Catalysis Today 172 (2011) 78–83

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic hydrodechlorination of trichloroethylene with 2-propanol over Pd/Al_2O_3

Martha Cobo [a], Carlos A. González [b], Edwin G. Sánchez [b], Consuelo Montes [b,*]

[a] Energy, Materials and Environment Research Group, Chemical Engineering Deparment, University of La Sabana, Campus Universitario Puente del Común, Km. 7 Autopista Norte, Bogotá, Colombia
[b] Environmental Catalysis Research Group, Universidad de Antioquia, Sede de Investigación Universitaria-SIU, A.A 1226, Calle 62 52-59, Medellín, Colombia

ARTICLE INFO

Article history:
Received 1 December 2010
Received in revised form 15 February 2011
Accepted 18 February 2011
Available online 9 April 2011

Keywords:
Hydrodechlorination
Palladium
Alumina support
Trichloroethylene
2-Propanol

ABSTRACT

Catalytic HDC of trichloroethylene (TCE) over 1 wt.% Pd/Al_2O_3 was carried out using 2-propanol, as solvent and hydrogen donor, in the presence of NaOH. The contribution of the homogeneous HDC reaction was important at 75 °C while at 25 °C thermal effects were less significant. 2-propanol dehydrogenation was evaluated at several reaction conditions and temperatures. It was found that NaOH is necessary for 2-propanol dehydrogenation. TOF of 0.001 s^{-1} for the HDC of 0.011 M TCE after 1-h reaction at 25 °C was obtained. Used catalyst samples (without any pretreatment) exhibited slightly lower activities than fresh ones. Surface area and dispersion of used catalyst samples decreased because of carbonaceous residues deposition. Treated catalyst samples recovered their surface area and HDC activity of fresh ones.

1. Introduction

Chlorinated organic compounds are widely used as solvents, extractants and degreasing agents. However, it is not possible to deny the extraordinary noxiousness of organic chlorine emissions and its devastating effect, not only to the environment, but also to public health. Important quantities of wastes containing these compounds are continuously generated [1,2]. Specifically, the Colombian electrical manufacturing industry uses TCE for degreasing metal parts. The process is performed at the TCE boiling point and the final residue is a dark liquid composed of TCE dissolved grease. Since incineration of chlorinated waste is banned in Colombia and appropriate treatment technologies are not available, these residues are stored thus, generating a toxicity problem [4]. Therefore, the development of appropriate TCE degradation technologies in organic matrices is needed.

Catalytic hydrodechlorination (HDC) of chlorinated compounds is considered as a viable, low cost and environmentally friendly method [5–7]. It has been applied to different types of chlorinated compounds such as polychlorinated benzenes (PCBzs), chlorophenols (CPs), polychlorinated biphenils (PCBs), dioxins and furans (PCDD/Fs), tetrachloroethylene (TTCE), trichloroethylene (TCE), etc. [8]. Ordóñez et al. [3] obtained around 60% conversion of TCE at room temperature over 200 mg of 5 wt.% $Pd/\gamma\text{-}Al_2O_3$ in the presence of alkaline compounds and using hydrogen as reducing agent at 5 Mpa. Under more severe conditions (50 °C, acid pH), they obtained total conversion. Nishijima et al., [9] and Concibido et al., [10] also used hydrogen and achieved high reaction rates over 10 wt.% Pd/C at 20 °C using methanol–water mixtures as solvent. He et al., [11] used Pd–Fe nanoparticles at pH 6 for the treatment of chlorinated compounds in aqueous phase but the iron phase underwent corrosion. Liquid hydrogen sources have been tested mostly for dioxin treatment in organic matrices [12–15]. Among them, 2-propanol has exhibited satisfactory performance with these toxic, stable compounds.

In this work we examine the feasibility of using 2-propanol as hydrogen source for the catalytic hydrodechlorination of TCE in organic matrices over 1 wt.% $Pd/\gamma\text{-}Al_2O_3$. Fresh and used catalyst samples were characterized by chemical analysis, BET surface area, H_2-chemisorption and FTIR. Spent catalyst samples were analyzed by TGA and regenerated by heat treatment and reduction in order to evaluate their stability.

2. Materials and methods

2.1. Catalyst preparation

Catalyst samples were prepared by impregnation, i.e. the required amount of palladium acetylacetonate (99%, Aldrich Chem.

* Corresponding author at: Universidad de Antioquia, Sede de Investigación Universitaria-SIU, Environmental Catalysis Research Group, Carrera 53, 61-30, Medellín, Colombia. Tel.: +574 2196605.
E-mail addresses: cmontes@udea.edu.co, montes.consuelo@gmail.com (C. Montes).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.02.064

Co., USA) was dissolved in acetone. Then, the required amount of γ-Al_2O_3 (99.97%, Alfa Aesar, USA) was added and the mixture rotoevaporated for 24 h. The resulting material was calcined in 50 mL/min flowing air to 400 °C (2 h) at a heating rate of 2 °C/min and reduced in flowing 5% H_2/N_2 to 300 °C (1 h) at 5 °C/min. Calcined and reduced catalyst samples containing a nominal loading of 1 wt.% Pd and 2 wt.% Pd were coded as PA1 and PA2, respectively.

2.2. Catalyst characterization

Elemental analysis was performed by atomic absorption in a Philips PU9200 apparatus. Single point BET surface area and pulse chemisorption were carried out in an AutoChem II 2920 Micromeritics instrument equipped with a TCD detector. For BET surface area experiments, catalyst samples were previously out gassed at 150 °C in a helium stream during 1 h to remove impurities. Then, a mixture of 30% N_2/He was allowed to flow through the samples previously immersed in a liquid nitrogen bath at −182 °C. Both the amount of adsorbed and desorbed N_2 was recorded. Total surface area was obtained from the amount of desorbed nitrogen using one point BET approximation. Pd dispersion and average active particle size was determined by pulse chemisorption by applying measured doses of 10% H_2/Ar to previously reduced catalyst samples (50-100 mg) in flowing 10% H_2/Ar at 300 °C. Chemisorption was performed at 100 °C to assure β-PdH desorption. H_2/Pd stoichiometry was established by oxygen titration in four consecutive experiments. FTIR measurements were performed in transmission mode using pressed disks (~20 mg) in a Cary/5E Varian apparatus. Before FTIR analyses, samples were heated under flowing dry 4% O_2/Ar at 200 °C for 1 h to remove undesired impurities from air. TGA/DTG of used samples was carried out in a TA instrument Q500. Around 10 mg catalyst samples were heated in 100 mL min^{-1} flowing air at 5 °C min^{-1} until 800 °C.

2.3. Catalytic tests

Catalytic tests were performed in a 50 mL round bottomed flask equipped with a thermocouple and a condenser, using 25 mL of 2-propanol and 30 mg of NaOH, maintaining a NaOH concentration of 0.03 M. The amount of catalyst varied between 50 and 200 mg and the temperature between 25 and 75 °C. TCE concentrations varied from 0.011 to 2.3 M (0.05–20% (v/v)). Reaction samples were taken at 5, 10, 30, 60, 120 and 180 min. The absence of heat and mass transfer limitations was assessed by the Koros–Nowak criterion (KN) modified by Madon–Boudart [16,17] and the catalyst Turnover Frequency (TOF) was calculated according to the following expression [16]:

$$\mathrm{TOF}(s^{-1}) = \frac{\text{initial reaction rate}\,(\mathrm{mols}^{-1}\mathrm{g}^{-1}\text{catalyst})}{\text{surface moles of active material per unit weight of catalyst}} \quad (1)$$

The surface moles of active material were calculated using Pd dispersion as determined by H_2-chemisoption experiments (see Table 1).

Recovered catalyst samples coded as PA1-used were tested in further HDC reactions to examine possible deactivation. PA1-used samples were also treated by calcination and reduction using the same temperature program applied to fresh catalyst samples. These samples were coded as PA1-reg. As previously reported [15], the production of hydrogen was estimated from the amount of acetone generated from the reaction mixture after 30-min reactions at different temperatures. TCE, 2-propanol and acetone were monitored in an Agilent 7890A GC equipped with a TCD detector, DB-5 (TCE) and CarboWax (2-propanol and acetone) columns, 30 m, I.D. 0.32 mm (Agilent, USA).

Table 1
Pd loading, BET surface area and metal dispersion of fresh, used and regenerated 1 wt.% Pd/Al_2O_3 catalyst samples.

Catalyst sample	Pd loading (%)	BET surface area (m^2/g)	Pd dispersion (%)
PA1	0.85	72.4	17.2
PA1-used	0.84	50.2	7.2
PA1-reg	0.85	62.9	14.7
PA2	2.2	76.8	17.4

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists Pd loading, BET surface area and Pd dispersion of fresh and spent catalyst samples. Active phase leaching was not detected from PA1 samples, neither after 180-min reaction (PA1-used) nor after being treated by calcination and reduction (PA1-reg). However, surface area and Pd dispersion of PA1-used samples decreased compared to fresh ones. BET surface area decrease of Pd supported catalysts has been previously attributed to porous obstruction by carbonaceous residues during HDC reactions [15,18,19]. Pd dispersion of PA1-used samples dramatically decreased. This has been related to Pd occlusion by carbonaceous residues [20]. When these residues were removed by temperature treatment, metal dispersion increased. FTIR spectra of fresh and used catalyst samples are compared in Fig. 1. The used catalyst exhibits a broader absorbance signal in the 2500–3500 cm^{-1} region, suggesting acidity changes during HDC reaction [21,22]. As previously reported [19,23] the Al_2O_3 acidity could increase due to HCl produced during HDC reaction, leading to increased carbon deposition and reduced surface area.

Fig. 2 shows typical TGA and DTG profiles of PA1-used samples after the HDC of 0.011 M of TCE at 25 °C. The DTG profile shows a peak at a temperature below 160 °C, attributed to the loss of physically adsorbed or occluded water and removal of physically adsorbed solvent [24,25]. Marécot et al. [25] established oxidation temperatures between 200 and 600 °C for carbonaceous deposits on supported palladium catalysts. Accordingly, weight loss in this temperature range (260–495 °C) is attributed to the combustion of organics where coke deposition on the (1 1 1) Pd planes desorbs around 250 °C whereas deposits on palladium atoms of lower coordination number like corners, edges or (1 0 0) Pd planes are eliminated around 600 °C [25]. The percent of total weight loss and temperature of the main combustion peaks of PA1-used catalyst are shown in Table 2. The largest weigh loss was found at 260 °C

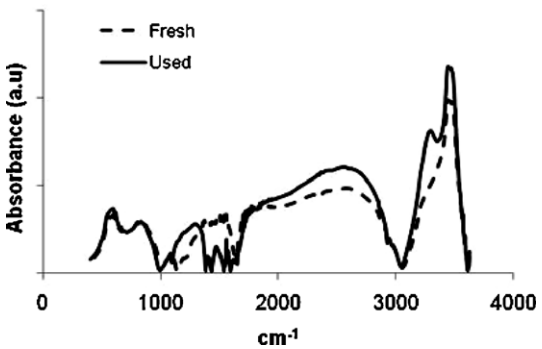

Fig. 1. FTIR spectra of 1 wt.% Pd/γ-Al_2O_3 fresh and used samples catalyst used in the HDC of 0.011 M of TCE at 25 °C. Reaction conditions: 2 g/L 1 wt.% Pd/γ-Al_2O_3, 0.011 M TCE and 0.030 M NaOH in 25 mL of 2-propanol at 25 °C.

Table 2
TGA weight loss and oxidation temperature of PA1-used.

Catalyst	Temperature range (°C)	Weight loss (%)	Oxidation temperature (°C)
1 wt.% Pd/Al_2O_3	20–160	1.3	60.0
	160–350	3.7	260.14
	350–600	2.6	491.84

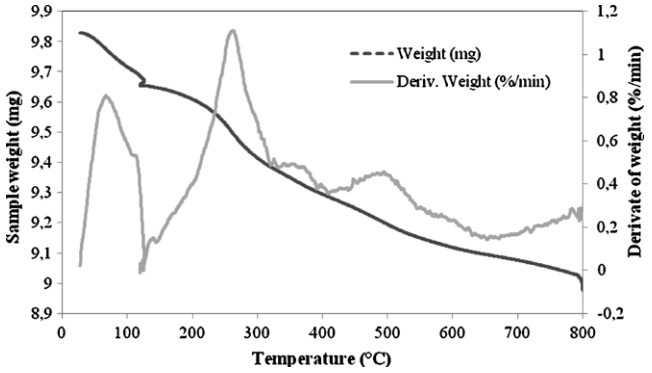

Fig. 2. TGA and DTG analysis of 1 wt.% Pd/catalyst used in the HDC of 0.011 M of TCE at 25 °C. Reaction conditions: 2 g/L 1 wt.% Pd/γ-Al_2O_3, 0.011 M TCE and 0.030 M NaOH in 25 mL of 2-propanol at 25 °C.

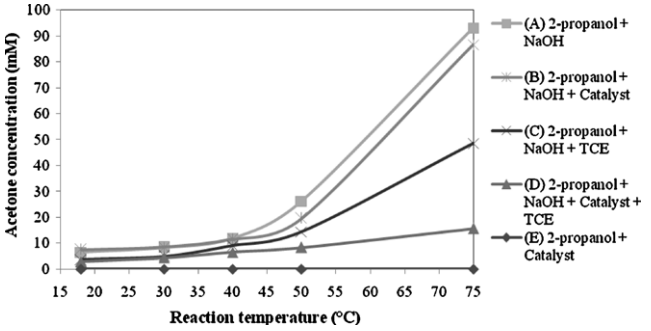

Fig. 3. Production of acetone in 2-propanol dehydrogenation reaction using different reaction conditions and temperatures. Concentrations: 0.03 M NaOH, 2 g/L 1 wt.% Pd/γ-Al_2O_3 and 0.011 M TCE in 25 mL of 2-propanol.

(3.7 wt.%) followed by desorption above 491 °C (2.6 wt.%), however, percent weight losses were lower than those reported for 1 wt.% Pd/Al_2O_3 catalyst samples used in liquid-phase dioxin HDC at 75 °C (between 4 and 7 wt.%) [15] and gas-phase HDC reactions over 225 °C (between 4 and 11.4 wt.%) [19]. Therefore, it appears that the deposition of carbonaceous residues decreases when the HDC reaction is carried out at low temperature. Carbonaceous residues can be originated by both TCE and 2-propanol. A direct relationship between the initial concentration of dioxins and carbonaceous residues on 1 wt.% Pd/Al_2O_3 catalyst samples was found [15]. Furthermore, these carbonaceous residues were mainly associated to C-OH species detected by XPS [15]. This kind of residues can be formed by acetone aldol condensation reaction, which is favored by the presence of a base during 2-propanol dehydrogenation [26].

3.2. Propanol dehydrogenation

Since this work deals with the feasibility of using 2-propanol as hydrogen source for TCE HDC, we measured acetone produced from this solvent after 30-min reaction, as a result of 2-propanol dehydrogenation according to the following scheme [23,27]:

$$CH_3 - CH(OH) - CH_3 \rightarrow CH_3 - C(O) - CH_3 + H_2 \quad (2)$$

Experiments were carried out at different reaction conditions and temperatures in the range 18–75 °C. Results are shown in Fig. 3. As expected, the higher the temperature the higher the 2-propanol dehydrogenation. The largest amount of acetone was recorded in the mixture 2-propanol + NaOH (experiment A). No acetone was detected in the absence of NaOH (experiment E: 2-propanol + catalyst). These results suggest that NaOH is required for 2-propanol dehydrogenation [27,28]. Without base, hydrogen generation is slow and the reactivity of our PA1 catalyst samples is not significant for this reaction. Fig. 3, traces B–D show the effect of PA1 catalyst samples and TCE on 2-propanol dehydrogenation in the presence of NaOH. TCE appears to inhibit 2-propanol dehydrogenation (trace C). Although a slight reduction of acetone was observed when PA1 catalyst was present in the mixture (trace B) a larger acetone drop was detected in the presence of TCE (trace D). This effect can be ascribed to NaOH neutralization by HCl formed during HDC of TCE, which reduces available base decreasing 2-propanol dehydrogenation. According to Eq. (2), available H_2 for HDC reaction ranges between 2.89 and 15.75 mM depending on reaction temperature (trace D) while TCE concentrations ranged between 0.011 and 2.3 M (Table 3), indicating that in the present experiments hydrogen is the limiting reactant.

3.3. Hydrodechlorination of trichloroethylene

The KN criterion to avoid mass and heat transfer effects [16,17] was evaluated by measuring TCE conversion over PA1 and PA2

Table 3
Turnover frequencies (TOF) of TCE HDC over 1 wt.% Pd/Al_2O_3.

Reaction no.	Initial TCE concentration (M)	Reaction temperature (°C)	Catalyst sample	Catalyst concentration (g/L)	Pd/catalyst weight (mol/g)	TOF (s^{-1})[a]
1	0.011	25	PA1	2	1.3E-3	1.0E-4
2	0.011	25	PA1	4	1.3E-3	7.2E-4
3	0.011	25	PA1	8	1.3E-3	3.7E-3
4	0.011	25	PA1[b]	2	1.3E-3	3.0E-5
5	0.011	45	PA1	4	1.3E-3	8.9E-4
6	0.011	75	PA1	4	1.3E-3	2.9E-3
7	2.3	75	PA1	4	1.3E-3	6.7E-1
8	2.3	75	PA1	$4 + H_{2(g)}$	1.3E-3	6.7E-1
9	0.011	25	PA1-used	2	5.8E-4	2.6E-3
10	0.011	25	PA1-reg	2	1.2E-3	1.3E-3

[a] TOF was measured using Pd loading and metal dispersion listed in Table 1. Reaction medium: 30 mM NaOH and different amounts of TCE in 25 mL of 2-propanol.
[b] Reaction carried out with no NaOH addition.

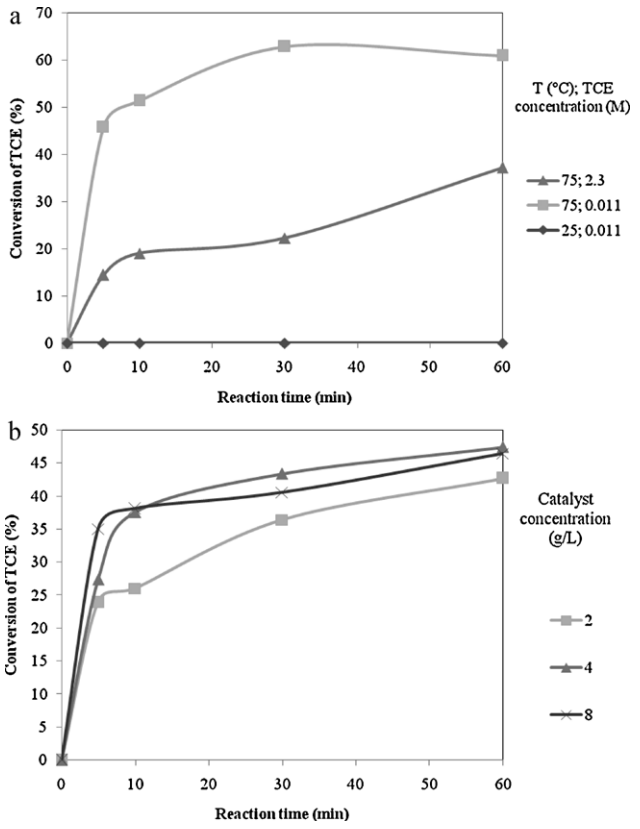

Fig. 4. Conversion of TCE (a) in the absence of catalyst at different TCE concentrations and reaction temperatures and (b) over different concentration of 1 wt.% Pd/γ-Al_2O_3 at 25 °C using 0.011 M TCE. Reaction medium: 0.030 M NaOH in 25 mL of 2-propanol.

catalyst samples having different Pd loadings and similar Pd dispersions (see Table 1). Percent conversion values were 75.28 and 75.16, respectively. HDC reactions of TCE with 2-propanol in the presence of NaOH were carried out using PA1 catalyst concentrations from 0 to 8 g/L. Fig. 4a shows TCE conversion profile in the absence of catalyst at different TCE concentrations at 25 and 75 °C. When 0.011 M (1000 ppmv) TCE initial concentration was used no HDC reaction at 25 °C was observed in the absence of catalyst, but at 75 °C up to 60% conversion was obtained after 30 min reaction. However, when 2.3 M or 20% v/v TCE concentration was used, TCE conversion at 75 °C decreased to about 36% after 60-min reaction in the absence of catalyst. Therefore, truly heterogeneous reaction occurs at low temperature for relatively low TCE concentrations.

Fig. 4b shows the effect of catalyst concentration on the HDC of 0.011 M TCE at 25 °C. Initial TOFs for these experiments (reactions 1–3) are listed in Table 3. Initial reaction rates increased with catalyst concentration (Table 3). Nevertheless, after 60-min reaction similar conversions were obtained (Fig. 4b).

Due to the important effect of NaOH on 2-propanol dehydrogenation (Section 3.2) TCE HDC experiments were performed without base addition at 25 °C using 2 g/L of PA1 catalyst samples. TCE concentration and conversion profiles are shown in Fig. 5. Less than 2% conversion was achieved after 1-h reaction and TOF was 3E-5 (reaction 4, Table 3). Ukisu and Miyadera [27] reported that HDC of 2,7-diclorodibenzo-p-dioxin (DCDD) using 2-propanol as a hydrogen source did not occur at 30 °C in the absence of NaOH. Similar behavior was found for HDC of a complex mixture of dioxins and furans [20]. In this way, NaOH plays an important role on HDC over Pd supported catalyst with 2-propanol as hydrogen donor. As it has been previously reported, NaOH facilitates the adsorption of

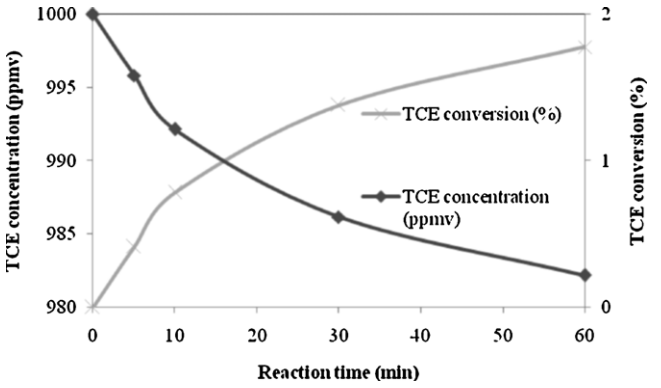

Fig. 5. Concentration and conversion profiles of TCE in the HDC reaction in the absence of NaOH. Reaction conditions: 2 g/L catalyst and 0.011 M TCE in 25 mL of 2-propanol at 25 °C.

the chlorinated compound [27], avoids catalyst poisoning by HCl [3,20], maintains the basicity of the system [20] and is required for 2-propanol dehydrogenation.

The effect of reaction temperature on TCE HDC over 4 g/L of PA1 catalyst sample is shown in Fig. 6a. The feature observed after 5- min reaction at 45 and 75 °C has been ascribed to reactant adsorption. Experiments performed over catalyst samples previously saturated with TCE for 2 h, filtered and dried before reactions did not present said adsorption peak. Table 3 lists initial TOF for these experiments (reaction 2, 5 and 6). At 75 °C TOF dramatically increased most likely due to thermal effects. Conversion profiles for higher TCE concentrations over PA1 at 75 °C are shown in Fig. 6b. Catalyst samples used with 2.3 M TCE at 75 °C were not pre-treated with TCE and the adsorption peak was present. Conversions of about 81% and 69% were obtained after 1- h reaction at initial TCE concentrations of 0.011 M and 2.28 M, respectively. In contrast, 60% and 37% conversions were obtained without catalyst under the same conditions (Fig. 3a). It is clear that at 75 °C the homoge-

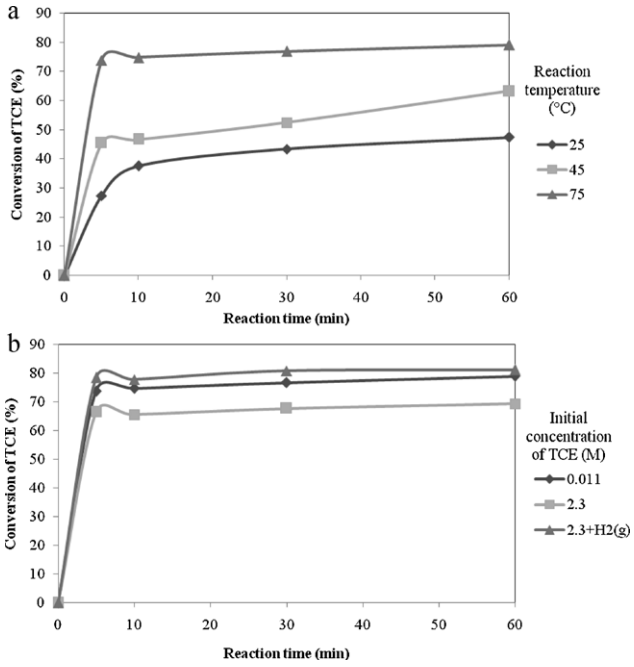

Fig. 6. Conversion of (a) 0.011 M TCE at different reaction temperatures and (b) different TCE initial concentration at 75 °C over 1 wt.% Pd/γ-Al_2O_3. Reaction medium: 4 g/L catalyst and 0.030 M NaOH in 25 mL of 2-propanol.

Table 4
pH of reaction mixture before and after 1-h TCE HDC.

TCE initial concentration (M)	pH initial	pH after 1-h reaction
0.011	12.40	12.37
2.3	12.42	12.32

Reaction conditions: 1 wt.% Pd/γ-Al_2O_3 catalyst, 30 mM NaOH and different amounts of TCE in 25 mL of 2-propanol at 25 °C.

neous reaction is significant. As listed in Table 3 (reactions 6 and 7), TOF increased when TCE initial concentrations varied from 0.011 to 2.26 M.

It is noticeable that complete TCE conversion was not achieved in this study. Transformation of aqueous 25.3 μM TCE, using excess molecular hydrogen, on 1 w/w% Pd/Al_2O_3 yielded ethane as the only reaction product [29]. Ordoñez et al. [3] observed this behavior on the HDC of wastewater TCE using 10 MPa $H_{2(g)}$ as hydrogen donor. They achieved 100% conversion when Na_2CO_3 was added during reaction, in order to maintain basic pH. They probed that at low pH, the HDC stopped. In order to determine pH changes in our reaction system, initial and final pHs were measured after 1-h reaction for HDC of 0.011 and 2.3 M TCE in the presence of 0.03 M NaOH in 2-propanol at 25 °C. Results are shown in Table 4. It is observed that a basic pH was maintained along the experiments without any additional NaOH addition. However, in the present work, hydrogen was the limiting reactant (see Section 3.2). Therefore, the observed TCE conversions do not correspond to ethane formation as would be expected under excess hydrogen. Assuming that TCE HDC lead to dichloroethylene (DCE) isomers (cis, trans, and 1,1), the maximum conversion obtained would be around 70% which agrees within experimental error with the values shown in Fig. 6b.

In order to improve hydrogen availability, HDC experiments were conducted adding 0.1 MPa $H_{2(g)}$ to the reaction system. Fig. 6b shows that in the presence of molecular hydrogen the conversion increased to 81% after 1-h reaction. Although H_2 solubility in 2-propanol at 75 °C and 0.1 MPa is only about 0.08 mol percent [15] it seems that hydrogen is supplied as it is being consumed, leading to conversion increase with time. TOF of this experiment is listed in Table 3 (reaction 8). Complete dioxin HDC conversion using 2-propanol in NaOH as the only hydrogen donor has been reported [15]. However, the levels of these organochlorinated compounds in environmental samples are in the order of pg or ng (10^{-12} to 10^{-9} g) and the hydrogen provided by 2-propanol to HDC reaction was enough for complete degradation. Those studies have demonstrated 2-propanol in NaOH as promising hydrogen supplier for liquid-phase HDC reactions.

Catalyst reuse and regeneration were evaluated under the conditions under which the homogeneous reaction was not significant (0.011 M TCE, 25 °C) and using 2 g/L PA1. However, since a small sample was used (50 mg) it was only possible one catalyst reuse. Besides, there were catalyst looses after filtration. Fig. 7 shows TCE concentration (a) and conversion (b) profiles during HDC of TCE over PA1 samples either used (PA1-used) or treated (PA1-reg) compared to a fresh catalyst sample (PA1). The treatment of used samples consisted of calcination and reduction under conditions similar to those of fresh catalyst samples. After 180-min reaction fresh catalyst samples exhibited 61% conversion, regenerated samples 58% and reused samples 55%. BET surface area and Pd dispersion were recovered after catalyst treatment. TOFs of the experiments performed over PA1-used and PA1-reg samples are listed in Table 3 (reactions 9 and 10). As Pd dispersion of PA1-used sample was lower, its TOF rose to 2.6E-3. However, since Pd dispersion of PA1 and PA1-reg are quite similar their TOFs are almost the same.

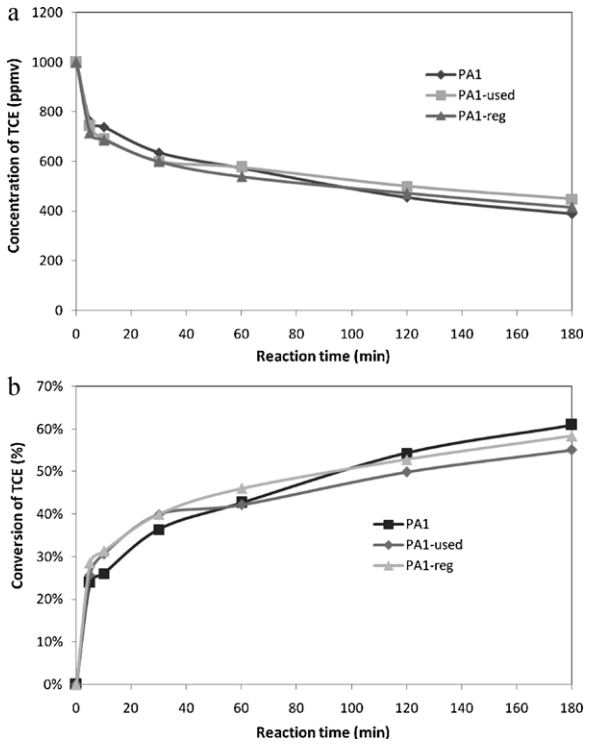

Fig. 7. Concentration (a) and conversion (b) profiles of TCE over fresh (PA1), used (PA1-used) and regenerated (PA1-reg) 1 wt.% Pd/γ-Al_2O_3 samples. Reaction conditions: 2 g/L catalyst, 0.011 M TCE and 0.030 M NaOH in 25 mL of 2-propanol at 25 °C.

4. Conclusions

In the presence of NaOH, 2-propanol provided hydrogen to carry out TCE HDC at room temperature. However, in this study hydrogen was the limiting reactant and most probably the HDC did not lead to ethane, as expected under excess hydrogen. In the absence of NaOH, 2-propanol dehydrogenation did not occur and the HDC reaction was not accomplished. At 25 °C TOFs were around 0.001 s^{-1} for the HDC of 0.011 M TCE over 2 g/L of PA1 catalyst samples with 2-propanol and 0.03 M NaOH. After 180-min reaction, used catalyst samples (without any pretreatment) exhibited BET surface area reductions and increased acidity, likely due to carbonaceous deposition. In spite of that, used catalyst samples (PA1-used) exhibited slightly lower activity than fresh ones. BET surface area of spent catalyst was recovered by calcination and reduction and the activity of treated samples (PA1-reg) was similar to fresh ones.

Acknowledgements

Authors are grateful to University of Antioquia for supporting this work through the project “Sostenibilidad 2009–2011”.

References

[1] N. Barrabes, D. Cornado, K. Foettinger, A. Dafinov, J. Llorcac, F. Medina, G. Rupprechter, J. Catal. 263 (2009) 239–246.
[2] L.H. Lash, D.A. Putt, P. Huanga, S.E. Hueni, J.C. Parker, Toxicology 235 (2007) 11–26.
[3] S. Ordóñez, B.P. Vivas, F.V. Díez, Appl. Catal., B 95 (2010) 288–296.
[4] M. Toro Gómez, N. Álvarez, J. Gómez Suárez, C. Sánchez, J. Serna Patiño. Actualización del inventario de emisiones atmosféricas en el Valle de Aburrá, con georeferenciación de estas. Inventario de emisiones de fuentes móviles–etrome–manual del usuario. Convenio Universidad Pontificia Bolivariana-Área Metropolitana del Valle de Aburrá No. 323, 2005–2006, 1.
[5] D. Richard, L.D. Nuñez, C. de Bellefon, D. Schweich, in: E. Lichtfouse, J. Schwarzbauer, D. Robert (Eds.), Environmental Chemistry, Springer GmbH, Berlin, 2005.

[6] C.B. Molina, A.H. Pizarro, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, Chem. Eng. J. 160 (2010) 578–585.
[7] W. Wu, J. Xu, H. Zhao, Q. Zhang, S. Liao, Chemosphere 60 (2005) 944–950.
[8] E.V. Golubina, E.S. Lokteva, S.A. Kachevsky, A.O. Turakulova, V.V. Lunin, Stud. Surf. Sci. Catal. 175 (2010) 293–296.
[9] W. Nishijima, Y. Ochi, T. Tsai, Y. nakano, M. Okada, Appl. Catal., B 51 (2004) 140.
[10] N.C. Concibido, T. Okuda, W. Nishijima, M. Okada, Tetrahedron Lett. 46 (2005) 3613–3617.
[11] F. He, D. Zhao, Appl. Catal., B 84 (2008) 533–540.
[12] Y. Ukisu, T. Miyadera, Appl. Catal., A 271 (2004) 165–170.
[13] S. Zinovyev, A. Shelepchikov, P. Tundo, Appl. Catal., B 72 (2007) 289–298.
[14] Y. Ukisu, Appl. Catal., A 349 (2008) 229–232.
[15] M. Cobo, J.A. Conesa, C. Montes de Correa, Appl. Catal., B 92 (2009) 367–376.
[16] R.J. Madon, M. Boudart, Ind. Eng. Chem. Fundam. 21 (1982) 438–447.
[17] M. Boudart, Chem. Rev. 95 (1995) 661–666.
[18] S. Ordoñez, H. Sastre, F.V. Díez, Thermochim. Acta 379 (2001) 25–34.
[19] E. López, S. Ordóñez, F.V. Díez, Appl. Catal., B 62 (2006) 57–65.
[20] M. Cobo, J.A. Conesa, C. Montes de Correa, J. Phys. Chem. A 112 (2008) 8715–8722.
[21] F. Liakath, A. Khan, Indian J. Pure Appl. Phys. 46 (2008) 12–19.
[22] J. Araña, J.M. Doña-Rodríguez, C. Garriga-Cabo, O. González-Díaz, J.A. Herrera-Melián, J. Pérez-Peña, Appl. Catal., B 53 (2004) 221–232.
[23] M. Legawiec-Jarzyna, A. Śrębowata, W. Juszczyk, Z. Karpiński, J. Mol. Catal. A 224 (2004) 171–177.
[24] W. Nishijima, Y. Ochi, T. Tsai, Y. Nakano, M. Okada, Appl. Catal., B 51 (2004) 135–140.
[25] P. Marécot, A. Akhachane, C. Micheaud, J. Barbier, Appl. Catal., A 169 (1998) 189.
[26] N.L. Allinger, M.P. Cava, D.C. DeJongh, C.R. Johnson, N.A. LeBel, C.L. Stevens, Organic Chemistry, second ed., Worth Publishers, New York, 1997.
[27] Y. Ukisu, T. Miyadera, Appl. Catal., B 40 (2003) 141–149.
[28] H. Junge, M. Beller, Tetrahedron Lett. 46 (2005) 1031–1034.
[29] G. Lowr y, M. Reinhard, Environ. Sci. Technol. 33 (1999) 1905–1910.