Spectroscopic studies of alumina supported nickel catalysts precursors: Part II – catalysts prepared from alkaline solutions[*]

S. Pasieczna-Patkowska* and J. Ryczkowski

*Maria Curie-Skłodowska University, Faculty of Chemistry,
Department of Chemical Technology, Maria Curie-Skłodowska Sq. 3,
20-031 Lublin, Poland
*tel. +48-81 537-55-24; fax: +48-81 537-55-65;
e-mail: spasiecz@hermes.umcs.lublin.pl*

Nickel alumina supported catalysts were prepared from alkaline solutions of hexaamminenickel nitrate by CIM and DIM methods (classical and double impregnation, respectively). The catalysts exhibited different nickel species due to the existence of various metal–support interaction strengths. As a consequence, the reducibility and other surface properties changed as a function of the preparation method. The aim of this work was to study the interaction between the metal precursor and alumina surface by means of FT-IR (Fourier transform infrared) and FT-IR/PAS (FT-IR photoacoustic spectroscopy).

1. INTRODUCTION

The activity and selectivity of supported metal catalysts are strongly influenced by the amount of metal, the size of dispersed metal particles, the preparation method and the support composition [1]. In order to improve the catalyst activity and its durability, it is necessary to obtain a well dispersed active phase in the catalyst. Highly dispersed catalysts can be obtained using several methods [2-6], but most of these techniques are quite complicated. It is possible to obtain small nickel crystallites by precipitation but such contacts are hardly reducible [4,7,8]. The classical methods of support impregnation result in

---

[*]This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

obtaining small metal crystallites but only at very low metal contents in the catalysts [6,9]. The preparation method called DIM is suitable for producing well dispersed nickel/alumina supported catalysts [10]. In this method there are two stages: the first one is the impregnation of inorganic support with disodium salt of ethylenediamminetetraacetic acid (H_2Na_2EDTA) solution and then, after drying, impregnation with the solution containing metal ions. Inorganic support is therefore preliminarily modified by EDTA, contrary to CIM [11], where this stage is not present.

The amount of metal ions adsorbed on the support surface and depth of penetration into the support pores are controlled during impregnation [12]. As impregnation pH level drops below the isoelectric point of the surface (IEPS) of the support material, the surface charge becomes predominantly positive and vice versa. The mobility and deposition of these ions to form dispersed phase on the surface are therefore largely influenced by the pH of the solution.

The aim of this work was to study the interaction between the metal precursor: alkaline solution of nickel ions (hexaamminenickel nitrate) and alumina support surface by means of FT-IR and FT-IR/PAS occurring during different preparation procedures: CIM and DIM. We will also compare our results to those previously achieved with usage of acidic solution of nickel ions [13].

2. EXPERIMENTAL

2.1. Preparation

Two series of catalysts were prepared. For the CIM, the appropriate quantity of γ-Al_2O_3 (CONDEA) previously calcined at 900°C (BET area 79.2 m^2/g) was impregnated with 3.6 wt. % solution of hexaamminenickel nitrate, calculated on the basis of the pure metal, for 1, 3, 5, 7, 15 and 30 minutes (samples N1-N6, respectively) at 293K. The solution of hexaamminenickel nitrate was prepared as follows: appropriate amount of nickel nitrate (POCh Gliwice) was dissolved in water and then 25% solution of ammonia was added until precipitation of nickel hydroxide was dissolved. After the precipitation was dissolved, small amount of ammonia was additionally added until pH of the solution has reached the value of 12.5.

Final concentration of hexaamminenickel nitrate ions in the impregnating solution was supposed to reach 5 wt. %, however, because of exceeding of solubility product, the sediment of crystalline hexaamminenickel nitrate has precipitated. Therefore, the solution before impregnation procedure was left for 24 h to achieve equilibrium between the precipitate and the solution. Actual concentration of such solution (3.6 wt. %) was determined using murexide titration [14].

For the DIM, the alumina support was initially impregnated with a 0.1M aqueous solution of the disodium salt of EDTA (POCh Gliwice) at 343K for 0.5 h. In the second step, the support with the adsorbed EDTA was impregnated with 3.6 wt. % solution of hexaamminenickel nitrate for 1,3,5,7,15 and 30 minutes (samples M1–M6, respectively) at 293K. Higher temperature of the impregnation process (as in the case of acidic solution of nickel nitrate [13]) caused decomposition of the hexaamminenickel nitrate, evolving the ammonia and precipitation of nickel hydroxide.

A small amount of precursor was subjected to the FT-IR measurements. High temperature treatment of the catalysts samples was as follows: calcination in air at 673K for 1 h, reduction was carried out in H_2 atmosphere at 773K for 3 h.

2.2. Methods

Total surface areas of the catalysts were determined from argon adsorption at liquid nitrogen temperature by the BET method in a volumetric apparatus ensuring a vacuum of at least $2 \cdot 10^{-6}$ kPa. The same apparatus was used for the determination of active surface areas of the reduced catalysts. The hydrogen adsorption was measured at room temperature, assuming the hydrogen binding stoichiometry to be 1:1 with a hydrogen atom taking an area of 0.0675 nm^2 [15]. The reduction degree of the nickel catalysts studied was determined by the volumetric method [16].
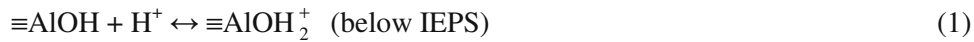
FT-IR and FT-IR/PAS measurements. FT-IR transmission spectra of the investigated samples, pressed in KBr pellets, were recorded by means of Bio-Rad (Excalibur 3000MX) spectrometer at 4 cm^{-1} resolution and maximum source aperture. Win-IR Pro software was used to control the spectrometer and to process data. Data were collected at room temperature (RT) under air. Interferograms of 256 scans were average for each spectrum.
Mid-infrared photoacoustic (mid-IR PA) data were collected with a Bio-Rad spectrometer and helium purged MTEC300 photoacoustic detector. The spectra were measured at RT at 4 cm^{-1} resolution. The spectra were normalized by computing the ratio of a sample spectrum to the spectrum of a MTEC carbon black standard. A stainless steel cup (diameter 10 mm) was filled with samples (thickness <6 mm). Before each data collection, the PA cell was purged with dry helium for 5 minutes. Interferograms of 1024 scans were average for each spectrum.

3. RESULTS AND DISCUSSION

On the alumina surface, with IEPS about 8.6, different hydroxyl groups are present. Reactions at the solid-liquid interface due to pH change can be described as follows [17,18]:
(i) Protonation/deprotonation of the surface:

$$\equiv AlOH + H^+ \leftrightarrow \equiv AlOH_2^+ \quad \text{(below IEPS)} \tag{1}$$

$$\equiv AlOH + OH^- \leftrightarrow \equiv AlO^- + H_2O \quad \text{(above IEPS)} \tag{2}$$

(ii) Dissolution of alumina

$$Al_2O_3 + 6H^+ \leftrightarrow 2Al^{3+} + 3H_2O \quad \text{(below IEPS)} \tag{3}$$

$$Al_2O_3 + 2OH^- + 3H_2O \leftrightarrow 2Al(OH)_4^- \quad \text{(above IEPS)} \tag{4}$$

During impregnation of alumina with acidic solutions (pH lower than IEPS) preferential adsorption of anions occurs, whereas in pH higher than IEPS cations adsorption occurs. Changes of solution pH have an influence on nickel ions adsorption on alumina surface.

In the previous paper [13] we exhibited that DIM allows to achieve alumina supported nickel catalysts with higher active surface area than using CIM, in the case of using acidic solution of nickel nitrate. Moreover, catalysts prepared with CIM had worse reducibility than analogical catalysts prepared using DIM. Application of EDTA in the first stage of impregnation in the case of catalysts prepared using DIM, probably prevents strong interaction between the Ni_{aq}^{2+} ions and the support. This may facilitate interaction with hydrogen (better reducibility of the catalysts made using DIM). Obtained results showed that DIM allowed to achieve better active surface area in comparison with the CIM, while wt. % of nickel was comparable [13].

During classical impregnation with acidic solution of Ni_{aq}^{2+}, nickel ions may bind with alumina surface through $\equiv AlOH_2^+$ and $\equiv AlOH$ groups. The opposite situation takes place during impregnation with alkaline solutions of Ni_{aq}^{2+} (more precisely $\left[Ni(NH_3)_n \right]_{aq}^{2+}$. In alkaline solutions $\equiv AlO^-$ and $\equiv AlOH$ groups are present, so preferential adsorption of cations occurs.

Despite the fact that real concentration of $\left[\text{Ni(NH}_3)_n\right]_{aq}^{2+}$ ions in alkaline solution was lower (3.6 wt. %) that in acidic solution (5 wt. %), active surface areas for analogical samples obtained using CIM and alkaline solution of nickel ions were relatively higher relative to obtained using acidic solution (Table 1). The quantity of introduced nickel was higher for catalysts obtained using acidic solution of nickel ions. Smaller mean crystallites size in the case of catalysts obtained using CIM may be the result of better mobility and deeper penetration of Ni^{2+}_{aq} in acidic environment [18].

Tab. 1. Physicochemical properties of studied catalysts.

Catalysts	Ni (wt. %)	Degree of metal reduction	Active surface area S_H (m^2/g_{cat})	Mean crystallites size (nm)	Catalysts	Ni (wt. %)	Degree of metal reduction	Active surface area S_H (m^2/g_{cat})	Mean crystallites size (nm)
N1	2.37	11.1	0.78	1.9					
N2	2.62	13.2	1.01	1.9	C3*	3.25	12.1	1.46	1.5
N3	2.73	20.6	2.09	1.5					
N4	2.93	27.4	2.43	1.9	C7*	3.45	20.0	2.30	1.7
N5	2.91	35.0	2.15	2.7					
N6	3.13	35.8	2.13	2.9					
M1	2.31	26.4	0.89	3.8					
M2	2.18	18.0	0.97	2.3	D3*	3.57	33.4	3.35	2.0
M3	2.34	23,2	1.24	2.5					
M4	2.45	27.2	1.50	2.5	D7*	3.70	34.0	4.04	1.7
M5	2.55	35.1	1.60	3.1					
M6	2.53	32.0	0.64	7.1					

* samples achieved using acidic solution of nickel ions [13]

Inverse situation takes place in the case of catalysts obtained via DIM. The usage of acidic solution during the second step of impregnation favors obtaining catalysts with relatively high active surface areas, whereas the application of alkaline solutions (pH=12.5) produces catalysts with lower active surface areas. The usage of DIM and alkaline solution of nickel ions causes decrease of metal reduction degree and increase of mean crystallites size in comparison to the catalysts obtained using DIM and acidic solution of nickel ions (Table 1). It is probable that DIM is not suitable method for obtaining catalysts when using alkaline solutions of nickel ions in the second step of impregnation process. In this case the process of adsorption of $\left[\text{Ni(NH}_3)_n\right]_{aq}^{2+}$ ions onto surface $\equiv\text{AlO}^-$ groups may be competitive with negligence of EDTA contribution. EDTA has a negative charge (EDTA^{4-}) in alkaline solution [19] and it may disturb its binding ability to the support surface. It may be that EDTA desorbs from the

support and forms the Ni-EDTA complex with $\left[Ni(NH_3)_n\right]^{2+}_{aq}$ ions, introduced during the second step of impregnation. Such argumentation may explain the lower content of nickel in the catalysts of M-series (Table 1).

The main sample handling problem in FT-IR analysis of solid materials is that nearly all materials are too opaque in their normal forms for direct transmission analysis in the mid-IR spectral region. The most broadly applicable mid-IR solution to the opacity problem is FT-IR/PAS. This spectroscopic technique has some limits in surface science and catalytical investigations [20,21]. However, it has broad range of applications, including adsorption experiments [22].

Figure 1 shows the photoacoustic spectra of the M-series catalyst precursors (before calcination and reduction). All the spectra are very similar – the presence of nickel nitrate is confirmed by the bands at 1440 and 1330 cm^{-1}. The time of impregnation has practically no influence on the peaks position.
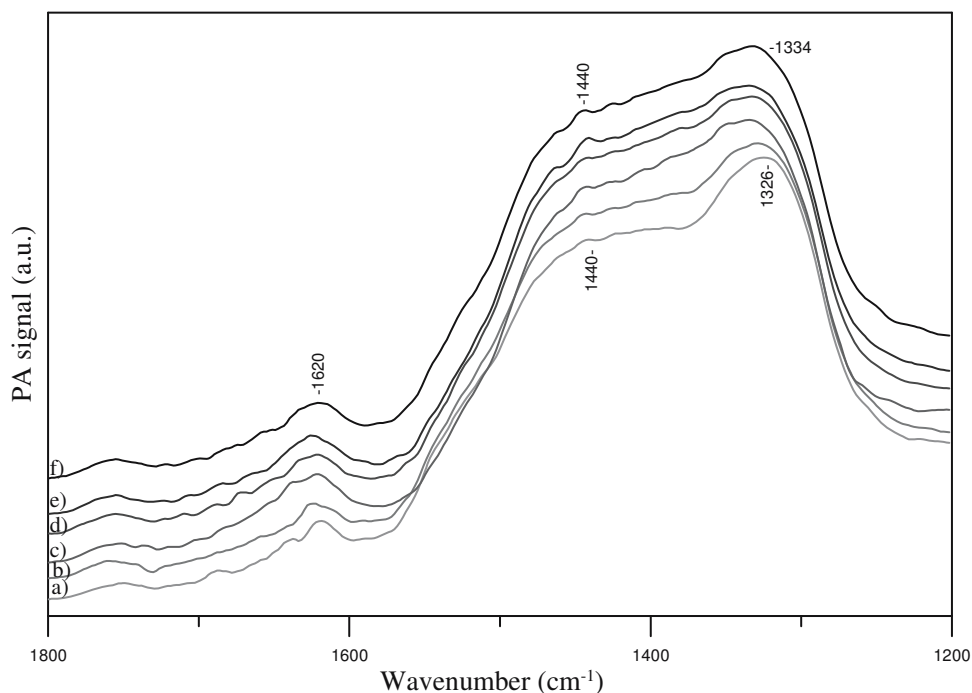

Fig. 1. PA spectra of M-series catalysts precursors in the range 1800-1200 cm^{-1}: a) M1, b) M2, c) M3, d) M4, e) M5, f) M6 catalyst precursor.

In the case of catalysts obtained via DIM, we attempted to interpret 3200–2600 cm^{-1} spectral range. This range provides information about vibrations of hydrocarbon group (C–H in CH$_2$) in EDTA molecule. For unbounded (pure) disodium salt of EDTA, the bands of C-H group are located at 3030 and 2780 cm^{-1} (Figure 2). Changes in intensity and shift of these bands towards 2950–2900 cm^{-1} region may be the evidence, that EDTA has bonded, without chelate creation, to alumina surface [13,23,24]. Disappearance of these bands for samples of M-series may be the evidence of Ni-EDTA complex creation, when the structure of EDTA gets stiffened [23]. There is also a possibility, as it was mentioned above, that during impregnation procedure a desorption process of Ni-EDTA complex occurs.
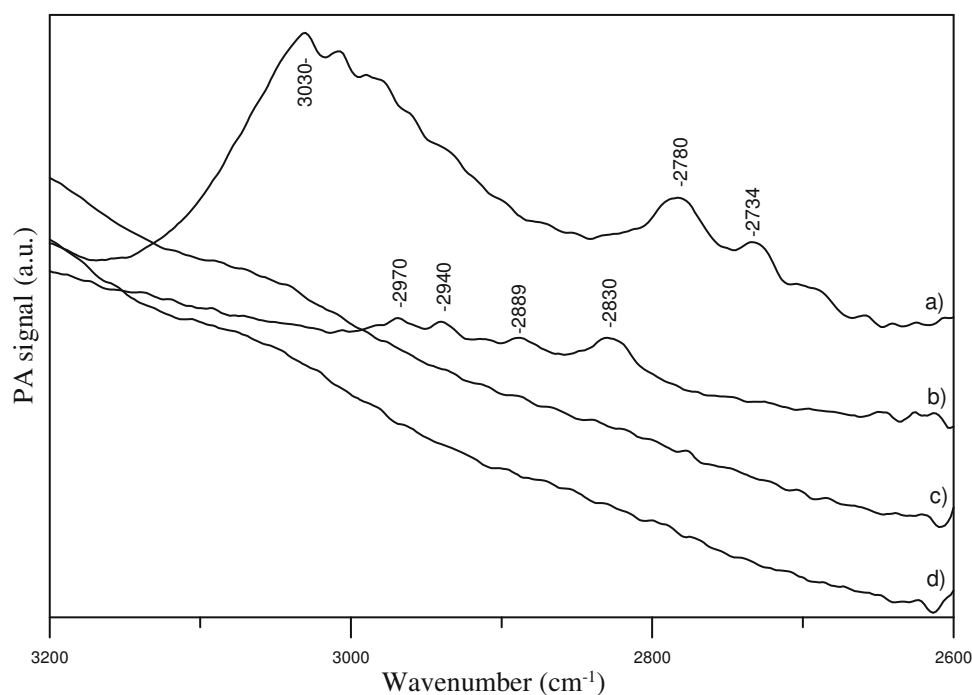

Fig. 2. PA spectra of: a) pure EDTA, b) EDTA adsorbed on Al$_2$O$_3$ and c) N2 sample, d) N4 sample in the range 3200–2600 cm^{-1}.

The most interesting changes can be observed in the range 1800–1200 cm^{-1} (Figure 3). The carboxyl group is known to give a strong band in the range 1735–1550 cm^{-1} associated with the C=O stretching vibration [25,26]. The band at 1606 cm^{-1} indicates that Ni-EDTA complex is formed – it is the band of asymmetric vibration of COO$^-$ groups. Its intensity decreases when impregnation

time increases. The intensity of symmetric stretching of the carboxyl group ($1398–1387$ cm^{-1}) slightly increases when impregnation time increases. Decrease of the intensity of asymmetric and simultaneous increase of symmetric stretching of this group may be the evidence for stabilization of the Ni-EDTA structure. However, it may also indicate, as it was mentioned while interpreting $3200–2600$ cm^{-1} spectral range, that Ni-EDTA complex desorbs from the support surface. At that time the prevalence of the processes occurring during classical impregnation may prevail. Similarity of the PA spectra of analogical precursors obtained via two different methods (CIM and DIM) may be the confirmation of this thesis (Figure 4).
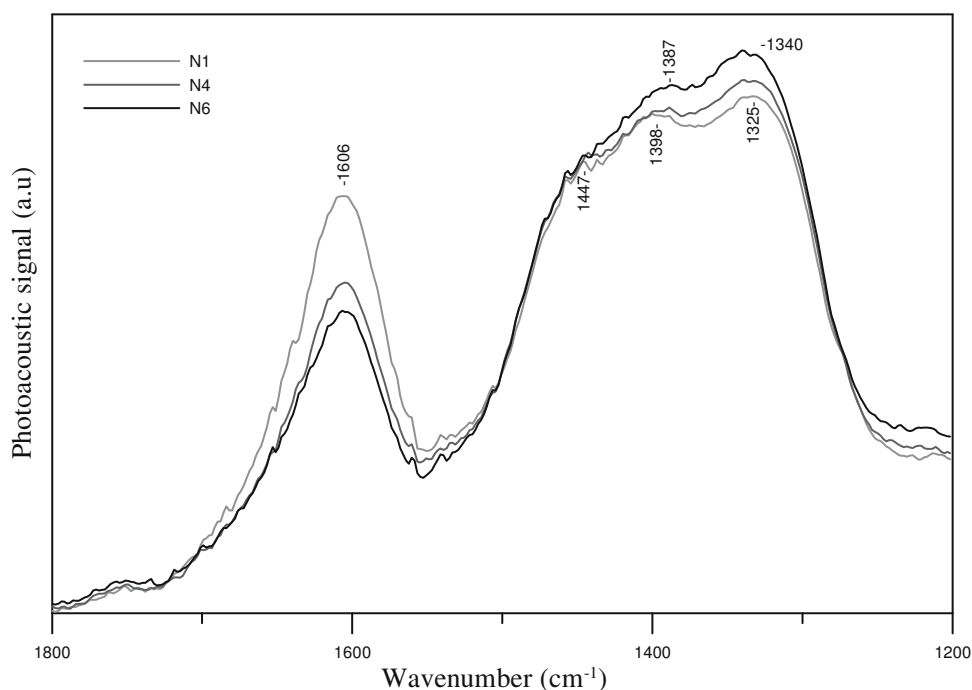

Fig. 3. PA spectra of the precursors obtained via DIM (N-series) in the range 1800–1200 cm^{-1} (for better readability only N1, N4 and N6 spectra were shown).

Described above changes on PA spectra of the N-series precursors and changes of active surface area (Table 1) prove that the processes occurring during impregnation via DIM and alkaline solution of nickel ions are different than those while using DIM and acidic solutions [13].
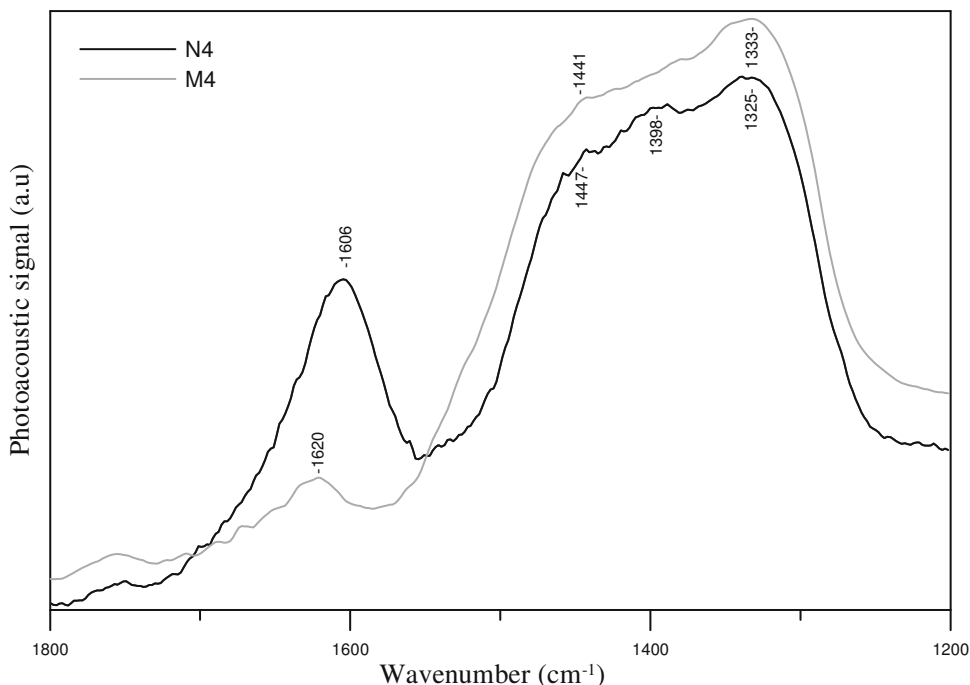
Fig. 4. PA spectra of N4 and M4 catalysts precursors in the range 1800-1200 cm^{-1}.

4. CONCLUSION

It has been shown that PAS is very useful tool for observation of various nickel species formed during impregnation procedure. Interpretation of the PA spectra of the precursors may facilitate prediction of some physico-chemical properties of achieved catalysts. It has been also shown that usage of alkaline solutions of nickel ions produces catalysts with higher active surface areas and higher degree of Ni reduction in comparison to those obtained using acidic solutions of Ni^{2+}_{aq} ions when using CIM and lower active surface areas and lower degree of Ni reduction when using DIM.

5. REFERENCES

[1] W. P. Halperin, *Rev. Mod. Phys.* 58, 533 (1998).
[2] L. Zhang, J. Lin, Y. Chen, *J. Chem. Soc. Faraday Trans.*, 88, 497 (1992).
[3] J.P. Brunelle, *Pure Appl. Chem.*, 50, 1211 (1978).
[4] J. Barcicki, W. Grzegorczyk, T. Borowiecki, A. Denis, D. Nazimek, A. Machocki, *Przem. Chem.*, 58, 419 (1979).
[5] M. Che, L. Bonneviot, C. Louis, M. Kermarec, *Mater. Chem. Phys.*, 13, 201 (1985).

[6] Z. G. Szabo, D. Kallo (Editors), in: *Contact Catalysis*, Vol. 2, Akademiai Kiado, Budapest, 1979.

[7] D. C. Puxley, I. J. Kitchener, C. Komodromos, N. D. Parkyns, *Stud. Surf. Sci. Catal.* 16, 237 (1983).

[8] L. N. Lewis, *Chem. Rev.*, 93, 2693 (1993).

[9] H. Hirai, Y. Nakao, N. Toshima, *J. Macromol. Sci. Chem. A* 13, 727 (1979).

[10] J. Barcicki, D. Nazimek, W. Grzegorczyk, T. Borowiecki, R. Frąk, M. Pielach, *React. Kinet. Catal. Lett.* 17, 169 (1981).

[11] B. C. Gates, *Chem. Rev.*, 95, 511 (1995).

[12] M. S. Heise, J. A. Schwarz, *J. Colloid Interface Sci.* 107, 237 (1985).

[13] S. Pasieczna-Patkowska, J. Ryczkowski, *Appl. Surf. Sci.* 253, 5910 (2007).

[14] F. J. Weltcher, *Analityczne zastosowanie kwasu wersenowego*, WNT, Warszawa, 1963.

[15] C. H. Bartholomew, R. B. Pannel, *J. Catal.* 65, 390 (1980).

[16] S. Pasieczna, *PhD Thesis*, UMCS, Lublin, 2006.

[17] U. Olsbye, R. Wendelbo, D. Akporiaye, *Appl. Catal. A* 152, 127 (1997).

[18] K. M. Hardiman, C. H. Hsu, T. T. Ying, A. A. Adesina, *J. Mol. Cat. A* 239, 41 (2005).

[19] C. F. Bell, *Principles and applications of metal chelation*, Clarendon Press, Oxford, 1977.

[20] G. Busca, *Catal. Today* 27, 323 (1996).

[21] J. Ryczkowski, S. Pasieczna, *J. Phys. IV* 109, 79 (2003).

[22] K. H. Michaelian, *Photoacoustic Infrared Spectroscopy*, Wiley, Hoboken, NJ, U.S.A., 2003.

[23] D. T. Sawyer, P. J. Paulsen, *J. Am. Chem. Soc.* 81, 816 (1959).

[24] D. T. Sawyer, J. M. McKinnie, *J. Am. Chem. Soc.* 82, 4191 (1960).

[25] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, p. 162, 1958.

[26] G. Socrates, *Infrared and Raman Characteristic Group Frequencies, Tables and Charts*, 3rd ed., Wiley, Chichester, p. 125, 2001.

CURRICULA VITAE
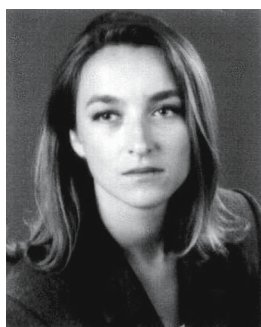
Sylwia Pasieczna-Patkowska. Born in Poland in 1974. Graduated from the University of Maria Curie-Skłodowska (UMCS) in Lublin (1998). Received his Ph.D. (2006) in physical chemistry from the University of Maria Curie-Skłodowska (UMCS) in Lublin. Since 2007 he is an adiunct at UMCS. Member of Polish Chemical Society (since 1998), Polish Catalysis Club (since 1998).

Janusz Ryczkowski. Born in Poland in 1959. Graduated from Nicolas Copernicus University in Toruń (1983). Received his Ph.D. and D.Sc. degree (1992 and 2004, respectively) in physical chemistry from the University of Maria Curie-Skłodowska in Lublin. Since 2007 university professor. Member of Polish Chemical Society (since 1984), Polish Catalysis Club (since 1993). Besides frequent short visits, he also made

long-term stay to Central Research Institute of Chemistry of the Hungarian Academy of Sciences (Hungary) and Ecole National Superieure de Chimie de Lille (France).

Within the Socrates Programme (Teaching Staff Mobility) he has visited partner European universities with a series of lectures. Moreover, he is a Faculty representative in the European Chemistry Thematic Network Association. As for today he has been a reviewer of many papers submitted to leading scientific journals. On the request of the Authorities of Quaid-i-Azam and Punjab Universitie (Pakistan) since 1994 eighteen times he was a reviewer of doctoral theses. Moreover, three times he was a referee for a professor position. Seven times he was a reviewer of the Polish Ph.D. thesis. His main field of interest is preparation of supported catalysts, catalyst's modification, their characterization, and application of infrared spectroscopy (including photoacoustic) in catalytic research. He published over 130 papers.