NO\textsubscript{x}-Assisted Soot Oxidation on Pt–Mg/Al\textsubscript{2}O\textsubscript{3} Catalysts: Magnesium Precursor, Pt Particle Size, and Pt–Mg Interaction

Liu Shuang, Wu Xiaodong,* Weng Duan, and Ran Rui

Laboratory of Advanced Materials, Department of Materials Science and Engineering, Tsinghua University, Beijing, China 100084

ABSTRACT: Pt–Mg/Al\textsubscript{2}O\textsubscript{3} soot oxidation catalysts were prepared by impregnating either magnesium acetate or magnesium nitrate on alumina-supported platinum catalyst. The influence of Mg addition on the structure and catalytic behaviors of Pt/Al\textsubscript{2}O\textsubscript{3} catalysts were investigated by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, transmission electron microscopy (TEM), H\textsubscript{2} chemisorption, thermogravimetric (TG) analysis, Fourier transform infrared spectroscopy (FTIR), NO\textsubscript{x} temperature-programmed desorption (NO\textsubscript{x}-TPD), NO temperature-programmed oxidation (NO-TPO), and soot temperature-programmed oxidation (soot-TPO). In spite of the coverage of surface Pt by magnesium species and the weakened oxidation resistance of Pt, the Pt–Mg/Al\textsubscript{2}O\textsubscript{3} catalyst derived from magnesium acetate exhibits a higher soot oxidation activity than that prepared with magnesium nitrate, which is mainly determined by the larger Pt particle size on this catalyst. Additionally, the synergistic effect between Pt and Mg enhances the NO oxidation activity and NO\textsubscript{x} storage capacity of Pt–Mg/Al\textsubscript{2}O\textsubscript{3} catalyst. More NO\textsubscript{x} is produced in the temperature range of soot oxidation on this catalyst than on the Mg-free Pt/Al\textsubscript{2}O\textsubscript{3} catalyst with a similar Pt particle size, which efficiently promotes the ignition of soot.

1. INTRODUCTION

Due to the environmental and health impacts of diesel soot and the pressure to comply with emissions regulations, efforts to reduce diesel soot emissions are ongoing and remain a challenging topic.\textsuperscript{1} Trapping on a filter, followed by oxidation, is an efficient means to eliminate of soot particulate matter. With the help of catalysts, the temperature of uncatalyzed oxidation of soot of over 600 °C can be significantly decreased.\textsuperscript{2}

As the catalytic oxidation of soot is a solid–solid reaction, the contact between catalyst and soot (“loose contact”) becomes the main limiting factor in the catalytic activity.\textsuperscript{3} To overcome this problem, the appropriate utilization of NO\textsubscript{x} in the exhaust gases turns out to be a good idea, as NO\textsubscript{x} is a much more powerful oxidant than O\textsubscript{2}, and if enough NO\textsubscript{x} is present in the exhaust gas, soot can be oxidized around 350 °C.\textsuperscript{4} Among the catalysts investigated, noble metals such as platinum are one of the most commonly applied kinds, as they can effectively catalyze oxidation of NO to NO\textsubscript{2}.\textsuperscript{5,6}

Nevertheless, the soot oxidation rate would be limited by the reduced NO\textsubscript{x} concentration in exhaust gas from modern engines. The NO\textsubscript{x} storage feature of alkali and alkaline earth metals can provide additional desorbed NO\textsubscript{x} at moderate temperatures and thus make them a promising component in soot oxidation catalysts. As a much more stable component than potassium, barium has received more and more attention in simultaneous removal of soot and NO\textsubscript{x} by Pt-containing NSR (NO\textsubscript{x} storage reduction) catalysts\textsuperscript{7–9} and simultaneous removal of NO\textsubscript{x} and soot.\textsuperscript{10–11} However, in these studies, Ba-containing catalysts always exhibit lower oxidation activity for soot, which may be attributed to the surface coverage of Pt by the barium species and the high stability of barium nitrates, which decompose at a temperature (around 600 °C) too high for the combustion of soot.\textsuperscript{3} Then the replacement of Ba by other alkaline-earth elements to maintain the NO\textsubscript{x} storage capacity may be a good choice. Due to the weaker alkalinity of magnesium than barium, the decomposition of magnesium nitrate is much easier than that of barium nitrate.\textsuperscript{12} On the other hand, as the chemical properties of metal precursor used in catalyst preparation play an important role in the interaction of the metals with each other and with the surface,\textsuperscript{13} the choice of magnesium precursor influences the surface distribution of Pt, which should be taken seriously.

The present work was aimed to gain deep insight into the textural properties and states of Mg and Pt species on Pt–Mg/Al\textsubscript{2}O\textsubscript{3} catalysts and their influence on soot oxidation performance. Thus, various physical and spectroscopic characterizations were performed to investigate the influence of magnesium precursors (nitrate and acetate) on Pt particle size, surface coverage of Pt, and NO\textsubscript{x} utilization for soot oxidation.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. Pt/Al\textsubscript{2}O\textsubscript{3} (PtAl-1) catalyst (1 wt %) was prepared by impregnating Pt(NO\textsubscript{3})\textsubscript{2} (17.01 wt %; Heraeus) on γ-Al\textsubscript{2}O\textsubscript{3} powders (BASF; 150 m\textsuperscript{2}/g). After impregnation, the sample was dried at 110 °C overnight and then calcined at 500 °C for 2 h. For comparison, the as-received catalyst was again calcined at 500 °C for 2 h. Another Pt/Al\textsubscript{2}O\textsubscript{3} catalyst was prepared by a successive calcination at 640 °C for 2 h to obtain a large average Pt particle size, which is denoted as “PtAl-2.” The Pt–Mg(NO\textsubscript{3})\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst (MgPtAl-1) was prepared by impregnating Mg(NO\textsubscript{3})\textsubscript{2} (AR, Beijing Modern Eastern) on the as-received PtAl-1 catalyst with a weight ratio of MgO:Al\textsubscript{2}O\textsubscript{3} = 2:8. Similarly, MgPtAl-2 was prepared by impregnating Mg(CH\textsubscript{3}COO)\textsubscript{2} (AR, Tianjin Yongda) on the as-received PtAl-1 catalyst. Both the Mg-containing catalysts were
then dried at 110 °C overnight and calcined at 500 °C for 2 h. Table 1 lists the compositions and preparation conditions of the four samples.

| Table 1. Compositions and Preparation Conditions of Catalysts |
|---------------------------------|--------------|-------------|
| catalyst | Pt (wt %) | MgO (wt %) | Al₂O₃ (wt %) | Mg precursor | calcination temp (°C) |
| PtAl-1 | 1 | 99 | 500 |
| PtAl-2 | 1 | 99 | 640 |
| MgPtAl-1 | 1 | 20 | 79 | Mg(NO₃)₂ | 500 |
| MgPtAl-2 | 1 | 20 | 79 | Mg(CH₃COO)₂ | 500 |

2.2. Catalyst Characterization. The powder X-ray diffraction (XRD) patterns were determined by a Japan Science D/Max-RB diffractometer employing Cu Kα radiation (λ = 0.15418 nm). The X-ray tube was operated at 40 kV and 30 mA. The X-ray diffractograms were recorded at 0.02° intervals in the range of 20° ≤ 2θ ≤ 80° with a scanning velocity of 4°·min⁻¹.

The specific surface areas of the samples were measured by use of the N₂ adsorption isotherm at −196 °C via the four-point Brunauer–Emmett–Teller (BET) method with an automatic surface analyzer (F-Sorb 3400, Gold APP Instrument). The samples were degassed at 200 °C for 2 h prior to the measurements.

Platinum dispersion of the catalysts was carried out on a Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD). For each experiment, approximately 0.1 g of catalyst was placed in an U-shaped quartz tube (i.d. = 10 mm) and reduced in a flow of 10% H₂/Ar (50 mL/min) while the temperature was ramped up to 400 °C at a rate of 10 °C/min and then held at 400 °C for 30 min in flowing He (50 mL/min) for degassing. After the sample was cooled down to 25 °C, the loop gas of 10% H₂/Ar (20 mL/min) was pulsed over the sample and the TCD signal was recorded until the peak area became constant. The percent dispersion was calculated by dividing the number of exposed surface Pt atoms (as determined by H₂ chemisorption) by the total amount of Pt in the catalyst. Mean Pt particle size (Dₚₐₑₑ) was determined from H₂ chemisorption data by the method presented in ref 14.

Transmission electron microscope (TEM) images were taken on a FEI Tecnai G² 20 instrument with an acceleration voltage of 200 kV. Mean Pt particle size was calculated from TEM images by averaging 50 points of Pt particles.

Thermogravimetric (TG) analysis experiments were conducted on a Mettler Toledo thermogravimetric analyzer. For each experiment, 15 mg of the sample was heated from ambient temperature to 500 °C at a heating rate of 10 °C/min. Reaction was carried out in air at a flow rate of 50 mL/min at the gauge pressure of 0.1 atm (10.1 kPa). The chamber blowing gas, N₂ (99.999% purity), was fixed at a flow rate of 20 mL/min.

Infrared spectra of CO adsorbed on the catalysts were recorded on a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. After a pretreatment in nitrogen at 500 °C for 30 min, the catalyst was cooled down to room temperature. The spectra were taken after exposure of the catalyst to 1% CO/N₂ for 30 min and then purging with N₂.

NO adsorption was recorded on the same apparatus. After pretreatment in nitrogen at 500 °C for 30 min and subsequent cooling down to 300 °C, the spectra were taken after exposure of the catalyst to 1000 ppm NO/10% O₂/N₂ for different times (1, 2, 5, 10, 20, and 30 min).

The NO temperature-programmed oxidation (TPO) tests were carried out in a fixed-bed reactor with the effluent gases monitored by an infrared spectrometer (Thermo Nicolet iS10). One hundred milligrams of catalyst powder was diluted with 300 mg of silica pellets, and this mixture was sandwiched by quartz wool in a tubular quartz reactor. A gas mixture of 1000 ppm NO/10% O₂/N₂ was fed at a flow rate of 500 mL/min. The reactor temperature was ramped to 600 °C at a heating rate of 10 °C/min.

The NO₂ temperature-programmed desorption (TPD) tests were performed in the same apparatus as that used in NO-TPO tests. Prior to the test, the sample powders were exposed in 1000 ppm NO/10% O₂/N₂ (500 mL/min) at 300 °C for 30 min and then cooled down to room temperature in the same atmosphere and flushed by N₂. Afterward, the NO and NO₂ desorption profiles were obtained by ramping the reactor from room temperature to 600 °C at a heating rate of 10 °C/min in a 10% O₂/N₂ stream.

2.3. Activity Measurement. Printex-U (Degussa) was used as a model soot. Its particle size was 25 nm and the specific surface area was 100 m²/g. Ten milligrams of soot and one hundred milligrams of catalyst powder were mixed by a spatula for 2 min for "loose contact" conditions. In order to prevent reaction runaway, 110 mg of the soot–catalyst mixture was diluted with 300 mg of silica pellets. The inlet gas mixture was 1000 ppm NO/10% O₂/N₂ with a total flow rate of 500 mL/min. The activities of the catalysts for soot oxidation were evaluated in a temperature-programmed oxidation (TPO) reaction apparatus at a heating rate of 10 °C/min. The activities of the catalysts for soot oxidation were evaluated in the same apparatus as that used in NO-TPO tests. T₁₀ and T₅₀ represented the temperature at which 10% and 50% of soot is oxidized. The downstream CO₂/(CO₂ + CO) ratio during soot oxidation was defined as the selectivity to CO₂. For comparison, the soot oxidation activities of the catalysts in a NO₃-free atmosphere were also measured in 10% O₂/N₂.

3. RESULTS

3.1. Solid Properties. Figure 1 shows the powder XRD patterns of the catalysts. All the samples exhibit characteristic peaks of γ-alumina. The peaks of crystalline MgO appear on both the magnesium-containing catalysts. The MgPtAl samples have similar crystallite sizes of MgO as shown in Table 2. MgAl₂O₄ spinel was not taken into consideration since the calcination temperature was only 500 °C.¹⁵ No sharp Pt peak at 2θ = 39.6° is observed, implying a high dispersion of platinum over all the catalysts.

As shown in Table 2, the impregnation of magnesium oxide leads to a slight decrease in the surface area of the catalysts due to the blocking effect on the support pores. However, such slight variations in the catalyst surface area should not result in any obvious differences in the catalytic performance of the catalysts.

3.2. H₂ Chemisorption and TEM. For Pt/Al₂O₃ and Pt/BaO/Al₂O₃ samples, Pereda et al.¹⁶ reported that the platinum dispersion results obtained by dissociation of H₂ chemisorption are reproducible. Table 2 shows the Pt dispersion and particle size for different samples obtained by H₂ chemisorption. Both
Table 2. Overview of BET, XRD, H₂ Adsorption, and TEM Results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET} (m²/g)</th>
<th>Crystallite size of MgO* (nm)</th>
<th>Particle size from H/Pt (nm)</th>
<th>Particle size from TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtAl-1</td>
<td>138</td>
<td>0.62</td>
<td>1.8</td>
<td>1−3 (1.8)</td>
</tr>
<tr>
<td>PtAl-2</td>
<td>134</td>
<td>0.32</td>
<td>3.5</td>
<td>2−5 (3.5)</td>
</tr>
<tr>
<td>MgPtAl-1</td>
<td>110</td>
<td>14</td>
<td>2.7</td>
<td>1−2 (1.8)</td>
</tr>
<tr>
<td>MgPtAl-2</td>
<td>117</td>
<td>15</td>
<td>3.6</td>
<td>2−5 (3.4)</td>
</tr>
</tbody>
</table>

*Calculated by Williamson–Hall equation from the XRD data. The data in parentheses represent the average diameter of platinum particles.

The addition of MgO and the calcination at a higher temperature (640 °C) lead to obvious decrease in H₂ adsorption, which means a larger Pt particle size or the partial covering of surface Pt by magnesium species.

To judge the specific factors accounting for the reduction of H₂ adsorption, high-resolution TEM images of the catalysts were obtained and are shown in Figure 2. As can be seen from Table 2, the Pt particle sizes calculated from H₂ chemisorption and those collected by TEM are consistent with each other for the Mg-free samples. However, for the Mg-containing samples, especially MgPtAl-1, the Pt particle sizes derived from H₂ chemisorption are much larger than those by TEM. These differences may result from the covering of Pt surface by Mg species, which reduces the exposed area of Pt and leads to a decrease of the H₂ uptake, just like the case of Pt-BaO/Al₂O₃ catalysts. The MgPtAl-2 catalyst has the largest Pt particle size among the three catalysts calcined at 500 °C, which may be due to the exothermic/endothermic decomposition of different magnesium precursors during the catalyst preparation, which will be discussed with the TG results. As the TEM images reflect the actual crystalline particle size of Pt and the decrease in H/Pt arises from both the covering of Pt surface with Mg species and the growth of Pt particles, the difference between these two results can be ascribed to the surface coverage of Pt particles. In this sense, it seems that the interaction between platinum nitrate and magnesium nitrate precursors during the catalyst preparation leads to a more serious covering of Pt surface.

3.3. Thermal Analysis. To identify the thermal decomposition processes of different magnesium precursors during the calcination, two Mg-containing samples before calcination at 500 °C were denoted as Mg(NO₃)₂/PtAl and Mg(Ac)₂/PtAl. The results of thermogravimetric analysis performed in air are shown in Figure 3. It can be seen from Figure 3a that the decomposition of magnesium nitrate presents endothermic peaks at 89 and 410 °C, corresponding to the congruent melting of its real [Mg(H₂O)₆](NO₃)₂ structure (and dissolved in its own water of crystallization) and the decomposition of magnesium nitrate, respectively. On the other hand, magnesium acetate experiences a quite different decomposition process. Melting of the salt and evaporation of the crystal water result in the first mass loss segment at around 85 °C. Since the decomposition of magnesium acetate in air is an oxidation reaction, which produces a lot of heat, a sharp exothermic peak area appears at around 319 °C in Figure 3b. This remarkable heat released locally would lead to the sintering of platinum particles or MgPtAl-2 that are not observed on the MgPtAl-1 (prepared with magnesium acetate) than those on MgPtAl-1 (prepared with magnesium nitrate) and PtAl-1.

3.4. IR Spectra of CO Adsorption. The addition of metal oxide additive would affect the oxidation state of platinum and the reactivity of active sites. Figure 4 presents the IR spectra of CO linearly adsorbed on the catalysts at room temperature under a N₂ stream after CO adsorption.

All the samples exhibit bands at 2083 and 2063 cm⁻¹, which were assigned to CO linearly adsorbed on terrace and step sites on Pt⁰ crystallites, respectively. Three overlapped bands at 2211, 2195, and 2180 cm⁻¹, which could be assigned to ν₁ and ν₃ of Pt⁴⁺(CO)₂ species, are observed on both MgPtAl-1 and MgPtAl-2 that are not observed on the PtAl catalysts. These results agree with the theory regarding the influence of support materials on the oxidation state of platinum reported by Yoshida et al. They proposed that electrophobic materials such as MgO can promote the oxidation of platinum through the stabilization of platinum oxo-anion species such as PtO₂⁻ by the surface electrophobic property of the support in a similar way to the formation of mixed oxides containing precious metal, or platinates, such as Mg₃PtO₄ and Sr₃MgPtO₆ with
tetravalent Pt. However, these compounds were not detected by XRD in our case due to the low loading amount of Pt.

The intensities of CO adsorption bands on PtAl-2, MgPtAl-1, and MgPtAl-2 are obviously lower than those obtained on PtAl-1, which should due to the reduced exposed area of surface platinum species as a result of sintering of Pt particles and/or covering effect of MgO deposition, which is consistent with the H2 chemisorption results.

3.5. NO Temperature-Programmed Oxidation. NO2 production is critical to soot catalytic oxidation in the presence of NO. Figure 5 shows the evolution of outlet NO2 concentration during the NO-TPO measurements. It is observed that more NO2 is produced on the PtAl-2 and MgPtAl-2 catalysts with larger Pt particles, and the onset temperatures are lower. It is noted that slightly more NO2 is generated at low temperatures (<ca. 300 °C) on MgPtAl-2 than on PtAl-2, which may be related to the better NOx storage capacity of the former catalyst and will be discussed with the NOx-TPO results. It has been reported that, for PtAl catalysts, the activity of platinum for NO oxidation increases with decreasing Pt dispersion.23 Nevertheless, for PtAl-2 and MgPtAl-2 in this work, the effect of Pt particle size seems to be ruled out since similar real sizes of Pt particles are observed on the TEM images of these two samples. On the other hand, the MgPtAl-1 sample with a similar real Pt particle size to PtAl-1 exhibits worse NO oxidation activity, which may be ascribed to the covering of surface Pt by MgO addition as suggested by H2 chemisorption.

It has been reported that oxidation of Pt to less active PtO and PtO2 may also deactivate the NO oxidation activity of Pt.24 Nevertheless, this influence is not so obvious on the MgPtAl-1 sample, which has a larger Ptδ+ ratio than the PtAl catalysts (confirmed by CO-IR results) but exhibits better NO oxidation activity.

3.6. Infrared Spectra of NO Adsorption. To identify the surface nitrates species formed on different catalysts during the reactions, NOx adsorption on the catalysts was investigated by IR spectroscopy. Prior to NOx adsorption, the catalysts were treated at 500 °C in N2 for 30 min to remove adsorbed species (e.g., H2O and CO2). After the samples were cooled down to 300 °C, NO and O2 were introduced to the sample cell. Figure 6 shows the spectra of different catalysts after exposure in 1000 ppm NO/10% O2/N2 for different time.

For the IR spectra of both MgPtAl samples, a weak band at 1230 cm⁻¹ due to nitrite species25 is observed within the first minute in Figure 6c,d. Other bands assigned to magnesium and alumina nitrates also appear at 1540 and 1297 cm⁻¹. The nitrate...
bands increase in intensity with time and have not reached a maximum even after 30 min. After 1 min, the nitrite band at 1230 cm\(^{-1}\) vanishes and is replaced by the nitrate band at 1297 cm\(^{-1}\), evidencing the conversion of nitrite to nitrate.\(^{25,26}\) It can be seen that the IR bands assigned to nitrate species are stronger on the MgPtAl catalysts than on the PtAl catalysts, and the formation of surface nitrates is accelerated. No significant difference is found between the nitrate bands of MgPtAl-1 and MgPtAl-2 catalysts except that the intensities of the latter are higher to some extent.

3.7. NO\(_x\) Temperature-Programmed Desorption. It should be kept in mind that the IR spectra of NO adsorption reflect only the surface adsorption properties of catalysts, and we cannot obtain qualitative information of possible NO\(_2\) release during soot TPO. Thus, further information about the decomposition amount and temperature of the adsorbed nitrate species was gained through thermal desorption studies. After exposure at 300 °C to 1000 ppm NO + 10% O\(_2\) for 30 min, the samples were exposed to 10% O\(_2\)/N\(_2\) and heated to 600 at 10 °C/min. The monitored results are shown in Figure 7.

As shown in Figure 7a, two NO\(_2\) desorption peaks are observed at 70 and 330 °C on PtAl-1, which are associated with desorption of weakly adsorbed NO\(_2\) and the decomposition of nitrates, respectively. A low-temperature NO desorption peak
appears at 60 °C, ascribed to desorption of weakly adsorbed 
NO in Figure 7b. It is noted that the high-temperature NO 
desorption peak lags just a few degrees (30 °C) above the high-
temperature NO2 peak. Thus, it is reasonable to suggest that 
the desorption of NO at high temperatures arises mainly from 
the thermodynamic-driven decomposition of NO3 and/or NO3 
dissociation on reducible metal sites during the TPD tests.27 
With respect to PtAl-1, NO3 and NO are released at similar 
temperatures on PtAl-2. The amount of NOx desorption is 
slightly larger on PtAl-2 (0.15 mmol of NO2/g of catalyst and 0.09 mmol of NO/g of catalyst) than on PtAl-1 (0.12 mmol 
NO2/g of catalyst and 0.07 mmol NO/g of catalyst). It may be 
related to the higher NO oxidation activity of PtAl-2, which 
provides to be adsorbed more readily than NO2 on the 
catalyst.28

The desorption curves of NOx formed on the Mg-containing 
catalysts are quite different from those of the PtAl samples. The 
nitrate-derived NO2 desorption peak on MgPtAl-2 is observed 
at 340 °C, which is retarded to 430 °C on MgPtAl-1. Besides 
this, the amount of NO2 desorbed from MgPtAl-2 (0.36 mmol/ 
g of catalyst) is twice that from MgPtAl-1 (0.18 mmol/g of catalyst). Under the given amount of alkaline earth metal 
additive, these significant differences should be mainly ascribed 
to the interaction between platinum and magnesium species. 
The MgPtAl-1 sample exhibits lower NO oxidation activity due 
to its smaller Pt particles. Then its NOx storage ability would 
be strictly limited since NOx can be stored on the support much 
more easily than NO, as indicated in ref 28. On the other hand, 
smaller Pt particles would go against the decomposition of the 
stored nitrate, which leads to a higher temperature of nitrate 
decomposition. In this way, the synergistic effect between 
platinum and magnesium species would obviously influence the 
NOx storage abilities of the catalysts.

It is interesting to compare the desorption behaviors of NOx 
asorbed on PtAl-1 and MgPtAl-1. It can be seen that the 
desorption temperature of NO2 lagged by about 100 °C, which 
is suggested to be due to formation of more stable magnesium 
nitrate compared with aluminum nitrate. In our previous 
study,29 it was presented that not only the amount of NO3 
production but also the match between soot oxidation 
temperature and NO2 generation temperature interval is 
important to NO3-assisted soot oxidation. In this sense, the 
delay of NO2 desorption temperature may not be good news 
for soot catalytic oxidation on MgPtAl-1. For MgPtAl-2, it is 
compensated by the stronger NO oxidation ability and nitrate 
catalytic decomposition of larger Pt particle size, resulting in an 
appropriate nitrate decomposition temperature interval for soot 
oxidation.

3.8. Soot Temperature-Programmed Oxidation. Figure 8 
panels a and b show the soot conversions with catalysts in the 
soot TPO measurements in 1000 ppm NO/10% O2/N2 and 10% 
O2/N2, respectively. The T50 and T10 values of the 
catalysts in the presence of NO follow the order MgPtAl-2 (432 
°C) < PtAl-2 (439 °C) < PtAl-1 (485 °C) < MgPtAl-1 (491 
°C) and MgPtAl-2 (339 °C) < PtAl-2 (361 °C) < PtAl-1 (405 
°C) < MgPtAl-2 (415 °C), respectively. These catalysts always 
yield a high CO2 selectivity (>98%). It indicates that the introduction of magnesium oxide efficiently promotes the ignition of soot by 
providing more nitrate-derived NO2.

The soot oxidation activities of the catalysts in the absence 
of NO are slightly weakened by the addition of magnesium oxide, 
with T50 shifting toward high temperatures by less than 10 °C 
as shown in Figure 8b. PtAl-1, with the highest dispersion of Pt, 
exhibits the lowest T50 values of the 
catalysts in the presence of NO is obviously decreased with 
the growth of platinum particles. Meanwhile, MgPtAl-2 shows a 
much lower T10 than the PtAl-2 sample, which has a similar 
average Pt particle size, indicating that the introduction of 
magnesium oxide efficiently promotes the ignition of soot by 
providing more nitrate-derived NO2.

The soot oxidation activities of different catalysts in NO + O2 and O2 have been confirmed 
reliable by repeating soot TPO tests. That is, the presence of NO influences the soot catalytic oxidation in a different way for 
the catalysts with magnesium oxide.

4. DISCUSSION

4.1. Exothermic/Endothermic Effects of Precursor 
Decomposition/Oxidation. It is known that Pt species 
become mobile and aggregate at temperatures above 600 °C to 
form larger particles.30 It has also been reported that Pt/Al2O3 
catalysts calcined at 450 and 500 °C have similar Pt dispersion, 
but a notable decrease of the Pt dispersion is observed when 
the calcination temperature is raised up to 550 °C.16 The larger 
Pt particle size of PtAl-2 with respect to PtAl-1 agrees with the 
above reports.

The choice of precursor can influence the structural 
properties and catalytic performances of platinum catalysts. A 
lot of work focusing on the Pt and Ba precursors of Pt−Ba/ 
Al2O3 has been published, indicating that catalysts prepared
with different precursors may have different dispersions of Pt. However, few works have discussed the thermal effects of precursors during the synthesis process. For example, Maeda et al. prepared Pt–Ba/Al catalysts with barium nitrate and barium acetate and identified the dispersion of platinum with H2 chemisorption. However, they did not confirm the Pt particle size by TEM and failed to point out the specific factor of lower dispersion of Pt on Pt–Ba/Al derived from barium acetate.

In the present study, both MgPtAl samples derived from magnesium acetate and magnesium nitrate exhibit similar MgO crystallite size as shown by XRD results, and the different Pt particle size should be attributed to different thermal behavior during catalyst preparation. As shown in Figure 9, during the calcination up to 500 °C in air, magnesium acetate experiences decomposition and oxidation, which release heat at about 3.52 kJ/g of catalyst with the assistance of platinum (calculated from the TGA results); however, magnesium nitrate experiences only a decomposition process, which even needs to absorb heat at about 0.3 kJ/g of catalyst. During the synthesis of MgPtAl-2, the intense exothermic combustion of the acetate salt surely heats the adjacent Pt particles and leads to sintering of Pt particles, which will never occur on MgPtAl-1 derived from magnesium nitrate.

4.2. Influence of Pt Particle Size on Catalytic Activity. It has been widely reported that the NO oxidation reaction is highly structure-sensitive; that is, the turnover frequency (TOF) increases with increasing Pt particle size.3,33 Although higher TOF does not necessarily mean higher NO oxidation activity (the surface area of Pt also needs to be taken into consideration), the NO oxidation activity is suggested to be in accordance with the NO TOF when the Pt particle size is no larger than 10 nm, which is the case here.37

As NO2 is a more powerful oxidant than O2, the oxidation of NO to NO2 is an important step in the mechanism of soot catalytic oxidation in the presence of NOx. On the other hand, the reaction at low temperatures is limited by the kinetics of soot oxidation. According to the experiments with soot oxidation by gaseous NO2, sufficient reaction rates are observed only above 300 °C.3 Figure 10 shows such a quasi-linear dependency of NO2 production above 300 °C in the NO-TPO experiments and that of TAG of soot oxidation in NO + O2 on the particle size of Pt. The catalysts with larger Pt particles produce more available NO2 and hereby assist the soot catalytic oxidation more efficiently. Additionally, larger Pt particles are reported to be more active for the catalytic oxidation of the intermediate products that produced during the soot oxidation. It is noted that the MgPtAl-2 catalyst, with smaller Pt particle size than PtAl-2, shows higher catalytic activities of NO and soot oxidation, which can be attributed to the synergistic effect between Pt and Mg that affects the NO oxidation and NOx storage capacity of Pt–Mg/Al2O3 catalyst.

4.3. Synergistic Effect between Pt and Mg. In spite of the coverage of surface Pt by magnesium species and the weakened oxidation resistance of Pt (confirmed by CO-IR), the MgPtAl-2 catalyst prepared with magnesium acetate precursor exhibits higher oxidation activity for soot and NO than PtAl-2 with a similar Pt particle size. As indicated by in situ diffuse reflectance Fourier transform (DRIFT) spectra and NOx-TPD, more surface nitrates are formed on the Mg-modified catalysts. The contribution of surface nitrates is mainly determined by the states of Pt and MgO species on the catalysts and their interaction.

Although Maeda et al. have reported that the smaller crystallite size of Ba(NO3)2 can make the oxidation of barium nitrates to barium nitrates easier, the XRD results show that both MgPtAl catalysts have similar crystallite sizes of MgO, so the crystallite size effect of MgO [or Mg(NO3)2] is likely to be ruled out. On the other hand, the desorption temperature of magnesium nitrate is much lower on MgPtAl-2 than on MgPtAl-1, which is mainly related to the larger particle size of Pt on the former catalyst. In our previous study, the nitrates and/or nitrate-derived NO2 can be considered as a “trigger” for the extensive oxidation of soot by oxygen; that is, the NO2 derived from NO oxidation and nitrate decomposition within an appropriate temperature interval (at 300–400 °C) acts as the main oxidant for soot catalytic oxidation. Again, PtAl-2 and MgPtAl-2, which yield more NO2 at 300–400 °C in the NOx-TPO experiments, exhibit lower Tag for soot oxidation than the other two catalysts, as shown in Figure 11. It is also noted that MgPtAl-1 presents a much lower Tag than PtAl-2, with similar Pt size and NO oxidation ability, which seems to be related to the additional NO2 generated from magnesium nitrate decomposition as revealed by the NOx-TPD results. At higher temperatures (>400 °C), the importance of NO2 is greatly weakened and O2 becomes the predominant oxidant for soot. Thus, the oxidation activity of MgPtAl-1 with less exposed Pt active sites is even lower than that of PtAl-1. That is, the participation of both large Pt particles and Pt–Mg interaction is important for obtaining superior soot oxidation activity of platinum catalyst.

![Figure 9. Scheme of growth of Pt particles on different catalysts during calcination.](image-url)

![Figure 10. NO2 production in NO-TPO and Tag of soot-TPO as a function of the Pt particle size measured by TEM.](image-url)
5. CONCLUSIONS

From the above experimental results, the following conclusions can be drawn:

(1) The particle size of Pt on MgPtAl catalyst prepared with magnesium acetate is remarkably larger than that on the catalyst derived from magnesium nitrate, which is determined by the exothermic/endothermic reaction of precursor decomposition during catalyst preparation. The growth of Pt particles improves the NO oxidation activity, and the produced NO2 efficiently promotes the catalytic oxidation of soot.

(2) The synergistic effect between Pt and Mg is proved to be important: a catalyst with large Pt particle size and surface magnesium species can produce NO- and nitrate-derived NO3 at an appropriate temperature interval for assisting soot catalytic oxidation. The magnesium nitrate-derived catalyst exhibits a weakened soot oxidation activity due to the partial covering of surface Pt active sites and increased desorption temperature of magnesium nitrate.

AUTHOR INFORMATION

Corresponding Author
*Telephone: +86-10-62792375. Fax: +86-10-62792375. E-mail: wuxiaodong@tsinghua.edu.cn.

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