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Transfer Dehydrogenation of 1-Phenylethanol Over Pd/C Under Mild Conditions: Effect of Reaction Conditions and Optimization of Catalytic Performance

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Abstract The catalytic activity of 5 wt% Pd/C has been evaluated using the liquid phase transfer dehydrogenation of 1-phenylethanol as a model reaction. The reaction parameters such as catalyst loading and stirring rate have been optimized to determine the required conditions to carry out the reaction under kinetic regime control. By performing the reaction under different temperatures, the value of apparent activation energy has been determined as being 61 kJ/mol. Furthermore, the influence of thermal treatment of 5 wt% Pd/C catalyst on its catalytic performance for the liquid phase transfer dehydrogenation of 1-phenylethanol has been investigated in a temperature range of 110–200 °C. The results reveal that the catalyst activity is strongly dependent on the ratio between Pd/PdO species. The fresh and used catalysts were characterized using a range of characterization techniques (XRPD, XPS, TEM, SEM-EDX, and BET) in order to investigate structure–activity relationships. The 5 wt% Pd/C exhibit high conversion (90%) and selectivity (91%) toward acetophenone under mild conditions. Moreover, the reusability tests have been carried out, and the results show that the catalyst preserves 80% of its initial catalytic activity after five cycles indicating the high stability of the 5 wt% Pd/C catalyst in the liquid phase transfer dehydrogenation of 1-phenylethanol. The influence of reaction conditions on the catalytic activity is also discussed.

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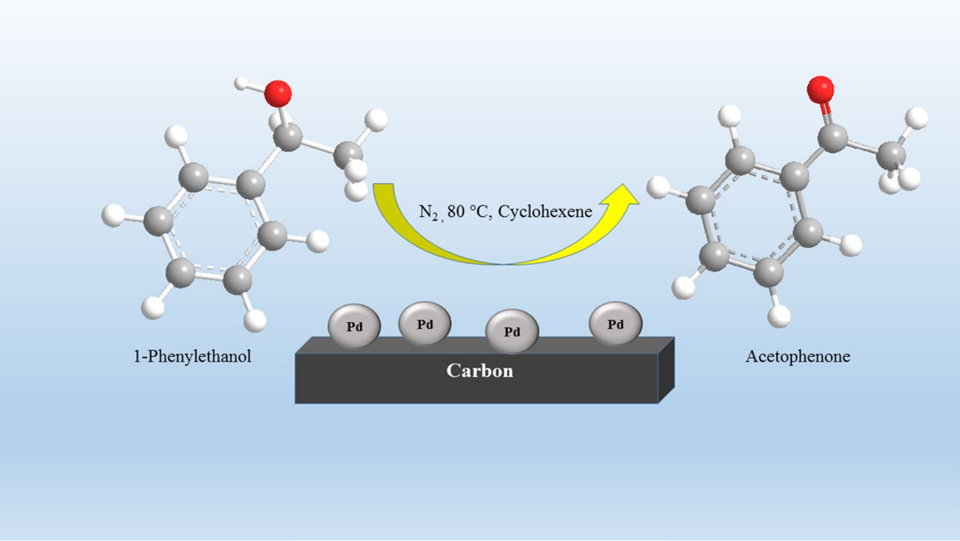
Graphical Abstract



Keywords Transfer dehydrogenation of alcohols · Palladium · Heterogeneous catalysis · Nanoparticles

1 Introduction

The transformation of alcohols to aldehydes or ketones is one of the most essential reactions in organic synthesis [1–3]. For this purpose, stoichiometric oxidants (typically, $KMnO_4$ and $K_2Cr_2O_7$) have been widely used in the fine chemicals industry [4, 5]. However, using these oxidants has its limitations due to the toxicity of the produced waste [2, 6, 7]. Thus, there has been wide use of molecular oxygen as a green oxidant to replace stoichiometric oxidants [6, 8–15] which is environmentally benign and a more "greener" method than the stoichiometric oxidation involving inorganic oxidants; nevertheless, an aerobic oxidation of alcohols is often linked with either safety concerns or problems of overoxidation, as it involves the use of flammable organic solvents [3, 12, 16].

An interesting alternative to aerobic conditions for the production of oxygenated products, such as aldehydes and ketones, can be the dehydrogenation of alcohols or the under anaerobic conditions with the utilization of unsaturated organic molecules as hydrogen acceptors, instead of molecular oxygen. In this case, the oxidative dehydrogenation is changed to transfer dehydrogenation, which overcomes the safety limitations of aerobic oxidation [15]. However, the number of heterogeneous catalysts that exhibits significant catalytic performance in this novel conversion of alcohol are limited, although the last decade a significant number of reports have shown the research growth of dehydrogenation studies in the presence and absence of hydrogen acceptor. The catalytic activity of supported metals such as palladium [5, 14, 15], copper [3, 16], gold [17] and ruthenium [18, 19] for the transfer dehydrogenation of alcohols has been investigated. One of the first reports showing the catalysed transfer dehydrogenation was reported by Hayashi's group [20] when they investigated the transfer dehydrogenation of the secondary allylic alcohol of D-glycals reporting that a 1/1 molar mixture of the corresponding ketones resulted when using DMF or MeCN as a solvent and $Sm(OTf)_3$ as a catalyst under Ar atmosphere and at 80 °C, and the yield was 60%. For the purpose of improving the selectivity, Hayashi et al. [5, 21] employed ethylene or nitrobenzene as a hydrogen acceptor and found that when allylic and aromatic alcohols were dehydrogenated with Pd/C as a catalyst, the yield was improved to be ~75–86% at 323 K, although the reaction times spanned several days. Baiker et al. [22–29] as pioneers in this area, reported systematic studies in the catalytic activity of supported palladium catalysts in the liquid phase transfer dehydrogenation of various aromatic and allylic alcohols. They analyzed the catalytic behavior of the Pd-based catalysts in cinnamyl alcohol transformation in both the presence and absence of oxygen, reporting that, in anaerobic conditions, the catalyst was deactivated, possibly owing to decarbonylation reactions and site blocking by CO [23]. Moreover, the authors employed cyclohexene as a hydrogen acceptor to examine Pd/Al_2O_3 catalysis of transfer dehydrogenation of aromatic alcohols [27]. Among the range of hydrogen acceptors that were assessed, cyclohexene was found to accelerate the reaction at a temperature of 80 °C as the other olefins formed oligomers which caused poisoning of the catalyst by blocking the active sites. In addition, the difference in the relative adsorption strength between the substrate and the olefin can influence the activity of the transfer dehydrogenation reaction [27]. In another study, the transfer dehydrogenation of benzyl alcohol in anaerobic conditions was investigated, and the results revealed compared to the selectivity values obtained in aerobic conditions of oxidation, a decrease in selectivity towards benzaldehyde formation. The authors pointed out that in anaerobic conditions, the results indicated that other by-products could be detected which formed by saturation of the aromatic ring or hydrogenolysis of the C–O, while the presence of oxygen inhibits the formation of these by-products resulting in increasing the selectivity toward benzaldehyde formation [28]. Shen et al. [3, 30] investigated the catalytic performance of Cu catalyst in the transfer dehydrogenation of primary aliphatic alcohols. They reported the influence of changing the support from Al_2O_3 to La_2O_3 on the activity of transfer dehydrogenation of 1-octanol towards 1-octanal as the desired product. This indicated that the use of Cu/Al_2O_3 was inactive in the transfer dehydrogenation process while the use of Cu/La_2O_3 increased the yield to 63%. They attributed this observation to the contribution of basic sites in $La_2O_{3,}$ which have a synergistic effect with the efficient spillover effect of Cu particles leading to an enhancement in the conversion of primary alcohol to the corresponding carbonyl compound. In contrast, Zecceria et al. [18, 31] reported high activity and selectivity for Cu/Al_2O_3 catalyzed transfer dehydrogenation of secondary alcohols, indicating that the oxidative transfer dehydrogenation of secondary alcohols is much easier than the transfer dehydrogenation of aliphatic alcohols and can be strongly affected by choice of hydrogen acceptor. To the best of our knowledge, the studies which investigate the influence of different parameters such as catalyst loading, stirring rate, the reaction's temperature and the determination of the apparent activation energy for the catalyzed liquid phase transfer dehydrogenation of alcohols are very limited. In this work, we report the catalytic activity of a commercial 5 wt% Pd/C and the influence of different parameters such as variation of stirring rate, substrate/metal molar ratio, reaction temperature and thermal treatment of the catalyst on the liquid phase transfer dehydrogenation of 1-phenylethanol as a model reaction under mild reaction conditions. By investigation the influence of these parameters, different regimes were identified, and the reaction parameters were optimized to carry out the transfer dehydrogenation reaction under kinetic regime control. The apparent activation energy for the anaerobic transfer dehydrogenation of 1-phenylethanol catalyzed by 5 wt% Pd/C was determined. Finally the effect of calcination treatment was investigated at relative mild heat treatment conditions (110–200 °C) for investigating the role of particle size and oxidation state of Pd in terms of catalytic performance.

2 Experimental

2.1 Materials and Chemicals

5 wt% Pd/C (catalogue number: 75,992), 1-phenylethanol (purity 98%), dodecane (purity ≥99%), and cyclohexene (purity 99%) were purchased from Sigma-Aldrich. All experiments were carried out using as a solvent toluene (purity ≥99.5), obtained from Fisher Scientific.

2.2 Catalyst Characterization

The fresh and used catalysts were characterized using X-ray powder diffraction (XRPD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) equipped with Energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller surface analysis (BET). X-ray powder diffraction (XRPD) patterns were recorded at ambient temperature on PAN analytical X'PertPRO diffractometer operated at 40 kV and 30 mA using the Cu- Kα radiation (1.54 A). Each sample was scanned from $2\theta = 10°$ to $2\theta = 80°$ for 30 min. XPS were recorded on a Kratos Axis Ultra DLD spectrometer using a monochromatic Al Kα X-ray source (100 W). Spectra were recorded at analyzer pass energies of either 160 eV (survey scans) or 40 eV (detailed scans). Binding energies were referenced to the C (1s) binding energy of adventitious carbon contamination, (284.7 eV) and data were quantified using CasaXPSTM v2.3.15, using sensitivity factors supplied by the manufacturer.

The morphology of the catalysts was examined with SEM on (Hitachi TM3030PLUS) equipped with a Quantax70 energy-dispersive X-ray spectroscope (EDX, Microanalysis System, Oxford Instrument) in order to determine the palladium content in the samples. Mean particle size and particle size distribution was determined by TEM. TEM images were recorded on a JEOL JEM 2100 LaB6 TEM model operating at 200 kV. Samples were prepared by dispersing the catalyst powder in high purity ethanol using ultra- sonication. 40 μL of the suspension was dropped on to a holey carbon film supported by a 300 mesh copper TEM grid before the solvent was evaporated. Particle size distributions and mean particle sizes were determined by measuring the size of over 300 particles from different areas.

In order to test for possible leaching of Pd after the reaction, the actual palladium content after the filtration of the reaction medium was measured by inductively coupled plasma-optical emission spectroscopy (ICP-MS) using an Agilent 7900 instrument. Surface area measurements were performed using a Quantachrome, NOVA 2200e equipment at liquid nitrogen atmosphere. Prior to the measurements, the samples were degassed for 2 h under dynamic vacuum at 227 °C. The total surface area was determined using the (Brunauer–Emmett–Teller) equation and the multi-point method.

The effect of heat treatment of the catalysts was carried by performing the calcination in Thermodyne 4800 Furnace under static air for 3 h at a temperature varying between 110 and 200 °C.

2.3 Transfer Dehydrogenation Reaction

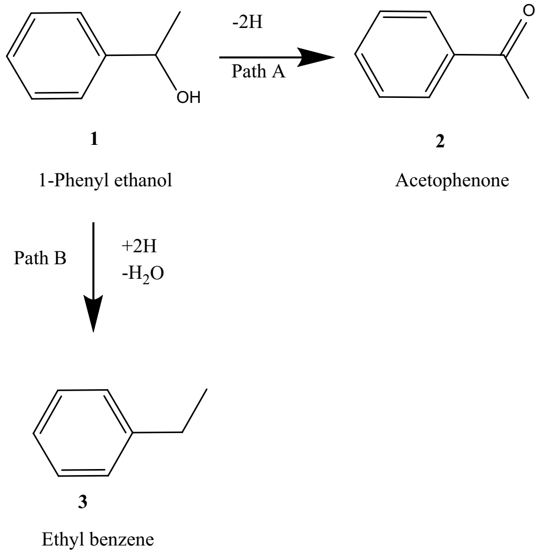
Experiments for the liquid- phase transfer dehydrogenation of 1-phenylethanol were carried out in a three-necked 100 ml round-bottom flask placed in an oil bath with a reflux condenser and a magnetic stirrer at a preset temperature (60–100 °C). The reactor was charged with 20 mL toluene as a solvent and the required amount of the catalyst before purging with N_2 for 30 min, then sealed with a nitrogen balloon (2 bar constant pressure). 1 g (0.008 mol) of 1-phenylethanol was added to (0.016 mol) of the hydrogen acceptor (cyclohexene) to maintain the 1-phenylethanol/cyclohexene molar ratio of (1:2) and injected into the sealed reactor.

2.4 Products Analysis

The progress of the reaction was monitored by analyzing the periodically removed samples using gas chromatography (GC) on Agilent 7890B with a column (CP-Wax 52 CB: 25 m × 0.53 mm × 2.0 µm) after adding dodecane as an external standard. GC-MS was used to determine the chemical identity of the products, and a comparison with authentic samples was carried out to ensure the chemical identity of the products.

3 Results and Discussion

Under the reaction conditions studied, the major products observed were acetophenone (2) and ethyl ether (3). Product (2) is mainly the desired product and product (3) is due to the side reaction of hydrogenolysis of the C–O bond shown in Scheme 1, and in agreement with the results reported earlier by as Keresszegi et al. [28] for the transfer dehydrogenation of 1-phenylethanol over Pd/Al_2O_3 catalyst in an Ar atmosphere. No conversion was observed for the blank reaction.



Scheme 1 Proposed reaction pathways for transfer dehydrogenation of 1-phenylethanol (*1*) to acetophenone (*2*) and the detected by-product (*3*) in the presence of 5 wt% Pd/C catalysts. Reaction conditions: 1 g of 1-phenylethanol, cyclohexene/1-phenylethanol molar ratio = 2 (mol/mol), T = 80 °C, 1-phenylethanol/Pd molar ratio = 416, stirring rate = 800 rpm

3.1 Optimization of the Reaction Parameters

In order to optimize the transfer dehydrogenation of 1-phenylethanol, several reaction parameters have been varied using a commercial 5 wt% Pd/C catalyst. The influence of stirring speed, the substrate to metal molar ratio and varying reaction temperature have been investigated. The main objective was to determine the different regimes (diffusion/kinetic regimes) of the liquid phase transfer dehydrogenation of 1-phenylethanol under varied experimental conditions.

3.1.1 Effect of Stirring Speed

The effect of stirring speed as another parameter that can influence the reaction regime was investigated by varying the stirring speed from 300 to 800 rpm (maximum value of the hot plate used). All other parameters were kept constant as follows: T = 80 °C, molar ratio of cyclohexene to 1-phenylethanol = 2, and 1-phenylethanol/Pd molar ratio = 416. Figure 1 illustrates the influence of stirring speed on the initial conversion of 1-phenylethanol (5 min) and the corresponding. Two regimes can be identified from this figure; the mass transfer limited regime occurred at lower speeding rates between 300 and 500 rpm where the conversion increased linearly from 8 to 20%, respectively, and the kinetic regime, which appeared at stirring speeds higher than 500 rpm where a

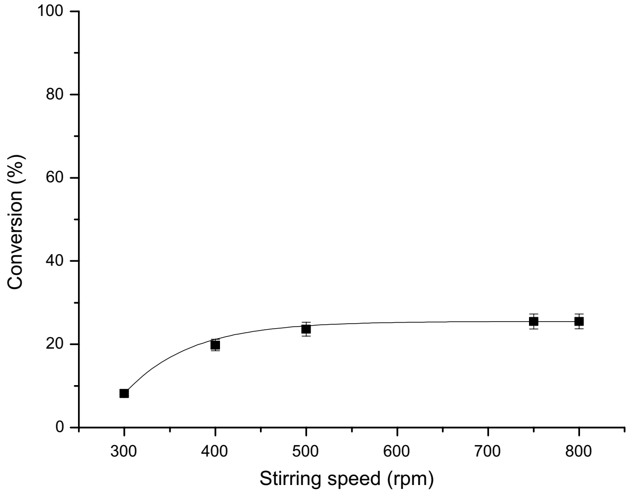


Fig. 1 Effect of stirring speed on the conversion values for the transfer hydrogenation of 1-phenylethanol over 5 wt% Pd/C. Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, T = 80 °C, 1-phenylethanol/Pd molar ratio = 416 and t = 5 min

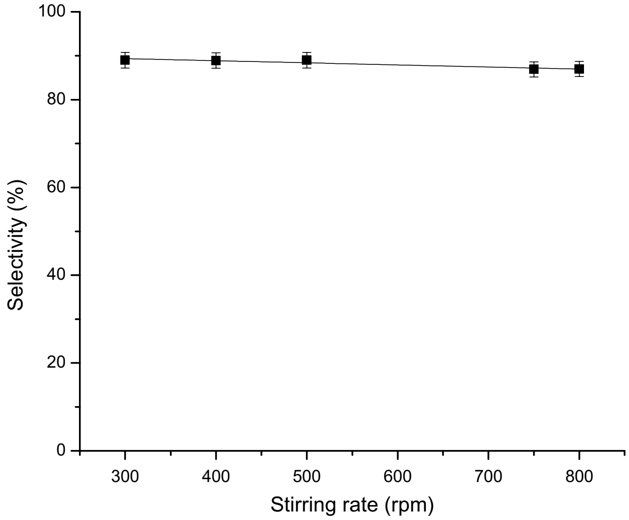


Fig. 2 Selectivity to acetophenone at different stirring rates. Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, T = 80 °C, 1-phenylethanol/Pd molar ratio = 416. Values of selectivity calculated at 50% conversion

slight change in the conversion was observed. By investigating the influence of stirring speed on the selectivity toward acetophenone (presented in Fig. 2), it appears that varying the stirring speed did not affect the selectivity values as they remain almost at the same level between 87 and 89%. Taking into account these results, and to ensure proceeding the reaction under kinetic controlled regime, a stirring speed of 800 rpm was used in the next optimization experiments.

3.1.2 Effect of Catalyst Amount

For that purpose, the effect of catalyst amount (substrate to metal molar ratio) was investigated by varying the 1-phenylethanol/Pd molar ratio from 174 to 3484 (mol/mol). In terms of mass of catalyst, the variation range was between 1 and 100 mg of 5 wt% Pd/C. All other parameters were kept constant as follows: T = 80 °C, the molar ratio of cyclohexene to 1-phenylethanol = 2, stirring speed = 800 rpm (at the maximum value of the hot plate used) and the reaction time = 6 h. Fig. 3 shows the conversion of 1-phenylethanol as a function of reaction time at different 1-phenylethanol/Pd molar ratio. The results indicate that by decreasing the 1-phenylethanol/Pd molar ratio from 3484 to 416 (equal to 1–40 mg of 5 wt% Pd/C), the conversion increased significantly from 20 to 81% respectively at reaction time = 2 h. Furthermore, it can be noticed that no considerable changes in conversion were observed after decreasing the 1-phenylethanol/Pd molar ratio from 416 to 174 (40–100 mg of Pd). The dependence of selectivity toward acetophenone formation on the catalyst amount is shown in Fig. 4, as it appeared almost independent from the 1-phenylethanol/Pd molar ratio, being always between 87 and 89% for the 5 wt% Pd/C catalyst. Therefore, the next optimization experiments were carried out with a 1-phenylethanol/Pd molar of 416 (catalyst mass of 40 mg).

To investigate whether the 1-phenylethanol/cyclohexene molar ratio can influence the catalytic activity, the reaction was carried out at different 1-phenylethanol/cyclohexene molar ratio as shown in Fig. 5a. It is clear that the conversion values after 30 min increased

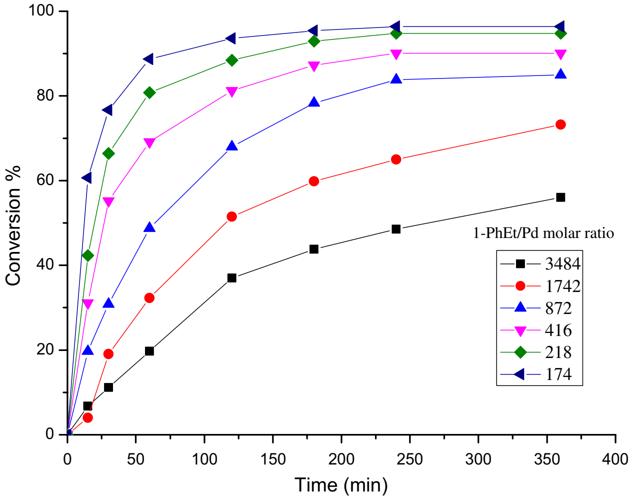


Fig. 3 Conversion of 1-phenylethanol as a function of reaction time at different 1-phenylethanol/Pd molar ratio. Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, T = 80 °C, stirring rate = 800 rpm

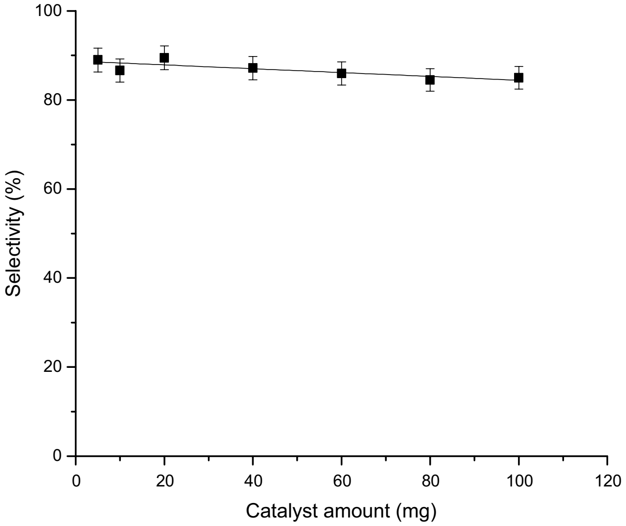


Fig. 4 Selectivity to acetophenone at different catalyst loading. Reaction conditions: (0.008 mol) 1-phenylethanol, (0.016 mol) cyclohexene, T = 80 °C and stirring rate = 800 rpm. Values of selectivity are calculated at 50% conversion

significantly from 43 to 55% by increasing the 1-phenylethanol/cyclohexene molar ratio from 1:1 to 1:2 respectively. Further increase in 1-phenylethanol/cyclohexene molar ratio to 1:4 resulted in a drop of conversion after 30 min to 32% associated with a drop in selectivity towards acetophenone from 87 to 65% as shown in Fig. 5b. These results indicate that the molar ratio between 1-phenylethanol and cyclohexene has a crucial impact on the catalytic activity and selectivity for this reaction. Thus, all the experiments were carried out at the molar ratio of 1:2 (1-phenylethanol/cyclohexene).

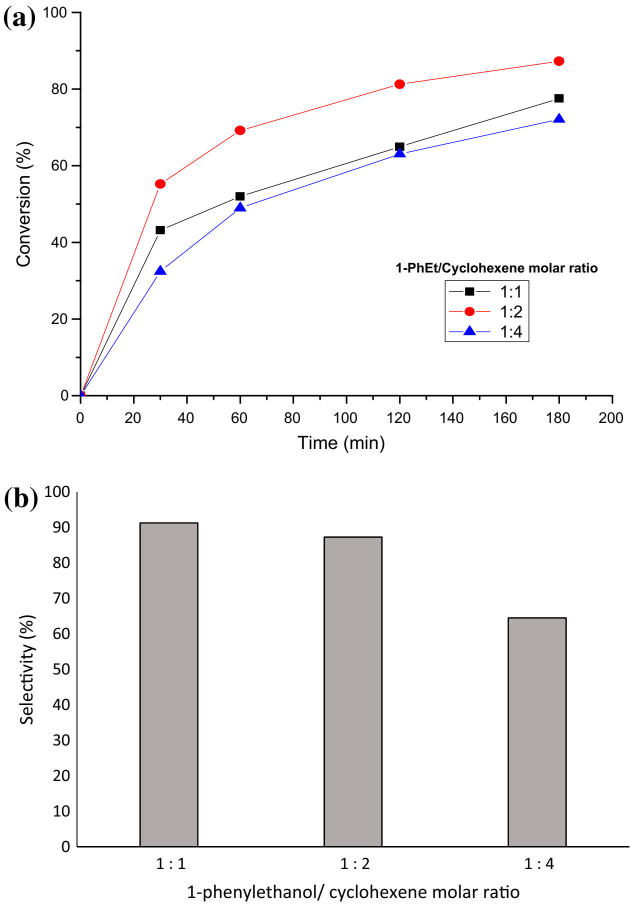


Fig. 5 Effect of 1-phenylethanol/cyclohexene molar ratio on **a** conversion values, and **b** selectively towards acetophenone. Reaction conditions: 1-phenylethanol/Pd molar ratio = 416, T = 80 °C and stirring rate = 800 rpm. Values of selectivity are calculated at 50% conversion

3.2 Effect of Temperature

The effect of temperature as an important factor that can influences the reaction rate of the transfer dehydrogenation of 1-phenylethanol was studied in the range from 60 to 100 °C at a molar ratio of cyclohexene to 1-phenylethanol = 2 and a molar ratio of 1-phenylethanol/Pd = 416, 800 rpm. As shown in Fig. 6, the conversion of 1-phenylethanol increased as the temperature increased. The reaction order was determined by applying zero and first order equations on the experimental data obtained at different temperatures as shown in Fig. S1 in the supporting information. The data fits well with the linear form of first order equation with correlation coefficient = 0.99 at all applied temperatures. The values of rate constant (k) for the reaction over the applied range of temperature are listed in Table 1 indicating the dependency of the transfer dehydrogenation of 1-phenylethanol on temperature, as the values of rate constant increases by a factor of 11 when the temperature increases from 60 to 100 °C. Subsequently, ln(k) versus 1/T was plotted in Fig. 7, and by using the Arrhenius equation, we able to report for the first time the value of apparent activation energy for the catalyzed liquid phase transfer dehydrogenation of 1-phenylethanol as being 61 kJ/mol for the 5% Pd/C catalyst.

3.3 Effect of Thermal Treatment

The catalytic performance of thermally treated 5 wt% Pd/C was studied on the liquid phase transfer dehydrogenation of 1-phenylethanol to evaluate the possible effect of particle size and oxidation state of Pd in terms of catalytic performance. Figure 8 shows the time online study of 5 wt% Pd/C calcined at 110, 150 and 200 °C. The results show that the conversion drops significantly by increasing the calcination temperature, as the conversion decreased from 91% in the non-calcined sample to 63% and 58% when using the 5 wt% Pd/C calcined at 110 and 150 °C, respectively. Completely

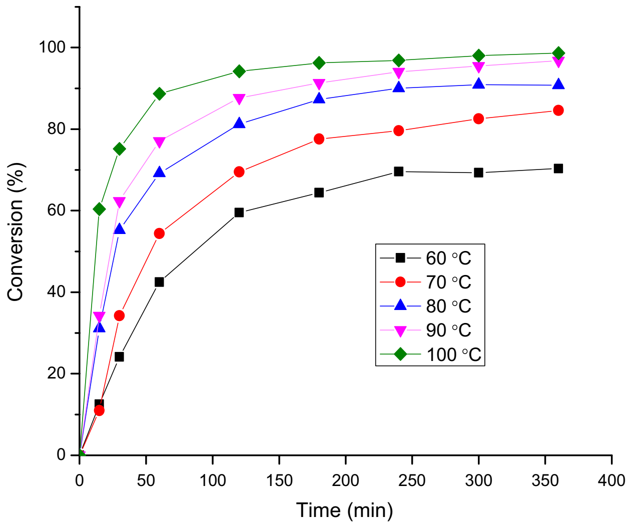


Fig. 6 Dependency of conversion of 1-phyenylethanol on temperature. Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, 1-phenylethanol/Pd molar ratio = 416 and rpm = 800

Table 1 Kinetic parameters for the anaerobic transfer dehydrogenation of 1-phenylethanol over 5 wt% Pd/C at different temperatures

Temperature (°C)	Rate equation	Correlation coefficient, R^2	k (min^{-1})
60	y = 0.004 x	0.989	0.0044
70	y = 0.0108 x	0.992	0.0108
80	y = 0.184 x	0.994	0.0184
90	y = 0.0202 x	0.989	0.0300
100	y = 0.05 x	0.998	0.0501

Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, 1-phenylethanol/Pd molar ratio = 416, stirring rate = 800 rpm and reaction time = 6 h

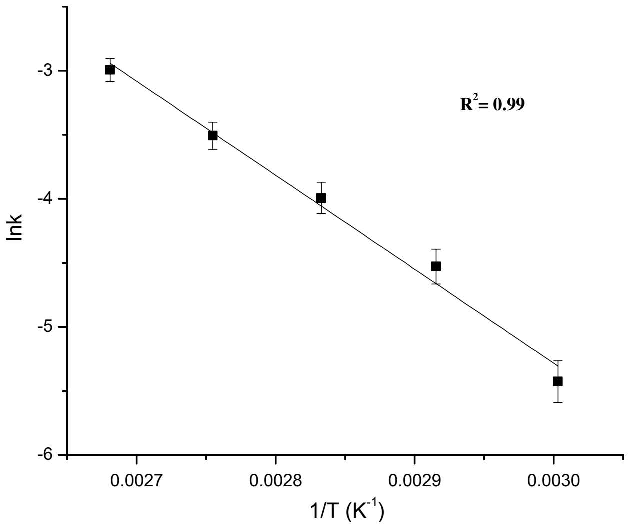


Fig. 7 Arrhenius's plot for the anaerobic transfer dehydrogenation of 1-phenylethanol over 5 wt% Pd/C. Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, 1-phenylethanol/Pd molar ratio = 416 and stirring rate = 800 rpm

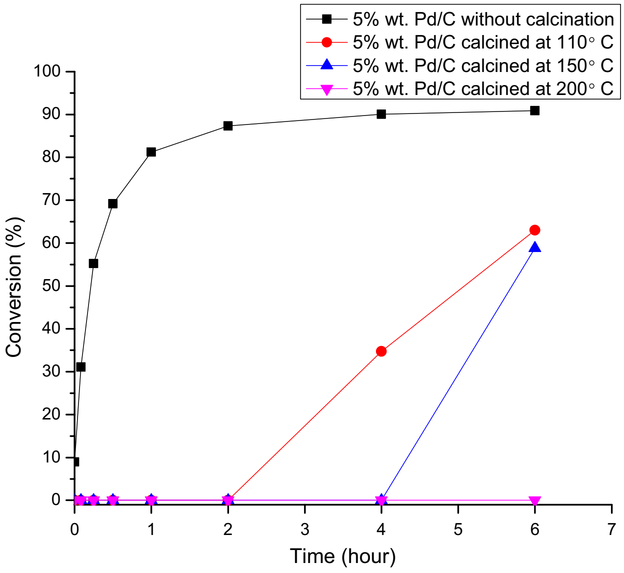


Fig. 8 Influence of thermal treatment of 5 wt% Pd/C on the catalytic performance in the liquid phase transfer dehydrogenation of the 1-phenylethanol. Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, 1-phenylethanol/Pd molar ratio = 416, T = 80 °C, stirring rate = 800 rpm

loss of catalytic activity was found when increasing the calcination temperature of the catalyst to 200 °C. Furthermore, an induction period was observed for the catalyzed liquid phase transfer dehydrogenation of 1-phenylethanol when using the calcined 5 wt% Pd/C catalysts at 110 and 150 °C. This induction period increased with increasing the calcination temperature from 110 to 150 °C as shown in Fig. 8, as the 5 wt% Pd/C calcined at 110 and 150 °C exhibited an induction period of 2 and 4 h, respectively before initiating the reaction. To interpret these results, it is important to evaluate the catalysts characterization results, in particular, in terms of the particle size and the oxidation state of Pd gained from the TEM and XPS analysis respectively. As shown in Table 2, the mean particle size calculated from TEM images for the thermally treated samples remain almost constant (~3 nm) when increasing the calcination temperature from 110 to 200 °C, while the palladium oxidation state was varied remarkably when increasing the calcination temperature. The Pd(0)/Pd(II) atomic ratio decreased by 75% after the thermal treatment of the 5 wt% Pd/C catalyst at 200 °C indicating the oxidation of Pd(0) to Pd(II) at relatively high temperature. This decrease in Pd(0) content in the catalyst is associated with a decrease in the catalytic performance, the higher content of Pd(0)

Table 2 Characterization data (TEM and XPS) of dried and calcined 5 wt% Pd/C and the corresponding catalytic performance

Catalyst	Pd(0)%	Pd(II)%	Pd(0)/Pd(II)[a]	Particle size (nm)	Conversion (%)
5 wt% Pd/C	52.70	47.30	1.11	3.34	91.0
5 wt% Pd/C calcined at 110 °C	52.54	47.46	1.11	3.20	63.0
5 wt% Pd/C calcined at 150 °C	44.95	55.05	0.82	3.60	58.0
5 wt% Pd/C calcined at 200 °C	22.71	77.29	0.29	3.20	0.0

Reaction conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, 1-phenylethanol/Pd molar ratio = 416, T = 80 °C, stirring rate = 800 rpm and reaction time = 6 h

[a] The calculations are based on Pd(0) and Pd(II) species only

on the catalyst, the higher catalytic performance in the liquid phase transfer dehydrogenation of 1-phenylethanol, which is in agreement with previous observations [12, 23, 27, 28]. As a result of increasing the Pd(II) content in the samples calcined at 150 and 200 °C, an induction period occurred during the first period of the reaction. This induction period is directly proportional to the percentage of Pd(II) in the catalyst, the higher Pd(II) content, the longer induction period was observed. The observed catalytic data during the induction period, can be explained based on the fact that the amount of Pd(0) increased during the induction period due to the chemical reduction of Pd(II) to Pd(0) via the dehydrogenation of alcohol and the formation of hydrogen that can act as a reducing agent [24, 26–29]. Consequently, a continuous increase in Pd(0)/Pd(II) ratio will take place within the induction period until reaching the required Pd(0)/Pd(II) to initiate the transfer dehydrogenation reaction of 1-phenylethanol.

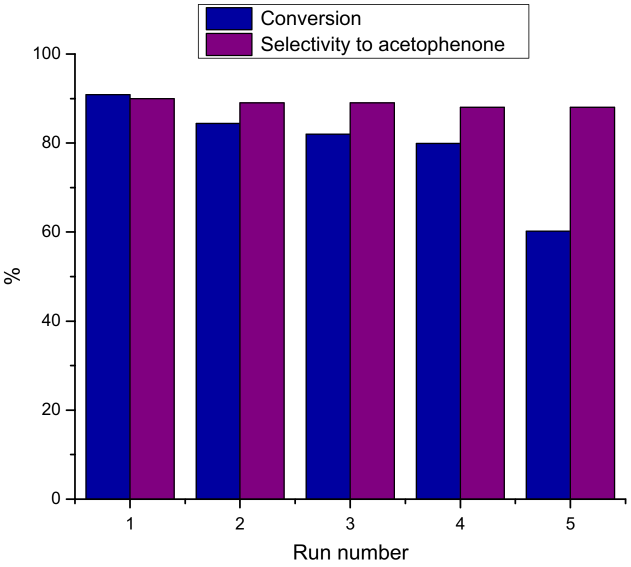


Fig. 9 Reusability of the 5 wt% Pd/C in the transfer hydrogenation of 1-phenylethanol at optimized conditions: (0.008 mol) of 1-phenylethanol, (0.016 mol) of cyclohexene, T = 80 °C, 1-phenylethanol/Pd molar ratio = 416 and stirring rate = 800 rpm

3.4 Re-usability Evaluation

In order to evaluate the catalytic stability of 5 wt% Pd/C catalyst, different batch runs were carried out at the optimized conditions (molar ratio of cyclohexene to 1-phenylethanol = 2, the molar ratio of 1-phenylethanol/Pd = 416, 80°C, and stirring speed of 800 rpm). After the liquid-phase transfer dehydrogenation reaction of 1-phenylethanol, the catalyst was separated using a simple filtration method and repeatedly washed with 10 mL of toluene at least five times. The separated catalyst was dried at room temperature for 24 h before being used in a new run. The recycling experiments were continued using the same catalyst and same experimental protocol for five cycles. Figure 9 revealed that the catalyst showed negligible changes in the catalytic activity as the conversion values remained approximately steady until the fourth run with constant values of selectivity to acetophenone. In the fifth cycle, the conversion value decreased by 20% from its original value. This decrease in activity can be possible attributed (i) to the deactivation of some active sites on the surface of the catalyst, (ii) leaching of Pd metal (iii) increase of Pd particle size. For investigating the possibility of Pd leaching, ICP-AES analysis was carried out after each run for the filtered solution to determine the concentration of leached palladium. The concentration of Pd after the first four runs was below the detectability limit of the instrument indicating the stability of the catalyst. After the fifth cycle, a negligible amount of leaching of Pd was detected (0.0002 ppm) and the leaching percentage considering the initial amount of Pd is 2.4×10^{-4}% indicating the stability of 5 wt% Pd/C catalyst during the liquid-phase transfer dehydrogenation reaction of 1-phenylethanol. Furthermore, the particle size distribution obtained from TEM images for the fresh and used 5 wt% Pd/C catalyst shows that there is no significant change in the particle size, as will be discussed in the catalyst characterization part, indicating that the decrease in the catalyst activity after the fourth cycle can be attributed to the deactivation of some active sites on the surface of the catalyst.

3.5 Catalyst Characterization

The fresh and used catalysts were characterized using a range of characterization techniques (XRPD, TEM, XPS, SEM-EDX and BET) to obtain information regarding the crystallite size, particle size, oxidation state, metal composition and surface area of the catalysts. Fig. S2 in the supporting information shows the XRPD patterns for the fresh and used 5 wt% Pd/C samples. For the fresh sample, the weak and broad diffraction peaks at 2θ = 40.10°, 46.74° and 67.60° correspond to (111), (200), and (220) planes which exhibit a typical XRPD pattern of a face-centered-cubic (fcc) lattice structure of metallic palladium [32]. This indicates the existence of palladium species in the metallic state. The broad peak that appears at 2θ = 43.8° relates to the (110) plane in PdO [33], which indicate the presence of Pd(II) species while the broad peak at 2θ = 24.17° relates to the plane (002) in activated carbon support [34]. The used sample presents the existence of all the peaks related to metallic Pd and the activated carbon as they appear in the fresh sample. Furthermore, the PdO peak (110) at 2θ = 43.8° has disappeared in the used sample while an enhancement of the Pd (220) peak at 67.60° has occurred indicating the reduction of Pd(II) to Pd(0) after the liquid phase transfer dehydrogenation of 1-phenylethanol.The results are consistent with those obtained from XPS analysis as we present in the following section.

The (111) peak for Pd was used to calculate the crystallite size of palladium according to Scherrer's equation. The calculated crystallite size for both the fresh and used catalysts are 5.7 and 5.8 nm respectively. This indicates that there is no significant agglomeration for the recycled catalyst as there is no significant change in crystallite size after the transfer dehydrogenation reaction. The results are consistent with those reported from TEM analysis and the EDX-elemental mapping.

XPS was conducted to obtain more information about the elemental composition of the surface and the oxidation state of Pd. Figure 10a shows the Pd(3d) core-level XPS spectra of the fresh and used 5 wt% Pd/C catalyst. The Pd($3d_{5/2}$) spin–orbit can be deconvoluted into two dominant peaks with a binding energy of 335.2 and 336.9 eV. The peak at 335.2 eV can be assigned to the metallic state of palladium while the other peak at 336.9 eV can be assigned to Pd(II) in PdO [35, 36]. In addition, a sub-peak appears at 338.5 eV, matching the values reported for Pd(IV) in PdO_2 [35, 37, 38]. The XPS spectrum of the used sample shown in Fig. 10b indicates that only the presence of Pd(0) can be detected after the transfer dehydrogenation reaction. The XPS results also allow us to determine the percentage of the respective oxidation states of Pd: 42% as Pd(0), 38% as Pd(II) and 20% as Pd(IV) in the fresh sample. The percentage of Pd(0) has increased to 100% in the used catalyst. This increase in Pd(0) after the reaction can be attributed to the reduction of Pd(II) to Pd(0) during the transfer dehydrogenation of 1-phenylethanol. This result is consistent with the XRPD data as the PdO peak (110) at 2θ = 43.8° has disappeared in the used sample due to the reduction of Pd(II) to Pd(0). Finally, The BET surface area of the 5 wt% Pd/C catalyst was measured. For the fresh and used catalysts the surface area was in similar range (934 m^2/g for the fresh catalyst compared with 928 m^2/g for the used catalyst).

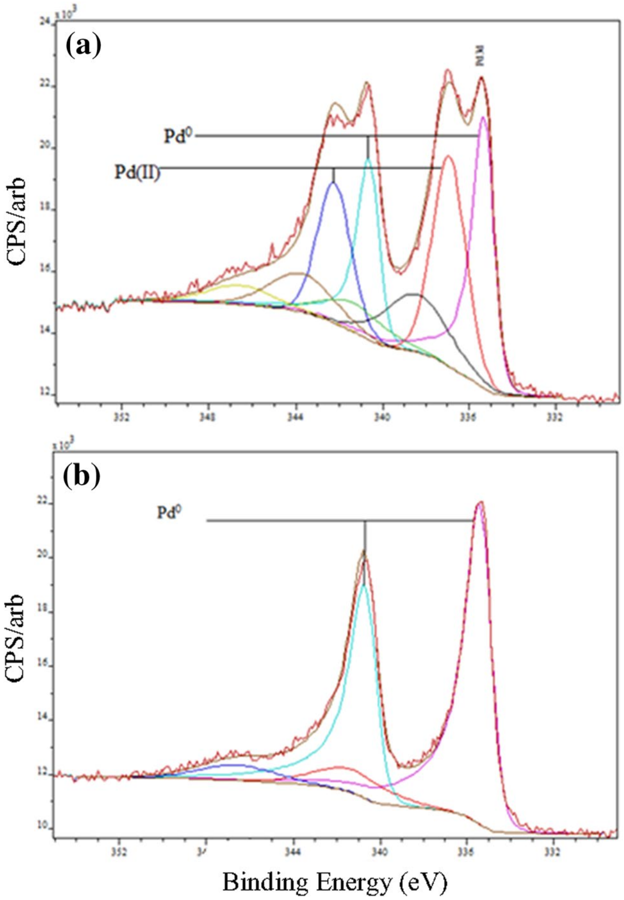


Fig. 10 Pd 3d core-level XPS spectra of the 5 wt% Pd/C catalyst **a** Fresh sample and **b** the used sample after the transfer dehydrogenation of 1-phenylethanol

For a detailed understanding of the effect of thermal treatment on the 5 wt% Pd/C catalyst, XRPD diffraction patterns and XPS spectra were recorded for the calcined catalysts before and after the transfer dehydrogenation of 1-phenylethanol. The samples were heat-treated at 110, 150, and 200 °C for 3 h under a steady flow of air (20 cm^3 min^{-1}). Fig. S3a in the supporting information illustrates the XRPD patterns of the thermally treated samples. All the peaks related to metallic palladium appears as the fresh sample at 2θ = 40.10°, 46.74° and 67.60° which correspond to (111), (200), and (220) planes respectively. The broad peak that appears at 2θ = 43.8° relates to the (110) plane in PdO [33]. It was also noted that a new peak at 2θ = 35.6° occurred in the sample treated at 200 °C. As previously reported, this peak can be attributed to PdO [33]. It is evident that the intensity of the Pd(111) peak decreases with increasing the calcination temperature, and the PdO(101) peak appears clearly in the sample calcined at 200 °C as shown in Fig. S3b in supporting information.

Figure S4 shows the Pd(3d) XPS spectra of thermally treated 5 wt% Pd/C catalyst. It can be noted that for all of the treated samples, the intensity of Pd(0) decreases remarkably, producing an increase in Pd(II) peak. This can be attributed to the oxidation of Pd(0) to Pd(II) during the thermal treatment process as it is expected. The oxidation process increases remarkably by increasing the temperature even at so low reaction temperature range. The ratio of Pd(0) to Pd(II) for the thermally treated samples calculated from XPS results are 1.11, 0.8, and 0.29 for the samples treated at 110, 150, and 200 °C, respectively. The decreases in Pd(0)/Pd(II) ratio indicates that there is a significant increase in Pd(II) species by increasing the calcination temperature as the percentage of Pd(II) increases by 30% when raising the temperature from 110 to 200 °C. This can be associated with the decrease in catalytic performance by increasing the calcination temperature as discussed earlier.

To confirm the loading of palladium onto the catalyst surface, the fresh and used catalysts were analyzed by SEM-EDX as shown in Fig. S5. It is evident that the transfer dehydrogenation reaction did not affect the morphology of the catalyst as there is no significant change in the morphology of the used sample. The EDX spectra confirm an average Pd loading of 5 wt% Pd/C in both samples. The elemental mapping images for the fresh and used

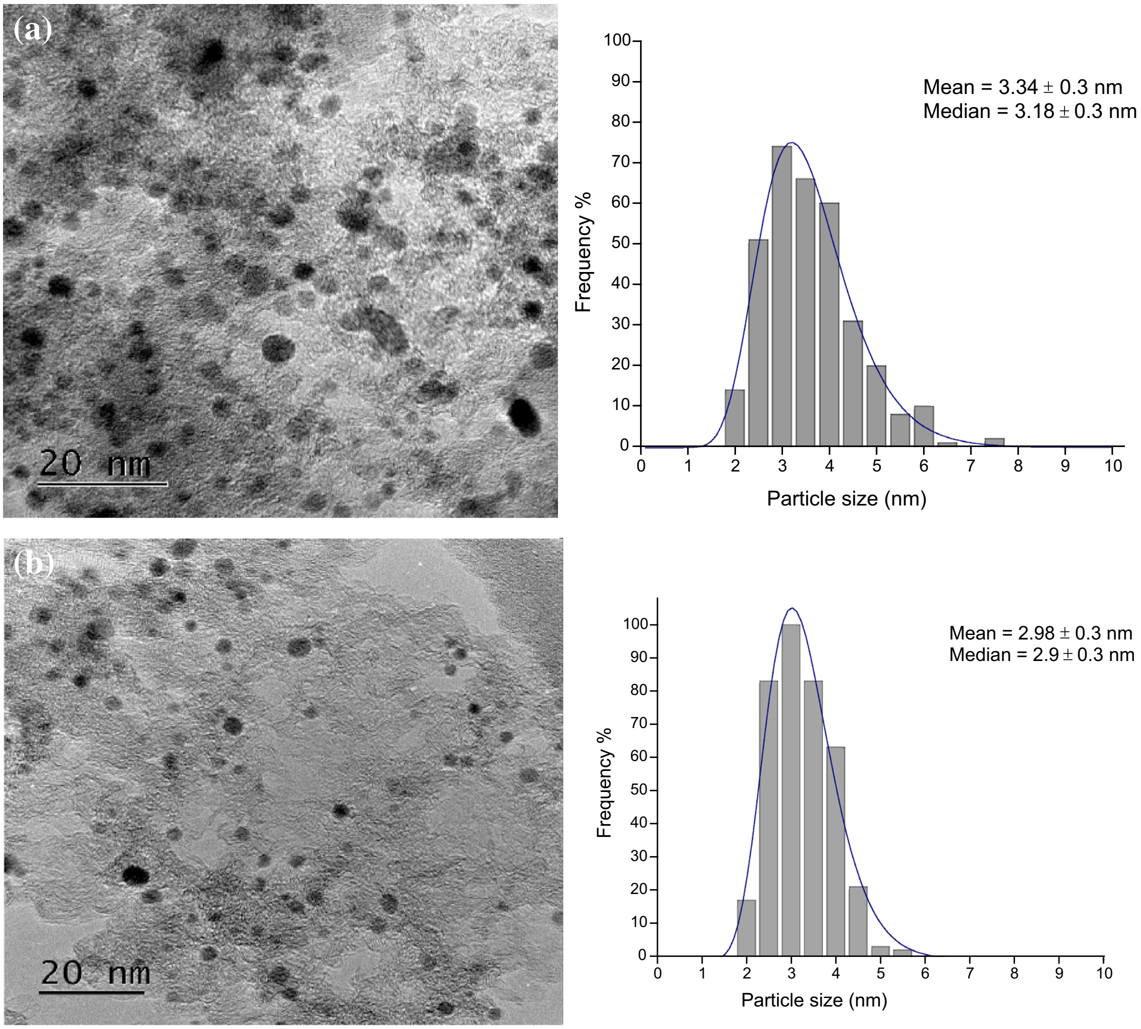


Fig. 11 TEM images of 5 wt% Pd/C and particle size distribution histograms for **a** fresh 5 wt%Pd/C and **b** used 5 wt% Pd/C

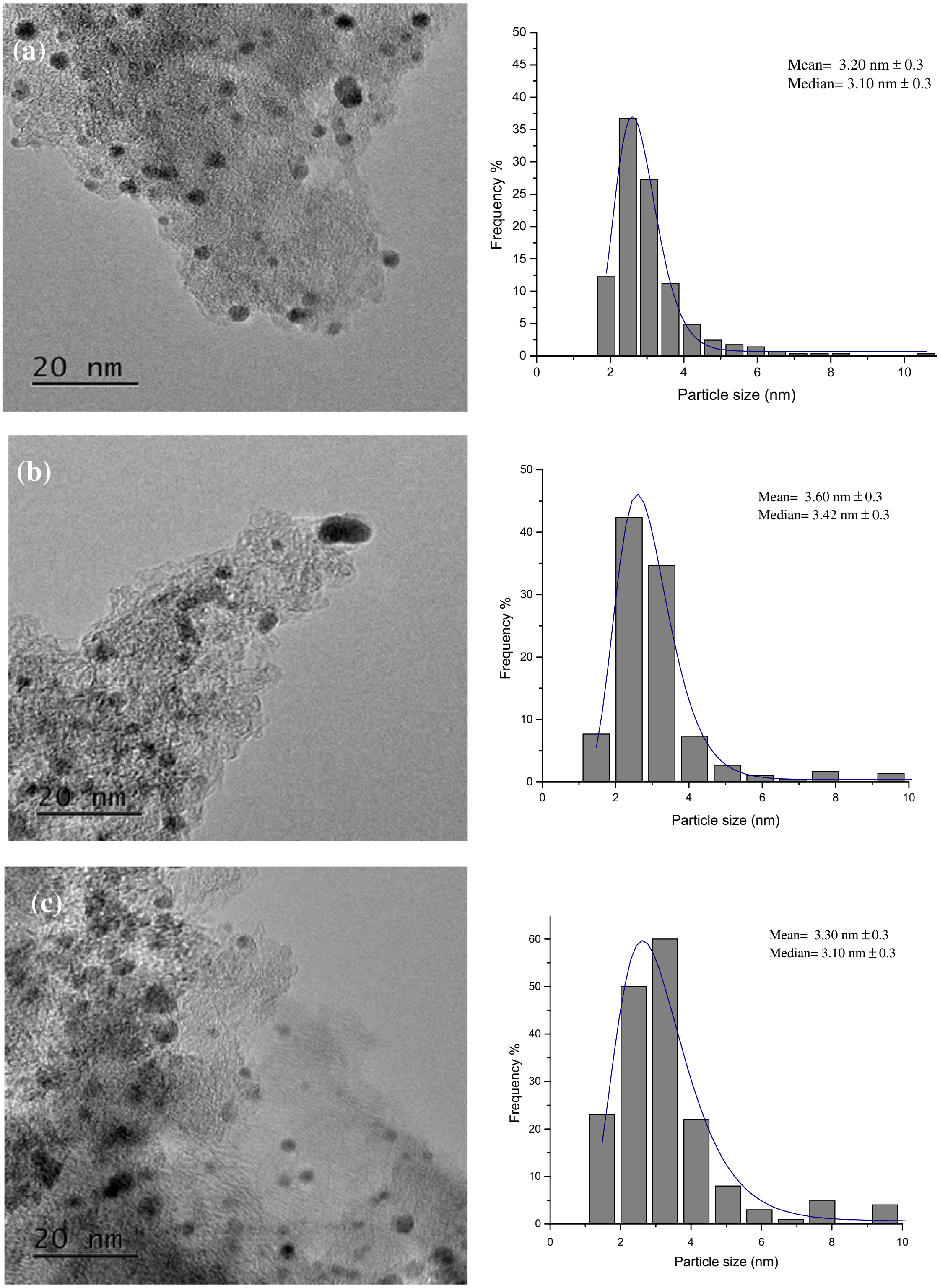


Fig. 12 TEM images and particle size distribution histograms for the of 5 wt%Pd/C calcined at **a** 110, **b** 150 and **c** 200 °C

catalyst are shown in Fig. S6. It can be noted that there is no significant change in the palladium and carbon mapping for the fresh and used samples, indicating that there is no indication of Pd agglomeration after the transfer dehydrogenation reaction of 1-phenylethanol. The results are consistent with TEM and XRPD results.

TEM images of the fresh and used 5 wt% Pd/C catalysts are shown in Fig. 11. Palladium particles were well dispersed on the carbon support, and the mean particle size for the fresh catalyst was 3.34 nm, which is in reasonable agreement with the crystallite size calculated from XRD (5.70 nm). Figure 11b shows the TEM image and particle size distribution of the used 5 wt% Pd/C catalyst. The mean particle size was 2.98 nm, which was not significantly different from that of the fresh 5 wt% Pd/C catalyst (3.34 nm), indicating that no Pd agglomeration occurred after recycling of the catalyst.

Figure 12 shows the TEM images for the thermal treated 5 wt% Pd/C catalyst. The mean particle size for the catalyst calcined at 110, 150, and 200 °C are 3.2, 3.6, and 3.3 nm, respectively. These values indicate that the effect of calcination on the 5 wt% Pd/C catalyst in the temperature range of 110–200 °C in negligible, and the growth of Pd particles is minimal within this range of temperature in agreement with STEM images (Fig. S7).

4 Conclusions

The present work reveals the successful utilization of a commercial 5 wt% Pd/C as an efficient and relative stable catalyst for the anaerobic liquid phase transfer dehydrogenation of 1-phenylethanol under mild reaction conditions. A number of reaction parameters were investigated for determining the different regimes of the 5 wt% Pd/C catalyzed anaerobic liquid phase transfer dehydrogenation of 1-phenylethanol, so we could distinguish between the mass transfer and kinetic regime. The optimal reaction conditions for the anaerobic transfer dehydrogenation reaction under kinetic regime control were found to be: 1-phenylethanol/Pd molar ratio of 416, 800 rpm, and 80 °C. The apparent activation energy for the transfer dehydrogenation reaction was determined with a value of 61 kJ/mol. In addition, the effect of thermal treatment of the catalyst on the catalytic performance was studied, and the structure–activity relationship was correlated using characterization results from TEM and XPS analysis. We found that under the optimized conditions, the transfer dehydrogenation of 1-phenylethanol is highly sensitive to the oxidation state of palladium. The higher content of Pd(0) in the catalyst, the higher catalytic performance in the liquid phase transfer dehydrogenation of 1-phenylethanol was observed. At the optimized reaction conditions, the 5 wt% Pd/C exhibits 91% conversion with 90% selectivity to acetophenone. Finally, the catalyst preserves around 80% of its initial catalytic activity after five cycles indicating the relative good stability of the 5 wt% Pd/C catalyst in the liquid phase transfer dehydrogenation of 1-phenylethanol.

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