

Studies of aging mechanisms of aftertreatment systems for diesel engines with the aim of developing methods for accelerated aging

Introduction

To meet the demand for heavy- and light-duty diesel vehicles on expansive markets while complying with current and future emission standards, it is necessary to reinsure the long-livety of the exhaust after-treatment techniques. Loss of catalytic performance may be associated with environmental as well as economical consequences. To aid the development in improving exhaust control components, such as the diesel oxidation catalyst (DOC), and optimise the use of raw materials, methods for accelerating the deactivation process are used. Catalysts can be aged in an engine-bench setup to simulate conditions in the field and thereby shorten the test procedure. The most resource efficient approach relies on using synthetic aging procedures to achieve such effect, which however has received limited attention in the field of DOCs. In order to establish and benefit from such procedure it is necessary to address critical sources of deactivation of vehicle- and lab-aged catalysts and determine to what extent the aging process can be correlated. Hence, this project comprises studies where a number of methods are used to characterise the performance and deactivation of model and commercial DOC subjected to aging in both real and synthetic environments [1, 2, 3]. Furthermore, within the scope of the project, fundamental processes behind catalyst deactivation have been studied, such as sintering mechanisms on well-defined model Pt catalysts, which are summarised below.

Results

Deactivation of model diesel oxidation catalysts

The purpose of this part of the study was to identify critical conditions for which significant degradation of catalyst performance occurs, with focus on chemical and thermal effects.

The actual washcoat compositions, amount adsorbed/desorbed C₃H₆, BET surface area, CO light-off temperature and Pt dispersion for each of the studied (fresh) catalysts are summarised in Table 1. The values correspond to the average characteristics of six samples prepared of each catalyst type (A)-(D). Variations in washcoat composition, e.g. the overall higher Al₂O₃ content in the Pt-Al₂O₃ catalyst, are to be expected due to difficulties in applying the exact same amount of washcoat on each catalyst. Adding ZSM-5 to the washcoat results in significant C₃H₆ adsorption in comparison to samples without ZSM-5, indicating that only small amounts are stored on the alumina. The commercial catalyst has a somewhat lower hydrocarbon storage capacity. The fraction of C₃H₆ that desorbs from TPD is roughly the same for the ZSM-5/Pt-Al₂O₃ and ZSM-5/Al₂O₃ catalysts, and slightly less for the commercial catalyst. Adding ZSM-5 does also increase the BET surface area. As for the remaining characteristics, the CO light-off temperature and Pt dispersion are similar, apart from the very low light-off temperature for the commercial catalyst.

TABLE 1

Characteristic data of the four catalysts when in the fresh state, showing mean values from six samples of each catalyst and corresponding standard deviation

	A: ZSM-5/Pt-Al ₂ O ₃	B: Pt-Al ₂ O ₃	C: ZSM-5/Al ₂ O ₃	D: Commercial
Al ₂ O ₃ (mg)	344 ± 16	386 ± 65	366 ± 21	n.a.
Pt (mg)	3.5 ± 0.2	3.9 ± 0.7	-	n.a. ^a
ZSM-5 (mg)	232 ± 11	-	244 ± 14	n.a.
C ₃ H ₆ adsorbed	930 ± 90	70 ± 40	960 ± 70	550 ± 20
C ₃ H ₆ desorbed (μmol/g _{washcoat})	520 ± 60	0	540 ± 60	260 ± 10
BET surface area (m ² /g _{washcoat})	285 ± 16	218 ± 16	273 ± 39	212 ± 7
T ₅₀ CO (°C)	103 ± 11	98 ± 9	-	7 ± 0
Pt dispersion (%)	53.2 ± 13.7	51.0 ± 7.5	-	49.7 ± 2.8

n.a. : Not available, ^a 1.1 wt.-% of the washcoat

Adding SO₂ to the synthetic exhaust has a clear impact on the CO light-off temperature as well as the Pt dispersion, as demonstrated in Fig. 1a-b. Results are obtained after oxidation and reduction at 500°C. Fig. 1a shows the CO conversion as function of temperature for catalyst (B) in the fresh state and after aging in H₂O vapor in absence (Cat. 1) and presence (Cat. 2) of SO₂. The CO T₅₀ values are approximately 100°C and 160°C for Cat. 1 and Cat. 2, respectively. Similar results are observed for catalyst (A) and (D). Sulfur species remaining after the pre-treatment, indicated by XPS, are most likely blocking the Pt sites, which furthermore is shown by the CO chemisorption Pt dispersion measurements. Fig. 1b shows the Pt dispersion in relation to the initial dispersion for catalysts (A), (B), and (D) (100% for a fresh catalyst) after deactivation, i.e. values should not be mistaken for actual values of dispersion. At both 670°C and 250°C the dispersion is lower for catalysts aged in atmospheres containing SO₂. It is particularly clear at 250°C as the thermal contribution to the deactivation is less pronounced. The most severe decrease in dispersion is achieved during conditions including both high temperature and poisoning by sulfur. Some further characteristics from aging in SO₂ atmosphere are discussed in the paragraphs below, first addressing the influence of water vapor.

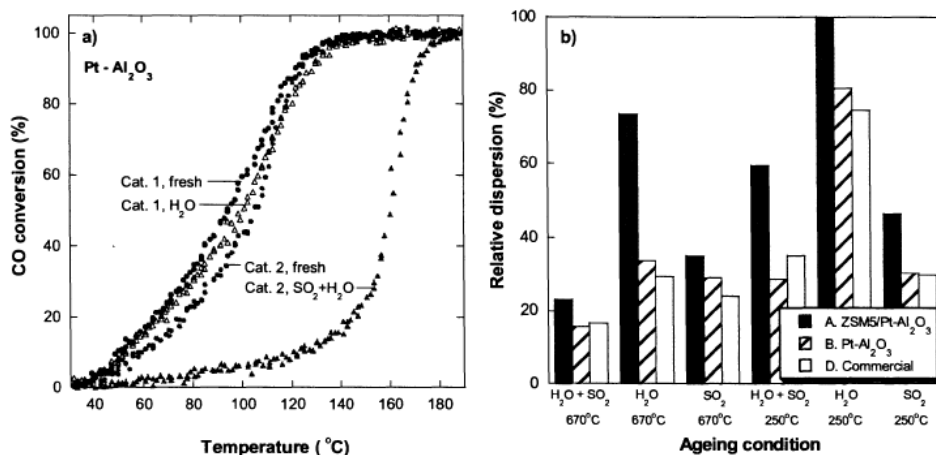


Fig. 1. a) CO conversion as function of temperature for two samples of the Pt-Al₂O₃ catalyst aged at 250°C in presence of H₂O (Δ) and H₂O + SO₂ (▲), including the fresh samples (●). b) Relative Pt dispersion for catalysts (A), (B) and (D) aged at different conditions. Note: 100% refers to the Pt dispersion of the corresponding fresh catalyst and not an absolute value of dispersion.

The most apparent contribution to the deactivation of the model catalysts from adding H₂O to the synthetic exhaust is the loss of hydrocarbon storage capacity at elevated temperatures. The effect is likely due to a combination of zeolite dealumination and collapse of the pore structure, as indicated by some of the BET measurements. Fig. 2 (I-II) show the temperature programmed desorption (TPD) spectra of catalyst (A) after exposure to C₃H₆ at 300 K. The monolith samples were aged in presence of H₂O at 670°C (I) and in presence of both H₂O and SO₂ at 250°C (II).

The concentrations of H₂, CO, C₃H₆, CO₂ and SO₂ are presented as functions of the catalyst temperature during the temperature ramp (concentrations equal to zero are excluded from the graphs), both for the fresh (f) and aged (a) catalyst. For the catalyst aged at 250°C a TPD spectrum was obtained before the pre-treatment (oxidation and reduction at 500°C) as well, denoted (a*) in the graph. Fig. 2 (I) shows that the amount desorbed hydrocarbon from the aged catalyst, C₃H₆(a), is much less in comparison to the fresh catalyst, C₃H₆(f). The observed CO signal is probably due to cracking of propene into ethene (sharing spectral peak with CO) at the elevated temperature. CO₂ may originate from a reaction by coke deposited during aging and H₂O in the washcoat. Complementary TPD spectra show that an atmosphere without H₂O has no effect on HC storage capacity at 670°C. From Fig. 2 (II) it is clear that the effect from aging at only 250°C is mainly reversible. The fresh catalyst has a similar spectrum (f) as in Fig. 2 (I). After aging and without any pre-treatment (a*) before the TPD, less HC is desorbed, C₃H₆(a*), and the bulk of the sulfur is also released, SO₂(a*). Following oxidation and reduction at 500°C, the HC signal is restored, C₃H₆(a), and also no further desorption of SO₂ can be seen, however not implying that it is completely removed, as indicated by the XPS data below. A similar behaviour with respect to this reversibility has been observed even without SO₂ in the aging atmospheres, suggesting that the zeolite is blocked by deposits of carbon species rather than sulfur.

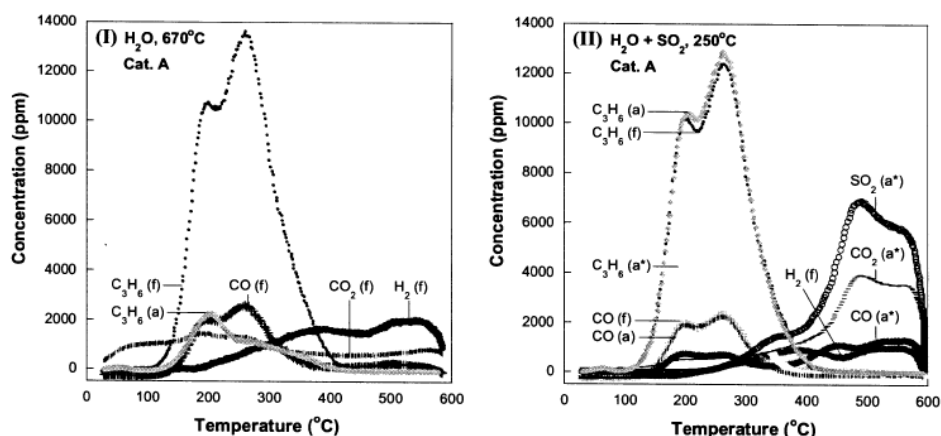


Fig. 2. C_3H_6 -TPD spectra; catalyst (A) aged in presence of H_2O at $670^\circ C$ (I), and in presence of both H_2O and SO_2 at $250^\circ C$ (II). Displaying concentrations for; fresh catalyst (f), aged catalyst without pre-treatment before the temperature ramp (a^*), and aged catalyst with pre-treatment (a), i.e. oxidation and reduction at $500^\circ C$. Concentrations equal to zero are excluded from the figure.

From analysis of adsorbed sulfur species on the washcoat of the catalysts it is clear that H_2O has further impact on the deactivation process. XPS data from analysis of catalyst (A) after aging at $250^\circ C$ in presence of SO_2 , with or without H_2O , are presented in Table 2. The S 2p peak has been studied in detail, both for the aged catalyst and after different pre-treatment procedures in a reactor setup mounted to the vacuum system of the XPS. Water vapor promotes the adsorption of sulfur species to some extent. The additional sulfur adsorbed onto the washcoat seem however to interact more weakly, as it is removed soon as the temperature is elevated during the pre-treatment procedures. What is more important is the treatment required to remove the sulfur completely, i.e. reduction at $700^\circ C$, after which only some traces are remaining. It should be noted that the XPS is highly surface sensitive and additional sulfur deeper within the bulk of the washcoat may remain. The effect of additional amounts of adsorbed sulfur as H_2O is present in the aging atmosphere is not reflected in the Pt dispersion data, or the CO light-off temperatures. BET measurements show however a more pronounced deactivation with respect to the specific surface area as SO_2 is combined with H_2O .

TABLE 2

The atomic concentrations of sulfur for the ZSM-5/Pt- Al_2O_3 catalyst aged at $250^\circ C$ in SO_2 and $SO_2 + H_2O$ atmospheres. The amount of sulfur is given for analysis directly following aging and after using a pre-(analysis)

treatment; CO oxidation, C₃H₆-TPD, oxidation at 500°C and 700°C (only for SO₂ + H₂O), reduction at 500°C and 700°C (only for SO₂ + H₂O).

Pre-treatment condition		S 2p atomic concentration (%)	
Atmosphere	Temp. (°C)	SO ₂ , 250°C	SO ₂ + H ₂ O, 250°C
-	-	2.9 ^a	4.5 ^a
CO + O ₂	200 (30°C/min)	2.5	3.0
C ₃ H ₆ -TPD	600 (40°C/min)	1.8	2.0
O ₂	500	1.6	1.5
H ₂	500	1.3	1.4
O ₂	700	1.3	n.d.
H ₂	700	0.3	n.d.

^a No pre-treatment
n.d. : Not determined

The effect of aging temperature can be seen in Fig. 1b when comparing aging at 250°C with 670°C for the different atmospheres. The most marked effect is seen in presence of only H₂O, since the contribution to the chemical deactivation is removed in absence of SO₂. As for the Pt dispersion, the BET surface area is also affected to some extent by elevated temperatures, which is likely to be connected to the deactivation of the zeolite and loss of hydrocarbon storage capacity. From studying CO conversion data of the catalysts it is clear that the effect of temperature is ruled out in presence of SO₂. At 250°C the temperature is sufficiently low for sulfur to adsorb, having a dramatic effect on CO T₅₀, as observed in Fig. 1a, while aging at 670°C in presence of SO₂ and H₂O do not result in significant amounts of sulfur deposits on the washcoat. The increased temperature is likely to inhibit adsorption, but once adsorbed, sulfur adheres even after exposure to oxidising atmosphere at 700°C.

Synthetic and vehicle aging correlations

Deactivation characteristics of a DOC subjected to controlled lab aging were compared to field-aged catalysts after 0, 80 000, and 160 000 km driving in order to establish the (dis)similarities between the two types of aging, and determine to what extent vehicle aging can be replaced by rapid synthetic aging. Emission tests confirmed the increasing deactivation of the field-aged catalysts, Fig. 3, and lab-scale measurements, Table 3, of CO oxidation, Pt dispersion and hydrocarbon storage capacity were used together with XPS, TEM, and SEM-EDS to compare the

performance with lab-aged catalysts. The synthetic aging was designed to account for a combination of thermal and chemical deactivation, Table 3 (a-e). The reference values for Pt dispersion and CO activity of the vehicle-aged catalyst could be approached using a 30h accelerated aging procedure combining poisoning at low temperature with (hydro)thermal treatment. A similar degree of Pt sintering was observed for both real and synthetic aging conditions (see Fig. 4), whereas differences arose from various contributions to the chemical deactivation. XPS showed that pre-oxidation and pre-reduction at 700°C was not sufficient to remove typical compounds of oil-derived catalyst poisons (P, Zn, Ca), which furthermore accumulated with mileage, on the vehicle-aged catalysts. The degree of sulfur poisoning of the lab-aged catalysts increased with the duration of low-temperature sulfur exposure and could not be fully recovered in oxidising atmospheres up to 700°C, which e.g. could be above the average for normal driving conditions. This also highlights the importance of using low-sulfur diesel fuel.

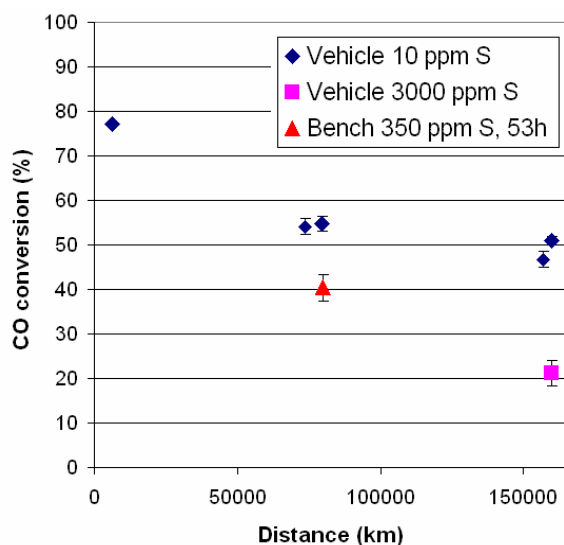


Fig. 3. CO conversion, obtained from CO emission measurements pre- and post converter (NEDC cycle), versus driving distance; vehicle-aged catalysts with 10 ppm sulfur in the fuel (◆), vehicle-aged catalyst with 3000 ppm sulfur in the fuel (■), and catalyst aged in engine bench for 53 h (350 ppm sulfur) (▲).

Table 3. Catalyst characteristics for different types of aging; vehicle-, bench-, and a selection of lab aging conditions (a)-(e). The results are obtained after heating the samples to 700°C prior to oxidation and reduction at 500°C. ^a Aging conditions apart from the regular model exhaust gas containing: C₃H₆: 400 ppm, C₃H₈: 200 ppm, CO: 1500 ppm, NO: 200 ppm, O₂: 5%, CO₂: 4%, Ar: balance, flow rate: 800 ml/min. ^b Amount desorbed from aged catalyst during temperature ramp to 700°C (no pre-treatment).

Aging	CO T ₅₀ (°C)	Pt dispersion (%)	C ₃ H ₆ ads. (µmol/g _{washcoat})	SO ₂ des. ^b (µmol/g _{washcoat})
0 km	7	49.7	546	0
80000 km, 10 ppm S	117	15.4	410	60
160000 km, 10 ppm S	130	9.1	420	180
160000 km, 3000 ppm S	162	5.2	360	4173
Engine bench 53h, 350 ppm S	136	8.0	248	6
Synthetic aging ^a				
Temp (°C) / Time (h)				
a) H ₂ O+SO ₂ , 250/15	96	16.2	544	1284
b) H ₂ O+SO ₂ , 670/15+250/15	138	8.6	324	1073
c) H ₂ O+SO ₂ , 670/7.5+250/7.5	116	8.6	203	825
d) H ₂ O, 670/15+250/15	113	10.9	233	0
e) H ₂ O, 670/7.5+250/7.5	57	15.7	274	0

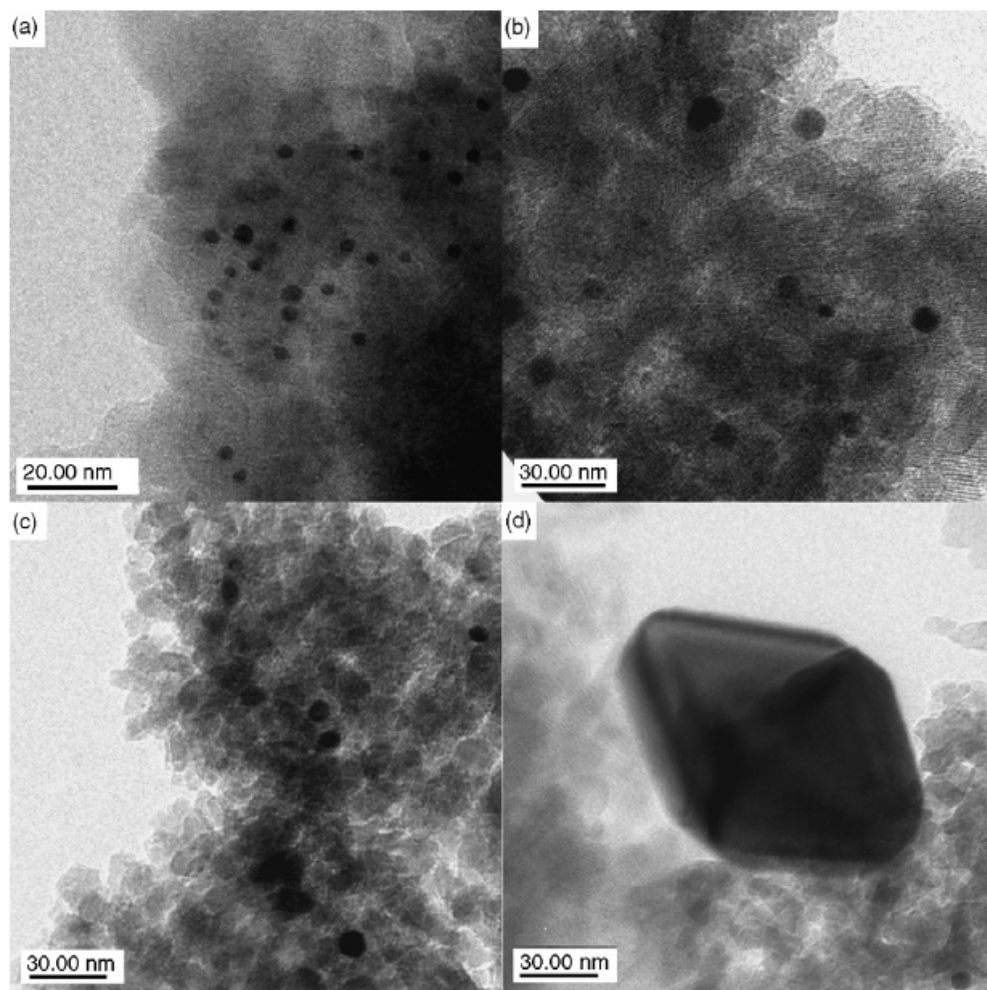


Fig. 4. TEM micrographs showing Pt particles for the fresh catalyst (a), vehicle-aged at 160,000 km (b), and lab-aged at 670°C (15 h) + 250°C (15 h) in presence of SO₂ and H₂O (c) and (d).

As part of investigating deactivation mechanisms in detail, a study is pursued on the sintering of Pt on model catalysts, focusing on the effect of support oxide and atmosphere. Vapor deposition allow support materials such as SiO₂, Al₂O₃, TiO₂ etc. to be used. Atmospheres are typically O₂/H₂ with additions of CO/SO₂/HC:s, and also H₂O. Oxidising atmosphere without mentioned additions result in the most significant sintering of Pt, Fig. 5, while additions of e.g. CO restrict the sintering. This is most likely due to reduction of mobile PtO_x species, i.e. the stoichiometry is largely the controlling factor. Typical events leading to Pt agglomeration has been confirmed using in-situ microscopy, i.e. coalescence of particles and indications of atomic migration, for

both oxidising and reducing atmospheres. Evaporation of volatile PtO_x species was also observed in O_2 . The effect of weak and strong metal-support interaction was demonstrated by the differences in merging times for colliding particles (time between collision and complete inclusion), e.g. increasing by a factor of 100 for Pt on CeO_2 compared to Pt on SiO_2 .

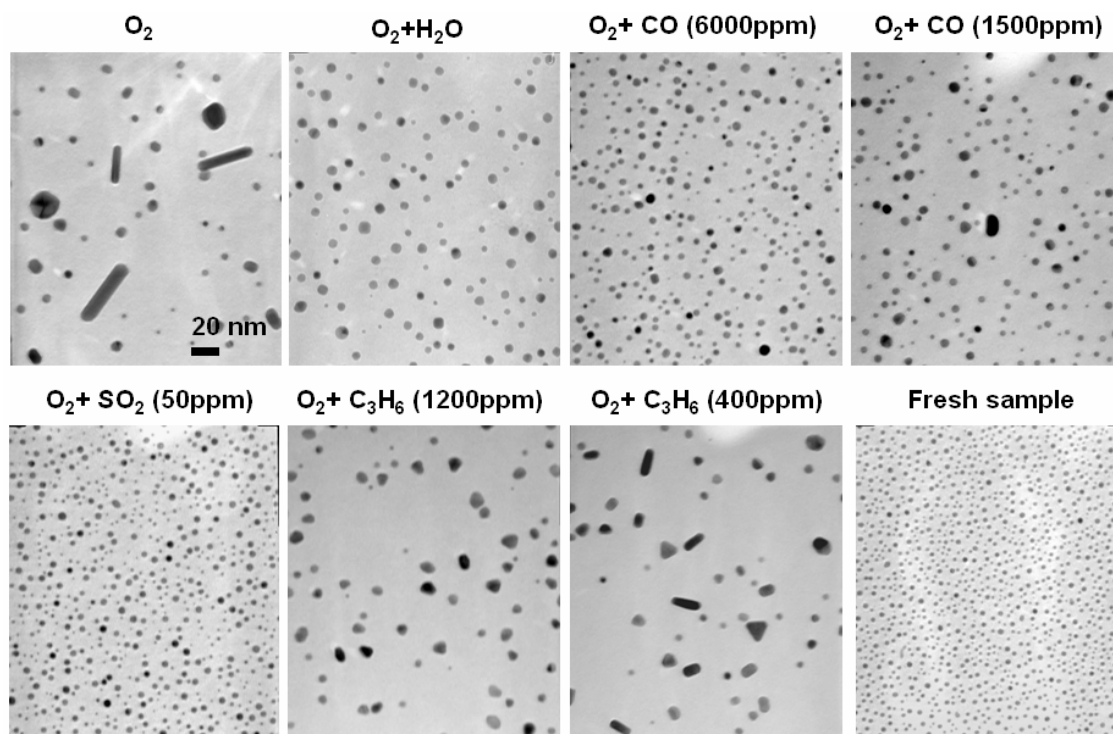


Fig. 5. Ex-situ sintering of Pt at 670°C, 7.5h, on SiO_2 substrate in different atmospheres.

Concluding remarks

Aging procedures are commonly developed to test the durability of catalysts through simulation of long-term vehicle operation. Synthetic aging is a convenient and resource efficient approach, which however has received limited attention in the field of diesel oxidation catalysts. In order to establish and benefit from such procedure, it is necessary to address critical sources of deactivation of vehicle- and lab-aged catalysts and determine to what extent the aging process

can be correlated. Hence, in the present study a number of methods were used to characterise the performance and deactivation of a commercial

Synthetic aging is sufficient for testing catalyst durability for long-term usage where loss of activity due to thermal deactivation and a general effect of chemical deactivation are of concern. In this respect, by adjusting the duration of the aging, temperature and composition of the exhaust gas (i.e. presence of catalyst poison), the deactivation can be adapted towards testing high temperature stability or resistance to poisoning (by sulfur) at low temperature, or a combination of both. Hence, a realistic aging procedure can be achieved where lab-scale measurements of typical characteristics like light-off temperatures can be correlated to the performance of corresponding vehicle-aged catalysts. The relationship between flow reactor measurements of such characteristics and emission data is however uncertain and only a full-scale lab aging procedure would connect the observed deactivation to actual emission levels. Lab aging is not sufficient if chemical deactivation is to be investigated in detail with respect to oil-derived poisons other than sulfur, which are unique to the process of deactivation of vehicle-aged catalysts.

1 The effects of sulfur dioxide, water and temperature on the deactivation of model diesel oxidation catalysts

Jonas Andersson, Magnus Skoglundh and Erik Fridell
Oral presentation at DECHEMA 10th International Symposium on Catalyst Deactivation (2006). Available in Book of Extended Abstracts, DECHEMA e.V., Frankfurt am Main, Germany, 2006, pp 91-96.

2 Deactivation of diesel oxidation catalysts: Vehicle and synthetic aging correlations

Jonas Andersson, Matilda Antonsson, Lisa Eurenus, Eva Olsson and Magnus Skoglundh
Applied Catalysis B: Environmental 72 (2007) 71-81.

3 Deactivation of diesel oxidation catalysts: Fundamental studies and methods for accelerated aging

Jonas Andersson
Licentiate thesis at the Department of Applied Physics/Competence Centre for Catalysis, Chalmers University of Technology, Göteborg, 2006.

