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# Durability of VOC catalysts in solvent emission oxidation

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## Abstract

The durability of four noble metal catalysts was investigated in solvent emission oxidation. Mono- and bimetallic catalysts (Pt, Pt–Pd) were supported on $\gamma$-$Al_2O_3$–La or $\gamma$-$Al_2O_3$–Ce washcoats and they were aged in industrial conditions for max. 25 months. The catalytic activities (light-off experiments with methane and *n*-butyl acetate) were determined before and after the ageing to compare the behaviour of catalysts. Catalysts were also characterized by BET and chemisorption measurements as well as with XRD, FTIR and SEM. According to the results, all the catalysts showed excellent stability after the ageing periods and no significant reduction in the activities were observed in the oxidation of *n*-butyl acetate. However, a small reduction in the activity of the catalysts was observed in the case of methane oxidation, which is related rather to poisoning or fouling of the catalysts than to thermal deactivation. This observation was also supported by other catalyst characterization methods.

*Keywords:* Industrial ageing; Solvent emission abatement; Noble metal catalysts

## 1. Introduction

Volatile organic compounds (VOCs) are one of the major contributors to the formation of photochemical ozone [1]. VOCs are emitted into the atmosphere from numerous sources including stationary, mobile and natural sources. One of the major stationary sources of VOC emissions is the usage of solvents [2,3], emissions of which are limited in EU countries by the Solvent Emissions Directive [4].

Catalytic oxidation has been applied to the abatement of VOCs for several years. It has been proven to be a feasible and cost-effective method in solvent emission abatement. A lot of research has been carried out in the selection of suitable catalysts in different abatement conditions. In general, the most popular catalysts are noble metals, but also different metal oxides are used [5,6]. In addition to catalytic activity, selectivity and durability are also important criteria when selecting the most suitable catalyst. Selectivity and durability become even more significant factors in the case of total oxidation of e.g. sulphurous or halogen-containing VOCs.

The deactivation of a catalyst is a significant matter both from the catalyst manufacturers' as well as the catalyst end users' point of view. The deactivation may be caused by several reasons, both physical and chemical, depending on the process where the catalyst is used. The durability of different catalytic materials in methane combustion or in gas turbine applications is widely studied (e.g. in references [7–9]) and it is mainly related to the high-temperature induced ageing, which is not likely present in the solvent VOC emission abatement. The main deactivation mechanisms over oxidation catalysts in solvent emission abatement are most probably fouling and chemical deactivation, although thermal shocks and abrasion of the catalytic surface may occur [10]. Libanati et al. [11] studied silica poisoning of bead VOC catalysts in industrial-scale oxidation of printing emissions and found out that silica penetrates into the catalyst bed and deposits in the micro pores of the catalyst. Vigneron et al. [12] have tested several different catalysts (in shape and in composition) in the abatement of VOC emissions originating from a coil-coating process. They reported poisoning by silicone and deactivation due to thermal stress as well as attrition. They did not find much benefit concerning poisoning resistance in using base metal oxide catalysts compared with noble metal catalysts. In spite of the lack of information concern-

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Fig. 1. Catalysts inside an ageing rack.

ing durability of the catalysts in solvent emission abatement, studies on e.g. poisoning of automotive catalysts by compounds present in lubrication oils and deactivation of methane oxidation catalysts by sulphur are available (e.g. [13–19]).

In general, the ageing of catalysts in solvent emission oxidation is a rather slow phenomenon. The expected time of usage for the monolithic catalysts in normal process conditions should be approximately 10–20 years. This argument is partially based on the experience gained from the catalytic oxidizer, which was installed some 10 years ago in Tikkurila, Finland [20]. However, more information on the durability of the catalysts and causes for possible deactivation is needed, and thus the durability of Pt and Pt–Pd catalysts in solvent emission abatement was studied in this research.

## 2. Experimental

In this study four different noble metal catalysts were aged in industrial conditions. Monometallic Pt catalysts and bimetallic Pt–Pd catalysts were supported on $\gamma$-$Al_2O_3$–Ce and $\gamma$-$Al_2O_3$–La washcoats. The noble metal contents of the catalysts were $1.76\,g\,l^{-1}$ (for bimetallic catalysts this is the total loading with the Pt/Pd ratio of 1:1).

The test catalysts were installed in an industrial-scale catalytic incinerator, close to a painting shop that uses solvent-based coating agents, the emissions of which are treated catalytically. The emission gas contains mostly *n*-butyl acetate, but some alcohols and other organic compounds are also found [21]. The pigments used in paints include e.g., magnesium silicate, titanium dioxide, iron oxide and tin oxide (information from the supplier), which may be potential catalyst poisons or more likely, may cause fouling of the catalytic surfaces.

The incinerator operates with flow-reversal at close to 350 °C and if the temperature exceeds 520 °C the incinerator will be shut down automatically. The temperature of the gas at the inlet of the incinerator fluctuates according to concentration and phase of the process. However, the temperature above the catalyst remains roughly constant, ~400 °C, regardless of the stage of incineration process [21].

The test catalysts, four of each, were placed inside a metal rack (Fig. 1) that had been installed into the reverse flow catalytic incinerator between the catalyst bed and the heat exchangers, which allows the raw emission gases to pass the sample catalysts in one flow direction and the once treated gas in the other flow direction. Prior to the ageing, the flow profile inside the incinerator was modeled with CFD calculations. The locations of the catalyst samples inside a rack were changed after every ageing period so, that those, which should be removed next, were placed at the maximum flow region. However, it is good to keep in mind, that the heat exchangers below and monolithic catalyst above the rack smooth the flow profile and differences in flow velocities over the reactor diameter are not very significant. The ageing periods of the catalysts were 3, 9, 16 and 25 months.

Characterization of fresh and aged catalysts was carried out by activity experiments (light-off measurements) and by different characterization methods (e.g., BET, chemisorption, SEM, XRD and FTIR). The light-off experiments were carried out in a tubular quartz reactor, which was heated from room temperature up to 800 °C. In these experiments, the GHSV was $\sim 31\,500\,h^{-1}$ and the concentrations of the model VOC compounds, *n*-butyl acetate and methane, were both 2000 ppm. *n*-Butyl acetate was selected to be the model compound due to the composition of the emissions in the painting shop. Methane was selected to be another model compound since it is known to be very difficult to oxidize (e.g. [10,22]), and therefore, the differences between activities of the tested catalysts can be observed more clearly.

The surface areas of the catalysts and CO chemisorption measurements were carried out for fresh and aged catalysts. Specific surface areas ($m^2\,g^{-1}$) were determined by Coulter Omnisorp 360CX according to the standard BET method. At first, the catalysts were outgassed in a vacuum at 140 °C for 16 h before the measurements. Surface areas were obtained from the $N_2$ adsorption isotherm at −196 °C by assuming the cylindrical shape of the pores. Chemisorption measurements (Micromeritics ASAP 2020 Surface area and porosity analyser) were carried out at 35 °C in order to determine the dispersion of noble metal particles and the amount of active metal in the catalyst. CO was used as the adsorbate gas with the assumption of a stoichiometry of 1:1 regardless of the particle size.

SEM–EDS, XRD and FTIR measurements were carried out to find out possible ageing-induced changes in the catalysts. A Jeol JSM-6400 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was used for high magnification imaging and elemental analysis. In the pretreatment stage, flat pieces of fresh and aged catalysts were cut and potted in epoxy in order to obtain side views of the catalysts. Prior to analysis, the samples were polished and coaled to avoid the accumulation of charge. The accelerating voltage and current in the measurements were 15 kV and 12 nA, respectively. X-ray diffraction (XRD) was used to investigate the bulk phases present in the samples. The XRD diffractograms presented in this study were recorded by a Siemens D5000 diffractometer employing nickel-filtered Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, 30 mA) at 0.020° intervals in the range of $20^\circ \le 2\theta \le 75^\circ$ directly from the catalyst foils. FTIR (Perkin Elmer Spectrum One) equipped with attenuated total reflectance (ATR) unit was used to give information on the bonds and bond strengths on the solid surface. The measurements were carried out at room temperature directly from the catalyst foils with the ATR unit. The spectra were measured in the range of $4000–650\,cm^{-1}$.

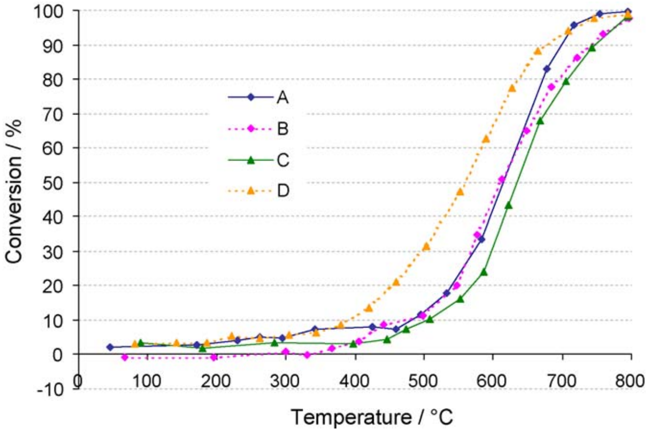

Fig. 2. Light-off curves for the fresh catalysts in methane oxidation.

## 3. Results and discussion

The light-off curves for the fresh catalysts in methane oxidation, presented in Fig. 2, show that bimetallic Pt–Pd catalysts (B and D) are slightly more active compared to similar monometallic Pt catalysts (A and C). Temperatures close to 800 °C are needed for the 100% conversion of methane.

In *n*-butyl acetate oxidation monometallic Pt catalysts were somewhat more active. However, 100% conversions of *n*-butyl acetate were achieved at around 500 °C with all the catalysts.

As Table 1 indicates, the light-off experiments with *n*-butyl acetate did not show significant differences between the catalysts, and therefore, methane oxidation is used in the evaluation of catalysts' activities. According to the repeated experiments, the accuracy of measurements is ±5 and ±10 °C for methane and *n*-butyl acetate, respectively.

Fig. 3a and b shows $T_{50}$ temperatures (temperature of 50% conversion) and the conversions at 750 °C for methane oxidation over the catalysts with different ages. The temperature of 750 °C was selected as the reference temperature, since it has been reported [9] that the mean temperature needed for the combustion of methane without a catalyst is about 825 °C and the possible effect of the gas phase oxidation when comparing the results is thus minor.

Table 1
Light-off temperatures ($T_{50}$) of the catalysts for methane and *n*-butyl acetate

| Ageing time | $T_{50}$ (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Methane | | | | *n*-Butyl acetate | | | |
| | A | B | C | D | A | B | C | D |
| Fresh | 610 | 610 | 635 | 555 | 250 | 240 | 230 | 260 |
| 3 months | 600 | 595 | 645 | 545 | 240 | 230 | 270 | 280 |
| 9 months | 670 | 650 | 620 | 460 | 250 | 250 | 280 | 280 |
| 16 months | 660 | 715 | 650 | 580 | 250 | 280 | 270 | 310 |
| 25 months | 670 | 650 | 680 | 610 | 240 | 290 | 270 | 290 |

The $T_{50}$ values of methane for the catalysts aged for 25 months are increased by approximately 50 °C (Fig. 3a). Similarly, conversions at 750 °C are decreased from the initial values (see Fig. 3b). The variation in both $T_{50}$ and conversions at 750 °C between the catalysts with different ages may be partly due to reversible poisoning. For example, Vigneron et al. [12] have reported similar variations in the ageing of VOC catalysts operating in the oxidation of coil-coating emissions, which were assumed to originate from reversible poisoning. Concentrations of the emissions after the industrial-scale incinerator were also measured when the catalyst samples were taken out from the incinerator. The calculated conversions were 96.9% (initial), 98.7% (9 months), 85.5% (16 months), 87% (25 months) [21]. These values are affected by the duration of the measurement and the operation phase of the incinerator, and thus the changes may not indicate reversible poisoning. For example, total conversions are usually higher when the inlet emission concentrations are higher, whereas for lower emission concentrations also the total conversions are lower. In addition, when the flow in the incinerator is reversed, a short peak of VOC concentration at the outlet occurs. Without continuous monitoring of the inlet and outlet concentrations in an industrial-scale incinerator, the possibility of reversible poisoning cannot be assured.

In general, catalysts C and D supported on γ-$Al_2O_3$–La seemed to be more active at 750 °C after 25 months of ageing.

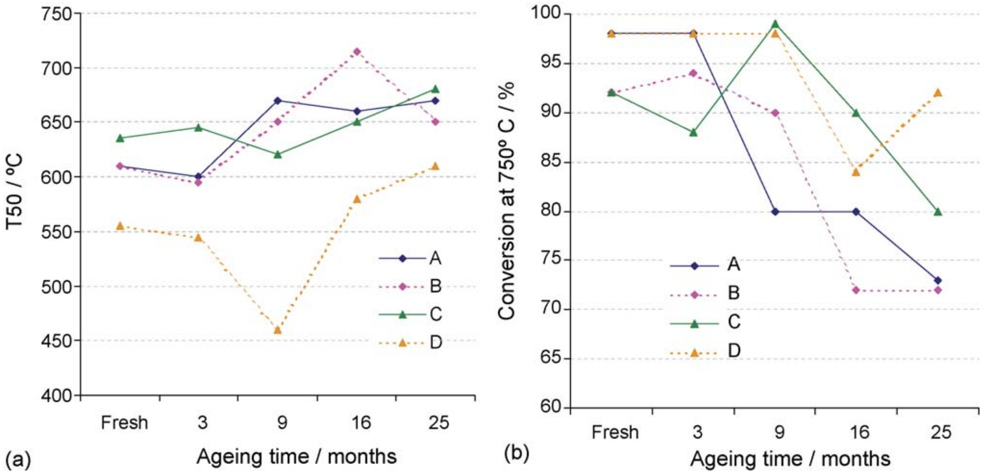

Fig. 3. (a) $T_{50}$ temperatures of methane oxidation and (b) conversions at 750 °C for fresh and aged catalysts.

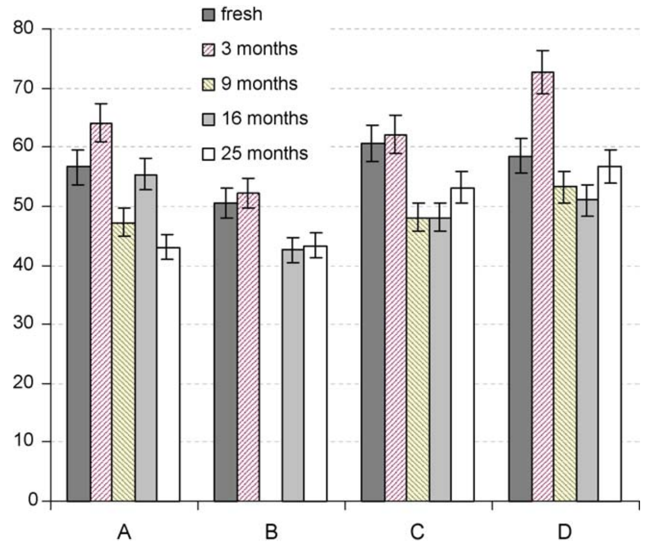

Fig. 4. Specific surface areas (BET, m$^2$ g$^{-1}$) of the catalysts.

A similar trend cannot be observed in $T_{50}$. When the effect of active metal is compared, it seems that $T_{50}$ of Pt–Pd catalyst D remains lower than the $T_{50}$ of the corresponding Pt catalyst (C). In addition, conversion at 750 °C for the 25 months old Pt–Pd catalyst is higher as well. Similar differences cannot be observed with catalysts A and B supported on γ-Al$_2$O$_3$–Ce. In the case of the abatement of solvent emissions, more important feature is the end conversion or total oxidation temperature than the $T_{50}$, and in general, it seems that La stabilization of a catalyst is more effective than Ce.

The specific surface areas (BET) of the catalysts for fresh and aged samples are presented in Fig. 4. In general, the surface areas decrease during ageing after the first increase in the surface area. The BET surface areas for catalysts C and D (γ-Al$_2$O$_3$–La washcoat) were slightly higher than for catalysts A and B after 25 months of ageing.

The chemisorption measurements of the catalysts show an increase in the metal dispersion after 3 months of ageing except with catalyst C. This is consistent with the observations of the BET measurements. It has been noticed during the earlier laboratory testing of fresh catalysts, that the light-off curves of these catalysts move towards the lower temperature region after certain time of usage, which is also noticed with catalysts A, B and C in Fig. 3a and catalyst B in Fig. 3b (see also Table 1). These phenomena are probably due to further calcinations of the catalysts, which is more pronounced with γ-Al$_2$O$_3$–Ce supported catalysts. The values of metal dispersion and metallic surface area are generally decreased when further ageing takes place. The metal dispersions as well as metallic surface areas of catalyst D remain almost unchanged during the whole ageing period. As a rule, they are smaller for catalysts C and D (supported on γ-Al$_2$O$_3$–La). However, the conversions at 750 °C for those catalysts are higher than for catalysts A and D. With catalysts A and B (supported on γ-Al$_2$O$_3$–Ce) that are 25 months old, the metal dispersions as well as metallic surface areas are decreased close to the values of catalysts C and D (γ-Al$_2$O$_3$–La). In general, γ-Al$_2$O$_3$–La seems to be a more stable washcoat than γ-Al$_2$O$_3$–Ce. Fig. 5a and b shows the changes in metallic dispersions and the metallic surface areas of the catalysts with different ages.

The SEM–EDS imaging of the catalysts did not show differences between the catalysts of different ages (see Fig. 6). This is also consistent with the XRD measurements, where no differences were observed between the fresh and aged catalysts (see Fig. 7). In SEM–EDS imaging, Si was observed in one sample aged for 25 months, which may indicate the possibility of poisoning due to the pigment compounds in the coating agents, since Si was not added into the washcoat material in the preparation stage of the catalysts. However, Si was not found in greater amounts, and does not affect the catalyst activity significantly, as proved in the light-off experiments.

The sintering of Pd is reported to be significant on these types of catalysts even below 800 °C in an air atmosphere in the presence of water vapour [23,24]. Furthermore, Hüttig temperatures for Pt (608 °C) and Pd (548 °C) as well as PdO (307 °C) may be momentarily exceeded on the surface of the catalyst during the operation of the incinerator, indicating the possible mobility of atoms [25]. However, the sintering or phase changes of γ-Al$_2$O$_3$-based washcoat is not that likely to occur at these temperatures

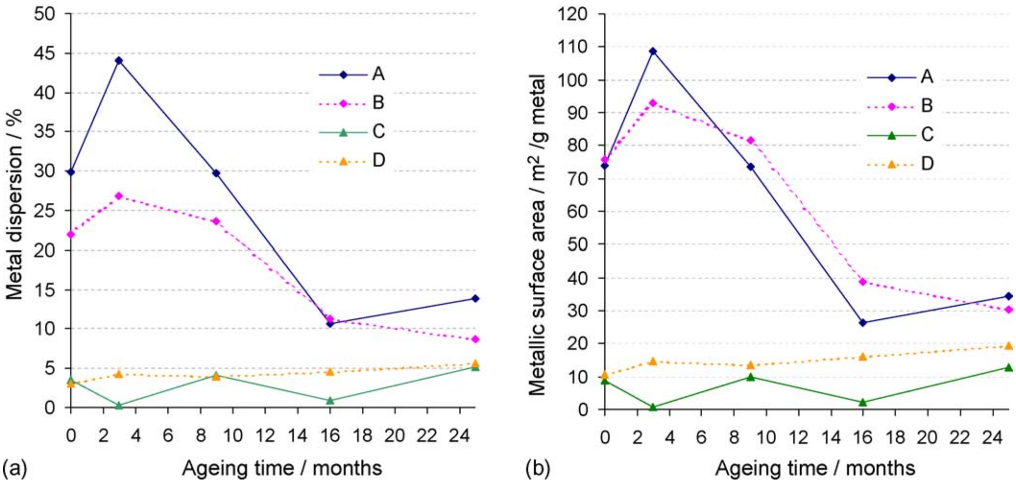

Fig. 5. Changes in (a) metal dispersions and (b) metallic surface areas of the catalysts with different ages.

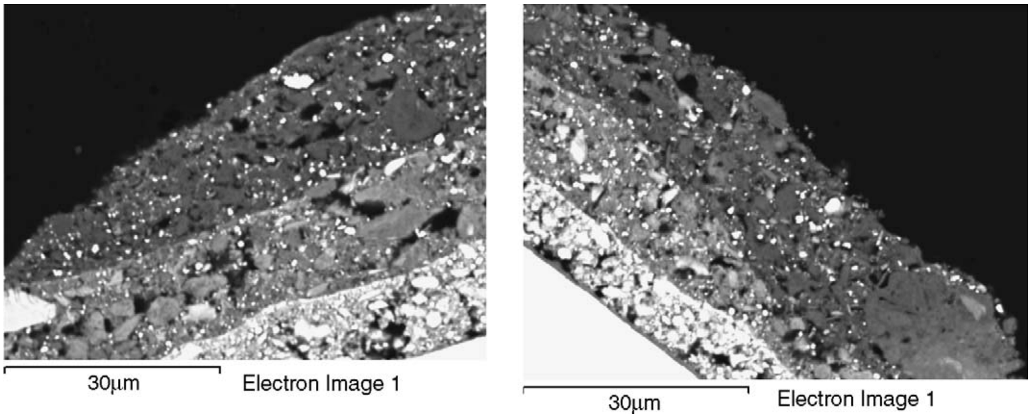

Fig. 6. SEM images of catalyst C. Fresh on the left hand side, 25 months old on the right hand side.

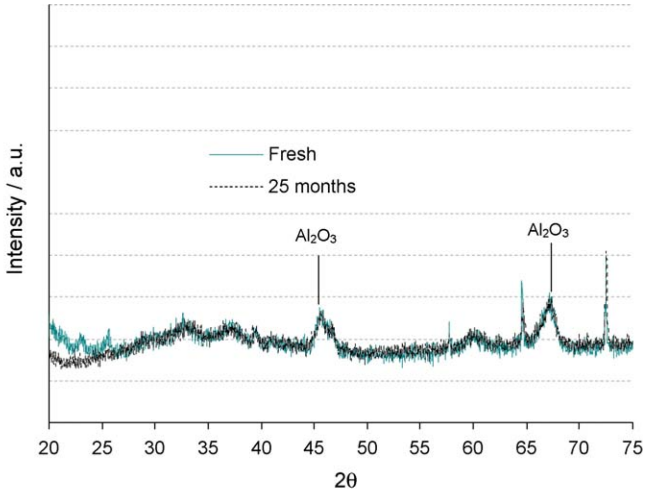

Fig. 7. XRD analysis for catalyst D as fresh and after 25 months of ageing.

[5]. In this case, thermal deactivation of catalysts during 25 months of industrial ageing is not significant if the process operates normally, which is supported by the XRD measurements that do not indicate significant crystallization (see Fig. 7).

FTIR measurements of fresh catalysts and catalysts aged for 25 months did not either show significant differences between the catalysts (see Fig. 8). A small stretching vibration was observed with catalysts B and D at around 1047 cm$^{-1}$, which may contribute to the Si–O–Si bond (at 1070–1040 cm$^{-1}$) or Si–OR bond (1100–1000 cm$^{-1}$). This could support our proposal about the possibility of slight Si-based poisoning of the catalysts. These catalysts are bimetallic, containing both Pt and Pd. The similar band was not observed with monometallic Pt catalysts.

## 4. Conclusions

In this paper the durability of four VOC catalysts in solvent emission abatement has been studied. It has been proven, that all the catalysts were highly stable throughout the whole 25 months long industrial ageing period. The activities of the catalysts did not decrease significantly according to *n*-butyl acetate light-off experiments. However, a slight decrease in methane oxidation activity was observed with all the catalysts. This decrease was more significant for catalysts supported on the γ-$Al_2O_3$–Ce washcoat, which had much higher initial metal dispersion and still higher dispersion after 2 years of operation. The $Al_2O_3$–La washcoat with lower initial metal dispersion and higher initial BET surface area is very stable in the used conditions and maintains initial values of metal dispersion and metallic surface areas better than the catalysts supported on the γ-$Al_2O_3$–Ce washcoat. Thereby alumina with lanthanum is more stable than

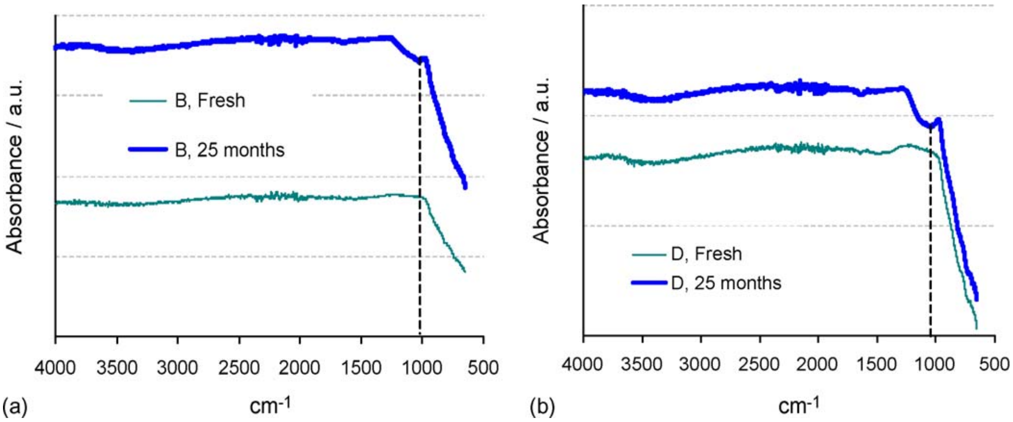

Fig. 8. IR spectra of (a) catalyst B and (b) catalyst D as fresh and aged.

alumina with cerium at least in these solvent VOC incineration conditions.

As expected, significant thermal ageing was not observed during the ageing period according to the XRD measurements, however, metal dispersions and surface areas were decreased. It seems that in industrial solvent emission oxidation conditions the most probable deactivation arises from the possibility that the compounds included in the coating pigments drift with the flow to catalytic surfaces. In these experiments significant deposition of those (silica-based) compounds was not observed by FTIR or by SEM–EDS. However, the decrease in methane oxidation activity, dispersion and metallic surface area as well as in BET surface area, probably indicate initial deactivation caused by poisoning or fouling. To conclude, the catalyst surface characteristics remained on the level, which do not show significant decrease in the activity of the 25 months old catalysts in the solvent VOC emission abatement.

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## References

[1] R.G. Derwent, M.E. Jenkin, S.M. Saunders, M.J. Pillinh, P.G. Simmonds, N.R. Passant, G.J. Dollard, P. Dumitrean, A. Kent, Atmos. Environ. 37 (2003) 1983–1991.

[2] Ministry of the Environment, 2002, Air Pollution Control Programme 2010, The Finnish national programme for implementation of Directive 2001/81/EC, approved by the Government on September 26, 2002, Ministry of the Environment 588e.

[3] Anon., Appl. Catal. B: Environ. 12 (1997) N13–N14.

[4] Directive 99/13/EC, EU Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations, Retrieved 5 February 2001 from the World Wide Web: http://www.esig.otg/direng.htm.

[5] R.E. Hayes, S.T. Kolaczkowski, Introduction to Catalytic Combustion, Gordon and Breach Science Publications, Amsterdam, 1997, p. 681.

[6] E.C. Moretti, Practical Solutions for Reducing Volatile Organic Compounds and Hazardous Air Pollutants, American Institute of Chemical Engineers (AIChE), USA, 2001, p. 150.

[7] P.O. Thevenin, A.G. Ersson, H.M.J. Kusar, P.G. Menon, S.G. Järås, Appl. Catal. A: Gen. 212 (2001) 189–197.

[8] J.G. McCarty, M. Gusman, D.M. Lowe, D.L. Hildenbrand, K.N. Lau, Catal. Today 47 (1999) 5–17.

[9] C.L. Pieck, C.R. Vera, E.M. Peirotti, J.C. Yori, Appl. Catal. A: General 226 (2002) 281–291.

[10] S. Ojala, Measurement and abatement of volatile organic compounds: focus on catalytic oxidation, Licentiate Thesis, Oulu, Finland, 2003.

[11] C. Libanati, D.A. Ullenius, C.J. Pereira, Appl. Catal. B: Environ. 15 (1998) 21–28.

[12] S. Vigneron, P. Deprelle, J. Hermia, Catal. Today 27 (1996) 229–236.

[13] J.B. Butt, E.E. Petersen, Activation, Deactivation and Poisoning of Catalysts, Academic Press, London, 1998, p. 495.

[14] T.C. Yu, H. Shaw, Appl. Catal. B: Environ. 18 (1998) 105–114.

[15] D. Beck, J.W. Sommers, Appl. Catal. B: Environ. 6 (1995) 185–200.

[16] D.L. Mowery, M.S. Graboski, T.R. Ohno, R.L. McCormick, Appl. Catal. B: Environ. 21 (1999) 157–169.

[17] T.N. Angelidis, S.A. Sklavounos, Appl. Catal. A: Gen. 133 (1995) 121–132.

[18] D.E. Angove, N.W. Cant, Catal. Today 63 (2000) 371–378.

[19] H.N. Rabinowitz, S.J. Tauster, R.M. Heck, Appl. Catal. A: Gen. 212 (2001) 215–222.

[20] S. Ojala, U. Lassi, R. Ylönen, R. Keiski, I. Laakso, T. Maunula, R. Silvonen, TAPPI J. 4 (2005) 9–14.

[21] S. Ojala, Katvoc-report, University of Oulu, Finland, Unpublished data.

[22] A.K. Neyestanaki, F. Klingstedt, T. Salmi, D.Yu. Murzin, Fuel 83 (2004) 395–408.

[23] U. Lassi, Deactivation correlations of Pd/Rh three-way catalysts designed for Euro IV emission limits, Doctoral Dissertation, Oulu University Press, Finland, 2003.

[24] U. Lassi, M. Hietikko, K. Rahkamaa-Tolonen, K. Kallinen, A. Savimäki, M. Härkönen, R. Laitinen, R.L. Keiski, Top. Catal. 30/31 (2004) 457–462.

[25] J.A. Moulijn, A.E. van Diepen, F. Kapteijn, Appl. Catal. A: Gen. 212 (2001) 3–16.