

# Transformation of cyclohexene on palladium catalysts: activity and deactivation

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## Abstract

The transformation of cyclohexene on palladium catalysts can take place via two competitive processes: disproportionation and dehydrogenation. A study conducted over a broad temperature range revealed that disproportionation prevails at low temperatures and dehydrogenation at high temperatures. When the reaction develops under continuous-flow conditions (viz. in a tubular reactor connected online to a mass spectrometer), a transition temperature exists for each catalyst above which hydrogen is formed in detectable amounts. Metal catalysts are strongly deactivated during the transformation of cyclohexene. This led us to examine the process by performing thermal programmed experiments, desorptions and thermal oxidations, which showed catalyst deactivation in this process to be the result of surface adsorption of benzene and carbon deposition. Finally, desorption and subsequent oxidation were found to effectively regenerate the catalysts, which thus regained their initial activity. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Palladium catalysts; Temperature-programmed reaction; Cyclohexene; Catalyst deactivation; Catalyst regeneration

## 1. Introduction

Cyclohexene (CHE) is widely used as a molecular probe in studies involving catalyst preparations [1–4]. This compound can undergo various transformations on transition metal catalysts depending on the particular metal and experimental conditions (temperature, presence or absence of hydrogen, hydrogen pressure). The main reactions involved in such transformations are dehydrogenation [5,6] and disproportionation [7,8].

While certain conditions occasionally exist where the two types of reaction can be examined separately, both are extensively overlapped in most cases. The disproportionation of CHE to benzene (BZ) and cyclohexane (CHA) is a frequently studied hydrogen-transfer reaction in metal catalysts. This is quite an interesting reaction since the reactant can act as both hydrogen donor and acceptor. The underlying mechanism is still largely speculative, the most interesting question remaining unanswered probably being how the hydrogen transfer takes place [6,9–11]. Moreover, it has been used as a model reaction for assessing catalysts [12–14].

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In this work, we studied the competitive disproportionation and dehydrogenation of CHE in a closed reactor and in the gas phase (under continuous-flow conditions), using 3% palladium catalysts on two different supports, viz. a sepiolite of the Pansil variety drawn from Vallecas (Madrid, Spain) and an  $\text{AlPO}_4\text{-SiO}_2$  mixed system. Because the catalyst is deactivated in the process, the origin of the deactivation and its potential regeneration were also investigated.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The catalysts used contained 3% Pd supported on (a) a Spanish sepiolite supplied by TOLSA (Vallecas) labelled SEP or (b) an 80:20  $\text{AlPO}_4\text{-SiO}_2$  mixed system labelled PM2. The procedure used to prepare the supports is described in detail elsewhere [15,16]. The metal was deposited by using the method of impregnation to incipient wetness, with  $\text{Na}_2\text{PdCl}_4$  as the precursor salt. The pretreated support was placed in a flask and supplied with appropriate amounts of precursor and aqueous sodium hydroxide. The flask was then placed on a rotavapor and stirred for 24 h, after which the solvent was evaporated in vacuo. Subsequently, the mixture was dried in a stove at 110–120°C for 24 h and ground to fine particles. Finally, the resulting powder was calcined in a furnace at a linearly increasing temperature up to 210°C, which was held for 30 min.

The deposited metal salt was reduced in a hydrogen flow system consisting of a furnace into which the material to be reduced was inserted inside a glass U-tube. The gas flow-rate was set at 120 ml  $\text{min}^{-1}$ . The reduction programme started at 110°C, which was held for 1 h and then raised linearly at 2°C  $\text{min}^{-1}$  up to 220°C, which was held for 10 min. The U-tube was then removed from the furnace and allowed to cool to room temperature under a hydrogen stream at a constant flow-rate. Thermal pro-

grammed reduction profiles confirmed that the temperature programme used ensured complete reduction of palladium on the support surface [17].

Supports and metal catalysts were characterized from nitrogen adsorption–desorption isotherms recorded on a Micromeritics ASAP 2000 porosimeter. Their specific areas were obtained by using the BET method [18]. The acid–base properties of the support were determined by using a thermal programmed desorption-mass spectrometric method with two different types of probe (pyridine for acid sites and  $\text{CO}_2$  for basic sites) as described elsewhere [19,20]. The mean particle size ( $d$ ), metal surface area ( $S$ ) and metal dispersion ( $D$ ) of the catalysts were determined by transmission electron microscopy (TEM).

## 3. Experimental set-up

Closed-system reactions were carried out in a Berghof reactor. The reactant mixture consisted of 6 ml (59.16 mmol) of CHE in methanol (total volume 20 ml) and 50 mg of catalyst  $\text{Pd}_3\text{SEP}$ . After an appropriate reaction time, the mixture was cooled down and analysed on a Hewlett-Packard 5890 gas chromatograph. Prior to the reactions proper, the absence of diffusion control was checked under the above-mentioned conditions. A shaking rate of 1700 rpm and a catalyst grain diameter less than 0.149 mm ensured the absence of diffusion control (internal and external).

Gas-phase isothermal reactions were conducted in a 150-mm (length)  $\times$  12 mm (ID) conventional continuous-flow reactor at atmospheric pressure and a constant temperature. A fresh catalytic bed containing 100 mg of  $\text{Pd}_3\text{PM2}$  was held between two layers of glass wool, the remaining reactor volume being packed with glass beads in order to ensure homogeneous mixing and complete vaporization prior to contact with the catalyst bed. The products emerging from the reactor were collected

Table 1  
Peaks monitored by the mass spectrum during the thermal programmed experiments

Compound	$m/z$	Relative intensity
Cyclohexene	82	40
Cyclohexane	84	72
1,3-Cyclohexadiene	79	100
Benzene	78	100
Hydrogen	2	100

and analysed in the gas chromatograph. Diffusional effects from the boundary layer and internal or external mass-transfer processes on catalytic runs were avoided by using appropriate operating conditions (viz. a reactor feed rate of 12 ml h<sup>-1</sup> and a nitrogen flow-rate of 120 ml min<sup>-1</sup>).

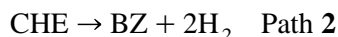
Temperature-programmed experiments [viz. reactions (TPR–MS), desorptions (TPD–MS) and oxidations (TPO–MS)] were carried out in a flow-through reactor that was fitted to a VG Sensorlab quadrupole mass spectrometer from Fisons Instruments/VG Quadrupoles (East Sussex, UK) operating in the Multiple Ion Monitoring mode. The temperature inside the reactor was controlled to within 1°C throughout each experiment by means of a thermocouple attached to its walls. Temperature-programmed reactions were carried out into two steps, viz. an isothermal period (100°C for 30 min) that was followed by a rise in temperature from 100 to

600°C at a constant rate of 10°C min<sup>-1</sup>. The gas feed was a nitrogen stream that was passed at a flow-rate of 50 ml min<sup>-1</sup> through a saturator loaded with CHE at 30°C. An amount of 100 mg of catalyst [Pd<sub>3</sub>PM2] was used. The entire process was monitored by a mass spectrometer. The monitored peaks for each compound and their relative intensities are shown in Table 1.

#### 4. Results and discussion

Table 2 summarizes the chemical textural and metal properties of the supports (SEP and PM2) and catalysts studied [Pd<sub>3</sub>SEP and Pd<sub>3</sub>PM2]. The most salient result is the decreased surface of the support upon deposition of the metal.

CHE can undergo two competitive transformation reactions, viz. disproportionation (path 1) and dehydrogenation (path 2):



The disproportionation reaction involves the redistribution of hydrogen among three CHE molecules to form CHA and BZ; on the other hand, the dehydrogenation reaction yields BZ and hydrogen. Both process can occur simultaneously to a varying extent depending on the experimental conditions. By examining changes

Table 2  
Textural, acid–base and metallic properties of the supports and catalysts studied

Properties	PM2	Pd <sub>3</sub> PM2	SEP	Pd <sub>3</sub> SEP
<i>Textural</i>				
Specific surface area, $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	402	241	121	71
Pore volume, $V_p$ (Å <sup>3</sup> )	0.36	0.30	0.36	0.32
Mean pore radius, $r_p$ (Å)	141	50	141	180
<i>Acid–base</i>				
Acidity (μmol <sub>PY</sub> g <sup>-1</sup> )	115	–	84	–
Basicity (μmol <sub>CO<sub>2</sub></sub> g <sup>-1</sup> )	–	–	46	–
<i>Metallic</i>				
Mean particle diameter, $d$ (Å)	–	62	–	144
Metal surface area, $S$ (m <sup>2</sup> g <sub>Pd</sub> <sup>-1</sup> )	–	81	–	35
Metal dispersion, $D$ (%)	–	18	–	8

in the CHA/BZ ratio, one can determine to what extent each reaction develops. Thus, a ratio of 2 is indicative of exclusive disproportionation; a ratio of zero indicates pure dehydrogenation; and a ratio of 0.5 means that both reactions take place to the same extent.

#### 4.1. Liquid-phase transformation of cyclohexene in a closed reactor

Fig. 1 shows the CHA/BZ ratios and initial reaction rates ( $\text{mmol s}^{-1} \text{g}_{\text{Pd}}^{-1}$ ) obtained in the transformation of CHE on catalyst  $\text{Pd}_3\text{SEP}$  over the temperature range 60–170°C in the closed reactor.

In a previous work [21], we found for the liquid-phase disproportionation of CHE in an open reactor, that the increasing temperatures and/or reaction time result in gradually decreasing CHA/BZ ratio as a result of the conversion of CHA originally formed in the disproportionation. In this work, the CHA/BZ ratio obtained at both low temperatures and contact times was close to 2 (i.e., pure disproportionation). This behaviour is showed in Fig. 1 (dotted line).

However, in a closed reactor the initial CHA/BZ ratio starts at about 1.3 (at 65°C) to

experience a further increase to reach 1.8 at around 90°C. Those results, in the low temperature range, seem to disagree with those obtained in open reactor [21]; however, those data were obtained at a very low CHE conversion (2% or lower) and therefore could be of low significance. Moreover, small differences in the CHZ/BZ ratio for the open and closed systems could be due to differences in the contact time. On the other hand, for higher CHE conversions, the behaviour is similar for that obtained in a open system [21]. Thus above 90°C, the ratio dropped abruptly to about 0.5 at 170°C. This suggests more extensive dehydrogenation at increased temperatures, so both reactions take place in the same extent at temperatures above 170°C. Moreover, at higher temperatures, CHA can be dehydrogenated to BZ lowering the final CHA/BZ ratio as reported previously [21]. The initial reaction rate increased gradually with increasing temperature, especially above 100°C, temperature at which the CHE conversion is high enough to get reliable results.

#### 4.2. Temperature-programmed experiments

Temperature-programmed reactions allow one to examine the transformation of CHE over a

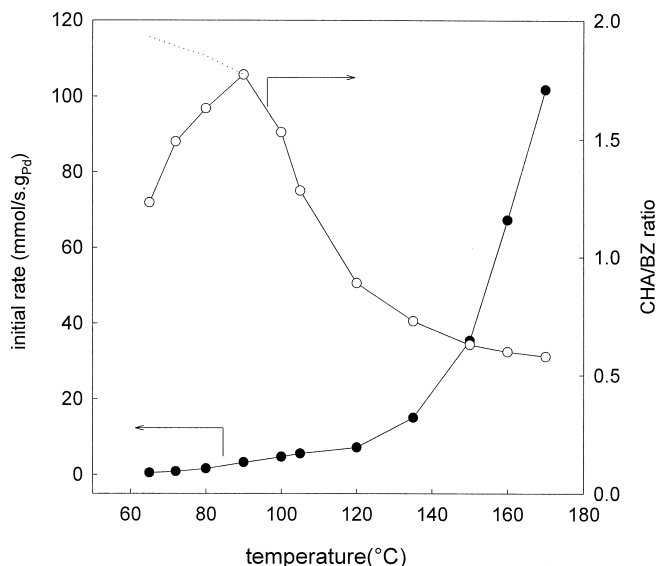


Fig. 1. Initial rates (●) and CHA/BZ ratios (○) obtained in the transformation of CHE on catalyst  $\text{Pd}_3\text{SEP}$  in a closed reactor.

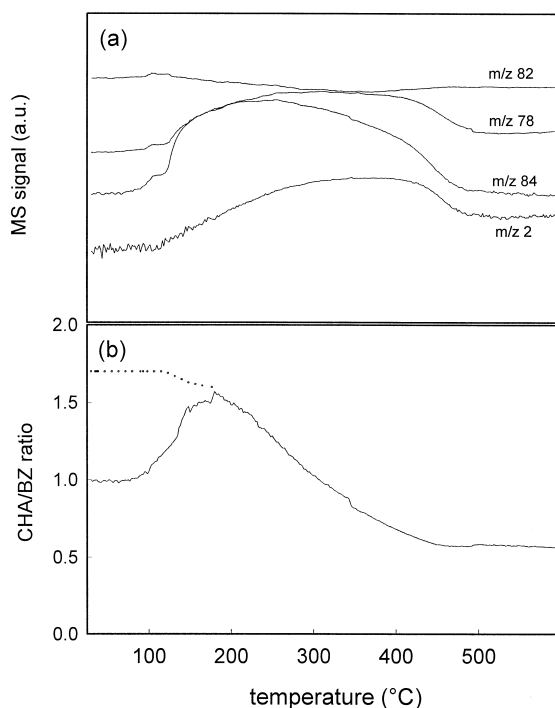


Fig. 2. TPR–MS profile for CHE on catalyst Pd<sub>3</sub>SEP. (a) Partial pressures recorded by the mass spectrometer [*m/z* 82 CHE, *m/z* 84 CHA, *m/z* 78 BZ, *m/z* 2 hydrogen]. (b) Variation of the CHA/BZ ratio.

broad temperature range. Fig. 2 shows the results for a thermal programmed process (TPR–MS) involving catalyst Pd<sub>3</sub>PM2 over the temperature range 100–600°C. Fig. 2a shows the variation of the four monitored signals (CHE, CHA, BZ and hydrogen), and Fig. 2b that of the CHA/BZ ratio, with temperature. As can be seen from Fig. 2b, changes in the CHA/BZ ratio with temperature are similar to those observed in the closed reactor (Fig. 1) except for a slight shift in the reaction temperatures. The values of CHA/BZ obtained at low temperatures have not been plotted since the CHA conversion was too low and therefore the results were not reliable. Moreover, small differences in that ratio could be accounted on differences in the contact time in both static and flow systems.

The CHA/BZ ratio peaks at 184°C, where disproportionation prevails over dehydrogenation (CHA/BZ = 1.63). Above this tempera-

ture, the ratio decreases — which indicates that dehydrogenation gains significance with respect to disproportionation — coinciding with a marked increase in the hydrogen signal and a decrease in the CHE signal (Fig. 2a). Temperature-programmed reactions of CHA as reactant (Fig. 3) confirmed that, above 185–190°C, CHA is also transformed into BZ and hydrogen.

Using a mass spectrometer coupled online to a flow reactor (i.e., an experimental set-up similar to that employed in our experiments), Rebhan and Haensel [7] obtained results similar to ours with a wide variety of metal catalysts. These authors identified a transition temperature, which we shall denote by  $\theta$ , in the competitive disproportionation–dehydrogenation of CHE below which no hydrogen was detected. For catalyst Pd<sub>3</sub>PM2, such a temperature ( $\theta$ ) is about 100°C. In addition, the transition temperature depends on the catalyst properties (viz. the specific metal and its proportion, its dispersion, the type of support used). Thus,  $\theta$  is 90°C for 5% Pd, 70°C for 66% Ni/Kieselguhr and 110°C for 0.8% Pt (all supported on alumina) as reported by Rebhan and Haensel [7].

#### 4.3. Gas-phase transformation of cyclohexene in a continuous-flow reactor

Isothermal reactions conducted over the temperature range from 150 to 250°C (above the

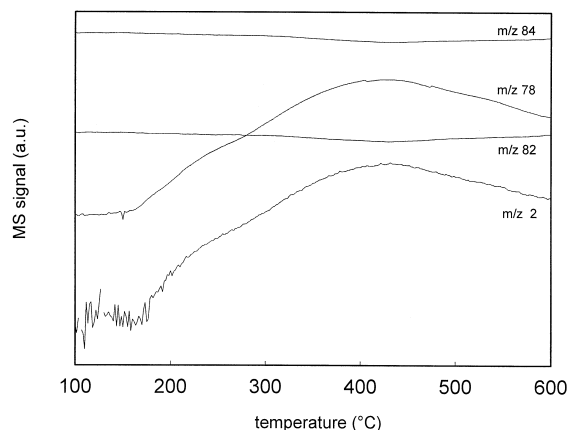


Fig. 3. TPR–MS profile for CHA on catalyst Pd<sub>3</sub>PM2 [*m/z* 82 CHE, *m/z* 84 CHA, *m/z* 78 BZ, *m/z* 2 hydrogen].

transition temperature) provided the activity profiles (total CHA conversion vs. time) shown in Fig. 4. As can be seen, the initial portion suggests rapid deactivation of the catalyst — the higher the reaction temperature the more marked the effect — followed by a more gradual decrease in catalytic activity that leads to a constant conversion. The origin of the deactivation was investigated by performing thermal programmed desorptions and oxidations in combination with mass spectrometry (TPD–MS and TPO–MS, respectively).

As can be seen from Fig. 5, which shows the product distribution profile and the variation of the CHA/BZ ratio with time at a given temperature (250°C), the CHA/BZ ratio decreased as the reaction developed. This indicates that as the reaction developed the dehydrogenation is favoured against disproportionation. If we accept that disproportionation requires large ensembles of active sites to closely adsorb three molecules of cyclohexene as stated in path **1**, then the deactivation of the catalyst reduces the population of such ensembles by poisoning part of the palladium active sites. This deactivation does not affect

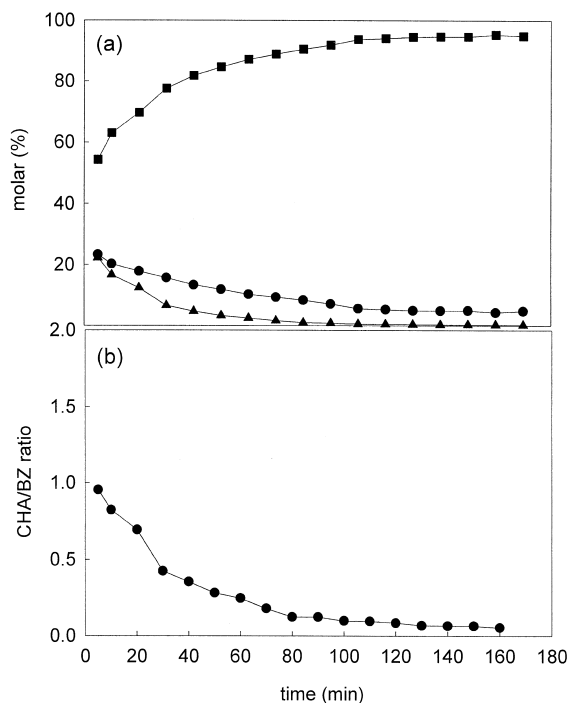


Fig. 5. (a) Product distribution profiles [(■) CHE, (●) BZ, (▲) CHA] and (b) variation of the CHA/BZ ratio with the reaction time, both at 250°C.

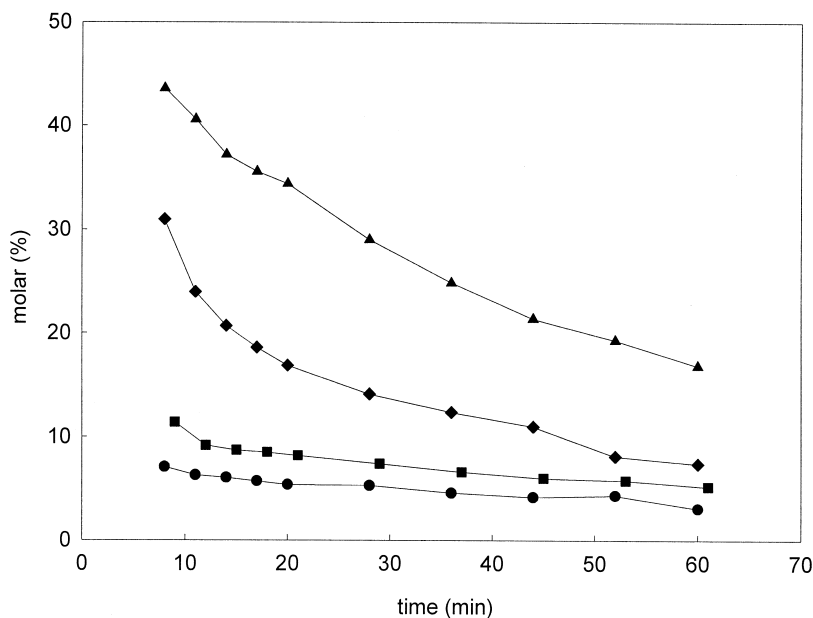


Fig. 4. Deactivation profiles obtained during the transformation of CHE on catalyst Pd<sub>3</sub>PM2 at (●) 150, (■) 200, (◆) 225 and (▲) 250°C.

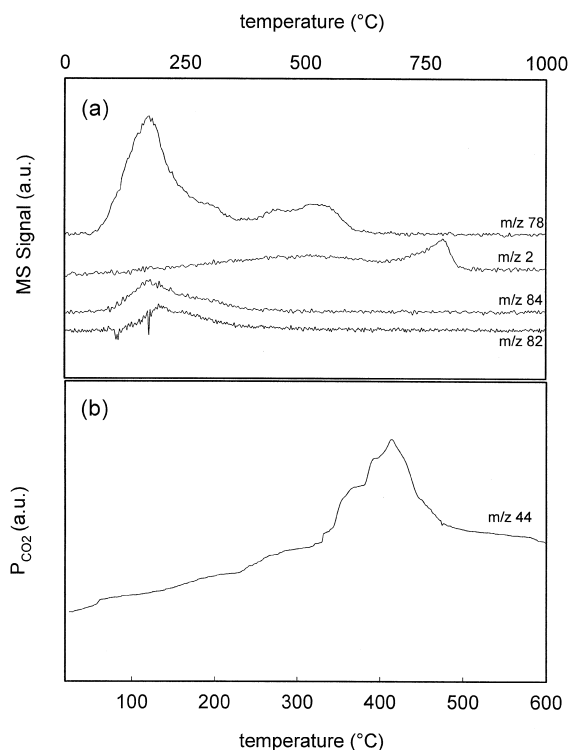


Fig. 6. TPD-MS (a) and TPO-MS profiles (b) obtained following isothermal reaction on catalyst Pd<sub>3</sub>PM2 at 200°C [*m/z* 82 CHE, *m/z* 84 CHA, *m/z* 78 BZ, *m/z* 2 hydrogen, *m/z* 44 carbon dioxide].

directly to dehydrogenation since single active sites are required according to path 2.

#### 4.4. Deactivation of the catalysts

In order to obtain more information about the primary causes of deactivation, we performed, after an isothermal reaction, TPD-MS and TPO-MS experiments. These experiences lead us to identify a two-fold origin for the previously observed catalyst deactivation phenomenon. Fig. 6 a and b shows the TPD-MS and TPO-MS profiles, respectively, obtained after an isothermal reaction on catalyst Pd<sub>3</sub>PM2 at 200°C. Thus, TPD-MS profiles (Fig. 6a) revealed the presence of strongly adsorbed species (largely BZ) on the catalyst surface. Also, a TPO-MS profile (Fig. 6b) run by using an oxygen stream containing 2% O<sub>2</sub> exhibited a CO<sub>2</sub> peak suggesting the presence of carbon on the catalyst surface. Therefore, the presence of both strongly adsorbed species and deposited carbon appears to be the origin of the catalyst deactivation.

Finally, we investigated the possibility of regenerating the catalyst after use in an isothermal reaction at 200°C. The process is summarized in Fig. 7. After the isothermal reaction (step 1), a clean-up operation with N<sub>2</sub> at 60 ml min<sup>-1</sup> at room temperature for 24 h was performed, followed by TPD to a final temperature of 220°C at a rate of 5°C min<sup>-1</sup>. A new reaction

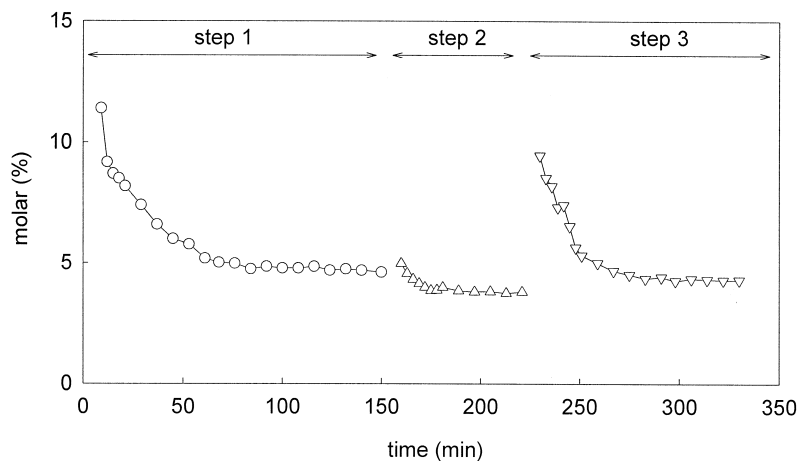


Fig. 7. Regeneration of catalyst Pd<sub>3</sub>PM2 after use in the isothermal transformation of CHE at 200°C.

(step 2) revealed that the catalyst was scarcely regenerated and hence that the strong deactivation observed was not exclusively due to the adsorption of BZ. In a subsequent experiment, the desorption process was followed by TPO with an oxygen stream containing 2% O<sub>2</sub> up to 220°C (at 5°C min<sup>-1</sup>) and by cooling to 110°C. The catalyst was then reduced in a stream of hydrogen containing 10% H<sub>2</sub> that was circulated at a flow-rate of 120 ml min<sup>-1</sup>. The last step (3) was a new reaction that provided conversions similar to those of the first profile.

This experiment seems to indicate that BZ desorbed at 220°C is not responsible for the deactivation of the catalyst. However, since the burn out of the carbon deposited lead to the regeneration of the initial activity, those carbonaceous species are mainly responsible for the loss of activity. We can not exclude, however, the effect of BZ strongly adsorbed on the catalyst since it could be considered as a precursor species that finally form the carbonaceous deposits (with a low H/C ratio). Mariey et al. [22] reached similar conclusions by using the FTIR technique in regeneration experiments involving acid zeolites.

## 5. Conclusions

The transformation of CHE on supported palladium catalysts can take place via two competitive reactions (viz. disproportionation and dehydrogenation) the extent of which can be inferred from the CHA/BZ ratio in the products. Based on the changes in both processes with temperature, disproportionation seems to prevail at low temperatures and dehydrogenation to compete with it to an increasing degree as the temperature is raised.

In continuous-flow reactions performed in a tubular reactor coupled online to a mass spectrometer, a point called the “transition temperature” ( $\theta$ ) exists below which no free hydrogen is detected. Such a temperature is characteristic of each catalyst [e.g.,  $\theta = 100^\circ\text{C}$  for Pd<sub>3</sub>PM2].

This suggests that the use of CHE as hydrogen donor in hydrogen-transfer reductions requires high temperatures (above  $\theta$ ) for hydrogen to be formed in the medium.

The strong deactivation of the catalyst observed in the isothermal reactions, which increases with increasing reaction temperature, could be assigned to the surface adsorption of various species (mostly BZ) and to the deposition of carbon, as inferred from the results of TPD and TPO experiments.

In any case, the catalyst regains virtually its whole activity by desorption, oxidation (to remove adsorbed species and deposited carbon) and reduction with molecular hydrogen.

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