

Study of the reaction conditions for the hydrodechlorination of pentachlorophenol on palladium catalysts

J.W. da-Silva^{a,*}, Roy E. Bruns^b, A.J.G. Cobo^a

^a *Laboratório de Desenvolvimento de Processos Catalíticos, Faculdade de Engenharia Química, Universidade Estadual de Campinas, Campinas, C.P. 6066, CEP 13083-852, SP, Brazil*

^b *Laboratório de Química Quântica e Quimiometria, Instituto de Química, Universidade Estadual de Campinas, Campinas, C.P. 6154, CEP 13083-970, SP, Brazil*

Received 23 March 2006; received in revised form 27 September 2006; accepted 5 December 2006

Abstract

Catalytic hydrodechlorination has been intensely studied recently since it seems to be a promising method for treating toxic organochlorine residues. In this context, the aim of this work is to study the reaction conditions for pentachlorophenol hydrodechlorination, conducted in a three-phase media with palladium catalysts. The study was carried on a commercial Pd/C catalyst and a Pd/TiO₂ catalyst, which was prepared by the dry impregnation technique from the PdCl₂ precursor. Preliminary catalytic tests indicated that for both catalysts, previous reduction significantly reduced their catalytic activities, while calcination at 573 K leads to active catalysts in the reaction. Owing to the undesirable retention of pentachlorophenol observed using the Pd/C catalyst, the Pd/TiO₂ system was used to study reaction conditions by means of a 2⁶⁻² fractional factorial design. One combination of levels of this design permitted establishing suitable reaction conditions for this hydrodechlorination.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrodechlorination; Pentachlorophenol; Palladium catalysts; Reaction conditions; Factorial design

1. Introduction

The endless quest for human welfare is an intrinsic characteristic of mankind. However, humanity has paid a high price for these activities, since the generation and inadequate discard of toxic compounds has accompanied the obtention of worthy final products [1]. To cope with this situation, communities around the world recently started movements to pressure their governments to establish rules for controlling the discharge of toxic matter into the environment. Among the toxic substances they try to control, a group that deserves special attention is the one formed by organochlorine compounds [2]. Such compounds present low biodegradability and are highly cumulative, a fact that may result in serious damages to human health and to

the environment [3]. Within that group, chlorophenols are one of the more important source of ambient contamination [4,5], because that, their production and applications are been slowed down in recent years [6]. Currently, a great deal of effort is being directed to destroy unwanted stocks and to depollute soils, ground and waste waters in which these compounds have accumulated. Among the most common processes for the destruction of these compounds are those based on electrochemistry, radiation, photochemistry and biotechnology, which result in low conversions and impractical scaling-up [7,8]. Also, there are the thermal methods, which include pyrolysis, hydrogenolysis, that need high energy inputs [9,10] and incineration, which can generate harmful dioxins/furans [11]. On the other hand, catalytic hydrodechlorination using palladium catalysts has been intensely studied over the last decade and is one of the most promising methods for treating toxic organochlorine residues [12–14].

In this context, the aim of this work is to study the reaction conditions, using factorial design, for the hydrodechlorination of pentachlorophenol (PCP) performed in a three-phase media on palladium catalysts.

* Corresponding author. Present address: Laboratório de Combustíveis alternativos, Departamento de Química Industrial, Universidade Federal do Maranhão, CEP 65058-580, São Luis, MA, Brazil. Tel.: +55 98 21098900 9871; fax: +55 98 21098245.

E-mail address: jwilson@ufma.br (J.W. da-Silva).

2. Experimental

2.1. Catalysts preparation

Two types of palladium catalysts were used in the present study: a commercial Pd/C and a prepared Pd/TiO₂, both with 5% nominal content in mass. The commercial Pd/C catalyst used in this study was kindly donated by the Degussa Company (reference E101 O/W, load no E1123L). On the other hand, the Pd/TiO₂ catalyst was prepared from commercial titania (Aldrich, 99%), with a specific surface area of 15 m² g⁻¹ in an anatase crystalline phase. The titania was treated so as to isolate particles with sizes varying from 37 to 88 μm. That size range was adopted taking into account that for catalyst particles larger than 100 μm, resistance to mass transfer intraparticles can be dominant [15]. After size separation, the support was dried at 393 K, for about 48 h. The PdCl₂ (Aldrich, 99%) was the palladium precursor used in the preparation of the Pd/TiO₂ system, which was carried on by dry successive impregnation. After impregnation, the solid Pd/TiO₂ was dried at 393 K, during 12 h. Next, a fraction of the dried solid was calcinated with a flow of synthetic air (30 cm³ min⁻¹), starting from room temperature until reaching 573 K with a 5 K min⁻¹ heating rate. Once attaining this final calcination temperature (573 K), the catalyst was maintained at 573 K for 3 h. With this procedure, the Pd/TiO₂ calcinated catalyst was obtained. In order to check whether this thermal treatment had any effect on the catalytic performance on the pentachlorophenol hydrodechlorination, a reduced Pd/TiO₂ catalyst was prepared, i.e., without previous calcination. This catalyst was obtained in a similar way to the Pd/TiO₂ calcinated catalyst, starting from solid Pd/TiO₂ dried at 393 K and at a heating rate of 5 K min⁻¹, from room temperature to 573 K under the flow of a 2 vol.% H₂/N₂ mixture (30 cm³ min⁻¹). Finally, the reduced Pd/TiO₂ catalyst was kept at a final reduction temperature of 573 K for 3 h.

The drying, calcination and reduction procedures had conditions defined based upon the studies conducted by Sales [16] and da-Silva [17], on the Pd/TiO₂ system and the TiO₂ support, respectively.

2.2. Catalytic tests

Liquid phase exploratory catalytic tests were conducted in a stainless steel stirred autoclave, by PARR Instruments Co, with 300 cm³ total capacity. In those tests, the commercial Pd/C catalyst as well as the prepared Pd/TiO₂ catalyst was used. Such tests assisted in the evaluation of these catalytic system behaviors for pentachlorophenol hydrodechlorination. In particular, exploratory tests were aimed at estimating the catalyst hydrodechlorination capacities, the diversities of products formed in the reaction and, also, the catalyst yields for chlorine free products.

The following reaction conditions were used for the exploratory tests: 393 K reaction temperature, 2.0 MPa hydrogen pressure in the reactor, 800 mg catalyst mass, 1000 rpm stirring rate, 4.0 mmol dm⁻³ pentachlorophenol initial concentration and 3 h of total reaction time. The choice of these reaction

conditions was based upon the fact that all compounds (substrate and products) proved to be stable at these conditions, for blank tests performed without catalyst. The experimental procedure adopted to conduct the exploratory catalytic tests was similar to the one used for the catalytic tests of the factorial design, detailed next.

For some exploratory tests, the commercial Pd/C catalyst was activated inside the reactor (in situ activation) before reaction onset. In this case, the in situ activation was conducted under hydrogen atmosphere following the already mentioned reaction conditions, but in the absence of the pentachlorophenol reagent. This treatment lasted 1 h, because, according to Sales [16], this suffices time to reduce the oxide layer that appears when metallic catalysts are exposed to air.

A factorial design was performed for the tests on the Pd/TiO₂ calcinated catalyst aimed at studying the reaction conditions for the pentachlorophenol hydrodechlorination conducted in a three-phase media. These designs provide a systematic, economical and robust statistical strategy for studying how potentially relevant experimental factors affect the properties of systems being studied [18,19]. The effects of six factors, listed in Table 1, on the pentachlorophenol conversion and the phenol yield were determined in this work. The choice of these factors as well as their respective levels, also given in Table 1, was based upon information available in the relevant literature [20] and in experience acquired by our research group on liquid phase catalytic reactions. Only two levels symbolically identified as the lower (–) and higher (+) ones for each factor were studied so that the number of necessary experiments would not be excessively high. Two level factorial designs involve the execution of experiments corresponding to all possible combinations of the low and high levels of all the factors. This permits the accurate determination of all possible main and interaction effects of the factors on the pentachlorophenol conversion and the phenol yield assuming these responses vary linearly with the changes in factor levels. Since a complete 2⁶ factorial design would necessitate the performance of 64 experiments only a fraction of these experiments was performed. A quarter fraction requiring only 16 experiments, a 2⁶⁻² fractional factorial design, was chosen since it permits the estimation of the main effects of all factors as well as possible synergistic and antagonistic effects due to the interaction of any two of these factors. The experiments performed for this fractional factorial design listed in standard order along with the corresponding results for pentachlorophenol conversion and the phenol yield are included in Table 1. It should be noted that the actual execution of these experiments was carried out in random order in accordance with recommended statistical procedure. In this way possible systematic error is not confounded with any of the factor effects.

The choice of the two blocks depicted in this design is due to the fact that the Pd/TiO₂ catalyst, prepared by means of the cited procedure, was obtained from repeated preparations. In principle, since the catalyst is the same, we expect that the block effect calculated for this design is not significant, which would confirm that the catalysts, obtained from repeated preparations, present the same performance, thus highlighting the efficiency

Table 1
 2^{6-2} factorial design: pentachlorophenol conversion (X) and phenol yield (R) results obtained using Pd/TiO₂ catalyst

		Factor		Level	
				(-)	(+)
1		Temperature (K)		333	383
2		H ₂ pressure (MPa)		0.5	2.0
3		Pd/TiO ₂ mass (mg)		500	800
4		Stirring rate (rpm)		200	1000
5		PCP concentration (mmol dm ⁻³)		2.0	4.0
6		Reaction time (h)		1	3
Block effect				1 ⁰ preparation	2 ⁰ preparation

Run	Order ^a	Factors							Responses	
		1	2	3	4	5 ^b	6 ^c	Block ^d	X (%)	R (%)
1	1 ⁰	-	-	-	-	-	-	-	40	0
2	8 ⁰	+	-	-	-	+	-	+	70	100
3	13 ⁰	-	+	-	-	+	+	+	77	81
4	10 ⁰	+	+	-	-	-	+	-	78	56
5	16 ⁰	-	-	+	-	+	+	-	87	100
6	3 ⁰	+	-	+	-	-	+	+	100	100
7	5 ⁰	-	+	+	-	-	-	+	60	76
8	11 ⁰	+	+	+	-	+	-	-	62	62
9	14 ⁰	-	-	-	+	-	+	+	100	100
10	9 ⁰	+	-	-	+	+	+	-	100	100
11	15 ⁰	-	+	-	+	+	-	-	74	86
12	2 ⁰	+	+	-	+	-	-	+	78	87
13	4 ⁰	-	-	+	+	+	-	+	95	100
14	6 ⁰	+	-	+	+	-	-	-	100	100
15	7 ⁰	-	+	+	+	-	+	-	100	100
16	12 ⁰	+	+	+	+	+	+	+	100	100

^a Run sequence.

^b $I_5 = 1235$.

^c $I_6 = 2346$.

^d $I_{\text{block}} = 124$.

of the preparation method. All factor effects as well as the block effect were calculated from the equation:

$$\text{Effect} = \bar{R}_+ - \bar{R}_- \quad (1)$$

where \bar{R}_+ and \bar{R}_- are the averages of all experiments at their high and low levels for the factors involved. For main factor effects and the block effect of Table 1 the signs used in this equation are the same as those in the corresponding columns in Table 1. For binary interaction effects the signs in the above equation are determined by multiplying the signs in the columns corresponding to the factors involved in the interaction. The actual calculations and corresponding graphs were carried out using software developed in our laboratories [21] as well as commercial software [22].

Catalytic tests based on the factorial design were also conducted in liquid phase in the same reactor used in the exploratory tests. Such tests were manipulated in accordance with the following procedure: the desired mass of pentachlorophenol (Aldrich, 98%) was dissolved in a base-aqueous solution of NaOH (Merck, 99%) with 0.35 mol dm⁻³ concentration. In the sequence, the resultant solution was transferred to the reactor's pot and afterwards the Pd/TiO₂ catalyst was added to it. Finally, the reactor was firmly locked and purged with nitrogen and, next,

with hydrogen. After the reaction temperature stabilized, the reactor was pressurized with hydrogen (99.999%), and the stirring was fixed at the desired value. This moment was considered the reaction onset.

Samples were collected from the reaction mixture at periodic intervals and their chemical compositions were established by gaseous chromatography [23]. The chromatograph HP 5890 Series II, by Hewlett-Packard, was equipped with FID and an OV-1701 capillary column (30 m × 0.25 mm × 0.25 μm).

Starting from the concentration values determined for the different components present in reaction media, the pentachlorophenol conversion (X) and the phenol yield (R) were calculated. The conversion is a measurement easily understood which indicates the catalytic activity for a certain reaction time, while the yield expresses the catalyst selectivity to obtain the desired product. The calculation of the conversion was done using its classical definition. As such, the expression adopted to calculate the yield was:

$$R(\%) = \frac{[\text{POH}]_t}{[\text{PCP}]_0 - [\text{PCP}]_t} \times 100 \quad (2)$$

where $[\text{PCP}]_0$ is the pentachlorophenol concentration at the reaction onset, $[\text{PCP}]_t$ and $[\text{POH}]_t$ are, respectively, the pen-

tachlorophenol and phenol concentrations for a given reaction time.

3. Results and discussion

3.1. Exploratory catalytic tests with Pd/C catalysts

Exploratory catalytic tests conducted with the in situ activated Pd/C catalyst revealed that it is a less active catalyst for the pentachlorophenol hydrodechlorination. In this case, there may have occurred a fast deactivation of the catalyst by chloride ions formed at the reaction onset [24].

In view of the poor performance obtained with the in situ activated Pd/C catalyst, the catalytic exploratory tests were repeated without any previous activation of the catalyst. At the end of that exploratory test, cyclohexanol was the only final product of the reaction, indicating that non-activated Pd/C catalyst, besides C–Cl bond hydrogenolysis, is also capable of performing benzene ring hydrogenation of pentachlorophenol. Nevertheless, the mass balance for the reaction confirmed that almost 40% of the pentachlorophenol fed into the reactor was neither present in the reaction media at the end of the reaction nor turned into any other product, even after 10 h of continuous reaction. Thus, the activated carbon capacity for retaining the pentachlorophenol was evaluated by means of an adsorption isotherm (Fig. 1).

This isotherm analysis revealed that for a Pd/C catalyst mass equal to the one used in the catalytic exploratory tests (800 mg), about 38% of the pentachlorophenol fed into the reactor would be retained by the activated carbon of that catalyst. This value is very close to the estimated pentachlorophenol retention (40%) determined by the exploratory catalytic test with the non-activated Pd/C catalyst. Even though the retention of significant amounts of components from the reaction media is not a general rule for the Pd/C catalysts [25], it is well known that this can occur in various types of activated carbon [26]. Therefore, results obtained with this particular Pd/C catalyst revealed that this support would not be proper, as a model catalyst, for estimating the pentachlorophenol hydrodechlorination reaction

conditions due to its high capacity for retaining, irreversibly, that substrate.

3.2. Exploratory catalytic tests with Pd/TiO₂ catalysts

Initially aiming at estimating the titania retention of pentachlorophenol, the adsorption isotherm for this chlorophenol was determined. The results obtained showed that the amount of pentachlorophenol retained by titania was less than 2%, being, thus, considered negligible for this study. This result is in accordance with other similar ones published in the literature [27].

Results of the exploratory catalytic tests using the reduced Pd/TiO₂ catalyst were similar to the ones presented by the Pd/C catalyst activated in situ, i.e., the catalytic activity was very low and the amount of dechlorinated products formed was also small. Once titania is stable in both, acid and basic medium [28,29], it is suitable for using in hydrodechlorination reactions [24,30]. That way, the behavior showed by the reduced Pd/TiO₂ catalyst, is likely the result of a fast deactivation of the referred catalyst by means of chlorine ions present in reaction media. Such a behavior is similar to the one shown by the Pd/C catalyst activated in situ. On the other hand, results of the catalytic tests using the calcinated Pd/TiO₂ catalyst showed that it has high performance in the pentachlorophenol hydrodechlorination. Besides that, and opposite to the commercial Pd/C catalyst non-activated in situ, which demonstrated selectivity to cyclohexanol, the calcinated Pd/TiO₂ tested catalyst was selective for the obtention of phenol. Therefore, this is likely a strong indication that the support nature may affect the type of dechlorinated compound that is obtained.

3.3. Catalytic tests for the 2^{6–2} factorial design

Based upon the results of the exploratory catalytic tests previously introduced, the experimental design techniques were applied to evaluate the more suitable reaction conditions for pentachlorophenol hydrodechlorination using the calcinated Pd/TiO₂ catalyst. Observation of the values in Table 1 shows that the tests number 6, 9, 10, 14, 15 and 16 led to conditions in which the pentachlorophenol hydrodechlorination occurred with catalyst maximized performance (100% pentachlorophenol conversion and 100% phenol yield). Nevertheless, prior to defining which of those tests presents the most adequate reaction conditions, it is instructive to check which of the investigated factors significantly affects the responses. This was done constructing a cumulative probability graph [18,19]. Statistically insignificant effects are expected to have small values caused by random experimental error and will be represented by points falling on a straight line passing close to the origin of the graph. On the other hand, the significant and most important effects will have points displaced from this line. These then indicate the factors that are important in the optimization process. Fig. 2 presents the cumulative probability graph for the effects of the 2^{6–2} factorial design for pentachlorophenol conversion. Factors 1 (reaction temperature), 2 (hydrogen pressure), 3 (catalyst mass), 4 (stirring rate), 6 (total reaction time) and the block effect (124) influence the pentachlorophenol conversion, while the pentachlorophenol

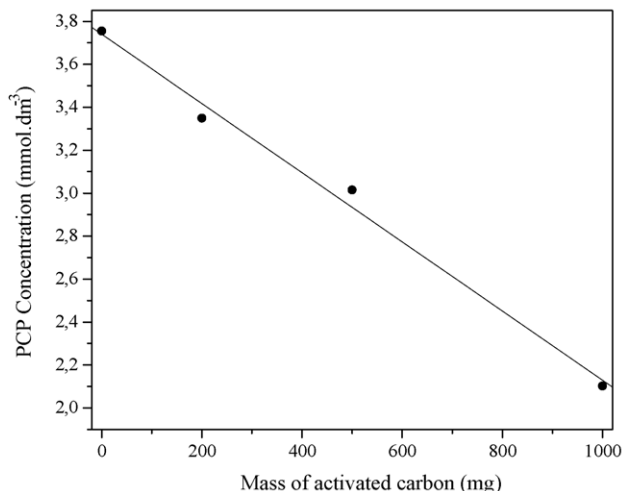


Fig. 1. Pentachlorophenol retention by activated carbon.

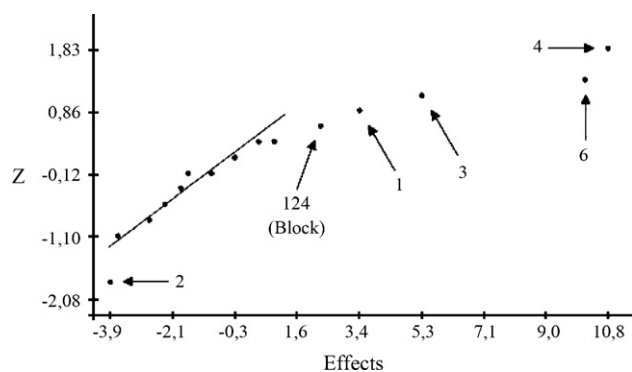


Fig. 2. Cumulative probability graph of the factor effects on the pentachlorophenol conversion using the Pd/TiO₂ catalyst.

initial concentration (factor 5) shows no effect at all on conversion. This result indicates that, probably, there are no limitations for pentachlorophenol mass transfer towards the catalyst surface [31], independent of the reaction conditions utilized in this work.

The cumulative probability graph of the factors effects on the phenol yield showed linear behavior centered close to the origin, indicating that none of the investigated factors significantly affect the phenol yield. This result states that the preferential formation of phenol is an intrinsic property of the Pd/TiO₂ catalyst.

Results presented in Table 2 allowed estimation of the degree of influence of each factor on the pentachlorophenol conversion. As it can be verified, the stirring rate (factor 4) and the total reaction time (factor 6) present higher effect values (above 10), strongly influencing the conversion. For both cases, since the value of the corresponding effect is positive, their higher level must be selected, i.e., 1000 rpm and 3 h, respectively for maximum conversion. Note that of the six results in the factorial with 100% conversion all have high levels for both these factors except for the low level for the stirring rate in run 6 and the lower retention time in run 14. In particular, the stirring rate's remarkable influence on conversion may indicate that at 200 rpm, hydrogen mass transfer, from the gaseous phase to the liquid phase [32], limits the reaction.

Moreover, the rest of the investigated factors have little effect on the pentachlorophenol conversion, especially in the case of the block effect (124), related with the repetition of the preparation of the Pd/TiO₂ system. This result indicates good reproducibility in catalyst preparation.

Consequently, according to the results of this factorial design and adopting economical criteria, run number 9 offers more advantageous reaction conditions. It has higher stirring rate

Table 2
Factors effects on the pentachlorophenol conversion using Pd/TiO₂ catalyst

Factor	Effect value
1	3.44
2	-3.94
3	5.44
4	10.8
6	10.2
124 (block effect)	2.44

values (1000 rpm) and reaction time (3 h), while the reaction was conducted at the lower temperature (333 K) and pressure (0.5 MPa), also using the smallest amounts of catalyst (500 mg) and pentachlorophenol (2.0 mmol dm⁻³).

4. Conclusions

Results obtained with the Pd/C system indicated that this solid is not adequate, in the condition of a model catalyst, to attain the objective aimed in this work due to its high capacity for retaining, irreversibly, pentachlorophenol.

Reduced Pd/C and Pd/TiO₂ catalysts are weakly active for pentachlorophenol hydrodechlorination in the liquid phase. However, the commercial Pd/C catalyst (non-activated in situ) is selective for cyclohexanol formation, while the calcinated Pd/TiO₂ catalyst is selective for phenol obtention.

The 2⁶⁻² factorial design showed that the stirring rate and the reaction total time had the most important influences on the pentachlorophenol conversion. On the other hand, none of the investigated factors had any influence whatever on the phenol yield.

The most adequate reaction conditions to perform the pentachlorophenol catalytic hydrodechlorination were established according to the factorial design results and economical criteria.

Acknowledgements

We would like to thank to the Degussa Company for supplying the Pd/C catalyst and its support, to FAEP/PRP/UNICAMP for the financial aid and to CAPES for the Ph.D. scholarship granted to José Wilson da Silva; to Prof. Dr. Wilson de Figueiredo Jardim, for valuable suggestions on the chemical analysis of the reaction media compounds.

References

- [1] M. Alexander, Environ. Sci. Tech. 29 (1995) 2713–2717.
- [2] R.C. Kirkwood, A.J. Longley, Clean Technology and Environment, Blackie Academic & Professional, London, 1995.
- [3] R.M. Sharpe, N.E. Skakkebaek, Lancet 341 (1993) 1392–1396.
- [4] U.S.EPA, The inventory of sources of dioxin in the United States, EPA/600/P-98/002Aa, 1998.
- [5] U.S. EPA, Chemical advisory and notice of potential risk: skin exposure to molten 2,4-dichlorophenol can cause rapid death, Advisory Document No. 8EHQ-14302, 2000.
- [6] U.S. EPA, OPPT Chemical Fact Sheets. Pollution Prevention and Toxics (7407). EPA 749-F-95-007a. Support Document: CAS No. 108-90-7 (1995).
- [7] L.N. Zanaevskii, V.A. Aver'yanov, Russ. Chem. Rev. 67 (1998) 713.
- [8] L.N. Zanaevskii, V.A. Aver'yanov, Y.A. Treger, Russ. Chem. Rev. 65 (1996) 617.
- [9] R. Louw, J.W. Rothuizen, R.C.C. Wegman, J. Chem. Soc., Perkin Trans. 2 (1973) 1635.
- [10] J.A. Manion, P. Mulder, R. Louw, Environ. Sci. Technol. 19 (1985) 280.
- [11] E. Goldberg, Sci. Total Environ. 100 (1991) 17.
- [12] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A 173 (2001) 329.
- [13] T.N. Kalnes, R.B. James, Environ. Prog. 7 (1988) 185.
- [14] C. Amorim, G. Yuan, P.M. Patterson, M.A. Keane, J. Catal. 234 (2005) 268–281.
- [15] Y. Shindler, Y. Malatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 40 (2001) 3301–3308.

- [16] E.A. Sales, Catalisadores de Paládio Suportados na Hidrogenação Seletiva de Hexadienos em Fase Líquida, Ph.D. Thesis, Faculdade de Engenharia Química/Universidade Estadual de Campinas, Campinas, Brasil, 1996.
- [17] J.W. da-Silva, A.J.G. Cobo, Appl. Catal. A: Gen. 252 (2003) 9–16.
- [18] G.E.P. Box, J.S. Hunter, W.G. Hunter, Statistics for Experimenters: Design, Discovery and Innovation, 2nd ed., Wiley–Interscience, New York, 2005.
- [19] R.E. Bruns, I.S. Scarminio, B. de Barros Neto, Statistical Design—Chemometrics, Elsevier, Amsterdam, 2006.
- [20] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 102 (2002) 4009–4091.
- [21] Instituto de Química/Universidade Estadual de Campinas (IQ/UNICAMP). The Laboratório de Química Quântica e Quimiometria download page. [<http://chemomatrix.iqm.unicamp.br>]. Accessed March 22, 2006.
- [22] Statistica for Windows, Statsoft, Inc., 2300 East 14th Street, Tulsa, OK, USA, 1999.
- [23] J.W. da-Silva, Tratamento de Resíduos Organoclorados Tóxicos: Avaliação das Condições Experimentais para a Hidrodescloração do Pentaclorofenol com Catalisadores de Paládio, Ph.D. Thesis, Faculdade de Engenharia Química/Universidade Estadual de Campinas, Campinas, Brasil, 2004.
- [24] M.A. Aramendía, V. Boráu, I.M. García, C.F. Jiménez, J.M. Marinas, F.J. Urbano, Appl. Catal. B 20 (1999) 101–110.
- [25] E. Auer, A. Freund, J.T. Pietsch, Appl. Catal. A 173 (1998) 259–271.
- [26] M. Streat, J.W. Patrick, M.J.C. Pérez, Water. Res. 29 (2) (1995) 467–472.
- [27] J. Matos, J. Laine, J.M. Herrman, J. Catal. 200 (2001) 10–20.
- [28] T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, B. Van Der Bruggen, G. Maes, J. Membr. Sci. 214 (2003) 21–29.
- [29] T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. Van Der Bruggen, G. Maes, J. Membr. Sci. 207 (2002) 73–89.
- [30] V. Felis, C. de Bellefon, P. Fouilloux, D. Schwiich, Appl. Catal. B 20 (1999) 91–100.
- [31] B. Coq, J.M. Cognion, F. Figuéras, D. Tournigant, J. Catal. 141 (1993) 21–33.
- [32] G.W. Roberts, in: P.N. Rylander, H. Greenfield (Eds.), The Influence of Mass and Heat Transfer on the Performance of Heterogeneous Catalysts in Gas/Liquid/Solid Systems, Academic Press, New York, 1976, pp. 1–48.