Trapping Mobile Pt Species by PdO in Diesel Oxidation

Catalysts: Smaller is Better

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Abstract

Pt is an active catalyst for treatment of diesel exhaust emissions but is known to sinter and form large particles under oxidizing conditions. Pd is added to suppress the sintering of Pt and improve the performance of the Pt catalysts through the formation of a Pt-Pd alloy. In a previous study, using model catalysts, we demonstrated that mobile Pt species can diffuse on the surface and get trapped on PdO particles, leading to the formation of metallic Pt-Pd alloys in flowing air at 650 °C. In this work we explore the implications of this trapping phenomenon to powder catalysts. We physically mixed Pt/MgAl₂O₄ and PdO/La-Al₂O₃ catalyst powders and aged them at 800 °C in air. Mobile Pt species emitted from the Pt/MgAl₂O₄ migrated through the vapor phase and were trapped by PdO nanoparticles located on the La-Al₂O₃ support. Since the Pt moved from the MgAl₂O₄ support to the PdO, we infer that PdO is better at trapping Pt than the MgAl₂O₄ support. We also investigated the effect of PdO particle size on the trapping efficiency for Pt. It was found that small PdO particles were more effective, leading to smaller size of Pt-Pd particles as confirmed by electron microscopy, x-ray diffraction and reactivity for methane oxidation.

Keywords: Diesel oxidation catalyst; Bimetallic Pt-Pd; Trapping Pt; Particle size effect

1. Introduction

Pt is a precious metal (0.003 ppb in the earth's crust) and is among the most active elements for NO oxidation in diesel oxidation catalysts (DOCs). However, Pt nanoparticles (NPs) sinter when the catalysts are used at high temperature under oxidizing conditions.[1] The mechanism of sintering is Ostwald ripening,[2] which results in the loss of active surface area and drop in reactivity after use. Due to the high cost and low abundance of Pt, it is important to develop strategies to improve the durability of Pt catalysts by slowing the rate of sintering of Pt. We have recently demonstrated that the formation of a volatile oxide of Pt plays a significant role in the degradation of Pt catalysts when heated in air at 800 °C.[3] The high vapor pressure of Pt oxides is a significant contributor to the rates of catalyst sintering. A recent report suggests that MgAl_2O_4 as a support could help slow the rates of Pt sintering because it is possible to stabilize small Pt particles due to a strong affinity between Pt and the (111) facets of the MgAl_2O_4 support.[4] This previous study found that after aging in air at 800 °C, a significant fraction of the Pt was present in the form of large particles as detected by XRD. The authors reasoned this growth of Pt occurred because of the limited availability of suitable sites on the spinel to stabilize Pt. In this study we explore whether the presence of PdO might help to trap this mobile Pt that leads to the growth of large particles.

It is known that the addition of a second metal, for example Pd, leads to improvements in the durability of Pt catalysts, the mechanisms are still a subject of study.[1, 5] Pd has a very low vapor pressure under oxidizing conditions due to the formation of the stable oxide PdO and we see very little sintering of Pd only catalysts when heated in air at 800 °C.[3] We have also found that the presence of Pt helps to keep Pd in metallic form,[6] and the Pd helps to lower the rates of emission of Pt to the vapor phase.[3] When Pt nanoparticles were deposited on a planar model SiO_2 support as a separate phase, heating for only 2 minutes at 650 °C in air caused the formation of bimetallic PtPd particles.[7] This previous work demonstrates that Pt species are mobile and can be effectively trapped by PdO at high temperatures in air, forming bimetallic PtPd particles which are thermodynamically more stable.[7]

The migration and vapor phase transport of precious metals in automotive exhaust catalysts has been documented in the literature. Cavataio et al. [8] pointed out that trace amounts of precious metals were transported from Pt-based DOC catalysts to the SCR catalyst, negatively impacting the performance of the SCR catalyst. Yu-Yao and Kummer[9] reported that they were able to prepare low concentration precious metal catalysts via vapor phase transport from a metal foil to an alumina or ceria-alumina support. The transport of precious metals has also been found to lead to formation of alloys and bimetallic nanoparticles, as in the case of physically mixed Pt and Pd[10] catalysts and also Pt, and Rh catalysts[11]. In this previous work, the results were influenced by the catalyst formulation, for example the same nominal ratio of Pt and Pd gave very different extent of volatilization and transport. The role of particle size and morphology was not explicitly studied.

The objective of the present work is to investigate the trapping capability of PdO by physically mixing Pt/ MgAl_2O_4 and PdO/ $\text{La-Al}_2\text{O}_3$ catalysts, followed by aging in flowing air at 800 °C. Detailed STEM-EDX analysis was used to investigate the location and composition of Pt-containing particles. We separately aged the PdO/ $\text{La-Al}_2\text{O}_3$ to generate PdO particles of differing size, so the role of particle size on the trapping capability of Pt could be studied.

Methane oxidation was used as a probe reaction and the results show that smaller PdO crystallites are more effective at trapping the mobile Pt, which appears to move from the spinel phase via vapor phase transport and is captured on the PdO particles.

2. Experimental

Catalyst preparation and aging

La-alumina was obtained from W. R. Grace (MI-386), contained 4 wt.% La_2O_3 , and had a BET surface area of $176 \text{ m}^2\text{g}^{-1}$. MgAl_2O_4 spinel support (surface area: $132 \text{ m}^2\text{g}^{-1}$) was synthesized following the method reported in the literature.[4] The Pt/La- Al_2O_3 and Pt/ MgAl_2O_4 catalysts (1 wt.% Pt) were prepared by incipient wetness by using an aqueous solution of chloroplatinic acid (8 wt.% H_2PtCl_6). The as-prepared catalyst materials were calcined at 450°C for 5 h in flowing air.

The PdO/La- Al_2O_3 catalysts (2 wt.% Pd) were prepared by incipient wetness using a 10 wt.% palladium(II) nitrate solution in 10 wt.% nitric acid. This sample was subjected to different thermal pretreatment to vary the PdO particle size. The PdO/La- Al_2O_3 catalysts were calcined in air at 350°C (6h) and 800°C (10 h and 50 h, respectively). These catalysts were denoted as PdO/La- Al_2O_3 -1, PdO/La- Al_2O_3 -2 and PdO/La- Al_2O_3 -3, respectively.

To investigate the trapping capability of PdO on Pt with different PdO sizes, Pt/ MgAl_2O_4 was physically mixed with the above three PdO/La- Al_2O_3 catalyst with a mass ratio of 1:1, respectively. The physical mixture was then aged at 800°C for 10 h in flowing air (100 mL/min). For comparison purposes, monometallic Pt/ MgAl_2O_4 and Pt/La- Al_2O_3 catalysts were also aged at 800°C for 10 h in flowing air (100 mL/min).

Characterization

XRD patterns for the samples were recorded with a Rigaku Smart Lab diffractometer using Cu K_α radiation and a Ni filter. N_2 physisorption was performed on a Quantachrome Autosorb-1. Scanning electron microscopy (SEM) was performed on a Hitachi S-5200. High resolution transmission electron microscopy was performed using a JEOL 2010F microscope. The powders were deposited on holey carbon support films after being dispersed in ethanol.

Methane oxidation

Methane oxidation[12] was used as a probe reaction to investigate the reactivity of these catalysts. We selected this reaction since it operates under lean conditions, where metallic Pd easily transforms into PdO. Hence, the reaction is useful for determining the extent of Pt-Pd contact, since the bimetallic nanoparticles remain in metallic form under oxidizing conditions [6]. The catalytic activity for methane oxidation over the physical mixtures (Pt/ MgAl_2O_4 -PdO/La- Al_2O_3) catalyst was measured in a plug-flow quartz tube reactor. A powder sample of 20 mg was placed in the middle of the reactor. Gas flow rates were measured by mass flow controllers. Reaction products were analyzed by an online micro-GC (Agilent 490). The reactant gas mixture contained 2% CH_4 , 5% O_2 and He as balance. Light-off

measurements were carried out with a heating rate of 2 K min⁻¹ from 100 °C to 600 °C, with aGHSV of 30000 h⁻¹.

3. Results and discussion

3.1. Sintering behavior of Pt nanoparticles supported on MgAl₂O₄ and La-Al₂O₃ at high temperature in oxidation conditions

The sintering behavior of monometallic Pt nanoparticles supported on MgAl₂O₄ and La-Al₂O₃ was first investigated. The XRD patterns of Pt supported on MgAl₂O₄ and La-Al₂O₃ before and after aging are shown in Fig. 1. No diffraction peaks corresponding to Pt nanoparticles was found on the XRD patterns of the fresh Pt catalysts, indicating that Pt NPs are highly dispersed on the support. However, the sharp diffraction peaks corresponding to Pt crystallites are observed on the XRD patterns of Pt/MgAl₂O₄ and Pt/La-Al₂O₃ catalysts after aging. Calculation based on the Scherrer equation indicated that the average crystallite sizes of Pt after aging for both of the catalysts are larger than 500 nm. This means that the Pt catalysts on MgAl₂O₄ and La-Al₂O₃ sintered significantly suggesting that these supports do not stabilize Pt when exposed to high temperatures under oxidizing conditions.

Fig. 1. XRD patterns of Pt nanoparticles supported on La-Al₂O₃ and MgAl₂O₄ before and after aging at 800 °C for 10 h in air. Scherrer analysis indicates the particle size of Pt > 500 nm, i.e., too large to be accurately determined by this technique.

The representative electron microscope images (SEM/TEM/STEM) of Pt/La-Al₂O₃ catalyst before and after aging in air are shown in Fig. 2. The Pt nanoparticles on the

Pt/La-Al₂O₃ catalyst before the high temperature treatment are small and the Pt sizes are in the range of 1-5 nm before aging (Fig. 2a). However, after aging at 800 °C in air, micrometer-scale Pt particles (1-4 μm) are formed (Fig. 2b and c). These results confirm the observations of the Pt/La-Al₂O₃ via XRD indicating the severe sintering seen after aging the catalysts in flowing air for 10 hours.

Fig. 2. Representative electron microscope images of Pt nanoparticles supported on La-Al₂O₃: (a) HAADF-STEM and (b) SEM image of as-prepared 1 wt.%Pt/La-Al₂O₃; (c) TEM image of the same catalyst after aging at 800 °C for 10 h in air.

The representative TEM/STEM images of Pt/MgAl₂O₄ catalyst before and after aging in air are shown in Fig. 3. The Pt nanoparticle sizes on the Pt/MgAl₂O₄ catalyst are less than 1 nm in diameter before aging (Fig. 3a). After aging at 800 °C in air, we see micrometer-scale Pt particles (0.5-1 μm) on the Pt/MgAl₂O₄ catalyst (Fig. 3b and c). However, we note that some Pt particles with size of < 1 nm still remain on the spinel support (Fig. 3d). Based on the distribution and density of these small Pt particles on spinel, and the morphology of the underlying support, we cannot infer the surface facets that might stabilize these small particles. The earlier study of Li et al.[4] concluded that the small Pt particles were present on the the MgAl₂O₄ (111) facets. The majority of the Pt is present in the form of large particles on the Pt/MgAl₂O₄ catalyst and we conclude that this catalyst also sintered significantly after aging under oxidizing conditions.

Fig. 3. Representative electron microscope images of Pt nanoparticles supported on MgAl_2O_4 : (a) fresh 1 wt.%Pt/ MgAl_2O_4 ; (b), (c) and (d) 1 wt.%Pt/ MgAl_2O_4 after aging at 800 °C for 10 h in air (arrows showing the Pt nanoparticles).

3.2. Preparation and characterization of PdO/La- Al_2O_3 catalysts with different PdO particle sizes

PdO/La- Al_2O_3 catalysts with different PdO particle sizes were prepared by varying the pretreatment of the catalyst. The XRD patterns of the three catalysts are shown in Fig. 4. The diffraction peaks corresponding to PdO are presented and the main phases on the three catalysts are PdO and La- Al_2O_3 . The sharper the diffraction peak of PdO, the larger are the PdO nanoparticles (Fig. 4b).

Fig. 4.(a) XRD patterns of Pd/La- Al_2O_3 with different PdO particle sizes; (b) the expanded XRD patterns of three PdO/La- Al_2O_3 over 30-38 ° (shaded rectangle in a).

Representative STEM images of the PdO/La-Al₂O₃ catalysts with different PdO particle sizes are shown in Fig. 5. The PdO/La-Al₂O₃-1 presents the PdO particles with around 1 nm (Fig. 5a). The PdO/La-Al₂O₃-2 showed that the PdO particle sizes are 5-10 nm and these particles have rough irregular surface consistent with the images seen from oxide particles (Fig. 5b). The PdO particle sizes on PdO/La-Al₂O₃-3 are 10-200 nm, much larger than those in the previously described samples (Fig. 5c and d).

Fig. 5. STEM images of PdO/La-Al₂O₃ with different PdO particle sizes: (a) PdO/La-Al₂O₃-1; (b) PdO/La-Al₂O₃-2; (c) and (d) PdO/La-Al₂O₃-3.

3.3. Characterization of physical mixtures (Pt/MgAl₂O₄+PdO/La-Al₂O₃) after aging at 800 °C in air

The XRD patterns of three physically mixed samples after aging at 800 °C in air are shown in Fig. 6. It can be seen that after aging at 800 °C for 10 h the main phases for the three samples include PtPd, PdO and MgAl₂O₄. Moreover, it is noteworthy that the diffraction peak corresponding to PtPd becomes sharper with the increase of initial PdO particle size, indicating that larger PdO leads to the formation of larger PtPd particles after mixing and aging. We also see the absence of a metallic Pt peak, suggesting that most of the Pt migrated to the alumina support and was converted to the Pt-Pd alloy.

Fig. 6. XRD patterns of three physical mixtures after aging at 800°C for 10 h in air.

Rietveld refinement analysis confirmed that the catalyst with smaller initial PdO crystallite size also led to smaller metallic PtPd crystallites (Table 1). With the increase in initial PdO particle size, the average crystallite size of PtPd particles increased. We also see an increase in the area of the Pt-Pd peak relative to the prominent reflection at $2\theta=37^\circ$ which serves as an internal standard. Likewise, we see less residual PdO in the sample after the aging of the physically mixed samples.

Table 1

X-ray diffraction analysis data of three physical mixtures after aging at 800 °C for 10 h in air

Catalyst	Pd/Pt atomic ratio	Initial PdO size (nm)	Final particle size (nm)		Diffraction peak area ratio	
			PtPd	PdO	$A_{\text{PtPd}(111)}/A_{\text{spinel}(311)}$	$A_{\text{PdO}(101)}/A_{\text{spinel}(311)}$
Pt/MgAl ₂ O ₄ +PdO/La-Al ₂ O ₃ -1	3.67	< 5	19.0	9.6	0.14	0.25
Pt/MgAl ₂ O ₄ +PdO/La-Al ₂ O ₃ -2	3.67	5	21.8	10.2	0.16	0.24
Pt/MgAl ₂ O ₄ +PdO/La-Al ₂ O ₃ -3	3.67	12	45.1	11.4	0.20	0.21

Representative STEM images of the physical mixtures after aging at 800 °C for 10 h in air are shown in Fig. 7. Large bimetallic PtPd particles (50-100 nm) are formed on all the physically mixed samples after aging and all these bimetallic PtPd particles are supported on La-Al₂O₃, rather than MgAl₂O₄, evidenced by STEM-EDX. However, there are very few of the large PtPd particles seen on Pt/MgAl₂O₄+ PdO/La-Al₂O₃-1 and the size of the PtPd particles seen on Pt/MgAl₂O₄-PdO/La-Al₂O₃-1 is comparatively smaller than on the other two samples. Furthermore, it is observed that these large bimetallic particles have smooth surfaces characteristic of a metallic phase, in contrast the oxide phase is very rough and irregular in shape as also seen previously.[7]

Fig. 7. STEM images of particles on the physical mixtures after aging at 800 °C for 10 h: (a) and (b) Pt/MgAl₂O₄-PdO/La-Al₂O₃-1; (c) Pt/MgAl₂O₄-PdO/La-Al₂O₃-2; (d) Pt/MgAl₂O₄-PdO/La-Al₂O₃-3.

3.4. Morphology and composition of PdO and PtPd particles revealed by STEM-EDX

The morphology and composition of the large particles in the air-aged physical mixtures was analyzed by STEM-EDX, and the STEM images and EDX results are shown in Fig. 8. It can be seen that the large particles contained both Pt and Pd, indicating that the Pt migrated to the PdO and was trapped there. The detailed spot EDX analysis showed that the composition of the large particles is not uniform, which means that the large particles are not single phase, explaining the discrepancy between XRD and TEM. Based on the composition and morphology of different locations on the large particles, we present a schematic illustration of the structure of these large particles in the inset. These results indicated that the large bimetallic PtPd have formed within the PdO, which now surrounds the metallic phase.

Fig. 8. STEM images and EDX analysis of physically mixed sample of Pt/MgAl₂O₄-PdO/La-Al₂O₃ after aging at 800 °C for 10 h in air (the inset is a schematic illustration of the locations of PtPd (light violet))

and PdO(gold) particles).

3.5. Methane oxidation as a probe reaction

In order to investigate the trapping efficiency of PdO on Pt for the mixed three samples, a catalytic reaction was chosen to probe the active surface area of the Pt-Pd phase. We cannot use CO oxidation since it would cause reduction of the PdO to Pd metal. Methane oxidation performed under lean conditions will not lead to any reduction of the PdO or to oxidation of the Pt-Pd phase [13, 14]. The methane activity as a function of temperature for the aged Pt/MgAl₂O₄ and the aged catalyst physical mixtures (Pt/MgAl₂O₄-PdO/La-Al₂O₃-1, Pt/MgAl₂O₄-PdO/La-Al₂O₃-2, Pt/MgAl₂O₄-PdO/La-Al₂O₃-3) is shown in Fig. 9. Fig. 9a shows the corresponding light-off curves for methane oxidation over PdO/La-Al₂O₃ before and after H₂ reduction at 250 °C for 6 h. From the curves, it can be seen that metallic Pd⁰ phase is more active than the PdO phase in methane oxidation at low temperatures. The superior activity of metallic Pd over PdO at low temperatures for methane oxidation has been reported in previous studies [15, 16], and it may be related to the unique sites created in coexisting Pd metal and oxide domains [17-20]. At high temperatures the Pd transforms into PdO which then constitutes the catalytically active phase [21]. The light-off curves of three physical mixtures (Fig. 8b and c) in methane oxidation showed that higher activity was obtained for the physically mixed sample when PdO/La-Al₂O₃ catalyst with smaller PdO particle size used as a trap. Since the aged Pt/MgAl₂O₄ presented negligible methane oxidation activity, it was concluded that the activity in these samples was mainly due to the presence of PdO and PtPd phases. Based on the XRD results above, all the three mixtures consisted of similar sized PdO after aging at 800 °C for 10 h. Therefore, the differences in activity of the three catalyst must be due to the differences in the surface area of the metallic Pt-Pd. Since the same weight of catalyst was used for the runs reported in Fig. 8, the physically mixed samples contain only half as much PdO in 8(b) as in 8(a). We conclude that the sample with smaller initial PdO particles provided higher methane oxidation activity due to the smaller crystallite size of Pt-Pd.

Fig. 9. Light-off curves for methane oxidation for catalysts (ramping rate: 2 °C/min): (a) PdO/La-Al₂O₃ catalyst before and after reduction at 250 °C in H₂ for 6 h; (b) three physical mixtures of 1 wt.% Pt/MgAl₂O₄ and 1 wt.% PdO/La-Al₂O₃ after aging at 800 °C in air for 10 h.

4. Summary and Conclusions

These results provide insight into the role of PdO in slowing the rate of sintering of Pt diesel oxidation catalysts. We show that the Pt sinters into large particles on both the

MgAl₂O₄ and La-Al₂O₃ supports, leading to formation of sub-micron sized Pt particles. When PdO nanoparticles were present in the catalyst, they were able to trap Pt even when these two components were present in physically different powders. It is clear that the MgAl₂O₄ support was not able to completely 'hold on to' Pt during heating in flowing air. Instead the Pt was transported through the vapor to the PdO phase which was present on the La-Al₂O₃ support. We also demonstrated that PdO crystallite size plays a role, smaller initial particles resulted in smaller PtPd particles with larger amounts of PdO left behind on the support. The PtPd particles that are formed are present in the vicinity of excess PdO which has not reacted with the Pt after high temperature aging. The high Pd:Pt ratio in the metallic core of the bimetallic particles suggest a fairly broad range of compositions where metallic particles of Pt:Pd may be stable under oxidizing conditions. The precise compositions of the phase stability envelope could not be determined in this study due to overlap with the PdO phase. The smaller Pt-Pd crystallite size after aging (~20 nm) contrasts with the Pt particle size on the La-Al₂O₃ and MgAl₂O₄ phase (>500 nm) after similar aging in air. In summary, our results illustrate an important role played by PdO which acts as a trap helping to slow the sintering of Pt in PtPd diesel oxidation catalysts. The formation of the metallic Pt-Pd phase leads to the observed enhancement in methane oxidation activity compared to PdO.

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Graphical abstract