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# Oxidation of Cyclohexane with Molecular Oxygen Catalyzed by $SiO_2$ Supported Palladium Catalysts

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**Abstract** The di(ethylthio)ethane palladium (**A**) and di(ethylthio)propane palladium (**B**) complexes have been immobilized on the surface of silica gel and these catalyst systems are shown to serve as effective supported Pd catalysts for cyclohexane oxidation with $O_2$ under solvent free condition. The supported catalyst **A** provides best results (overall ca. 16.2% conversion, with a selectivity of 72 or 24% for cyclohexanol or cyclohexanone, respectively, which are further promoted in the presence of 2-pyrazinecarboxylic acid which acts as a co-catalyst (overall ca. 21.2% conversion).

**Keywords** Heterogeneous system · Pd catalysts · Cyclohexane · Dioxygen · Mechanism

## 1 Introduction

Selective oxidation of hydrocarbons by supported transition metal catalysts [1–4] with dioxygen produces oxigenated products, such as epoxides, ketones, aldehydes, alcohols and acids that find wide applications [5]. Oxidation catalysts account for about 18% of the total catalyst used in the USA [6]. Therefore, establishment of greener oxidation prosseses is much importance [7]. Most of cyclohexane oxidation processes involve more than two reaction stages, and tend to use either chlorine or organic peroxides. In the first case, chlorinated organic intermediates are neutralized to form organic oxygenates and producing huge amounts of chloride salts and lesser, but significant, amounts of toxic chlorinated organic by-products. The other alternative, i.e. the use of peroxides is expensive [8] and accompanied by the formation of the by-products and therefore it is economically disadvantageous. So the prospect of operate with the ideal "green" oxidant, i.e. dioxygen for oxidative functionalization reactions of cyclohexane, constitute main aims of the current study [9, 10]. A contribution towards widening the use of Pd in catalysis is also an objective of this work.

We have selected cyclohexane as the substrate in view of the relevance of its partially oxidized products (cyclohexanol and cyclohexanone, *known as KA oil*) for the production of adipic acid, which are further used in the manufacture of nylon-6,6 [11]. Normally, cobalt naphthenate or cobalt acetate have been used for the industrial oxidation reaction, with dioxygen as oxidant, at above 150 °C, and only a low conversion (ca. 4%) is achieved to obtain a high selectivity (ca. 85%) towards a mixture of KA oil [12]. Studies have been undertaken to develop new selective catalytic systems with a higher activity under mild conditions using different oxidizing agents (e.g. $H_2O_2$, TBHP, $O_2$ and O) [13, 14]. Heterogeneous catalysts are often oxides or metal cations incorporated in inorganic supports (e.g. silica, alumina, zeolites or aluminophosphates), while promoters can be used to reduce the induction period and to increase the selectivity for the target products [15, 16]. The other oxidation catalysts, transition metal-substituted heteropoly compounds (heteropolyoxometalates), can exhibit activity towards the oxidation of alkanes, quite effectively [13, 17]. In this article we report that di(ethylthio)ethane palladium (**A**) and di(ethylthio)propane palladium (**B**) catalysts have been

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immobilized on the surface of silica and these catalyst systems act as efficient and selective heterogeneous catalysts for the oxidation of cyclohexane by molecular oxygen, under solvent free condition.

## 2 Experimental

### 2.1 Materials and Methods

Trimethoxy(vinyl)silane ($C_5H_{12}O_3Si$); 1,2-ethanedithiol ($HSCH_2CH_2SH$); 1,3-propanedithiol ($HS(CH_2)_3SH$); palladium(II)acetate ($Pd(O_2CCH_3)_2$); picolinic acid ($C_6H_5NO_2$); bromotrichloromethane ($BrCCl_3$); diphenylamine $(C_6H_5)_2NH$; cyclohexane ($C_6H_{12}$); silica gel ($SiO_2$), (Aldrich); 2-pyrazinecarboxylic acid ($C_{12}H_{10}N_4O_3$); 2,6-pyridinedicarboxylic acid ($C_7H_5NO_4$), triphenylamine $(C_6H_5)_3N$ (Janssen) were used as received.

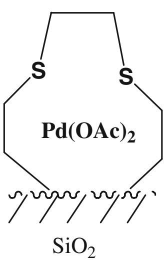
All the synthetic work was performed under dinitrogen atmosphere using standard Schlenk techniques. The solvents were dried and degassed by standard method. The silica supported di(ethylthio)ethane palladium (**A**) and di(ethylthio)propane palladium (**B**) catalysts were prepared according to literature procedures [18].

### 2.2 Preparation of Dithio Ligand, Supported on Silica

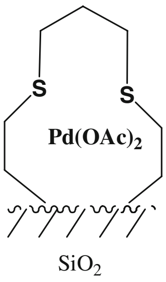
The timethoxy(vinyl)silane, $C_5H_{12}O_3Si$ (67 mL, 0.44 mol) was added separately with 1,2-ethanedithiol (20 mL, 0.2 mol) or 1,3-propanedithiol (20 mL, 0.2 mol) in Schlenk and the reaction mixtures were stirred for 1 h at room temperature. After that the volatiles were removed by vacuum at 100 °C and the resultant colourless oil [18] was separately dissolved in toluene (20 mL) and the solution was add to silica gel (15 g, each) and mixture refluxed, for 8 h. After the completion of the reaction, the mixture was filtered and the modified silica residue was washed with MeOH and then it was dry to obtain the modified silica gel.

### 2.3 Preparation of Final Pd Supported Catalysts

A solution of palladium acetate, $Pd(C_2H_3O_2)_2$ (0.16 g, 0.7 mmol) in THF (40 mL) was added separately to silica gel supported di(ethylthio)ethane (2 g) or di(ethylthio)propane (2 g). The reaction mixture was stirred for 12 h and the colorless material was filtered from orange solid. It was washed with THF and then dried under vacuum at 60 °C to obtain the final silica supported di(ethylthio)ethane palladium (**A**) catalyst and silica supported di(ethylthio)propane palladium (**B**) catalyst. All the analytical results are in accordance with the data reported elsewhere [18]. The final structures of Pd catalysts are given below:



Silica supported di(ethylthio)ethane palladium catalyst (**A**)



Silica supported di(ethylthio)propane palladium catalyst (**B**)

### 2.4 Instrumentation

Infrared spectra (4,000–400 $cm^{-1}$) were recorded on a Jasco FTIR-430 spectrometer in transmission mode using KBr pellets. $^1H$, $^{13}C$ and $^{29}Si$ solid NMR spectra were recorded on a Varian Unity 400 spectrometer at ambient temperature. The C, H, N and O, S elemental analyses results were carried by CE440 Elemental analyzer. Gas chromatography (GC) was carried out with a FISONS Instruments GC 8000 series gas chromatograph equipped with a FID detector and a DB-WAX capillary column (length: 30 m; internal diameter: 0.32 mm). GC-MS analysis was performed by using this spectrometer with a coupled gas chromatograph Carlo Erba Instruments, Auto/HRGC/MS. Thermogravimetric analysis (TGA) of the catalyst was performed at a Setaram TG/DTA/DSC-92 instrument. The palladium metal content of the final catalyst was determined by Inductive Couple Plasma (ICP) using a Perkin Elmer Plasma-400 (the sample was digested in hot $H_2SO_4 + HF + HNO_3$ solution).

### 2.5 Typical Oxidation Procedure

The oxidation reactions were preformed in a high pressure stainless steel cylindrical rocking batch reactor (22 mL capacity), provided with a gas delivery inlet and a pressure gauge. The inside temperature was controlled by a suitable thermocouple for temperature sensing. In typical conditions, 3.0 mL (27.8 mmol) of neat cyclohexane and 20 mg of supported Pd catalyst were used for 8 h. At the end of the reactions, the supported catalysts, whose colours had turned into light brown, were separated from the solutions by filtration, and washed three times with acetone. The supported catalysts could be reactivated for further use by heating in an air oven at 60 °C for 8 h. The reaction products were analyzed by GC (30 μL of hexanone added as internal standard to 1.0 mL of the filtered final reaction solution). The temperature of injection of the chromatograph was 240 °C (see Sect. 2.3). The initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min to 180 °C, and held at this temperature for 1 min. Helium was used as the carrier gas. They were further analysed by GC-MS measurements. The yields (moles of product per mole of cyclohexane) were estimated.

## 3 Results and Discussion

We have tested silica gel supported di(ethylthio)ethane palladium catalyst (**A**) and silica gel supported di(ethylthio)propane palladium catalyst (**B**) in the oxidation reaction of cyclohexane by dioxygen to obtain cyclohexanol, cyclohexanone and by-products (i.e. *n*-valeric acid, succinic acid, adipic acid, it was conform by HPLC analysis.): the experimental results show that they serve as effective heterogeneous catalysts for such a reaction without the need of using any additive (run 4, Table 1). The supported palladium **A** catalyst provides the best conversion results (overall ca. 16.2% conversion, run 4, Table 1, with $p(O_2) = 10$ atm, 150 °C, 10 h) in comparison with those of the other silica gel supported Pd (**B**) catalyst (overall ca. 11.4% conversions to cyclohexanol and cyclohexanone of 8.1 and 2.1%, respectively, with $p(O_2) = 10$ atm, 150 °C, 10 h) and therefore we focused our catalytic studies on the former supported Pd (**A**) catalyst. Blank experiments with unmodified silica, but without the Pd catalyst, were also examined, giving maximum conversions to cyclohexanol and cyclohexanone of 1.1 and 0.3%, respectively (under the same conditions of run 4, Table 1). This low conversions, although detectable, activity can result, at least in part, from the effect of the autoclave walls [19], but this was not investigated further, in the present study, in view of its low significance. The strong smell at the end of the reaction, when carried out in the presence of the Pd catalysts, indicated the product formation which was further confirmed by GC and GC-MS analyses that allow to quantify the amounts of KA oil as the main products and very little amount of acids formed as by product. As a result of the chemical reaction, the colour of the supported Pd (**A** and **B**) catalysts changed to dark brown. The cyclohexane conversions and the effects of temperature, time, oxygen pressure, amount of catalyst, other catalysts and co-catalysts are summarized in Tables 1–4.

The *effect of temperature* on the oxidation reaction of cyclohexane was examined by varying it up to 200 °C (Table 1, runs 1–6 and Fig. 1 for $p(O_2) = 10$ atm, 10 h time). For each of the products, the conversion increases slowly until ca. 125 °C (overall 10.4%) beyond which a sharp increase occurs until 150 °C (overall 16.2%). At 200 °C, an overall conversion of 20.5% is achieved but the

**Table 1** Effect of temperature on the oxidation of cyclohexane by dioxygen in the presence of silica gel supported palladium (**A**) catalyst[a]

| Run no. | Temperature (°C) | Percentage conversion[b] | | | |
|---|---|---|---|---|---|
| | | Over all | Cyclohexanol | Cyclohexanone | Other products |
| 1 | 75 | 3.8 | 2.4 | 0.7 | 0.7 |
| 2 | 100 | 7.3 | 4.8 | 1.5 | 1.0 |
| 3 | 125 | 10.4 | 7.3 | 2.2 | 0.6 |
| 4 | 150 | 16.2 | 11.7 | 3.9 | 0.7 |
| 5 | 175 | 18.0 | 12.8 | 4.3 | 0.9 |
| 6 | 200 | 20.5 | 13.4 | 4.4 | 2.7 |

[a] Reaction conditions (unless stated otherwise): supported Pd (**A**) catalyst = 25 mg, $O_2$ pressure = 10 atm, $C_6H_{12}$ = 3.0 mL, 10 h, micro reactor = 18 mL capacity, measured at 24 °C

[b] Molar yield (%) based on moles of product per mole of cyclohexane

**Table 2** Effect of pressure on the oxidation of cyclohexane by dioxygen in the presence of silica gel supported palladium (**A**) catalyst[a]

| Run no. | Oxygen pressure (atm) | Percentage conversion | | | |
|---|---|---|---|---|---|
| | | Over all | Cyclohexanol | Cyclohexanone | Other products |
| 1 | 5 | 6.4 | 4.5 | 1.5 | 0.4 |
| 2 | 10 | 16.2 | 11.7 | 3.9 | 0.7 |
| 3 | 15 | 18.1 | 12.3 | 4.5 | 1.7 |
| 4 | 20 | 19.8 | 11.9 | 5.2 | 2.8 |
| 5 | 25 | 21.4 | 12.2 | 5.6 | 3.6 |

[a] Reaction conditions (unless stated otherwise): supported Pd (**A**) catalyst = 25 mg, temp. = 150 °C, $C_6H_{12}$ = 3.0 mL, 10 h, micro reactor = 18 mL capacity, measured at 24 °C

**Table 3** Effect of reaction time on the oxidation of cyclohexane by dioxygen in the presence of silica gel supported palladium (**A**) catalyst

| Run no. | Time (h) | Percentage conversion | | | |
|---|---|---|---|---|---|
| | | Over all | Cyclohexanol | Cyclohexanone | Other products |
| 1 | 5 | 2.6 | 2.0 | 0.6 | 0 |
| 2 | 10 | 16.2 | 11.7 | 3.9 | 0.7 |
| 3 | 15 | 17.8 | 12.5 | 3.7 | 1.6 |
| 4 | 30 | 20 | 13.2 | 3.8 | 3.0 |

[a] Reaction conditions (unless stated otherwise): supported Pd (**A**) catalyst = 25 mg, temp. = 150 °C, $C_6H_{12}$ = 3.0 mL, 10 h, micro reactor = 18 mL capacity, measured at 24 °C

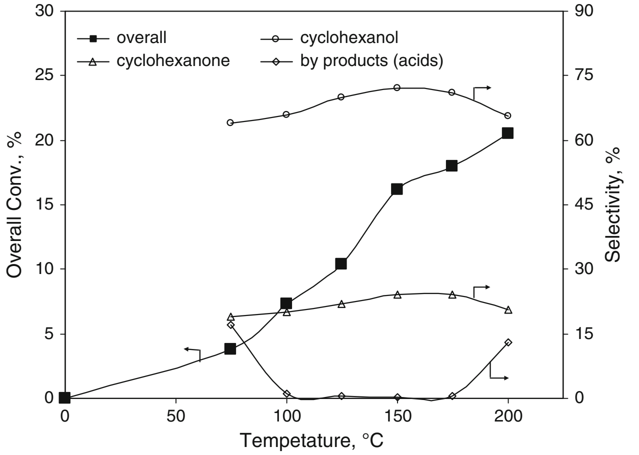


**Fig. 1** Temperature effect on cyclohexane conversion and selectivity, upon oxidation by $O_2$, in the presence of the silica gel supported Pd (**A**) catalyst ($p(O_2)$ = 10 atm, reaction time = 10 h, Catal. = 25 mg)

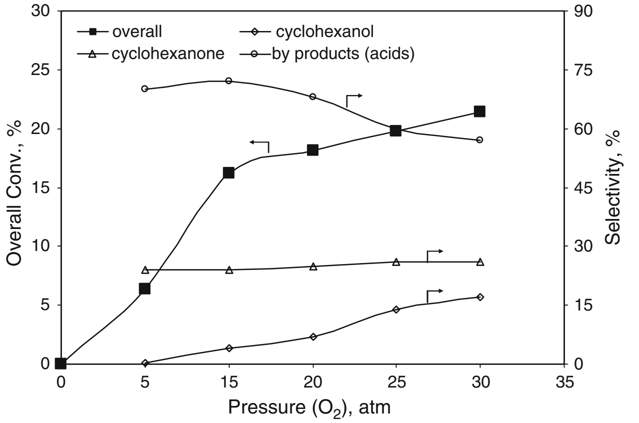


**Fig. 2** Pressure effect on cyclohexane conversion and selectivity, upon oxidation by $O_2$, in the presence of the silica gel supported Pd (**A**) catalyst (temp. = 150 °C, time = 10 h, Catal. = 25 mg)

reaction temperature was not allowed to go beyond this value due to the formation of a slight amount of an unidentified black material. The dependence of the selectivity with the temperature is shown in Fig. 1 which indicates little effect in the 100–175 °C range, with relatively good cyclohexanol and cyclohexanone selectivities. However, at 150 °C or a higher temperature, these products are clearly the major ones.

The *effect of oxygen pressure* was also investigated. The alkane conversion markedly increases with $p(O_2)$ until 25 atm (Fig. 2, at 150 °C, 10 h time) but only slightly beyond this pressure (overall conversion of 16.2 and 19.8% for 10 and 20 atm, runs 2 and 4, Table 2, respectively). The increase of the conversion with the $O_2$ pressure is consistent with the promotion of the solubility of this gas with the pressure. Above 5 atm, the selectivity towards cyclohexanol decreases and cyclohexanone remains practically constant up to 25 atm (Fig. 2), whereas the relative amount of by-products acids increases from 5 to 25 atm. Hence the use of $O_2$ pressures above 25 atm is not advantageous due to formation of unidentified black material.

The *effect of the reaction time* was studied (Fig. 3, runs 1–4, Table 3) in the range 5–20 h reaction (at constant temperature, 150 °C, and $p(O_2)$ = 10 atm) and it was observed that the conversions towards the desired cyclohexanol and cyclohexanone products does not greatly increase after the 10 h (e.g., the overall conversion of cyclohexane into the KA oil increases from 16.2 to 20%, for 10 to 30 h). Moreover, extending the reaction time above 10 h results in a decrease of the selectivity (Fig. 3) towards such products, concomitant with a more pronounced increase of the formation of by-products was observed. The increase of the amount of the supported palladium (**A**) catalyst leads to a growth of the overall conversion (3.2–22.1% for 5–45 mg, respectively, Fig. 4). The selectivity towards the main product, i.e. cyclohexanol

**Table 4** Carboxylic acid effects as co-catalysts on cyclohexane oxidation by dioxygen catalyzed by silica gel supported palladium (**A**) catalyst[a]

| Run no. | Carboxylic acid (as co-catalyst) | Percentage conversion | | |
|---|---|---|---|---|
| | | Over all | Cyclohexanol | Cyclohexanone |
| 1 | Picolinic acid | 16.4 | 11.8 | 3.6 |
| 2 | 2,6-pyrazine-dicarboxylic acid | 17.8 | 12.4 | 4.1 |
| 3 | 2,3-pyrazine-dicarboxylic acid | 18.1 | 12.8 | 4.2 |
| 4 | 3-amino-2-pyrazine-carboxylic acid | 19.9 | 14.0 | 4.6 |
| 5 | 2-pyrazine-carboxylic acid | 21.2 | 14.9 | 5.1 |

[a] Same conditions as those indicated for the run 4 in Table 1

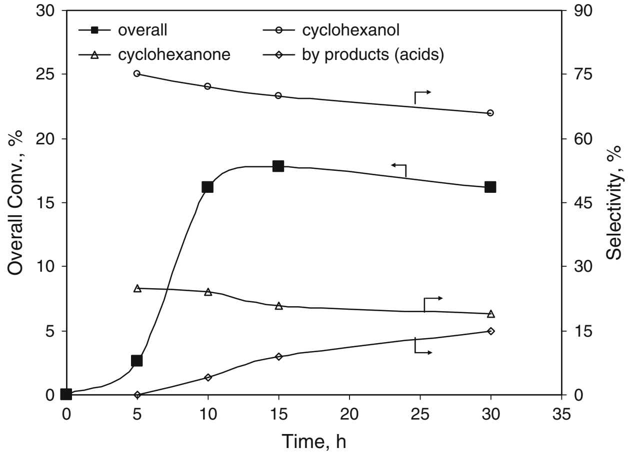


**Fig. 3** Time effect on cyclohexane conversion and selectivity, upon oxidation by $O_2$, in the presence of the silica gel supported Pd (**A**) catalyst (temp. = 150 °C, $p(O_2)$ = 10 atm, Catal. = 25 mg)

and cyclohexanone are nearly similar, ca. ~70 and ~23%, respectively, in between 5 and 45 mg catalyst amount.

We have checked some carboxylic acids as possible co-catalysts (Table 4). Pyrazinecarboxylic acid promotes the reaction considerably, increasing the overall conversion (from 16.2 to 21.2%, run 4, Table 1 and 4, Table 4). A promoting effect of the same acid was also observed by us for supported V-complexes and by Shul'pin and Süss-Fink [20–22] and conforms by DFT calculations [23], in the peroxidative oxidation of alkanes, in various homogeneous systems with V-species. 2,3-Pyrazinedicarboxylic acid, 2,6-pyrazinedicarboxylic acid and 3-amino-2-pyrazine-carboxylic acid have a less pronounced effect, while picolinic acid is almost inactive.

The TGA of the freshly silica supported Pd (**A**) catalyst shows that it is stable up to ca. 293 °C (Fig. 5). In addition, after being used, the catalyst can be reactivated by heating and recycled, still displaying activity. Thus, after cyclohexane oxidation (run 4, Table 1), the catalyst was filtered off, washed three times with acetone and dried in an oven at 100 °C for 1 h. It was then used again, under the same reaction conditions, leading to further (although lower) overall conversion of cyclohexane 9.9%. The preservation of most of the catalytic activity is consistent with the ICP analysis that shows only a partial metal loss upon use. In fact, the freshly supported Pd (**A**) catalyst shows 0.26 wt.% of palladium whereas after run 4, Table 1, followed by separation, washing and drying of the catalyst, a metal content of 0.19 wt.% is still present. These observations also indicate that the Pd is negligible leached out during the reactions.

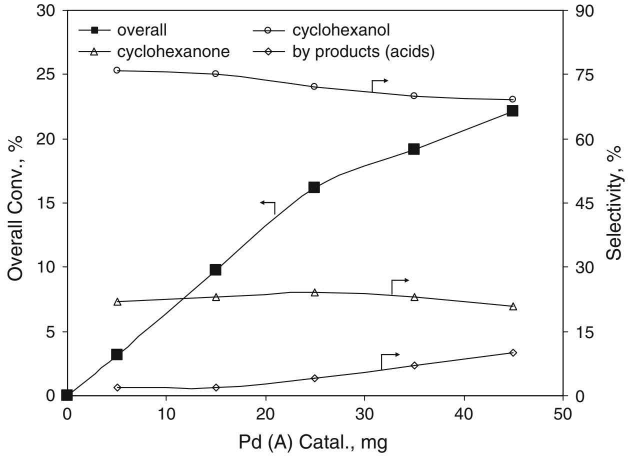


**Fig. 4** Silica supported Pd (**A**) catalysts effect on cyclohexane conversion and selectivity, upon oxidation by $O_2$ (temp. = 150 °C, $p(O_2)$ = 10 atm, 10 h time = 10 h)

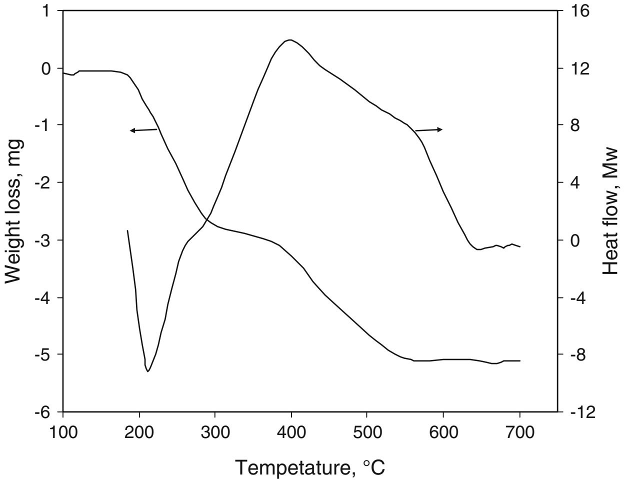


**Fig. 5** TGA of the freshly silica gel supported Pd (**A**) catalysts

## 3.1 Proposed Reaction Mechanism

Alkane oxidation reactions can occur [24] via a free-radical chain process, via coordination of the substrate and via catalytic oxygen transfer. In the current study, the involvement of a free radical mechanism is supported by the inhibition of the catalytic activity when performing the reactions in the presence of $BrCCl_3$ or $(C_6H_5)_2NH$, i.e. a carbon- and an oxygen-radical trap, respectively.

Hence, the oxidation is proposed to proceed via the cyclohexyl radical ($Cy^\bullet$) obtained by reaction of cyclohexane (CyH) with $O_2$ upon homolytic C–H bond cleavage (slow induction period). Oxidation of $Cy^\bullet$ by $O_2$ would form the alkylperoxy radical $CyOO^\bullet$ which could react in two ways: (i) decomposition to the final products, i.e. cyclohexanol (CyOH) and cyclohexanone (Cy(-H)=O), also with formation of $O_2$; (ii) H-atom abstraction from the alkane to form the alkyl hydroperoxide CyOOH, whose homolytic decomposition to alkyloxy ($CyO^\bullet$) (O–O bond cleavage) and alkyl peroxy ($CyOO^\bullet$) (O–H rupture) could be catalyzed by a Pd catalyst. The alcohol (CyOH) could then be formed either by H-abstraction from the alkane (CyH) by $CyO^\bullet$ or (see (i) above) by decomposition of the $CyOO^\bullet$ to yield also cyclohexanone. This type of mechanism has been proposed [13, 14, 25] for catalysts in which the metal has two available oxidation states of comparable stability, a property that is not unusual in Pd catalyst chemistry [26].

The conceivable involvement of the hydroperoxide CyOOH is substantiated by the promotion of the detected amount of CyOH with a decrease in that of the ketone Cy(–H)=O, when the final reaction solution is treated with an excess of $PPh_3$ prior to GC analysis, according to a reported method [27]. The final reaction solution is then deoxygenated by $PPh_3$ to give CyOH (with formation of $Ph_3PO$), thus eliminating the CyOOH decomposition to both CyOH and Cy(–H)=O in the GC analysis under usual experimental conditions (run 3, Table 1). The above $PPh_3$ treatments are typically not higher the 12%. Its shows the hydroperoxide CyOOH still present in reaction solution. Another interesting result of the current study is the detection of carboxylic acid as by products, i.e. *n*-valeric acid, succinic acid, adipic acid (in little amount) in the oxidation reactions of cyclohexane. This indicates the occurrence of metal promoted C–C bond cleavage of the cyclohexane which concomitantly further oxidized to the furnish carboxylic acids, in spite of the considerably mild reaction conditions employed. It also appears that the oxidation process get promoted by the presence of acid since the amount of carboxylic acid as by products increases in the presence of a carboxylic acid co-catalyst [21] (Table 4).

## 4 Conclusions

On the basis of above discussion, we conclude that the di(ethylthio)ethane palladium (**A**) and di(ethylthio)propane palladium (**B**) immobilized on silica gel, catalyze the cyclohexane oxidation with molecular oxygen (the ideal "green" oxidant) to cyclohexanol (the major product) and cyclohexanone, under moderate conditions. The supported palladium (**A**) catalyst provides the best activity, overall conversion ca. 16% with 94% selectivity towards those products, reaching, under typical optimize conditions ($pO_2 = 10$ atm, at 150 °C for 10 h). The higher activity of the supported palladium (**A**) catalyst is observed, in comparison with the other supported palladium (**B**) catalyst. The carboxylic acids can act as co-catalysts and 2-pyrazinecarboxylic acid is the most effective one among those tried. The TGA analysis of the Pd (**A**) catalyst shows the catalyst is stable up to 293 °C and ICP analysis indicates that the metal does not leach out markedly for at least 20 h of oxidation reaction. Experiments with radical traps and initiators provide some supporting testimony in favour of a free-radical mechanism.

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