

# Heterogeneous Epoxidation of *n*-octene, Cyclooctene and Styrene Using a Chitosan 4-Salicylidinepalladium (II) Catalyst under Aerobic Conditions

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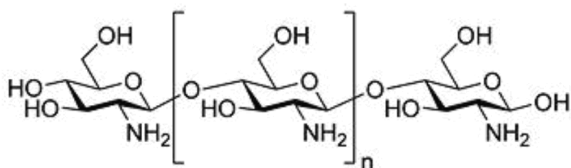
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**Abstract:** Chitosan (CS) has been condensed with 4-salicylidene to form a 2CS-Hdhba Schiff-base. The heterogeneous catalytic epoxidations of *n*-octene, cyclooctene and styrene have been achieved by employing a [Pd(dhba(H<sub>2</sub>O)Cl)] complex as a catalyst in the presence of oxygen at atmospheric pressure at 358 K. The influence of reaction temperature, reaction time and amount of catalyst on the epoxidation processes has also been investigated. The catalyst is easily recovered from the epoxidation reaction mixtures even after 10 catalytic cycles.

**Keywords:** Chitosan, Schiff-base, *n*-octene, Cyclooctene, Heterogeneous.

## 1. INTRODUCTION

Chitosan (CS; Figure 1) is a β-(1→4) linked biopolymer of 2-amino-2-deoxy-D-glucose (glucosamine) repeat unit [1-3], *i.e.*, it is a N-deacetylated derivative of chitin. Chitosan is the most abundant free amino polysaccharide that occurs naturally. Beside its non-toxicity, it has wide range of applications [4] because the free amino groups enable various chemical modifications of the polymeric chain to be undertaken, including the formation of Schiff-bases and subsequently metal complexes [5].



**Figure1:** Structure of Chitosan.

Polymer-supported metal complexes with high activity and selectivity are of great interest because they can be easily recovered from the reaction mixtures [6]. In this respect, several catalytic systems using CS as a support have been developed [7-12]. Functionalization of CS to afford suitable coordination sites has also been accomplished and this has resulted in catalysts for oxidation reactions, such as the Suzuki and Heck reactions [13, 14]. Schiff-bases derived from CS and substituted salicylaldehyde complexes of copper, cobalt and palladium have been reported to act

as efficient catalysts in the cyclopropanation of styrene [15] and the oxidation of cyclohexene [16] and cyclohexane (in the presence of molecular oxygen without any solvent) [17]. A cross linked, chitosan salicylaldehyde-supported palladium complex is an efficient catalyst in the Heck reaction of acrylic acid with iodobenzene at 60 °C [18].

The epoxidation of olefins is an important chemical reaction as epoxides are versatile synthetic intermediates in the chemical industry [19]. Such selective epoxidation of unsaturated hydrocarbons can be achieved by the use of transition metal complexes catalysts and these reactions have received considerable attention lately [20-22]. However, these homogeneous catalysts suffer from several disadvantages, such as difficult separation procedures and the loss of precious metal complexes in the reactions [23]. These problems can be solved by anchoring the homogeneous catalysts onto chemically modified support materials [23]. Numerous epoxidation systems based on the use of alkyl peroxides [24, 25-27], hydrogen peroxide [28-31] and molecular oxygen [32-39] as oxidants have been reported. Molecular oxygen (without a reductant product) or H<sub>2</sub>O<sub>2</sub> (with only H<sub>2</sub>O as a product) in particular have been widely studied because of the environmental benefits and the lower costs involved than when using other oxidizing agents [35, 36, 40, 41].

We present here a continuation of our previous research on the synthesis of transition metal salicylidene Schiff-base complexes anchored on solid supports [33, 42, 43] and their application as efficient catalysts for the epoxidation of olefins. The objective of this study was to use the chemically modified CS complex, [Pd(2CS-dhba)Cl(H<sub>2</sub>O)], where 2CS-dhba is

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the supported 4-salicylidene Schiff-base, as a heterogeneous catalyst for the epoxidation of *n*-octene, cyclooctene and styrene in the presence of molecular oxygen under aerobic conditions. The influence of the reaction temperature, reaction time and amount of catalyst on the mechanism of the epoxidations was also investigated.

## 2. EXPERIMENTAL

### 2.1. Materials

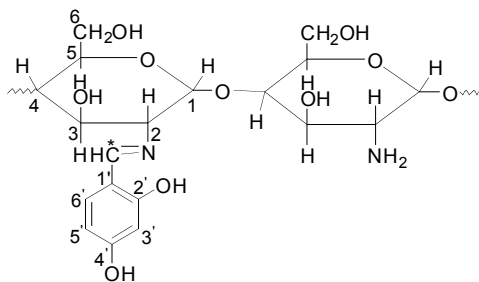
All manipulations were performed under aerobic conditions using materials and solvents as received from the commercial suppliers. The olefins, *n*-octene and cyclooctene, were of extra pure quality and were obtained from Sigma-Aldrich Chemie GmbH, Germany. Chitosan (CS) with a molecular weight of 161 and 0% degree of acetylation was obtained from BiobasicInc, UK.

### 2.2. Instrumentations

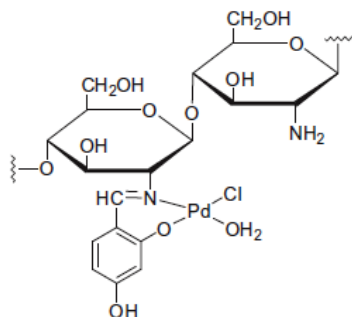
The epoxidation products formed were analyzed by GC-mass spectrometry in the Mass Spectroscopy Unit in the Department of Chemistry, McGill University, Montreal, Quebec, Canada.

### 2.3. Syntheses

The Schiff-base 2CS-Hdhba and the palladium complex, [Pd(dhba(H<sub>2</sub>O)Cl)], were synthesized by the literature methods [42] (Figure 2 and 3).



**Figure 2:** Structure of Schiff-base 2CS-Hdhba.



**Figure 3:** Structure of [Pd(2CS-dhba)Cl(H<sub>2</sub>O)].

## 2.4. Epoxidation Process

In a typical experiment, a Pyrex tube (20 mL) was charged with the olefin (2.0 mL) and the catalyst, [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] (15 mg). The tube was filled with molecular oxygen and the reaction mixture was stirred and heated at 358 K. The reactions products were identified and analyzed after 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 h using GC-mass spectrometry. Control experiments were conducted under similar conditions.

## 3. RESULTS AND DISCUSSION

The development of new, highly efficient heterogeneous catalysts is an active and important area in the commercial production of fine chemicals. Many opportunities present themselves in terms of the significant developments in the tailoring of solid supports, which allow a rich variety of surface functionalities and properties to be developed, along with the unprecedented control of physical features such as porosity, pore connectivity and high surface area. Key challenges include making full use of this palette of materials in the drive towards sustainable manufacturing.

Transition metal complex-promoted oxidation reactions are of considerable current interest because of their relevance to organic chemistry [44, 45]. Schiff-base transition metal complexes have become highly valuable catalysts in the epoxidation of alkenes when using readily available oxygen donors such as molecular oxygen, H<sub>2</sub>O<sub>2</sub>, NaOCl or PhIO [46-50]. On the other hand, anchoring of transition metal complexes on solid supports can provide efficient catalysts, which are easy to handle and may possibly exhibit improved selectivity and activity [16, 46, 51, 52].

In the present work, the ability of the chitosan 4-hydroxysalicylidene Schiff-base (2CS-Hdhba) complex, [Pd(2CS-Hdhba)Cl(H<sub>2</sub>O)], to catalyze the epoxidation of olefins has been systematically examined in the presence of molecular oxygen as co-oxidant. The epoxidations are performed without the presence of a reducing agent; the reactions are inexpensive, environmental friendly and easy to perform [46]. Since such modified chitosan Schiff-base complexes are not easily soluble in common solvents, the oxidation processes were undertaken under heterogeneous catalysis conditions.

In general, linear and cyclic alkenes can be directly oxidized to the corresponding epoxyalkanes by

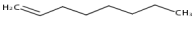
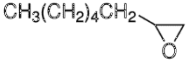
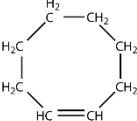
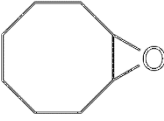
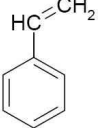
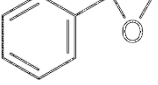
molecular oxygen or H<sub>2</sub>O<sub>2</sub> at 353-363 K without any reductant [46, 53]. The results of the epoxidation of *n*-octene, cyclooctene and styrene [Pd(dhba)(H<sub>2</sub>O)Cl] in the presence of molecular oxygen as a co-oxidant are presented in reported in Table 1. The epoxidation of the olefins could be increased by raising the reaction temperature up to 358 K; high temperatures (e.g., 353 K) are known to help initiate the epoxidation process [46,54]. The most interesting point observed is the complete absence or sometimes the presence of just very small amounts of alcohol, aldehyde or ketone as by-products as detected by the GC-mass spectrometry. This observation indicates the high selectivity of the epoxidations under the experimental conditions employed. Similar results have been described in the epoxidations of *n*-octene by modified HY-zeolite-APTSSal and the Pd(MCM-41-N-(Hdhba)<sub>2n</sub>(dhba)Cl(H<sub>2</sub>O)) {(MCM-41-N-(Hdhba)<sub>2</sub>(dhba) Schiff-base [33] and N-(3-(trimethoxysilyl)-propylethylenediamine anchored onto mesoporous silica, MCM-41, and 4-salicylidene [43] using molecular oxygen and aqueous 30% H<sub>2</sub>O<sub>2</sub>-0.2M NaHCO<sub>3</sub> as co-oxidants, respectively. The relation between the epoxidation percentage and reaction time at 358 K shows that the highest catalytic activity occurs during after a 10 h period.

The stability of the catalyst unit, {Pd(II)/2CS-dhba}, at high temperature is the main point to be considered

The TG thermo gram of [Pd(dhba)(H<sub>2</sub>O)Cl] indicates its stability up to 150 °C [42]. The TG curve shows decomposition steps in the 155–377, 378–520 and 521–700 °C temperature ranges due to the elimination of (Cl<sub>2</sub> and CS), C<sub>7</sub>H<sub>5</sub>NO and C<sub>5</sub>H<sub>9</sub>O fragments, respectively, eventually leaving a PdO residue [42]. Thus, under the experimental conditions employed for the epoxidations, the catalyst integrity is maintained. Moreover, the catalyst is stable after up to ten runs (Table 1), but it does undergo some degradation over a 10 h period, as evidenced by a slight metal loss.

Oxidation of olefins, cyclooctene, *n*-octene and styrene, in the presence of [Pd(2CS-dhba)Cl(H<sub>2</sub>O)], using molecular oxygen as oxidant at 358 K, yields the corresponding epoxyalkane as the main product. Without the catalyst, the reaction does not take place. Initial activities for *n*-octene, cyclooctene and styrene epoxidation are 93.0, 80.6 and 16.5%, which are much higher percentages than are those observed for CS and 2CS-Hdhba (1.2 and 1.7%) under identical reaction conditions. These results suggest that the active center for the epoxidations is chiefly the Pd(II)/2CS-dhba species. The related literature shows the catalytic activity sequence as cyclooctene > styrene > *n*-octene. Recently, we have reported that the sequence of oxidation of olefins in presence of [Pd(MCM-41-N-(Hdhba)<sub>2</sub>(dhba)Cl(H<sub>2</sub>O)], using 30% H<sub>2</sub>O<sub>2</sub>-0.2M NaHCO<sub>3</sub> as oxidant at 353 K is

**Table 1: Epoxidation of Olefins by [Pd (2CS-dhba)Cl(H<sub>2</sub>O)] in Presence of Molecular Oxygen for 10 h at 358 K\***

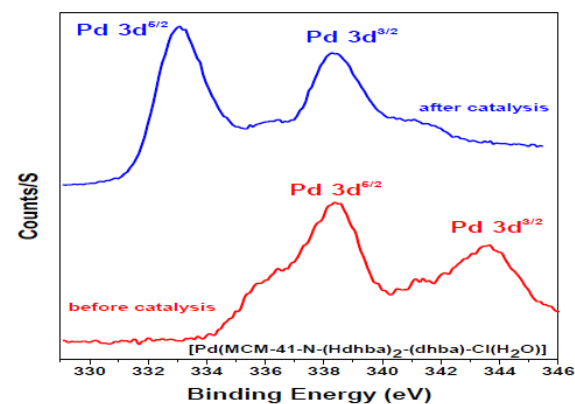
Olefin	Epoxide	CS	Epoxide % 2CS-Hdhba	[Pd(2CS-dhba)Cl(H <sub>2</sub> O)]
 n-Octene	 Epoxyoctane	1.2	1.7	93.0 (99.9) 383 <b>(89.9)<sup>c</sup></b>
 cyclooctene	 Epoxycyclooctane	1.02	1.44	80.6 (88.3) 397 <b>(77.6)<sup>c</sup></b>
 Styrene	 Styrene oxide	-- <sup>b</sup>	0.76	16.5 (77.2) 87 <b>(11.2)<sup>c</sup></b>

Selectivity in parentheses and TON (mmol of epoxide/mmol of catalyst) bold and underline, <sup>b</sup> no epoxide detected by GC. <sup>c</sup> Large scale in italics (using 1.5 g of [Pd(2CS-dhba)Cl(H<sub>2</sub>O)], olefin (50 mL), molecular oxygen was filled 250 mL Pyrex flask, at 358 K for 10 h.)

cyclooctene>*n*-octene> styrene; the high pH value (using 30% H<sub>2</sub>O<sub>2</sub>–0.2M NaHCO<sub>3</sub>) may play a role in the activity of epoxidation of cyclooctene [43]. Our present results differ, viz., the sequence is *n*-octene>cyclooctene> styrene. The low pH and the steric effects, based on  $\pi$ - electron density (in the case of styrene), may decrease the possibility of electrophilic addition resulting in the epoxidation [25, 43, 55]. Furthermore, linear olefins can easily approach the catalyst active sites [33, 43, 47]. The efficiency of epoxidation is raised by increasing the reaction temperature (343–363 K), as has been reported previously [33, 47]. The complex [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] shows high selectivity for the epoxidations (99.9–77.2%) with small amounts of by-products being detected by GC analysis (diols and/or aldehydes) [56]. It is thought that epoxidation of linear and cyclic olefins may proceed through a radical chain mechanism [33, 47, 57]. At 358 K, the oxidation could be initiated by radicals present in the system and the peroxide (ROO $\cdot$ ) thereby generated would be catalytically decomposed by the Pd(II) complex [through the reduction of Pd(II) to Pd(0)].

After the oxidation processes, the XPS spectra of the remaining catalyst, [Pd(2CS-dhba)Cl(H<sub>2</sub>O)], were examined (Figure 4). The binding energies of Cl<sub>2p</sub>, O<sub>1s</sub> and N<sub>2p</sub> and Pd<sub>3d 5/2</sub> are nearly the same as are those of the original catalyst [43, 58]. The active site of the catalyst should be able to undergo reversible redox transformations *i.e.*, the Pd ion should readily changes its oxidation state from Pd(II) to Pd(0) and *vice versa*, confirming the regeneration of the active catalyst after oxidation [43]. In addition, the stability of the catalyst was also established after each run by IR, UV-vis and solid-state <sup>13</sup>C-NMR spectroscopy. Similar results have been obtained for HY-anchored Fe(III)-APTSSal, M(II)-APTSSal (M(II) = Mn, Co, Ni, Cu, Pd), Ag(I)-APTSSal and WO<sub>2</sub><sup>2+</sup>-APTSSal, and [Pd(MCM-41-N-(Hdhba)<sub>2</sub>(dhba)Cl(H<sub>2</sub>O))] complexes [33, 43, 47]. The

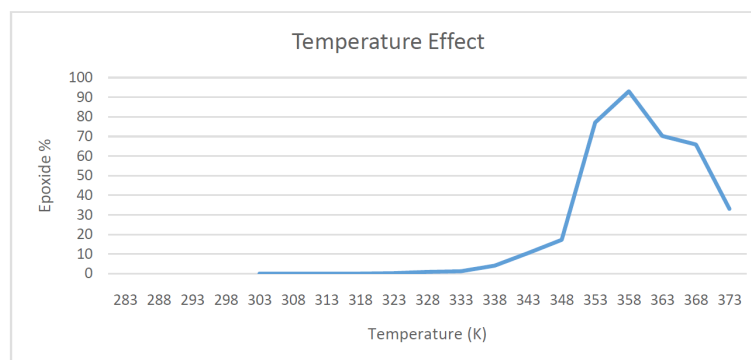
catalytic activities of the filtrates from the washings of the first and second time use of the catalyst were examined to ascertain their possible re-use, but very poor activities were observed. In an effort to find the optimal conditions of the epoxidation of the olefins under study in presence of molecular oxygen, *n*-octene was chosen as a model substrate for a detailed investigation.



**Figure 4:** XPS of [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] (red = before catalysis process, blue = after catalysis process).

### Influence of Temperature of the Epoxidation Reactions

Figure 5 illustrates the epoxidation of *n*-octene, using [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] at different temperatures. It is clear that the epoxidation increases with increasing the temperature from 343 to 373 K, as below 343 K it is difficult to initiate the process [40, 41]. Only very small amounts of epoxides were detected at room temperature. Upon raising the temperature to 358 K, however, both the yields and selectivity's were increased. The epoxyoctane yield was 17.2% after 10 h at 348 K, which quickly increased up to 93.0% at 358 K. With a further increase in temperature to 368 K, the epoxidation of *n*-octene dropped to 65.9%. The



**Figure 5:** Effect of temperature in the catalytic epoxidation of *n*-octene using 15 mg of [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] in presence of molecular oxygen as co-oxidant.

selectivity for epoxide production was affected by the temperature, which increased from 41.0% at 348 K to the maximum (99.9%) at 358 K and then quickly fell to 70.0% at 368 K. When the temperature was set too low, it was difficult to initiate the reaction. When the temperature was too high, polymerization of substrate occurred followed by an increase in the amounts of byproducts (diols and/or aldehydes) [33, 42, 47]. Also, decomposition of the catalyst may have taken place [33, 47].

### Influence of the Epoxidation Reaction Time

Figure 6 shows the relationship between the conversion percentage of *n*-octene to epoxy-octane using [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] at the reaction time at 358 K. The catalytic activity becomes very high after 10 h. At the beginning of the reaction, no epoxyoctane was detected but the yield gradually increased to 11.4% in 2.5 h, 19.8% in 5 h, and 93.0% in 10 h, showing an induction period characteristic of a radical reaction. However, the epoxyoctane selectivity was approximately increased to 99.9% after 10 h, and then it began to decrease as there action time was increased (12 h). Elongation of the reaction time may have led to the over oxidation of *n*-octene through double bond cleavage as well as polymerization of octene, which reduces the extent of the epoxide formation and the selectivity [43].

### Effect of the Amount of Catalyst on the Epoxidation Reaction

Figure 7 shows the relationship between epoxy-octane percentage and the amount of the catalyst applied at 358 K for 10 h using [Pd(2CS-dhba)Cl(H<sub>2</sub>O)]. When the amount of the catalyst was increased from 5 to 15 mg, the yield of epoxyoctane was increased from

29.2 to 93.0%; *i.e.*, when the amount of catalyst reached 15 mg, the epoxidation percentage and selectivity reached their maximum values. Upon increasing the amount of catalyst from 15 to 20 mg, a clear decrease in the yield (from 93.0 to 80.2%) was observed. This was due to more byproducts being produced based on the increased number of active centers in the catalyst [43]. The highest catalytic activity of the catalysts was observed when using 15 mg, which illustrates the high turnover numbers observed in the catalytic processes and the possibility of using these catalysts in industry.

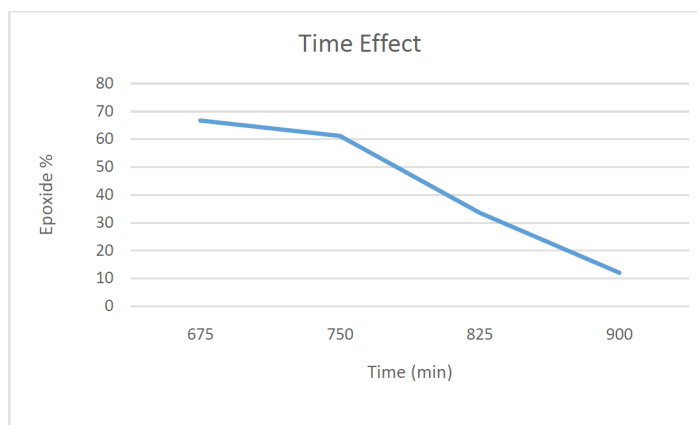
### Mechanism of Epoxidation

As the olefin can easily approach the catalyst active sites [41, 59], all the reported catalysts in this study show high selectivity in 1,2-epoxide formation (93–16.5%). As mentioned earlier, the catalytic activity of modified chitosan Schiff-base (2CS-Hdhba) complexes for the epoxidation of alkenes in the presence of molecular oxygen as co-oxidant may involve a radical chain mechanism at high temperature [41,60 but the metal ion may also play a role of catalyzing chain initiation and epoxide formation [16, 40, 41].

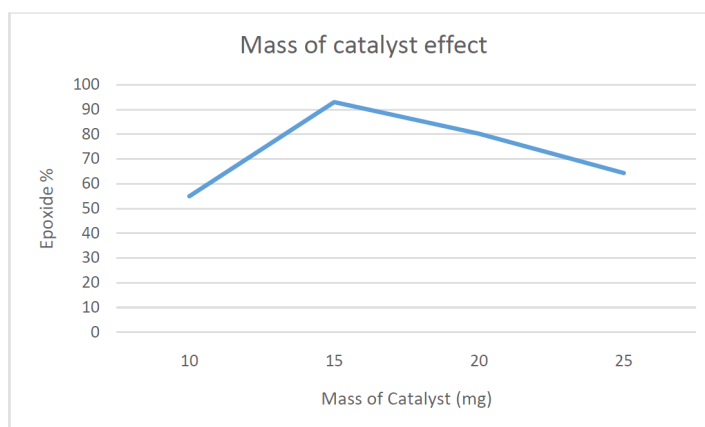
At high temperature, 358 K, the oxidation of olefins (*n*-octene, cyclooctene and styrene) is initiated by radicals presented in the system (equation 1).

$RH \rightarrow R\cdot + O_2 \rightarrow ROO\cdot$  Very fast step initiated by radicals in solution (1)

Thereby generated is catalytically decomposed by Pd(II), [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] catalyst through reduction to Pd(0) [43]. This feature was supported by XPS spectra of the catalyst before and after the epoxidation process (Figure 4). The *in situ* reduction of Pd(II) to Pd(0) was taken place [43]. The XPS spectra



**Figure 6:** Effect of reaction time in the catalytic epoxidation of *n*-octene using 150 mg of [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] at 358 K in presence of molecular oxygen as co-oxidant.



**Figure 7:** Effect of amount of catalyst in the catalytic epoxidation of *n*-octene using [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] at 358 K for 10 h in presence of molecular oxygen as co-oxidant.

were characterized by two pairs of Pd<sub>3d</sub> peaks and the binding energies (BEs) of 333.1, 338.4 eV are assigned to Pd(0) species for 3d-5/2 and 3d-3/2, respectively [43].

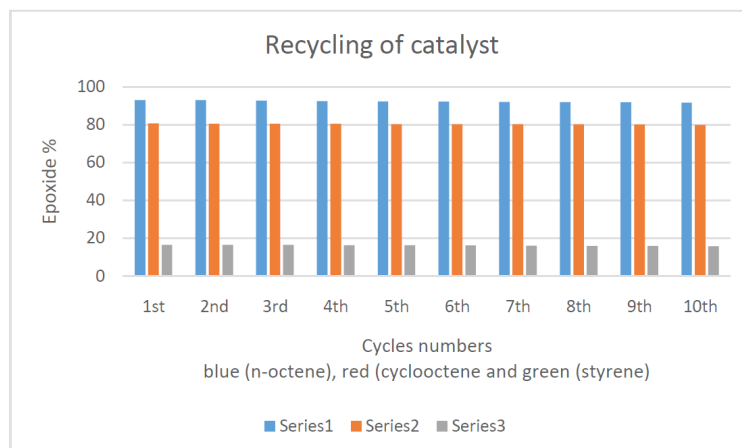
### Large Scale Epoxidations

Large-scale epoxidations were also examined. A Pyrex flask (250 mL) was charged with the [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] catalyst (1.5 g) and olefin (50 mL) and then filled with molecular oxygen. The resulting reaction mixture was stirred and heated at 358 K for 10 h. These large-scale experiments could be easily carried out using the same procedure as for the experimental scale reactions. *n*-Octene, cyclooctene and styrene were oxidized to their corresponding epoxides with yields of 89.9, 77.6 and 11.2%, respectively. The epoxide yields obtained were at nearly the same level for both the large- and experimental-scale reactions, even though the large-scale reactions involved about 50 times more material than did those for the

experimental-scale ones [43, 61].

### Catalyst Recycling

A significant advantage of heterogeneous catalysis is the ability to easily remove the catalyst from the reaction mixture and reuse it for subsequent reactions until the catalyst is sufficiently de-activated. Thus, the stability of the catalyst was studied by recycling the recovered catalyst. At the end of the reactions, the solid catalysts were separated from the reaction medium by centrifugation at 3500 rpm for 10 min, thoroughly washed with ethanol, air-dried and then reused under similar reaction conditions. The recovered catalysts showed as light lower catalytic activity in successive runs. After the 10<sup>th</sup> oxidation process, the XPS spectra of the catalysts were examined (Figure 4). No significant changes in the oxidation state of Pd(II) were noted following the recovery of the catalyst, confirming the regeneration of the active catalyst after oxidation (Figure 8). In addition, the XPS, IR and UV-vis. spectra



**Figure 8:** Recycling of the catalyst for ten times using [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] at 358 K for 10 h in presence of molecular oxygen as co-oxidant.

of the original and recovered catalyst exhibited no significant differences in the characteristic bands indicating that the catalyst is quite stable under the applied oxidizing conditions.

## CONCLUSIONS

The chitosan 4-hydroxysalicylaldehyde Schiff-base (2CS-Hdhba) complex, [Pd(2CS-dhba)Cl(H<sub>2</sub>O)] was found to be an efficient catalyst for epoxidation of *n*-octene, cyclooctene in presence of molecular oxygen under atmospheric pressure at 358 K for 10 h in an aerobic heterogeneous system. The catalyst was easily separated from the epoxidation reactions and could be recovered reused up to ten times.

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