



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

## **Sulfur Poisoning Effects on Modern Lean NO<sub>x</sub> Trap Catalysts Components**

Downloaded from: <https://research.chalmers.se>, 2022-10-11 21:22 UTC

Citation for the original published paper (version of record):

De Abreu Goes, J., Kristoffersson, A., Olsson, L. (2019). Sulfur Poisoning Effects on Modern Lean NO<sub>x</sub> Trap Catalysts Components. *Catalysts*, 9(6). <http://dx.doi.org/10.3390/catal9060492>

N.B. When citing this work, cite the original published paper.

Article

# Sulfur Poisoning Effects on Modern Lean NO<sub>x</sub> Trap Catalysts Components

Jesus Emmanuel De Abreu Goes <sup>1,2</sup>, Annika Kristoffersson <sup>1</sup> and Louise Olsson <sup>2,\*</sup> 

<sup>1</sup> Volvo Cars, SE-405 31 Gothenburg, Sweden; [jesus.emmanuel.de.abreu.goes@volvocars.com](mailto:jesus.emmanuel.de.abreu.goes@volvocars.com) (J.E.D.A.G.); [annika.kristoffersson@volvocars.com](mailto:annika.kristoffersson@volvocars.com) (A.K.)

<sup>2</sup> Competence Centre for Catalysis, Chemical Engineering, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

\* Correspondence: [louise.olsson@chalmers.se](mailto:louise.olsson@chalmers.se)

Received: 29 April 2019; Accepted: 24 May 2019; Published: 28 May 2019



**Abstract:** In the present work, a series of different materials was investigated in order to enhance the understanding of the role of modern lean NO<sub>x</sub> trap (LNT) components on the sulfur poisoning and regeneration characteristics. Nine different types of model catalysts were prepared, which mainly consisted of three compounds: (i) Al<sub>2</sub>O<sub>3</sub>, (ii) Mg/Al<sub>2</sub>O<sub>3</sub>, and (iii) Mg/Ce/Al<sub>2</sub>O<sub>3</sub> mixed with Pt, Pd, and Pt-Pd. A micro flow reactor and a diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) were employed in order to investigate the evolution and stability of the species formed during SO<sub>2</sub> poisoning. The results showed that the addition of palladium and magnesium into the LNT formulation can be beneficial for the catalyst desulfation due mainly to the ability to release the sulfur trapped at relatively low temperatures. This was especially evident for Pd/Mg/Al<sub>2</sub>O<sub>3</sub> model catalyst, which demonstrated an efficient LNT desulfation with low H<sub>2</sub> consumption. In contrast, the addition of ceria was found to increase the formation of bulk sulfate species during SO<sub>2</sub> poisoning, which requires higher temperatures for the sulfur removal. The noble metal nature was also observed to play an important role on the SO<sub>x</sub> storage and release properties. Monometallic Pd-based catalysts exhibited the formation of surface palladium sulfate species during SO<sub>2</sub> exposure, whereas Pt-Pd bimetallic formulations presented higher stability of the sulfur species formed compared to the corresponding Pt- and Pd-monometallic samples.

**Keywords:** lean NO<sub>x</sub> traps; sulfur poisoning; platinum; palladium; magnesium; ceria

## 1. Introduction

Stringent exhaust gas emission and fuel economy regulations, such as the European Real Driving Emission (RDE) and US Tier 3, have encouraged the development of advanced lean burn gasoline and diesel engines for their improved fuel economy and reduced greenhouse gas emissions. The implementation of these engines are, however, constrained by the need of catalytic systems in their lean exhaust to control the nitrogen oxide (NO<sub>x</sub>) emissions. Current NO<sub>x</sub> reduction technologies, such as NO<sub>x</sub> storage and reduction (NSR; also known as lean NO<sub>x</sub> trap, LNT), and selective catalytic reduction (SCR), are indeed expected to require more efficient NO<sub>x</sub> abatement materials and strategies to cope with these regulations.

Lean NO<sub>x</sub> trap is an effective NO<sub>x</sub> reduction strategy able to attain high NO<sub>x</sub> conversions over a wide range of temperatures without the need of additional on-board reductants [1,2]. It can also be used in combination with SCR catalysts to achieve low NO<sub>x</sub> emissions. In fact, the combination of a close-coupled LNT and downstream SCR catalysts has been considered crucial to meet the forthcoming NO<sub>x</sub> emission regulations [3]. The LNT catalyst complements SCR performance at low operating temperatures, and produces ammonia during the rich regeneration phase that can partially replace

urea [4]. Nevertheless, the LNT system is highly susceptible to sulfur, and its performance can be severely affected as  $\text{NO}_x$  storage sites are blocked by sulfur [5–7]. Sulfates formed on the  $\text{NO}_x$  storage sites have higher thermal stability than nitrates and nitrites and, therefore, their decomposition needs very high temperatures and alternating rich/lean exhaust mixtures [8,9]. This does not only lead to higher fuel consumption due to regular desulfation events, but may also cause structural deactivation of the catalyst, such as sintering of precious metals and the formation of mixed oxides (e.g.,  $\text{BaAl}_2\text{O}_4$  for the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{BaO}$  at high temperatures), affecting the overall  $\text{NO}_x$  storage and reduction activity of the catalyst [10–12].

Therefore, the sulfur tolerance of modern LNT catalysts should be improved by replacing the  $\text{NO}_x$  trapping material with a component with lower affinity towards sulfation, and with enhanced desorption of sulfur species during regeneration. Barium is frequently employed as a storage material because of its high thermal stability, however, it is responsible for the major LNT catalyst deterioration due to its high affinity for sulfation [13]. Ji et al. [14] studied the incorporation of ceria to Ba-based LNT catalysts and determined to provide a positive impact on LNT performance in the presence of sulfur. Ceria was found to enhance sulfur tolerance of the LNT catalyst by storing sulfur species, which mitigates the sulfation of barium sites. Rohr et al. [13] however, determined that barium is selectively poisoned in the presence sulfur over alumina and ceria. This may be attributed to the less alkaline nature of Ce and  $\text{Al}_2\text{O}_3$  compared to Ba, which might lower the ability of Ce and  $\text{Al}_2\text{O}_3$  to store sulfur and, therefore, result in more severe sulfation of the Ba phase [15]. Nevertheless, the amount of S stored on non-Ba oxides can be anyhow significant, delaying the Ba sulfation [16]. In other studies, Kylhammar et al. investigated the effect of MgO addition on the sulfation and desulfation behavior. They reported that  $\text{Al}_2\text{O}_3$ -MgO-based samples form less stable sulfur species by releasing  $\text{SO}_x$  already below 500 °C. Other studies have shown that the addition of MgO can also enhance the  $\text{NO}_x$  trapping performance and minimize irreversible precious metal sintering upon severe thermal aging treatments [17–19]. Nevertheless, the sulfur poisoning and regeneration behavior on MgO-CeO<sub>2</sub>-based LNT catalysts have not been investigated yet to the best of our knowledge. Additionally, there is very limited work done on the influence of the noble metal nature on the  $\text{SO}_x$  storage and release properties for MgO and MgO-CeO<sub>2</sub> materials.

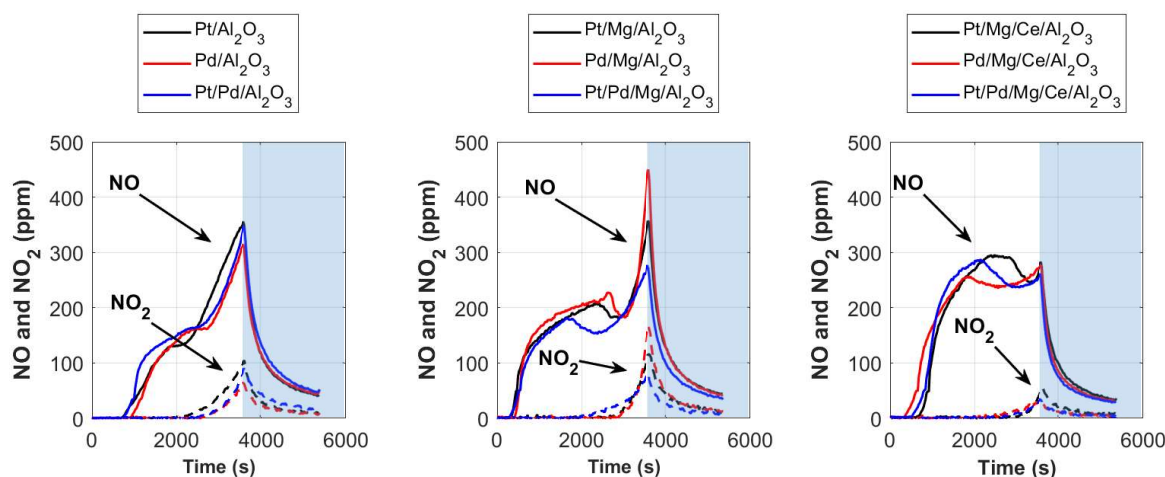
In this study, a number of different LNT components is investigated as regenerable  $\text{NO}_x$  traps. This effort aims to enhance the understanding of the role of modern LNT materials on the sulfur poisoning and regeneration characteristics. We, therefore, studied different metal oxides that are sufficiently basic for  $\text{NO}_x$  storage, such as  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and MgO, but less basic than BaO in order to minimize the sulfur poisoning. Nine different types of model catalysts were prepared, which mainly consisted of three compounds: (i)  $\text{Al}_2\text{O}_3$ , (ii) Mg/ $\text{Al}_2\text{O}_3$ , and (iii) Mg/Ce/ $\text{Al}_2\text{O}_3$  mixed with Pt, Pd, and Pt-Pd.

## 2. Results

### 2.1. $\text{NO}_2$ -TPD Experiments

In order to investigate the stability of the formed nitrates,  $\text{NO}_2$ -temperature programmed desorption experiments were conducted over all samples according to the experimental procedure described earlier. Firstly, the NO and  $\text{NO}_2$  profiles over the  $\text{NO}_2$  adsorption and Ar flushing steps are presented in Figure 1. The data clearly indicates that the adsorption of  $\text{NO}_2$  leads to NO release in the gas phase. The NO formation is most probably associated to both  $\text{NO}_2$  disproportionation and  $\text{NO}_2$  decomposition reactions, which are well known in the literature [20–23]. The formation of NO increases in the order of PGM- $\text{Al}_2\text{O}_3$  < Mg- $\text{Al}_2\text{O}_3$  < Mg-Ce- $\text{Al}_2\text{O}_3$ , where PGM denotes precious group metal. This is most likely because of the increase of  $\text{NO}_2$  storage sites available for the disproportionation reaction by introducing Mg and Ce into the catalyst formulation. Additionally, Table 1 summarizes the results of  $\text{NO}_2$ -TPD experiments over the  $\text{NO}_2$  adsorption and Ar flushing steps, which includes the total  $\text{NO}_x$  adsorbed (Total  $\text{NO}_x$  Ads). The total amount of  $\text{NO}_x$  adsorbed was determined by

subtracting the cumulative outlet  $\text{NO}_x$  concentration over the  $\text{NO}_2$  adsorption and Ar flushing steps from the total amount of  $\text{NO}_x$  introduced into the system over the same period of time. The amount of  $\text{NO}_x$  stored was slightly higher for PGM- $\text{Al}_2\text{O}_3$  samples compared with Mg-containing catalysts, which probably indicates that Mg can block Al sites, resulting in a reduced  $\text{NO}_x$  storage capacity.



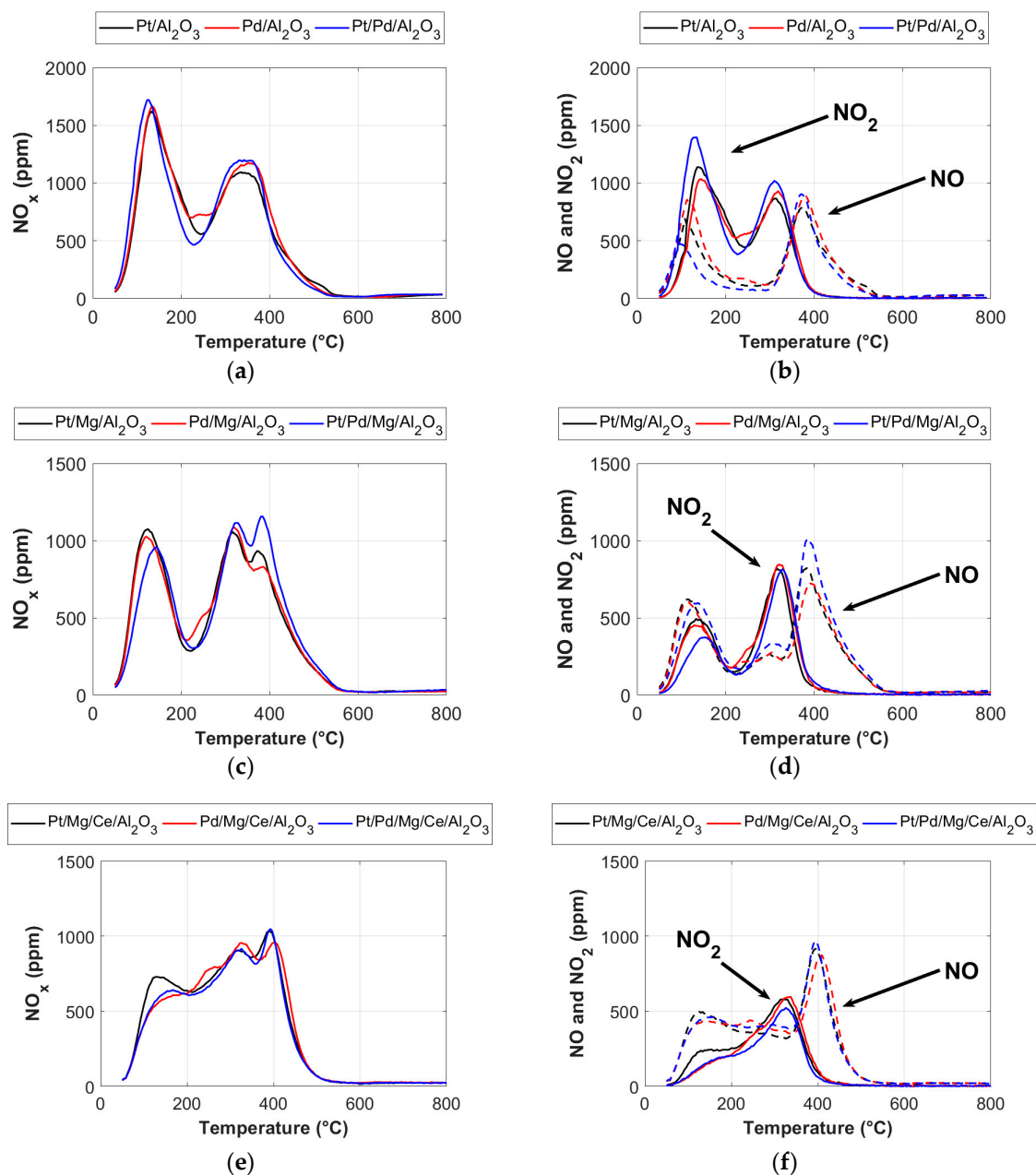
**Figure 1.** NO and  $\text{NO}_2$  profiles over the  $\text{NO}_2$  adsorption and Ar flushing (light blue) steps.

**Table 1.** Summary of TPD experiment for all samples tested: total amount of  $\text{NO}_x$  adsorbed, amount of NO and  $\text{NO}_2$  desorbed during temperature ramp, and the temperature at 20% (T20) and 90% (T90) of  $\text{NO}_x$  released.

Sample	Total $\text{NO}_x$ Ads ( $\mu\text{mol}$ )	NO Des. ( $\mu\text{mol}$ )	$\text{NO}_2$ Des. ( $\mu\text{mol}$ )	T20 $\text{NO}_x$ ( $^\circ\text{C}$ )	T90 $\text{NO}_x$ ( $^\circ\text{C}$ )
Pt/ $\text{Al}_2\text{O}_3$	37.3	13.8	18.2	141	417
Pd/ $\text{Al}_2\text{O}_3$	38.9	15.6	18.1	146	417
Pt/Pd/ $\text{Al}_2\text{O}_3$	37.2	11.9	20.8	132	406
Pt/Mg/ $\text{Al}_2\text{O}_3$	35.3	15.4	11.5	142	438
Pd/Mg/ $\text{Al}_2\text{O}_3$	34.5	15	11.5	142	435
Pt/Pd/Mg/ $\text{Al}_2\text{O}_3$	37.1	17.3	10	160	442
Pt/Mg/CeO <sub>2</sub> / $\text{Al}_2\text{O}_3$	35.5	16.6	9.4	165	424
Pd/Mg/CeO <sub>2</sub> / $\text{Al}_2\text{O}_3$	35.8	16.8	8.7	191	435
Pt/Pd/Mg/CeO <sub>2</sub> / $\text{Al}_2\text{O}_3$	36	17	7.5	184	428

Regarding the desorption temperature, Table 1 numerically summarizes the results over the TPD step, containing the amount of NO and  $\text{NO}_2$  desorbed, and temperature at 20% (T20) and 90% (T90) of  $\text{NO}_x$  released. Note that the total amount of NO (NO Des.) and  $\text{NO}_2$  ( $\text{NO}_2$  Des.) desorbed over the TPD step is slightly lower than the total  $\text{NO}_x$  adsorbed during  $\text{NO}_2$  adsorption and Ar flushing steps (see Table 1). This could be because of temperature variations in the mass-spectrometer during the temperature ramping, leading to small experimental deviations. Moreover, Figure 2 shows the NO,  $\text{NO}_2$ , and total  $\text{NO}_x$  profiles as a function of the catalyst temperature. The total  $\text{NO}_x$  profiles are particularly used to properly assign the  $\text{NO}_x$  desorption peaks to their corresponding components, and compare their magnitudes with other catalyst groups. Clear differences in  $\text{NO}_x$  desorption profiles are presented, which suggests that the LNT formulation certainly influence the  $\text{NO}_x$  storage stability. Two  $\text{NO}_x$  desorption peaks were evident for PGM- $\text{Al}_2\text{O}_3$  samples, with their maximum approximately at 130 and 330  $^\circ\text{C}$ , respectively. Note that the magnitude of the low temperature maxima is slightly larger compared to the high temperature peak. The low temperature peak could be attributed to the removal of weakly adsorbed  $\text{N}_2\text{O}_4$  and  $\text{NO}_2^{+\delta}$  species, whereas the high temperature desorption peak could be associated to the decomposition of nitrate species from alumina sites [24,25]. Mg- $\text{Al}_2\text{O}_3$  samples show a similar TPD-profile with an additional peak located around 380  $^\circ\text{C}$ , ascribed to the decomposition of  $\text{NO}_x$  stored on magnesium sites [26]. The TPD spectra of Mg-Ce- $\text{Al}_2\text{O}_3$  samples in contrast show a shoulder around 160  $^\circ\text{C}$  and two intense peaks located around 330 and 380  $^\circ\text{C}$ ,

respectively. Thereby, the results suggest that the presence of Mg and Ce into the LNT formulation certainly impact the stability of  $\text{NO}_x$  stored species. In fact, PGM-Mg- $\text{Al}_2\text{O}_3$  and PGM-Mg-Ce- $\text{Al}_2\text{O}_3$  samples presented up to 36 °C higher T90 temperatures compared to PGM- $\text{Al}_2\text{O}_3$  samples (see Table 1). This is most likely due to the formation of more strongly bound nitrate species in presence of Mg and Ce compared to PGM- $\text{Al}_2\text{O}_3$  samples [25,26]. Moreover, most of the  $\text{NO}_x$  stored was desorbed as NO for PGM-Mg- $\text{Al}_2\text{O}_3$  and PGM-Mg-Ce- $\text{Al}_2\text{O}_3$  samples because of the  $\text{NO}_2$  dissociation at high temperatures (above 350 °C) over noble metal sites [27]. It should also be noted that the experiments do not emphasize a considerable impact of the precious metals used on the nature and amount of the  $\text{NO}_x$  released.



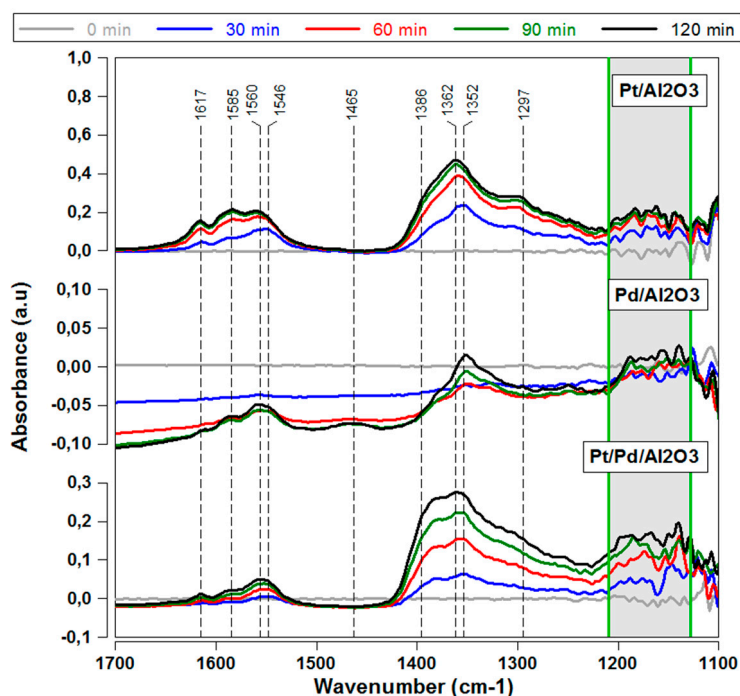
**Figure 2.**  $\text{NO}_x$  release as a function of the catalyst temperature during the TPD experiment for all samples. The total  $\text{NO}_x$  release profile is shown on the left, while the  $\text{NO}_2$  and NO release profiles are shown on the right for the same group of samples. (a,c,e) show the total  $\text{NO}_x$  profiles, while (b,d,f) show the NO and  $\text{NO}_2$  profiles for PGM- $\text{Al}_2\text{O}_3$ , Mg- $\text{Al}_2\text{O}_3$  and Mg-Ce- $\text{Al}_2\text{O}_3$  groups of samples, respectively.

## 2.2. Sulfur Adsorption Characteristics—DRIFTS Experiments

The sulfation behavior of modern LNT compounds are discussed in this section, including the effects of SO<sub>x</sub> poisoning on precious metals, magnesium, and cerium compounds. The sulfation mechanism was studied through DRIFT spectroscopy experiments.

### 2.2.1. Influence of Sulfur on Different Precious Metal Species

The mechanism of SO<sub>x</sub> adsorption over LNT compounds was studied by DRIFT spectroscopy. Figure 3 shows the DRIFTS spectra of Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, and Pt/Pd/Al<sub>2</sub>O<sub>3</sub> samples after the exposure to 50 ppm SO<sub>2</sub> and 8% O<sub>2</sub> for 2 h at 200 °C in the range from 1100–1700 cm<sup>-1</sup>. The spectrum presented represent a subtraction between the reference spectra recorded after pre-treatment at 200 °C and the spectra taken during the SO<sub>x</sub> storage period. The corresponding spectra for Pt/Al<sub>2</sub>O<sub>3</sub> show a substantial increase in the intensity of absorbed sulfur species on alumina. The band at 1352 cm<sup>-1</sup> was quickly formed after 30 min of SO<sub>2</sub> exposure with a weak shoulder at 1386 cm<sup>-1</sup>. Both absorbance bands were assigned to the formation of surface aluminum sulfate species [13,28,29]. These bands increased in intensity and shifted to higher frequencies with extended SO<sub>2</sub> exposure. The observed shift has been previously reported by several authors [30–32], ascribed to either pure frequency shift of a single band caused by the change in the strength of molecular interactions or the combined effect of two overlapping bands that differ in relative intensity. The shift in frequency is observed only after 90 min of sulfur poisoning. In this case, we therefore suggest that the resultant increase in frequency of the band at 1352 cm<sup>-1</sup> is induced by the formation of bulk aluminum sulfate species, centered approximately at 1362 cm<sup>-1</sup>, overlapping the surface aluminum sulfate band. Furthermore, a shoulder appeared approximately at 1297 cm<sup>-1</sup> attributed to chemisorbed molecular SO<sub>2</sub> on alumina [33,34], and SO<sub>3</sub> on Pt [35]. The Pt/Al<sub>2</sub>O<sub>3</sub> spectrum also has a wide band from ~1210 cm<sup>-1</sup> to lower wavenumbers, which corresponds to the formation of bulk aluminum sulfate [34,36].



**Figure 3.** DRIFT spectra from 1100 to 1700 cm<sup>-1</sup> for Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, and Pt/Pd/Al<sub>2</sub>O<sub>3</sub> samples after exposure to 50 ppm SO<sub>2</sub> and 8% O<sub>2</sub> at 200 °C for 0, 30, 60, 90, and 120 min. The blue band represents the frequency range for bulk aluminum sulfates formed over the samples tested (<1210 cm<sup>-1</sup>).



The spectrum at high wave numbers obtained from the SO<sub>2</sub> exposure of Pd and Pt supported on Al<sub>2</sub>O<sub>3</sub> is also shown in Figure 3. Similar to Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the Pd/Al<sub>2</sub>O<sub>3</sub> exhibit an intense band at 1352 cm<sup>-1</sup> with a shoulder near 1386 cm<sup>-1</sup>, both assigned to surface aluminum sulfate [29–31,34]. Likewise, bulk aluminum sulfate were also formed at lower wavenumber (<1200 cm<sup>-1</sup>). Additionally, a weak absorbance band was shown around 1465 cm<sup>-1</sup> after 2 h of SO<sub>2</sub> + O<sub>2</sub> exposure, which corresponds to sulfates formed on Pd sites [34,37–39]. This band was not observed for Pt/Al<sub>2</sub>O<sub>3</sub> sample, which clearly indicates that monometallic Pd-based catalysts are more prone for sulfur poisoning than Pt sites. This is in agreement with previous investigations [40–43]. Lampert et al. [40] indeed reported an important increase in the activation energy after exposing Pd-based catalysts to sulfur species because of the formation of a PdO-SO<sub>3</sub> complex and, therefore, the decrease of the overall catalyst activity. On the contrary, these species apparently spill over rapidly from Pt sites to the alumina surface, which contribute to the resistance of Pt sites to sulfur poisoning [34]. Nevertheless, it is also well known that even the Pt-based catalysts eventually lost activity over time with exposure to sulfur [43].

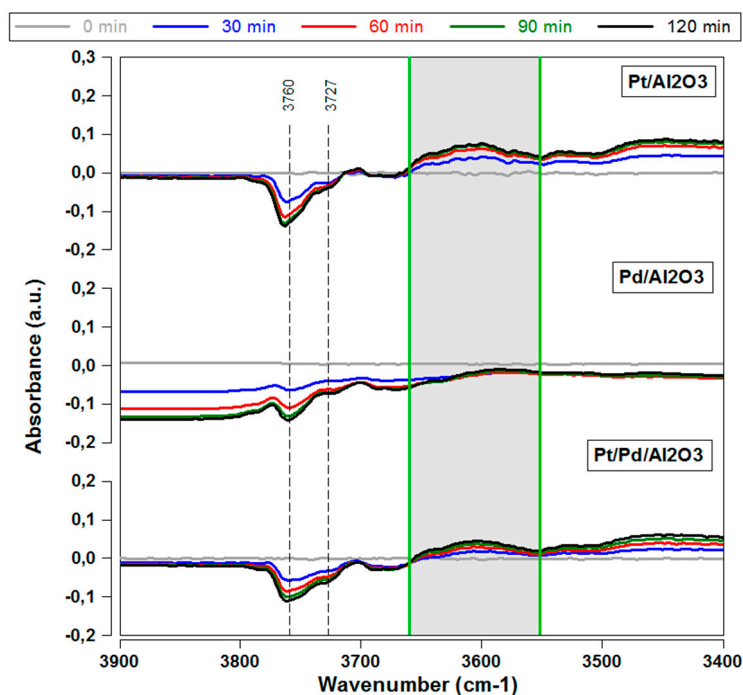
From Figure 3, it is also clear that when Pt/Pd/Al<sub>2</sub>O<sub>3</sub> sample was exposed to SO<sub>2</sub> under oxidizing conditions, surface aluminum sulfate species (1352, and 1386 cm<sup>-1</sup>) were formed, in addition to bulk aluminum sulfates (<1210 and 1362 cm<sup>-1</sup>). Furthermore, the absence of the peak at approximately 1465 cm<sup>-1</sup> associated with PdSO<sub>4</sub> demonstrates that no stable sulfates are formed on Pd surface for Pt-Pd bimetallic samples under the conditions investigated. These results are consistent with the study by Sadokhina et al. [44], where Pd/Pt/Al<sub>2</sub>O<sub>3</sub> was more resistant to sulfur poisoning compared to Pd/Al<sub>2</sub>O<sub>3</sub> during methane oxidation.

Focusing on the hydroxyl region presented in Figure 4, all samples developed negative peaks at ~3760 and ~3727 cm<sup>-1</sup>, in addition to a wide absorbance band from ~3660 cm<sup>-1</sup> to lower wavenumbers. These peaks have been attributed to the interaction of SO<sub>2</sub> with hydroxyl groups on alumina (~3760 and ~3727 cm<sup>-1</sup>) [29,34,45], and hydrogen-bounded sulfite species (<3660 cm<sup>-1</sup>) [34]. Although no sulfites were observed for PGM-Al<sub>2</sub>O<sub>3</sub> samples from the DRIFT spectra presented in Figure 3, it is suggested that the surface aluminum sulfates are also hydrogen-bonded to alumina OH-groups, producing the same effect on the OH stretching frequency [29]. Additionally, during SO<sub>2</sub> + O<sub>2</sub> exposure, all samples developed absorbance bands between 1540 and 1620 cm<sup>-1</sup> (see Figure 3). These peaks are most likely attributed to the adsorption of different species over alumina, where the peak at 1617 cm<sup>-1</sup> is particularly associated with water bound to the alumina surface as a result of the release of OH groups from the alumina surface [4,29,37]. The peaks developed between 1540 and 1585 cm<sup>-1</sup> are attributed to the interaction of the weakly absorbed SO<sub>2</sub> species with Al<sup>n+</sup> Lewis acid sites [46].

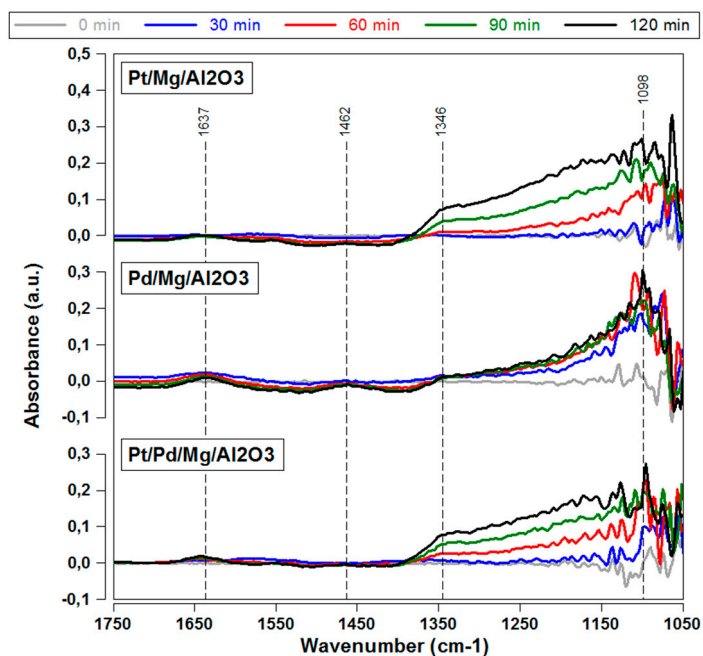
### 2.2.2. Influence of Sulfur on Magnesium Compound

Figure 5 shows the in situ DRIFTS spectra for Pt/Mg/Al<sub>2</sub>O<sub>3</sub>, Pd/Mg/Al<sub>2</sub>O<sub>3</sub>, and Pt/Pd/Mg/Al<sub>2</sub>O<sub>3</sub> samples during the exposure to 50 ppm of SO<sub>2</sub> and 8% O<sub>2</sub> for 2 h at 200 °C. Similar spectrum were observed for all three samples, characterized predominantly by a broad band centered at 1098 cm<sup>-1</sup>. This band can be attributed to asymmetric stretches of surface-bound SO<sub>3</sub> (sulfate) on MgO sites [6,47,48]. A second adsorption band is observed at 1346 cm<sup>-1</sup> most probably due to the formation of surface aluminum sulfate [29,30,34]. Compared with the PGM-Al<sub>2</sub>O<sub>3</sub> samples (see Figure 3), the intensity of the surface aluminum sulfate peak is low, indicating that only small amounts were formed. In fact, surface aluminum sulfate was primarily observed for Pt/Mg/Al<sub>2</sub>O<sub>3</sub> and Pt/Pd/Mg/Al<sub>2</sub>O<sub>3</sub> catalysts, whereas practically no surface aluminum sulfate could be identified for Pd/Mg/Al<sub>2</sub>O<sub>3</sub> sample. This in turn means that the introduction of Mg in the LNT catalyst formulation leads to lower formation of surface aluminum sulfate. This can be attributed to the partial coverage of the Al<sub>2</sub>O<sub>3</sub> surface with magnesium, and/or the higher affinity of Mg for S than Al<sub>2</sub>O<sub>3</sub> [4,6,49]. Interestingly, the shoulder observed at 1297 cm<sup>-1</sup> for PGM-Al<sub>2</sub>O<sub>3</sub> samples did not evolve for Mg-Al<sub>2</sub>O<sub>3</sub> catalysts, suggesting that Mg could prevent the formation of either chemisorbed molecular SO<sub>2</sub> on alumina or bulk aluminum sulfates during SO<sub>2</sub> exposure. In addition, Pd/Mg/Al<sub>2</sub>O<sub>3</sub> sample showed weak bands at ~1462 and ~1637 cm<sup>-1</sup>

assigned to palladium sulfates ( $\text{PdSO}_4$ ) [34,37–39], and water bound to the catalyst surface (probably on alumina) [4,29,37], respectively. The latter was also weakly observed for the  $\text{Pt/Pd/Mg/Al}_2\text{O}_3$  catalyst.



**Figure 4.** DRIFT spectra from  $3400\text{--}3900\text{ cm}^{-1}$  for  $\text{Pt/Al}_2\text{O}_3$ ,  $\text{Pd/Al}_2\text{O}_3$ , and  $\text{Pt/Pd/Al}_2\text{O}_3$  samples after exposure to 50 ppm  $\text{SO}_2$  and 8%  $\text{O}_2$  at  $200\text{ }^\circ\text{C}$  for 0, 30, 60, 90, and 120 min. The blue band represents the frequency range for hydrogen-bounded sulfite species formed over the samples tested ( $<3660\text{ cm}^{-1}$ ).

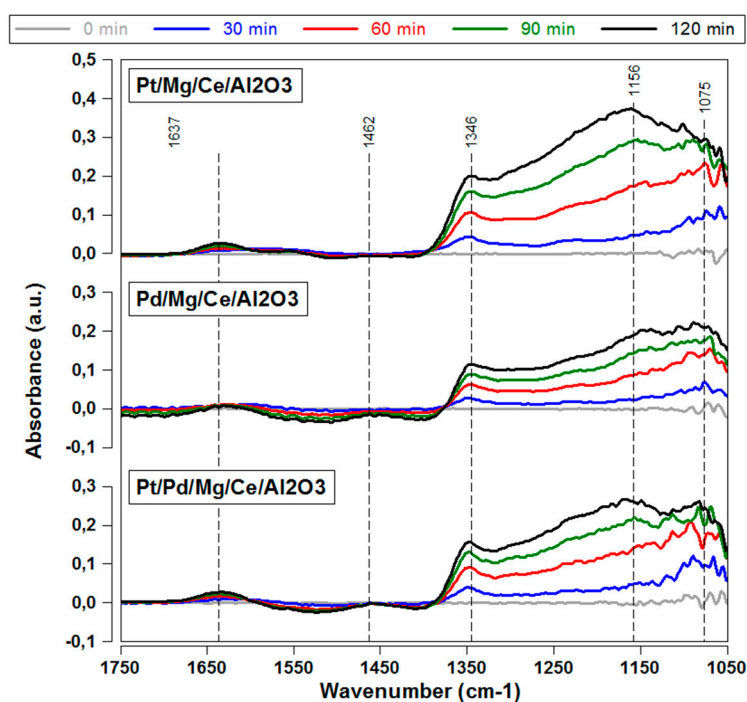


**Figure 5.** DRIFT spectra from  $1000\text{ to }1700\text{ cm}^{-1}$  for  $\text{Pt/Mg/Al}_2\text{O}_3$ ,  $\text{Pd/Mg/Al}_2\text{O}_3$ , and  $\text{Pt/Pd/Mg/Al}_2\text{O}_3$  samples after exposure to 50 ppm  $\text{SO}_2$  and 8%  $\text{O}_2$  at  $200\text{ }^\circ\text{C}$  for 0, 30, 60, 90, and 120 min.



### 2.2.3. Influence of Sulfur on Ceria Compound

In situ DRIFTS spectra as a function of time are presented in Figure 6 for Pt/Mg/Ce/Al<sub>2</sub>O<sub>3</sub>, Pd/Mg/Ce/Al<sub>2</sub>O<sub>3</sub>, and Pt/Pd/Mg/Ce/Al<sub>2</sub>O<sub>3</sub> samples exposed to SO<sub>2</sub> + O<sub>2</sub> at 200 °C. Interestingly, Ce-Mg-Al<sub>2</sub>O<sub>3</sub> samples showed relatively similar sulfated DRIFTS spectra compared with Mg-Al<sub>2</sub>O<sub>3</sub> catalysts (see Figure 5). The primary differences are the more pronounced peak at 1346 cm<sup>-1</sup> and the presence of a new adsorption band at 1156 cm<sup>-1</sup>. According to the literature, the bands at 1346 and 1156 cm<sup>-1</sup> correspond to surface and bulk sulfates [30,32,49,50], respectively. The surface sulfate can be either formed on Al<sub>2</sub>O<sub>3</sub> and/or ceria sites [29,30,32,34,49], whereas bulk sulfate is mostly associated with ceria sites [32,49]. The 1156 cm<sup>-1</sup> band can be also associated with bulk MgSO<sub>4</sub> [48], however, this is not likely since it was not observed for Mg-Al<sub>2</sub>O<sub>3</sub> samples (see Figure 5). In addition, the band at 1098 cm<sup>-1</sup> (for Mg-Al<sub>2</sub>O<sub>3</sub>) was slightly shifted to 1075 cm<sup>-1</sup> for Ce-Mg-Al<sub>2</sub>O<sub>3</sub> samples. This adsorption band can be assigned to the formation of surface magnesium and/or cerium sulfates. Note also that the bands at 1346 and 1075 cm<sup>-1</sup> were quickly formed after 30 min of SO<sub>2</sub> exposure, whereas the adsorption band at 1156 cm<sup>-1</sup> appeared only after 90 min when the band at 1075 cm<sup>-1</sup> began to be saturated. This implies that in the presence of ceria, the sulfur starts to accumulate on the surface of the catalyst, and subsequently converts into bulk sulfate when the surface becomes saturated. This is in agreement with previous studies [38,51].

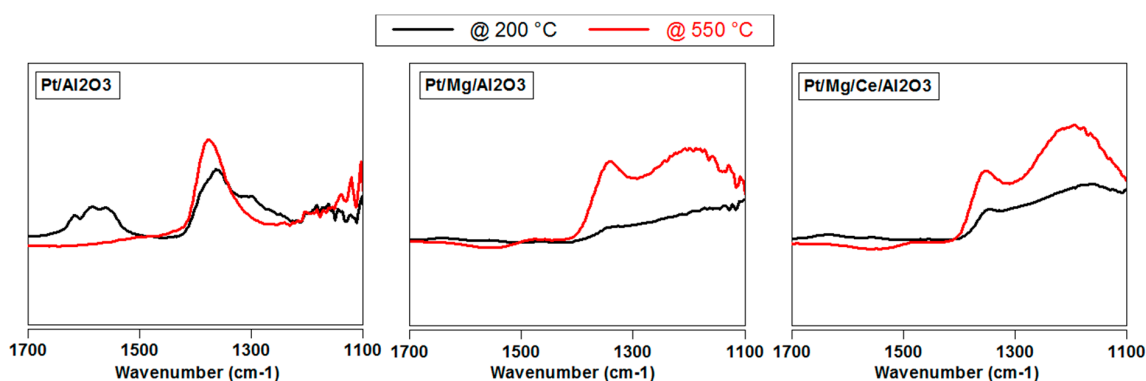


**Figure 6.** DRIFT spectra from 1000 to 1700 cm<sup>-1</sup> for Pt/Mg/Ce/Al<sub>2</sub>O<sub>3</sub>, Pd/Mg/Ce/Al<sub>2</sub>O<sub>3</sub>, and Pt/Pd/Mg/Ce/Al<sub>2</sub>O<sub>3</sub> samples after exposure to 50 ppm SO<sub>2</sub> and 8% O<sub>2</sub> at 200 °C for 0, 30, 60, 90 and 120 min.

### 2.2.4. Influence of Catalyst Temperature on SO<sub>2</sub> Poisoning

Identifying the stability of the sulfur species formed is crucial for an efficient desulfation event to recover the catalyst activity. Therefore, in order to better understand the stability of sulfur on various LNT components, DRIFTS spectra were collected from Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/Mg/Al<sub>2</sub>O<sub>3</sub>, and Pt/Mg/Ce/Al<sub>2</sub>O<sub>3</sub> samples during a temperature ramp. The samples were first exposed to 50 ppm of SO<sub>2</sub> and 8% O<sub>2</sub> for 2 h at 200 °C, and then the temperature was risen from 200 °C to 550 °C at a rate of 20 °C/min with the same feed composition (50 ppm of SO<sub>2</sub> and 8% O<sub>2</sub>). Spectra were collected at each temperature and are presented in Figure 7, using a background spectrum taken before the SO<sub>2</sub> adsorption at 200 °C. An increase in intensity is clearly seen for all three samples as the temperature increases, in particular

the bands related to surface- and bulk-like sulfates. In fact, a new adsorption peak at  $\sim 1190\text{ cm}^{-1}$  was identified for Pt/Mg/Al<sub>2</sub>O<sub>3</sub> at 550 °C, assigned to the formation of bulk MgSO<sub>4</sub> [48]. The bulk sulfate band indeed dominated the spectrum for Mg and Mg-Ce containing catalysts at 550 °C, indicating that both Mg and Ce play critical roles in increasing the sulfation for LNT catalysts. This is in good agreement with the results reported by Colussi et al. [38] and Boaro et al. [52]. Bulk sulfate bands were also shifted to higher wavenumbers by increasing the catalyst temperature, whereas, under such condition, surface-like sulfate remained at same vibrational frequency. On the contrary, bands observed over the  $\sim 1400$  to  $\sim 1600\text{ cm}^{-1}$  range at 200 °C for Pt/Al<sub>2</sub>O<sub>3</sub> sample were removed at 550 °C, which indicate that these species left the surface or were converted into other species. It should be noted that the SO<sub>2</sub> saturation was not achieved during the sulfur exposure at 200 °C and this can be seen by examining Figures 5 and 6, where it is clear that the intensities are increasing significantly between 90 and 120 min of exposure. However, the time for the ramping is only 17.5 min, and when comparing the large differences between the spectra at 200 and 550 °C in Figure 7, with the spectra in Figures 5 and 6 after 90 and 120 min exposure time, respectively, it is clear that the temperature plays a critical role.



**Figure 7.** DRIFTS spectra for Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/Mg/Al<sub>2</sub>O<sub>3</sub>, and Pt/Mg/Ce/Al<sub>2</sub>O<sub>3</sub> samples after SO<sub>2</sub> adsorption at 200 °C and a temperature ramp at 550 °C. The reference spectrum was taken before SO<sub>2</sub> adsorption at 200 °C. The gas composition during adsorption and subsequent temperature ramp was 50 ppm SO<sub>2</sub> and 8% O<sub>2</sub>.

Overall, the catalyst temperature clearly influences SO<sub>2</sub> adsorption by (a) increasing the amount of species formed (higher sulfation rate), (b) endorsing the migration of surface sulfate species to occupy more stable sulfate configurations (higher bulk-like sulfate species formed), and (c) removing weakly absorbed species during SO<sub>2</sub> exposure.

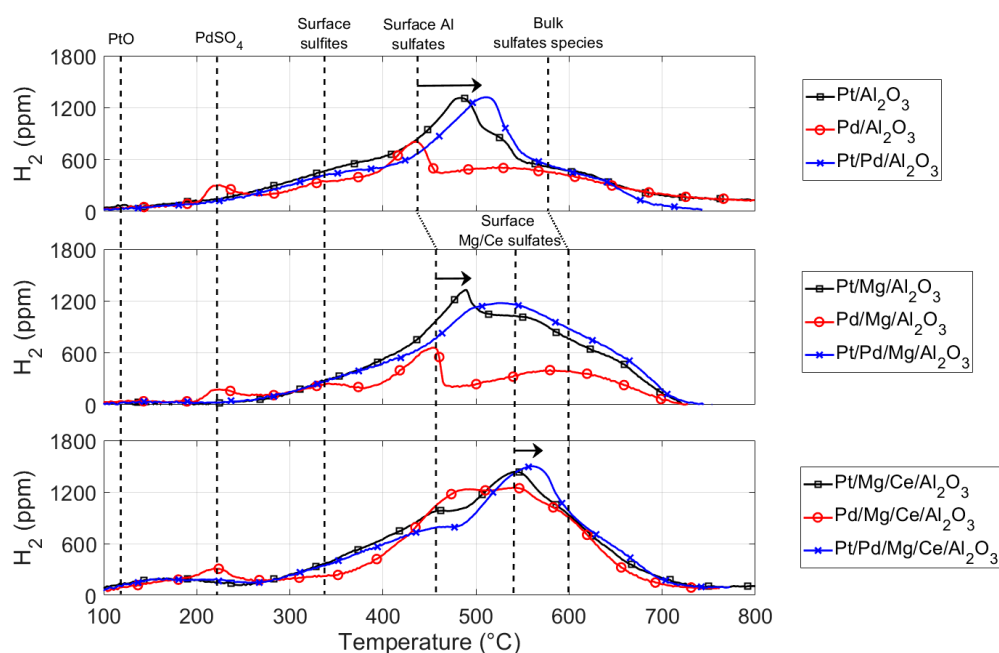
### 2.3. Sulfur Regeneration

The influence of the LNT catalyst formulation on the sulfur regeneration was investigated over nine different model LNT catalysts by performing H<sub>2</sub>-TPR experiments. Prior to testing, the samples were sulfated in a gas feed containing 50 ppm SO<sub>2</sub> and 8% O<sub>2</sub> for 8 h at 200 °C. Table 2 numerically summarizes the results of the H<sub>2</sub>-TPR experiment, including total H<sub>2</sub> consumption, and the temperatures at 20% (T20) and 90% (T90) of SO<sub>2</sub> released. Likewise, Figure 8 displays the resulting H<sub>2</sub> consumption profiles for all pre-sulfated samples. All reduction reactions involving hydrogen consumption have been reported in the Appendix A. The H<sub>2</sub> consumption peaks were identified as the reduction of PdSO<sub>4</sub> (peak centered at 223 °C for Pd-monometallic [39]), surface sulfites (337 °C [53]), surface aluminum sulfates (from 437 °C to 510 °C), surface magnesium/ceria sulfates (542 °C [14,54]), and bulk-like sulfates species (579 °C [38]). Surface aluminum sulfates and bulk-like sulfates were slightly shifted towards higher temperatures (+20 °C) for Mg-Al<sub>2</sub>O<sub>3</sub> and Mg-Ce-Al<sub>2</sub>O<sub>3</sub> samples. This is probably because of the formation of more strongly bound sulfate species in presence of Mg compared to PGM-Al<sub>2</sub>O<sub>3</sub> samples [54]. Likewise, the reduction of surface aluminum sulfates were shifted

towards higher temperatures for the bimetallic samples. This, therefore, implies that the sulfur species formed were more stable in the bimetallic catalysts than in corresponding monometallic Pt and Pd samples. It should be also noted that the reduction of Pd-monometallic catalysts took place at lower temperatures (with lower H<sub>2</sub> consumption; see Table 2) with respect to other samples. For instance, the corresponding reduction peak for surface aluminum sulfates was observed at 437 °C and 480 °C for Pd- and Pt-monometallic samples, respectively. This is totally consistent with the results reported by Wilburn and Epling [34]. They found that Pd makes the formed sulfur species less strong compared to Pt containing samples due to the poor oxidizing capabilities of Pd [34].

**Table 2.** Summary of H<sub>2</sub>-TPR experiment for PGM-Al<sub>2</sub>O<sub>3</sub> samples tested: amount of SO<sub>2</sub> stored after poisoning, H<sub>2</sub> consumption, and temperatures at 20% (T20) and 90% (T90) of SO<sub>2</sub> released.

Sample	H <sub>2</sub> Consumption (μmol)	T20 SO <sub>2</sub> (°C)	T90 SO <sub>2</sub> (°C)
Pt/Al <sub>2</sub> O <sub>3</sub>	52	401	652
Pd/Al <sub>2</sub> O <sub>3</sub>	38.3	386.9	661.9
Pt/Pd/Al <sub>2</sub> O <sub>3</sub>	46.2	409.4	653.1
Pt/Mg/Al <sub>2</sub> O <sub>3</sub>	48.8	487.8	689.7
Pd/Mg/Al <sub>2</sub> O <sub>3</sub>	24	351.2	694.7
Pt/Pd/Mg/Al <sub>2</sub> O <sub>3</sub>	50.7	508.3	713.8
Pt/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	62.8	482.5	714.6
Pd/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	57.7	475.3	674.3
Pt/Pd/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	61.3	506	701.7

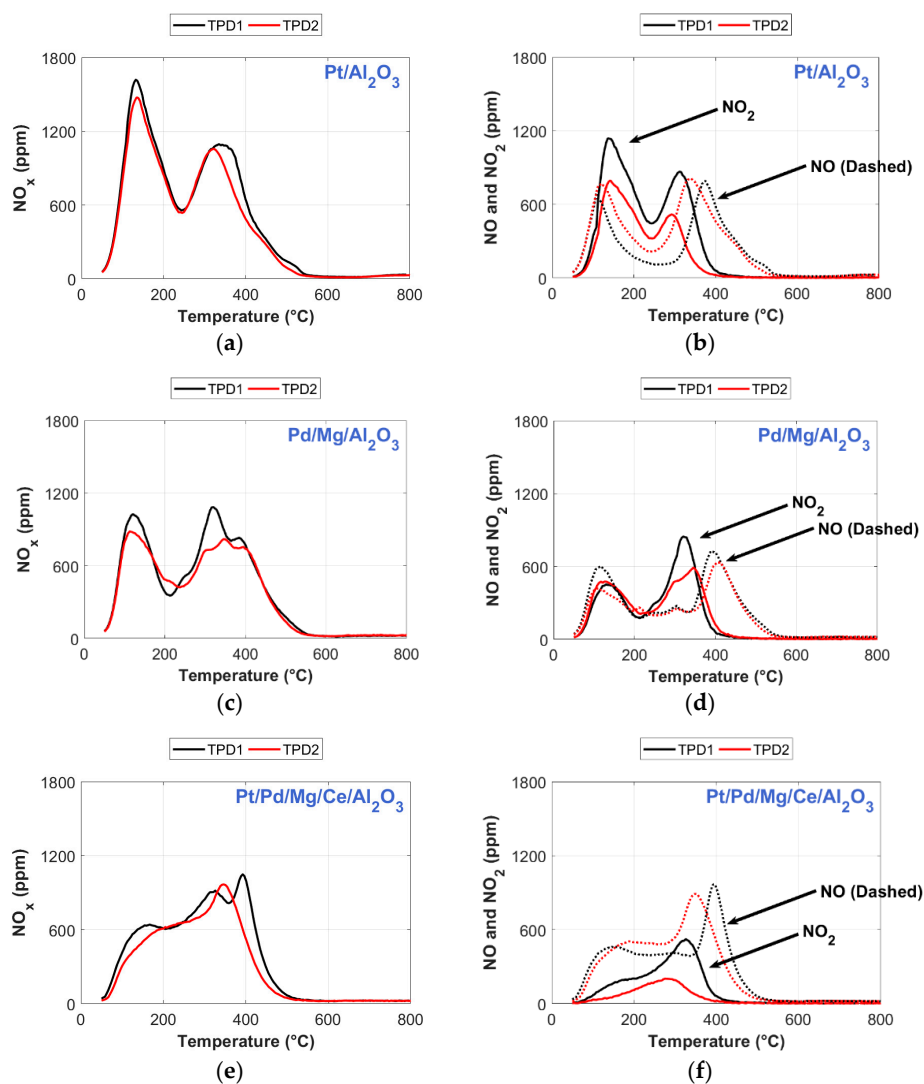


**Figure 8.** H<sub>2</sub> consumption for all samples during H<sub>2</sub>-TPR experiment in a flow of 1600 ppm of H<sub>2</sub> with a ramp rate of 5 °C/min.

#### 2.4. Temperature Programmed Desorption (TPD) after Sulfur Regeneration

In order to evaluate the effectiveness of H<sub>2</sub>-TPR in removing sulfur species and recovering the catalytic activity, a subsequent NO<sub>2</sub>-TPD experiment (TPD2) was carried out and compared with previous NO<sub>2</sub>-TPD test (TPD1, before SO<sub>2</sub> poisoning). The samples were exposed to the same experimental procedure as in TPD1. A quantitative analysis of the amount of NO<sub>x</sub> adsorbed and released during TPD1 and TPD2 experiments is reported in Table 3. Figure 9 compares TPD1 and TPD2 spectra for Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Mg/Al<sub>2</sub>O<sub>3</sub>, and Pt/Pd/Mg/Al<sub>2</sub>O<sub>3</sub> samples during the desorption step. The amount of the total NO<sub>x</sub> released was decreased after sulfation, ranging the reduction between

6% and 15%. This can be particularly observed for Ce containing catalysts probably because of the large formation of very stable bulk sulfates during the SO<sub>2</sub> exposure (according to DRIFTS spectra). Therefore, these results indicate that sulfur removal was not completely achieved during the H<sub>2</sub>-TPR test. In fact, some SO<sub>2</sub> were desorbed during the temperature ramping of the TPD2 experiment, whereas a small amount of SO<sub>2</sub> was also released during the NO<sub>2</sub> exposure, implying that sulfates were probably replaced by nitrates (see Supplementary Information; see Figure S1). The remaining sulfur probably then affected the NO<sub>x</sub> desorption performance by deactivating sites in proximity to the interface between the precious metal and Al<sub>2</sub>O<sub>3</sub> support [39,49,55]. Moreover, most of the NO<sub>x</sub> stored was desorbed as NO for all samples during TPD2, which substantially increased compared to TPD1 (except for Pd/Mg/Al<sub>2</sub>O<sub>3</sub>; see Table 3). This is probably because of the increase in the Pt-NO formation during NO<sub>2</sub> exposure by the oxidation of the accumulated sulfur species on the precious species [5], as presented below:



**Figure 9.** TPD spectra for Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Mg/Al<sub>2</sub>O<sub>3</sub> and Pt/Pd/Mg/Al<sub>2</sub>O<sub>3</sub> samples. The total NO<sub>x</sub> release profile is shown on the left, while the NO<sub>2</sub> and NO release profiles are shown on the right for same group of samples. The experiments were performed before (TPD1) and after (TPD2) SO<sub>2</sub> poisoning. (a,c,e) show the total NO<sub>x</sub> profiles (TPD1 and TPD2), and (b,d,f) show the NO and NO<sub>2</sub> profiles (TPD1 and TPD2) for Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Mg/Al<sub>2</sub>O<sub>3</sub> and Pt/Pd/Mg/Ce/Al<sub>2</sub>O<sub>3</sub> samples, respectively.

**Table 3.** Total NO<sub>x</sub> adsorbed (NO<sub>x</sub> Ads), and NO/NO<sub>2</sub> desorbed during temperature programmed desorption experiments performed before (TPD1) and after (TPD2) SO<sub>2</sub> poisoning. Note that TPD2 was performed after the temperature programmed reduction experiment.

Sample	TPD1			TPD2		
	NO <sub>x</sub> Ads (μmol)	NO Des. (μmol)	NO <sub>2</sub> Des. (μmol)	NO <sub>x</sub> Ads (μmol)	NO Des. (μmol)	NO <sub>2</sub> Des. (μmol)
Pt/Al <sub>2</sub> O <sub>3</sub>	37.3	13.8	18.2	35.7	17.4	11.3
Pd/Al <sub>2</sub> O <sub>3</sub>	38.9	15.6	18.1	37.4	17.5	13.1
Pt/Pd/Al <sub>2</sub> O <sub>3</sub>	37.2	11.9	20.8	36	16.1	13.9
Pt/Mg/Al <sub>2</sub> O <sub>3</sub>	35.3	15.4	11.5	34.4	16.9	7.7
Pd/Mg/Al <sub>2</sub> O <sub>3</sub>	34.5	15	11.5	34.1	13	11.1
Pt/Pd/Mg/Al <sub>2</sub> O <sub>3</sub>	37.1	17.3	10	36.8	18.8	6.9
Pt/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	35.5	16.6	9.4	36.7	17.9	4.2
Pd/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	35.8	16.8	8.7	37.2	17.5	4.1
Pt/Pd/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	36	17	7.5	37	17.6	3

### 2.5. Interpretation of the Sulfur Poisoning and Regeneration Results

An outstanding performance of Pd/Mg/Al<sub>2</sub>O<sub>3</sub> model catalyst was clearly observed throughout this work. Its promising features include the ability to release most of the stored NO<sub>x</sub> at reasonable temperature, the ability to release the sulfur trapped at relatively low temperatures (T<sub>90</sub> < 700 °C), and an efficient sulfur removal with low H<sub>2</sub> consumption. After the temperature programmed regeneration procedure performed, the remaining sulfur on Pd/Mg/Al<sub>2</sub>O<sub>3</sub> barely impacted the NO<sub>x</sub> storage stability characteristics. In contrast, ceria-containing catalysts required higher temperatures for sulfur removal compared to other samples, probably caused by a large formation of very stable bulk sulfates during SO<sub>2</sub> poisoning procedure, as reported from DRIFTS measurements. Bounechada et al. [32] indeed suggested that the high dynamic oxygen storage capacity (OSC) of ceria-containing materials leads to the diffusion of surface sulfates into the bulk, blocking some pores and inhibiting the access to active sites. Meanwhile, the remaining sulfur species on Ce-containing catalysts certainly affected the NO<sub>x</sub> stored stability by reducing the amount of NO<sub>x</sub> released after sulfation.

Even though the experiments did not demonstrate a strong effect of the precious metal nature on the stability of the NO<sub>x</sub> stored, they certainly played an important role in the sulfur poisoning and regeneration characteristics. We found that the addition of platinum on the LNT formulation facilitates the SO<sub>2</sub> adsorption with the formation of bulk and surface sulfate species. As discussed above, the sulfur species formed on Pt sites might quickly spill over to neighboring Al<sub>2</sub>O<sub>3</sub> sites, resulting in surface aluminum sulfate formation. The resultant increase in surface aluminum sulfate might, therefore, promote the formation of very stable bulk sulfate species, observed on the DRIFTS measurements. In contrast, monometallic Pd-based catalysts barely exhibited bulk sulfate species probably because of the formation of PdO-SO<sub>3</sub> complexes, limiting the overall catalyst activity. Likewise, monometallic Pd-based catalysts exhibited better sulfur regeneration capabilities compared to other model samples tested (see Figure 8), mostly characterized by a reduced reductant consumption and lower regeneration temperatures. This is probably because Pd makes the formed sulfur species weaker compared to Pt containing samples because of the poor oxidizing capabilities of Pd. Meanwhile, bimetallic samples showed similar characteristics as the monometallic Pt-based catalysts, nevertheless more stable sulfur species were formed for Pt-Pd samples investigated. This catalytic behavior of the bimetallic samples can be attributed to the presence of electron-deficient Pt species isolated on the Pd surface [56]. These species have been reported for Pt-highly-loaded bimetallic samples (Pt > 75%) [57]. Therefore, the electron donor character of the reductant (H<sub>2</sub>) might weaken the affinity between the Pt clusters and the reductant, resulting in a modification of the overall apparent activation energy [56].

### 3. Experimental

#### 3.1. Catalyst Preparation

Nine different model catalysts were prepared using the incipient wetness impregnation method of commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Sasol, Puralox SBA200, Brunsbüttel, Germany) and 20 wt% Ce-doped Al<sub>2</sub>O<sub>3</sub> (Sasol, Puralox SCFa-160/Ce20, Brunsbüttel, Germany), both thermally treated in air at 750 °C for 4 h to remove impurities and stabilize the structure prior to impregnation. A full list of the catalysts prepared as well as their formulations is found in Table 4. All catalysts contained the same total number of precious metal (PGM) moles equivalent to 2 wt% Pt. Pt and Pd were first impregnated onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ce-doped Al<sub>2</sub>O<sub>3</sub> powders using a solution of Pt(NO<sub>3</sub>)<sub>2</sub> (Heraeus GmbH, 14.93 wt% Pt, Hanau, Germany) and Pd(NO<sub>3</sub>)<sub>2</sub> (Heraeus GmbH, 16.37 wt% Pd, Hanau, Germany), respectively. Samples were subsequently dried at 100 °C in air overnight and then calcined at 550 °C for 2 h.

**Table 4.** Component contributions by mass percent for the three groups of samples prepared: precious metals-alumina (PGM-Al<sub>2</sub>O<sub>3</sub>), magnesium-alumina (Mg-Al<sub>2</sub>O<sub>3</sub>), and magnesium-ceria- alumina (Mg-Ce-Al<sub>2</sub>O<sub>3</sub>).

Group	Sample	Pt	Pd	Al <sub>2</sub> O <sub>3</sub>	Mg	CeO <sub>2</sub>
PGM-Al <sub>2</sub> O <sub>3</sub>	Pt/Al <sub>2</sub> O <sub>3</sub>	2	-	98	-	-
	Pd/Al <sub>2</sub> O <sub>3</sub>	-	1.09	98.9	-	-
	Pt/Pd/Al <sub>2</sub> O <sub>3</sub>	1.6	0.2	98.2	-	-
Mg-Al <sub>2</sub> O <sub>3</sub>	Pt/Mg/Al <sub>2</sub> O <sub>3</sub>	2	-	88	10	-
	Pd/Mg/Al <sub>2</sub> O <sub>3</sub>	-	1.09	88.9	10	-
	Pt/Pd/Mg/Al <sub>2</sub> O <sub>3</sub>	1.6	0.2	88.2	10	-
Mg-Ce-Al <sub>2</sub> O <sub>3</sub>	Pt/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2	-	68	10	20
	Pd/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	-	1.09	68.9	10	20
	Pt/Pd/Mg/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.6	0.2	68.2	10	20

Bimetallic samples were prepared by sequential wet impregnation of Pt and Pd based on a commercial LNT catalyst with a Pt/Pd ratio of 80% Pt and 20% Pd [2]. First, 1.6 wt% Pt/Al<sub>2</sub>O<sub>3</sub> was prepared as described above in the case of monometallic samples. After calcination at 550 °C for 2 h, a solution containing the palladium precursor was prepared and added drop-wise to the catalyst powder. The catalyst was subsequently dried and calcined at 550 °C for 2 h.

Catalysts containing 10 wt% Mg were then prepared by a dilution of C<sub>4</sub>H<sub>6</sub>MgO<sub>4</sub>·4H<sub>2</sub>O (Sigma-Aldrich, St. Louis, MO, USA) in milliQ water. The precursor solution was added drop-wise to PGM/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and PGM/Ce-Al<sub>2</sub>O<sub>3</sub> slurries followed by drying in air overnight at 100 °C and calcining at 550 °C for 2 h.

#### 3.2. Catalytic Evaluation Experiments

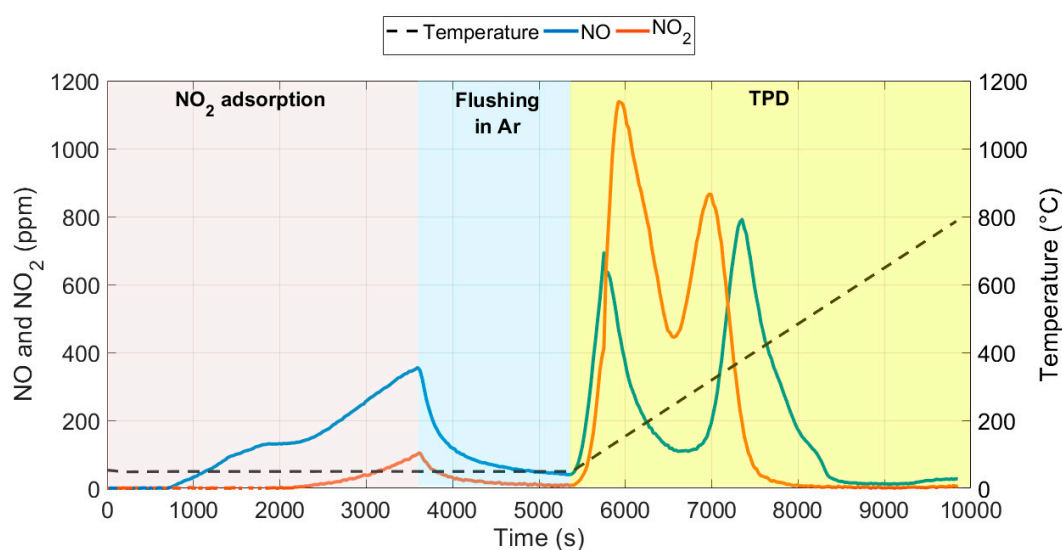
The catalytic evaluation experiments were conducted in a vertical quartz tube mounted in an electric furnace as a part of Setaram Sensys DSC instrument (Digital Scanning Calorimeter, Caluire, France). The catalyst powder (~70 mg) was placed inside the tube on a porous quartz bed. A flow of 20 mL/min was sent into the catalyst-containing tube and the gases were taken from a larger gas flow to enhance the transient response of the system. Multiple mass flow controllers (Bronkhorst Hi-Tech Low- $\Delta$ P Flow, Ruurlo, Netherlands) were employed to control the inlet gas composition, whereas the outlet gas composition was analyzed with a Hiden HPR-20QUI mass spectrometer (MS): NO (m/z = 30), NO<sub>2</sub> (m/z = 46), H<sub>2</sub> (m/z = 2), O<sub>2</sub> (m/z = 32), SO<sub>2</sub> (m/z = 64), and Ar (m/z = 20). The NO–NO<sub>2</sub> spectral interference was considered for the data analysis. Calibration curves were collected before each experiment for the quantitative analysis using diluted gaseous mixtures. All experiments were carried out in nearly isothermal conditions at atmospheric pressure with Ar balance. Prior to testing, all samples were pre-treated at 500 °C for 1 h in a flow containing 2% H<sub>2</sub>. The experimental campaign consisted of NO<sub>2</sub>-temperature programmed desorption and H<sub>2</sub>-temperature programmed reduction



experiments, which are described in detail below. It is important to remark that the experimental campaign was conducted in the absence of CO<sub>2</sub> and water. It is well known that the presence of H<sub>2</sub>O and CO<sub>2</sub> in the exhaust stream have an effect on the catalyst surface and consequently on the reaction chemistry. We have used these conditions in order to facilitate the comparison between NO<sub>x</sub> and SO<sub>x</sub> interactions.

### 3.2.1. NO<sub>2</sub>-TPD Experiments

NO<sub>2</sub> temperature programmed desorption (NO<sub>2</sub>-TPD) experiments were carried out to compare the thermal stability of NO<sub>x</sub> stored species among the catalysts prepared. The samples were first exposed to 900 ppm NO<sub>2</sub> for 1 h at 50 °C and then flushed in Ar for 30 min. The temperature was subsequently increased to 800 °C with a ramp rate of 10 °C/min in Ar. The experimental procedure is also illustrated in Figure 10 for Pt/Al<sub>2</sub>O<sub>3</sub>.



**Figure 10.** Reaction protocol for TPD experiment for Pt/Al<sub>2</sub>O<sub>3</sub>.

Same experimental procedure was repeated over all samples after SO<sub>2</sub> poisoning and H<sub>2</sub>-TPR experiments (described below) in order to evaluate the effectiveness of H<sub>2</sub>-TPR in removing sulfur species and recovering the catalytic activity by comparing both NO<sub>2</sub>-TPD results.

### 3.2.2. SO<sub>2</sub> Poisoning and H<sub>2</sub>-TPR Experiments

Hydrogen temperature programmed reduction experiments were conducted over the model catalysts in order to examine the stability of sulfur species stored during a SO<sub>2</sub> poisoning procedure. The samples were first subjected to 50 ppm SO<sub>2</sub> and 3% O<sub>2</sub> for 8 h at 200 °C. The temperature was then decreased to 50 °C in presence of Ar. Thereafter, a flow containing 1600 ppm of H<sub>2</sub> was introduced for 1 h at 50 °C, followed by increasing the temperature to 800 °C with a ramp rate of 5 °C/min in presence of H<sub>2</sub>. The temperature was subsequently maintained constant at 800 °C for 30 min in 1600 ppm of H<sub>2</sub>.

### 3.3. DRIFT Spectroscopy

In situ FTIR spectroscopy experiments were conducted in diffusive reflectance mode (DRIFTS) to follow the evolution of surface species during SO<sub>2</sub> poisoning. The experiment set-up consisted of a BRUKER Vertex 70 spectrometer (Billerica, MA, USA) equipped with a Harrick Praying Mantis DR stainless steel reaction cell and a nitrogen-cooled MCT detector. The reaction cell contains a sample cup with a porous grid, where approximately 70 mg of catalysts powder was placed. The sample was then covered by a dome equipped with two ZnSe windows. The feed gases were flown through the sample via separate mass flow controllers (Bronkhorst Hi-Tech Low- ΔP Flow, Ruurlo, Netherlands),

providing a total gas flow of 100 mL/min for all experiments. All samples were pretreated in 1% H<sub>2</sub> at 500 °C for 1 h and then exposed to 3% O<sub>2</sub> for 10 min. Thereafter, the temperature was reduced to 200 °C in Ar flow and a background spectrum was collected. The feed gas was then switched to 50 ppm SO<sub>2</sub> and 3% O<sub>2</sub> for 2 h at 200 °C. During this time, infrared spectra were acquired every 60 s between 650 and 4000 cm<sup>-1</sup> with a spectral resolution of 2 cm<sup>-1</sup>.

The evolution and stability of sulfur species were then evaluated for Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/Mg/Al<sub>2</sub>O<sub>3</sub>, and Pt/Mg/Ce/Al<sub>2</sub>O<sub>3</sub> samples during a temperature ramp. Immediately after SO<sub>2</sub> poisoning, the temperature was raised from 200 °C to 550 °C at a rate of 20 °C/min in a feed containing 50 ppm of SO<sub>2</sub> and 8% O<sub>2</sub>. DRIFTS spectra were collected every 60 s during the temperature ramp, and then subtracted to the background spectrum collected before SO<sub>2</sub> poisoning at 200 °C.

#### 4. Conclusions

A comparable investigation among nine different LNT model catalysts were performed with the purpose of studying the sulfur poisoning and regeneration characteristics on modern LNT components. The model samples consisted of three compounds: (i) Al<sub>2</sub>O<sub>3</sub>, (ii) Mg/Al<sub>2</sub>O<sub>3</sub>, and (iii) Mg/Ce/Al<sub>2</sub>O<sub>3</sub> mixed with Pt, Pd, and Pt-Pd. Temperature programmed reaction and DRIFTS spectroscopy results showed that palladium and magnesium are key components in the development of modern LNT catalysts. They provide appropriate NO<sub>x</sub> release temperature range, outstanding regeneration capabilities, and low reductant consumption. This was especially evident for Pd/Mg/Al<sub>2</sub>O<sub>3</sub> sample, which presented an excellent performance during the testing campaign performed. However, monometallic Pd-based catalysts exhibited the formation of surface palladium sulfate species during SO<sub>2</sub> exposure, which might limit the catalytic performance of the catalyst. Alternatively, it was therefore suggested that Pt-Pd bimetallic formulations could provide some improvements of the catalytic behavior of monometallic Pd catalysts since the formation of surface palladium sulfate was not observed during SO<sub>2</sub> exposure. However, the higher stability of sulfur species was observed for the bimetallic samples investigated. Furthermore, it was found that the addition of ceria into LNT formulations leads to the increased formation of bulk sulfate species. This is probably because of the high dynamic oxygen storage capacity property of ceria-containing materials which results in the diffusion of surface sulfates into the bulk.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/9/6/492/s1>, Figure S1: SO<sub>2</sub> desorption profile during TPD2 for Pt/Al<sub>2</sub>O<sub>3</sub>.

**Author Contributions:** Conceptualization, J.E.D.A.G., A.K. and L.O.; Methodology, J.E.D.A.G. and L.O.; Data Acquisition, J.E.D.A.G.; Data Analysis, J.E.D.A.G. and L.O.; Writing—original draft, J.E.D.A.G.; Writing—Review & Editing, J.E.D.A.G., A.K. and L.O.; and Supervision, A.K. and L.O.

**Acknowledgments:** This study is a collaboration between Volvo Car Corporation and Competence Centre for Catalysis at Chalmers University of Technology. We gratefully acknowledge the financial support from Volvo Car Corporation and the Swedish Foundation for Strategic Research (ID15-0030).

**Conflicts of Interest:** The authors declare no conflict of interest.

#### Appendix A

The reduction reactions that involved hydrogen consumption are reported below:



where *M* denotes metal oxides as SO<sub>x</sub> absorbents. Likewise, the reduction reaction for the precious metals is:



## References

1. Ottinger, N.A.; Toops, T.J.; Pihl, J.A.; Roop, J.T.; Choi, J.-S.; Partridge, W.P. Sulfate storage and stability on representative commercial lean NO<sub>x</sub> trap components. *Appl. Catal. B Environ.* **2012**, *117–118*, 167–176. [[CrossRef](#)]
2. De Abreu Goes, J.E.; Olsson, L.; Berggrund, M.; Kristoffersson, A.; Gustafson, L.; Hicks, M. Performance Studies and Correlation between Vehicle- and Rapid-Aged Commercial Lean NO<sub>x</sub> Trap Catalysts. *SAE Int. J. Engines* **2017**, *10*, 1613–1626. [[CrossRef](#)]
3. Johnson, T.; Joshi, A. Review of Vehicle Engine Efficiency and Emissions. *SAE Int. J. Engines* **2018**, *11*, 1307–1330. [[CrossRef](#)]
4. Choi, J.-S.; Partridge, W.P.; Pihl, J.A.; Daw, C.S. Sulfur and temperature effects on the spatial distribution of reactions inside a lean NO<sub>x</sub> trap and resulting changes in global performance. *Catal. Today* **2008**, *136*, 173–182. [[CrossRef](#)]
5. Dawody, J.; Skoglundh, M.; Olsson, L.; Fridell, E. Kinetic modelling of sulfur deactivation of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> and BaO/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage catalysts. *Appl. Catal. B Environ.* **2007**, *70*, 179–188. [[CrossRef](#)]
6. Liu, Y.; He, H.; Xu, W.; Yu, Y. Mechanism of Heterogeneous Reaction of Carbonyl Sulfide on Magnesium Oxide. *The J. Phys. Chem. A* **2007**, *111*, 4333–4339. [[CrossRef](#)] [[PubMed](#)]
7. Rohr, F.; Göbel, U.; Kattwinkel, P.; Kreuzer, T.; Müller, W.; Philipp, S.; Gélin, P. New insight into the interaction of sulfur with diesel NO<sub>x</sub> storage catalysts. *Appl. Catal. B Environ.* **2007**, *70*, 189–197. [[CrossRef](#)]
8. Lafossas, F.-A.; Manetas, C.; Mohammadi, A.; Kalogirou, M.; Koltsakis, G.; Samaras, Z.; Iida, M.; Inoue, M. Sulfation and Lean/Rich Desulfation of a NO<sub>x</sub> storage Reduction Catalyst: Experimental and Simulation Study. *Int. J. Engine Res.* **2015**, *16*, 197–212. [[CrossRef](#)]
9. Hadl, K.; Ratzberger, R.; Eichlseder, H.; Schuessler, M.; Linares, W.; Pucher, H. Sulfur Poisoning of a NO<sub>x</sub> Storage Catalyst—A Comprehensive Modelling Approach. *SAE Int. J. Engines* **2016**. [[CrossRef](#)]
10. Olsson, L.; Blint, R.J.; Fridell, E. Global Kinetic Model for Lean NO<sub>x</sub> Traps. *Ind. Eng. Chem. Res.* **2005**, *44*, 3021–3032. [[CrossRef](#)]
11. AL-Harbi, M.; Epling, W.S. Investigating the Effect of NO Versus NO<sub>2</sub> on the Performance of a Model NO<sub>x</sub> Storage/Reduction Catalyst. *Catal. Lett.* **2009**, *130*, 121–129. [[CrossRef](#)]
12. Benramdhane, S.; Millet, C.-N.; Jeudy, E.; Lavy, J.; Blasin-Aubé, V.; Daturi, M. Diesel Lean NO<sub>x</sub>-Trap Thermal Aging and Performance Evolution Characterization. *Oil Gas Sci. Technol. Rev. IFP Energies nouvelles* **2011**, *66*, 845–853. [[CrossRef](#)]
13. Rohr, F.; Peter, S.D.; Lox, E.; Kögel, M.; Sassi, A.; Juste, L.; Rigaudeau, C.; Belot, G.; Gélin, P.; Primet, M. On the Mechanism of Sulphur Poisoning and Regeneration of a Commercial Gasoline NO<sub>x</sub>-Storage Catalyst. *Appl. Catal. B Environ.* **2005**, *56*, 201–212. [[CrossRef](#)]
14. Ji, Y.; Toops, T.J.; Crocker, M. Effect of Ceria on the Sulfation and Desulfation Characteristics of a Model Lean NO<sub>x</sub> Trap Catalyst. *Catal. Lett.* **2009**, *127*, 55–62. [[CrossRef](#)]
15. Easterling, V.; Ji, Y.; Crocker, M.; Ura, J.; Theis, J.R.; McCabe, R.W. Effect of ceria on the desulfation characteristics of model lean NO<sub>x</sub> trap catalysts. *Catal. Today* **2010**, *151*, 338–346. [[CrossRef](#)]
16. Choi, J.-S.; Partridge, W.P.; Lance, M.J.; Walker, L.R.; Pihl, J.A.; Toops, T.J.; Finney, C.E.A.; Daw, C.S. Nature and Spatial Distribution of Sulfur Species in a Sulfated Barium-Based Commercial Lean NO<sub>x</sub> Trap Catalyst. *Catal. Today* **2010**, *151*, 354–361. [[CrossRef](#)]
17. Basile, F.; Fornasari, G.; Gambatesa, A.; Livi, M.; Vaccari, A. Reactivity of Mg-Ba catalyst in NO<sub>x</sub> storage/reduction. *Catal. Today* **2007**, *119*, 59–63. [[CrossRef](#)]
18. Jeong, S.; Youn, S.; Kim, D.H. Effect of Mg/Al ratios on the NO<sub>x</sub> storage activity over Pt-BaO/Mg–Al mixed oxides. *Catal. Today* **2014**, *231*, 155–163. [[CrossRef](#)]
19. Luo, J.; Gao, F.; Karim, A.M.; Xu, P.; Browning, N.D.; Peden, C.H.F. Advantages of MgAlO<sub>x</sub> over γ-Al<sub>2</sub>O<sub>3</sub> as a Support Material for Potassium-Based High-Temperature Lean NO<sub>x</sub> Traps. *ACS Catal.* **2015**, *5*, 4680–4689. [[CrossRef](#)]
20. Nova, I.; Castoldi, L.; Prinetto, F.; Dal Santo, V.; Lietti, L.; Tronconi, E.; Forzatti, P.; Ghiotti, G.; Psaro, R.; Recchia, S. NO<sub>x</sub> Adsorption Study over Pt–Ba/Alumina Catalysts: FT-IR and Reactivity Study. *Top. Catal.* **2004**, *30*, 181–186. [[CrossRef](#)]
21. Scotti, A.; Nova, I.; Tronconi, E.; Castoldi, L.; Lietti, L.; Forzatti, P. Kinetic Study of Lean NO<sub>x</sub> Storage over the Pt–Ba/Al<sub>2</sub>O<sub>3</sub> System. *Ind. Eng. Chem. Res.* **2004**, *43*, 4522–4534. [[CrossRef](#)]

22. Forzatti, P.; Castoldi, L.; Lietti, L.; Nova, I.; Tronconi, E. Chapter 6 Identification of the reaction networks of the NO<sub>x</sub> storage/reduction in lean NO<sub>x</sub> trap systems. In *Studies in Surface Science and Catalysis*; Granger, P., Párvulescu, V.I., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Volume 171, pp. 175–208.
23. Lietti, L.; Daturi, M.; Blasin-Aubé, V.; Ghiotti, G.; Prinetto, F.; Forzatti, P. Relevance of the Nitrite Route in the NO<sub>x</sub> Adsorption Mechanism over Pt–Ba/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> Storage Reduction Catalysts Investigated by using Operando FTIR Spectroscopy. *ChemCatChem* **2012**, *4*, 55–58. [[CrossRef](#)]
24. Prinetto, F.; Ghiotti, G.; Nova, I.; Lietti, L.; Tronconi, E.; Forzatti, P. FT-IR and TPD Investigation of the NO<sub>x</sub> Storage Properties of BaO/Al<sub>2</sub>O<sub>3</sub> and Pt–BaO/Al<sub>2</sub>O<sub>3</sub> Catalysts. *J. Phys. Chem. B* **2001**, *105*, 12732–12745. [[CrossRef](#)]
25. Lindholm, A.; Currier, N.W.; Dawody, J.; Hidayat, A.; Li, J.; Yezerets, A.; Olsson, L. The influence of the preparation procedure on the storage and regeneration behavior of Pt and Ba based NO<sub>x</sub> storage and reduction catalysts. *Appl. Catal. B Environ.* **2009**, *88*, 240–248. [[CrossRef](#)]
26. Svedberg, P.; Jobson, E.; Erkkfeldt, S.; Andersson, B.; Larsson, M.; Skoglundh, M. Influence of the storage material on the storage of NO<sub>x</sub> at low temperatures. *Top. Catal.* **2004**, *30*, 199–206. [[CrossRef](#)]
27. De Abreu Goes, J.; Kristoffersson, A.; Wentworth, T.; Olsson, L. Detailed Characterization Studies of Vehicle and Rapid Aged Commercial Lean NO<sub>x</sub> Trap Catalysts. *Ind. Eng. Chem. Res.* **2018**. [[CrossRef](#)]
28. Uy, D.; Wiegand, K.A.; O'Neill, A.E.; Dearth, M.A.; Weber, W.H. In Situ UV Raman Study of the NO<sub>x</sub> Trapping and Sulfur Poisoning Behavior of Pt/Ba/γ-Al<sub>2</sub>O<sub>3</sub> Catalysts. *J. Phys. Chem. B* **2002**, *106*, 387–394. [[CrossRef](#)]
29. Abdulhamid, H.; Fridell, E.; Dawody, J.; Skoglundh, M. In situ FTIR study of SO<sub>2</sub> interaction with Pt/BaCO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage catalysts under lean and rich conditions. *J. Catal.* **2006**, *241*, 200–210. [[CrossRef](#)]
30. Waqif, M.; Saur, O.; Lavalley, J.C.; Perathoner, S.; Centi, G. Nature and mechanism of formation of sulfate species on copper/alumina sorbent-catalysts for sulfur dioxide removal. *J. Phys. Chem.* **1991**, *95*, 4051–4058. [[CrossRef](#)]
31. Xie, S.X.; Yu, Y.B.; Wang, J.; He, H. Effect Of SO<sub>2</sub> on the performance of Ag-Pd/Al<sub>2</sub>O<sub>3</sub> for the selective catalytic reduction of NO<sub>x</sub> with C<sub>2</sub>H<sub>5</sub>OH. *J. Environ. Sci.* **2006**, *18*, 973–978. [[CrossRef](#)]
32. Bounechada, D.; Fouladvand, S.; Kylhammar, L.; Pingel, T.; Olsson, E.; Skoglundh, M.; Gustafson, J.; Di Michiel, M.; Newton, M.A.; Carlsson, P.-A. Mechanisms behind sulfur promoted oxidation of methane. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8648–8661. [[CrossRef](#)] [[PubMed](#)]
33. Mitchell, M.B.; Sheinker, V.N.; White, M.G. Adsorption and Reaction of Sulfur Dioxide on Alumina and Sodium-Impregnated Alumina. *J. Phys. Chem.* **1996**, *100*, 7550–7557. [[CrossRef](#)]
34. Wilburn, M.S.; Epling, W.S. SO<sub>2</sub> adsorption and desorption characteristics of bimetallic Pd-Pt catalysts: Pd:Pt ratio dependency. *Catal. Today* **2017**. [[CrossRef](#)]
35. Li, Y.; Shen, M.; Wang, J.; Wan, T.; Wang, J. Influence of sulfation and regeneration on Pt/Al<sub>2</sub>O<sub>3</sub> for NO oxidation. *Catal. Sci. Technol.* **2015**, *5*, 1731–1740. [[CrossRef](#)]
36. Mowery, D.L.; McCormick, R.L. Deactivation of alumina supported and unsupported PdO methane oxidation catalyst: the effect of water on sulfate poisoning. *Appl. Catal. B Environ.* **2001**, *34*, 287–297. [[CrossRef](#)]
37. Yu, T.-C.; Shaw, H. The effect of sulfur poisoning on methane oxidation over palladium supported on γ-alumina catalysts. *Appl. Catal. B Environ.* **1998**, *18*, 105–114. [[CrossRef](#)]
38. Colussi, S.; Arosio, F.; Montanari, T.; Busca, G.; Groppi, G.; Trovarelli, A. Study of sulfur poisoning on Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> methane combustion catalysts. *Catal. Today* **2010**, *155*, 59–65. [[CrossRef](#)]
39. Wilburn, M.S.; Epling, W.S. Sulfur deactivation and regeneration of mono- and bimetallic Pd-Pt methane oxidation catalysts. *Appl. Catal. B Environ.* **2017**, *206*, 589–598. [[CrossRef](#)]
40. Lampert, J.K.; Kazi, M.S.; Farrauto, R.J. Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles. *Appl. Catal. B Environ.* **1997**, *14*, 211–223. [[CrossRef](#)]
41. Ohtsuka, H. The selective catalytic reduction of nitrogen oxides by methane on noble metal-loaded sulfated zirconia. *Appl. Catal. B Environ.* **2001**, *33*, 325–333. [[CrossRef](#)]
42. Gélin, P.; Primet, M. Complete oxidation of methane at low temperature over noble metal based catalysts: A review. *Appl. Catal. B Environ.* **2002**, *39*, 1–37. [[CrossRef](#)]
43. Lapisardi, G.; Gélin, P.; Kaddouri, A.; Garbowski, E.; Da Costa, S. Pt–Pd bimetallic catalysts for methane emissions abatement. *Top. Catal.* **2007**, *42*, 461–464. [[CrossRef](#)]
44. Sadokhina, N.; Smedler, G.; Nylén, U.; Olofsson, M.; Olsson, L. Deceleration of SO<sub>2</sub> poisoning on PtPd/Al<sub>2</sub>O<sub>3</sub> catalyst during complete methane oxidation. *Appl. Catal. B Environ.* **2018**, *236*, 384–395. [[CrossRef](#)]

45. Knözinger, H.; Ratnasamy, P. Catalytic Aluminas: Surface Models and Characterization of Surface Sites. *Catal. Rev.* **1978**, *17*, 31–70. [[CrossRef](#)]
46. Hamzehlouyan, T.; Sampara, C.S.; Li, J.; Kumar, A.; Epling, W.S. Kinetic study of adsorption and desorption of SO<sub>2</sub> over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. *Appl. Catal. B Environ.* **2016**, *181*, 587–598. [[CrossRef](#)]
47. Wang, J.-A.; Li, C.-L. SO<sub>2</sub> adsorption and thermal stability and reducibility of sulfates formed on the magnesium–aluminate spinel sulfur-transfer catalyst. *Appl. Surf. Sci.* **2000**, *161*, 406–416. [[CrossRef](#)]
48. Schneider, W.F.; Li, J.; Hass, K.C. Combined Computational and Experimental Investigation of SO<sub>x</sub> Adsorption on MgO. *J. Phys. Chem. B* **2001**, *105*, 6972–6979. [[CrossRef](#)]
49. Kylhammar, L.; Carlsson, P.-A.; Skoglundh, M. Sulfur promoted low-temperature oxidation of methane over ceria supported platinum catalysts. *J. Catal.* **2011**, *284*, 50–59. [[CrossRef](#)]
50. Kylhammar, L.; Carlsson, P.-A.; Ingelsten, H.H.; Grönbeck, H.; Skoglundh, M. Regenerable ceria-based SO<sub>x</sub> traps for sulfur removal in lean exhausts. *Appl. Catal. B Environ.* **2008**, *84*, 268–276. [[CrossRef](#)]
51. Li, J.; Theis, J.; Chun, W.; Goralski, C.; Kudla, R.; Ura, J.; Watkins, W.; Chattha, M.; Hurley, R. Sulfur Poisoning and Desulfation of the Lean NO<sub>x</sub> Trap. *SAE Tech. Pap.* **2001**. [[CrossRef](#)]
52. Boaro, M.; de Leitenburg, C.; Dolcetti, G.; Trovarelli, A.; Graziani, M. Oxygen Storage Behavior of Ceria–Zirconia-Based Catalysts in the Presence of SO<sub>2</sub>. *Top. Catal.* **2001**, *16*, 299–306. [[CrossRef](#)]
53. Hamzehlouyan, T.; Sampara, C.; Li, J.; Kumar, A.; Epling, W. Sulfur Poisoning of a Pt/Al<sub>2</sub>O<sub>3</sub> Oxidation Catalyst: Understanding of SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> Impacts. *Top. Catal.* **2016**, *59*, 1028–1032. [[CrossRef](#)]
54. Jeong, S.; Kim, D.H. Sulfation and Desulfation Behavior of Pt-BaO/MgO-Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> Storage Reduction Catalyst. *J. Nanosci. Nanotechnol.* **2016**, *16*, 4411–4416. [[CrossRef](#)] [[PubMed](#)]
55. Epling, W.S.; Campbell, L.E.; Yezerets, A.; Currier, N.W.; Parks, J.E. Overview of the Fundamental Reactions and Degradation Mechanisms of NO<sub>x</sub> Storage/Reduction Catalysts. *Catal. Rev.* **2004**, *46*, 163–245. [[CrossRef](#)]
56. Navarro, R.M.; Pawelec, B.; Trejo, J.M.; Mariscal, R.; Fierro, J.L.G. Hydrogenation of Aromatics on Sulfur-Resistant PtPd Bimetallic Catalysts. *J. Catal.* **2000**, *189*, 184–194. [[CrossRef](#)]
57. Rades, T.; Pak, C.; Polisset-Thfoin, M.; Ryoo, R.; Fraissard, J. Characterization of bimetallic NaY-supported Pt-Pd catalyst by EXAFS, TEM and TPR. *Catal. Lett.* **1994**, *29*, 91–103. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).