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Catalytic hydrodechlorination of dichloromethane in the presence of traces of chloroform and tetrachloroethylene

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Abstract

The gas phase dichloromethane hydrodechlorination was studied in the absence and in the presence of traces of chloroform and tetrachloroethylene over 0.3–0.7 wt.% Pd supported on commercial alumina or sol–gel titania. Turnover frequencies (TOFs), rate constants, reaction orders and activation energies were determined. Catalysts with the higher palladium loadings on both supports were much more active. A decreased activity was observed when traces of chloroform or tetrachloroethylene were added to the feed stream. However, the deactivation effect was lower over alumina-supported catalysts. Selected catalysts were characterized by chemical analysis, BET, chemisorption, TGA and TPR.

Keywords: Dichloromethane; Chloroform; Tetrachloroethylene; Pd-supported catalysts; Catalytic hydrodechlorination; TOF; Kinetics

1. Introduction

Chlorinated volatile organic compounds (CVOCs) such as dichloromethane, chloroform and tetrachloroethylene are solvents typically found in industrial waste streams and have a negative impact in public health and ecology [1–3]. Incineration of waste containing these compounds is most widely used but it may lead to more dangerous products such as phosgene, dioxins and furans. So there is a renewed interest to develop friendlier disposal methods. The heterogeneous catalytic hydrodechlorination of aromatic and aliphatic compounds over Ni-, Pd-, Pt- and Rh-based catalysts has been reported but, available kinetic data on hydrodechlorination are still limited [4–7]. Besides, only few works deal with the simultaneous hydrodechlorination of mixtures of organochlorinated compounds [8]. Díez and coworkers found important inhibition effects when mixtures of tetrachloroethylene (TTCE), trichloroethene (TCE) and 1,1-dichloroethene (DCE) were hydrodechlorinated over commercial 0.5 wt.% Pd/Al_2O_3 catalyst samples [8]. Therefore, a Langmuir–Hinshelwood model considering adsorption of organochlorinated compounds and hydrogen over the same active sites was postulated for hydrodechlorination of binary and ternary mixtures of TTCE, TCE, and DCE in toluene as solvent [8]. In another work [9], the same model was found to be representative for hydrodechlorination of tetrachloroethylene (TTCE)–chlorobenzene (CBZ) mixtures.

Dichloromethane (DCM) is a difficult compound to be eliminated displaying not only low conversions [6,9–11] but also a high amount of chlorinated by-products (regarding retention of chlorine on the catalytic surface) [12]. Additionally, according to EPA reports [13], dichloromethane is released into the environment in large quantities. Malinowski et al. [11] studied the effect of metal dispersion on the activity of $Pd/\gamma\text{-}Al_2O_3$ on DCM hydrodechlorination using Pd loadings between 1 and 5 wt.%. Their results showed that poorly dispersed catalysts displayed higher turnover frequencies. In agreement with previous works, we have found that alumina or sol–gel titania are the most suitable Pd supports for dichloromethane hydrodechlorination [14,15]. In this study we report kinetic parameters for dichloromethane hydrodechlorination over alumina- and titania-supported catalysts containing different

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Pd loadings (lower than 1 wt.%). Furthermore, taking into account that industrial emissions contain traces of several organochlorinated compounds [6,16], the effect of the presence of traces of chloroform and tetracholoroethylene on the kinetic parameters of dichloromethane hydrodechloriantion was also studied. Catalytic tests were performed under differential conditions and turnover frequencies, reaction orders and rate constants were obtained. These parameters are required for the implementation of kinetic models to compare catalyst performance and reproduce experimental data [17].

2. Experimental

2.1. Catalyst preparation and characterization

Sol–gel titania was prepared following a previously reported procedure [14,15]. Samples of as synthesized sol–gel titania were calcined in air at 600 °C to remove organic residues. Anatase phase with a surface area of 43 m^2/g was obtained. Palladium was incorporated by incipient wetness impregnation on sol–gel titania and commercial alumina (γ-Al_2O_3), both pretreated at 300 °C, using palladium(II) acetylacetonate as precursor salt [15]. The amount of palladium salt was varied as to obtain several samples containing 0.3–0.7 wt.% Pd/TiO_2 and 0.3–0.7 wt.% Pd/γ-Al_2O_3. Catalyst samples were then heated under static conditions in a muffle furnace at 300 °C to remove organic residues from Pd precursor.

XRD of fresh catalyst samples were performed in a diffractometer Philips 3710, using Cu Kα radiation in the range, $2\theta = 20$–$80°$. Palladium loading was determined by atomic absorption. BET analysis was carried out by nitrogen adsorption in a Micromeritics ASAP 2010. Thermogravimetric analysis was performed in a 2950 TGA HR V6.1[a] apparatus modulated until 1000 °C.

2.2. Catalytic tests

Catalytic tests were carried out in a pyrex plug flow tubular reactor under steady-state conditions. Before reaction, palladium catalysts were sieved to 250–180 μm and reduced at 300 °C in flowing 5% H_2/N_2. Catalyst samples were mixed with silicon carbide (SiC) so a bed height/particle diameter ratio of 100 was obtained. Initial reaction rates were obtained by varying dichloromethane concentration from 350 to 750 ppm in excess hydrogen ($H_2/CH_2Cl_2 = 10$), and using 25 mg catalyst, total flow 120 mL/min, GHSV 0.20 gcat min/L, temperatures between 100 and 200 °C and atmospheric pressure. In order to reach steady-state conditions it was necessary to stabilize the system for about one hour. A FTIR gas analyzer (Temet) equipped with a 2 L cell, optical step of 240 cm and operated at 120 °C was used to monitor reactants and products.

The effect of the presence of chloroform and tetrachloroethylene was studied using the ratios: $CH_2Cl_2:CHCl_3 = 5:1$, $CH_2Cl_2:C_2Cl_4 = 5:1$, $CHCl_2:CHCl_3:C_2Cl_4 = 15:1:1$.

Temperature-programmed reduction (TPR) and chemisorption studies were carried out in a Micromeritics AutoChem II 2920 equipped with a TCD. For TPR experiments, samples were pretreated at 300 °C in flowing 4% O_2/Ar. Afterwards, they were cooled down at room temperature in flowing Ar. Reduction in flowing 9% H_2/Ar was carried out from 25 to 800 °C at 10 °C/min. Palladium dispersion by hydrogen chemisorption was determined at 100 °C. Catalysts were initially pretreated in 9% H_2/Ar heating at 2 °C/min from room temperature to 300 °C and this temperature was kept for 1 h. Afterwards, samples were cooled down at 100 °C in flowing Ar and hydrogen pulses were introduced until saturation. Turnover frequencies (TOFs) were calculated on the basis of the Pd dispersion values (H/Pd) obtained by chemisorption.

3. Results and discussion

3.1. Nitrogen adsorption

Textural properties of supported palladium catalysts on alumina and sol–gel titania are listed in Table 1. Nitrogen adsorption–desorption isotherms shown in Figs. 1 and 2 are of type I hysteresis typical of mesoporous materials with cylindrical channels, uniform pore size and shape, and narrow pore size distribution [16]. Isotherms did no significantly change with palladium loading.

3.2. Thermogravimetric analysis (TGA)

TGA and DTG of fresh and used 0.6 wt.% Pd/γ-Al_2O_3 samples are shown in Fig. 3. Both fresh and used samples exhibit similar weight losses until 200 °C. The weight loss in this region is attributed to elimination of physisorbed water and solvent. At temperatures between 200 and 800 °C a weight loss of 3.45 wt.% was observed for fresh catalyst samples, while used catalyst samples lost about 5.67 wt.%. These weight losses can be attributed to combustion of organic residues from palladium(II) acetylacetonate. Nevertheless, weight losses of used samples were larger suggesting the formation of coke [17,18].

3.3. Hydrogen chemisorption

Results of chemisorption analysis of fresh and used catalyst samples are listed in Table 2. Catalysts with higher palladium loading, exhibited lower dispersion, and larger particle size.

Table 1
Textural properties of Pd/γ-Al_2O_3 and Pd/TiO_2 samples

Catalyst	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
γ-Al_2O_3	105.28	12.88	0.34
0.6% Pd/γ-Al_2O_3[a]	80.83	21.46	0.43
0.4% Pd/γ-Al_2O_3[a]	96.09	ND	ND
TiO_2	43.80	14.02	0.15
0.7% Pd/TiO_2[b]	38.51	9.33	0.090
0.4% Pd/TiO_2[b]	38.23	ND	ND

N.D.: not determined.

[a] Pd/γ-Al_2O_3 treated in static air at 300 °C before and after impregnation.

[b] Pd/TiO_2, sol–gel TiO_2 support, catalyst calcined in static air at 300 °C before and after Pd impregnation.

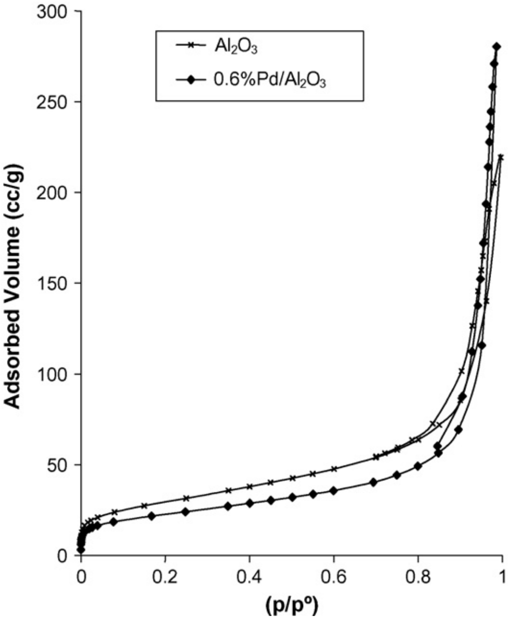

Fig. 1. Nitrogen adsorption–desorption isotherms of γ-Al_2O_3 and 0.6 wt.% Pd/γ-Al_2O_3 samples, calcined under static conditions in air at 300 °C before and after palladium impregnation.

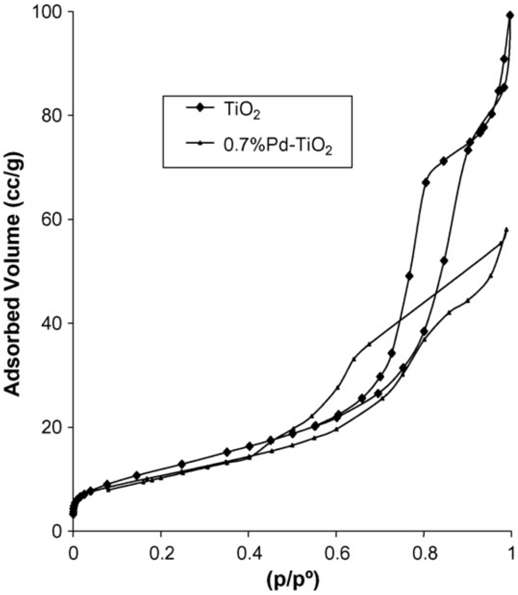

Fig. 2. Nitrogen adsorption–desorption isotherms of sol–gel titania and 0.7 wt.% Pd/TiO_2 samples, pretreated under static conditions in air at 300 °C before and after palladium impregnation.

Furthermore, for similar palladium loadings on both supports sol–gel titania-supported catalysts exhibited lower Pd dispersions. This result was expected given the lower surface area of sol–gel titania compared to that of alumina support (see Table 1).

3.4. Temperature-programmed reduction (TPR)

TPR profiles of γ-Al_2O_3 and TiO_2-supported palladium catalyst samples are shown in Figs. 4 and 5. A negative H_2-consumption peak at 60 °C observed in both figures is associated with decomposition of palladium hydride, β-PdH, as has been reported [19–22]. In general, palladium can absorb hydrogen at low temperature (β-PdH is typically formed at temperatures lower than 10 °C) and release it around 80 °C, due to thermal instability of these species. Another negative peak at 150 °C, observed in the TPR profile of a 0.7 wt.% Pd/TiO_2 sample is associated with the presence of organic residues from the Pd precursor [14]. In line with previous reports [15,23] TPR of commercial γ-alumina shows no peak corresponding to hydrogen consumption in the temperature range evaluated demonstrating the stability and resistance to reduction of this material.

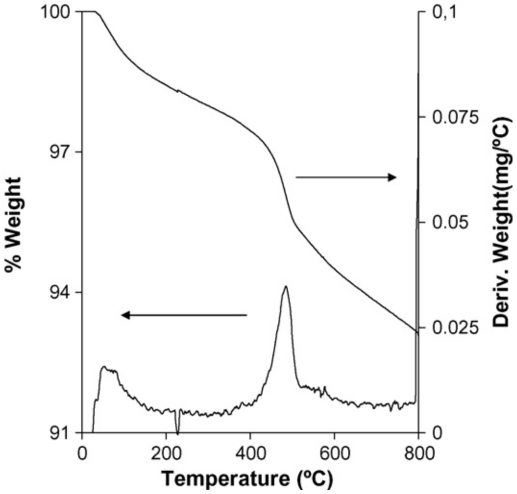

Fig. 3. TGA and DTA of used 0.6 wt.% Pd/γ-Al_2O_3 samples.

3.5. Catalytic tests

Initially, blank tests were carried out with the empty reactor and over γ-alumina and sol–gel titania supports. Results presented in Fig. 6 show that γ-alumina is more active than titania for dichloromethane hydrodechlorination, while very low conversions are obtained with the empty reactor indicating that under the studied conditions thermal hydrodechlorination is not significative. Ordóñez et al. [23] suggested that in the absence of catalyst hydrodechlorination might occur due to the presence of catalytic centers on their stainless steel reactor wall,

Table 2
Hydrogen chemisorption of Pd/γ-Al_2O_3 and Pd/TiO_2 samples

Catalyst	% Palladium loading	Dispersion (%)	Particle size (nm)
Pd/γ-Al_2O_3[a]	0.3	72.5	1.5
Pd/γ-Al_2O_3[a]	0.4	64.8	1.7
Pd/γ-Al_2O_3[a]	0.6	55.5	2.0
Pd/γ-Al_2O_3[b]	0.6	39.6	2.9
Pd/TiO_2[a]	0.3	67.0	1.7
Pd/TiO_2[a]	0.4	58.6	1.9
Pd/TiO_2[a]	0.7	36.7	3.1

[a] Pretreated in static air at 300 °C (before and after palladium impregnation) and reduced in flowing hydrogen at 300 °C.

[b] Pretreated in static air at 300 °C (before and after palladium impregnation) and reduced in flowing hydrogen at 400 °C.

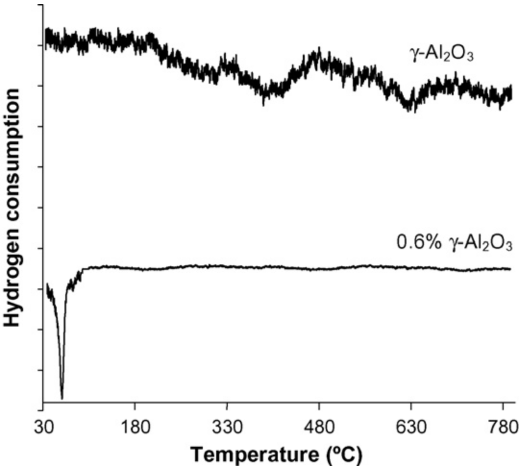

Fig. 4. H_2-TPR profiles of fresh γ-Al_2O_3 and 0.6 wt.% Pd/γ-Al_2O_3 samples.

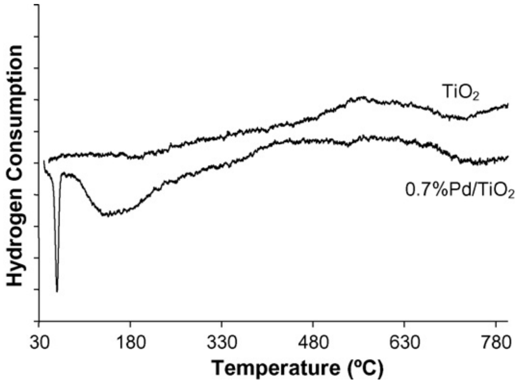

Fig. 5. H_2-TPR profiles of fresh TiO_2 and 0.7 wt.% Pd/TiO_2 sol–gel samples.

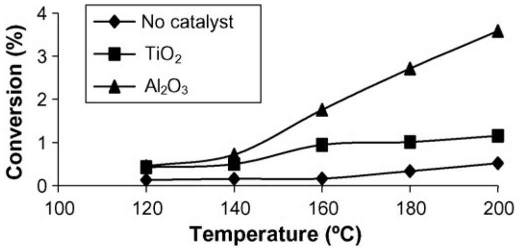

Fig. 6. Conversion (%) of dichloromethane hydrodechlorination without catalyst and over γ-alumina and titanium dioxide supports. Twenty-five milligrams of support, concentration of CH_2Cl_2 550 ppm, $H_2/CH_2Cl_2 = 10$.

probably generated by hydrogen chloride produced during reaction.

TOF values of dichloromethane hydrodechlorination are presented in Fig. 7 and Table 3. Catalytic activity increases not only with palladium loading but also with temperature and dichloromethane concentration. As can be observed in Table 2 the larger the particles the lower the dispersion. Aramendia et al. [24] proposed that chlorine formed during reaction could migrate into catalyst bulk and thus smaller Pd particles would be rapidly saturated with chlorine, which in turn would poison catalyst surface leading to low activity. So, larger particles appear to be more resistant to deactivation by HCl.

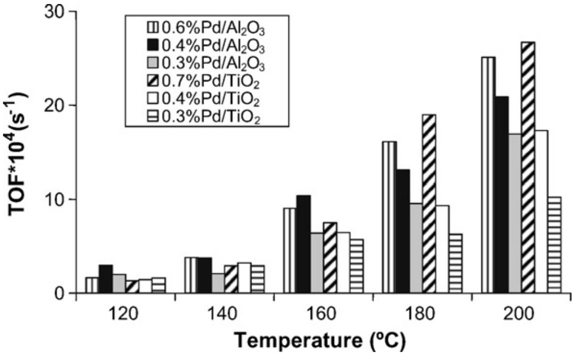

Fig. 7. TOF (s^{-1}) of dichloromethane hydrodechlorination over palladium supported on γ-alumina and sol–gel titania catalyst samples. Twenty-five milligrams of catalyst, 550 ppm of CH_2Cl_2, $H_2/CH_2Cl_2 = 10$.

Activation energies were obtained from Arrhenius equation, $k_A = A\,e^{-E/RT}$, where k_A, A, E, R, T correspond to rate constant, frequency exponential factor, activation energy, gas constants and absolute temperature, respectively. Reaction orders, rate constants and activation energies are listed in Tables 4 and 5. Reaction orders were similar for all catalysts. Specific rate constants increased with temperature and palladium loading. Samples of 0.7 wt.% Pd/TiO_2 were more sensitive to temperature (rate constants between 0.089 and 13.80 (L/gcat min)) than 0.6 wt.% Pd/γ-Al_2O_3 (rate constants between 0.10 and 12.28 L/gcat min). Activation energies values vary between 22 and 31 kcal/mol. Mori et al. [25] obtained activation energies between 9 and 15 kcal/mol for different reaction products during hydrodechlorination of 1,1,1-trichloroethane over Pd/SiO_2. Each value was ascribed to an intermediate of different nature.

Table 3
TOF values of dichloromethane hydrodechlorination at 200 °C

Catalyst	Dichloromethane concentration (ppm)	TOF ($\times 10^4$ s^{-1})
0.7% Pd/TiO_2	359	14.45
	454	25.16
	554	26.62
	608	29.26
0.6% Pd/Al_2O_3	365	16.57
	420	21.48
	460	22.35
	555	25.11

$H_2/CH_2Cl_2 = 10$.

Table 4
Kinetic parameters for dichloromethane hydrodechlorination over alumina and titania-supported Pd catalysts

Catalyst	Reaction order	k, 120 °C ($\times 10^3$ L/gcat min)	k, 200 °C (L/gcat min)
0.3% Pd/γ-Al_2O_3	1.20	8.63	7.26
0.4% Pd/γ-Al_2O_3	1.16	19.56	7.40
0.6% Pd/γ-Al_2O_3	1.19	102.24	12.28
0.3% Pd/TiO_2	1.11	8.40	7.32
0.4% Pd/TiO_2	1.18	63.43	7.50
0.7% Pd/TiO_2	1.20	89.46	13.77

Table 5
Activation energies, E_a (kcal/mol) for dichloromethane hydrodechlorination over alumina and sol–gel titania-supported Pd catalysts

Catalyst sample	$E_a \pm 0.10$ kcal/mol	Correlation coefficient
0.3% Pd/γ-Al_2O_3	31.16	0.95
0.4% Pd/γ-Al_2O_3	27.42	0.94
0.6% Pd/γ-Al_2O_3	22.12	0.96
0.3% Pd/TiO_2	31.28	0.99
0.4% Pd/TiO_2	30.90	0.93
0.7% Pd/TiO_2	23.30	0.95

Activation energies obtained in this work are close to each other. Lower values correspond to catalyst samples with higher palladium loadings. The limiting step for hydrodechlorination has been assigned to the C–Cl bond cleavage on the palladium surface [8,9]. If reaction kinetics is dominated by this step, activation energies correspond to the necessary energy for breaking this bond. TOF results for fresh catalysts confirm that at a given temperature and dichloromethane concentration, alumina-supported palladium catalysts are more active than titania supported ones. However, the most active catalyst between 180 and 200 °C was 0.7 wt.% Pd/TiO_2, even though, it is worth mentioning that among tested catalysts it contains the highest Pd loading.

3.6. The effects of chloroform and tetrachloroethylene

The use of binary and ternary mixtures of dichloromethane, chloroform and tetrachloroethylene was evaluated over 0.6 wt.% Pd/γ-Al_2O_3 and 0.7 wt.% Pd/TiO_2 catalyst samples. As can be observed in Fig. 8, important mixture effects are found for hydrodechlorination of dichloromethane and chloroform on both catalyst types. Activity decrease is more appreciable over sol–gel titania-supported Pd catalyst samples. Since 0.6 wt.% Pd/Al_2O_3 appeared to be less inhibited by the presence of chloroform, we evaluated the effect of feeding ternary mixtures (dichloromethane, chloroform and tetrachloroethylene) and the effect of different pretreatments over 0.6 wt.% Pd/Al_2O_3 catalyst samples.

Fig. 9 shows TOFs values for hydrodechlorination of binary and ternary mixtures of dichloromethane chloroform and tetrachloroethylene on 0.6 wt.% Pd/γ-Al_2O_3. Chloroform has a greater inhibition effect than tetrachloroethylene but both chloroform and tetrachloroethylene compete for active sites so deactivation was more pronounced when the ternary mixture was used. Similar results were obtained by López et al. [9] for binary and ternary mixtures of tetrachloroethylene, chlorobencene, and dichloromethane. The impact was more severe on the ternary system.

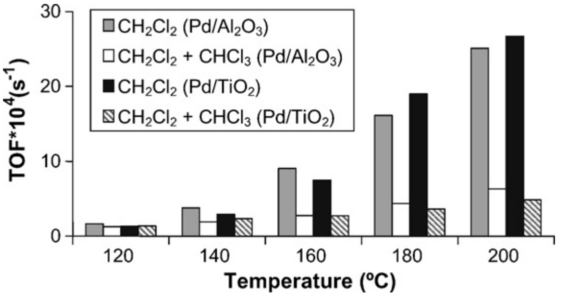

Fig. 8. The effect of chloroform on dichloromethane hydrodechlorination over 0.7 wt.% Pd/TiO_2, 0.6 wt.% Pd/γ-Al_2O_3. $H_2/CH_2Cl_2 = 10$, $H_2/CHCl_3 = 50$, 25 mg of catalyst, 0.12 L/min.

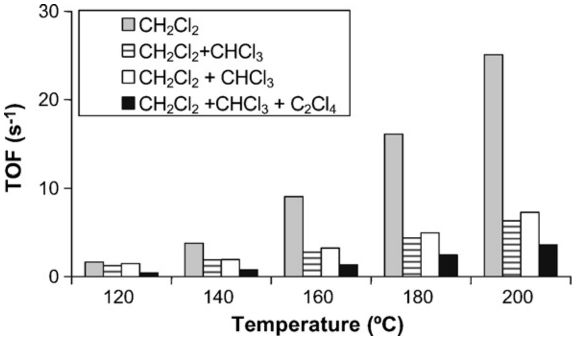

Fig. 9. The effect of both chloroform and tetrachloroethylene on dichloromethane hydrodechlorination over 0.6 wt.% Pd/γ-Al_2O_3. Twenty-five milligrams of catalyst, 0.12 L/min.

3.7. Catalyst pretreatment

Samples of 0.6 wt.% Pd/γ-Al_2O_3 were submitted to different pretreatment conditions (see Fig. 10). The use of a low heating rate under an inert atmosphere allows both an adequate water and hydroxyl removal favoring dichloromethane hydrodechlorination. Bae et al. [26], found that an inert gas as helium did not adsorb over Pt/γ-Al_2O_3 catalyst surface, whereas gases such as O_2 or CO adsorbed more strongly than the chlorinated compounds or hydrogen, inducing a more drastic catalyst deactivation. This may explain why pretreatment under an inert atmosphere was more effective in this work. TOF values of a sample pretreated under inert atmosphere and air were 3.84×10^{-3} and 2.48×10^{-3} s^{-1}, respectively. Before reduction, thermal treatment below 500 °C [27] is recommended to favor catalyst dispersion. In the present work palladium catalysts were pretreated in static air at 300 °C before catalytic runs.

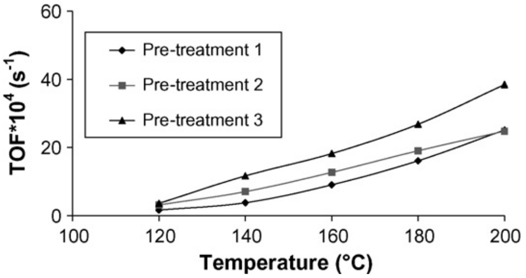

Fig. 10. Effect of different pretreatment conditions on dichloromethane hydrodechlorination over 0.6 wt.% Pd/γ-Al_2O_3. Pre-treatment 1: calcination in static air up to 300 °C and reduced in flowing hydrogen up to 300 °C. Pre-treatment 2: calcination in static air at 300 °C and reduction in flowing hydrogen at 400 °C. Pre-treatment 3: heating in flowing helium at 500 °C, and in flowing air at 700 °C, then impregnation with palladium and reduction in flowing hydrogen at 300 °C.

As shown in Fig. 10, alumina activation at high temperature leads to a considerable higher activity, which is attributed to changes on support acidity [28]. Increasing acidity of alumina influences the chemical (electronic) state of palladium [28,29]. High temperature pretreatment of Pd/Al_2O_3 generates Lewis acidity of γ-Al_2O_3 and, at the same time, induces Pd–alumina interactions leading to the formation of active Pd–Al species [30]. Peri et al. [28], found that alumina, itself, even after activation by high temperature pretreatment, is not active, however the presence of palladium plays an important role. Cordi et al. reported [31] that Lewis sites were obtained during pre-calcination of alumina at 600 °C in flowing O_2 before palladium impregnation with a $PdCl_2$ solution. These electrophilic sites were characterized by the absence of hydroxyl groups on aluminum atoms and can be obtained by dehydroxylation of the alumina surface, allowing the transformation of their Brønsted sites [32]. In general, Lewis sites, which strongly adsorb organochlorinated compounds, are favored at high temperatures [33]. Therefore, as shown in Fig. 10, the observed variation in reactivity when different pretreatment conditions were used might be due to changes in support acidity. Lebedeva et al. [34] reported a high ability of alumina to retain chlorine ions when catalysts were calcined and reduced at high temperatures. Other authors have pointed out that the acidity of alumina plays an important role on chlorocarbon adsorption and dechlorination rate increases with the support ability to adsorb organochlorinated compounds [35]. Fig. 10 also shows that catalysts reduced at 400 °C, exhibit a slight hydrodechlorination activity enhancement compared to those reduced at 300 °C. Chemisorption results show that reduced catalyst samples at 400 °C contain larger Pd particles, suggesting that the reaction is structure sensitive.

4. Conclusions

Empirical kinetic parameters for dichloromethane hydrodechlorination over Pd-supported alumina and sol–gel titania catalyst samples were determined. A pseudo-first-order reaction appears to be a reasonable assumption. Activation energies varied between 22 and 32 kcal/mol. Catalysts with higher palladium loading showed larger particle size and lower dispersion and exhibited higher hydrodechlorination activity. For similar palladium loadings, alumina-supported catalysts exhibited more activity for dichloromethane hydrodechlorination than sol–gel titania supported ones. Besides, they were less deactivated by the presence of dichloromethane and chloroform mixtures. However, both catalysts were highly deactivated when tetrachloroethylene was added to the dichloromethane-chloroform binary mixture. Alumina pretreatment in flowing air at 500 °C and then, in flowing helium at 700 °C before Pd impregnation lead to more active catalysts for dichloromethane hydrodechlorination.

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