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Palladium-Based Catalysts with Improved Sulphur Tolerance for Diesel-Engine Exhaust Systems

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Elma van der Lingen

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Abstract Palladium-based catalysts have been developed for the diesel exhaust system with an emphasis on their sulphur tolerance during the simultaneous oxidation of CO and HC. Promising materials include Au–Pd–Pt, Co–Pd–Pt and Ni–Pd–Pt supported on Al₂O₃ or TiO₂ and Pd–Pt/MoO₃–Al₂O₃ with the Al₂O₃ support modified with MoO₃ monolayer.

Keywords Palladium · Sulphur tolerance · Diesel exhaust

1 Introduction

Until full transition is made to a hydrogen economy and zero emission of greenhouse gases, strict emission regulations must be met. Excluding carbon dioxide pollution, automobile emission abatement is primarily concerned with carbon monoxide (CO), unburnt hydrocarbons (HC), nitrogen oxides and particulate matter, especially carbonaceous particulates from diesel engines [1]. Ricardo [2] has projected a global increase in the demand for diesel driven vehicles soon, but a Pd-based diesel oxidation catalyst (DOC) cannot be used as it is intolerant to sulphur. Pd-rich systems favour hydrogen adsorption by forming the metal hydride, and the hydrogen is more strongly adsorbed by sulphur than Pd itself [3]. Therefore, in addition to maintaining active, highly dispersed and thermally stable nano-particles, catalyst poisoning by formation of metal-hydrogen and metal-sulphur bonds must be avoided [4].

Besides, the catalytic efficiency of Pt-only autocatalysts drops noticeably after operating at high temperatures due to sintering, but Pd–Pt alloys are comparatively less vulnerable [5]. Skoda et al. [6] showed that synthesis procedure can modify surface properties of alloys and catalytic properties of materials with similar composition can be customised. Micheaud et al. [7] confirmed that different preparation methods for Pd–Pt/Al₂O₃ resulted in various morphologies and during reaction, temperature variation created surface enrichment of Pd as PdO. Moreover, dissolved elements migrating from the bulk to the surface of binary alloys and a chemisorbing gas can modify the surface further. It is now commonly accepted that the best way to improve sulphur resistance of noble metal catalysts is to modify their electronic properties by creating electron deficient species either by bimetallic interaction or by metal interaction with acid sites on the support [8]. A *Süd Chemie* patent [9] indicates the inclusion of a vanadium-based sulphur oxidation suppressant in its Pt autocatalyst. We therefore present potential sulphur-tolerant Pd-based DOCs.

2 Experimental Methods

Catalysts were prepared by co-impregnation, oven dried in air at 110 °C for 16 h, calcined in flowing air at 500 °C for 4 h, reduced in 30% H₂ balanced with N₂ at 500 °C for 1 h and then aged in a gas stream of 10% H₂O and 50 ppm SO₂ in a balance of air at 500 °C for 24 h. The catalysts were tested for concurrent CO and propane oxidation in a purpose-built micro-reactor operated from room temperature to 600 °C under an artificial gas mixture simulating realistic diesel exhaust-gas conditions but without particulate matter, comprising of 10% H₂O, 10% CO₂, 12% O₂ with

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350 ppm CO, 500 ppm NO, 500 ppm C₃H₈ and 20 ppm of SO₂ in a balance of nitrogen flowing at a gas hourly space velocity of 30,000 h⁻¹ [10].

3 Results and Discussion

3.1 Catalyst Activity

Fresh catalysts exhibited the highest activity. For CO oxidation, Pt-only catalysts were the best, followed by Pd–Pt alloys, and lastly the Pd-only formulation. Significant shifts of the light-off curves to higher temperatures after ageing proved the low sulphur tolerance of Pd/Al₂O₃ as Fig. 1 shows. It was established early that the effect of sulphur was pronounced in Pd-poisoning. For example, in CO oxidation the temperature at 50% CO conversion (T_{50}) of fresh Pd–Pt/TiO₂ catalyst was 145 °C. The sample aged in steam only, shifted the T_{50} value to 165 °C while that of the sample aged in SO₂ shifted to 180 °C, leading to the conclusion that the effect of sulphur was greater, far and above that of thermal ageing. With equal metal weight loading, the most active and resilient catalyst for HC oxidation was 0.5wt%Pd–0.5wt%Pt/Al₂O₃ bimetallic, but the ternary systems performed even much better by operating in the cold start regime of below 300 °C [11]. Figure 2 presents evidence for low temperature CO light-offs, particularly at room temperature and for HC oxidation T_{50} values of the aged Pd/Al₂O₃, Pd–Pt/Al₂O₃ and Au–Pd–Pt/Al₂O₃ catalysts shifted from 380° to 370° to 290 °C, respectively, signifying the synergistic effect of the metals. Active and sulphur-tolerant materials supported on Al₂O₃ or TiO₂ included Au–Pd–Pt [12], Co–Pd–Pt and Ni–Pd–Pt, besides Pd–Pt/MoO₃–Al₂O₃ catalyst where the modified

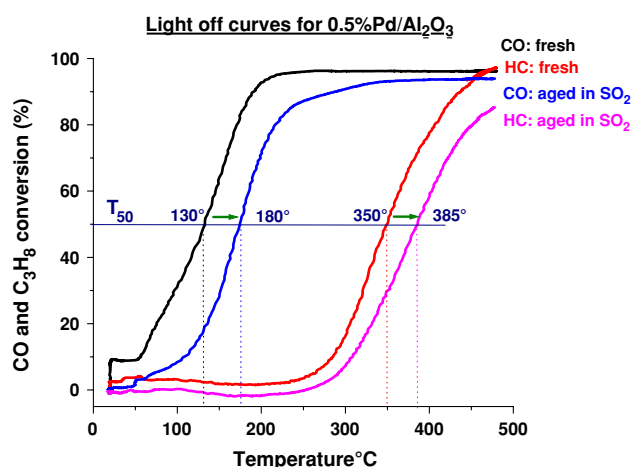


Fig. 1 Light-off curves for CO and HC oxidation using a 0.5%Pd/Al₂O₃ catalyst

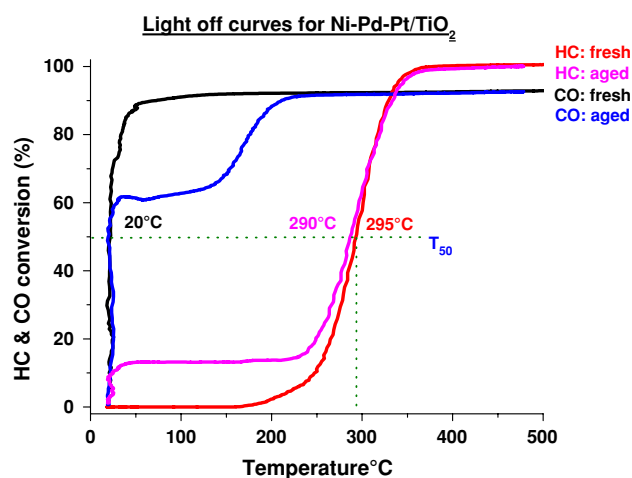


Fig. 2 Light-off curves for CO and HC oxidation using Ni–Pd–Pt/TiO₂ catalyst

Al₂O₃ support incorporated MoO₃ monolayer coverage. Table 1 gives a summary of the T_{50} values and their corresponding shifts (ΔT_{50}) after exposure to SO₂. The presence of Pt seemed to enhance catalytic activity and incorporating nickel proved beneficial as one, it may act as a scavenger of sulphur, believed to be stored as NiS under rich conditions and released as SO₂ in the lean-burn cycle [1] and two, it was observed that better alloy formation existed in the nickel-containing samples. In addition, nickel-containing samples were comparably more active than Pd-only formulation as they did not show sintering after thermal ageing, which implied that probably nickel had a role of preserving the crystallites from phase transformation, change of morphology and possibly the alloy composition. However, the possible formation of Ni(CO)₄ at ambient temperatures makes some of these materials highly hazardous with potential emission in exhaust fumes, and in some countries prospective prohibition of Ni-containing auto catalysts by legislation is high. Ni(CO)₄ is classified in Group 1 as a possible human carcinogen but nickel alloys are placed in Group 2B because there is inadequate evidence [13]. Nevertheless, it was observed that both the Ni–Pd–Pt and Co–Pd–Pt catalysts were so active that they would give almost total CO oxidation at room temperature.

It is for this reason we believe that proper alloy formation between metals in the ternary systems is imperative in order to prevent the development of carbonyls. Metal segregation as found in some samples is unattractive because it would promote carbonyl formation. We however, submit that the strong inter-metallic bonds in the ternary systems would retain the nickel within the alloys and significantly reduce CO reaction with the nickel to form metal carbonyls.

Table 1 The T_{50} shifts and ΔT_{50} values of the Al_2O_3 and TiO_2 -supported catalysts

Catalyst	CO oxidation (T_{50})		ΔT_{50}	HC oxidation (T_{50})		ΔT_{50}
	Fresh ($^{\circ}\text{C}$)	Aged ($^{\circ}\text{C}$)		Fresh ($^{\circ}\text{C}$)	Aged ($^{\circ}\text{C}$)	
2% Pd–MoO ₃ /Al ₂ O ₃	145	210	65	255	420	165
Pd–Pt–MoO ₃ /Al ₂ O ₃	25	65	40	345	275	–70
Au–Pd–Pt/Al ₂ O ₃	25	35	10	390	290	–100
Co–Pd–Pt/Al ₂ O ₃	25	20	–5	300	315	15
Ni–Pd–Pt/Al ₂ O ₃	35	25	–10	335	285	–50
Au–Pd–Pt/TiO ₂	35	190	155	265	275	10
Co–Pd–Pt/TiO ₂	20	20	0	310	285	–25
Ni–Pd–Pt/TiO ₂	20	20	0	295	290	–5

Another approach to improving the sulphur tolerance of Pd-based catalysts is by the metal interaction with acid sites on the support since it is thought that the SO_2 being acidic in nature will not find repose on acidic surfaces. We therefore developed a novel method of depositing a monolayer of molybdena (MoO_3) on Al_2O_3 support, upon which the precious metals were impregnated [14]. The Pd-only formulation performed dismally with very high T_{50} values for both CO and HC oxidation especially after ageing. However, with Pd–Pt bimetallic deposited on the MoO_3 monolayer, the catalytic performance and particularly the sulphur tolerance significantly improved. For example, in CO oxidation the T_{50} values of Pd–MoO₃/Al₂O₃ improved from 210 $^{\circ}\text{C}$ to 65 $^{\circ}\text{C}$ with Pd–Pt–MoO₃/Al₂O₃ while in HC oxidation the T_{50} value of Pd–MoO₃/Al₂O₃ dropped from 420 $^{\circ}\text{C}$ to 275 $^{\circ}\text{C}$ in Pd–Pt–MoO₃/Al₂O₃ bimetallic. This suggests that a combination of both inter-metallic interaction and surface acidity improves the sulphur tolerance of these materials considerably.

3.2 Catalyst Characterisation

3.2.1 BET Surface Area

Catalyst deactivation was attributed largely to the effect of sulphur and to a lesser extent, thermal ageing. A limited loss of low-temperature catalyst activity was linked to physical degradation of the support. Micro-pore closure rendered some active sites inaccessible for reaction. There was a substantial drop in the surface area, see Table 2.

Table 2 The BET specific surface areas for the fresh and aged catalyst

Catalyst	Bulk support	Fresh catalyst	Aged catalyst
Ni–Pd–Pt/Al ₂ O ₃	200	190	172
Ni–Pd–Pt/TiO ₂	51	46	41

3.2.2 Temperature Programmed Reduction (TPR)

TPR analysis showed that Pd in fresh, calcined and reduced Au-containing samples adsorbed H_2 , a phenomenon that was absent in well alloyed Ni–Pd–Pt systems, see Fig. 3. Negative peaks at higher temperatures confirmed desorption of H_2 and hence symptomatic of segregation of the Pd species [15], or formation of Pd-rich phases in the Au–Pd–Pt systems, validating our suspicion that the samples were poorly alloyed.

3.2.3 X-Ray Diffraction (XRD)

Powder XRD patterns of Au–Pd–Pt/Al₂O₃ catalysts showed that with addition of metal alloys on the bulk support, diffraction peaks of metallic Au emerged at 38.5, 44.5, 64.5 and 77.5° [2 θ] angle [16], while the peak at 33.5° [2 θ] angle in the aged catalyst was attributed to palladinite (PdO), see Figs. 4 and 5. It is believed that segregation of Pd as PdO in Au-containing catalysts resulted in a comparatively depressed low-temperature activity and lower sulphur tolerance. Prominent Au reflection peaks in Au–Pd–Pt/Al₂O₃ indicated poorer alloy formation in comparison to the Au–Pd–Pt/TiO₂ catalyst. Conversely, the Ni–Pd–Pt/Al₂O₃ catalyst showed superior alloy formation, with minute quantities of PdO showing from the diffraction peak at 34.5° [2 θ] angle in the aged catalyst only. Both the fresh and aged samples indicated diffraction peaks at 40 and 47° [2 θ] angles, typical of metallic Pt. In our systems, the conspicuous absence of the (210) reflection peak of palladium sulphide (PdS) at around 31° [2 θ] angle led to the conclusion that catalyst deactivation arose from the lack of proper metallic interaction as a result of PdO formation in preference to the formation of PdS as a catalyst poison.

Phase diagrams [17] specify that Au–Pd and Pd–Pt binary systems are totally miscible below 1000 $^{\circ}\text{C}$, giving substitutional alloys and sometimes with solid reactions

Fig. 3 TPR profiles for Ni–Pd–Pt/TiO₂ and Au–Pd–Pt/TiO₂ catalysts

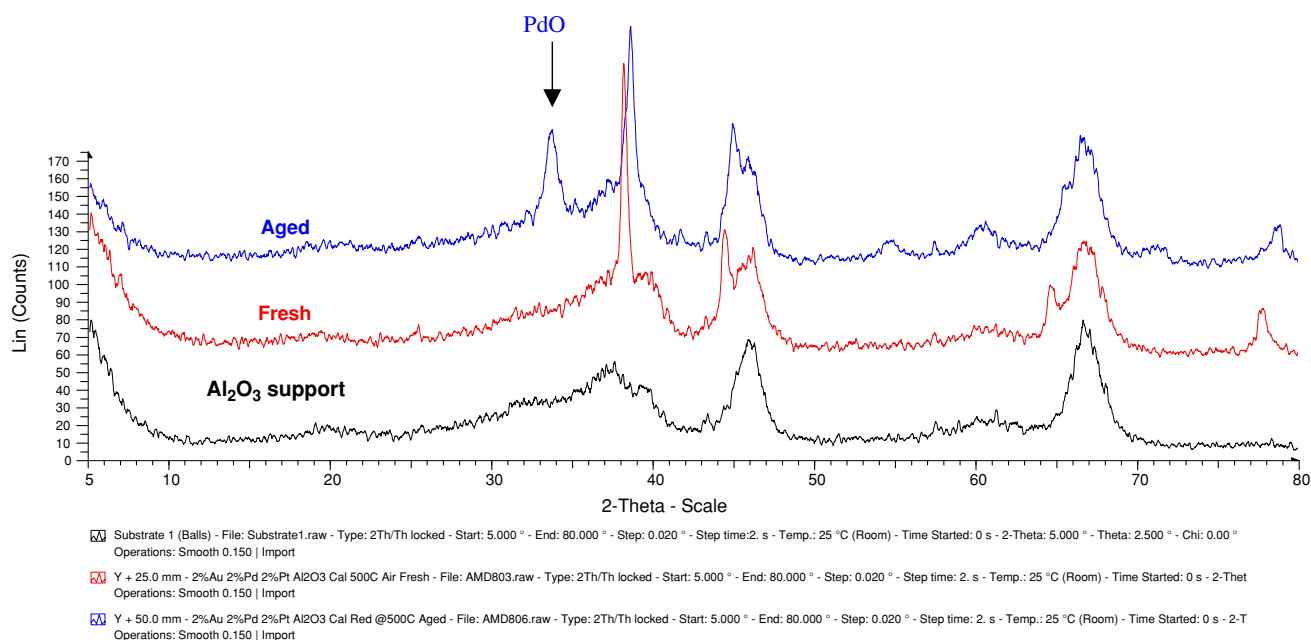
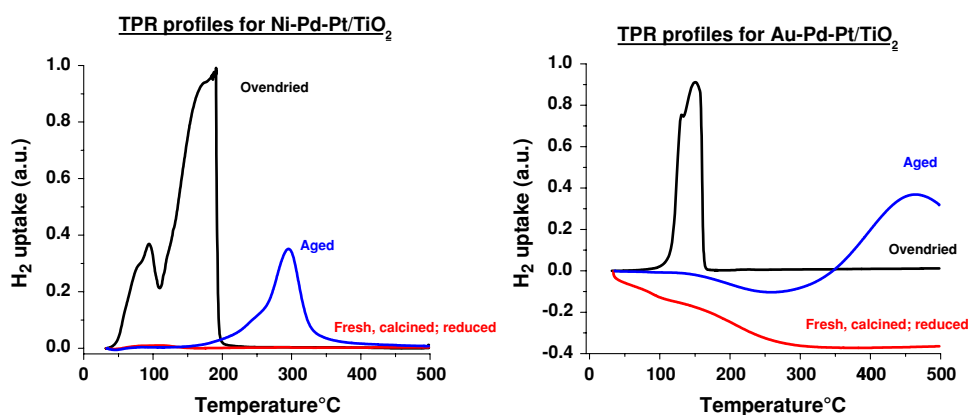


Fig. 4 P-XRD patterns of Au–Pd–Pt/Al₂O₃ catalysts with notable PdO in aged catalyst

producing Au₃Pd and AuPd₃ compounds. However, Au and Pt are partially miscible depending on temperature and composition. For example, below our calcination temperature of 500 °C they are totally immiscible unless the Pt composition in Au is below 15%. Thermodynamically, we could probably explain for the Au and Pd segregation in Au–Pd–Pt catalysts as shown by XRD. Due to the Au: Pd: Pt ratio of 1:1:1, there was some degree of immiscibility leading to poor alloy formation. On the other hand, for the Ni–Pd–Pt ternary system, all their various binary systems indicate that Ni–Pd, Ni–Pt and Pd–Pt are totally miscible below 1000 °C also giving mainly single phase alloys and sometimes producing some Ni₃Pt and NiPt compounds. It is therefore clear that all compositions in the Ni–Pd–Pt

ternary system were miscible and consequently leading to proper alloy formation.

3.2.4 High Resolution Scanning Electron Microscope (HRSEM)

The XRD patterns of fresh and aged Au–Pd–Pt catalysts were considerably different due to crystallite growth in the aged samples, which developed new XRD reflection peaks, also exemplified by the HRSEM micrographs in Figs. 6 and 7. In contrast, the HRSEM analysis of Ni–Pd–Pt catalysts did not show any significant sintering after ageing as shown in Figs. 8 and 9. All the characterisation techniques used, that is, HRSEM, TPR and XRD analysis attested to

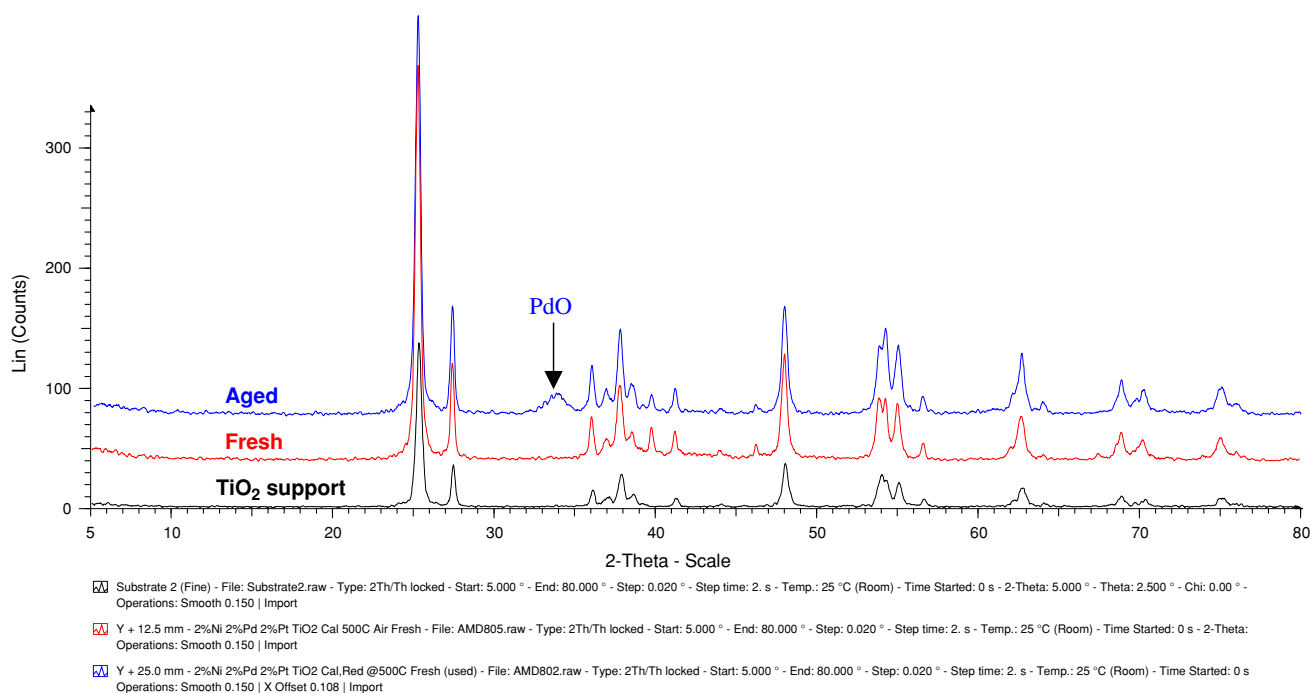


Fig. 5 P-XRD patterns of Ni–Pd–Pt/TiO₂ showing minute quantities of PdO in the aged catalyst

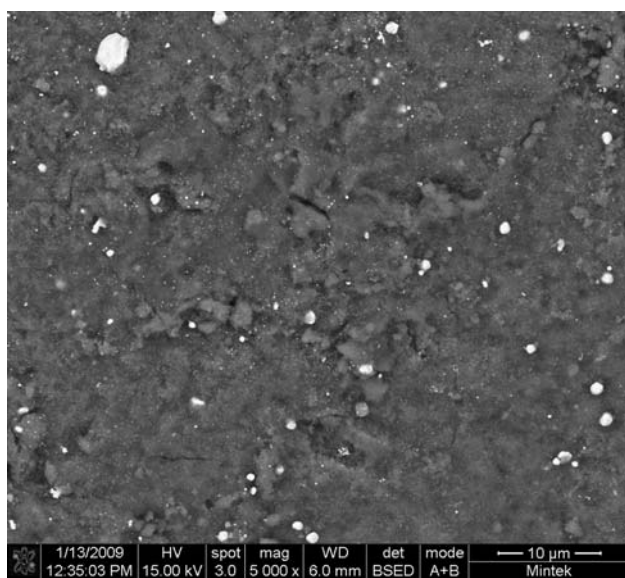


Fig. 6 HRSEM backscattered image of fresh Au–Pd–Pt/TiO₂ catalyst; mag. 5000×

the fact that Ni–Pd–Pt produced better and more robust alloys than Au–Pd–Pt, which portrayed segregation of the metals in the samples.

4 Conclusion

Poisoning of automotive catalysts by sulphur is a complex phenomenon, involving the noble metals, washcoat

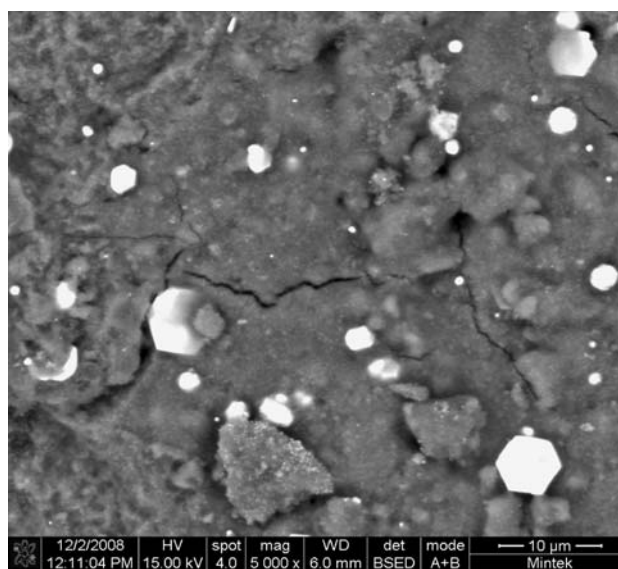


Fig. 7 HRSEM backscattered image of aged Au–Pd–Pt/TiO₂ catalyst; mag. 5000×

components, operating conditions such as temperature and the exhaust gas composition. In our findings, deactivation of Pd-only catalysts was attributed largely to the effect of sulphur but well-alloyed Pd-ternary systems showed improved performance. For simultaneous CO and HC oxidation, the most active and sulphur tolerant catalysts were Au–Pd–Pt, Co–Pd–Pt and Ni–Pd–Pt supported on bulk Al₂O₃ or TiO₂ besides Pd–Pt–MoO₃/Al₂O₃. Supporting evidence from TPR and XRD analysis showed that

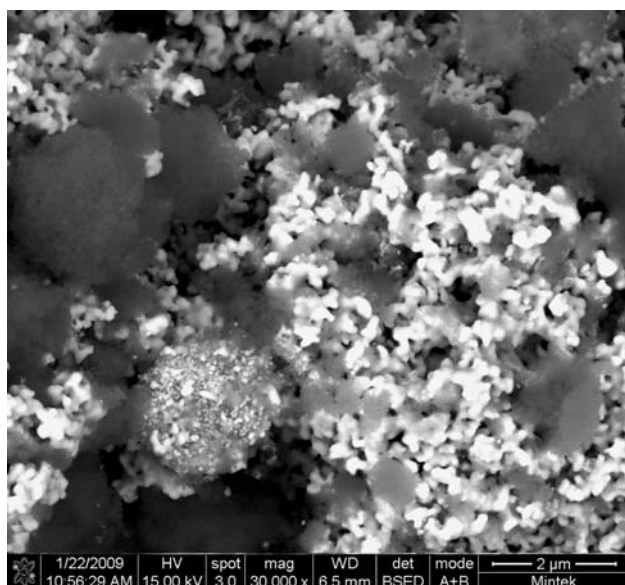


Fig. 8 HRSEM backscattered image of fresh Ni–Pd–Pt/TiO₂ catalyst; mag. 30000×

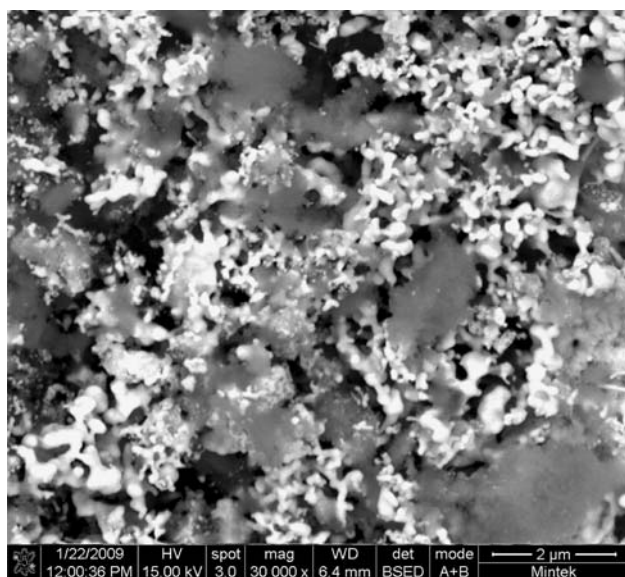


Fig. 9 HRSEM backscattered image of aged Ni–Pd–Pt/TiO₂ catalyst; mag. 30000×

segregation of Pd as PdO was the origin of catalyst deactivation stemming from poor alloy formation. BET surface area analysis indicated that a drop in surface area leads to a significant loss in low-temperature catalyst activity.

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