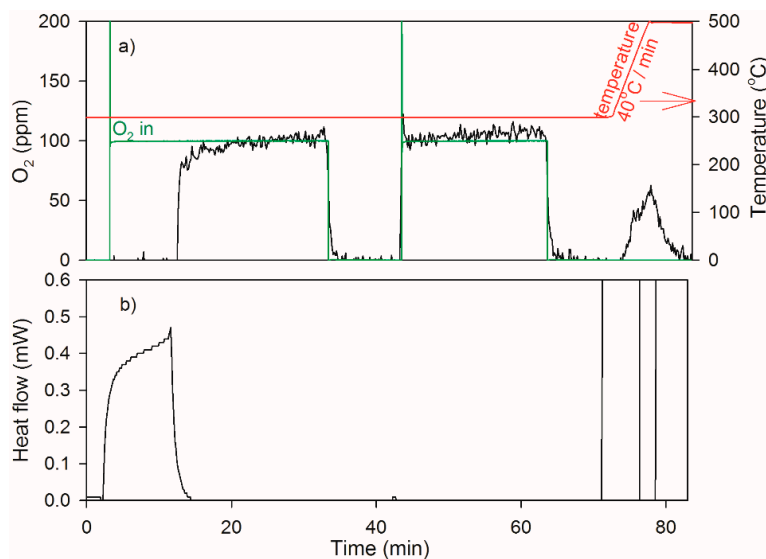
The heat of adsorption (in kJ/mol) of NO at adsorption temperatures 50 °C, 100 °C, and 150 °C are displayed in Figure 4. Moreover, there are some variations between individual tests, likely due to the very small heat release (in the range of 0.1 mW) and the experiments were, therefore, repeated to increase the accuracy. At 50 °C, 100 °C, and 150 °C, the respective average heats of adsorptions are 206, 204, and 195 kJ/mol, with corresponding standard deviations of 9.8, 11.2, and 2.6 kJ/mol. Thus, the NO heat of adsorption was quite constant in this temperature interval. It should be noted that, for the adsorption temperature of 150 °C, N<sub>2</sub> production was observed during NO adsorption period and this means that the heat of adsorption measured is a combination of adsorption heat for NO, dissociation of NO and formation of N<sub>2</sub>. This could be the reason for that this adsorption heat being slightly lower than the others. For adsorption temperatures of 50 °C and 100 °C the values are very similar (206 and 204 kJ/mol). Our results on supported platinum on alumina are in agreement with heat of adsorption measured over single-crystal platinum surfaces, where Fiorin *et al.* [19] reported values of 182 kJ/mol on Pt (111) and 192 kJ/mol on Pt (211). However, the values found by Wartnaby *et al.* [17] for NO on Pt (110) is slightly lower (160 kJ/mol).



**Figure 4.** Averaged adsorption heats of NO at adsorption temperatures of 50 °C, 100 °C, and 150 °C over 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Experimental details are described in Section 3.

### 2.3. Heat of Adsorption during O<sub>2</sub> TPD Experiments

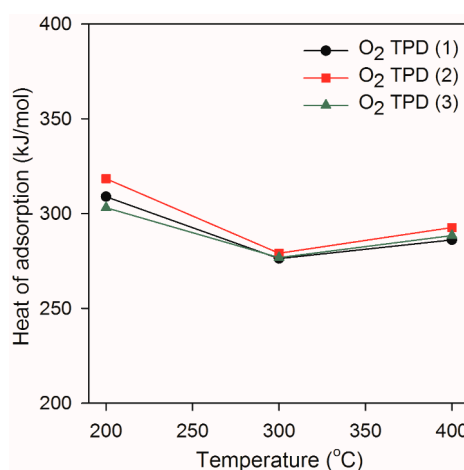
Additionally, for the O<sub>2</sub> TPD experiments, 100 ppm was dosed and three adsorption temperatures were investigated (200 °C, 300 °C, and 400 °C) and the results for the adsorption temperature at 300 °C are shown in Figure 5. In the same way as for the NO TPD, there is a clear exotherm observed when starting the oxygen adsorption. However, the exotherm is much larger, since the heat of adsorption of oxygen is higher compared to NO. During the Ar period between the oxygen steps, no O<sub>2</sub> desorption is visible, which also is the reason why no O<sub>2</sub> re-adsorption is observed in the second step. The oxygen storage corresponded to 0.96 μmol, which gives an O coverage of 1.6 per Pt surface sites (considering the dispersion of 12%). Thus, subsurface oxygen was produced. This is in line with an earlier study by Olsson and Fridell [22], where Pt/Al<sub>2</sub>O<sub>3</sub> was exposed to 200 ppm O<sub>2</sub> for 5 min, 8.1% O<sub>2</sub> for 5 min, and 8.1% O<sub>2</sub> for 4.5 h, respectively, at 350 °C, which resulted in oxygen coverage of 1.0, 1.6, and 2.4. In the present experiments, our catalyst was exposed to oxygen for quite a long time (30 min) and it is, therefore, reasonable that some sub-surface oxygen was produced. Finally, a temperature ramp was conducted to 500 °C and only small amounts of oxygen was desorbing. The desorbed amount corresponded to only 23% of the stored oxygen, hence, large amount of oxygen is remaining on the surface, which clearly shows the large binding strength of oxygen to the platinum sites.



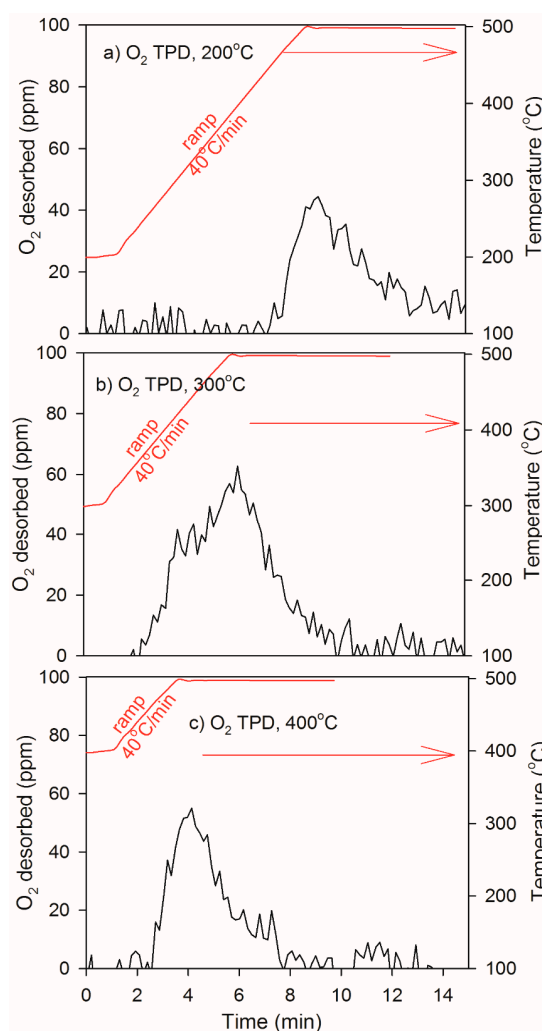
**Figure 5.** (a) Oxygen concentration and temperature as a function of the time and (b) the corresponding heat flow during O<sub>2</sub> TPD at 300 °C for 2 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>. Experimental details are described in Section 3.

From the adsorption part of the TPD experiments, the heat of adsorption is derived and the results are displayed in Figure 6. In order to determine experimental variance and reproducibility, the experiments were repeated and the results for three repeated experiments at each temperature are shown in Figure 6. At 200 °C, 300 °C, and 400 °C the respective average heats of adsorptions are 310, 278, and 289 kJ/mol with corresponding standard deviations of 7.7, 1.5, and 3.3 kJ/mol. At higher adsorption temperature the loosely bound species will not adsorb, which results in higher heat of adsorption, which we previously found for NH<sub>3</sub> adsorption on Cu/SSZ-13 [23], and is also the case in this study comparing 400 °C and 300 °C. These results are also in line with the amount of O<sub>2</sub> desorbed (see Figure 7), where 0.25 μmol is desorbed after 400 °C TPD, while 0.41 μmol for the TPD at 300 °C. This is also in line with the study by Wartnaby *et al.* [17] who observed that the oxygen adsorption heat decreases with the oxygen coverage. Surprisingly, the heat of adsorption of oxygen at 200 °C is higher than the other two temperatures. In addition, the O<sub>2</sub> desorption peak is significantly smaller, where only 0.30 μmol is released for the TPD at 200 °C, but for TPD at 300 °C the corresponding value is 0.41 μmol. It should be noted that at higher temperatures formation of Pt-oxides have been suggested based on TPD experiments [24] and the formation of these species is an activated process. These results are in line with the study by Olsson *et al.* [24], where larger amounts of O<sub>2</sub> was desorbing during the TPD at 300 compared to 200 °C. It should be noted that the heat of adsorption is the difference between activation energy for desorption minus the activation energy for adsorption, and if the activation energy for adsorption is higher, it can result in a lower heat of adsorption, which we observe at 300 °C. Thus, we suggest that the reason for the lower heat of adsorption at 300 °C compared to 200 °C could be the formation of some platinum oxides/subsurface oxygen that has a lower heat of adsorption (due to formation via an activated process) compared to chemisorbed oxygen. Moreover, our results for the heat of adsorption of oxygen on Pt/Al<sub>2</sub>O<sub>3</sub> at atmospheric pressure (310 kJ/mol, 278 and 289 kJ/mol for adsorption temperatures of 200 °C, 300 °C, and 400 °C, respectively) is in line with single crystal measurements at UHV conditions where, for example, Brown *et al.* [18] reported an initial heat of adsorption of oxygen of  $316 \pm 34$  kJ/mol for Pt (110), which decreased with increasing coverage. Moreover, Wartnaby *et al.* [17], received an initial heat of adsorption of 335 kJ/mol for O<sub>2</sub> on Pt (110) at 300 K. Thus, interestingly, the ΔH of oxygen on platinum seems not to be sensitive to the effect of the support, since similar results are observed for single crystals. Moreover, these results also show that similar results are retrieved at atmospheric pressure as for UHV.





**Figure 6.** Averaged adsorption heats of oxygen for adsorption temperatures of 200 °C, 300 °C, and 400 °C over 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Experimental procedures are described in Section 3.



**Figure 7.** The amounts of the oxygen desorbed during temperature ramp for O<sub>2</sub> TPD at adsorption temperatures (a) 200 °C, (b) 300 °C, and (c) 400 °C. Experimental details are described in Section 3.

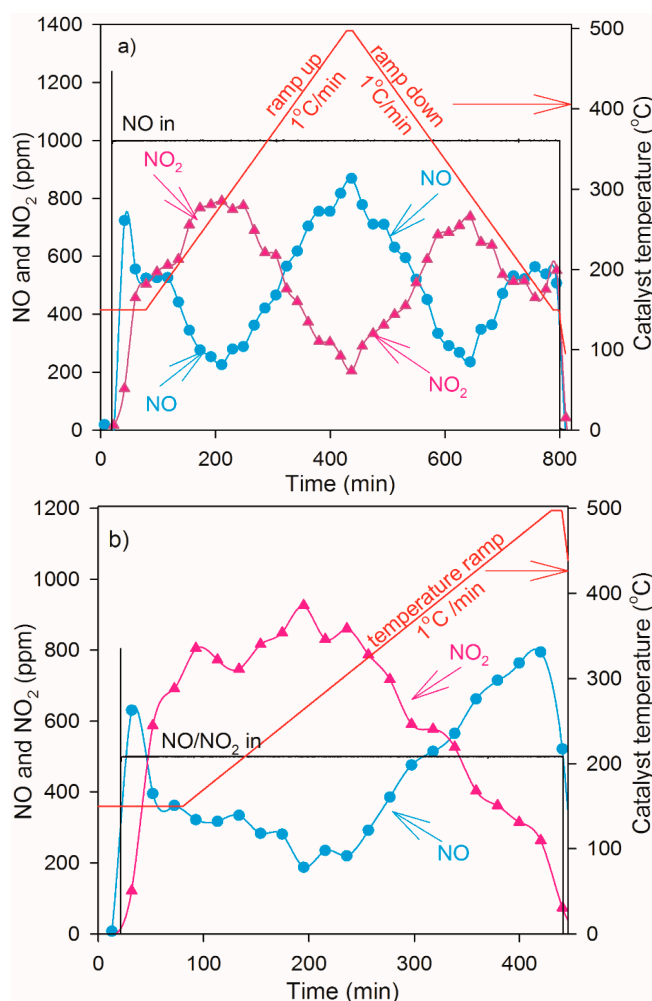
#### 2.4. NO Oxidation and NO<sub>2</sub> Dissociation Reaction

NO oxidation on supported platinum is investigated in this study first with only NO and O<sub>2</sub> as reactants. The increase in NO<sub>2</sub> concentration followed by its decrease and opposite trend for NO

concentration during a temperature ramp from 150 °C to 500 °C (ramp 1 °C/min) is shown in Figure 8a. The reason for the observed decrease in NO oxidation at higher temperatures is due to thermodynamic equilibrium [25]. The results clearly show that the catalyst is active for NO oxidation. Regarding the NO concentration profile, when NO and O<sub>2</sub> are simultaneously dosed into the system, there is a short initial overshoot of NO during the first minutes of the experiment (Figure 8a). The reason for this is probably NO formation during the storage of nitrates from the NO<sub>2</sub> produced, according to:



where S is a storage site. In addition, there appears to be a hysteresis behavior, where the catalyst is more active for NO oxidation during ramp up compared to ramp down. This can be due to Pt-oxides formation during the ramp up [26], which are less active for NO oxidation [22].

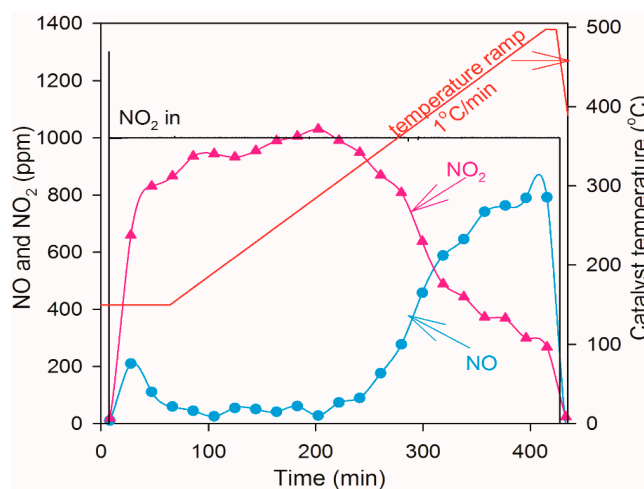


**Figure 8.** Evolution of NO and NO<sub>2</sub> concentrations as function of the time during (a) NO oxidation and (b) (NO + NO<sub>2</sub>) oxidation over 2 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>. Experimental procedures are described in Section 3.

Figure 8b shows the evolution of NO and NO<sub>2</sub> concentrations over the Pt catalyst during simultaneous dosing of 500 ppm NO and 500 ppm NO<sub>2</sub> with 8% O<sub>2</sub>. When the catalyst is oxidized with a mixture of (NO and NO<sub>2</sub>) at 150 °C, nitrates and/or nitrites are first formed on the catalytic surface (same as in Figure 8a). This results in NO production, which are clearly seen by the NO concentration being higher than the inlet NO. A decrease in NO and an increase in NO<sub>2</sub> is then observed during the temperature ramp from 150 to 500 °C.



Finally, the  $\text{NO}_2$  dissociation was studied and Figure 9 shows the NO and  $\text{NO}_2$  concentration profiles as a function of temperature during  $\text{NO}_2$  dissociation starting at  $150^\circ\text{C}$ . Initially, there is a production of NO observed, and as discussed above, this relates to the formation of nitrates on the alumina. It requires high temperatures before an increasing production of NO is seen during  $\text{NO}_2$  dissociation (starts at about  $310^\circ\text{C}$ ), which is significantly higher compared to the start of NO oxidation, which was actually already active at the lowest temperature of the experiment, *i.e.*,  $150^\circ\text{C}$  (see Figure 8a). According to our earlier study where we developed a kinetic model for NO oxidation and  $\text{NO}_2$  dissociation, we found, based on Gibbs free energy analysis, that for  $\text{NO}_2$  dissociation the rate-determining step is oxygen desorption [24]. Thus, the reason for the low activity for  $\text{NO}_2$  dissociation observed in Figure 9 is the slow desorption of oxygen, and indeed the heat of adsorption for oxygen is very high; therefore, the activation energy for  $\text{O}_2$  desorption is very high.



**Figure 9.** The NO and  $\text{NO}_2$  profiles as function of the time during  $\text{NO}_2$  dissociation over 2 wt. % Pt/ $\text{Al}_2\text{O}_3$  catalyst. Experimental procedures are described in Section 3.

### 3. Experimental Section

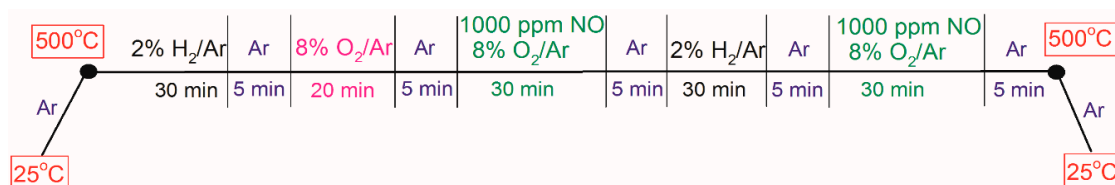
#### 3.1. Synthesis of 2 wt. % Pt/ $\gamma\text{-Al}_2\text{O}_3$ Powder Catalyst

The used catalyst in this study was synthesized by a conventional wetness impregnation method of  $\gamma$ -alumina (Puralox Sasol SBA-200, Hamburg, Germany) with an appropriate concentration of an aqueous solution containing the Pt precursor in the form of  $\text{Pt}(\text{NO}_3)_2$  (W.C. Heraeus GmbH, Hanau, Germany) corresponding to a Pt loading of 2 wt. %. The commercial  $\gamma\text{-Al}_2\text{O}_3$  powder was pre-calcined at  $750^\circ\text{C}$  for 2.5 h before the synthesis in order to prevent the phase changes after metal deposition. After 2 h of vigorous stirring at room temperature, the resulting solution was freeze dried (ScanVac Cool Safe™) at the temperature of liquid nitrogen for 24 h. The obtained 2 wt. % Pt/ $\text{Al}_2\text{O}_3$  was then ground into a powder and calcined at  $500^\circ\text{C}$  for 2 h in air.

#### 3.2. Microcalorimeter Measurements

The experimental setup consisted of a differential scanning calorimeter (Setaram Sensys DSC, SETARAM Instrumentation, Caluire, France) instrument with two vertical quartz tube reactors. One micro-reactor served as the reference and the second was used for loading the powder catalyst. An amount of 100 mg of 2 wt. % Pt/ $\text{Al}_2\text{O}_3$  was loaded onto the sintered quartz bed in the micro-reactor for  $\text{N}_2\text{O}$  dissociation and the TPD experiments, while 40 mg of catalyst was used for the NO, NO +  $\text{NO}_2$  oxidations, and  $\text{NO}_2$  dissociation. The inlet gas flow composition was controlled by Bronkhorst mass flow controllers (Bronkhorst High-Tech B.V., Ruurlo, The Netherlands). The composition of the reaction products was analyzed with a Hiden Analytical HPR 20 quadrupole mass spectrometer (MS, Hiden

Analytical Ltd., Warrington, England) equipped with a capillary probe connected directly to the exit of the second reactor. The reaction products were monitored by recording the MS signals for each compound. The fragmentation in the MS of  $\text{NO}_2$  to produce mass 30 (for NO) and  $\text{N}_2\text{O}$  to produce mass 28 (for  $\text{N}_2$ ) is considered in the calibration and data analysis. The total flow rate was  $20 \text{ mL} \cdot \text{min}^{-1}$  at room conditions in all of the experiments described below. Prior to the desired experiments, the catalysts were subjected to a degreening procedure. Figure 1 shows an overview of the degreening sequence. As is shown in the Figure 10, the sample was conditioned two times in 2%  $\text{H}_2$  at 500 °C for 30 min each, followed by exposure in a mixture of 1000 ppm NO + 8%  $\text{O}_2$  at the same temperature for 30 min. The sample was also treated with 8%  $\text{O}_2$  at 500 °C for 20 min, as is depicted in Figure 10. The degreening treatment was intended to stabilize the catalyst, so that it should return to the same reproducible state under identical reaction conditions.



**Figure 10.** Series of conditions for the degreening procedure carried out for 2 wt. % Pt/ $\text{Al}_2\text{O}_3$  catalyst.

The degreened catalyst was subjected to various transient experiments:  $\text{O}_2$  TPD at three different temperatures (200 °C, 300 °C, and 400 °C), with NO TPD at 50 °C, 150 °C, and 150 °C. The samples were pre-treated using 2%  $\text{H}_2$  at 500 °C for 20 min. After pre-treatment, the catalysts were exposed to 100 ppm  $\text{O}_2$  at the target temperatures (200 °C, 300 °C, or 400 °C) in two steps: in the first step the samples were exposed to oxygen for 30 min followed by an inert period for 10 min; in the second step the catalysts were flowed with oxygen for 20 min. Thereafter, the temperature was raised to 500 °C at a ramping rate of  $40 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  in an Ar stream. The NO TPD tests were performed in the same way as for  $\text{O}_2$  TPD, but using 50 ppm NO in the storage phases instead. The NO TPD experiments were conducted at three temperatures: 50 °C, 100 °C, and 150 °C, respectively.

The surface Pt dispersion was evaluated by  $\text{N}_2\text{O}$  dissociation based on the  $\text{N}_2$  produced during the experiment performed at 100 °C. It was assumed that the number of formed  $\text{N}_2$  molecules is equal with the number of surface noble metal sites [20], which we have used successfully for Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{BaO}/\text{Al}_2\text{O}_3$ , previously [27]. The degreened sample was pre-treated with 2%  $\text{H}_2$  at 500 °C for 30 min, followed by decreasing to the desired temperature (100 °C) in Ar.  $\text{N}_2\text{O}$  dissociation experiment was then performed in which the catalysts were exposed to 200 ppm  $\text{N}_2\text{O}$  at 100 °C for 1 h.

In order to evaluate the Pt behavior when NO and  $\text{NO}_2$  are fed either independently and/or simultaneously in the reactor, various experiments were designed such as: NO oxidation, (NO +  $\text{NO}_2$ ) oxidation, and  $\text{NO}_2$  dissociation. Prior to each of these experiments, the degreened sample was pre-treated following the same procedure as used for TPD experiments. In these experiment the catalyst was exposed to either of the three gas mixtures (1000 ppm NO and 8%  $\text{O}_2$ , 500 ppm NO, 500 ppm  $\text{NO}_2$  and 8%  $\text{O}_2$  or 1000 ppm  $\text{NO}_2$  and 8%  $\text{O}_2$ ) at 150 °C for 1 h. Afterwards, the temperature was raised to 500 °C at a rate of  $1 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  while exposing the catalyst to the same gas mixture and the sample was maintained at 500 °C for 10 min. For the NO oxidation case, the sample was also cooled in the same gas mixture to 150 °C at  $1 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ .

#### 4. Conclusions

In this study we have shown that it is possible to measure the heats of adsorption of NO and oxygen on a functional oxidation catalyst, *i.e.*, Pt supported on  $\text{Al}_2\text{O}_3$ , using microcalorimeter experiments at atmospheric pressure. For reproducible results it was important that the catalyst was stabilized by a thorough degreening treatment. The heats of adsorption were, in most cases,

comparable to those reported for measurements on single crystal platinum surfaces. The results from this work can be used when developing kinetic models for DOC. The main findings in this study is (i)  $\Delta H$  for oxygen adsorption of Pt/Al<sub>2</sub>O<sub>3</sub> as a function of temperature, (ii) platinum oxide formation may result in lowering of  $\Delta H$ , (iii)  $\Delta H$  for oxygen is changing at higher temperatures due to repulsive interactions, and (v)  $\Delta H$  for NO adsorption on Pt/Al<sub>2</sub>O<sub>3</sub>. The results, in a more detailed description, can be found in the following sections:

The initial averaged values of the adsorption heats of oxygen are 310 kJ/mol at 200 °C and it declines to 278 kJ/mol at 300 °C, followed by its increase to 289 kJ/mol at 400 °C. At 300 °C a greater quantity of oxygen was adsorbed compared to the TPD at 200 °C, indicating the formation of platinum oxides via an activated process. Oxygen, as platinum oxides, might have a lower heat of formation compared to chemisorbed oxygen formed mainly at 200 °C, which could be due to that oxide formation likely being an activated process which reduces the  $\Delta H$  ( $\Delta H$  = activation energy for decomposition of Pt oxides – activation energy for formation of Pt oxides). The smaller increase in the heat of adsorption from 300 to 400 °C indicates coverage dependence of the heat of adsorption in this temperature range.

For nitric oxide, the initial heat of adsorption for a fresh sample is 206 kJ/mol (at 50 °C) and 195 kJ/mol (at 150 °C). At the lowest adsorption temperature (50 °C) no N<sub>2</sub> formation was observed indicating that the heat of adsorption of 206 kJ/mol is associated with NO adsorption. Over the examined temperature range the heat of adsorption of NO appeared nearly constant. A slight apparent decrease at only the highest temperature, 150 °C, was likely due to interference from side reactions (NO dissociation and N<sub>2</sub> formation).

The catalyst was demonstrated to be active for NO oxidation, (NO + NO<sub>2</sub>) oxidation, and NO<sub>2</sub> dissociation. A higher temperature was required for light-off of NO<sub>2</sub> dissociation compared to NO oxidation, which is consistent with the observed high adsorption heats for oxygen since oxygen desorption has been suggested to be the rate-limiting step for NO<sub>2</sub> dissociation.

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