

TAED – IR studies of bleach activator for peroxide-based detergents

J. Ryczkowski* and S. Pasieczna

Faculty of Chemistry, Department of Chemical Technology,

Maria Curie-Skłodowska University,

pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland

tel. +48-81 537-55-96; fax: +48-81 537-55-65;

e-mail: ryczkows@hermes.umcs.lublin.pl

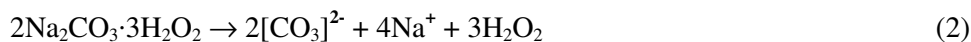
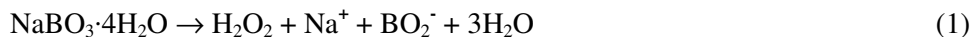
In the present work IR studies are discussed. The studies concerned TAED (tetraacetyl ethylenediamine) bleach activator applied for peroxide-based detergents. It was stated that infrared spectra of the coloured TAED granules available in the washing powders are of the same nature as the spectrum of commercial chemical reagent, and there is no influence of the colourant applied. Depending on the temperature treatment an alkaline TAED solutions can undergo transformation and degradation. Moreover, the presence of hydrogen peroxide in the alkaline TAED solution accelerates its transformation. There can be observed TAED-inorganic support interaction, which nature depends on the pH of the solution.

1. INTRODUCTION

It has long been established that peroxygen bleaches that generate hydrogen peroxide in the wash (such as perborate and percarbonate) are excellent stain removal and textile whitening agents and that they are less aggressive to fabric dyes than chlorine bleaches.

Dissolution of sodium perborate or sodium percarbonate under alkaline wash conditions leads to the formation of the perhydroxyl ion (OOH⁻) [1]:

* Author to whom all correspondence should be addressed.



The perhydroxyl anion is an effective bleaching agent at temperatures above 60°C, but is insufficiently active to be effective in washes at below this temperature or in short wash cycles. However, the perhydroxyl ion can be made to react with compounds to produce peroxygen bleaches that are effective at lower temperatures. TAED is such a compound and is known as a perborate or percarbonate bleach activator.

The TAED-system was described for the first time in 1959 and has now been used successfully in European heavy-duty detergents. TAED is produced on a large industrial scale in a two-stage sequence from ethylenediamine and acetic anhydride at 150°C (Figure 1) [2].

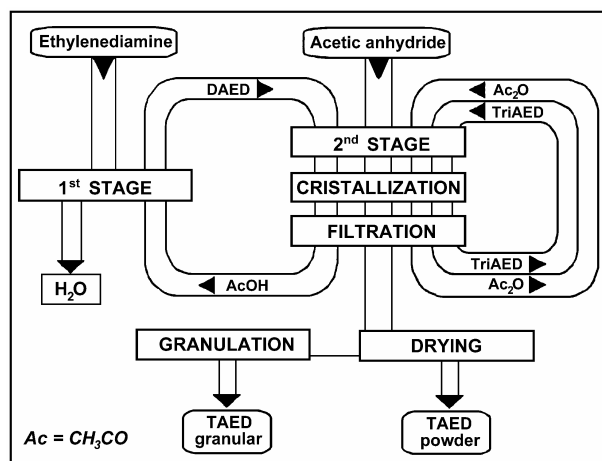


Fig. 1. Scheme of TAED production (Hoechst).

A continuous reaction procedure guarantees a product purity of more than 99%. The water of reaction, which is the sole by-product, can be disposed of without any problems in a biological clarification plant. TAED contains two active groups, from which two molecules of oxidizing and disinfecting peracetic acid are released in the presence of H₂O₂. Because of its low molecular weight of 228, 140 mg active oxygen are thus available per gram of the activator. From environmental aspects, the biodegradability of a detergent additive is of critical

importance. TAED is totally mineralized to the extent of more than 95% in a clarification plant within 28 days. No stable metabolites are observed on degradation. The N-C bond is not the cause of biological stability if it can undergo biological hydrolysis [3,4].

To improve the performance of household detergents, manufacturers have used sodium perborate as a bleaching agent together with a bleaching activator (up to 2% in the detergent formulation) whose role is to permit the bleaching to occur at lower temperature [5]. Among the bleaching activators, TAED is one of the most widely used [6].

One mole of TAED reacts with two moles of the perhydroxyl anion (nucleophilic attack) to form two moles of the effective peracetate anion and one mole of the biodegradable by-product DAED (diacetyl ethylenediamine; Figure 2) [1,7,8]. The remaining two acetyl groups on DAED cannot be displaced by peroxide in the wash bath. The perhydrolysis reaction is rapid under alkaline conditions.

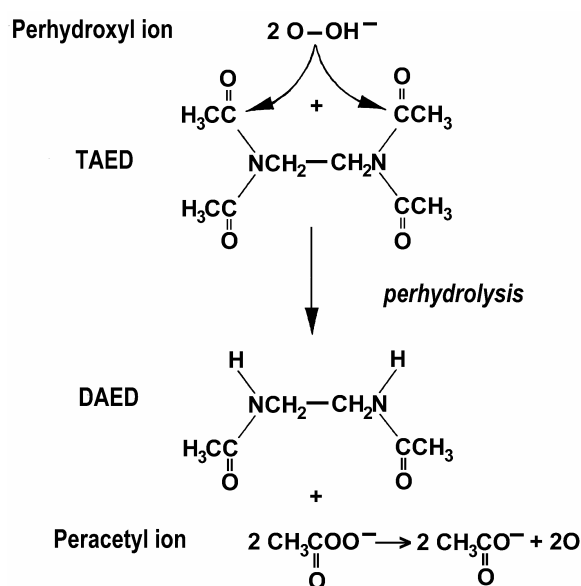


Fig. 2. Schematic reaction of TAED (Warwick International).

The optimum pH for bleaching activity of the TAED activated peroxygen system is approximately 9.5. However, the bleach system will work effectively over a fairly broad pH range (8.5 – 10.5). As a consequence of its inherent reactivity, TAED is sensitive to oxidizing agents and hydrolysis under alkaline conditions. Therefore, in order to prevent premature reaction with perborate or

moisture during storage of the detergent powder, the TAED should be suitably protected by detergent compatible materials. For this reason producers supplies TAED in granulated forms, e.g., product contains 92% ($\pm 2\%$) active TAED formulated as a coated/granulated product. The product has several colors (mainly white, green, blue; Fig. 3) to choose depending on users' choice (Warwick International).

The chemical nature of the blue colorant is a copper phthalocyanine complex CI (colour index) 74160 pigment blue 15 [9]. The green pigment is a similar metal complex (polybromochloro copper phthalocyanine) – CI 74265 pigment green 36 [1].

According to the growing number of patents concerning its use in detergent formulations, TAED will be found more often in detergents and therefore in the natural media. In spite of its fairly low concentration in detergent formulations, TAED and TAED's by-products (e.g.: ethylenediamine, acetic acid, TriAED - triacetyl ethylenediamine) might have an impact on the environment. TAED is very slightly lipophilic and TriAED (one of the most usual TAED by-product) very hydrophilic. TriAED can therefore affect bacteria cells less than TAED. TAED by-products could thus have less effect on aquatic life than TAED itself [10].

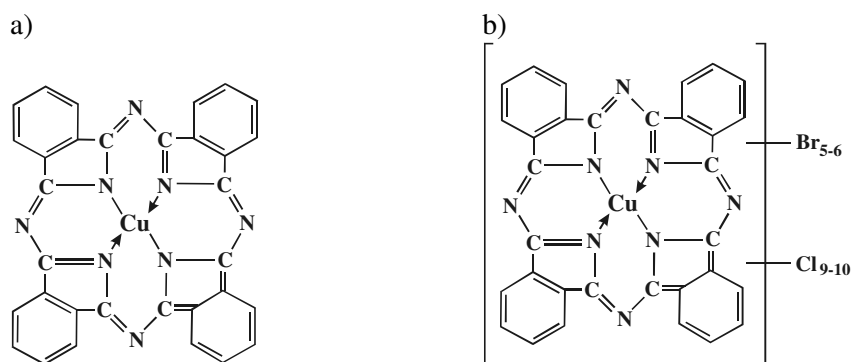


Fig. 3. Structural formulae of the pigments which are present in the TAED granules: a) pigment blue 15, b) pigment green 36 (Warwick International).

A collaborative study has been carried out concerning the IR spectrophotometric determination of TAED in raw materials [11]. As a result it was found the analytical transmission band ($1706 \pm 2 \text{ cm}^{-1}$) for the quantitative determination of TAED. However, there is no other IR data characterizing this popular nowadays compound. In this work a preliminary spectroscopic results concerning TAED bleach activator are delivered.

2. EXPERIMENTAL

White, granulated commercial chemical reagent (N,N,N',N' – tetraacetyl ethylenediamine – TAED) was supplied by Fluka Chemika. Its IR spectrum serves as the base for subsequent experimental data obtained. Colored granules (blue and green) from the commercial washing powders (mechanically isolated from the powder mixture) available on the market were characterized (by means of IR), too. Next part of investigations was devoted to the adsorption of TAED from the alkaline solution on the inorganic oxides characterized by the different IEPS - isoelectric point of the surface [12,13]: V₂O₅, SiO₂, TiO₂, ZrO₂, ZrO₂-La (7 wt. % La₂O₃), γ -Al₂O₃, and La₂O₃. TAED solubility in water is up to 10⁻³ mol/l [5,9]. To increase the concentration, the appropriate amount of TAED, calculated for 0.1 mol/l solution, was transferred to the measuring flask, diluted in water, and alkaline by sodium hydroxide for complete dissolution. Resulted pH solution was within the range as it is using washing powder during normal washing procedure (pH ~9.5). Following, supports samples were impregnated at room temperature (RT) by the alkaline TAED solution (0.5 h), dried in the oven (100°C) and then analysed. FT-IR transmission spectra of the investigated samples, pressed in KBr pellets, were recorded using Bio-Rad Excalibur 3000MX spectrometer. Win-IR Pro software was used to control the spectrometer and to process data. Spectra were measured at RT at an 8 cm⁻¹ resolution. The average of 1024 scans was used for the transformation.

3. RESULTS AND DISCUSSION

Commercially important imidic bleach activator (TAED) was not extensively studied by IR. Its infrared spectrum is rich in well shaped bands (Fig. 4).

The most characteristic vibration at 1707 cm⁻¹ can be attributed to C=O stretching, known in the literature as an amide I band (1740-1670 cm⁻¹) [14]. This one was described in the literature as a transmission band for the quantitative determination of TAED [11]. Another significant vibration related to C-N stretching, and known as amide III band (1235-1165 cm⁻¹) is located at 1192 cm⁻¹.

Figure 5 presents spectrum of the commercial chemical reagent compared with the spectra of coated/granulated color product taken from the commercial washing powders.

As seen, there is a good correlation between spectra. Moreover, there is no influence of the colorants (Fig. 3), which are present in the color TAED granules.

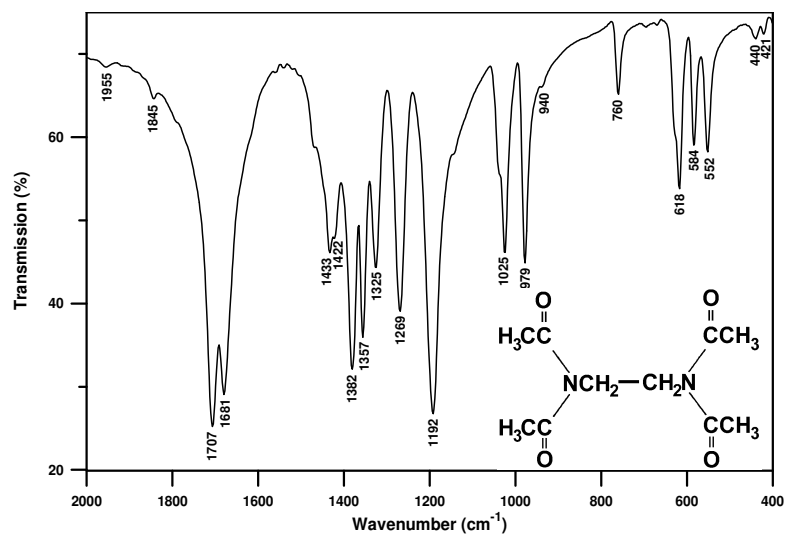


Fig. 4. Mid IR spectrum of TAED.

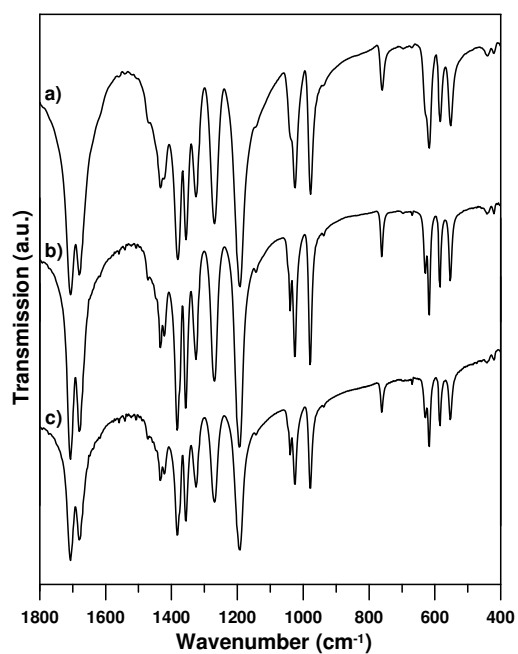
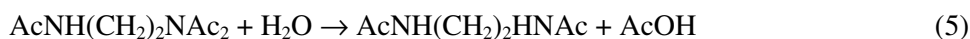
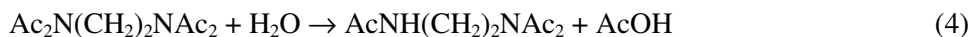


Fig. 5. FT-IR spectra of TAED as: a) chemical reagent, and colored granules from washing powders, blue and green (b and c, respectively).

The permission level of the copper in the washing powder is less than 1 ppm [2], so the existing amount of the colorants is probably below the detection limit of the spectroscopy technique applied. This is the reason that recorded spectra are in good agreement.

As it was pointed out in the experimental section, TAED is slightly soluble in water and is going hydrolysis process (favored in acidic medium) to form TriAED (equation (4)) and DAED (equation (5)) [5]:



Separate experiment with isolated DAED show that it is inert. The low reactivity of DAED is typical of amides and due to resonance stabilization of the amide bond [7]. However, it was confirmed, that TAED in the presence of iron(III) undergoes further degradation and photodegradation [7].

Prior to the adsorption experiments an alkaline TAED solution was subjected to temperature treatment. An appropriate amount of the solution was evaporated and remaining solid residues were measured in a transmission mode (Fig. 6).

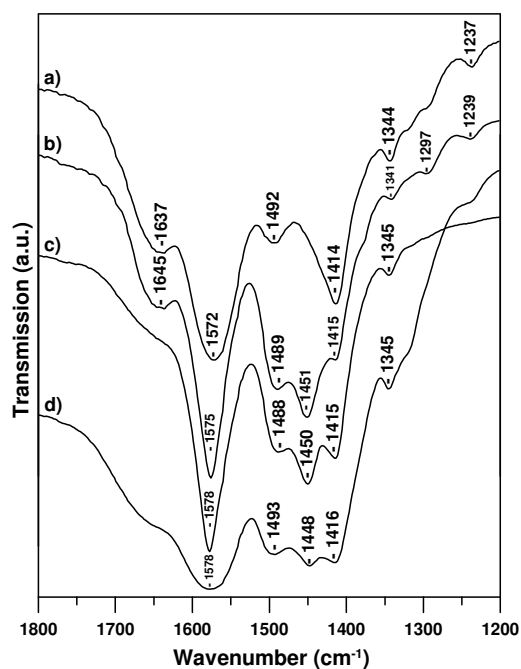


Fig. 6. Transformed TAED* from the alkaline solution evaporated at: a) 30°C, b) 50°C, c) 80°C, and d) 95°C.

Depending on the temperature treatment an alkaline TAED solutions undergo: transformation (Fig. 6a), partial degradation (Fig. 6b and c), and deep degradation (Fig. 6d). According to equation (5) the product of TAED transformation (here denoted as TAED*) should be DAED. An additional experiments have been done. Saturated TAED aqueous solution was prepared and divided into two parts. First one left unchanged, and the second was slightly alkalined. Following both solutions (“neutral” and alkalined, respectively) were treated by hydrogen peroxide, and left until there was not observed oxygen formation. As before, an appropriate amount of the solutions were evaporated (at 30°C) and remaining solid residues were analysed (Fig. 7).

An addition of H₂O₂ to the neutral solution cause partial transformation of TAED (compare Figs 4a and 7a). Observed changes in bands position and their intensities allow to conclude that intermediate compound (Fig. 7a) is not an “initial” TAED, and still it is not TAED*. The neutral TAED solution was evaporated at 50°C, too. IR spectrum of solid residue (not presented here) was similar to those presented in Figure 7a. This is an indication that neutral TAED solution treated with hydrogen peroxide is not so sensitive for temperature treatment. According to the equation (4) an intermediate product of TAED partial transformation could be TriAED. Based on the IR results it can be stated that the solid residue from the alkaline and H₂O₂ treated TAED solution (Figure 7b) are of the same nature as TAED* (Fig. 6a). In this case the presence of hydrogen peroxide only accelerates the transformation. The only product of TAED transformation can be DAED [1,7]. This means, that presented spectra (Figs 6a and 7b), described as TAED*, should be characteristic for DAED.

Finally, samples of inorganic oxides characterized by the different IEPS (starting from the lowest value) [12,13]:



were impregnated by the TAED* solution, than dried and subjected to IR analysis (Figs 8 and 9).

The obtained spectra were compared with the spectrum of TAED*. This comparison allow to conclude if there is any interaction between adsorbed TAED* and inorganic oxides surface. The characteristic of the recorded spectra is changed with the increasing value of the IEPS. For the oxides with IEPS = 1.8 – 3.0 (Fig. 8) there can be observed an interaction with the adsorbed TAED*, then there is almost no interaction (IEPS = 6.6 – 7), and finally (IEPS ≥ 8) again appears. However, the latest one is weaker than the first one. This can suggest three different modes of TAED* adsorption in which supports hydroxyls (–OH₂⁺, –OH, –O[–]) are involved:

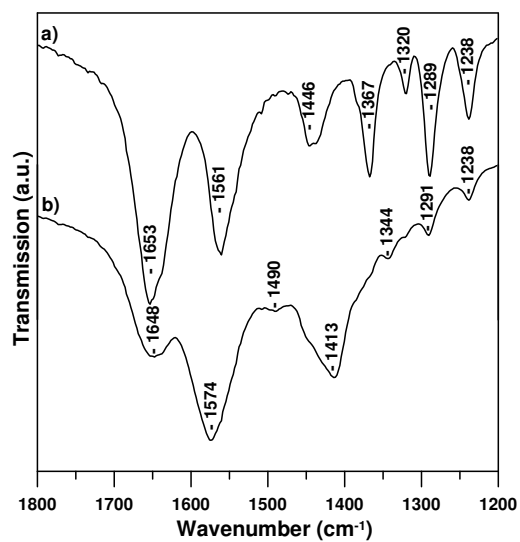


Fig. 7. IR spectra of solid residues obtained after evaporation TAED solutions treated with H₂O₂: a) neutral, b) alkaline.

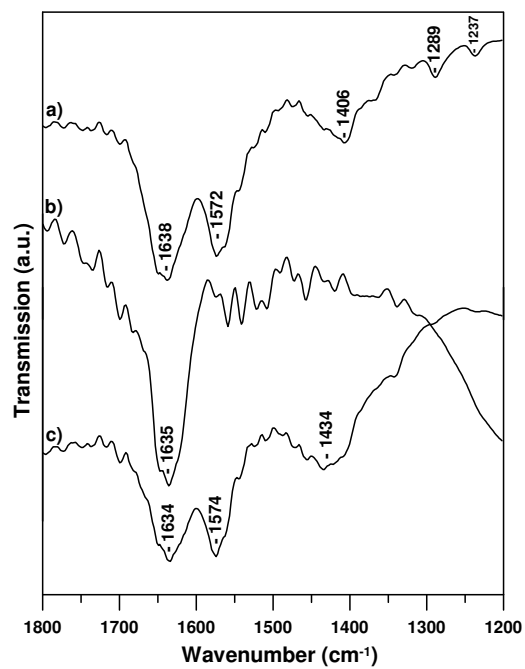


Fig. 8. IR spectra of TAED* adsorbed on: a) V₂O₅, b) SiO₂, c) TiO₂.

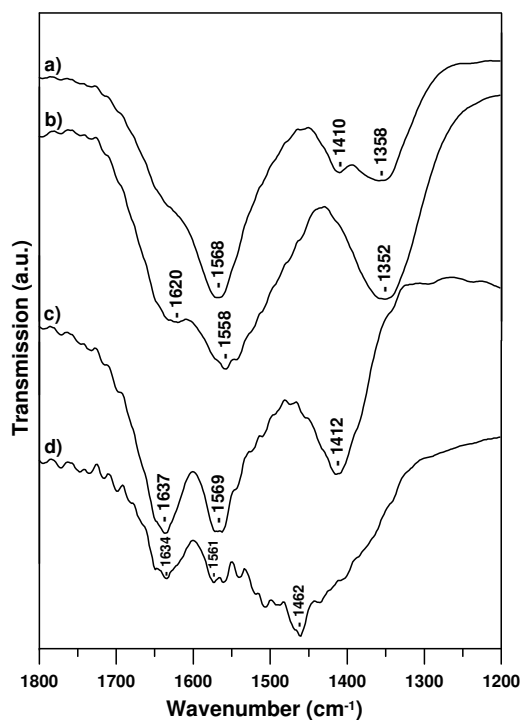


Fig. 9. IR spectra of TAED* adsorbed on: a) ZrO₂, b) ZrO₂-La, c) Al₂O₃, d) La₂O₃.

- a) –OH₂⁺ with C=O group (hydrogen bond for oxides characterized by low IEPS value),
- b) –OH with the whole TAED* molecule (Van der Waals interaction for oxides with the IEPS value around 7), and
- c) –O⁻ with hydrogen (hydrogen bond for oxides characterized by IEPS value ≥ 8).

As far as the projection to environment is concerned, this work provides information about the fate of TAED or more precisely its transformation by-product TAED*. Adsorption phenomena, particular in an acidic aquatic environments, can have an influence on the biodegradability of TAED*. However, aquatic environments are open systems and other factors (e.g., the presence of metal ions, photodegradation) can have a major impact on the biodegradation process.

4. CONCLUSIONS

In the present work there was shown mid IR spectrum of TAED. It was stated that infrared spectra of the coloured TAED granules available in the washing powders are of the same nature as the spectrum of commercial chemical reagent, and there is no influence of the colourant. Depending on the temperature treatment an alkaline TAED solutions undergo: transformation, partial degradation, and deep degradation. An addition of hydrogen peroxide to the neutral TAED aqueous solution causes its partial transformation. The presence of H₂O₂ in the alkalined TAED solution accelerates the transformation to TAED* (DAED). There can be observed TAED*-inorganic support interaction, which is stronger in an acidic environment, weaker in an alkalic one, and very weak in neutral.

Abbreviations used in the text:

CI – colour index	RT – room temperature
DAED – diacetyl ethylenediamine	TAED – tetraacetyl ethylenediamine
FT-IR – Fourier transform infrared	TAED* – transformed TAED
IEPS – isoelectric point of the surface	TriAED – triacetyl ethylenediamine
IR – infrared	

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CURRICULA VITAE



Janusz Ryzkowski. 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. He is an official correspondent for Applied Catalysis News Brief (since 1994), 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 Supérieure 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 several papers submitted to leading scientific journals. On the request of the Authorities of Quaid-i-Azam University (Pakistan) since 1994 eight times he was a reviewer of doctoral theses. Recently 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 80 papers.



Sylwia Pasieczna was born in Lublin, Poland in 1974. She studied chemistry at Maria Curie-Skłodowska University, graduated in 1998. She is a member of Polish Chemical Society (since 1998) and Polish Catalysis Club (since 1998). At present she is an assistant at the Department of Chemical Technology at Maria Curie-Skłodowska University in Lublin. Her main field of interest is an application of different techniques in the area of infrared spectroscopy for surface and catalysts characterization.