Development of a regeneration procedure for commercial automotive three-way catalysts

Henrik Birgersson

KTH Chemical Engineering
and Technology

Licentiate Thesis 2004

KTH – Royal Institute of Technology
Department of Chemical Engineering and Technology
Chemical Technology
SE-100 44 Stockholm, Sweden

TRITA-KET R204
ISSN 1104-3466
ISRN KTH/KET/R--204--SE

Abstract

Car exhaust catalysts were introduced in the early 1980's, to limit the release of pollutants such as hydrocarbons, carbon monoxides and nitrogen oxides. These catalysts contain noble metals such as palladium (Pd), platinum (Pt) and rhodium (Rh) and are able to simultaneously abate all three of the above-mentioned pollutants, hence the name three-way catalyst (TWC). The exposure to high temperatures (800-1000 °C) during operation and the presence of additives in petrol such as lead, calcium, silicon, magnesium, manganese, chromium, sulphur and phosphorus will after a certain time start to lower the overall effectiveness of the catalyst. These effects are either of a mechanical or a chemical nature. High temperatures reduce the active area by causing the noble metals to agglomerate and sinter whereas the additives alter the activity by either fouling the pores of the support material (phosphorus) or by interacting with the metals (sulphur and lead).

The main objective of this work was to develop a method to redisperse the catalytically active sites, comprising Pd, Pt and Rh on the washcoat surface, in an effort to regain lost catalyst activity. For this purpose, a wide spectrum of different commercial car exhaust catalysts containing varying noble metal loadings, aged under various driving conditions and with mileages ranging from 30 to 100 000 km were evaluated.

The influence of a thermal treatment in a controlled gas atmosphere, such as oxygen or hydrogen and a redispersing agent, e.g. chlorine, on the activity of TWC was investigated by means of laboratory-scale activity measurements. Several complementary characterisation methods such as SEM/TEM, XRD, BET and TPR were used to verify the effects of the regeneration treatments on the catalyst morphology (Paper I). Partial regeneration of catalyst activity and noble metal dispersion was achieved after thermal treatment in an oxygen-chlorine rich atmosphere at temperatures below 500 °C.

Finally, an investigation of the effects of an oxy-chlorine thermal treatment for regeneration of a ‘full-scale’ commercial automotive three-way catalyst was performed. Catalyst activity and performance prior to and after the oxy-chlorine thermal treatment was measured on a test vehicle in accordance with the European driving cycle (EC2000). The catalyst surface was further characterised using XRD and EDX (Paper II). Improved catalyst activity for a high mileage catalyst could be observed, with emissions lowered by approximately 30 to 40 vol% over the EC2000 driving cycle.

Keywords: *deactivation, fouling, sintering, poisoning, palladium, rhodium, regeneration, dispersion, thermal gas treatment, oxy-chlorine, TWC, automotive catalyst*

Sammanfattning

Bilavgaskatalysatorn introducerades i början av 1980-talet för att minska utsläppen av föroreningar som kolväten, koloxid och kväveoxider. Dessa katalysatorer består av ädelmetaller såsom palladium (Pd), platina (Pt) och rodium (Rh) och kan samtidigt minska mängden av alla tre nämnda föroreningar, därav namnet trevägskatalysator. Katalysatorn utsätts för höga temperaturer (800-1000 °C) under drift, detta tillsammans med förekomsten av tillsatser till bensinen såsom bly, kalcium, kisel, magnesium, mangan, krom, svavel och fosfor försämrar med tiden katalysatorns effektivitet. Dessa effekter är endera av mekanisk eller kemisk natur. Höga temperaturer minskar den aktiva ytan genom at ädelmetaller ansamlas och sintrar medan tillsatserna ändrar aktiviteten antingen genom att sätta igen porerna i bäraren (fosfor) eller genom att interagera med metallerna (svavel och bly).

Det huvudsakliga målet med detta arbeta har bestått i att utveckla en metod för att redispergera de katalytiskt aktiva sätena, bestående av Pd, Pt och Rh på bärarytan, i ett försök att återfå förlorad katalytisk aktivitet. För detta ändamål utvärderades ett brett spektrum av olika kommersiella bilavgaskatalysatorer med varierande halt av ädelmetall, åldrade under skiftande körbetingelser och med en körsträcka på mellan 30 och 100 000 km.

Inflytandet av värmebehandling i en kontrollerad gasatmosfär, såsom syre eller väte med tillsats av ett redispergerande ämne, t.ex. klor, på trevägskatalysatorns aktivitet undersöktes medelst försök i laboratorieskala. Ett antal kompletterande karakteriseringsmetoder som SEM/TEM, XRD, BET och TPR användes för att utröna effekten av den regenerande behandlingen på katalysatorns morfologi (artikel I). En partiell regenerering av både katalysatorns aktivitet och ädelmetallernas dispersion kunde iakttas efter värmebehandling i en syre-klor rik miljö vid temperaturer under 500 °C.

Slutligen utfördes en undersökning av effekterna av en termisk behandling i en syre-klor rik miljö på en ’full-skale’ kommersiell katalysator. Katalysatorns aktivitet och prestanda före och efter behandling uppmättes i ett testfordon i enlighet med den europeiska körcykeln (EC 2000). Katalysatorns yta karakteriserades vidare med XRD och EDX (artikel II). Förbättrad katalytisk aktivitet för en katalysator med högt miltal kunde iakttas, med en sänkning av utsläppen med uppskattningsvis 30 till 40 vol% över hela EC 2000 körcykeln.

Nyckelord: *deaktivering, förorening, sintring, förgiftning, palladium, rodium, regenerering, dispersion, termisk gasbehandling, syre-klor, TWC, bilavgaskatalysator*

List of papers

This thesis is based on the following publications, referred to by their Roman numerals. The papers are appended at the end.

I. *Thermal gas treatment to regenerate spent automotive three-way exhaust gas catalysts (TWC)*
H. Birgersson, M. Boutonnet, S. Järås, L. Eriksson, Appl. Catal. B 54 (2004) 193.

II. *Regeneration of spent commercial automotive three-way exhaust gas catalysts (TWC)*
H. Birgersson, L. Eriksson, M. Boutonnet, S. Järås, submitted for publication in Appl. Catal. B.

Other Publications

Other publications on catalysis not included in this thesis.

1. *Deactivation and regeneration of spent three-way automotive exhaust gas catalysts (TWC*)
H. Birgersson, M. Boutonnet, S. Järås, L. Eriksson, Top. Catal. 30 (2004) 433.
2. *Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO_2 and Al_2O_3*
J. Agrell, H. Birgersson, M. Boutonnet, I. Melián-Cabrera, R.M. Navarro, J.L.G. Fierro, J. Catal., 219 (2003) 389.
3. *Steam reforming of methanol over a Cu/ZnO/Al_2O_3 catalyst: A kinetic analysis and strategies for suppression of CO formation*
J. Agrell, H. Birgersson, M. Boutonnet, J. Power Sources, 106 (2002) 247.

Contents

1 Introduction 1
1.1 Scope of the thesis 2
2 Automotive three-way catalysts (TWC) 3
3 Aging phenomena of the automotive three-way catalyst 5
3.1 Chemical deactivation 5
3.2 Thermal deactivation 6
4 Investigation of regeneration procedures for TWC 7
5 Regeneration of TWC at laboratory scale (Paper I) 8
5.1 Catalysts 8
5.2 Experimental 8
5.2.1 KTH equipment set-up (Regeneration) 8
5.2.2 AVL MTC small-scale experiment set-up (Activity tests) 9
5.3 Characterisation 10
5.3.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) 10
5.3.2 Transmission electron microscopy (TEM) 11
5.3.3 X-Ray Diffraction (XRD) 12
5.3.4 Temperature programmed reduction (TPR) 13
5.3.5 Brunauer, Emmet and Teller analysis (BET) 14
5.4 Results from laboratory-scale studies 14
6 Regeneration of full scale TWC (Paper II) 17
6.1 AVLMTC full-scale activity tests 17
6.2 Results from full scale activity tests 18
7 Conclusions 20
8. Acknowledgment 22
References 23

Appendices: Papers I-II

1 Introduction

Since the end of World War II there has been a steady increase in the production of motor vehicles, amounting up to 55 million per year worldwide at the present time. North America was the largest producer of vehicles during the 1950's, to be surpassed by a steadily increasing market in Europe at the end of the 1960's. To date, new and ever-growing transportation sectors in Asia and Latin America are estimated to lead to an increase in the world vehicle fleet by over 100% by 2030. With approximately 800 million vehicles currently in service, the impact of such a growth on already heavily strained road networks and the environment is substantial. Emissions of primarily hazardous gases stemming from the vehicle propulsion system, such as spark-ignition or diesel engines, are serious culprits in rural areas. Such gases, mainly composed of unburnt or partially burnt hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_X) and particulates, cause smog, acid rain and various human health problems [1,2], to name a few effects. Strategies to control air pollution thus became necessary, starting with the first major clean air act in 1970, when the first regulations to control emissions were implemented in the US. Since then, new standards have continuously been introduced in an effort to tackle air pollution due to ever increasing emissions. Strategies incorporating more efficient engines and the introduction of a catalytic exhaust after-treatment were and still are the main solutions to stay within ever more stringent legislation [3-5]. A schematic representation of a vehicle equipped with a TWC after-treatment system is shown in Fig. 1.1.

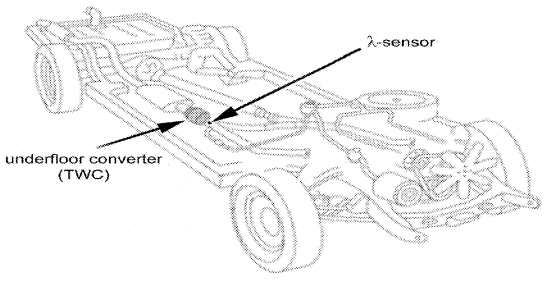

Figure 1.1 Schematic of a vehicle equipped with a TWC

The first automotive converters were oxidising catalysts for the removal of HC and CO as CO_2 and H_2O. Later on, the introduction of the lambda feedback control system enabled the removal of all emissions, including NO_X [6,7]. This was accomplished by altering the exhaust gas composition between a fuel lean (oxidising environment) and fuel rich (reductive environment) for the removal of NO_X as N_2. The catalyst system is prone to lose activity over time, due to phenomena such as thermal aging and chemical contamination of the active sites. Temperatures spanning up to 1000 °C due to heavy load driving and the abundance of additives in lubricating oils are the main culprits.

1.1 Scope of the thesis

Finding a procedure for the regeneration of spent three-way catalysts was the main incitement for the work, which was a part of a European Commission-funded project 'Regencats'. The thesis is divided into two parts.

The first part (Paper I) deals with the application and evaluation of a variety of thermal regeneration procedures on smaller monolith fragments extracted from commercial automotive three-way catalysts (TWC), utilising gases such as hydrogen, oxygen, chlorine and their mixtures.

The second part (Paper II) concludes with a scale-up of the most successful regeneration procedure. Experiments were performed on a Volvo 245 test vehicle, utilising a low and a high mileage catalyst, respectively.

2 Automotive three-way catalysts (TWC)

The current three-way catalysts consist of either a ceramic (cordierite) or a metallic (stainless steel) honeycomb structure called a monolith, usually with 1 mm large square cross sections or channels divided by thin 0.1 mm porous walls. The number of channels usually varies between 400 and 600 cells per square inch (cpsi). Placed upon the ceramic substrate lies a highly porous alumina-based washcoat. The washcoat is impregnated by the noble metals constituting the active sites, amenable for the removal of the hazardous exhaust gases (CO, HC and NO_X) [6,7]. The layout of such a TWC is shown in Fig. 2.1.

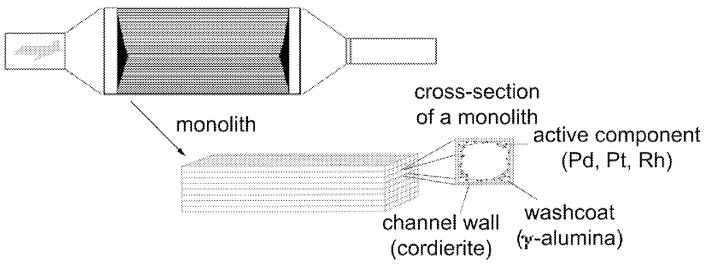

Figure 2.1 Structural design of the monolithic converter in an automotive catalyst

The washcoat comprises a high surface-area γ-alumina (100-200 m^2/g), capable of maintaining a stable structure even at high temperatures. Typically, the washcoat constitutes about 10 - 15 wt% of the final monolith. The washcoat is loaded with numerous base-metal oxides such as La_2O_3 and or BaO, thus increasing the thermal stability of γ-Al_2O_3 [8,9]. CeO_2 and ZrO_2 act as oxygen donor sites or oxygen storage components (OSC) [10-15]. The purpose of the latter two is threefold: first, to stabilise the precious metals; second to stabilise the oxygen concentration on the catalyst during driving, third; to increase the catalyst's tolerance for poisons.

The precious metals consist of either a palladium (Pd) or platinum (Pt) and rhodium (Rh) mixture. The amount of active material impregnated on the washcoat is approximately 1 - 2 wt% of the washcoat [6], or 1-2 g/l (catalyst monolith volume) for Pt and 1-5 g/l for Pd. Rhodium is most effective in the

reduction of NO_X gases, whilst platinum or palladium is more efficient in the oxidation of CO and hydrocarbons [16-18].

The name three-way catalyst stems from the catalyst's ability to simultaneously reduce and oxidise the mentioned three pollutants that is CO, NO_X and HC. This is achieved by the incorporation of an O_2 or lambda (λ) sensor, which is placed before the catalyst. The sensor consists of an electrically conductive solid electrolyte made of stabilised zirconia with electrodes of high surface area Pt. One electrode is located in the exhaust stream and senses the O_2 content relative the concentration on the reference electrode, positioned outside the exhaust in the surrounding air. The lambda sensor generates a voltage, in the order of 100 to 900 mV, depending on the current oxygen content. The air fuel ratio can thus be controlled by the interaction of the lambda sensor's voltage signal and the on-board computer system, keeping the exhaust gas within a specific air-fuel ratio [6,7].

The possible reaction mechanisms occurring on the catalyst are as follows [6,7]:

Oxygen storage abilities of CeO_2:

Fuel rich conditions (λ<1): $2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$ (1)

Fuel lean conditions (λ>1): $Ce_2O_3 + \frac{1}{2}O_2 \rightarrow 2CeO_2$ (2)

Steam reforming abilities of CeO_2:

$CO/HC + H_2O \rightarrow H_2 + CO_2$ (3)

Oxidation reactions (Pt/Pd) under fuel lean conditions:

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ (4)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (5)

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad (6)$$

NO_x reduction (Rh) under fuel rich conditions:

$$2CO + 2NO \rightarrow 2CO_2 + N_2 \quad (7)$$

$$C_xH_y + \left(2x + \frac{y}{2}\right)NO \rightarrow xCO_2 + \frac{y}{2}H_2O + \left(x + \frac{y}{4}\right)N_2 \quad (8)$$

$$H_2 + NO \rightarrow H_2O + \frac{1}{2}N_2 \quad (9)$$

3 Aging phenomena of the automotive three-way catalyst

The automotive three-way catalyst (TWC) is exposed to a harsh environment both thermally and chemically. The exhaust gas temperature for a warm engine varies from 300 to 400 °C during idling mode to 1000 °C or more during full load driving. Metals are prone to undergo a loss of catalyst surface and active sites due to: (I) sintering or aging phenomena after prolonged exposure to high temperatures; (II) chemisorption or poisoning of the catalyst surface by reactants, products or impurities in the exhaust; (III) fouling or the deposition of 'debris' or particles plugging pores and blocking the active surface; (IV) component volatilisation, a loss of promoter or active material through vaporization; (V) phase change and noble metal-base metal or metal/metal oxide-support interactions [19-28].

3.1 Chemical deactivation

The whole of the automotive catalyst undergoes a deactivation during its operation. The front section of the catalyst sees the highest concentration of pollutants and is therefore usually the most heavily fouled part, whereas the rearmost part is the least deactivated [25,26]. High quantities of various contaminants originating from fuel as well as additives in the lubricating oils can be detected, leading to a cumulative increase of quantity over driving

time, as illustrated in Fig. 3.1. In this figure, the composition of contaminating materials in the front inlet and rear outlet of a high mileage catalyst is reported. Sulphur originated from the fuel whilst phosphorus, calcium, zinc and nickel are oil additives. Iron is due to debris from the engine or the exhaust gas manifold.

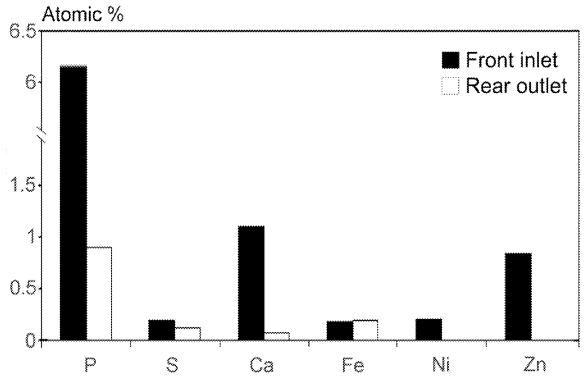

Figure 3.1 Contaminants on the washcoat for front and rear part of a TWC

Some of these contaminants can be removed from the catalytic system by a weak acid-based treatment, relying on the solubility of the respective species in acid. Such studies were reported by Angelidis et al. [26], where the obtained results were of varying success.

3.2 Thermal deactivation

Surface and bulk metals become increasingly 'mobile' at higher temperatures and crucial temperatures are the so-called Hüttig and Tamman temperatures, lying at one third and one half of the respective melting points. At these temperatures, a restructuring of the washcoat surface and the bulk, with pore collapse in the support, crystal growth and agglomeration of both noble and washcoat metals occur, resulting in an encapsulation of active sites. Fig. 3.2 illustrates the increase in pore size on a fresh catalyst and a vehicle-aged sample of the same type.

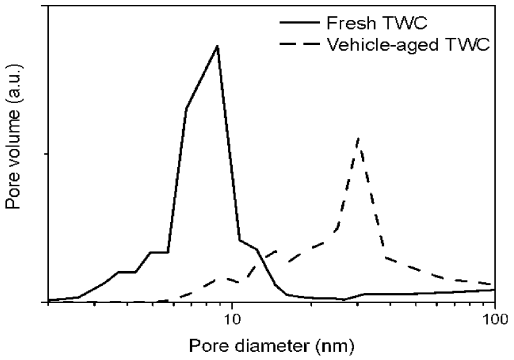

Figure 3.2 BET profiles showing the pore size distribution of a fresh and an aged TWC

This form of deactivation has been thought of as an irreversible mechanism, although early studies in the 1970's and 1980's using oxygen or hydrogen-rich gases at elevated temperatures hinted at the possibility to break or fracture larger crystallites [29-32]. The introduction of halogen gases into the treatment atmosphere eased the redispersion rate due to lowering of the metal vapour pressures, caused by a metal oxy-chlorine intermediate [33-38]. Hence, it is a more 'rapid' and 'aggressive' procedure for treating catalysts, in comparison with applying air or hydrogen regeneration only.

4 Investigation of regeneration procedures for TWC

In this thesis, the possibility to 'clean' the catalyst surface by removing combustible contaminants clogging the active surface as well as a studying the behaviour of larger metal crystallites under various thermal gaseous treatments were the main objectives. Starting with procedures conducted in oxygen or hydrogen-rich atmospheres at temperatures ranging from 300 °C to 700 °C, the effect of temperature and treatment time on the stability of the noble metal and metal oxide support particles was evaluated. Based on these experiments and the conclusions that could be drawn, it was hypothesised that the addition of chlorine, either in liquid or gaseous form, might enhance regeneration of the catalysts (Paper I). Indeed, subsequent experiments with a chlorine-rich environment confirmed this hypothesis and full-scale experiments (Paper II) were initiated, focusing on the thermal treatment in a

chlorine-rich atmosphere. Real simulated driving conditions allowed for rigorous testing and evaluation of the regeneration method.

5 Regeneration of TWC at laboratory scale (Paper I)

Small cylindrical catalyst fragments (radius 20 mm; height 30 mm) were cut out from commercial TWCs obtained from car or scrap yard companies, enabling a faster screening of a large number of different catalysts, both regarding activity and morphological changes.

5.1 Catalysts

The catalysts were supplied from Ford Spain or Fevar, a Belgian scrap yard company, and included driving conditions ranging from extra-urban to urban in countries such as Spain, Belgium and Finland. Unused (fresh) samples of each catalyst type were available for comparative studies, such as activity and characterisation.

5.2 Experimental

5.2.1 KTH equipment set-up (Regeneration)

A tubular stainless steel reactor with an internal diameter of 22 mm was used in all regeneration experiments. The steel reactor was placed in a heating furnace capable of reaching temperatures exceeding 700 °C. A catalyst fragment was inserted inside the reactor and the temperature increased at a rate of 10 °C/min. A given gas mixture was then introduced and premixed before entering the area containing the catalyst fragment. The gas flow through the reactor was 230 ml/min. Temperatures were continuously measured at the inlet and outlet of the reactor using a Vips TT100 temperature-logger. The schematic of the experimental apparatus is demonstrated in Fig. 5.1.

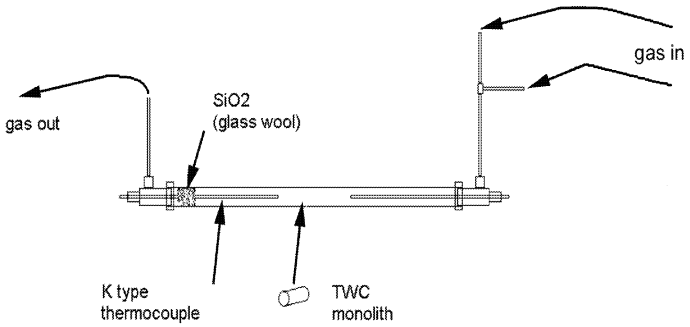

Figure 5.1 Experimental set-up for regeneration treatments

5.2.2 AVL MTC small-scale experiment set-up (Activity tests)

Activity tests were carried out in a quartz tube reactor with an internal diameter of 22 mm, a schematic of which is shown in Fig. 5.2. Both mixtures of synthetic gas and/or real exhaust gas could be used to simulate real driving conditions. During such dynanometer tests, which may be carried out at different motor engine loads, the gas flow rates were varied from 24 000 h^{-1} to 100 000 h^{-1}. The gas entering the reactor was preheated to a temperature of 220 °C to ensure no condensation of exhaust gases prior to entering the quartz reactor. The maximum temperature was set to 550 °C and the heat raised at a maximal rate of 20 °C/min while the cooling rate was 10 °C/min. Measurements of regulated emissions were in accordance with the test procedure using the Horiba 9000 system. Emissions were continuously sampled via heated coils to a Horiba 9000 analysis system [39] according to the European directive 96/69/EC and the emissions were measured as follows: carbon monoxide (CO) using a non-dispersive infrared analyser (NDIR); total unburned hydrocarbons (HC) using a flame ionisation detector (FID); nitrogen oxides (NO_x) by means of a chemiluminescence analyser (CLA).

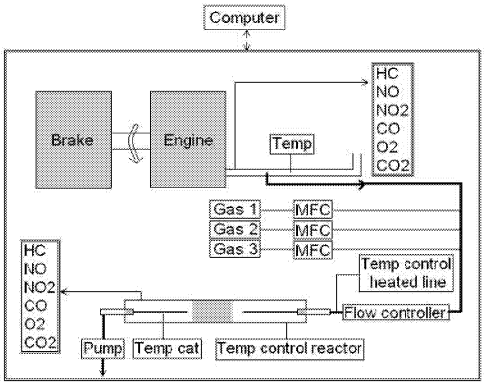

Figure 5.2 Equipment set-up for small-scale activity measurements

5.3 Characterisation

To obtain information regarding the composition and structure of the washcoat and noble metal surface, a wide variety of characterisation techniques were utilised. A brief description follows together with a discussion of the main results from the characterisation.

5.3.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

Surface phase morphology such as particle size, distribution and shape are easily studied by means of the SEM/EDX technique. The SEM instrument scans a small sample surface with a probe of electrons (5-50 kV). Backscattered or emitted electrons from the sample later produce an image on a cathode-ray tube. The order of magnification lies at around 20-50 000; depending on sample composition a resolution of length scales down to 5 nm is possible. Elemental composition of the catalyst surface is obtainable by the EDX. A typical SEM micrograph showing the ceramic substrate and the washcoat can be found in Fig. 5.3.

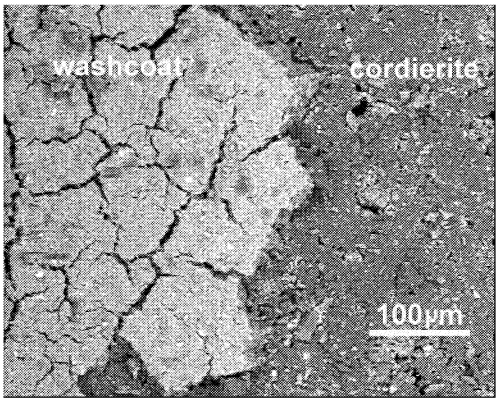

Figure 5.3 SEM image of a TWC monolith

Two different SEM instruments were employed in this work: a Zeiss digital scanning microscope DSM 940 equipped with a Link QX2000 EDX-system and a JEOL JSM-840 microscope with a germanium detector for energy dispersive X-ray analysis.

5.3.2 Transmission electron microscopy (TEM)

Higher resolutions in comparison to SEM are achievable with a TEM, where a more intense electron beam, ranging from 100 kV and higher, is utilised. An order of magnification up to 1 000000 is possible, with resolutions of 0.5 nm. The study of the washcoat of a three-way catalyst by TEM at a higher resolution is of great importance since it is the 'only' method, which can give information about the size and the distribution of the noble metal particles. Sintering after exposure to high temperatures on a noble metal particle is illustrated in Fig. 5.4.

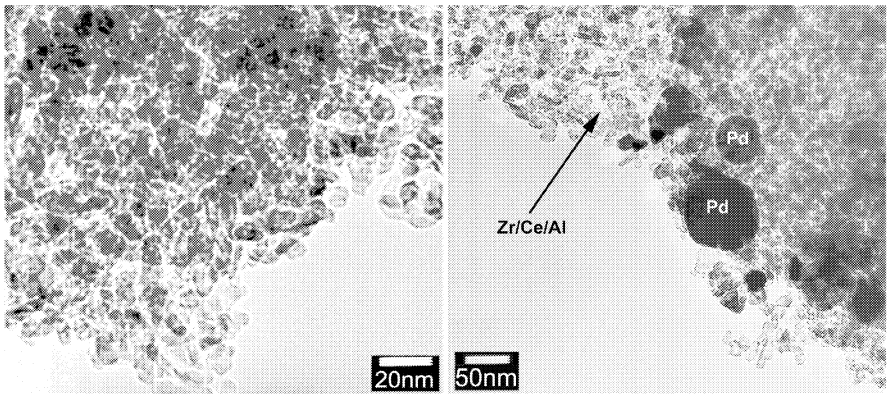

Figure 5.4 TEM micrographs of catalysts: (left) fresh catalyst and (right) aged

A JEOL 2000FX transmission electron microscope (TEM), running at 200 kV, was used throughout the experimental characterisation.

5.3.3 X-Ray Diffraction (XRD)

XRD allows for studies of the composition of the bulk structure, due to the high energy of the x-ray beam penetrating deep into the washcoat. The x-rays are diffracted by the crystalline phases in the sample according to Bragg's law, from which a quantitative estimate of crystallite size based on width and height of the diffraction peak can be made. Diffraction patterns further give 'fingerprint' information about the phase compositions in the sample. The effects of aging or sintering are apparent by the degree of line intensification of the aged sample together with the appearance of new peaks due to chemical contamination of the washcoat surface, as illustrated in Fig. 5.5.

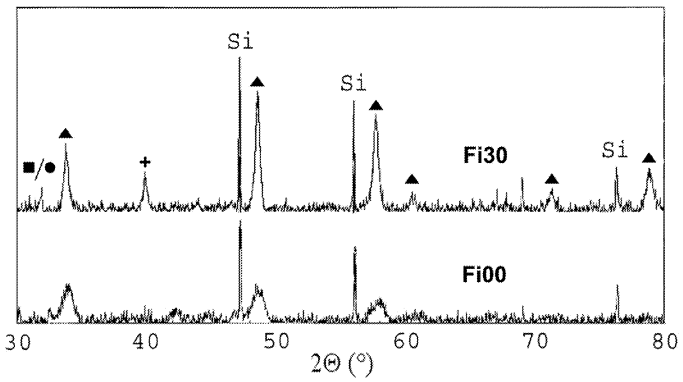

Figure 5.5 X-ray diffractograms of the catalysts Fi30 (aged) and Fi00 (fresh): ZrO (■), $Zr_{1-X}Ce_XO_2$ (▲), $CePO_4$ (●) and Pd (+)

A Siemens D5000 XRD, using monochromatic Cu Kα radiation and scanning 2θ from 30 to 80° in the scan mode (0.02°, 1 s), was used. Subsequent phase identification was performed using a reference database (JCPDS files) supplied with the equipment.

5.3.4 Temperature programmed reduction (TPR)

The washcoat and the metals placed upon its surface consist of a vide variety of metal oxides. By introducing a gas, such as hydrogen, and by increasing the temperature over a certain temperature interval, metal reduction will take place. Noble metals and surface-bound metals are more easily reduced and thus their peaks occur at lower temperatures, whilst bulk metals follow at higher temperatures. The ease by which metals are reduced or the shape, width and height (i.e. hydrogen uptake), of the peaks allows for an estimation of the metal surface composition and the accessibility of the metallic active sites. The influence of sintering and chemical contamination on two catalyst fragments originating from two different parts of a TWC catalyst was observed using TPR studies. Fig. 5.6 shows the obtained TPR profiles, where a less sintered and contaminated rear outlet (Ro30) is compared with the front inlet (Fi30) originated from the same catalyst. Loss of hydrogen uptake and higher temperatures required to reduce the surface and noble metals are interesting features.

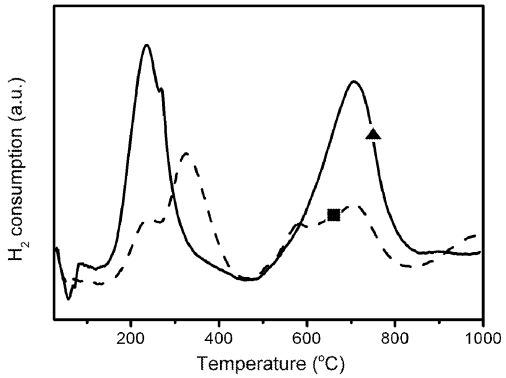

Figure 5.6 Temperature-programmed reduction profiles for the rear outlet (▲) and front inlet (■) of a TWC catalyst

TPR combined with chemisorption experiments, where a gas such as carbon monoxide (CO) is pulsed in small amounts over the sample, allows for an estimation of the metal dispersion. This, by the formation of a monolayer over the precious metals until saturation is reached in chemisorption.

5.3.5 Brunauer, Emmet and Teller analysis (BET)

Measurements of pore size distribution and surface area of small monolith cylinders (radius 12mm; height 30 mm) were obtained on a Micromeritics ASAP 2010 instrument by adsorption/desorption of nitrogen at liquid nitrogen temperature. BET analysis was carried out on whole monoliths *priori* and *posteriori* to thermal gas treatment and allowed for comparative results, utilising the same monolith.

5.4 Results from laboratory-scale studies

Regaining lost activity stemming from thermal deactivation, where metals have undergone structural changes inducing large and bulky crystallite structures, is not ‘easy’ by any means. Complex metal compositions found in a TWC, placed there to uphold a stable and high catalytic activity in a harsh exhaust gas environment, make a ‘successful’ regeneration more difficult.

Experiments were based on how parameters such as treatment temperature, time and gas composition would influence the washcoat material as well as the precious metals placed thereon. These experiments were performed to identify potential regeneration methods. From the obtained results, the following conclusion can be drawn:

Oxygen treatments did not result in any significant changes in the catalyst activity or its structure. However, catalyst segments with a high noble metal loading and located close to the front section of the TWC, being exposed to the highest temperatures and chemical deactivation, showed a certain response to oxygen treatment. Activity measurements performed on two samples of oxygen/air treated catalysts, both extracted from the front section of a commercial TWC, one carrying a high noble metal (Fi30) loading (approximately 6000 mg/l) versus a catalyst containing one third of the metal concentration (Fi59), are displayed in Fig. 5.7.

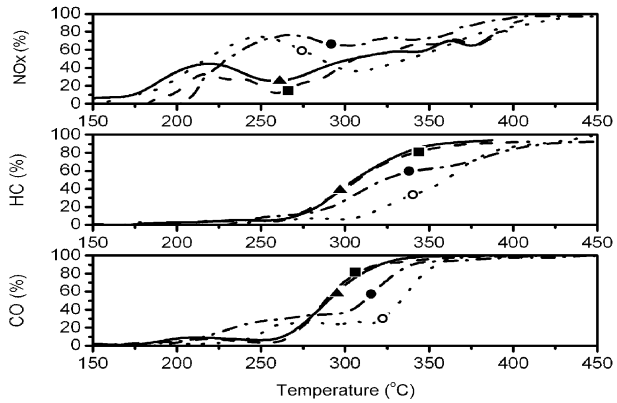

Figure 5.7 Influence of the temperature on the conversion of NO_X, HC and CO for Fi59 (▲), oxygen-treated Fi59 (■), Fi30 (o) and oxygen-treated Fi30 (●)

Screening the catalyst surface of Fi30 by means of TEM indicated a minute removal of the largest noble metal crystallites, around 100 nm in size. TPR measurements, where the reduction profiles exhibit an increase in the hydrogen uptake from surface-bound metals (including noble metals), further verified the feasibility of the regeneration treatment, hinting at an increase in the metal accessibility. But the 'joy' proved short-lived as repetitive activity

measurements demonstrated the lack in stability of the Fi30 catalyst, with the activity dropping back to the same level as prior to oxygen thermal treatment. The observable change in activity was thus most likely due to a temporary 'cleaning' effect of the washcoat surface.

Changing the treatment gas to hydrogen, whilst retaining the same temperature and time intervals as previously during the oxygen treatment, did not give rise to any detectable changes in the catalysts. A loss in activity was even observable at temperatures higher than 700 °C, comparable with similar loss in activity for oxygen-treated catalysts in the same treatment temperature interval.

Based on the results from these trials with oxygen or hydrogen, the addition of a halogen gas such as chlorine was tested. Chlorine possesses properties, which can influence the mobility/volatility of metals through the formation of M_XO_YCl complexes. The main incitement was to try to control the formed mobile intermediate in an effort to increase the dispersion of the metals, in particular the noble metals. Keeping the chlorine concentration and treatment temperature within certain boundaries is crucial, as can be seen in Fig. 5.8, where 'pure' palladium was removed from the catalyst during treatment and later captured on glass wool placed at the cold outlet of the oven.

Keeping the temperature below 500 °C combined with a treatment time of 30 to 60 minutes and a low chlorine gas content, e.g. 0.6 vol% in air was found to

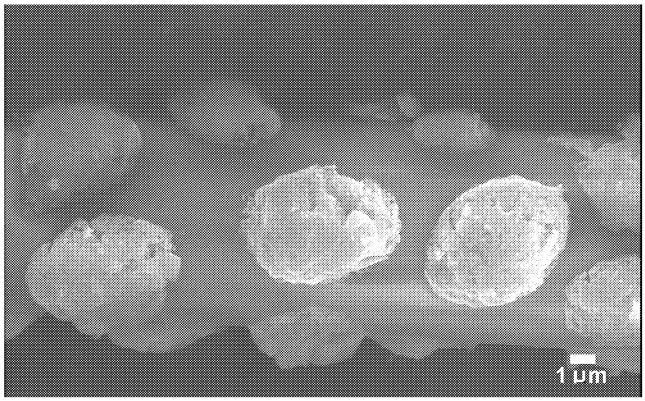

Figure 5.8 SEM image of 'porous' Pd particles caught on glass wool

be one of the most versatile regeneration procedures. Both heavily front inlet (Fi47) and less sintered rear outlet (Ro47) catalyst samples could be treated with success at both faster ignition rates and markedly higher noble metal dispersion. Fig. 5.9 shows the HC conversion *vs.* temperature for Fi47 and Ro47 before and after regeneration.

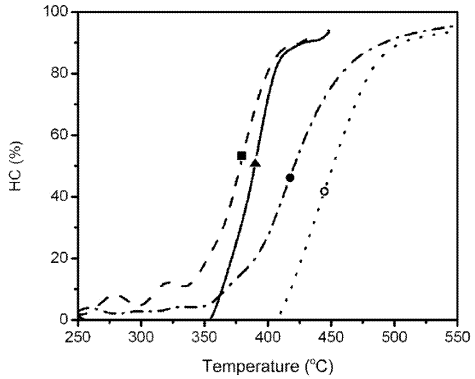

Figure 5.9 Influence of the temperature on the conversion of HC for Ro47 (▲), oxygen-chlorine treated Ro47 (■), Fi47 (o) and oxygen-chlorine treated Fi47 (●)

Chlorine-regenerated samples are more stable against prolonged exposure to exhaust gas after regeneration, and aging the catalyst in air for 16 hours at 800 °C did not remove all the regained activity.

6 Regeneration of full scale TWC (Paper II)

6.1 AVLMTC full-scale activity tests

Full-scale dynanometer tests allow for a more dynamic measurement of the catalyst activity. Here, factors such as varying exhaust gas composition and exhaust gas temperature are more easily studied in comparison to using fixed gas and temperature ramps, e.g. the 'mini-cuts' reactor. The applied test method EC2000 is standardised and consists of two parts; the first 780 s representing urban driving conditions (UBC) and the final 400 s comprising a higher speed part, the so-called extra urban driving cycle (EUDC), as illustrated in Fig. 6.1.

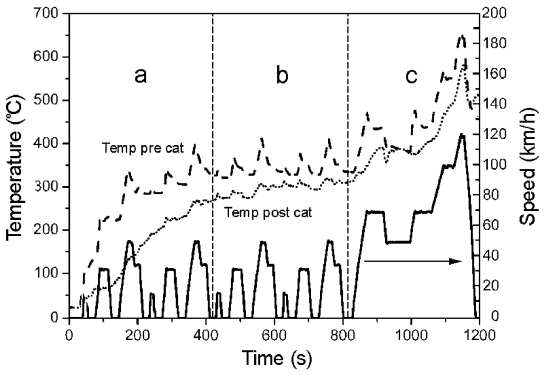

Figure 6.1 EC2000 dynanometer test procedure

Exhaust gases were measured continuously during the procedure and combined with the results from a constant volume sampler (CVS), where an average for a given part of the driving cycle can be obtained (in g/km). Both catalysts were mounted on a test vehicle, Volvo 245. No optimisation of catalyst *vs*. car engine was performed and any changes in activity are based on catalyst behaviour before and after regeneration.

6.2 Results from full scale activity tests

During the first part of the EC2000 driving cycle, the TWC is heated from room temperature to its 'operating zone/window', which lies at 300 °C to 700 °C. The initial phase, the cold-start period is responsible for the release of the highest amount of contaminants, since the catalyst quickly reaches close to 100% conversion once it is has ignited. A fast ignition response together with a fast response to transient periods are thus of importance during the evaluation of the 'full-scale' activity measurements.

Two different automotive catalysts were studied: a high mileage catalyst (catalyst I) and a low mileage catalyst (catalyst II) with a less chemically and thermally deactivated catalyst surface. Catalyst fragments were removed from both catalysts and used in preceding characterisation, as illustrated in Fig 6.2, with contaminant composition measured by EDX.

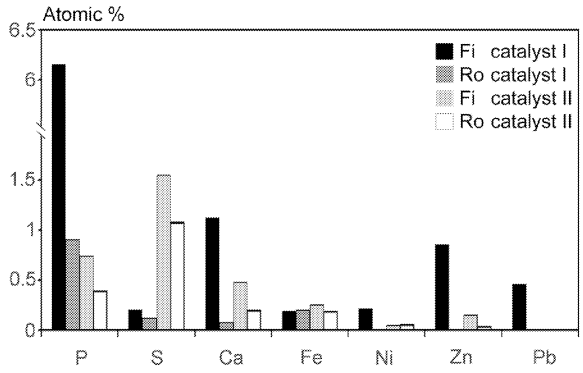

Figure 6.2 Contaminants on the washcoat for front and rear parts of catalyst I (high mileage) and catalyst II (low mileage)

The previous 'lab-scale' measurements hinted at a possible regeneration of a wide variety of catalysts, relatively independent of catalyst status, such as degree of sintering or chemical fouling. These measurements were based on a pre-defined exhaust gas composition together with a specific ignition-ramp (10 °C/min). During 'full-scale' measurements the catalyst is exposed to a more dynamic environment, with the engine being exposed to a higher fuel-air ratio (lambda below 1) to ease the engine start-up, followed by subsequent emissions and exhaust gas temperatures stemming from brake and acceleration steps, as defined by the EC2000 driving cycle. Criteria such as catalyst metal composition, structure and size will have a noticeable impact on the overall catalyst efficiency. For the 'full-scale' experiments performed in this work no catalyst adjustment was carried out, since the activity of the catalyst before and after regeneration is the relevant feature, and not achieving current Euro 3 standards, with emission levels for CO at 2.3 g/km, HC 0.2 and NO_X 0.15 g/km.

Of the two catalysts tested, only the high mileage catalyst (catalyst I) showed any significant improvement in the catalytic activity after oxy-chlorine thermal treatment. Emissions from both cold ('light-off' behaviour) and warm-engine phase ('dynamic' behaviour) of the EC2000 driving cycle were reduced, with an overall reduction of emissions for CO, HC and NO_X by 45 %, 32 % and 35 %, respectively. It proved more difficult to attain any noticeable improvements

on the low mileage catalyst (catalyst II). High activity was observed in both the 'cold-engine' and 'warm-engine' phases of the EC2000 driving cycle prior to regeneration. The results after oxy-chlorine treatment did not improve the overall activity of the catalyst.

7 Conclusions

Several methods for regeneration of commercial three-way automotive catalysts (TWC) have been derived and investigated in this thesis. The common denominator for these methods is a thermal treatment, which was applied for various gaseous atmospheres at lab-scale, as can be seen in Table 7.1.

Table 7.1 Applied regeneration procedures

Oxygen treatment	
Temp. 500 to 700 °C Treatment time >3 hours	Proved to be more successful on catalysts with a higher noble metal loading which are also more heavily sintered
Hydrogen treatment	
Temp. 300 to 700 °C Treatment time >1 hours	Did not give rise to any detectable changes in the catalysts. A loss in activity was even observable at temperatures higher than 700 °C.
Chlorine (0.5-5 vol%) in oxygen	
Temp. 300 °C Treatment time >0.5 hours	Regeneration of catalysts with lower metal loading and not as heavily sintered
Chlorine (<1 vol%) in oxygen	
Temp. 500 °C Treatment time <1 hour	Regeneration of catalysts with lower metal loading and not as heavily sintered Possible losses of noble metals from the catalyst must be taken into consideration
Hydrochloric acid pre-treatment, followed by a thermal regeneration in oxygen	
Temp. 300-500 °C Treatment time <1 hour	Hydrochloric acid solutions can be used instead of gases. Dilute liquids should be used to better control the amount of chlorine interacting with the catalyst surface.

The results obtained at lab-scale gave that the full-scale test was made on oxy-chlorine treated catalysts.

The main mechanism for catalyst regeneration of TWC is redispersion of the active sites (e.g. noble metals) on the catalyst washcoat. Both ‘small-scale’ and ‘full-scale’ activity measurements and characterisation of the catalyst surface structure, laid the basis for the catalytic performance evaluation.

The scale-up experiments were found to be more demanding in terms of evaluation of catalyst restructuring after regeneration, especially so on relatively fresh catalysts, with effects such as catalyst composition and catalyst-(relative)-car engine playing a more significant role in the catalyst performance during the full-scale activity test.

The best results from the light-off ‘small-scale’ experiments were obtained on the Fi30 catalyst, with a lowering of the T_{50} (temperature at which conversion reaches 50%) of approximately 50 °C, 60 °C and 20 °C for CO, HC and NO_X, respectively, in comparison to the untreated reference. For the ‘full-scale’ activity evaluation only the high mileage catalyst responded to regeneration, by a reduction of emissions by 45 %, 32 % and 35 % for CO, HC and NO_X, respectively, over the 1200s long EC2000 test.

The proposed method can be applied without dismantling the on-board catalyst, as opposed to the present treatment of spent TWC catalysts, which involves the extraction of noble metals. As such, the oxy-chlorine thermal treatment constitutes a novel and simple alternative for efficient regeneration of spent automotive catalysts.

8. Acknowledgment

The European Commission is highly acknowledged for providing the financial means through project no. G5RD-CT-2000-00376 (Regencats) to make this thesis possible.

I would like to thank my supervisors Associate Professor Magali Boutonnet and Professor Sven Järås for their supervision and support.

Further I would like to thank all my colleagues, former and present, at Chemical Technology and Chemical Reaction Engineering.

Thanks also to:

Dr. Lars Eriksson at AVLMTC for his help and input, especially with the 'mini-cuts' reactor and all the 'problems' it brought and still brings.

Dr. Christina Hörnell for helping me with the linguistics and valuable input.
Inga Groth for her assistance with the analytical instruments.

Dr. Johan Agrell and Ulf Nylén, former and present room compadres, for the 'strange talks' and for allowing 'Bertha-the palm tree' and me to stay in the room.

Last, but not least, I would like to thank my family for their support over the years, especially Erik, for his valuable input.

References

[1] H.L. MacLean, L.B. Lave, Prog. Energy Combust. Sci. 29 (2003) 1.

[2] US Environmental Protection Agency, www.epa.gov, accessed October 27, 2004.

[3] R.J. Farrauto, R.M. Heck, Catal. Today 51 (1999) 351.

[4] M. Shelef, R.W. McCabe, Catal. Today 62 (2000) 35.

[5] D.S. Lafyatis, G.P. Ansell, S.C. Bennett, J.C. Frost, P.J. Millington, R.R. Rajaram, A.P. Walker, T.H. Ballinger, Appl. Catal. B 18 (1998) 123.

[6] G.C. Koltsakis, A.M. Stamatelos, Prog. Energy Combust. Sci. 23 (1997) 1.

[7] R.M. Heck, R.J. Farrauto, Appl. Catal. A 221 (2001) 443.

[8] T. Kobayashi, T. Yamada, K. Kayano, Appl. Catal. B 30 (2001) 287.

[9] T.E. Hoost, K. Otto, Appl. Catal. A 91 (1992) 39.

[10] D. Duprez, C. Descorme, T. Birchem, E. Rohart, Top. Catal. 16/17 (2001) 49.

[11] M.H. Yao, R.J. Baird, F.W. Kunz, T.E. Hoost, J. Catal. 166 (1997) 67.

[12] H. Vidal, J. Kašpar, M. Pijolat, G. Colon, S. Bernal, A. Cordón, V. Perrichon, F. Fally, Appl. Catal. B 30 (2001) 75.

[13] L.F. Liotta, A. Macaluso, A. Longo, G. Pantaleo, A. Martorana, G. Deganello, Appl. Catal. A 240 (2003) 295.

[14] H.W. Jen, G.W. Graham, W. Chun, R.W. McCabe, J.P. Cuif, S.E. Deutsch, O. Touret, Catal. Today 50 (1999) 309.

[15] R.D. Monte, J. Kašpar, Top. Catal. 28 (2004) 47.

[16] Z. Hu, F.M. Allen, C.Z. Wan, R.M. Heck, J.J. Steger, R.E. Lakis, C.E. Lyman, J. Catal. 174 (1998) 13.

[17] Y. Cai, H.G. Stenger, C.E. Lyman, J. Catal. 161 (1996) 123.

[18] Y.J. Mergler, B.E. Nieuwenhuys, J. Catal. 161 (1996) 291.

[19] C.H. Bartholomew, Appl. Catal. A 212 (2001) 17.

[20] P. Forzatti, L. Lietti, Catal. Today 52 (1999) 165.

[21] J.R. González-Velasco, J.A. Botas, R. Ferret, M.P. González-Marcos, J-L. Marc, M.A. Gutiérrez-Ortiz, Catal. Today 59 (2000) 395.

[22 A. Martínez-Arias, M. Fernández-García, A. Iglesias-Juez, A.B. Hungría, J.A. Anderson, J.C. Conesa, J. Soria, Appl. Catal. B (1992) 151.

[23] V. Kröger, M. Hietikko, U. Lassi, J. Ahola, K. Kallinen, R. Laitinen, R.L. Keiski, Top. Catal. 31 (2004) 469.
[24] C.E. Hori, H. Permana, K.Y. Simon, A. Brenner, K. More, K.M. Rahmoeller, D. Belton, Appl. Catal. B 16 (1998) 105.
[25] D.D. Beck, J.W. Sommers, C.L. DiMaggio, Appl. Catal. B 11 (1997) 257.
[26] T.N. Angelidis, S.A. Sklavounos, Appl. Catal. A 133 (1995) 121.
[27] C. Battistoni, V. Cantelli, M. Debenedetti, S. Kačiulis, G. Mattogno, A. Napoli, Appl. Surf. Sci. 144 (1999) 390.
[28] T. Luo, J.M. Vohs, R.J. Gorte, J. Catal. 210 (2002) 397.
[29] R.M.J. Fiederow, S.E. Wanke, J. Catal. 43 (1976) 34.
[30] J.E. Stulga, P. Wynblatt, J.K. Tien, J. Catal. 62 (1980) 59.
[31] T.J. Lee, Y.G. Kim, J. Catal. 90 (1984) 279.
[32] R.M.J. Fiedorow, S.E. Wanke, Appl. Catal. B 14 (1997) 249.
[33] H. Lieske, G. Lietz, H. Spindler, J. Völter, J. Catal. 81 (1983) 8.
[34] G. Tonetto, M.L. Ferreira, D.E. Damiani, J. Mol. Catal. A 171 (2001) 123.
[35] G. Lietz, H. Lieske, H. Spindler, W. Hanke, J. Völter, J. Catal. 81 (1983) 17.
[36] K. Foger, H. Jaeger, J. Catal. 92 (1985) 64.
[37] Z.C. Zhang, B.C. Beard, Appl. Catal. A 188 (1999) 229.
[38] C. Contescu, D. Macovei, C. Craiu, C. Teodorescu, J.A. Schwartz, Langmuir 11 (1995) 2031.
[39] Horiba Group, www.horiba.com/flash.htm, accessed October 27, 2004.