

Materials analysis with Rutherford backscattering spectrometry; application to catalysts

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MATERIALS ANALYSIS WITH RUTHERFORD BACKSCATTERING
SPECTROMETRY; APPLICATION TO CATALYSTS

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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_2O_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 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/cm² with atomic number Z , can be deduced from the sharp peaks in the RBS spectra. The yield is given as $Y = N_\alpha N_Z (d\sigma/d\Omega) \Omega$, where N_α

is the number of beam particles arriving at the target, $(d\sigma/d\Omega)$ is the differential cross-section and Ω is the solid angle of the detector. The height of the continuum in the spectrum at low energies is given as $H=N_{\alpha}c(d\sigma/d\Omega)\Omega(\delta E/\epsilon)$, where c is the atomic concentration of the substrate element (usually $c=1$), δE is the energy per channel in the spectrum and ϵ is the stopping power ($\text{eV at}^{-1} \text{cm}^2$). 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_{α} and Ω 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. ZrO₂/SiO₂/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 ZrO₂/SiO₂/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

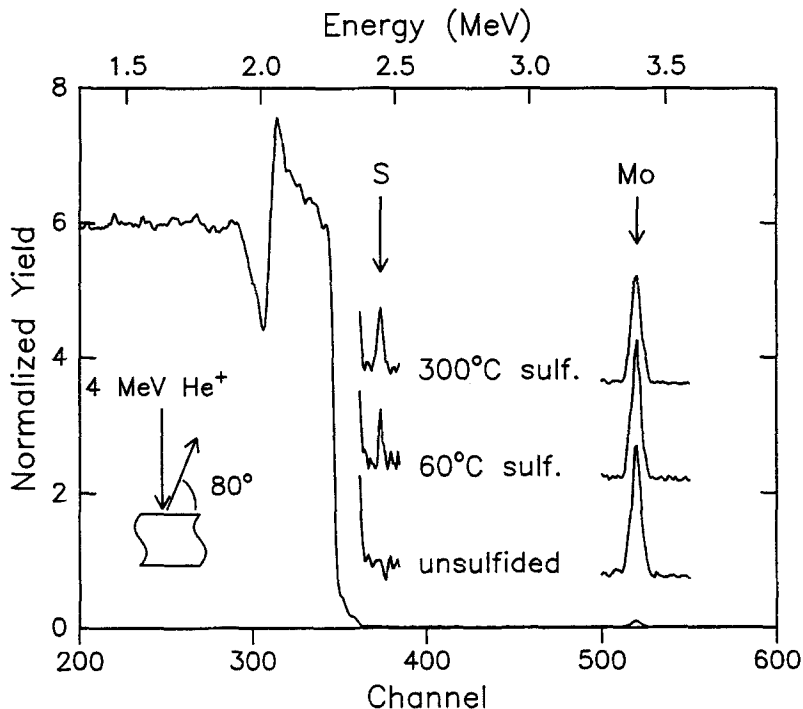


Fig. 1. Rutherford backscattering spectrum of a $\text{ZrO}_2/\text{SiO}_2/\text{Si}(100)$ model catalyst prepared by impregnation from an aqueous solution of zirconium nitrate, measured with an incident beam of 3.94 MeV He^+ ions

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 $(5.7 \pm 0.2) \times 10^{15} \text{ atoms cm}^{-2}$, while Hf corresponds to $(7 \pm 1) \times 10^{13} \text{ atoms cm}^{-2}$.

2. $\text{Rh}/\text{Al}_2\text{O}_3/\text{Al}$

In this case $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ solutions, with different acidities, have been applied onto $\text{Al}_2\text{O}_3/\text{Al}$ supports. The Al_2O_3 layer was 50 \AA thick. The 3.94 MeV He^+ beam entered the sample perpendicular to the surface and the backscattered particles were

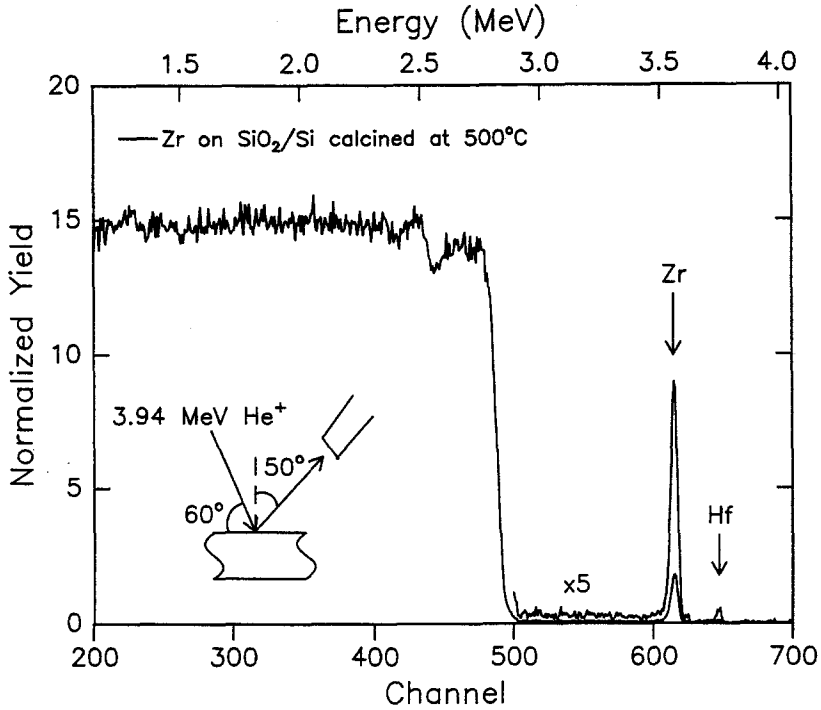


Fig. 2. Upper-energy part of the RBS spectrum showing the Rh peak for three different pH values, as measured with a 3.94 MeV He^+ beam

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 Al_2O_3 and Al. Only at pH=4 is the Rh confined to the surface with an areal density of $(1.4 \pm 0.2) \times 10^{15}$ atoms cm^{-2} . The bulk materials contain only a small fraction ($\text{Rh}/\text{Al} = 5 \times 10^{-7}$). RBS information provides here useful hints for the preparation, while XPS produced a result of $\sim 10^{14}$ atoms cm^{-2} , independent of the pH.

3. $\text{MoO}_2\text{Cl}_2/\text{SiO}_2/\text{Si}(100)$

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

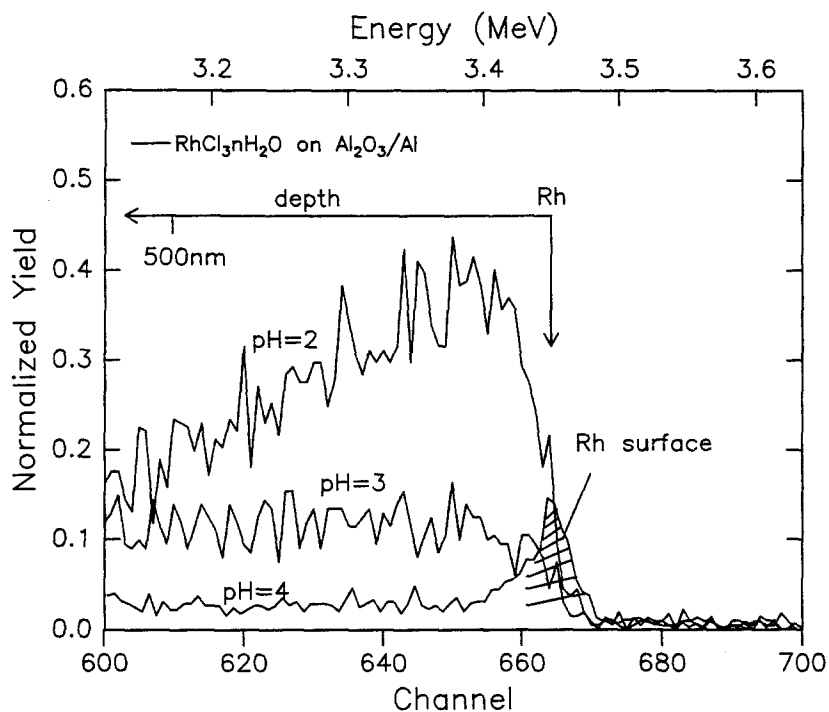


Fig. 3. RBS spectra of unsulfided and sulfided samples at 60°C and 300°C of a $\text{MoO}_2\text{Cl}_2/\text{SiO}_2/\text{Si}(100)$ model catalyst. Beyond channel 350 the scale is expanded by a factor of 20. The low-energy ridge is due to silicon, including a resonance

pollution. The model catalyst was prepared by spincoating liquid molybdenum oxychloride onto a $\text{SiO}_2/\text{Si}(100)$ support. After dry-

ing the sulfidation was studied by leading H_2S over the catalyst at different temperatures between 30 and 300°C. Consistent results between XPS and RBS were only obtained when the MoO_2Cl_2 was thin enough for XPS to analyze the full layer ($< 30 \text{ \AA}$). 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 $\sim 10^{15} \text{ atoms cm}^{-2} \text{ Mo}$, which corresponds to $\sim 1/3$ monolayer, thus to a surface coverage of $\sim 30\%$.

CONCLUSION

The results in this paper on $\text{ZrO}_2/\text{SiO}_2/\text{Si}$, $\text{Rh}/\text{Al}_2\text{O}_3/\text{Al}$ and $\text{MoO}_2\text{Cl}_2/\text{SiO}_2/\text{Si}(100)$ 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.

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