



Applications of High Sensitivity-Low Energy Ion Scattering (HS-LEIS) in heterogeneous catalysis

H.R.J. ter Veen^{a,1}, T. Kim^b, I.E. Wachs^b, H.H. Brongersma^{a,*}

^a Calipso BV, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Operando Molecular Spectroscopy & Catalysis Laboratory, Chemical Engineering Department, Lehigh University, Bethlehem, PA 18015, USA

ARTICLE INFO

Article history:

Available online 26 November 2008

Keywords:

High Sensitivity-Low Energy Ion Scattering (HS-LEIS)
Heterogeneous catalysis
Surface analysis
MoO₃/TiO₂ catalyst

ABSTRACT

High Sensitivity-Low Energy Ion Scattering (HS-LEIS) is a sensitive analysis technique for the outermost atomic layer of a sample. On a heterogeneous catalyst, this outermost atomic layer is the precise location where the catalytic processes take place. Based on the principles of classical mechanics, HS-LEIS determines the mass of surface atoms by measuring the energy from ions that are scattered from the surface. Examples with pure oxides, mixed oxides and supported metal oxide catalyst samples are presented to demonstrate the sensitivity, the ease of quantification, the availability of information about layers immediately beneath the surface (relevant for the dispersion of the active catalytic component on the surface of the catalyst) as well as the potential for High Throughput Experimentation (HTE) due to the short analysis times.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In heterogeneous catalysis, reactions take place at the outermost atomic layer of solid catalysts. Therefore, the availability of a technique that analyzes the chemical composition of this layer is of crucial importance in the fundamental study of catalysis as well as in the optimization of industrial catalysts. Low Energy Ion Scattering is a unique tool that provides quantitative compositional information about the outermost atomic layer of a material. For many years, important contributions to the application of LEIS to catalytic materials have been made by the groups of Cocke, Hercules and Houalla, Taglauer and Knözinger, Hoflund, Grünert and Brongersma. See reviews [1–3] and other references to the literature [4–7]. A problem of LEIS is the damage to the samples by the bombarding ions. The development of High Sensitivity-LEIS has enabled the use of such low ion doses that the damage is negligible, while the mass resolution has been improved. This has given a new impulse to the application to catalysts.

HS-LEIS compares favorably to XPS (ESCA) since the information depth for XPS is several nanometers (~20 layers) whereas HS-LEIS is specific for the outermost atomic layer. HS-LEIS also compares favorably to SIMS, since quantification of HS-LEIS results is straightforward.

The principle behind the LEIS technique is depicted in Fig. 1. A noble gas ion with a known primary energy E_i is aimed at the surface. The incident ion beam is perpendicular to the surface. There, this ion collides with a surface atom in a binary collision. The energy of the backscattered ion (E_f) is determined by the classic laws of mechanics (conservation of momentum and conservation of energy) and is given by

$$E_f = k^2 \left(\frac{m_2}{m_1}, \theta \right) E_i \quad (1)$$

In this, m_1 and m_2 are the masses of the primary ion and scattering surface atom, respectively, while θ is the back scattering angle (determined by the geometry of the instrument). In the HS-LEIS experiment, θ , m_1 and E_i are known and E_f is measured with a dedicated energy analyzer. The factor k^2 is a known function of m_2/m_1 and θ . The k^2 function increases monotonously from 0 for $m_2/m_1 = 1$ to 1 for $m_2/m_1 \rightarrow \infty$ (if $\theta > 90^\circ$). Thus, the mass of the scattering surface atom can be calculated from Eq. (1). Only surface atoms with a mass higher than the mass of the primary ion can be measured since the primary ion will scatter in the forward direction if it scatters from very light atoms. In the derivation of Eq. (1) it has been assumed that the target atom is at rest. It has been shown before that, although the vibrational energy of the surface atoms is orders of magnitude smaller than the primary energy of the ion, Doppler broadening will give a detectable increase in the peakwidth [8].

The HS-LEIS instrument is very sensitive and typically exhibits detection limits on the order of several ppm for high

* Corresponding author.

E-mail address: H.Brongersma@Calipso.nl (H.H. Brongersma).

¹ Present address: Tascon GmbH, Heisenbergstr. 15, 48149 Münster, Germany.

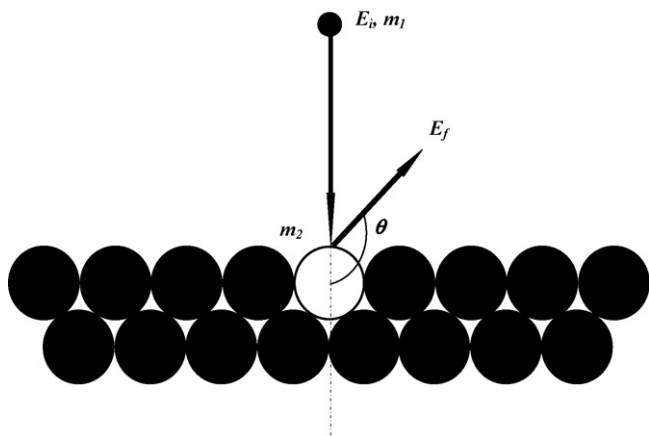


Fig. 1. Schematic representation of the ion scattering process. The energy, E_i , and mass m_1 of the primary ion are controlled in the experiment. The scattering angle, θ , is fixed for the instrument geometry. The final energy, E_f , is measured, which yields the mass of the surface atom, m_2 .

values of m_2/m_1 , while mass resolution is good for low values of m_2/m_1 . In many cases, the HS-LEIS spectra are recorded with different primary ions since the HS-LEIS analyst is free to choose the primary ion. The spectra with $^4\text{He}^+$ ions will give the best information in terms of mass resolution and sensitivity for lighter surface atoms. In general, elements with masses in the range from 12 to 60 amu can be positively identified with $^4\text{He}^+$. It is perfectly possible to use $^4\text{He}^+$ ions for higher masses, but element identification will be problematic. For example, if it is known that a sample contains only Pt, Co and alumina then analysis with $^4\text{He}^+$ ions will be sufficient, since in that case higher mass resolution is not required. However, when a positive identification for unknown heavier surface atoms is needed, the mass resolution can be improved by using $^{20}\text{Ne}^+$ ions.

A typical HS-LEIS spectrum is shown in Fig. 2. The sample is a mixed oxide catalyst, cleaned with atomic oxygen (to remove hydrocarbons from exposure to atmosphere) prior to analysis. The surface is analyzed with 3 keV $^4\text{He}^+$ ions (Fig. 2a). Peaks for oxygen ($m = 16$ amu), aluminum (27 amu) and vanadium (51 amu) can be recognized in the spectrum, as well as a peak at 2500 eV. This high energy peak is due to elements that are too heavy to separate with $^4\text{He}^+$. By switching to 3 keV $^{20}\text{Ne}^+$ ions (Fig. 2b) the elements in this peak can be separated and are identified as molybdenum (96 amu) and tellurium (118 amu). If needed, $^{40}\text{Ar}^+$ ions can be used to discriminate between even heavier surface atoms. Similarly, $^3\text{He}^+$ ions are preferred for the analysis of very light elements (<20 amu).

2. Sensitivity and sputter damage

HS-LEIS is orders of magnitude more sensitive than conventional LEIS. In HS-LEIS, the scattered ions are collected from all azimuth angles and the HS-LEIS analyzer is imaging the ions onto a position sensitive detector. The latter makes it possible to simultaneously detect scattered ions of different energies. As a result, the ratio of the LEIS signal to the primary ion current is orders of magnitude higher in HS-LEIS. As a consequence of this enormous increase in sensitivity it is possible to perform Static LEIS. Good LEIS spectra are obtained while less than 0.5% of a monolayer is sputtered from the sample surface. An example of Static LEIS spectra of a dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst containing a two-dimensional monolayer of surface MoO_x species on the TiO_2 support is shown in Fig. 3 together with the reference spectra of pure MoO_3 and TiO_2 samples [9]. For each of the spectra

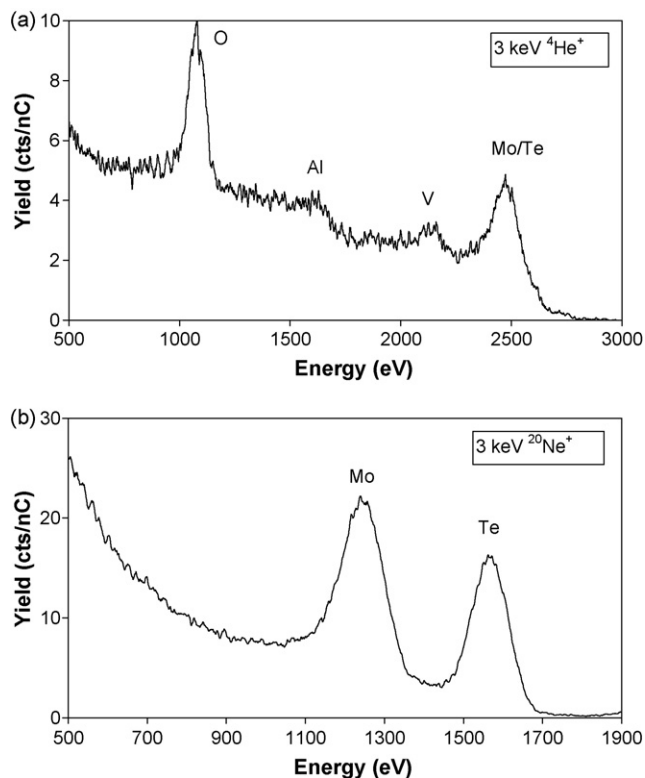


Fig. 2. HS-LEIS spectra of a mixed oxide catalyst. In the 3 keV $^4\text{He}^+$ spectrum of (a), the peaks of O, Al and V can be identified. The last peak consists of contributions from Mo and Te that cannot be separated with 3 keV $^4\text{He}^+$ ions. In the 3 keV $^{20}\text{Ne}^+$ spectrum of (b), these peaks are clearly separated.

only 0.2% of a monolayer was sputtered from the surface. This is generally considered to be well below the static limit.

3. Quantification

As long as the experimental conditions are chosen with care (E_i cannot be too low, θ is large and no grazing angles are used), for a given primary ion, primary ion energy and scattering surface atom, the HS-LEIS peak is proportional to the amount of scattering surface atoms [3]. This means that quantification is straightforward. Backgrounds are subtracted from the peaks, the peaks are integrated and peak areas are proportional to the surface fraction of the atoms. Thus, when a pure reference of the element is analyzed, peak areas from the unknown samples can be expressed

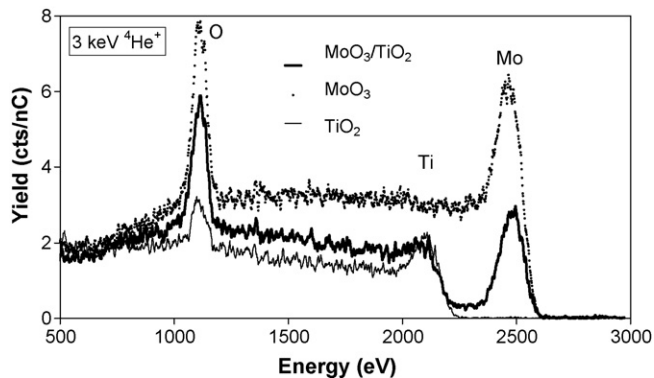


Fig. 3. Static HS-LEIS spectra (3 keV $^4\text{He}^+$) of dehydrated supported 5.3% $\text{MoO}_3/\text{TiO}_2$ catalyst and pure MoO_3 and TiO_2 references. During the experiment approximately 0.2% of a monolayer is sputtered from the sample surface.

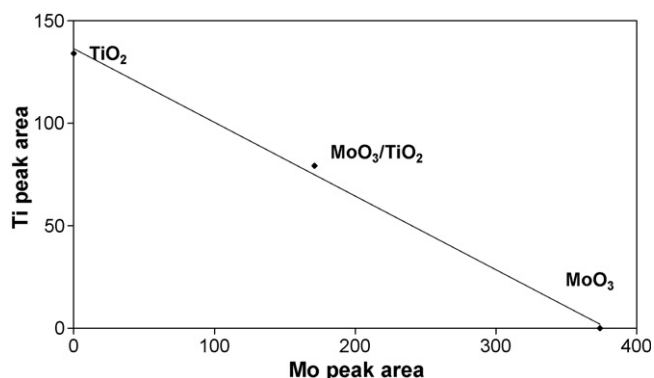


Fig. 4. Calibration plot for the spectra from Fig. 3. The Mo/Ti ratio for the supported $\text{MoO}_3/\text{TiO}_2$ catalyst sample was 44/56.

as fractions of the peak area for the pure element yielding surface fractions for the unknown samples.

Another typical procedure makes use of a calibration plot. The area of one peak is plotted as a function of the area of another peak for a number of samples. If there are no other elements to consider and if Vegard's law holds (i.e., there is no significant excess volume of mixing), these data points will form a straight line. The calibration plot for the Static LEIS spectra from Fig. 3 is shown in Fig. 4. From the spectrum and the references, it is determined that the Mo/Ti ratio for the dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst surface is 44/56. This surface composition is consistent with the surface Mo density of 4.6 Mo atoms/ nm^2 for the supported $\text{MoO}_3/\text{TiO}_2$ catalyst relative to 8 Mo atoms/ nm^2 for pure MoO_3 [9,10]. The HS-LEIS detection of exposed TiO_x sites from the underlying TiO_2 support also reflects the generally lower surface density of supported metal oxide phases at monolayer coverage relative to that found in their corresponding unsupported pure oxides.

Fig. 4 is an example of a calibration plot, containing data points for the dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst sample and two pure references. In many cases, it is not necessary to use pure reference samples. A set of unknowns will be sufficient to obtain surface fractions of the various elements. If the experiment from Fig. 4 would have been performed on a set of supported $\text{MoO}_3/\text{TiO}_2$ catalysts with varying amounts of Mo on the surface, the (Mo peak area, Ti peak area) data points for all the samples would have been on the same straight line. By fitting the line for the supported $\text{MoO}_3/\text{TiO}_2$ catalyst and extrapolating to the x - and y -axis, the sensitivity factors can be found. Thus, as long as the set of samples is large enough and the surface concentrations vary sufficiently, so that a good fit can be obtained, pure reference samples are not needed.

The surface roughness has a small influence on the HS-LEIS spectra [11]. In Fig. 5a, the 4.5 keV $^4\text{He}^+$ spectrum for highly dispersed silica powder is compared to the spectrum of a 100 nm thick SiO_2 layer on a Si wafer. In a similar way, in Fig. 5b, the 4.5 keV $^4\text{He}^+$ spectrum for highly dispersed γ -alumina powder is compared to the spectrum of a 100 nm thick Al_2O_3 layer on a Si wafer. All samples were treated with atomic oxygen, prior to analysis. It can be seen that the peak is slightly lower for the powder samples. This is due to the fact that a small part of the surface atoms cannot be seen by the analyzer due to shadowing effects from other powder particles. At the same time, the background on the low energy side of the peak is slightly higher for the powder samples. This background is due to scattering from deeper lying atoms (see below). The surface atoms that are shadowed by other powder particles are now contributing as deeper lying atoms, thereby raising the background at the low energy side of the peak. It is worth mentioning that the LEIS spectra for α -alumina and

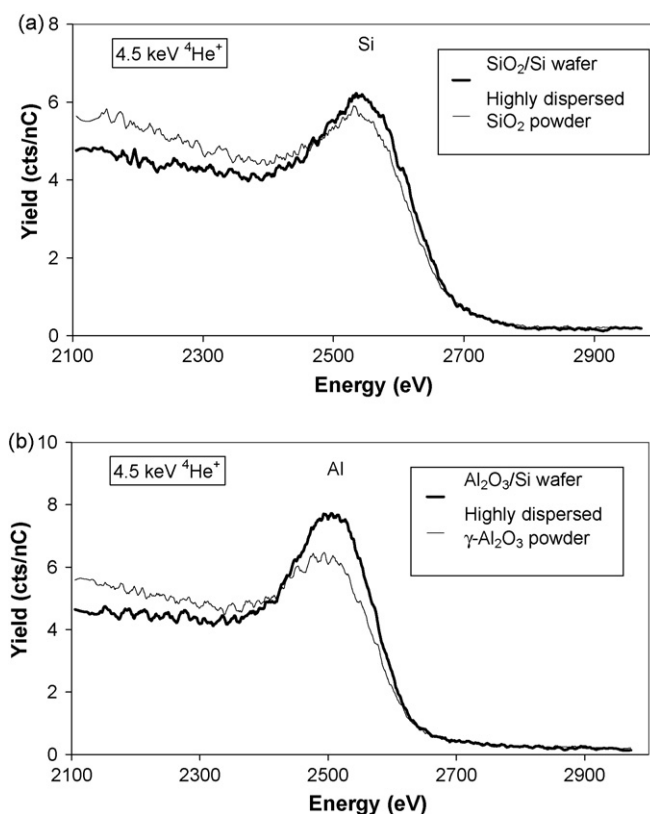


Fig. 5. Effect of surface roughness on 4.5 keV $^4\text{He}^+$ HS-LEIS spectra. (a) Comparison between highly dispersed SiO_2 powder and SiO_2 on a Si wafer and (b) comparison between highly dispersed $\gamma\text{-Al}_2\text{O}_3$ powder and Al_2O_3 on a Si wafer.

γ -alumina also differ significantly because of the different surface termination [12]. In the present case, it is not clear what the structure of the Al_2O_3 layer on Si is.

It is clear that there is no effect of surface roughness on the peak position and that the effect of the surface roughness on the peak area here is of the order of 10–20%. Given that quantification errors of that magnitude (5–25%) are generally accepted in XPS [13], this should not be considered a problem. In addition, all peaks within a LEIS spectrum are affected in the same way. Therefore, peak area ratios are not affected by surface roughness. Also, samples with similar topology have similar effects on the spectra. Therefore, when quantifying LEIS results, one should strive to use reference samples with a surface roughness similar to the sample being quantified to minimize the influence of surface roughness. Usually, this is not a problem.

4. Information about deeper layers and dispersion of active material

HS-LEIS is surface sensitive since noble gas ions are used as primary ions that are neutralized when they enter the solid. The resulting neutral noble gas atoms may still scatter from deeper layers and leave the sample but they are not detected since the analyzer only detects ions.

In some cases, a fraction of these scattered noble gas atoms can be re-ionized when they leave the surface. Since these particles have lost energy while traveling through the material, these re-ionized particles show up in the spectrum at the low energy side of the peak. When these particles have scattered from atoms close to the surface, only a small amount of energy is lost. These atoms are represented in the spectrum by the signal close to the peak. Deeper lying atoms are represented in the spectrum by a signal at much lower energies than the peak energy. If the scattering atoms are

present in a continuous layer, this phenomenon manifests itself as a continuous tail on the low energy side of the peak. The shape of this tail gives information about the distribution of the studied element over deeper layers. On flat surfaces (e.g. samples from microelectronics industry) one typically obtains information about layers up to a depth of 10 nm. For supported catalysts or other highly disperse samples, the useful information depth is much lower. This is not due to the technique, but due to the topology of the sample, where at a depth of a few nanometers the composition will be equal to the bulk composition. However, this information is very useful in the determination of the dispersion of an active catalytic component on the surface of the catalyst, since it yields quantitative information about the amounts of the active component in the outermost atomic layer and in the second layer.

The HS-LEIS Mo peak region in the 3 keV $^4\text{He}^+$ spectra of the pure MoO_3 powder and the dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst are presented in Fig. 6a and b, respectively. The surface peak is separated from the background through a fitting procedure. The ratio of background to surface peak is clearly lower for the dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst. For the pure MoO_3 powder, the Mo is distributed over all layers that give rise to a high background. For the dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst, the Mo on the catalyst sample is mainly in the outermost atomic layer of the sample. There is very little Mo in deeper layers and, therefore, the background is very low. A comparison of the ratios of background height to peak area for the two samples results in an amount of Mo in the second layer of 26% (where this value is 100% for MoO_3 powder). The partial clustering of the surface MoO_x species may be related to the presence of some residual moisture since crystalline MoO_3 nanoparticles are absent in this sample [9].

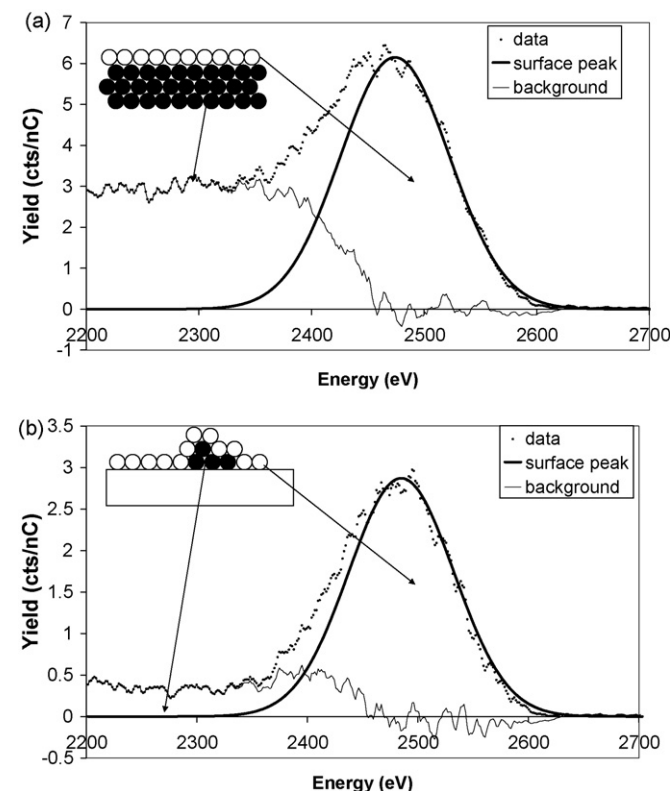


Fig. 6. Comparison of the Mo peak (3 keV $^4\text{He}^+$ spectra) for (a) pure MoO_3 and (b) dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst. The ratio of the background height to peak area is much lower for the supported $\text{MoO}_3/\text{TiO}_2$ catalyst than for the bulk MoO_3 powder indicating little Mo in the second atomic layer of the catalyst. A quantitative comparison showed that the second layer contains 26% Mo for the supported $\text{MoO}_3/\text{TiO}_2$ catalyst relative to 100% Mo for MoO_3 .

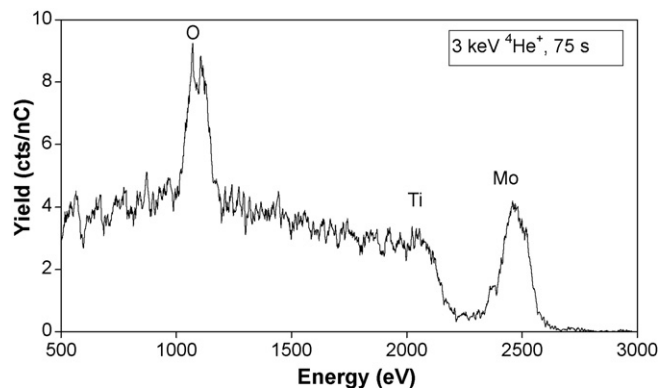


Fig. 7. HS-LEIS spectrum of the dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst (3 keV $^4\text{He}^+$) acquired in 75 s.

5. Other applications

The high surface sensitivity of HS-LEIS has been used to obtain detailed information on the catalytic processes themselves. From the signal reductions upon poisoning by coke or sulfur, information was obtained on the sites that were poisoned [14,15]. Guliants et al. [16] used such signal reductions by various probe molecules to obtain insight in the active sites on complex catalysts (VNbMoTeO_x) used for the selective oxidation of propane to acrylic acid.

The sensitivity of HS-LEIS is high enough to obtain good quality spectra in a short time. In general, data acquisition times are of the order of 10 min/spectrum. However, due to the fast electronics for signal processing, shorter analysis times can be achieved with relative ease. The 3 keV $^4\text{He}^+$ spectrum of the same dehydrated supported $\text{MoO}_3/\text{TiO}_2$ catalyst is shown in Fig. 7 with an acquisition time of 75 s. It would be possible to record $^4\text{He}^+$ and $^{20}\text{Ne}^+$ spectra for an array of 24 samples in 2 h. Currently, a sample stage with the ability to hold 48 samples is under commercial development. The samples are treated simultaneously in a pretreatment chamber and enter the HS-LEIS analysis chamber without exposure to atmosphere. This makes HS-LEIS an excellent candidate for High Throughput Experimentation (HTE) surface analysis of heterogeneous catalysts.

6. Conclusions

High Sensitivity-Low Energy Ion Scattering (HS-LEIS) is an attractive technique for the surface analysis of heterogeneous catalysts. It is very surface specific and samples the outermost atomic layer. It is flexible since the operator has a choice of primary ions and primary ion energies. This makes it possible to optimize for sensitivity as well as specificity for the different elements. In this way, all elements from C and higher can be analyzed. The HS-LEIS measurement can be operated in a Static mode, essentially non-destructive, due to the high sensitivity of the analyzer. Sputter damage below 0.5% of a monolayer is routinely achieved while the quality of the spectra is more than sufficient. HS-LEIS yields quantitative information, not only in terms of elemental composition of the outermost atomic layer, but also in terms of the distribution of elements in the layers immediately beneath the outermost atomic layer.

Acknowledgements

The authors wish to thank Prof. Dr. Vadim Guliants (Chemical Engineering Department, University of Cincinnati, Cincinnati, OH, USA) for providing the mixed oxide catalyst sample and Drs. Ally

Chan and Simon Bare (UOP, Des Plaines, IL, USA) for providing the Al₂O₃/Si and SiO₂/Si samples. The Lehigh contribution was supported by the U.S. Department of Energy–Basic Energy Sciences grant DE-FG02-93ER-14350.

References

- [1] B.A. Horrell, D.L. Cocke, *Catal. Rev. Sci. Eng.* 29 (1987) 447.
- [2] H.H. Brongersma, G.C. van Leerdam, in: H.H. Brongersma, R.A. van Santen (Eds.), *Fundamental Aspects of Heterogeneous Catalysis Studied by Particle Beams*, Plenum Press, 1991., p. 283, NATO ASI B 265.
- [3] H.H. Brongersma, M. Draxler, M. de Ridder, P. Bauer, *Surf. Sci. Rep.* 62 (2007) 63.
- [4] S. Labich, E. Taglauer, H. Knözinger, *Top. Catal.* 14 (2001) 153.
- [5] S. Rondon, M. Houalla, D.M. Hercules, *Surf. Interface Anal.* 26 (1998) 329.
- [6] L.E. Briand, O.P. Tkachenko, M. Guraya, X. Gao, I.E. Wachs, W. Grünert, *J. Phys. Chem. B* 108 (2004) 4823.
- [7] S.D. Gardner, G.B. Hoflund, M.R. Davidson, H.A. Laitinen, D.R. Schryer, B.T. Upchurch, *Langmuir* 7 (1991) 2140.
- [8] J.B. Theeten, H.H. Brongersma, *Rev. Phys. Appl.* 11 (1976) 57.
- [9] T. Kim, Ph.D. Thesis, Lehigh University, Bethlehem, PA, USA (2007).
- [10] H. Hu, I.E. Wachs, S.R. Bare, *J. Phys. Chem.* 99 (1995) 10897.
- [11] W.P.A. Jansen, A. Knoester, A.J.H. Maas, P. Schmit, A. Kytökiivi, A.W. Denier, v.d. Gon, H.H. Brongersma, *Surf. Interface Anal.* 36 (2004) 1469.
- [12] H.H. Brongersma, P.A.C. Groenen, J.P. Jacobs, *Science of ceramic interfaces 2*, in: J. Nowotny (Ed.), *Materials Science Monographs*, vol. 81, Elsevier, 1994., p. 150.
- [13] D.E. Newbury, et al., *Advanced Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press, New York, 1986.
- [14] J.M.A. Harmsen, W.P.A. Jansen, J.H.B.J. Hoebink, J.C. Schouten, H.H. Brongersma, *Catal. Lett.* 74 (2001) 133.
- [15] P.A.J. Ackermans, G.C.R. Krutzen, H.H. Brongersma, *Nucl. Instrum. Methods B* 45 (1990) 384.
- [16] V.V. Guliants, R. Bhandari, A.R. Hughett, S. Bhatt, B.D. Schuler, H.H. Brongersma, A. Knoester, A.M. Gaffney, S. Han, *J. Phys. Chem. B* 110 (2006) 6129.