Catalysis Letters Vol. 96, Nos. 3–4, July 2004 (© 2004)

Cyclohexene reactivity over palladium acetate supported in liquid phase

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Received 8 April 2004; accepted 30 April 2004

The competitive reactions of cyclohexene: disproportionation and dehydrogenation were studied over a supported-liquid phase catalyst (SLPC) of palladium acetate solved in a stationary phase employing two different techniques: pulsed and flow micro-reactor, where the products of reaction are analysed by gas chromatography. The effect of the liquid phase (comparing an aliphatic phase, squalane, with a polar phase, Triton), the reaction environment (comparing He, N_2 and air) and the process conditions (temperature and reactant concentration) have been studied. Although continuous deactivation was observed in all the cases, the catalyst supported on the apolar phase presents better performance, whereas the disproportionation reaction only takes place at no oxidant conditions and the operation conditions only affect to the selectivity of the reaction. A kinetic model for the reaction, taking into account the catalyst deactivation has been proposed, and kinetic and deactivation constant were calculated by fitting the model to the experimental data. Arrhenius parameters were obtained from measured data at several temperatures.

KEY WORDS: cyclohexene disproportioning; cyclohexene dehydrogenation; supported-liquid-phase catalysts.

1. Introduction

Cyclohexene (CHE) can react according to different reaction pathways yielding different reaction products depending on the catalyst and experimental conditions. Therefore, it is used a probe in studies involving and comparing catalyst preparations. The main reactions involved in this transformation are dehydrogenation and disproportionation, both usually occurring simultaneously [1]. The disproportionation of CHE to benzene (BZ) and cyclohexane (CHA) is an interesting hydrogen-transfer reaction since the reactant can act as a hydrogen donor, in the case of the formation of BZ, and as a hydrogen acceptor, in the case of CHA. Because of this, this reaction was widely studied [1–6].

Catalytic reactions have traditionally involved either homogeneous or heterogeneous catalysts. The major disadvantages of homogeneous catalysts are the problem of separating the latter (usually very expensive) from the products at the end of the reaction, lower conversions, back-mixing, corrosion and fouling of the reactor materials. The range of suitable solvents is often limited by the solubility characteristics of the catalysts. On the other hand, the main potential advantages of homogeneous systems for the same reaction are higher selectivities, the more efficient use of the catalyst atoms, and the easy reproducibility of catalyst preparation. Consequently, considerable attention has been paid to the physical or chemical fixation of homogeneous catalysts on organic or inorganic supports to combine the advantages of homogeneous and heterogeneous catalysis. One of the most successful methods for achieving these purposes consists of dissolving the homogeneous catalysts in a high boiling solvent and supporting this solution on a porous or non-porous carrier. Catalysts so prepared, called *supported-liquid-phase catalysts* (SLPC), can be used as conventional heterogeneous catalysts, for example, in fixed bed reactors.

Although this technique was developed in 1960s and was devoted to the development of catalysts for different organic reactions, such as the hydroformylation of propylene, the isomerisation of quadricyclene to norbornadiene, oxidation of SO_2, conversion of ethylene to acetaldehyde [7–17], etc., the interest in this technique has grown in the last few years. In recent years, SLPC has been applied to selective oxidation (oxidation of ethylene for producing acetaldehyde, catalysed by $PdCl_2$ and $CuCl_2$, and the acetoxylation of acetylene to produce vinyl acetate, catalysed by potassium acetate and palladium acetate) [18], and the Heck reaction of iodobenzene and butyl acrylate in toluene in the presence of triethylamine [19]. Other recent studies deal with the development of methodologies for working with SPLC catalysts in reverse flow reactors [20] and with the modelling of SLPC processes [21, 22].

Gas–liquid chromatography (GLC) constitutes an important tool in the area of catalysis and, particularly, for the study of reaction kinetics. The most frequent application of GLC in kinetic studies has been as an analytical device separated from the reactor. It has also been used in the micro-reactor technique, were the reaction device (micro-reactor) is connected directly to the entrance of the chromatographic column. This

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technique allows, in a very simple way, the study of reaction kinetics when very small reactant samples and conversions are dealt with. Micro-reactors, owing to their small dimensions, have many advantages over the conventional lab-size reactors because they consume less space, materials, and energy, and have shorter response times [23].

In this work, the competitive disproportionation and dehydrogenation of CHE catalysed by palladium acetate solved in a stationary phase (SLPC) has been studied. Specifically, two different liquid phases have been studied: squalane and Triton-X305. The first one is a branched paraffinic solvent with a boiling point of 215 °C, whereas the second one has aromatic and oxygenated structures in the molecule and a boiling point of 101 °C. The effect of different operating parameters (such as temperature, carrier gas or space time) on both the selectivity and the deactivation of the SLPC catalysts was studied, and a deactivation model developed. Reaction studies have been carried out in a micro-reactor, while feeding the CHE either in pulses or as continuous feed.

2. Experimental

2.1. Catalyst preparation

The preparation of the SLPC was carried out in two steps: first, the support, (Chromosorb P-AW, 60–80 mesh, pre-dried at 110 °C for 24 h) was suspended in a solution of the liquid phase: Triton-X305 (Fluka, 70%) or Squalane (Fluka, > 99%) in chloroform (Panreac, 99%). The suspension was kept stirred for 5 h under a nitrogen atmosphere. Later, solvent was removed in a rotavapor by progressive heating. Once the impregnated support is dried, palladium acetate (final catalyst will contain 3% PdAc), dissolved in an appropriate solvent (chloroform), is added to the support and this solvent is subsequently eliminated in the rotavapor.

The second solvent, which contains the palladium acetate, must be chosen in order to avoid the precipitation of metallic palladium when the mixture was heated at 70 °C for the evaporation of the solvent [13]. In the present work, chloroform and acetone have been used.

The composition of the different catalysts prepared and the structure of the liquid phases, are indicated in table 1.

2.2. Experimental

The reaction device used in this work was a micro-reactor. The micro-reactor consists of a small tube of pyrex glass (0.25 inch internal diameter, 5 cm length and with 0.54 g catalyst), packed with the catalyst and connected directly to the analytical chromatographic column, inside the oven of the chromatograph. The analytical column has been packed with a stationary phase of Triton X-305 (15%) on Chromosorb P-AW (60/80 mesh). A Hewlett-Packard 5750 chromatograph with thermal conductivity detector was used. The micro-reactor was operated either under continuous-flow of CHE or using the pulse technique with 0.1/0.2 μL of CHE injected into the carrier gas stream, before the reactor, at equal intervals. The temperature of analysis has been fixed at 80 °C and the carrier gas flow at 30 mL/min in the micro-reactor studies. Mass balance closures were checked in all the experiments by injecting known amounts of reactants and products directly in the analytical column.

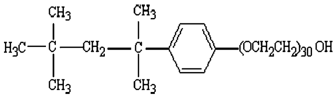
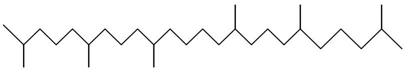
3. Results and discussion

3.1. Pulsed micro-reactor

Prior to catalytic experiments, the reaction was carried out in absence of palladium, that is, the micro-reactor was filled with the support of the SLPC impregnated with a 15% of the liquid phases (as it is used in this work) in order to discard the existence of reaction without catalyst. No chemical reaction was observed below 180 °C (100 °C in the case of triton), maximum temperature allowed by the oven.

The reaction was first studied in the micro-reactor to compare the performance of the two liquid phases mentioned in table 1. A sample of 2 μL of CHE was injected into the carrier gas flowing through the

Table 1
Composition of the catalysts

Catalysts	I	II
Liquid phase	Triton-X305	Squalane
% liquid phase	15	15
% PdAc	3	3
	 **Triton-X305**	 **Squalane**

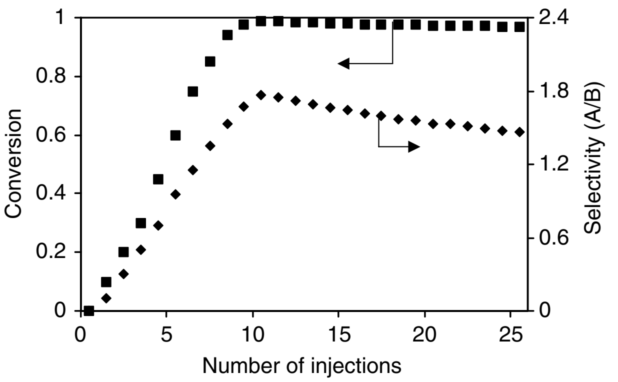


Figure 1. Variation of the conversion and the selectivity with the number of injections in the pulsing micro-reactor using catalyst I (Triton X-305).

micro-reactor (5 cm of length with 0.1–0.54 g of catalyst) at regular intervals. The conversion of CHE and the selectivity to CHA (expressed as mol of CHA produced by mol of BZ) versus. the injection number are shown in figure 1 for a catalyst load of 0.54 g of catalyst, with Triton as liquid phase. Under the same conditions, CHE was fully converted when squalane was used as liquid phase. Hence, the experiment was carried out with a catalyst load of only 0.1 g. Results corresponding to this experiment are shown in figure 2.

For both SLPC catalysts a common behaviour is observed, *viz*., an induction period, in which the conversion and selectivity for CHA increase with the number of injections. Also, after reaching a maximum value, the conversion and selectivity for CHA decrease, which means that the catalyst undergoes a deactivation process.

The behaviour of the catalyst can be explained considering the mechanism proposed in the literature [1–4,6,24]. A broad number of reaction paths take place, with a complicate interrelation between the different regimes. Five different paths in the reaction of CHE with Pd (II) were found [4], each of them with a different reaction rate. From their results, it can be concluded that the reaction of CHE in a neutral solution of palladium acetate, in absence of other oxidants, takes place in the following way; initially, some palladium (II) is reduced by the hydrocarbon, producing a metallic precipitate that is very active as an heterogeneous catalyst and a molecule of BZ. Then, the CHE disproportionates by means of an heterogeneous reaction that can be interrupted in the presence of regenerative agents that regenerate the palladium metal: in some occasions the reaction shows an induction period that ends with the appearance of deposited metal. Later on, the reaction takes place very quickly.

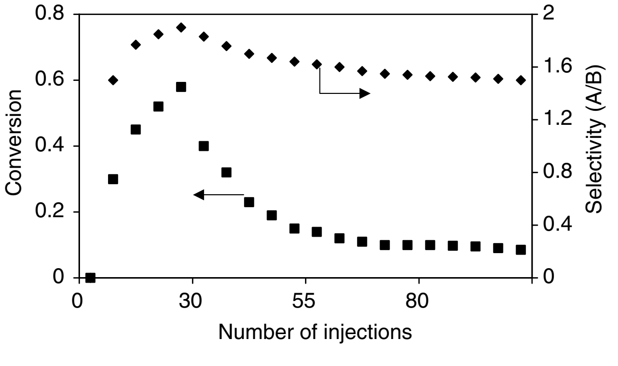
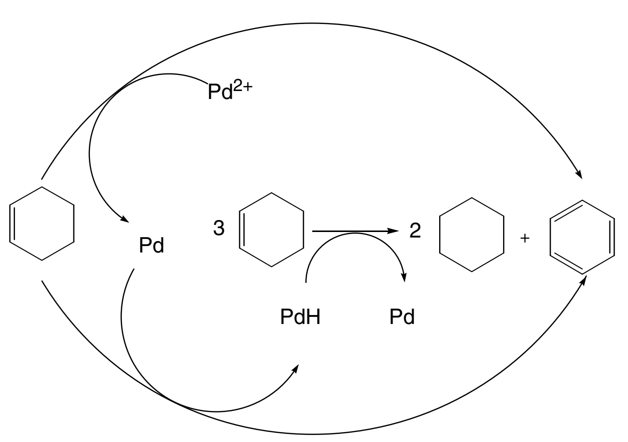


Figure 2. Variation of the conversion and the selectivity with the number of injections in the pulsing micro-reactor using catalyst II (squalane).

The disproportionation mechanism might be explained by the transfer of a hydrogen atom from the molecule of CHE to the metal on the surface, which is further transferred to another CHE molecule attached to the surface. The hydrogen atom can be transfered to an oxidant if it is present, and CHE will be oxidised to benzene. The reaction pathway is shown in scheme 1.



Scheme 1. Reaction pathaway for dehydrogenation and disproportionation of CHE over an homogeneous Pd(II) catalyst.

The reaction can be expressed as two competitive reactions, dehydrogenation (path I) and disproportionation (path II)

$$\mathrm{CHE} \rightarrow \mathrm{BZ} + 2\mathrm{H_2} \qquad [\mathrm{I}]$$

$$3\mathrm{CHE} \rightarrow 2\mathrm{CHA} + \mathrm{BZ} \qquad [\mathrm{II}]$$

Both processes can occur simultaneously depending on the experimental conditions. The ratio CHA/BZ can determine the extent of each reaction. Thus, a ratio of 2 indicates that only the disproportionation reaction takes place, whereas a ratio of 0.5 indicates that both reactions take place to the same extent.

Considering the above-mentioned mechanism, the initial induction period could be explained since disproportionation reactions involve the redistribution of hydrogen among three CHE molecules. Therefore, the main role of the catalyst is hydrogen transportation. At this point, the interaction between reduced palladium and hydrogen is stronger than that corresponding to

Pd^{2+} ions, which is its form in the SLPC catalyst. On the other hand, reaction I yields pure hydrogen, which is able to reduce Pd^{2+} to Pd at the operation conditions. So, in the first injections reaction I takes place primarily, and as H_2 is formed and reduces Pd^{2+} ions, reaction II then assumes importance. This is the cause for observing an important induction period both in the conversion (only one reaction pathway is taking place) and the selectivity for CHA. The amount of hydrogen formed by dehydrogenation of cyclohexene, even in the case of full conversion for this reaction, was two orders of magnitude lower than the needed for the total reduction of the Pd (II) present in the catalyst (in this case, one pulse of cyclohexene yields 1.4×10^{-7} mol of hydrogen, whereas for reducing all the palladium content of the catalyst 2×10^{-5} mol of H_2 are needed). So it can be inferred that both palladium species are present in the catalyst in all the experiments.

The fast catalyst deactivation may be caused by two phenomena: (i) side reactions of CHE or the reaction products (CHA and BZ); and (ii) decomposition of the stationary phases (Triton X-305) by reaction with the catalysts. It has been found [1] using TPO-MS and TPD-MS techniques, that the deactivation of heterogeneous palladium catalysts could be either due to the strong adsorption of BZ or to coke deposits generated from the adsorbed BZ. In our case, the adsorption of BZ could play an important role, as it can act as a Lewis base, stabilizing the Pd^{2+} ions. By doing so, it favours the presence of the less active form. This would explain the sharp decrease in the selectivity to CHA, since direct dehydrogenation of CHA over the oxidised palladium may occur. The presence of carbonaceous deposits, does not seem to be so important in this study, since the CHE is fed in pulses, which hinders the formation of these deposits.

Regarding the role of the liquid phases, the difference observed between Triton and squalane might be caused either by differences in their boiling points or in their chemical structures. Both factors lead to a better performance with squalane, since it has a higher boiling point (215 versus 101 °C for Triton), and is a paraffinic compound. Furthermore, Triton has aromatic and oxygenated functional groups which are electron donors, stabilizing the Pd^{2+} species, which are less reactive. For this reason, further experiments were carried out using squalane as the liquid phase.

3.2. Continuous micro-reactor

The reaction was further investigated in the same micro-reactor, with continuous feed of CHA using 1 g of catalyst II. The operating conditions were: flow rate 25 mL/min, CHE concentration of 7.3×10^{-4} mol/L in He, and N_2 and air as carrier gases. Figure 3 shows the cyclohexene conversion as a function of time in a experiment carried out at 80 °C. As expected, the catalysts behave similarly for N_2 and He and results are in a good agreement with the behaviour observed with the pulse technique. Again, an initial period of induction was observed, followed by a period of continuous deactivation.

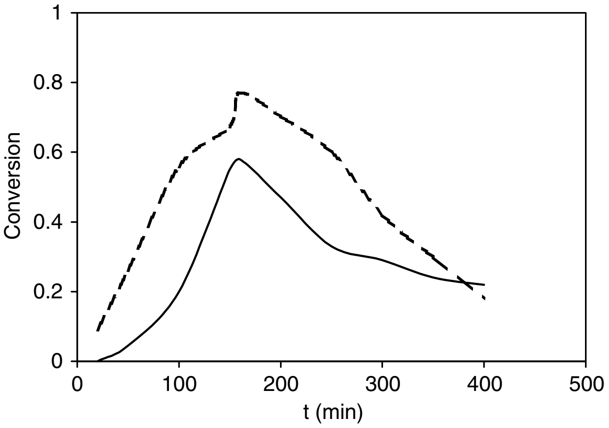


Figure 3. Conversion of CHE in the continuous micro-reactor with different carrier gases at 80 °C: nitrogen (continuous line), air (discontinuous line).

In contrast, the results obtained when air was used as the carrier gas are very different from those using nitrogen or helium. So, although the total conversion is higher when working with air, only the dehydrogenation reaction takes place, and appreciable yields for the formation of CHA are not observed. This behaviour is explained by considering that oxygen can react with the hydrogen adsorbed on Pd^0, and can even oxidise Pd^0 to Pd^{2+} so reaction (I) is favoured whereas reaction (II) disappears. This effect is noted clearly in this work, because there is not cyclohexane, except at the initial of the reaction at very low conversion.

Due to the high enthalpy of the reactions involved, it has been necessary to work with low flows of reactant and use the saturation of the diluting gas technique to feed the micro-reactor. Nevertheless, some small in-

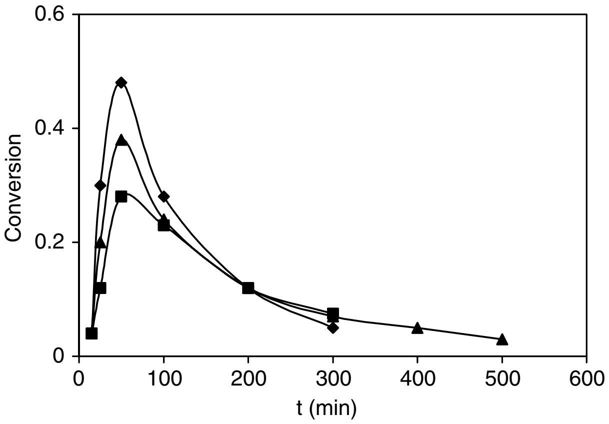


Figure 4. Variation of the conversion with the reaction time for several operation temperatures, with catalyst II: 55 °C (■), 60 °C (▲), 65 °C (◆).

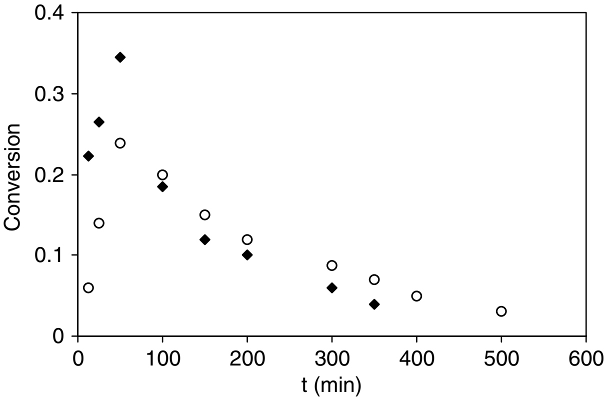


Figure 5. Variation of the conversion with the reaction time for two concentrations of CHE at the entrance of the micro-reactor: 7.3×10^{-4} mol/L (o), 11×10^{-4} mol/L (◆).

creases of below 1–1.5 °C in the catalyst bed were observed in the pulsed micro-reactor due to the small injections of the reactant, the variation of temperature in the catalyst being negligible.

The effects of the concentration of CHE ($7–11 \times 10^{-4}$ mol/L) and the temperature (55–65 °C) were also studied in the continuous micro-reactor. The results obtained are shown in figures 4 (temperature) and 5 (concentration). It was observed that the maxima in the conversion increase with the temperature and the concentration of the reactant. In all these experiments, it was observed that the selectivity remains almost constant (CHA/BZ equal to 1.4–1.6) in spite of the variation in the conversion with temperature and CHE inlet concentration.

4. Kinetic modelling

It is widely accepted that the determination of the kinetic constants in cases where the catalyst suffers fast deactivation must be determined independently of the deactivation constants. In many cases, it has not been possible to separate the reaction and deactivation processes, so it has been necessary to determine simultaneously the kinetic parameters for the main reaction and the deactivation reaction. The procedure consists of combining the kinetic and deactivation equations [25], and fitting the resulting model to the experimental results.

The deactivation rate (assuming that it is not dependent on the reactant concentration), can be expressed as

$$-\frac{da}{dt} = k_a a^{\beta} \tag{1}$$

where a is the ratio of the actual reaction rate and the reaction rate at the beginning of a given experiment. Independent deactivation is assumed, since, as mentioned before, there are several concomitant causes leading to catalyst deactivation (and it is fair to consider independent deactivation rather than have any dependence on product or reactant concentrations).

The design equation for the micro-reactor can be written as

$$\frac{Y_{Eo} - Y_{Ef}}{W/F} = (-\bar{r}_E) \approx (-r_{Eo}) \tag{2}$$

where Y_{Eo} and Y_{Ef} represent the molar fractions of the reactant (CHE) at the entrance and the exit of the micro-reactor, W is the mass of catalyst, F the molar flow rate of the reactant and $(-\bar{r}_E)$, the total reaction rate per unit mass of catalyst. The subscript, o, in $(-\bar{r}_{Eo})$ indicates that the reaction rate is considered taking the reactant concentration at the inlet of the micro-reactor.

If the reaction is considered to be first order with respect to the reactant in reactions (I) and (II), the kinetic equation for the global reaction rate will be written as

$$(-r_{Eo}) = k_1 \Theta_{Ac} C_{Eo} a + k_2 \Theta_{P} C_{Eo} a \tag{3}$$

where Θ_{Ac} and Θ_p represent the concentrations of palladium acetate and metal palladium on the catalyst, measured in mol/g catalyst. By combining equations 2 and 3, the following equation is obtained:

$$X = 1 - \frac{Y_{Ef}}{Y_{Eo}} = \frac{W C_{Eo} a}{Y_{Eo} F}(k_1 \Theta_{Ac} + k_2 \Theta_{P}) \tag{4}$$

where X is the total conversion of CHE, a variable that is measured experimentally.

It will be necessary to express Θ_{Ac},Θ_{P} and a as a function of t. If equation (1) is integrated, then

(a) if $\beta = 1$

$$a = \exp(-k_a t) \tag{5}$$

(b) if $\beta \neq 1$

$$a = [(\beta - 1)k_a t + 1]^{1/(1-\beta)} \tag{6}$$

A mass balance on the palladium acetate and metal palladium gives the following expression:

$$-\frac{d\Theta_{Ac}}{dt} = \frac{d\Theta_{P}}{dt} = k_1 \Theta_{Ac} C_{Eo} a \tag{7}$$

so

$$\Theta_{P} = \Theta_{AcO} - \Theta_{Ac} \tag{8}$$

If the equations for a are taken into account, and the equations are integrated, the following is obtained:

(a) if $\beta = 1$

$$\Theta_{AcO} = \Theta_{Ac} \exp\left[-\frac{k_1 C_{Eo}}{k_a}\{1 - \exp(-k_a t)\}\right] \tag{9}$$

(b) if $\beta \neq 1$

$$\Theta_{AcO} = \Theta_{Ac} \exp\left[\frac{k_1 C_{Eo}}{k_a(2-\beta)}\left[\{(\beta - 1)k_a t + 1\}^{(2-\beta)/(1-\beta)} - 1\right]\right] \tag{10}$$

If equations (9)/(10), (8) and (5)/(6) are substituted in equation (4), an expression of the following type is obtained:

$$X = \Gamma(t) \tag{11}$$

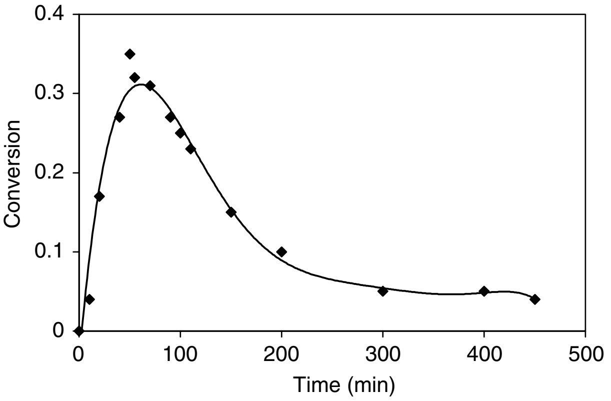


Figure 6. Example of the agreement of the proposed model with experimental data: experimental points (◆), theoretical data (■).

where Γ is a function that depends on the parameters, k_1, k_2, k_a and β, that are fitted to the experimental data.

The data corresponding to the experiments carried out in the continuous micro-reactor with squalane catalysts have been fitted to this empirical deactivation model, figure 6. The reaction conditions for this experiment are: 15 mL/min total feed flow rate, molar fraction of CHE $(Y_{E\text{o}}) = 0.04$ and reaction temperature = 55–65 °C. The fitting of the parameters which correspond to the experimental data of figure 4, was made numerically, combining the MARQUARDT method (code BSOLVE) with the isolation variable method. The results are indicated in table 2.

Figure 7 shows the Arrhenius plot for these reactions (in order to obtain the Arrhenius parameters, the data of table 2 were used). Both reactions fit the model quite well.

As figure 4 demonstrates, the deactivation of the catalyst is faster at higher temperatures. The deactivation of the catalyst with increasing reaction temperature could be attributed to the surface adsorption of the various species (principally BZ) [1]. A change in the order of deactivation is observed as the temperature increases. Although a more detailed study is needed to confirm this hypothesis, it suggests that at lower temperatures, the deactivation mechanism is different than at the two highest temperatures, for which the deactivation orders are very similar.

Table 2
Parameters values for the experiments shown in figure 6

T (°C)	k_1 (g cat/mol-g min)	k_2 (g cat/mol-g min)	k_a	β	Square difference
55	8.7×10^{-7}	5.4×10^{-7}	1.4×10^{-2}	1.2	0.0014
60	1.4×10^{-6}	8.5×10^{-7}	3.3×10^{-2}	1.5	0.0015
65	2.0×10^{-6}	1.1×10^{-8}	4.3×10^{-2}	1.5	0.0046

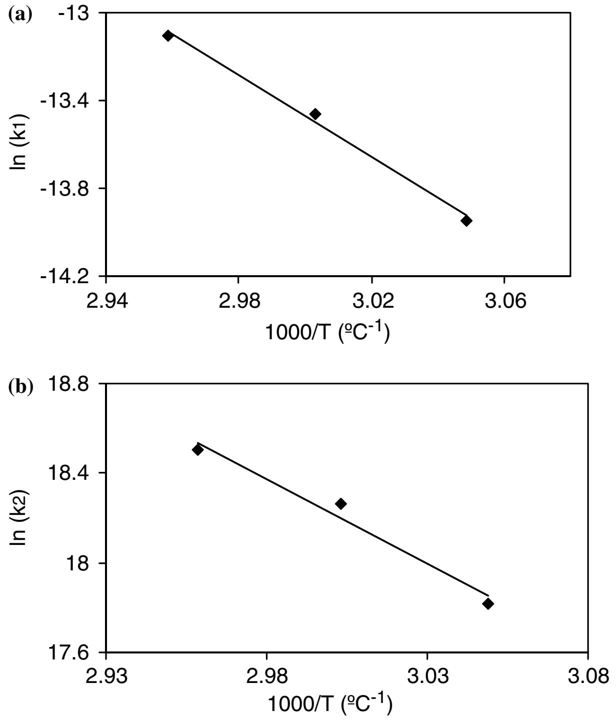


Figure 7. Fitted (continuous line) and experimental data (■) for the CHE reaction with PdAc in squalane using the pulse micro-reactor technique.

5. Conclusions

The transformation of CHE in CHA on a supported liquid phase catalyst of palladium acetate takes place *via* disproportionation and dehydrogenation. When helium or nitrogen are used as the carrier gas, disproportionation seems to prevail, and when air is used, dehydrogenation is the only reaction that takes place. The experimental data were modelled successfully for micro-reactor operation.

In the reaction study with the pulsed micro-reactor, the effects of activation and deactivation of catalyst during its life were observed.

Symbols

a	deactivation parameter
BZ	benzene
C_i	concentration of component I
CHA	cyclohexane
CHE	cyclohexene
E_A	activation energy
F	gas flow
K	deactivation constant
k_1	kinetic constant for reaction 1
k_2	kinetic constant for reaction 2
$(-r_E)$	rate of reaction per catalyst mass

$(-r_{Eo})$	rate of reaction considering the concentrations of the reactants at the inlet of the micro-reactor
t	time
TCD	thermal conductivity detector
W	catalyst mass
X	total conversion of cyclohexene
Y_{Ef}	molar fraction of cyclohexene at the exit of the micro-reactor
Y_{Eo}	molar fraction of cyclohexene at the entrance of the micro-reactor
β	deactivation order
Θ_{Ac}	palladium acetate concentration on the catalyst
Θ_{AcO}	initial palladium acetate concentration on the catalyst
Θ_{P}	palladium concentration on the catalyst

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