The growth mechanism of nickel in the preparation of Ni/Al_2O_3 catalysts studied by LEIS, XPS and catalytic activity

J.-P. Jacobs [a], L.P. Lindfors [b], J.G.H. Reintjes [a], O. Jylhä [b]
and H.H. Brongersma [a,1]

[a] *Faculty of Physics and Schuit Institute of Catalysis,*
Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] *Neste Oy, Technology Center, PO Box 310, FIN-06101 Borgå, Finland*

Received 24 September 1993; accepted 11 January 1994

A series of Ni/Al_2O_3 catalysts prepared from vapor phase by the atomic layer epitaxy (ALE) technique have been studied. A model is proposed for the growth mechanism of nickel in its oxidic form on alumina, from sequences of treatments with $Ni(acac)_2$ and air. In the study activity measurements were combined with surface analysis by LEIS and XPS. During the first preparation sequence (< 5 wt% Ni) atomically dispersed nickel is obtained on the alumina support. The nickel atoms are catalytically inactive, but act as nuclei for the growth of the catalytically active Ni-species during the subsequent preparation sequences. The highest utilization of nickel atoms in the hydrogenation of toluene was obtained when the nickel nuclei were covered with one layer of active nickel species.

Keywords: Ni/Al_2O_3 catalysts; growth mechanism; hydrogenation of toluene; surface characterization; ALE; LEIS; ISS; XPS

1. Introduction

Supported nickel catalysts are widely used in a number of industrial processes such as hydrogenation. The activity of the supported catalysts is strongly dependent on the preparation method used and on the choice of reagents and support. In order to keep up with the increasing demands regarding the performance of catalysts, a thorough understanding of the mechanisms involved in the catalyst preparation is important. In this study, the growth mechanism of nickel on alumina in the preparation of Ni/Al_2O_3 catalysts from vapor phase by ALE, was studied using low-energy ion scattering (LEIS or ISS) and X-ray photoelectron spectroscopy (XPS).

---

[1] To whom correspondence should be addressed.

The characteristic feature of ALE is the controlled build-up of surface structures [1]. This is achieved by a sequential introduction of different reagents in saturating gas–solid reactions. The active species or their precursors, introduced from vapor phase, saturate the surface by chemisorption. Thus, the loading of the active species is determined by the ability of the support to bind the reactant, not by dosing of the reactant [2]. The Ni/Al_2O_3 catalysts were prepared in the oxidic form by chemisorbing nickel acetylacetonate, $Ni(acac)_2$, onto alumina followed by the removal of ligand residues with air treatment [3]. The nickel content was regulated by the number of reaction cycles.

In low-energy ion scattering spectroscopy (LEIS) a beam of monoenergetic ions is directed towards the surface to be analysed. The information on the surface of a specimen is obtained from the energy distribution of the ions that are scattered back by the surface. Conservation of energy and momentum during the collision with a surface atom ensures that for given experimental conditions (incident energy, type of ion and scattering angle) the scattered ion energy only depends on the mass of the surface atom from which it was scattered [4]. An energy spectrum of the scattered ions is thus equivalent to a mass spectrum of the surface atoms. It has been demonstrated earlier that when inert gas ions, such as He^+ or Ne^+ are used to probe the surface, the information comes exclusively from ions scattered by the outermost atomic layer of the solid [4].

Recent investigations proved the value of the technique even when studying rough insulating surfaces, such as catalysts in general [5,6]. A review of LEIS in catalysis research and recent developments have been reported elsewhere [7,8].

The activity of the catalysts was evaluated in gas phase hydrogenation of toluene in a laboratory scale fixed bed reactor after in situ reduction of the accessible nickel species. In addition to a model proposal for the growth mechanism of nickel on alumina, the aim was to study the effect of alumina pretreatment, prior to the catalyst preparation, on the characteristics and activity of the catalysts. It is well known that the interaction between metal oxide supports and active species is crucial for the catalytic performance. Several studies dealing with the interaction between nickel and alumina have been reported [9–12]. The interaction can be varied e.g. by pretreating the support and thus influencing the number, strength and nature of the bonding sites between the active species and the support. The dispersion of the active species and their resistance towards agglomeration as well as the activities of the catalysts are strongly dependent on this interaction.

2. Experimental

2.1. CATALYST PREPARATION

The alumina used as support (AKZO 000-1.5E) was crushed and sieved to a size of 0.15–0.35 mm. It was then heat treated in air at various temperatures to vary the θ/γ phase ratio. The preparation of the Ni/Al_2O_3 catalysts by ALE has been discussed in more detail elsewhere [3]. The interaction between $Ni(acac)_2$ and alumina was restricted to chemisorption by the proper choice of reaction temperature. Surface saturation was ensured by using an excess of reactant. The chemical nature of the nickel species was changed by removing the ligands with air at elevated temperatures at the end of each sequence.

The nickel growth mechanism was studied using an alumina having a θ/γ phase ratio of ~ 0.25 as support (catalysts Ni-1, Ni-2, Ni-4_b, Ni-6, Ni-8 and Ni-10 in table 1). The nickel content was varied from 3 to 21 wt% by changing the number of preparation sequences from one to ten.

In order to study the effect of alumina pretreatment on the activity, three catalysts containing $\sim$ 10 wt% nickel were prepared on the alumina having θ/γ phase ratios of $\sim$ 0, 0.25 and 0.30 (catalysts Ni-4_a, Ni-4_b and Ni-4_c, respectively, in table 1).

2.2. CATALYST CHARACTERIZATION

The nickel content was determined using X-ray fluorescence (XRF). Possible crystalline nickel species and alumina phase ratios were determined by means of X-ray diffraction. The specific surface area, SA, pore volume, PV, and average pore diameter, d_p, of the alimuna and the catalysts were determined using nitrogen adsorption and condensation (BET-analysis) [3]. The values of the SA, PV and d_p were between 125 and 155 m^2/g, 0.3 and 0.4 cm^3/g, and 100 and 115 Å, respectively, for all catalysts. The corresponding values for the pure θ and γ alumina were 120 and 190 m^2/g, 0.45 and 0.49 cm^3/g, and 150 and 100 Å, respectively.

The surface compositions of the catalysts were studied using low-energy ion scattering (LEIS) and X-ray photoelectron spectroscopy (XPS).

The LEIS characterization was performed with the LEIS apparatus NODUS, of which the basic design has been described elsewhere [13]. In its setup it is nowadays possible to compensate for surface charging, when the ion beam is directed onto the target, by flooding the surface using thermal electrons from all sides. The base pressure of the ultra high vacuum (UHV) system is 1×10^{-9} mbar and will

Table 1
Number of preparation sequences, corresponding Ni-loadings and hydrogenation activity of catalysts

Catalyst, No. of prep. seq.	Ni (wt%)	Activity (g_{MECH}/g_{Ni} h)	Activity (g_{MECH}/g_{Cat} h)
Ni-1, 1	3.0	5	<1
Ni-2, 2	5.9	60	4
Ni-4_b, 4	10.8	205	22
Ni-6, 6	14.0	140	20
Ni-8, 8	17.2	130	22
Ni-10, 10	20.7	135	28

increase during operation to 8×10^{-9} mbar. This is due to the inert gas of the ion beam, which does not affect the measurements. Prior to the LEIS measurements the catalysts were treated in 20 mbar oxygen at ~ 250°C for 15 min in order to remove contamination by water and hydrocarbons. The scattering conditions were kept constant during the experiments. Therefore, the LEIS signals of the different catalysts can be compared in an absolute sense. A typical LEIS spectrum of the studied catalysts is shown in fig. 1. The signals for the various elements are the peak heights with respect to the background on the high energy side of the peak. Instead of peak heights one can also use peak areas. The numbers are then different, but it does not effect the conclusions.

The catalysts along with the pure alumina were also analyzed using XPS. The photoelectron spectra were measured with an X-probe model 101 spectrometer manufactured by Surface Science Instruments (VG Fisons, Mountain View, CA) equipped with a monochromatized Al Kα X-ray source. A flood gun was used to minimize sample charging. For the analysis the Ni $2p_{3/2}$ signal with its corresponding satellite were used. High resolution spectra of the elements of interest and wide scan survey spectra were run for each sample. The relative surface composition in atomic per cent was calculated from high resolution spectra for aluminum, nickel and oxygen. The atomic surface composition was calculated from the Ni $2p_{3/2}$, Al 2p and O 1s peak intensities using atomic sensitivity factors provided by the instrument manufacturer. The background pressure during data acquisition was lower than 10^{-8} mbar.

The activity of the catalysts was studied in the hydrogenation of toluene to methylcyclohexane. The catalysts were tested in a differential fixed bed vertical tubular reactor following a similar procedure as described elsewhere [14]. The catalysts were reduced in situ in flowing hydrogen at 500°C (0.5 mol/h) at atmospheric

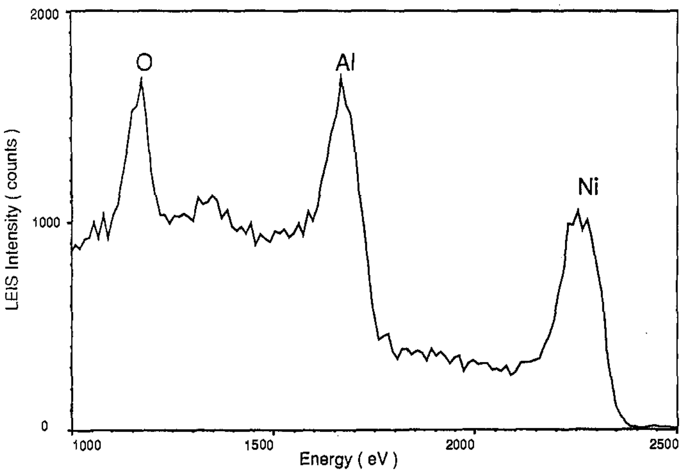

Fig. 1. Typical LEIS-spectrum of an alumina supported nickel catalyst (A3) ($^4He^+$, primary energy of 3 keV).

pressure prior to testing. The reactor was operated at atmospheric pressure, $T_r \sim 175°C$ at a molar ratio of hydrogen to toluene, n_{H_2}/n_T, of ~ 3.1. Methylcyclohexane (MECH) and unreacted toluene (T) along with traces of methylcyclohexene were detected in the on-line GC analysis of the product flow.

3. Results and discussion

3.1. THE NICKEL GROWTH MECHANISM IN THE CATALYST PREPARATION

3.1.1. Activity in the hydrogenation of toluene

In table 1 the production rate calculated in grams of produced MECH per gram of nickel/catalyst and hour are shown. The results describe the steady-state performance of the catalysts. The selectivity to MECH was always above 95%.

3.1.2. Surface characterization

LEIS was used for the study of the nickel growth. The surface composition was studied as a function of the number of preparation sequences (nickel loadings) ranging from one to ten (catalysts Ni-1 to Ni-10 in table 1) along with the pure alumina which was used as support in the preparation of the catalysts. Each sample was measured twice, except for catalysts Ni-6 and Ni-4_c, which were measured four times. The LEIS intensities were reproducible, with a deviation of less than 5% between measurements of the same sample. The average LEIS signals are shown in fig. 2 as a function of nickel content.

As expected, the nickel signal increases and the aluminum signal decreases with increasing nickel loadings. This indicates that nickel is shielding the aluminum. However, as can be seen from fig. 2, the LEIS nickel signal does not increase line-

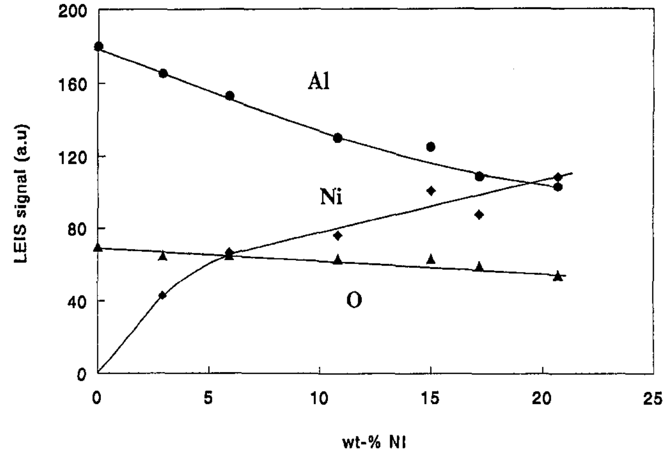

Fig. 2. LEIS-intensities of nickel (■), aluminum (◆) and oxygen (●) for various nickel loadings.

arly with the nickel loading: starting from the second preparation sequence, i.e. at nickel loadings above 5 wt%, the rate of increase of the LEIS Ni-signal decreases. Thus, more and more of the deposited nickel grows on nickel instead of on uncovered alumina. The theoretical monolayer coverage of nickel as NiO on a support having a specific surface area of ~ 130 m^2/g, i.e. similar to that of the alumina used in the catalyst preparation was calculated. Both the crystal ionic radii of the elements and unit cell dimensions for NiO (cubic), were used. The monolayer coverage was determined to be ~ 13 wt% Ni.

It appears from fig. 2 that, at a nickel loading corresponding to the theoretical monolayer coverage, only half of the nickel atoms are visible with LEIS. Thus, one can assume that nickel is present in clusters of NiO. It one assumes atomical dispersion of nickel during the first preparation sequence, it is possible to approximate the number of Ni atoms which would be detected by LEIS. This exercise can also be performed for the XPS results, which are presented in fig. 3. One should keep in mind that LEIS probes only the topmost atomic layer while in XPS several layers are seen. LEIS is, therefore, much more sensitive for spreading behavior than XPS. Combining these results and the activity measurements, as shown in fig. 4, a model for the nickel growth in the preparation of Ni/Al_2O_3 catalysts via ALE using $Ni(acac)_2$ as a starting compound is proposed.

3.1.3. Model for the growth mechanism

During the first reaction sequence a high nickel dispersion is ensured both by avoiding condensation of reactants and by the steric hindrance of the acac ligands, making it impossible for nickel atoms to cluster. The theoretical monolayer coverage of the surface complexes of $Ni(acac)_2$ on the alumina used in these experiments

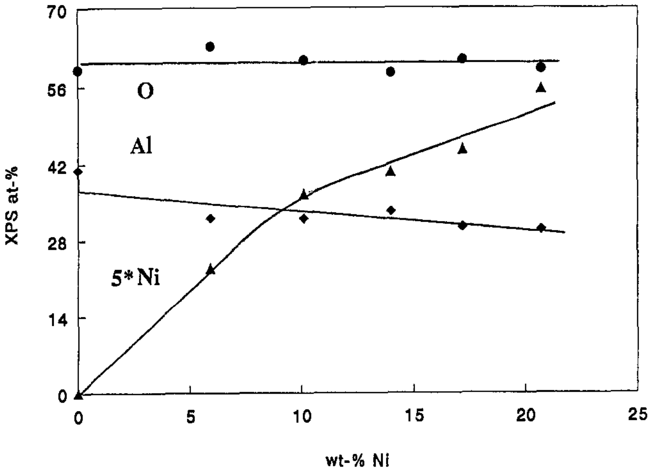

Fig. 3. XPS results in atomic per cent nickel (■), aluminum (◆) and oxygen (●) for various nickel loadings, where Ni + Al + O = 100 at%.

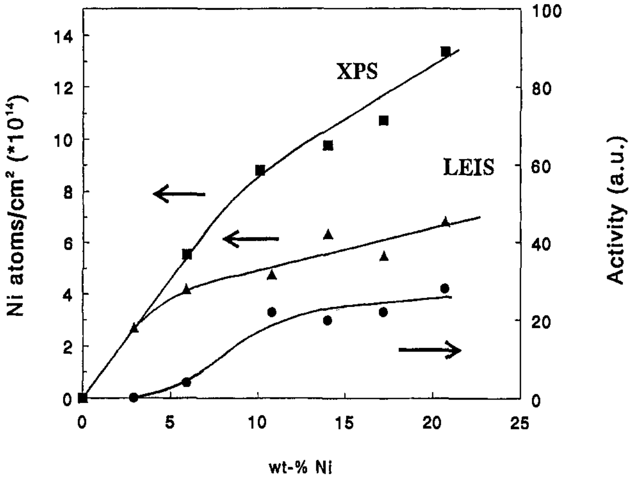

Fig. 4. Results of the LEIS (▲), XPS (■) and activity (●) measurements as a function of Ni loading on the catalyst.

corresponds well with the nickel obtained by XRF (3.0 wt%). The atomically dispersed nickel was found to be catalytically inactive in the hydrogenation of toluene (table 1, fig. 4). This seems reasonable, since these Ni-atoms will interact with the strongest binding sites on the alumina support. It is also well known that the dissociation of H_2, an important step in hydrogenation reactions on nickel catalysts, requires two nickel atoms.

At 2–4 reaction sequences with $Ni(acac)_2$ and air, (5–10 wt% Ni), the nickel signal obtained by XPS still increases linearly while the LEIS signal for nickel increases less fast. This suggests that the well dispersed nickel atoms, strongly bonded to the alumina during the first sequence, act as nuclei for the growth of nickel clusters and are thus screened from observation by LEIS. The catalytic activity increases dramatically (fig. 4) during cycles 2–4. At these Ni-loadings the weakly bonded nickel can interact well with the gaseous reactants. As XPS also detects the subsurface layers, it cannot identify the initial growth of the clusters. LEIS, however, is sensitive to the topmost layer only and can thus detect the formation of clusters after the first ALE sequence. After the second sequence, there is about twice as much Ni deposited on the surface, as shown by the doubled XPS signal, whereas the LEIS signal increases only by ~ 50% (fig. 4). This indicates that the nickel species from the second sequence shield the nickel nuclei obtained during the primary reaction in the first sequence.

At higher nickel loadings, ~ 10–20 wt% Ni, both the hydrogenation activity and the surface composition measured by LEIS do not change much. This indicates that the ratio between the number of nickel species accessible for the hydrogenation and the total number of nickel atoms has decreased by a factor of 2 when the nickel content has increased from 10 to 20 wt%: The nickel oxide clusters are growing, covering catalytically active nickel from previous sequences. At 20 wt% (10 sequences), about one fourth of the deposited Ni is detected by LEIS and about half is detected by XPS. Thus, the size of the nickel clusters exceeds the information depth of XPS. We suggest that the clusters have grown from an average thickness of two NiO layers after four preparation sequences to an average thickness of four NiO layers after ten preparation sequences. This proposal is supported by the XRD results: When the catalysts containing less than 14 wt% nickel were studied by means of X-ray diffraction, the nickel species were found to be XRD-amorphous. For the catalysts containing more than 14 wt% nickel, a peak broadening in the X-ray diffractograms was observed in the region of 43–44° 2θ corresponding to NiO. However, the intensity was very low. Even for the catalyst containing more than 20 wt% Ni, the crystallite size of the nickel oxide species was estimated to be below 40 Å, using a profile fitting program and the Scherrer formula. It seems likely, by combining the results obtained from LEIS, XPS and XRD measurements, that the nickel clusters are small, even at nickel loadings of $\sim$ 20 wt%.

At even higher loadings the nickel/alumina ratio observed by LEIS has been reported to increase [15]. This should increase the total activity of the catalyst. In this investigation, however, there was not enough data to confirm this. Although the LEIS results of similar studies [15,16] in general show good agreement with our results, one should keep in mind that the catalysts have been prepared in a different way in this work and that the growth mechanism is dependent on the nickel compound, alumina and the preparation method/conditions used.

3.2. EFFECT OF ALUMINA PRETREATMENT ON ACTIVITY AND SURFACE COMPOSITION

In order to study the effect of alumina pretreatment on the catalyst activity, three catalysts (Ni-4_a, Ni-4_b and Ni-4_c) were tested in the hydrogenation of toluene. The surfaces of the fresh catalysts were studied using LEIS. The only variable in the preparation of the catalysts was the pretreatment of the alumina. The alumina phases were investigated by XRD. The XRD-patterns of the alumina as received (pure γ-alumina), after heating at 950°C for 6 hours (pure θ-alumina), and mixtures of these aluminas were studied and used as reference samples. It was then possible to determine the alumina phase ratios in the catalysts.

In table 2 the Al/O ratio of the aluminas and the Ni signals of the corresponding catalysts observed by LEIS are shown along with the hydrogenation activities. There appears to be a correlation between the hydrogenation activity and the phase ratio of the alumina; with increasing θ/γ phase ratio, both the activity and the LEIS Ni-signal increase. Nickel seems to grow more dispersed on the alumina when the fraction of the θ phase is increased from 0 to 0.3. The available bonding sites and especially the reducibility of nickel seem to be higher on the mixture of aluminas, containing less OH-groups than the pure γ-alumina.

Table 2
Hydrogenation activity and LEIS signals of catalysts prepared on alumina having various phase ratios

Catalyst, Ni-loading (wt%)	θ/γ Al_2O_3 phase ratio	Activity, (g_{MECH}/g_{Ni} h)	Activity (g_{MECH}/g_{Cat} h)	LEIS Al/O signal ratio [a]	LEIS Ni signal [a]
Ni-4_a, 10.8	~ 0	120	13	2.8	68
Ni-4_b, 10.8	0.25	205	22	2.7	76
Ni-4_c, 10.1	0.30	230	23	2.5	83

[a] The LEIS signals are the peak heights in the energy spectra.

4. Conclusions

The growth mechanism of nickel was studied in the sequential preparation of Ni/Al_2O_3 catalysts via ALE, by bringing $Ni(acac)_2$ vapor into contact with an alumina support and removing the acac ligands with air. Activity measurements were combined with LEIS and XPS surface analyses in order to develop a model for the nickel growth process.

Nickel brought into contact with alumina during the first preparation sequence bonds with the heterogeneous surface. These nickel species, the so-called nucleation centers, are atomically dispersed but catalytically inactive since they interact strongly with the alumina. During the first preparation sequence, the atomic dispersion of nickel is ensured by the steric hindrance of the acac ligands in $Ni(acac)_2$, making it impossible for nickel atoms to cluster.

During the 2–4 sequences (5–10 wt% Ni), nickel grows on the nucleation centers but also to some extent on unoccupied sites on the support. This can be seen in the slopes of the LEIS signals and catalytic activity as a function of the number of preparation sequences (fig. 4). During the 6–10 sequences (10–20 wt% Ni), both the LEIS signal and the activity remain relatively constant (figs. 2 and 4), since nickel is growing on nickel. Thus, the highest activity in the hydrogenation of toluene, i.e. the maximum nickel utilization, was obtained at a Ni-loading of ~ 10 wt% nickel.

Acknowledgement

Our sincere thanks go to Dr. M. Lindblad and MSc. U. Lehtovirta (Microchemistry Ltd.) for their contribution in the preparation of the catalysts and to Dr. J. Vilhunen (Neste Oy) for the XRF/XRD measurements. The investigations were supported in part by the Netherlands' Foundation of Chemical Research (SON) with financial aid from the Netherlands' Organization for the Advancement of Scientific Research (NWO).

References

[1] T. Suntola, Mater. Sci. Rep. 4 (1989) 261.

[2] M. Lindblad and L.P. Lindfors, in: *New Frontiers in Catalysis*, Proc. 10th Int. Congr. on Catalysis, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadmiai Kiado, Budapest, 1993) p. 1763.

[3] M. Lindblad, L.P. Lindfors and T. Suntola, Catal. Lett., submitted.

[4] H.H. Brongersma and P.M. Mul, Surf. Sci. 35 (1973) 303.

[5] G.C. van Leerdam, J.-P. Jacobs and H.H. Brongersma, Surf. Sci. 268 (1992) 45.

[6] M. Skoglundh, L.O. Löwendahl, P.G. Menon, B. Stenbom, J.-P. Jacobs, O. van Kessel and H.H. Brongersma, Catal. Lett. 13 (1992) 27.

[7] H.H. Brongersma and G.C. van Leerdam, *Fundamental Aspects of Heterogeneous Catalysis Studied by Particle Beams*, NATO-ASI Series B 265, eds. H.H. Brongersma and R.A. van Santen (Plenum Press, New York, 1991) p. 283.

[8] H.H. Brongersma, R.H. Bergmans, L.G.C. Buijs, J.-P. Jacobs, A.C. Kruseman, C.A. Severijns and R.G. van Welzenis, Nucl. Instr. Meth. B 68 (1992) 207.

[9] S. Narayanan and K. Uma, J. Chem. Soc. Faraday Trans. I 81 (1985) 2733.

[10] S. Narayanan and G. Sreekanth, J. Chem. Soc. Faraday Trans. I 85 (1989) 3785.

[11] C.H. Bartholomew and R.J. Farrauto, J. Catal. 45 (1976) 41.

[12] S.L. Chen, H.L. Zhang, J. Hu, C. Contescu and J.A. Schwarz, Appl. Catal. 73 (1991) 289.

[13] H.H. Brongersma, N. Hazewindus, J.M. van Nieuwland, A.M.M. Otten and A.J. Smets, Rev. Sci. Instr. 49 (1978) 707.

[14] L.P. Lindfors, T. Salmi and S. Smeds, Chem. Eng. Sci. 48 (1993) 3813.

[15] M. Wu and D.M. Hercules, J. Phys. Chem. 83 (1979) 2003.

[16] S. Kastzelan, J. Grimblot and J.P. Bonnelle, J. Phys. Chem. 91 (1987) 1503.