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A differentially pumped pressure cell for *in situ* low-energy ion scattering analysis of catalysts during reactions

W. P. A. Jansen, A. W. Denier v. d. Gon,^{a)} G. M. Wijers, Y. G. M. Rikers, and H. H. Brongersma

Department of Applied Physics and Schuit Institute of Catalysis, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

P. W. v. d. Hoogen, J. A. M. de Laat, T. M. Maas, E. C. A. Dekkers, and P. Brinkgreve

Central Design and Engineering Facility, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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A differentially pumped pressure cell has been developed to enable *in situ* low-energy ion scattering (LEIS) analysis of catalysts during chemical reactions. The cell is fully compatible with an electrostatic analyzer and is, therefore, very well suited to study rough, highly dispersed catalysts. The pressure cell is a continuous flow cell (space velocity $1.2 \times 10^3 \text{ s}^{-1}$) and allows observation of dynamic surface reactions with various, perfectly mixed gases at fully controlled partial pressures and temperatures up to 800 K. The design decreases the pressure gap by three orders of magnitude. This offers ample opportunities such as the determination of specific adsorption sites, surface coverages of different species during reactions, and information on growth processes, poisoning or chemically induced segregation. As an example, an *in situ* LEIS study of the CO oxidation over Pt is presented. By combining *in situ* LEIS and quadrupole mass spectroscopy, both the surface and gas composition could be monitored during this reaction. © 2002 American Institute of Physics. [DOI: 10.1063/1.1433949]

I. INTRODUCTION

Many of the traditional techniques that can more selectively probe the nature of the active site of catalyst surfaces, like x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), and low-energy ion scattering (LEIS) have mostly been applied under ultrahigh vacuum (UHV) conditions. Although examination before and after a reaction using these techniques has greatly contributed to our knowledge, it is difficult to probe nucleation sites and transient phases in static studies of postreacted catalysts. Adsorbates may completely restructure a catalyst surface and surface phases that are unstable in high vacua may well play a critical role in catalysis.¹ Hence, dynamic studies of catalysts are key to a deeper understanding of mechanisms of reactions, surface structural evolution, and the processes of activation and deactivation.^{1,2}

A very suitable technique to study catalysis is LEIS.^{3–6} The high neutralization probability of the probing low-energy noble gas ions in combination with an electrostatic analyzer (ESA) limits the information depth of this technique to a *single* atomic layer.^{4,5} Hence, using LEIS selective information on the gas–surface interface, exactly the place where catalysis takes place, can be obtained. *In situ* application of this technique offers ample opportunities, such as the determination of specific adsorption sites, surface coverages of different species during reactions, and information on

growth processes, poisoning, or chemically induced segregation. Nevertheless, only a very limited number of LEIS studies^{7–12} have been carried out *in situ*. Except for Ref. 7, where the reaction of Br and O with W was studied, the purpose of all these studies was monitoring growth processes and they applied time of flight (TOF) instead of an ESA, whereas for LEIS analysis of rough highly dispersed catalysts, an ESA is much more appropriate than TOF.¹³

Here, we present a differentially pumped pressure cell to enable *in situ* LEIS analysis of catalysts during reactions with an ESA. The pressure cell is physically compatible with the existing energy resolved ion scattering spectroscopy (ERISS) LEIS setup⁶ and does not restrict its operation. The design decreases the pressure gap by three orders of magnitude. With only minor modifications, the cell can also be used for other surface science techniques such as SIMS and XPS. The subsequent sections deal with the restrictions for environmental LEIS and the design features with respect to the vacuum system and reactor design. Experimental results are added to illustrate possibilities of environmental LEIS with the differentially pumped pressure cell.

II. DESIGN DIFFERENTIALLY PUMPED PRESSURE CELL

A. Limitations for environmental LEIS

The signal attenuation in a gas layer, which limits the maximum environmental pressure in which LEIS can be successfully applied, depends on the type of gas layer and the probing ions. As a rule of thumb, the cross section for signal loss (σ) is proportional to $1/\sqrt{E}$ of the probing ions (where E

^{a)} Author to whom all correspondence should be addressed; electronic mail: a.w.denier.van.der.gon.@tue.nl

FIG. 1. LEIS signal loss as a function of Ar pressure and path length of 10 keV He^+ ions through the vacuum system, as calculated using the cross section for ion-gas interactions (see Ref. 14). The contour lines show constant signal attenuation with the attenuation factor.

is the primary energy of the probing ions). Lin *et al.*¹⁴ performed detailed studies of the interaction of low-energy ion beams with gases. For 10 keV He^+ ions in Ar gas, they experimentally determined a cross section for signal loss of $\sigma = 1.3 \times 10^{-19} \text{ m}^2$. In Fig. 1, we show the attenuation of the LEIS signal as a function of the gas pressure and path length of the ions in the reactor for $\sigma = 1.3 \times 10^{-19} \text{ m}^2$ (note that the remaining LEIS signal equals 1-attenuation, as plotted in Ref. 13). Using this graph it is easy to determine the limiting pressure for environmental LEIS analysis for a specific setup, which is determined by the path length of the ions and the signal attenuation of the ions that is acceptable in a specific experiment. For a typical path length of 0.1 m and an attenuation of 90%, this would result in $1 \times 10^{-2} \text{ mbar}$. This presents the ultimate limit possible for a given path length and acceptable attenuation. In practice, however, the pressure limit for LEIS is generally imposed by the maximum operating pressure of the multichannel plates or channeltrons that are included in most LEIS detectors.¹³ The maximum operating pressure of channeltrons and multichannel plates is in the low 10^{-4} mbar range,¹⁵ however, at such pressures, there is a serious risk for discharge. Therefore, pressures below 10^{-6} mbar are used in practice.

Chemical reactions have successfully been studied at pressures in the 10^{-8} mbar range using low-energy electron diffraction and AES,¹⁷ however, real-life catalysis takes place at pressures $\geq 1 \text{ bar}$ (which is referred to as the so-called pressure gap). To minimize the required extrapolation, a huge pressure gradient has to be accomplished between the sample and the detector. The reactor and the detector cannot be separated by use of a window, however, since any window would completely neutralize the probing ions and obstruct LEIS analysis. Another way of accomplishing a pressure gradient is to use a nozzle to dose gases on the sample. A nozzle could increase the pressure at a sample in a LEIS setup by 1 or 2 orders of magnitude in comparison to the environment with the detector. However, a nozzle also introduces extreme pressure gradients over the sample ($\sim 10\%$ over $\varnothing 1 \text{ mm}$). To avoid strong pressure gradients over the sample, differentially pumping has been used here instead of a nozzle.

TABLE I. The objectives and specifications of the differentially pumped pressure cell.

●	The pressure cell should be fully compatible with the existing UHV LEIS setup that uses a double toroidal analyzer. This requires the cell to be bakable, retractable, and in agreement with the geometry of the ERISS LEIS detector.
●	Pressures $P \leq 1 \times 10^{-3} \text{ mbar}$ at the sample in the reactor of the pressure cell correspond to pressures $P \leq 1 \times 10^{-6} \text{ mbar}$ in the surrounding UHV.
●	At the center of the sample, $\Delta P \leq 1\%$ over $\varnothing 3 \text{ mm}$.
●	Computer controlled positioning with $\pm 0.01 \text{ mm}$ accuracy in the X, Y, and Z directions.
●	Admittance of two perfectly mixed reactant gases with fully controlled partial pressure ratios.
●	Effective suppression of wall reactions in the reactor of the pressure cell.
●	Real-time monitoring of the gas composition in the reactor during <i>in situ</i> LEIS.
●	During <i>in situ</i> LEIS, temperatures in the range $RT \leq T \leq 800 \text{ K}$, with stability better than $\pm 0.6 \text{ K}$.
●	Flashing up to 1500 K without breaking UHV before starting <i>in situ</i> LEIS.
●	Thermometry during <i>in situ</i> LEIS with an absolute accuracy $\pm 2 \text{ K}$ and a relative accuracy $\pm 0.1 \text{ K}$.

B. Vacuum system

1. General principle of the differentially pumped pressure cell

Table I summarizes the objectives and the specifications of the differentially pumped pressure cell, which is schematically shown in Fig. 2. A bellows (bellows B1 in Fig. 2) mounted on a standard conflat 160 flange connects the pressure cell to the main vessel and allows the cell to be placed between the manipulator containing the sample and the analyzer, and to retract it when it is not needed. A second bellows (B2) allows the manipulator to move upward, contacting the bellows and thereby sealing the reactor from the UHV environment. A gas inlet is provided to introduce reactant gases into the reactor. Holes and circular slits are provided to allow entrance and exit of the incident and scattered ions, respectively. A turbomolecular pump provides differential pumping to the area directly above the reactor. A quadrupole mass spectrometer has been installed in the UHV chamber for real-time monitoring of chemical reactions, and the sampleholder and the interior of the reactor are coated with titanium nitride to suppress wall reactions. In the reactor, samples can be heated and the sample temperature can be measured using either a thermocouple or fluoroptic thermometry.

2. Differential pumping

Figures 3(a) to 3(c) show cross sections of the differentially pumped pressure cell and the sampleholder, the numbers in parentheses refer to numbers in these figures. The sample (3) is placed in the reactor. Since neither the incom-

FIG. 2. Schematic view of the rotational symmetric LEIS analyzer and the differentially pumped pressure cell. In this text, the phrase “(differentially pumped) pressure cell” refers to the ensemble that is enveloped by the dashed line, the so-called “reactor” is shaded.

ing nor the outgoing ions should be blocked, the pressure cell has holes ($\varnothing$ 1 mm) in the center for the incoming beam and conical circular slits at $\theta=145^\circ$ for the outgoing ions (see Fig. 2). The widths of the conical circular slits are chosen in accordance with the dimensions of the maximum incoming beam diameter ($\varnothing$ 1 mm) and the acceptance of the analyzer (2°). The ESA uses only 320° of the azimuthal angle range, its dead angle has been used for a fluoroptic temperature probe (8) and the attachment of the central part of the circular slits. The requirement that the pressure over a $\varnothing$ 3 mm sample should be constant within 1% imposes, given the

described geometry, a minimum height of 4 mm for the reactor. Given the 4 mm height, the most efficient way to obtain a gradient of 3 orders of magnitude is to use two restrictions in series. Starting from the sample and using 3 mm thick material for the first restriction (7), the conductance of the first beam hole C_1 is $3 \times 10^{-2} \text{ l s}^{-1}$ and the conductance of the first circular slit C_2 is 1.4 l s^{-1} . Assuming an effective pump rate of 100 l s^{-1} in the surrounding UHV, the pressure would be some 70 times lower at the detector than at the sample. To further reduce the pressure, a second restriction (9) has been applied. Using 8 mm material for the second restriction, the conductance of the second beam hole C_3 is again $3 \times 10^{-2} \text{ l s}^{-1}$. The conductance of the second circular slit C_4 is 5.2 l s^{-1} . This is much higher than that of C_2 since the second slit has a larger radius. The thickness of the first restriction (3 mm) and the height of the intermediate space between the two restrictions (7 mm) have been chosen in a way to optimize the total pressure drop. For the same reason, the tubing to the pump in the intermediate space is widened outside the circular slit in order to maximize the effective pump rate. In this way, a 52 l s^{-1} turbomolecular pump (Hycone 60) provides an effective pump rate of 15 l s^{-1} between the two restrictions. This, in combination with an effective pump rate of $\sim 100 \text{ l s}^{-1}$ in the UHV, results in a pressure drop of 3 orders of magnitude between the sample and the UHV provided the leakage from the bottom of the pressure cell into the UHV is negligible ($\ll 1.4 \text{ l s}^{-1}$).

FIG. 3. Cross sections of the differentially pumped pressure cell (a) and (c) and the sampleholder. (1) manipulator, (2) sampleholder, (3) sample, (4) heat and electrical restriction (alumina), (5) bellows allowing alignment and air tight sealing of the pressure cell, (6) gas inlet, (7) first restriction with beam hole for incoming and circular slit for outgoing ions, (8) fluoroptic fiber, (9) second restriction with beam hole for incoming and circular slit for outgoing ions, (10) UHV, (11) analyzer, (12) bellows allowing positioning of the pressure cell, (13) UHV vessel, (14) conflat 160 flange connecting the pressure cell to the UHV LEIS setup, (15) guidance/alignment, (16) microvalve gas inlet, (17) connection with gas manifold, (18) approach switches, (19) thermocouple, (20) frame, (21) holder, and (22) heater.

3. Sampleholder

To minimize the leakage from the bottom of the pressure cell into the UHV, a special sampleholder has been designed. Figure 3(b) shows a schematic of this sampleholder, which allows accommodation of samples up to $\varnothing$ 8 mm. The sampleholder consists of two parts, a holder (21) with a hole in its center to allow electron-beam heating (see Sec. IIC 3) and a frame (20) that can be sealed over a sample or a cup containing a (powder) sample. The frame itself can be sealed airtight to the holder using the elasticity of its three tabs. Both the holder and the frame have been fabricated from stainless steel and are coated with titanium nitride. As will be explained in Sec. IIC 2, this coating suppresses wall reactions. By pressing the topline of the frame onto the alumina ring (4), at the bottom of bellows (5) the bottom of the pressure cell becomes sealed (leakage $\sim 0.04 \text{ l s}^{-1}$) from the UHV. Note the leakage from the bottom of the pressure cell into the UHV is $\leq 1.4 \text{ l s}^{-1}$.

4. Positioning and alignment of the differentially pumped pressure cell

The pressure cell can be retracted to the edge of the UHV chamber using bellows (12) to allow compatibility with the existing LEIS setup and to enable fast sample transfer without breaking UHV. When the pressure cell has been retracted to the edge of the UHV chamber, samples can be transferred in and out the LEIS setup via a loadlock, thus without breaking the UHV. If the manipulator containing the sample (1) is positioned at its lowest height, the pressure cell can be positioned between the sample and the analyzer. After the pressure cell has been positioned under the analyzer, the manipulator height can be increased to seal the pressure cell from the UHV by pressing bellows (5). In this way, the sample height is put in the focal plane of the analyzer, while the bellows allow the accommodation of different sample heights.

Both the pressure cell and the sample are positioned using computer controlled manipulators. The position of the manipulator containing the samples (1) can be positioned in all directions within 0.01 mm. The pressure cell can be automatically moved along a single axis from the edge of the UHV chamber to its working position between the sample and the analyzer, and vice versa. When the pressure cell approaches its working position within 0.5 mm, its precise position is fine tuned to within ± 0.01 mm using a so-called approach switch (18) (Baumer Electric type IWRM 12I9501). The position at the edge of the UHV chamber is less critical and is controlled with an endswitch. The movement of the pressure cell has been aligned to the existing setup by tilting the guidance of the pressure cell (15).

In the ERISS LEIS setup, secondary electrons that are produced by the primary ion beam can be imaged, since the primary ion beam can be electrostatically deflected synchronous with imaging of the secondary electrons. Using secondary electron imaging, the sample position can be visualized when the pressure cell is retracted to the edge of the UHV chamber. When the pressure cell is positioned between the sample and the analyzer, the secondary electrons show the

FIG. 4. Schematic of the gas manifold that allows the introduction of two different gases into the pressure cell at different pressures and for different pressure ratios. Via the bellows, the manifold is connected to the gas inlet of the pressure cell at (17) in Fig. 3(c).

position of the beam hole in the cell. This allows one to check the alignment of the sample and the pressure cell with a spatial resolution of some $10 \mu\text{m}$.

C. Reactor design

1. Gas handling

Of essential importance for environmental LEIS is of course the transport of gases in and out of the differentially pumped pressure cell. Molecular flow conditions assure perfect mixing of different gases. Therefore, a gas manifold has been designed that allows mixing of two reactant gases under molecular flow conditions (Fig. 4). To obtain molecular flow conditions from the point where the different gases meet, the different reactant gases are first put in separate reservoirs (sphere A and B in Fig. 4). The spheres can be evacuated down to $\sim 10^{-2}$ mbar using a rotary pump, they can be filled using adjustable needle valves. The pressure in each sphere can be measured gas independently with an absolute accuracy of 4×10^{-2} mbar using capacitance diaphragm gauges (Varian CeramiCel VCMT12TAA). Each sphere is connected to a $\varnothing$ 4 mm tube that is led over a cold trap (liquid nitrogen) towards a microvalve. This home-built microvalve (16) consists of a pinhole $\varnothing$ $15 \mu\text{m}$ that can be opened/closed by hand. The pinhole has been sunken in a plate to avoid defor-

mation during closing. The small dimensions of the pinhole, together with the dimensions of the tubing between the pinhole and the pressure cell, assure molecular flow if the pressure in each sphere is kept below 20 mbar. Then, gases are perfectly mixed and concentration gradients are absent in the pressure cell. Pressures of 20 mbar in the spheres correspond to 3×10^{-4} mbar at the sample.

The pressure in the reservoirs can be measured easily, however, the direct measurement of the pressure in the reactor containing the sample (3) is very difficult. By assuring molecular flow conditions in all parts of the gas inlet, the partial pressure ratio in the pressure cell becomes equal to the pressure ratio of the reservoirs in the gas manifold.¹⁶ The absolute pressure in the reactor as a function of the pressure in the reservoir spheres has been calculated. The uncertainty in this calculation is largely determined by the uncertainty in the sizes of the pinholes in the microvalves in the gas inlet. The ratio between the calculated and measured value of this size appeared to be a factor 1.6. To minimize the error in the calculations of the pressure in the reactor, the experimentally determined size is used. Therefore, the calculated pressure in the reactor is expected to be reliable up to at least a factor 1.6.

To assure a stable pressure in the reactor of the pressure cell during experiments, both the volume ratio and the pressure ratio between the spheres and the reactor are chosen relatively high, 5×10^3 and $\sim 10^5$, respectively. Therefore, only 0.4% of the gas in the spheres is used per hour, which keeps the pressure drop during experiments at an insignificant level.

To obtain a homogeneous gas inlet into the reactor of the pressure cell, the gas is led into the reactor via a circular ring containing four holes. For homogeneity, the conductance of these holes (each $2.3 \times 10^{-3} \text{ s}^{-1}$) is six times lower than the conductance of the circular ring, and the holes are divided over the ϕ direction in a way that corrects for the pressure drop over the ring (at $\phi = 30^\circ$, 126° , 214° , and 298° , respectively). The gas outlet is determined by the leakage through the beam hole and the slit for the outgoing ions (effective pump rate 1.5 s^{-1}). At 4 mm height, the total solid angle of these openings is constant within 1% over $\phi 3 \text{ mm}$ around the center of the sample. Together with the molecular flow conditions in the reactor this results in pressure variations below 1% over the central $\phi 3 \text{ mm}$. The volume of the reactor is 1.2 cm^3 , hence the reactor has a very high refresh rate (space velocity of $1.2 \times 10^3 \text{ s}^{-1}$).

2. Monitoring chemical reactions and suppressing wall reactions

Outside the pressure cell in the UHV, there is a quadrupole mass spectrometer [(QMS) Balzers Prisma 200]. Approximately 25% of the gases leaving the pressure cell leaks, under molecular flow conditions, into the UHV. When, after saturation, adsorption and desorption at the walls are in equilibrium, the ratios of the partial pressures of the different gases in the pressure cell can be measured using the QMS in the UHV. Since the dimensions of the UHV chamber are $<1 \text{ m}$ and the average velocity of gas molecules at room

temperature is typically $\sim 4 \times 10^2 \text{ m s}^{-1}$, the gas concentrations measured in the QMS represent instantaneously the concentration ratios in the pressure cell.

The most important problem that remains with regard to the quantification of the reactant and product gases is that of wall reactions.¹⁷ Unless otherwise mentioned, the entire pressure cell has been made from stainless steel. To suppress wall reactions, the sampleholder and the interior of the reactor surrounding the sample have entirely been coated with titanium nitride, except for a 1 mm thick alumina ring ($\phi 12.5 \text{ mm}$). The relatively inert alumina ring (4), that is attached to the base of bellows (5), provides a heat barrier and electric isolation between the sampleholder and the pressure cell. The titanium nitride coated surface will oxidize very fast, however, after oxidation titanium nitride is very inert, like gold, another material that is commonly applied to suppress wall reactions. However, titanium nitride is much more durable and stable than gold. Gold molecules are rather mobile and may therefore end up covering the sample. The use of TiN also reduces adhesion and prevents seizing.

It is also important to retract the pressure cell during sputtercleaning, otherwise material will be deposited on the interior of the pressure cell. Such material would probably be active and cause undesirable background rates.

3. Heating and thermometry

By radiating the back of a sample from a Ta spiral ($\phi 0.4 \text{ mm}$) underneath the sampleholder (22), the sample temperature can be increased up to $\sim 1300 \text{ K}$. Moreover, electron-beam heating can be applied since the voltage of the sample can be increased to $+1 \text{ keV}$ with respect to the rest of the setup including the Ta spiral. Using electron-beam heating, temperatures up to 2500 K can be easily reached. However, if the pressure cell is placed over the sample, the temperatures have to be kept below 800 K because of the bellows (5). Since the pressure cell can be retracted and repositioned without breaking the UHV, electron-beam heating can be used for *in situ* cleaning and restructuring (single crystal) metal samples before starting a measurement session using the pressure cell.

The sample temperature can be determined using a K-type thermocouple that is pressed by a spring into a conical hole in the sampleholder (19). The difference between the temperature as determined using the thermocouple and the actual sample temperature has been calibrated using an *in situ* remote fluoroptic thermometer (8) (Luxtron 712). A fiberoptic probe has been mounted in the pressure cell (8) to allow *in situ* use of the remote fluoroptic thermometer. The fluoroptic thermometer has an absolute accuracy of $\pm 2 \text{ K}$, and stability better than $\pm 0.1 \text{ K}$ over 1 h. In order to prevent electrical field disturbances during LEIS, the all silica probe ($\phi 0.34 \text{ mm}$) of this thermometer has been jacketed with a titanium nitride coated stainless steel tube ($\phi 0.5 \text{ mm}$) that sticks out 1 mm. To probe the temperature close to the sample center (at 2.7 mm) without physically blocking the ingoing and outgoing ions, the probe has been placed in the dead angle of the ESA, bent under an angle of 45° towards the surface. The only disadvantage of fluoroptic thermometry

FIG. 5. The relation between the sample temperature as obtained with a thermocouple pressed into the sampleholder and the actual sample temperature as determined with a remote fluoroptic thermometer. The open circles have been measured in UHV, the solid diamonds have been measured in an oxygen atmosphere ($P_{O_2} = 2 \times 10^{-4}$ mbar).

is that this method requires that a phosphorescent paste is put on the sample. However, calibration showed a reproducible difference between the sample temperature measured using the fluoroptic thermometer and the temperature as determined using the thermocouple (Fig. 5). Therefore, the fluoroptic thermometer is only used to calibrate the thermocouple reading. The thermocouple provides the input for a proportional integer differential controller (Eurotherm 900 EPC) that is used to control the heating and sample temperature in the temperature range $\sim 300 \text{ K} < T < 800 \text{ K}$. In practice, a sample-temperature stability of $\pm 0.6 \text{ K}$ is obtained (typical 98% interval over several hours as determined with the fluoroptic thermometer). Figure 5 shows the relation between the real sample temperature (as determined by the fluoroptic thermometer) and the thermocouple signal. The solid diamonds are measured in 2×10^{-4} mbar O_2 , the open circles in UHV, hence, the presence of gases in the pressure cell does not significantly influence the absolute temperature, or the stability of the temperature.

4. Spatial and time resolution

Two important parameters with regard to the monitoring of chemical reactions are of course both the spatial and time resolution of the detection system. Concerning the time resolution: it takes typically a few minutes to collect a complete LEIS spectrum. If one is only interested in the presence of one element, the time scale can be significantly reduced to about 0.01 s by monitoring only the intensity at the top of a LEIS peak versus time. Any process requiring faster analysis would need significant improvements of instrumentation.

The spatial resolution of LEIS is inherently limited by the damage of the sample surface by the ion beam. The limitation is determined by the ion dose by which the surface becomes damaged and by the sensitivity of the analyzer and detector. In Ref. 13, it has been shown that for an energy and angle resolved ion scattering (EARISS) type analyzer, which is applied in the ERISS LEIS setup, the minimum allowed

beam diameter is $3 \mu\text{m}$ if a dose of 1×10^{15} ions/cm² is allowed. Any smaller beam size would damage the surface significantly before the analysis is complete, thus resulting in nonsurface-specific information. To realize different beam spot diameters, apertures ranging from 3 mm down to $5 \mu\text{m}$ can be inserted in the beamline. The apertures are used as object for the lens that determines the beam spot diameter at the target and enable focusing to a beam diameter of less than $5 \mu\text{m}$ at the sample surface.

D. Pressure cell for XPS and SIMS

So far the pressure cell has only been described in combination with a LEIS setup, however, the principle can also be used in combination with, e.g., XPS or SIMS. To do so, the holes for the incoming and outgoing particles should be adapted to the geometry of the XPS/SIMS setup. Since these holes determine the pressure gradient, the height of the reactor may have to be changed as well. For the rest, the design can be used as it is. A calculation for the geometry of a ESCA200—a widespread XPS analyzer from Gammatdata AB, formerly Scienta—shows that a decrease of the pressure gap of 3 orders of magnitude is feasible.

III. FIRST RESULTS

To check the alignment of the pressure cell, LEIS measurements have been performed comparing a gold sample outside the pressure cell in an UHV environment and the same sample inside the pressure cell in an argon atmosphere (at various pressures up to 2.4×10^{-4} mbar). Since the inert sample and the inert gas will not react, the LEIS signals

FIG. 6. 3 keV $^4\text{He}^+$ LEIS spectra of Au measured in UHV (1×10^{-10} mbar) and in Ar at 8×10^{-5} mbar and 2.4×10^{-4} mbar.

(a)

(b)

FIG. 7. (a) 3 keV $^3\text{He}^+$ LEIS spectra obtained before (solid line) and during the CO oxidation (open circle) over Pt. The LEIS measurements clearly show that the Pt gets poisoned by Ni. (b) QMS spectra showing the concentration of masses 28 amu (CO), 32 amu (O_2), and 44 amu (CO_2). After ~ 15 min, the CO_2 production has virtually stopped because of poisoning of the Pt.

should remain constant. The LEIS spectra in Fig. 6 show that indeed both the peak energy, the full width at half maximum of the peak, and the gold yield/nC (from which the gold surface concentration is determined) remain constant within the experimental errors (<6 eV, <12 eV, and $<2\%$, respectively). Hence, differences in LEIS spectra between samples kept in UHV and in gaseous environments—up to total pressures of at least 2.4×10^{-4} mbar—can be completely ascribed to changes at the gas-surface interface due to the interaction with the gaseous environment. Regarding Fig. 1

(a)

(b)

FIG. 8. (a) 3 keV $^3\text{He}^+$ LEIS spectra obtained before (solid line) and during the CO oxidation (open circles) over Pt. The absence of Ni in the spectra confirms the effectiveness of the cold trap. (b) QMS spectra showing the concentration of masses 28 amu (CO), 32 amu (O_2), and 44 amu (CO_2). Using a cold trap to remove $\text{Ni}(\text{CO})_4$, a constant CO_2 production (conversion 53%) is obtained.

and the pathlength in the pressure cell, signal losses due to the gaseous environment are expected to become significant at pressures $P \geq 1 \times 10^{-3}$ mbar.

The following experiment illustrates the possibilities of environmental LEIS with the pressure cell. In this experiment, O_2 ($P_{\text{O}_2} = 8 \times 10^{-5}$ mbar) and CO ($P_{\text{CO}} = 3 \times 10^{-5}$ mbar) are converted to CO_2 over Pt at 524 K. Before starting the reaction, the Pt has been cleaned by so-called vacuum oxypolishing (1 h at 1073 K in $P_{\text{O}_2} = 1.5 \times 10^{-7}$ mbar) followed by flashing in UHV up to ~ 1400 K. The 3 keV $^3\text{He}^+$ LEIS spectrum taken before the reaction

[solid line Fig. 7(a)] shows that in this way clean Pt is obtained. A second LEIS spectrum [open circles Fig. 7(a)], was measured during reaction. The QMS signals of O₂, CO, and CO₂ in Fig. 7(b) show that the CO₂ production dies within ~15 min. Comparison of the LEIS spectra taken before and during reaction shows that the Pt gets poisoned by Ni. The Ni poisoning can be explained by reaction with Ni(CO)₄ which is formed if CO gas gets in contact with stainless steel (gas bottle and tubing). However, if the cold trap in the gas inlet (Fig. 4) is used, the Ni(CO)₄ is effectively removed from the CO gas. Figures 8(a) and 8(b) show the LEIS and QMS signals under the same reaction conditions when the CO gas is let over a cold trap. Now the conversion remains constant for more than 1 h (53%) and the LEIS spectra do not show any sign of poisoning by Ni.

The experiments described show that the differentially pumped pressure cell enables *in situ* LEIS analysis. The pressure cell allows for *in situ* LEIS at 10⁻³ mbar, while the pressure at the multichannel plates is kept at 10⁻⁶ mbar. If the multichannel plates are used in the low 10⁻⁴ mbar range (risking a discharge) the pressure cell allows for *in situ* LEIS at 10⁻¹ mbar. In spite of the short pathlength in the reactor (1 cm) a pressure of 1×10⁻¹ mbar corresponds to signal losses of 93% or 45% in the gas layer for 10 keV He⁺ and Ne⁺, respectively. Hence, even though the pressure cell allows one to perform *in situ* LEIS there remains a pressure gap between LEIS and catalysis. Although the pressure cell presented here reduces this pressure gap by three orders of magnitude, the gap between the LEIS analysis and industrial relevant catalysis conditions is still very large. However, even at pressures $P \leq 10^{-3}$ mbar there are already ample opportunities for *in situ* LEIS that can considerably contribute to our knowledge of catalysis such as, the determination of specific adsorption sites, surface coverages of different spe-

cies during reactions, and information on growth processes, poisoning or chemically induced segregation.

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¹G. A. Somorjai, *Top. Catal.* **8**, 1 (1999).

²P. L. Gai, *Top. Catal.* **8**, 97 (1999).

³P. G. Menon, *Appl. Catal.*, A **207**, N2 (2001).

⁴E. Taglauer, in *Fundamental Aspects of Heterogeneous Catalysis Studied by Particle Beams*, edited by H. H. Brongersma and R. A. van Santen, NATO ASI B (Plenum New York, 1991), Vol. 265, p. 301.

⁵H. H. Brongersma, P. A. C. Groenen, and J.-P. Jacobs, in *Science of Ceramic Interfaces II*, edited by J. Nowonty (Elsevier, New York, 1994), p. 113.

⁶W. P. A. Jansen, M. Ruitenbeek, A. W. Denier v.d. Gon, J. W. Geus, and H. H. Brongersma, *J. Catal.* **196**, 379 (2000).

⁷H. H. Brongersma, G. C. J. v.d. Ligt, and G. Rouweler, *Philips J. Res.* **36**, 1 (1981).

⁸A. R. Kraus, O. Auciello, G. J. Lamich, D. M. Gruen, J. A. Schultz, and R. P. H. Chang, *J. Vac. Sci. Technol. A* **12**, 1943 (1994).

⁹A. R. Kraus, J. Im, J. A. Schultz, V. S. Smentkowski, K. Waters, C. D. Zuiker, D. M. Gruen, and R. P. H. Chang, *Thin Solid Films* **270**, 130 (1995).

¹⁰Y. Lin, A. R. Kraus, O. H. Auciello, Y. Nishino, D. M. Gruen, R. P. H. Chang, and J. A. Schultz, *J. Vac. Sci. Technol. A* **12**, 1557 (1994).

¹¹Y. Fujii, K. Nakajima, K. Namuri, K. Kimura, and M. Mannami, *Surf. Sci.* **318**, L1225 (1994).

¹²R. Pfanzelter, T. Igel, and H. Winter, *Surf. Sci.* **375**, 13 (1997).

¹³A. W. Denier v.d. Gon, R. Cortenraad, W. P. A. Jansen, M. A. Reijme, and H. H. Brongersma, *Nucl. Instrum. Methods Phys. Res. B* **161**, 56 (2000).

¹⁴Y. Lin, A. R. Kraus, R. P. H. Krauss, R. P. H. Chang, O. H. Auciello, D. M. Gruen, and J. A. Schultz, *Thin Solid Films* **253**, 247 (1994).

¹⁵Philips Photonics, Electron multipliers, Philips Export B. V. (1990).

¹⁶D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).

¹⁷D. W. Blakely, E. I. Kozak, B. A. Sexton, and G. A. Somorjai, *J. Vac. Sci. Technol.* **13**, 1091 (1976).