



STABILITY OF Pd/SiO₂ AND Pd-Tl/SiO₂ CATALYSTS IN HYDRODECHLORINATION OF 2,4-DICHLOROPHENOL

Aleksandra KRÓLAK, Izabela WITOŃSKA, Natasza KRAWCZYK, Magdalena FRAJTAK
and Stanisław KARSKI*

Institute of General and Ecological Chemistry, Technical University of Lodz, ul. Żeromskiego 116, 90-924 Lodz, Poland

Received November 5, 2010

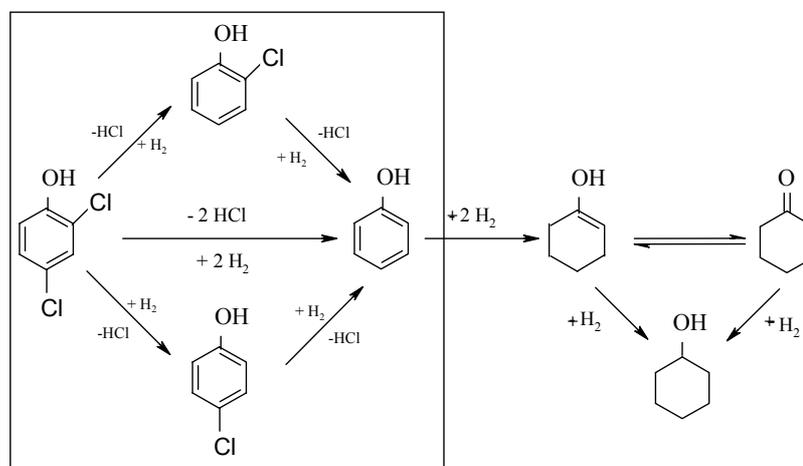
The influence of thallium addition on the activity and selectivity of supported palladium catalysts in the reaction of hydrodechlorination of 2,4-dichlorophenol to phenol was studied. Bimetallic Pd-Tl/SiO₂ catalysts, containing 5 wt. % of Pd and 1-5 wt. % of Tl, are characterized by high activity in hydrodechlorination of 2,4-dichlorophenol. The addition of thallium into supported palladium leads to the improvement of selectivity toward phenol and stability in the studied process. The XRD and ToF-SIMS studies proved the presence of intermetallic compounds Pd_xTl_y-type, which probably modify the catalytic properties of Pd-Tl/SiO₂ catalysts in hydrodechlorination of 2,4-dichlorophenol.

INTRODUCTION

Chlorophenols belong to an important group of organic compounds, which are commonly used for manufacturing pesticides, herbicides, biocides, wood preservatives, pharmaceuticals and dyes.¹⁻³ The wide application of chlorophenols in different branches of chemical industry may be the reason for their easy penetration to the natural environment. These compounds have toxic, mutagenic, possibly carcinogenic properties and they are also very stable in the environment.⁴⁻⁸

Because of these facts, the development of efficient methods of chlorophenol elimination is necessary. Catalytic hydrodechlorination (HDC) applied to mono- and bimetallic systems is a promising technology for the removal of chloroorganic compounds. The advantages of this method include easy elimination of hydrochloric acid and no dioxin or dibenzofuran formation.

The HDC process of 2,4-dichlorophenol over palladium and bimetallic palladium based catalysts can run according to the following scheme:⁹⁻¹¹



* Corresponding author: karski@p.lodz.pl

In this paper, we present the stability, activity and selectivity of Pd/SiO₂ and Pd-Tl/SiO₂ catalysts in hydrodechlorination of 2,4-dichlorophenol. What is more, the catalytic properties of Pd-Tl/SiO₂ catalysts will be connected with physicochemical properties of those systems.

RESULTS AND DISCUSSION

In the process of hydrodechlorination of 2,4-dichlorophenol in the liquid phase, supported palladium catalysts are characterized by good activity.¹²⁻¹⁶ In the open literature, the influence of many factors such as the kind of support, type of salt, method of catalysts preparation and amount of active phase etc. on the catalytic activity in this process have been considered. The role of the addition of second metal into palladium-based systems in the hydrodechlorination process in the liquid phase has been investigated only in few

papers.¹⁷⁻²⁰ In our study of hydrodechlorination of 2,4-dichlorophenol in the liquid phase we observed the influence of thallium addition into 5%Pd/SiO₂ catalysts on both activity and selectivity (Fig. 1).

An addition of Tl to 5%Pd/SiO₂ catalysts leads to the change of both activity and selectivity in the studied reaction of hydrodechlorination of 2,4-dichlorophenol in the liquid phase. The introduction of thallium in the amount of up to 5 wt.% practically causes only a slight change in the activity. Additionally, bimetallic Pd-Tl/SiO₂ catalysts are characterized by higher selectivity towards phenol in comparison with monometallic systems. Especially, the system with the lowest amount of thallium (5%Pd-1%Tl/SiO₂) is characterized by the highest selectivity to phenol (Table 1). From the presented results, it can be seen that the selectivity to cyclohexanone increases for the bimetallic catalysts with a higher amounts of thallium.

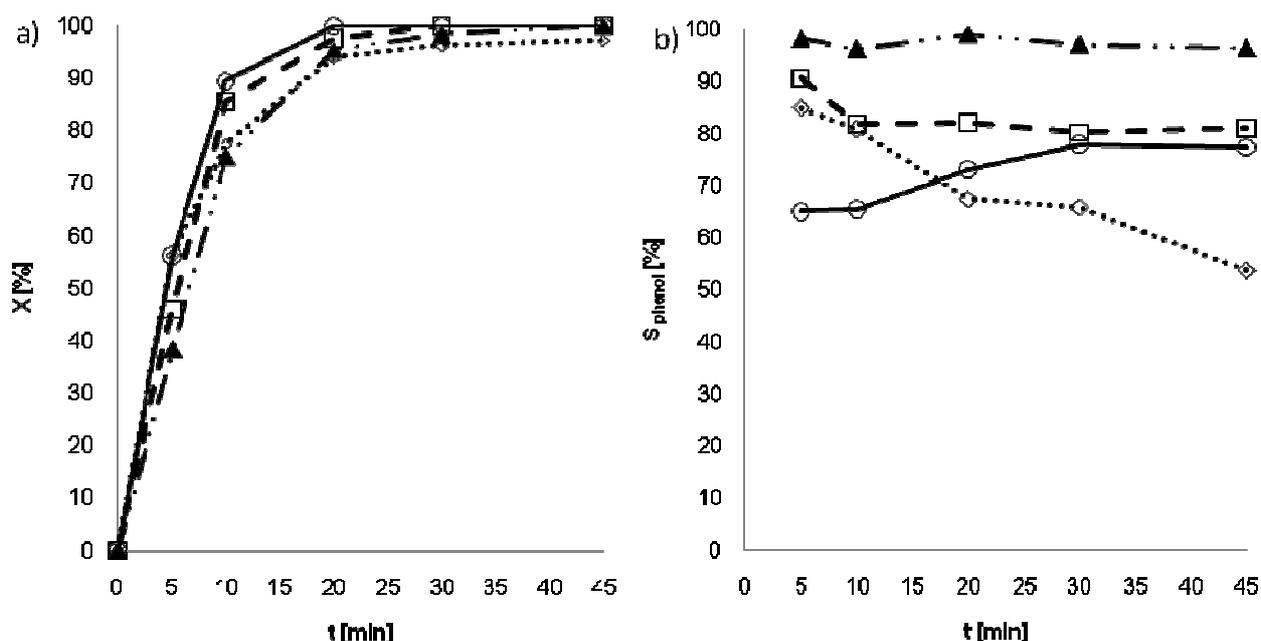


Fig. 1 – a) Conversion of 2,4-dichlorophenol as a function of time of hydrodechlorination over Pd-Tl/SiO₂ catalysts containing always 5wt.% of palladium and respectively: ▲ – 1wt.%; □ – 3wt.%; ○ – 5wt.% of thallium. In comparison, the conversion of ◇- 5%Pd/SiO₂ catalysts in this process is presented b) Selectivity towards phenol in the reaction of hydrodechlorination of 2,4-dichlorophenol over the same catalysts as a function of time.

Table 1

Activity and selectivity to final products in the reaction of hydrodechlorination of 2,4-dichlorophenol over Pd-Tl/SiO₂ catalysts

Catalyst	X [%]	S _{2-CP} [%]	S _{4-CP} [%]	S _{Phenol} [%]	S _{Cyclohexanone} [%]	S _{Cyclohexanol} [%]
5%Pd-1%Tl/SiO ₂	100	-	-	96,52	3,48	-
5%Pd-3%Tl/SiO ₂	100	-	-	81,09	18,91	-
5%Pd-5%Tl/SiO ₂	100	-	-	77,44	22,56	-

Our earlier studies performed for Pd-Tl/SiO₂ catalysts in oxidation of glucose and lactose show the presence of intermetallic compounds Pd_xTl_y type, which determine the catalytic properties of these systems.²¹⁻²² Therefore, we assume that the selectivity of palladium-thallium catalysts in the reaction of hydrodechlorination of 2,4-dichlorophenol in the liquid phase is probably connected with the presence of intermetallic compounds on the surface. Intermetallic compounds Pd_xTl_y type were not observed only for the catalyst 5%Pd-1%Tl/SiO₂ by XRD technique (Table 2), which is characterized by the highest selectivity to phenol. The presence of Pd_xTl_y compounds in bimetallic systems probably favour the formation of cyclohexanone. However, for the 5%Pd-1%Tl/SiO₂ catalyst, the presence of intermetallic compounds was stated by ToF-SIMS technique, but the intensity of PdTl⁺ secondary ions was very low. This fact indicates the low concentration of intermetallic compounds on the surface of this catalyst, what may be the reason of small selectivity to cyclohexanone.

Similarly, temperature-programmed reduction studies prove an existence of strong interactions between Pd and Tl in Pd-Tl/SiO₂ systems.

Fig. 2 presents TPR profiles obtained for 5%Pd/SiO₂, 5%Tl/SiO₂ and Pd-Tl/SiO₂ bimetallic systems after calcination in O₂ at 500°C for 2h. The calcined 5%Pd/SiO₂ samples show two low temperature reduction peaks located in the temperature range of 25-200°C. This seems to be connected with the formation of two different forms of palladium oxide in the first stage of contact between the samples and oxygen. The addition of thallium leads to the decrease of the intensity of reduction effects on the thermograms. On the TPR spectrum of 5%Pd-1%Tl/SiO₂, 5%Pd-3%Tl/SiO₂ and 5%Pd-5%Tl/SiO₂ catalysts the reduction peak at the temperature about 110°C is detected. The position of this peak is another than the position of the peaks observed for pure

palladium. The appearance of this maxima on the thermogram of the bimetallic catalysts might indicate the formation of a certain Pd_xTl_yO_z oxide type. The existence of this form could lead to the formation of intermetallic compounds in the reduction atmosphere. For those systems the formation of Pd_xTl_y phases was indicated by XRD and ToF-SIMS study.

In Fig. 3 the stability of mono- and bimetallic systems in the reaction of hydrodechlorination of 2,4-dichlorophenol in an aqueous phase was shown. The stability of catalysts was estimated on the basis of activity changes during seven 45-minute-long measurement cycles. The process of reduction was conducted for the steady amount of catalyst ($m_{\text{cat}} = 0,4 \text{ g}$) without its removal from the reaction mixture in the subsequent cycles. After each 45-minute-long measurement cycle, a new portion of 2,4-dichlorophenol ($m_{2,4\text{-dichlorophenol}} = 0,04 \text{ g}$) was introduced to the reaction mixture. In the reaction mixture, only the concentration of 2,4-dichlorophenol was analysed and on the basis of these values the stability of catalysts was estimated. The problem of the selectivity studies versus long time of the reaction run is being investigated now.

In the case of monometallic catalyst 5%Pd/SiO₂, a systematical decrease in its activity was observed in each measurement cycle. In the 7th measurement cycle, the conversion of 2,4-dichlorophenol falls to the value of about 65%. This phenomenon is observed also for the bimetallic system 5%Pd-3%Tl/SiO₂ but the changes in activities were less significant. In this case, even in the 7th measurement cycle, the conversion of 2,4-dichlorophenol is not lower than 85%. Therefore, the addition of thallium to palladium catalysts, which lead to the formation of intermetallic Pd_xTl_y compounds, causes a significant improvement of their stability in the process.

Table 2

The results of XRD and ToF-SIMS analysis of reduced Pd-Tl/SiO₂ catalysts

Catalyst	*XRD Analysis			**ToF-SIMS Analysis		
	Pd	Tl	Pd _x Tl _y	Pd ⁺	Tl ⁺	Pd _x Tl _y ⁺
5%Pd/SiO ₂	+	-	-	+	-	-
5%Pd-1%Tl/SiO ₂	+	-	-	+	+	+
5%Pd-3%Tl/SiO ₂	+	-	+	+	+	+
5%Pd-5%Tl/SiO ₂	+	+	+	+	+	+

* On the base of ICDD PDF-2 of obtained diffractograms of mono- and bimetallic catalysts

** On the base of the obtained ToF-SIMS (+) spectra of mono- and bimetallic catalysts

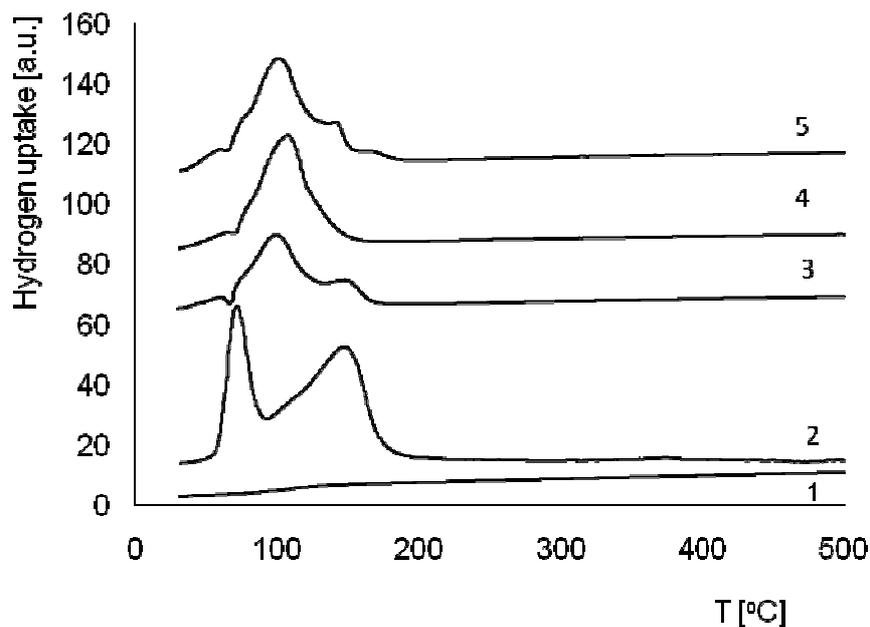


Fig. 2 – Temperature programmed reduction (TPR) profiles of 1) 5%Ti/SiO₂; 2) 5%Pd/SiO₂; 3) 1%Ti-5%Pd/SiO₂; 4) 3%Ti-5%Pd/SiO₂ and 5) 5%Ti-5%Pd/SiO₂ catalysts. Samples which underwent preliminary calcinated in O₂ at 500°.

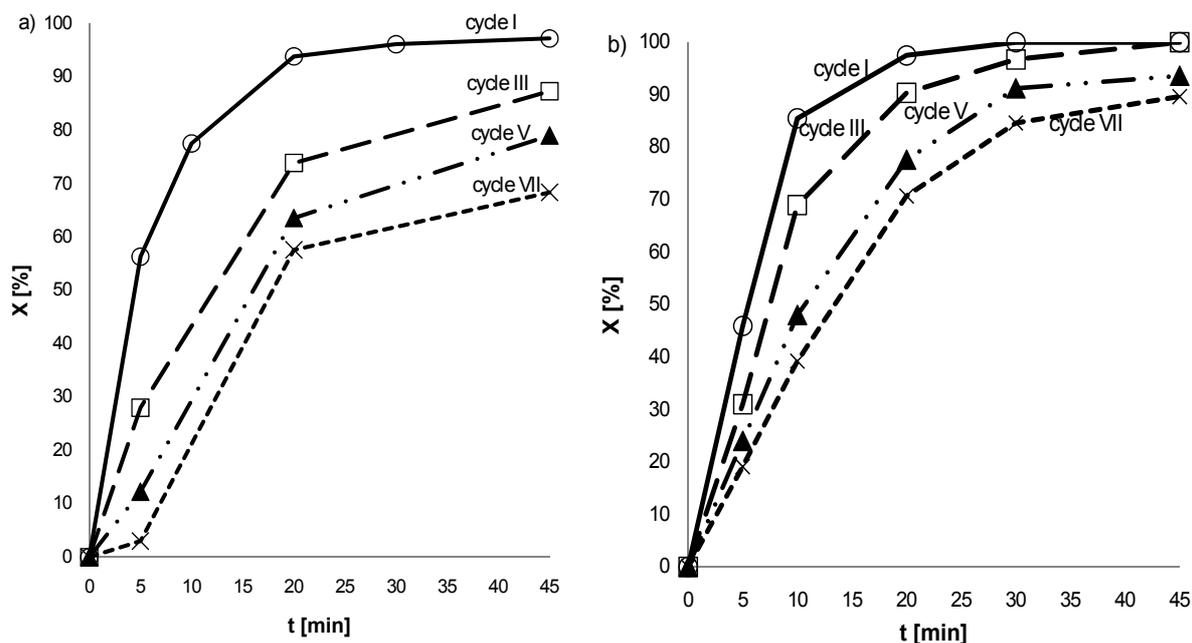


Fig. 3 – Stability of a) 5%Pd/SiO₂ and b) 5%Pd-3%Ti/SiO₂ in the reaction of 2,4-dichlorophenol hydrodechlorination as a function of time.

EXPERIMENTAL

1. Catalysts preparation

Catalyst containing 5 wt.% of palladium supported on silica (Aldrich, 250m²/g) was prepared from water solutions of PdCl₂ (a.q., POCh Gliwice S.A.) by aqueous impregnation. The water was evaporated at an increased temperature (353 K)

under vacuum. The catalyst was dried in air at 383K for 6 h, calcinated at 773K for 2 h in air atmosphere and then reduced in hydrogen atmosphere for 2 h at 533 K. Bimetallic Pd-Ti/SiO₂ catalysts containing 5 wt.% Pd and 1, 3, 5 wt.% Ti were obtained from 5%Pd/SiO₂ catalyst by repeated impregnation of this system with water solution of Ti₂CO₃ (a.q., POCh Gliwice S.A.) according to the procedure described above.

2. Catalytic measurements

The hydrodechlorination of 2,4-dichlorophenol solution (100 mg/dm³) was performed in a thermostated glass reactor of 400 mL equipped with a stirrer, a hydrogen supply system, a burette containing NaOH (0,01 mol/L) and a pH electrode.

The reaction was conducted at room temperature, at pH = 7 and for the steady amount of catalyst ($m_{\text{cat}} = 0.4$ g). The mixture was stirred at 500 rpm and hydrogen was bubbled through at 2.0 l/min. Samples of the reaction medium were taken systematically, filtered and analyzed using a liquid chromatograph coupled with a variable wavelength UV detector Varian 9050. The analytical wavelength was 210 nm. The reaction products were separated on a Zorbax SB-C18 column 250mm×4.6mm ID, using water solution of MeOH as a mobile phase. The reaction products were also detected by GC (Hewlett Packard 5890 with FID detection; packed column 8% Carbowax 1540 on Chromosorb W, 1500mm×8mm ID) for the full analysis of the mixture of cyclohexanone / cyclohexanol.

Catalytic results are expressed as conversion (X, %) and selectivities (S, %). Those parameters were defined as:

$$X = \left[1 - \left(\frac{C_{2,4DCP}}{C_{0,2,4DCP}} \right) \right] \cdot 100\%$$

$$S = \left[\frac{C_P}{C_{0,2,4DCP} - C_{2,4DCP}} \right] \cdot 100\%$$

where $C_{0,2,4DCP}$ is a molar concentration of 2,4-dichlorophenol at the beginning of the hydrodechlorination process, $C_{2,4DCP}$ is a molar concentration of 2,4-dichlorophenol after time t , C_P is a molar concentration of phenol after time t .

3. Characterization of catalysts

3.1. Powder X-ray diffraction (XRD)

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer. The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40KV and 30 mA. Divergent optics were used in a Bragg–Brentano (flat-plate sample) geometry, with fixed divergence ($1/2^\circ$) and antiscatter (1°) slits. Incident and receiving 0.04 rad Soller slits were used to limit axial divergence, and a nickel filter on the receiving side was used to eliminate $\text{CuK}\beta$ radiation. Data were collected in the range $20 - 90^\circ 2\theta$, with step 0.0167° and exposition per one step of 20 s. A PANalytical X'Celerator detector based on Real Time Multiple Strip technology capable of measuring the intensities simultaneously in the 2θ range of $2,122^\circ$ was used. Crystalline phases were identified by referring to ICDD PDF-2 (ver. 2004) data base.

3.2 Time of fly secondary mass spectrometry (ToF-SIMS)

The secondary ions mass spectra were recorded with a TOF-SIMS IV mass spectrometer manufactured by Ion-Tof GmbH, Muenster, Germany. The instrument was equipped with Bi liquid metal ion gun and high mass resolution time of flight mass analyzer. During the measurement, the analyzed area was irradiated with the pulses of 25 keV Bi_3^+ ions at 10 kHz repetition rate and an average ion current 0.6 pA. The analysis time was 30 s for both positive and negative secondary ions giving an ion dose below static limit of 1×10^{13} ions/cm². Secondary ions emitted from the bombarded surface were mass separated and counted in time of flight (ToF) analyzer.

The catalyst samples were prepared by pressing pellets.

3.3. Temperature-programmed reduction (TPR) measurements

The measurements were carried out in AMI-1 (Altamira) apparatus. The catalyst samples (0,05g), prior to the TPR measurements were calcined at 500°C for 2h in the mixture of oxygen-argon (10 vol.% of O₂) at a flow rate of 30 cm³·min⁻¹. TPR runs were performed in the temperature range 20-500°C, using a mixture of hydrogen-argon (10 vol.% of H₂) at a flow rate of 30 cm³/min and a linear temperature growth of 10 °C·min⁻¹.

CONCLUSION

Bimetallic Pd-Tl/SiO₂ catalysts, containing 5 wt. % of Pd and 1-5 wt. % of Tl, are characterized by high activity in the hydrodechlorination of 2,4-dichlorophenol. The addition of thallium into supported palladium leads to the improvement of selectivity toward phenol and stability in the studied process.

The ToF-SIMS measurements showed the presence of intermetallic compounds in all studied bimetallic catalysts. For the palladium-thallium catalysts supported on silica the intermetallic phases Pd_xTl_y-type were also detected by XRD. This method enables the detection of only relatively high concentrations of intermetallic compounds in the bimetallic catalysts when the degree of crystallinity of the sample is sufficient. Due to this limitation the identification of intermetallic phases on the surface of 5%Pd-1%Tl/SiO₂ system was not possible with the use of the XRD technique. The results of temperature programmed reduction prove the occurrence of interactions between metallic components in Pd-Tl/SiO₂ systems.

The high activity, selectivity and stability of Pd-Tl/SiO₂ systems containing up to 3 wt. % of thallium constitute a promise to their possible application in the chemical industry.

REFERENCE

1. S. Ramamoorthy and S. Ramamoorthy, "Chlorinated Organic Compounds in the Environment", CRC Press: Boca Raton, FL., 1997.
2. F. Muller and L. Caillard, "Chlorophenols. Ullmann's Encyclopedia of Industrial Chemistry", Wiley-VCH Verlag GmbH&Co KGaA, Weinheim, 2000.
3. M. Czaplicka, *Sci. Total Environ.*, **2004**, 322, 21-39.
4. Proposition 65, Office of Environmental Health Hazard, EPA, State of California, USA, 2005.
5. C.B. Molina, A.H. Pizarro, M.A. Gilarranz, J.A. Casas and J.J. Rodriguez, *Chem. Eng. J.*, **2010**, 160, 578-585.
6. J.B. Hoke, G.A. Gramiccioni and E.N. Balko, *Appl. Catal. B Environ.*, **1992**, 1, 285-296.

7. L. Calvo, A. F. Mohendo, J. A. Casas, M.A. Gilarranz and J.J. Rodriguez, *Carbon*, **2004**, *42*, 1371-1375.
8. M.A.Keane, *J. Chem. Biotech.*, **2005**, *80*, 1211-1222.
9. G. Yuan and M.A. Keane, *Catalysis Today*, **2003**, *88*, 27-36.
10. G. Yuan and M.A. Keane, *Chem. Engin. Sci.*, **2003**, *58*, 257-267.
11. J. Wie, X. Xu, Y. Liu and D. Wang, *Water Res.*, **2006**, *40*, 348-354.
12. S. Gómez-Quero, F. Cárdenas-Lizana and M.A. Keane, *Ind. Eng. Chem. Res.*, **2008**, *47*, 6841-6853.
13. S. Gómez-Quero, F. Cárdenas-Lizana and M.A. Keane, *AIChE Journal*, **2010**, *56*, 756-767.
14. Guang Yuan and M.A. Keane, *Ind. Eng. Chem. Res.*, **2007**, *46*, 705-715.
15. G.Yuan and M.A. Keane, *Chem. Eng. Sci.*, **2003**, *58*, 257-267.
16. L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano and J.J. Rodríguez, *Appl. Catal. B Environ.*, **2006**, *67*, 68-76.
17. Y. Gao, F. Wang, S. Liao, D. Yu and N. Sun, *React. Funct. Polym.*, **2000**, *44*, 65-69.
18. M.A. Keane, S. Gómez -Quero, F. Cárdenas-Lizana and W.Shen, *ChemCatChem*, **2009**, *1*, 270-278.
19. N. Lingaiah, P.S. Prasad, P.K. Raa, L.E. Smart and F.J. Berry, *Appl. Catal. A Gen.*, **2001**, *213*, 189-196.
20. I. Witońska, A. Królak and S. Karski, *J. Mol. Catal. A: Chemical*, **2010**, *331*, 21-28.
21. S. Karski, I. Witońska and J. Goluchowska, *J. Mol. Catal. A Chem.*, **2006**, *245*, 225-230.
22. S. Karski and I. Witońska, *Kinet. Catal.*, **2004**, *45*, 256-259.