Materials analysis with Rutherford backscattering spectrometry; application to catalysts

Citation for published version (APA):

DOI:
10.1007/BF02062199

Document status and date:
Published: 01/01/1993

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl

providing details and we will investigate your claim.
Rutherford Backscattering Spectrometry (RBS) is shown to be a powerful tool in the analysis of model catalysts. The surface coverage of various metals on thin SiO$_2$ layers on Si and thin Al$_2$O$_3$ layers on Al can be accurately measured while simultaneously depth profiles of the metals are obtained. The scattering technique is briefly reviewed and several applications concerning the preparation of model catalysts by wet chemical methods are presented.

INTRODUCTION

Commonly applied surface sensitive spectroscopies which are used to characterize the surface composition of catalysts are X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES). These techniques serve to identify factors in the catalyst preparation but are usually limited in obtaining quantitative results due to the inhomogeneous charging of powder samples. The use of model catalysts which consist of thin (1-5 nm) oxide layers on Si or Al reduces this problem considerably and also facilitates the study of the chemical environment due to the reduced linewidths in XPS.
The sensitivity, however, remains restricted to the surface when no sputtering is applied and the accuracy of quantification remains limited by charging as well as by intrinsic uncertainties in the basic physical processes of the techniques. High energy ion scattering techniques such as RBS are quantitative and are sensitive to large depths, depending on the energy of the particles and the stopping power. At the Department of Chemical Technology of Eindhoven University of Technology (EUT) research is carried out on wet chemical preparation methods of model catalysts normally applied on powders and the samples are also analyzed by RBS at the Faculty of Technical Physics. Examples are presented in which Rh, Zr, Mo and S are deposited and characterized.

EXPERIMENTAL ANALYSIS METHODS

Commonly applied nuclear techniques were carried out with the 30 MeV AVF cyclotron at EUT. Rutherford backscattering spectra were measured with a beam of 3.94 MeV $\text{He}^+$. The resulting overall energy resolution was measured to be 18 keV. As the energy of the beam is higher than 2 MeV, which is usually employed for RBS, the scattering cross-sections for the atoms with $Z \leq 20$ have to be assessed. The energy threshold for non-Rutherford behavior of scattering cross-sections is dependent on the scattering angle and can be estimated theoretically [1]. For Si and Al a deviation of 4% from the Rutherford cross-section is predicted at a scattering angle of 100° with an incident ion energy of 4.4 MeV and 4.1 MeV, respectively. Experiments revealed deviations above approximately 3.7 MeV at a scattering angle of 165°.

Surface "impurities" or thin films of heavy elements show up in RBS spectra as sharp peaks separated from the low-energy ridges due to the low-Z substrate supports like Si or Al. The elemental concentrations expressed as $N_z$ in atoms/cm$^2$ with atomic number $Z$, can be deduced from the sharp peaks in the RBS spectra. The yield is given as $Y=N_z\alpha$ where $N_\alpha$
is the number of beam particles arriving at the target, \( (d\sigma/d\Omega) \) is the differential cross-section and \( \Omega \) is the solid angle of the detector. The height of the continuum in the spectrum at low energies is given as \( H = N_a c (d\sigma/d\Omega) \Omega (\delta E/\epsilon) \), where \( c \) is the atomic concentration of the substrate element (usually \( c=1 \)), \( \delta E \) is the energy per channel in the spectrum and \( \epsilon \) is the stopping power (eV at \( -1 \) cm\(^2\)). The appearance of the continuum in the spectra provides an opportunity to calculate the areal density of the heavy elements without the use of a dose measurement. In the ratio \( Y(Z)/H \) (determined from the same spectrum) both \( N_a \) and \( \Omega \) vanish and the areal density of atoms \( Z \) can be calculated by using the Rutherford cross-sections and the stopping power.

### RESULTS FOR MODEL CATALYSTS

1. **\( \text{ZrO}_2/\text{SiO}_2/\text{Si}(100) \)**

Zirconium oxide is of interest as a catalyst for isosynthesis, methanol synthesis and catalytic cracking and as a support for other catalysts [2]. Preparation of supported model systems by wet chemical methods has the disadvantage that the amount of deposited zirconia, whether from nitrate or from ethoxide is not known. Although Zr concentrations can be estimated from angle dependent XPS, RBS offers a more direct way to determine the Zr concentration. Figure 1 shows the RBS spectrum of a \( \text{ZrO}_2/\text{SiO}_2/\text{Si}(100) \) model catalyst prepared by impregnation from a solution of zirconium nitrate in water. The spectrum shows sharp peaks at 3.554 MeV corresponding to Hf (a known impurity of Zr) and a broad continuum below 2.8 MeV due to the Si substrate. The structure between 2.5 and 2.8 MeV is attributed to a nuclear resonance. The amount of Zr on the sample has been calculated from Fig.1 from the ratio of the integrated Zr peak and the Si signal height below channel 350. This region corresponds to incident He ions which have slowed down to an energy of \(< 3.7 \) MeV just before scattering, which is
Fig. 1. Rutherford backscattering spectrum of a ZrO$_2$/SiO$_2$/Si(100) model catalyst prepared by impregnation from an aqueous solution of zirconium nitrate, measured with an incident beam of 3.94 MeV He$^+$ ions the empirical limit for Rutherford scattering in Si. In this way the Zr concentration can be calculated from the Zr and Si cross-sections and the stopping power of He in Si. The concentration of Zr thus determined is $(5.7 \pm 0.2) \times 10^{15}$ atoms cm$^{-2}$, while Hf corresponds to $(7 \pm 1) \times 10^{13}$ atoms cm$^{-2}$.

2. Rh/Al$_2$O$_3$/Al

In this case RhCl$_3$nH$_2$O solutions, with different acidities, have been applied onto Al$_2$O$_3$/Al supports. The Al$_2$O$_3$ layer was 50 Å thick. The 3.94 MeV He$^+$ beam entered the sample perpendicular to the surface and the backscattered particles were
detected at an angle of 15° with respect to the normal on the surface. Figure 2 shows the upper part of the spectrum, containing only the Rh "peak". At pH=2 and 3 the peaks are smeared out to lower energy, indicating that Rh has penetrated into the Al₂O₃ and Al. Only at pH=4 is the Rh confined to the surface with an areal density of (1.4±0.2)x10¹⁵ atoms cm⁻². The bulk materials contain only a small fraction (Rh/Al=5x10⁻⁷). RBS information provides here useful hints for the preparation, while XPS produced a result of ~ 10¹⁴ atoms cm⁻², independent of the pH.
This catalyst is used in the petrochemical industry for upgrading high molecular fraction of crude oil or coal derived liquids which contain sulfur and nitrogen. This catalyst helps removing these compounds (hydrodesulfurization, hydrodenitrogenation) and thus are important for controlling environmental pollution.

The model catalyst was prepared by spincoating liquid molybdenum oxychloride onto a $SiO_2/Si(100)$ support. After dry-
ing the sulfidation was studied by leading H2S over the cata-
lyst at different temperatures between 30 and 300°C. Consis-
tent results between XPS and RBS were only obtained when the
MoO2Cl2 was thin enough for XPS to analyze the full layer
(<30 Å). Figure 3 shows the RBS spectra of 3 cases (unsulfided
and sulfided at 60°C and 300°C). It appears that only above
100°C was full sulfidation obtained with Mo:S=1:2. We found
~10^{15} atoms cm^{-2} Mo, which corresponds to ~1/3 monolayer, thus
to a surface coverage of ~30%.

CONCLUSION

The results in this paper on ZrO2/SiO2/Si, Rh/Al2O3/Al and
MoO2Cl2/SiO2/Si(100) demonstrate that flat conducting model
catalysts can successfully be prepared by the same wet chemical
procedures as are used in the preparation of powder catalysts.
Although it has not been proved yet that these systems are
indeed catalytically active, the possibility is offered to
study surface chemical aspects of catalyst preparation by means
of surface spectroscopies that are either not applicable, or
not applicable to their full potential on powder catalysts.
RBS forms a useful supplement in the range of surface analysis
techniques applied to catalysts which offers quantification and
non-destructive depth information.

REFERENCES

2. A.M. de Jong, L.M. Eshelman, L.J. van IJzendoorn, J.W.
   and references therein.