

Coarsening of Pt particles in a model NO_x trap

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The effects of temperature and atmosphere on the coarsening of Pt particles in a model NO_x trap (Pt/BaO/Al₂O₃) were examined by XRD, TEM, and CO chemisorption. The main finding, that the most significant particle growth occurs at elevated temperatures under oxidizing conditions, is relevant to NO_x trap durability.

KEY WORDS: NO_x trap; automotive-exhaust catalyst; platinum; particle coarsening.

1. Introduction

Lean-burn internal combustion engines are attractive for transportation applications because they are more efficient than those operating under stoichiometric conditions. Pollutants in the exhaust gas from vehicles powered by lean-burn engines cannot be removed in the usual way, however, since the normal three-way catalyst is unable to reduce nitric oxide (NO) in the presence of excess oxygen.

A solution to this problem is to catalytically convert NO to a solid, prototypically barium nitrate, and store it in a “NO_x trap” during fuel-lean operation [1]. The NO_x trap is regenerated by periodically shifting engine operation to stoichiometric or slightly fuel-rich conditions, under which the barium nitrate becomes unstable, releasing NO_x that is reduced in the usual manner. The operating temperature range for the NO_x trap is thus determined by the activity of the catalyst used to form the solid nitrate (defining the lower limit) and the stability of the nitrate under lean conditions (defining the upper limit). A typical range is approximately 200–500 °C.

Although the NO_x trap works well initially, its performance usually degrades over time. One reason for this is a slow accumulation of sulfate, derived from the combustion of fuel sulfur, which effectively competes with the nitrate for storage space. The sulfate is more stable than the nitrate, but it can be removed by an occasional exposure to rich conditions at a somewhat higher temperature than that used for normal regeneration of the NO_x trap [2].

Another reason for the degradation in performance of the NO_x trap is a loss in activity of the catalyst used to form the solid nitrate. Typically, the catalyst is platinum supported on a high-surface-area oxide, and its loss in activity is thought to result from loss of platinum surface area due to coarsening of the sup-

ported particles of platinum. There is no known practical way of restoring the platinum surface area, but as the present observations reveal, it is possible to largely avoid severe platinum-particle coarsening by carefully limiting high-temperature exposure of the NO_x trap to rich conditions.

2. Experimental details

A model NO_x trap was made with γ -Al₂O₃ from Alfa-Aesar, using an aqueous solution of Ba(NO₃)₂ to impregnate the alumina (with excess solution removed in a rotary evaporator) to a level equivalent to the composition BaO·6Al₂O₃. The material was then calcined at 750 °C before impregnation with Pt (2 wt%), by the incipient wetness method, from an aqueous solution of H₂PtCl₆. The model trap was finally calcined at 350 °C and reduced at 500 °C in a N₂ stream containing H₂ (1%) and H₂O (10%). For comparison, a simple Pt/Al₂O₃ catalyst (i.e., without Ba) was also prepared, following the same procedures.

Samples were aged in a quartz tube furnace at temperatures in the range 600–950 °C under an atmosphere consisting of flowing N₂ with H₂O (10%) and either H₂ (1%) or O₂ (0.006%, 0.05%, 0.5%, or 6.7%). Heating (and cooling) was performed under pure N₂, and time at temperature under the variable atmosphere was typically 3 h, although some samples were aged for longer times (up to 40 h) under even higher oxygen concentration (13%).

X-ray diffraction (XRD) patterns were obtained with a Scintag X2 diffractometer using CuK_α radiation. Samples were loosely packed in a shallow cavity (1 mm deep and 12 mm in diameter) cut into a “zero-background” quartz sample holder. Transmission electron microscopy (TEM) images were obtained with a JEOL-2010F microscope, equipped with an energy-dispersive X-ray spectrometer. Samples were dispersed

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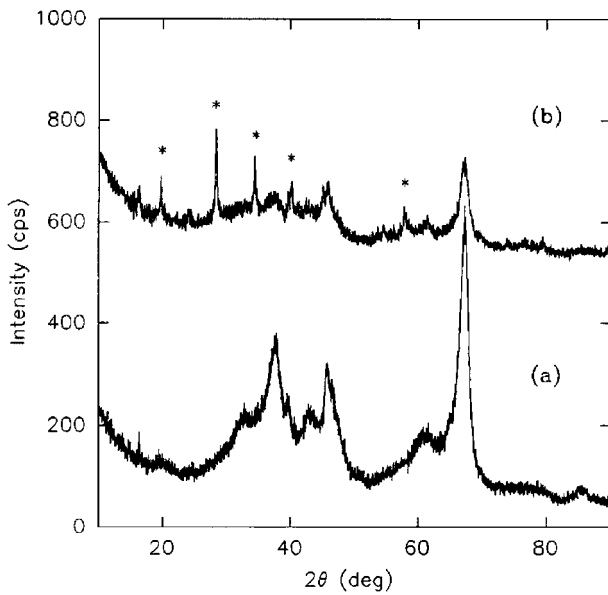


Figure 1. XRD patterns from samples of (a) alumina and (b) $\text{Ba}(\text{NO}_3)_2$ -impregnated alumina, both calcined at 750°C . Asterisks mark some of the more intense BaAl_2O_4 peaks.

onto holey carbon films supported on copper grids. CO-chemisorption results were obtained with an ASDI volumetric apparatus. Samples of 0.2–0.3 g were pre-treated in H_2 , typically at 500°C for 20 min, prior to CO uptake measurements.

3. Results

XRD patterns from the alumina and the $\text{Ba}(\text{NO}_3)_2$ -impregnated alumina, both after 750°C calcination, are shown in figure 1. Two effects of the addition of Ba are evident, the attenuation of $\gamma\text{-Al}_2\text{O}_3$ peaks due to the

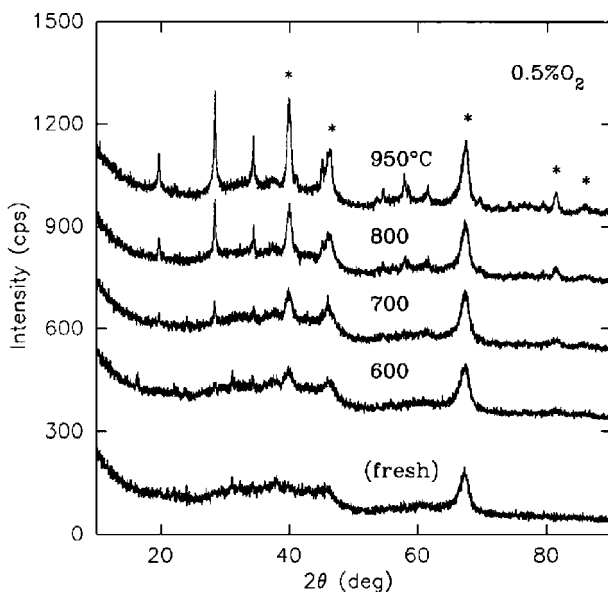


Figure 2. XRD patterns from samples of a fresh trap and traps aged at 600, 700, 800, and 950°C in 0.5% O_2 . Asterisks mark Pt peaks.

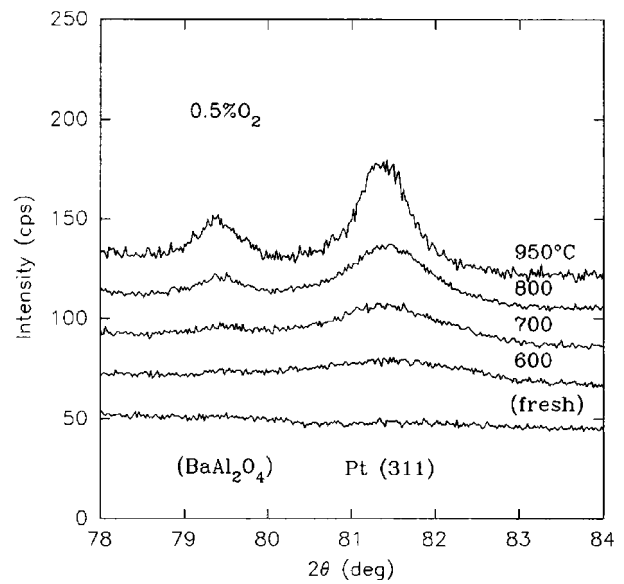


Figure 3. XRD patterns from samples of a fresh trap and traps aged at 600, 700, 800, and 950°C in 0.5% O_2 .

diminished penetration of X-rays into the sample, and the development of new peaks due to the formation of BaAl_2O_4 . Several of the more intense BaAl_2O_4 peaks are marked with asterisks in figure 1(b).

After completion of the preparation of the model trap, the BaAl_2O_4 peaks were gone, as shown at the bottom of figure 2. This reflects the process, not shown here but described in detail elsewhere (G.W. Graham *et al.*, submitted), of leaching of Ba^{2+} from the aluminate and precipitation of BaCO_3 during the aqueous process of Pt incorporation, followed by (partial) elimination of CO_2 from the BaCO_3 during the reduction step. Subsequent aging treatments in 0.5%

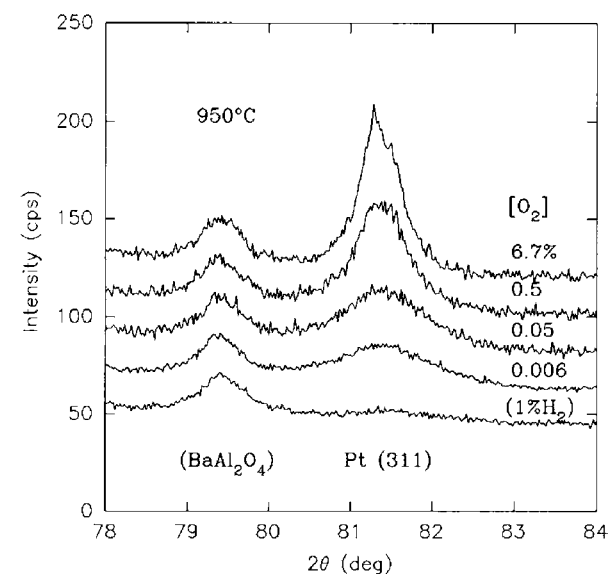


Figure 4. XRD patterns from samples of traps aged at 950°C in 1% H_2 , 0.006% O_2 , 0.05% O_2 , 0.5% O_2 , and 6.7% O_2 .

O₂ led to the reappearance of the BaAl₂O₄ peaks as well as the development of Pt peaks, as shown in the upper portion of figure 2. The Pt peaks in the pattern obtained after the treatment at 950 °C are marked with asterisks, (though only two of them, above 80°, are free of interference from the support).

An expanded view of these patterns, taken around the region of the Pt(311) reflection, is shown in figure 3. Both the amplitude and the inverse width of the Pt peak increased with aging temperature, starting from zero in

the fresh trap. These variations are due to coarsening of the Pt particles. According to the Scherrer equation, an average particle size can be computed from the inverse width of the peak, corrected for instrumental factors. For small enough particles, the peak may be too broad to resolve, however. Assuming that most of the Pt contributes to the peak in the sample aged at 950 °C, the average particle size in this sample would thus be 18 nm. The average particle size in the fresh sample, on the other hand, should be at least an order of magnitude smaller. Since the intensity of the peak, as determined using standard Scintag fitting procedures, increases monotonically with aging temperature, particle sizes in samples aged at intermediate temperatures would be consistent with a simple bimodal distribution, where only a fraction of the Pt is in particles of average size corresponding to the inverse peak width, and the remainder is in particles of average size comparable to that in the fresh trap.

The effect of aging atmosphere on the XRD pattern of samples heated at 950 °C is shown in figure 4. In this case, there was no change in the BaAl₂O₄ peak, but the Pt peak varied in a way that parallels figure 3. Specifically, the Pt peak from the sample heated in 1% H₂ is comparable to that from the fresh trap, and the effect of increasing oxygen concentration is comparable to that of increasing temperature. The intensity of the Pt peak does not change much between 0.5 and 6.7% O₂, but the width of the latter is less, corresponding to an average particle size of 27 nm.

Typical TEM images obtained from a sample of the fresh trap, a sample of the trap that had been aged at 950 °C in 1% H₂, and a sample of the trap that had been aged at 950 °C in 6.7% O₂ are shown in figure 5(a)–(c), respectively. Energy dispersive spectroscopy (EDS) established that the dark, relatively round objects in these images are Pt particles. Histograms of Pt particle size measured from a number of images like those in figure 5 are shown in figure 6(a)–(c). For comparison, a histogram of Pt particle size measured from images obtained from a sample of Pt/Al₂O₃ catalyst that had been aged at 950 °C in 1% H₂ is shown in figure 6(d). In accordance with the XRD results, the Pt particles in the fresh trap are 1–3 nm in size, those in the trap that had been aged at 950 °C in 1% H₂ are somewhat larger, 2–6 nm, and those in the trap that had been aged at 950 °C in 6.7% O₂ are either much larger, 6–40 nm, or more nearly comparable, 1–5 nm, to those in the fresh trap. The Pt particles in the Pt/Al₂O₃ catalyst that had been aged at 950 °C in 1% H₂ are somewhat smaller than in the correspondingly aged trap.

Additionally, electron diffraction (together with EDS) confirmed the presence of crystalline support phases in samples that had been aged at 950 °C. Figure 7(a), for example, shows a high-resolution TEM image from a sample of the Pt/Al₂O₃ catalyst that had been aged in 1% H₂. The lattice planes are due to κ -Al₂O₃ (also found by XRD), which was apparently

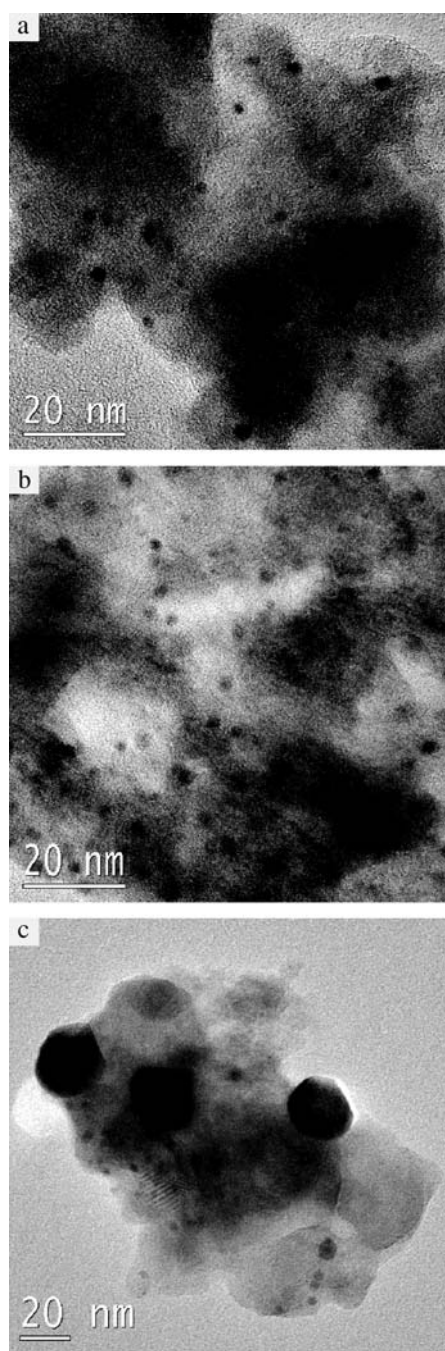


Figure 5. Representative TEM images of (a) fresh trap, (b) trap aged at 950 °C in 1% H₂, and (c) trap aged at 950 °C in 6.7% O₂.

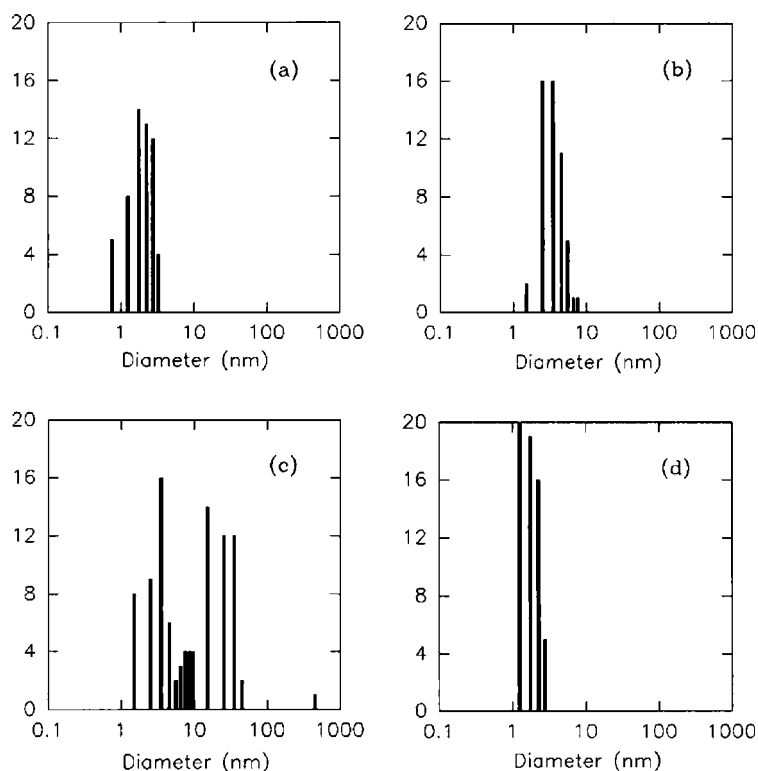


Figure 6. Histograms of Pt particle size measured from images like those in figure 5 together with that of (d) Pt/Al₂O₃ catalyst aged at 950 °C in 1% H₂.

able to form in any of the 950 °C-aged samples without Ba. The image in figure 7(b), taken from a sample of the trap that had been aged in 6.7% O₂, shows a large Pt particle supported on BaAl₂O₄.

CO-chemisorption results are summarized in table 1, and selected values are plotted in figure 8, as a function of aging temperature. These show that essentially all the

trends, as well as the orderings with respect to aging temperature and atmosphere, that were observed by XRD and TEM are roughly reproduced by CO-chemisorption, although quantitative relationships are poor in some instances. For example, the CO/Pt ratio for samples of trap aged at 950 °C in O₂ generally decreases with increasing [O₂], but the CO/Pt ratio varies by only a

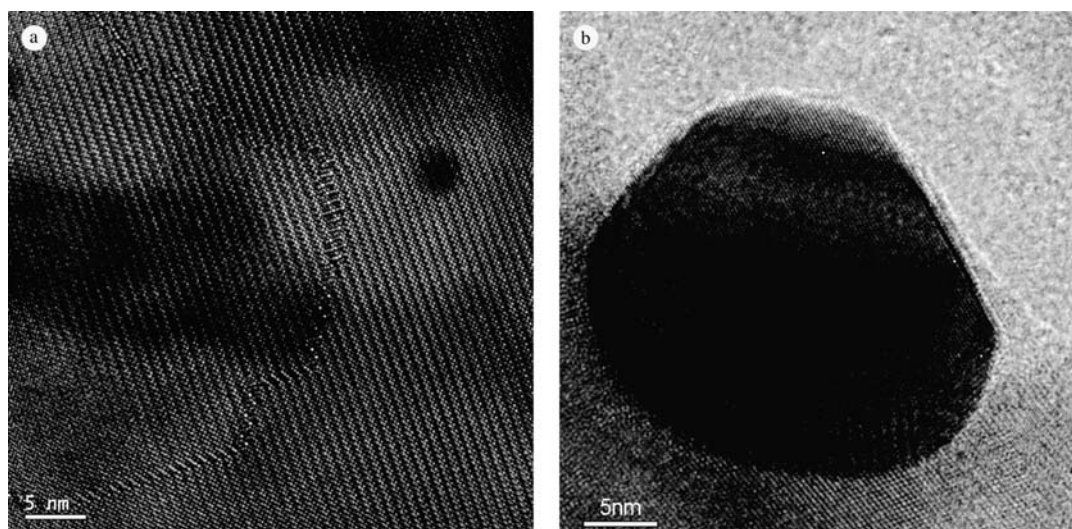


Figure 7. High-resolution TEM images of (a) small Pt particle on κ -Al₂O₃ from a sample of Pt/Al₂O₃ catalyst aged at 950 °C in 1% H₂ and (b) large Pt particle on BaAl₂O₄ from a sample of trap aged at 950 °C in 6.7% O₂.

Table 1
CO chemisorption results

Aging conditions	Pretreatment	CO/Pt	
		Model NO _x trap	Pt/Al ₂ O ₃ catalyst
(Fresh)	350 °C/10 min	0.307	0.574
	500 °C/20 min	0.285	0.541
950 °C/1%H ₂ /3 h	350 °C/20 min		0.186
	500 °C/20 min	0.115	
600 °C/0.5%O ₂ /3 h	500 °C/20 min	0.063	
600 °C/13%O ₂ /3 h	500 °C/20 min	0.084	
600 °C/13%O ₂ /17 h	500 °C/20 min	0.051	
600 °C/13%O ₂ /40 h	500 °C/20 min	0.048	
700 °C/0.5%O ₂ /19.5 h	500 °C/20 min	0.025	
800 °C/0.5%O ₂ /3 h	500 °C/20 min	0.032	0.018
950 °C/0.006%O ₂ /3 h	500 °C/20 min	0.042	
950 °C/0.05%O ₂ /3 h	500 °C/20 min	0.044	0.032
950 °C/0.5%O ₂ /3 h	500 °C/20 min	0.029	
950 °C/6.7%O ₂ /3 h	500 °C/20 min	0.022	0.003

factor of 2 between 0.006 and 6.7% O₂ whereas the Pt surface area deduced from XRD varies by approximately a factor of 5. The difference between trap and catalyst at large Pt/CO ratio, where the Pt/CO ratio of the catalyst is larger than that of the trap by a factor of 2, appears to reflect a real difference in particle size, according to the TEM observations, but the significance of their reversal at small Pt/CO ratio is not clear.

4. Discussion

As shown by the three methods used in this investigation, the presence of oxygen in the aging atmosphere dramatically accelerates the coarsening of Pt particles in

both model traps and supported catalysts that are aged at high temperature. This is likely due to vapor-phase transport of volatile oxides of Pt, one of the known mechanisms for Pt-particle coarsening [3]. Though previously recognized, the degree to which the aging atmosphere can affect loss of Pt surface area may not be fully appreciated in connection with NO_x trap technology. Detailed knowledge of this phenomenon should, in fact, be useful for achieving enhanced NO_x trap durability through the proper selection of engine control strategies.

As mentioned in the Introduction, the functional parameter space of the NO_x trap spans the relatively low-temperature range from approximately 200 to

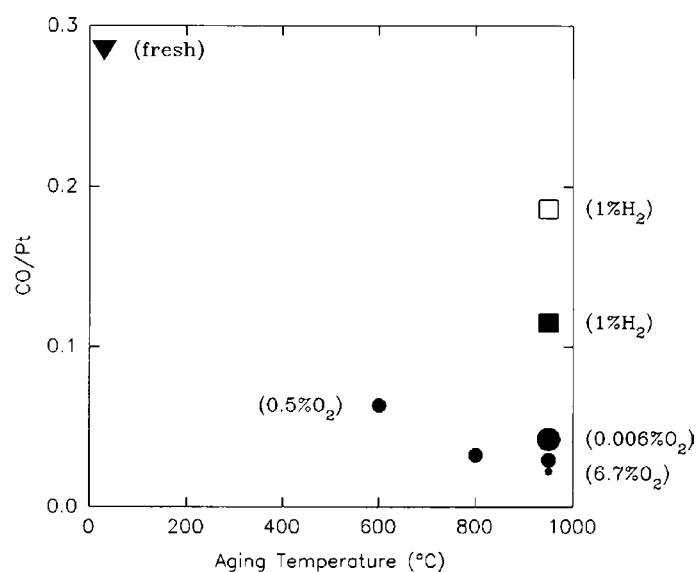


Figure 8. Selected CO chemisorption values as a function of aging temperature. Solid symbols are from trap samples, and the open symbol is from a Pt/Al₂O₃ catalyst sample.

500 °C, with somewhat higher temperatures occasionally required for removal of sulfates (though under rich conditions). Any loss of Pt surface area that takes place under these conditions is thus regarded as a necessary consequence of operation. The significantly greater loss that could occur at the much higher temperatures produced in certain situations, such as vehicle acceleration or high-speed driving, can be avoided, however, if the NO_x trap is protected from exposure to oxygen while hot. In practice, this is possible if the trap temperature and exhaust gas oxygen are monitored and used to provide the necessary engine air-to-fuel-ratio control.

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