Coke deposition on automotive three-way catalysts studied with LEIS

J.M.A. Harmsen [a,b], W.P.A. Jansen [b,c], J.H.B.J. Hoebink [a,b], J.C. Schouten [a,b] and H.H. Brongersma [b,c,*]

[a] *Laboratory of Chemical Reactor Engineering, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*
E-mail: H.H.Brongersma@tue.nl
[c] *Calipso LEIS Expertise Centre, PO Box 513, 5600 MB Eindhoven, The Netherlands*

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LEIS measurements have been performed on fresh and used commercial three-way catalysts ($Pt/Rh/CeO_2/\gamma\text{-}Al_2O_3$). The catalysts showed a significant decrease in the platinum surface concentration of approximately 50% after use in hydrocarbon oxidation at cold-start conditions, and could be completely regenerated. The selectivity towards the outermost atomic layer of LEIS allowed a one to one correlation between the surface Pt concentration as detected with LEIS and that obtained by kinetic modelling. This supports recent assumptions on selective deactivation. Conventional surface science techniques such as XPS, SIMS or AES would have yielded ambiguous results since their probing depths are not limited to the outermost atomic layer.

KEY WORDS: coke deposition; automotive catalysis; regeneration; low-energy ion scattering (LEIS); ion scattering spectroscopy (ISS)

1. Introduction

Nowadays, most cars are supplied with a monolith converter, which contains a so-called three-way catalyst to diminish the emission of harmful components present in the car exhaust gas [1]. The catalyst converts simultaneously carbon monoxide, uncombusted hydrocarbons, and oxides of nitrogen to carbon dioxide, water, and nitrogen. After a cold start, however, the temperature of the catalyst is too low for an effective conversion (*viz.*, $T < 600$ K), resulting in emissions of toxic pollutants. The rates of conversion of the reactants are then completely determined by the intrinsic chemical reaction kinetics. Therefore, for a further optimisation of the exhaust gas converter and the control system, currently an air/fuel ratio based feedback controller, a full understanding of the process is necessary, notably the kinetics of the reactions involved. The influence of the driver, reflected by FTP tests (federal test procedure), as well as the delay of the sensor/controller system cause steep and frequent changes in the composition of the exhaust gas from the car engine [2]. This indicates the need for modelling of the transient kinetics. Transient kinetic modelling, based on elementary reaction steps, yields a detailed model, capable of predicting accurately the conversions of all components over the automotive catalyst. Such a model can be used to improve the performance of the monolith converter *via* model predictive control [3].

During the cold-start period, which will take generally about 100 s, the engine is normally operated at rich conditions in order to ensure its operation. This will result in a large excess of carbon monoxide and unburned hydrocarbons in the exhaust gas that partly adsorb onto the catalytic surface. Partial decomposition of these adsorbed components during the monolith heat-up will lead to the presence of carbonaceous deposits on the catalytic surface, which will block active sites of the catalyst, until the deposits can be burned off. The latter will not occur until the end of the cold-start period, at $T \approx 600$ K. Carbon deposits from CO on Pt/CeO_2 and Rh/CeO_2 catalysts have been imaged by means of TEM [4], and also ethylene is notorious for depositing carbonaceous species on noble metal catalysts [5–8]. This means that deposition of carbonaceous species contributes significantly to the emissions during the cold-start period. Recent kinetic studies [9,10] on ethylene and acetylene oxidation in the framework of automotive catalysis endorsed the involvement of carbonaceous species, notably the selective deactivation of noble metal sites with respect to oxygen adsorption. The intention of this study is to provide an independent, quantitative confirmation of the decrease of noble metal sites, as estimated from the recent kinetic studies [9,10].

A real exhaust gas contains hundreds of different hydrocarbons [11–13]. Ethylene and acetylene have been chosen to represent these hydrocarbons. Ethylene, with a relatively large abundance in an exhaust gas [13], represents the hydrocarbons, which can be oxidised quite easily, among which aromatics [14,15]. Acetylene was chosen mainly because of both its large inhibitive effect and high concentration after a cold engine start, as discussed recently [10].

In this study low-energy ion scattering (LEIS) has been used to quantify the coke formation on a commercial three-way catalyst with a characteristic noble metal loading of 0.48 wt%. Using LEIS the elemental composition of the

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[*] To whom correspondence should be addressed.

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outermost atomic layer of a catalyst can be determined in a quantitative way. Hence, if the catalyst surface is partly covered with carbon this will both be detected by observing the presence of carbon and by measuring the disappearance of the underlying material. Therefore, LEIS can reveal whether the carbon is deposited on the carrier material or on the noble metals. Techniques like XPS, Auger electron spectroscopy (AES) or secondary ion mass spectroscopy (SIMS), do not provide this information since their probing depths are not limited to the outermost atomic layer which leads to ambiguous results [16]. For instance – assuming $\theta = 45°$, Mg Kα X-rays, inelastic mean free path of 3.07 nm for Pt_{4f} in C [17], and a carbon monolayer thickness of 0.2 nm [18] – a surface that is totally covered with one atomic layer of carbon still gives about 91% of the Pt XPS signal of a clean Pt sample. While a Pt surface that is only half covered with two monolayers of C would give the same 91% Pt signal. Therefore, XPS cannot be used to determine the part of the Pt surface that is covered with C. The XPS signal of the C atoms can also not be used, since C can also be on the support. Hence, quantification of the carbon coverage does not make sense. The same kind of ambiguity will be encountered when using AES or SIMS. Moreover, matrix effects will further complicate the analysis when using SIMS. The information depth of LEIS, however, is limited to one atomic layer [19,20] and allows quantification of the noble metal area loss. Moreover, the high sensitivity of LEIS towards noble metals enables detection down to concentrations of some 10 ppm of a monolayer. This opens a unique possibility to quantitatively verify the kinetic modelling. In general it will thus be possible with LEIS to study the nucleation site of coke formation.

The noble metal surface areas of fresh and used commercial catalysts as detected with LEIS, have been compared with the corresponding values as estimated from kinetic modelling of the acetylene and ethylene oxidation at cold-start conditions, to verify the outcome of the latter [9,10].

2. Experimental

2.1. Catalyst (pre-)treatment

A commercial $Pt/Rh/CeO_2/\gamma$-Al_2O_3 catalyst, as used for coating monoliths, has been provided by d**mc²** A.G. (Hanau, Germany) as a powder with a mean particle diameter of 12 μm. The powder is pressed, crushed, and sieved to obtain a fraction with pellet diameters between 0.11 and 0.15 mm. To enhance isothermicity during kinetic measurements in a fixed-bed reactor, 0.92 g of catalyst is diluted with 1.4 g of inert α-Al_2O_3 (0.15–0.21 mm).

In order to enable reproducible kinetic experiments the following pre-treatment is carried out. The catalyst is heated to 773 K in a steady flow of He. Then the catalyst is oxidised during 1 h by a stream containing 25 vol% oxygen. Next the catalyst is kept under flowing He for 30 min in order to purge reversibly adsorbed oxygen, followed by reduction in a He stream containing 5 vol% H_2 at 773 K for 2 h. Finally, the catalyst is allowed to cool down to reaction temperature under a He stream.

2.2. Kinetic experiments

Different batches of the thus pre-treated $Pt/Rh/CeO_2/\gamma$-Al_2O_3 catalyst have been used in transient ethylene oxidation experiments at cold-start conditions (393–443 K), and in transient acetylene oxidation experiments at cold-start conditions (503–543 K). During the transient experiments, the catalyst material is alternately exposed to He flows with either 0.15 kPa hydrocarbons or 0.5 kPa O_2 at frequencies between 0.05 and 0.25 Hz for a period of two weeks. More detail on the transient experiments can be found in [9,10], concerning the ethylene and acetylene oxidation, respectively.

2.3. LEIS experiments

In LEIS (also known as ion scattering spectroscopy or ISS) experiments, low-energy noble gas ions are scattered by atoms in the exposed surface. According to the laws of conservation of energy and momentum, the energy spectrum of the back-scattered ions is equivalent to the mass spectrum of the target atoms. The information depth of LEIS is limited to one atomic layer, because of the high neutralisation probability of the noble gas ions.

Prior to LEIS analysis the catalyst samples have been compacted into pellets at 300 MPa. Recently, we have shown that compaction at 300 MPa does not influence the surface composition [21]. LEIS selectively probes the outermost atomic layer, hence surface contaminants would obscure the intrinsic composition. Therefore, the contaminants have to be removed before analysis of the intrinsic composition is possible. To clean the fresh, and to regenerate the used three-way catalyst samples, an atomic oxygen beam has been applied. The use of atomic oxygen allows very effective cleaning at low temperatures (*ca.* 310 K). After the oxidative cleaning, the catalysts are reduced at 573 K in 20 kPa H_2 flowing at 2.6 mmol/min for 10 min.

After evacuation, hydrogen from the reduction treatment remains on the catalyst surface. This remaining hydrogen can be selectively removed by sputtering, since the sputter rate for hydrogen is usually 10–50 times higher than that for other elements [22]. From LEIS measurements as a function of ion dose, it appeared that hydrogen was removed upon a He dose of 2×10^{15} ions/cm². Between a He dose of 2×10^{15} and 10×10^{15} ions/cm², the surface composition of the catalyst remained constant. The sputter rate of Ne is typically ten times higher than for He. Therefore, all presented measurements are carried out using either a He dose between 2×10^{15} and 9×10^{15} ions/cm² or a Ne dose between 0.2×10^{15} and 1×10^{15} ions/cm².

All LEIS measurements have been performed in the UHV Calipso LEIS set-up. This set-up, which has been developed at the Eindhoven University of Technology, is equipped with a sensitive double-toroidal analyser and a large position-sensitive detector. These allow a large part of the energy

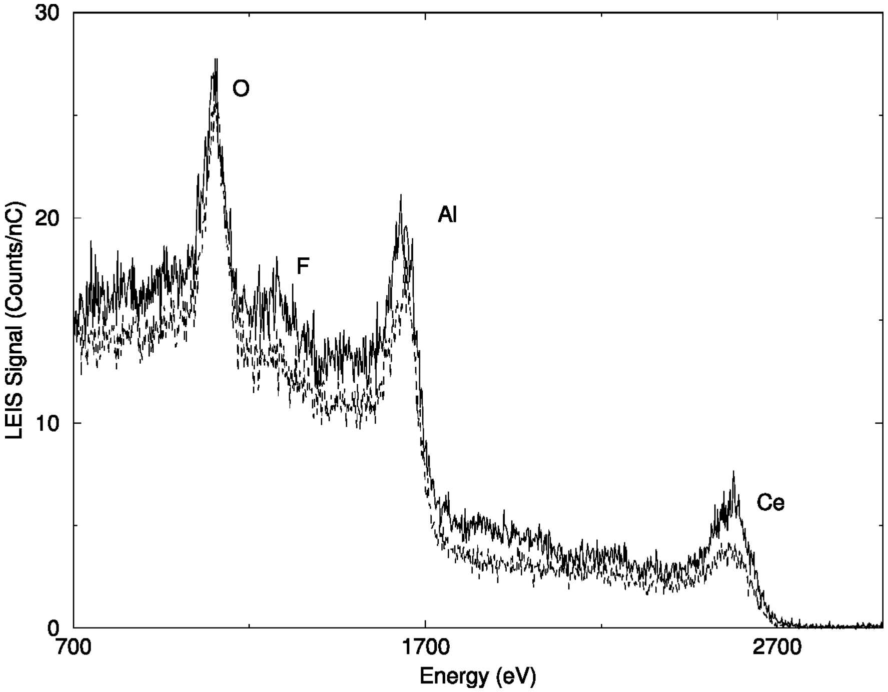

Figure 1. Two LEIS spectra obtained with 3 keV ^{4}He on a fresh (—) and a used (- - -) three-way catalyst.

spectrum to be measured simultaneously [23]. Since the sensitivity of this set-up is about a factor 1000 higher than that of conventional LEIS, it is now possible to detect as little as some 10 ppm of a monolayer Pt on a supported catalyst.

To analyse the surface composition of the three-way catalyst before and after use in the ethylene and acetylene oxidation, 3 keV ^{4}He ions have been used. Moreover, 3 keV Ne ions have been used to allow separation of Pt from the Ce in the catalyst carrier. Unfortunately, Rh cannot be observed since the expected Rh surface concentration is *ca.* ten times lower than the Pt surface concentration because of segregation [24]. Moreover, the Rh peak is on the low-energy side of the huge Ce peak. Hence a small Rh peak is indiscernible from the Ce background of the catalyst carrier. The beam was rastered over an area of 1×1 mm^2 during measurements. In the Calipso LEIS set-up the primary ion beam is directed perpendicular towards the target, and ions scattered over 145° with respect to the incoming beam are detected. During the experiments the catalyst samples were prevented from charging by flooding with low-energy electrons from all directions.

3. Results

3.1. LEIS analysis of the catalyst carrier

Figure 1 shows LEIS spectra of a fresh (solid line) and a used (dotted line) Pt/Rh/CeO_2/γ-Al_2O_3 three-way catalyst. The spectra have been measured with a 3 keV ^{4}He dose of 6×10^{15} ions/cm^2, and are therefore selectively representing the outermost atomic layer of the catalyst. From this figure, it can be seen that the catalyst surface exposes not only large amounts of Ce, O, and Al, but also a significant amount of F. Additional measurements on the support materials revealed that the F originates from the γ-Al_2O_3 support material. Like other surface contaminants, F will obscure underlying catalyst constituents. Since the F content differs from sample to sample, it hampers exact quantification of the composition of the catalyst support. However, the Al peak area is about twice as high as the Ce peak area. In combination with the fact that Ce is much heavier and therefore more easily detected than Al, this shows that there is much more Al in the surface than Ce. This is in agreement with the bulk analysis of the diluted three-way catalyst being 11 wt% CeO_2 and 89 wt% γ-Al_2O_3 [25].

3.2. LEIS analysis of the Pt surface area after acetylene oxidation

To allow separate determination of Pt and Ce, 3 keV Ne ions have been used. Figure 2 shows the Pt LEIS signals for a fresh three-way catalyst (dash line), the catalyst after use in the acetylene oxidation (thick solid line), and the catalyst after regeneration following use in the acetylene oxidation (thin solid line). Prior to the LEIS measurements, the fresh catalyst has been cleaned using atomic oxygen, whereupon it was reduced at 573 K. As has been described in the previous section, these treatments have been carried out to reveal the intrinsic catalyst surface. To regenerate the catalyst after use in the acetylene oxidation, the same treatment has been applied. The figure shows the Pt signal decreased 50±5% after use in the acetylene oxidation at cold-start conditions. This

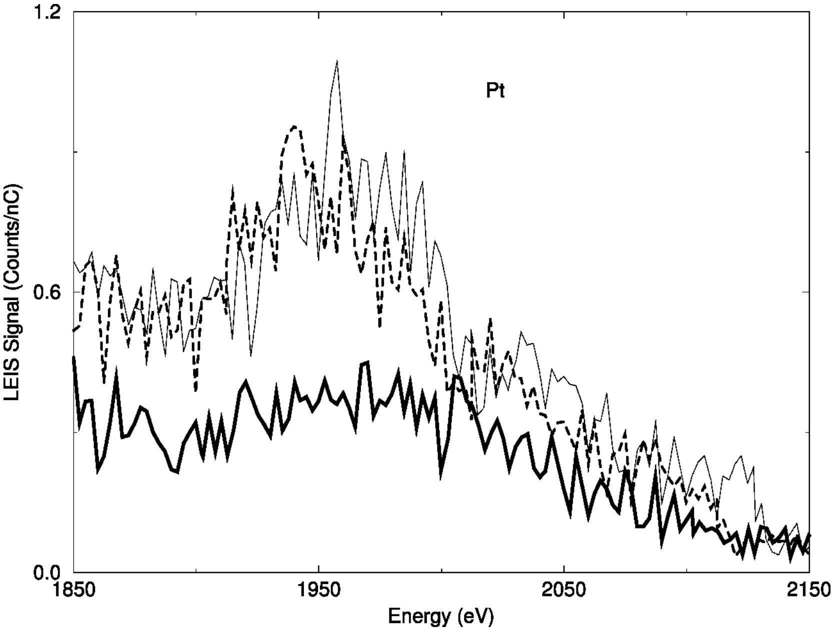

Figure 2. Three LEIS spectra obtained with 3 keV Ne on a fresh (- - -), a used (—) and a regenerated (—) three-way catalyst. The figure shows a drop in the Pt surface area after use in acetylene conversion at cold-start conditions. After regeneration the Pt surface area is fully restored.

decrease in Pt signal can be explained in two ways, either half of the Pt is covered by some other material, or severe sintering took place during use. An eightfold volume increase of the Pt particles due to sintering is needed to explain a 50% signal decrease. This is highly improbable during use at 543 K, especially since both the fresh and the used catalyst have been exposed to 773 K during the pre-treatment. As shown in figure 2, the Pt surface concentration could be completely restored after regeneration.

LEIS data are generally independent of the chemical environment (*i.e.*, no matrix effects) [19,20]. Therefore, the sensitivity for Pt can be calibrated against a reference sample with a well-known Pt surface atomic density. The Pt surface concentration of the three-way catalyst has been calibrated against a sputter-cleaned pure polycrystalline Pt sample. From this, it was learned that the Pt surface concentration in the fresh three-way catalyst equals approximately 0.040% of a monolayer. However, this concentration is obtained on a three-way catalyst that has been diluted with inert α-Al_2O_3. If correction for the dilution is applied, a Pt surface concentration of 0.098% of a monolayer for the pure fresh three-way catalyst is found. If 50% of this amount is covered with carbonaceous species, this cannot be detected in the carbon LEIS signal, since the sensitivity for carbon is too low. However, the high sensitivity for Pt allows detection of the Pt surface concentration loss.

The Pt surface concentration can be entirely restored during regeneration, or cleaning. This proves that no sintering took place during use. The loss in Pt signal is due to a 50 ± 5% coverage of the Pt with carbonaceous species, deposited during acetylene oxidation. These carbonaceous species can be effectively removed using atomic oxygen and a consecutive reduction at 573 K.

Table 1
The Pt surface concentration normalised to a fresh three-way catalyst.

	LEIS	Kinetic modelling
Fresh three-way catalyst	1	1
Three-way catalyst used in acetylene conversion	0.50 ± 0.05	0.4 ± 0.1
Three-way catalyst used in ethylene conversion	0.49 ± 0.05	0.6 ± 0.1
Regenerated three-way catalyst	1.1 ± 0.1	–

3.3. Comparison between LEIS analysis and kinetic modelling

LEIS analysis reveals that three-way catalysts that have been used in ethylene oxidation at cold-start conditions show a 51 ± 5% decrease in Pt surface concentration as well. Table 1 summarises the relative Pt surface concentrations found with LEIS and compares them to those obtained with kinetic modelling by Harmsen *et al.* [9,10]. The experimental error margin for LEIS analysis is mainly caused by the determination of the Pt peak area. Since both peak area determinations have an accuracy of 7%, a 10% error margin is estimated for the peak area ratio of the fresh and the used catalyst.

For the data obtained by kinetic modelling, the error estimation is more difficult, because the statistical data from transient regression analysis is unreliable, due to the fact that successive measurements in time are not independent. The kinetic modelling results revealed a 60 and 40% reduction of the Pt surface concentration in case of acetylene and ethylene, respectively. This is of the order of magnitude of the 50% reduction found in the LEIS experiments. This value of 50% Pt surface reduction has been used in model simulations of the ethylene and acetylene conversion. It was found that this value of 50% could also well describe the experimental data. This indicates an uncertainty of approximately 0.1 for the kinetic modelling results in the normalised Pt surface concentration. This error margin is given in table 1.

Consequently, the observed 50 ± 5 or 51 ± 5% decrease in Pt surface concentration after use in, respectively, acetylene or ethylene oxidation, as found with LEIS, agrees quantitatively with the noble metal area loss found in kinetic modelling.

4. Conclusions

LEIS analysis shows a Pt surface concentration of about 0.098% of a monolayer in a fresh commercial three-way catalyst. After use in either acetylene or ethylene oxidation at cold-start conditions, a decrease of 50 ± 5% of the Pt surface concentration is observed with LEIS. The Pt surface concentration can be completely restored by exposing the used catalyst to atomic oxygen and a subsequent reduction at 573 K. Therefore, the observed Pt loss is not due to sintering, but due to deposition of carbonaceous species during the hydrocarbon oxidation. The observed loss in Pt surface area with LEIS agrees quantitatively with the noble metal area loss as found in kinetic modelling of acetylene and ethylene oxidation, being 60 ± 10 and 40 ± 10%, respectively [9,10]. As such, the current results support earlier assumptions on selective catalyst deactivation with respect to the oxygen adsorption. Hence, this study shows that LEIS can be successfully applied to quantitatively investigate coke formation on commercial supported three-way catalysts. This kind of information is believed to be unique for surface analysis.

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