Polymer-supported palladium-imidazole complex catalyst for hydrogenation of substituted benzylideneanilines

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ABSTRACT

The polymer-supported palladium-imidazole complex catalyst was synthesized and characterized by various techniques such as elemental analysis, IR spectroscopy and TG analysis. The physico-chemical properties such as bulk density, surface studies by BET method and swelling studies of catalyst in different solvents were investigated. XPS studies were carried out to identify the oxidation state of palladium in the catalyst. The morphology of the support and the catalyst was studied using scanning electron microscope. Using the synthesized catalyst, hydrogenation of benzylideneaniline and a few of its para substituted derivatives was carried out at ambient conditions. The influence of variation in temperature, concentration of the catalyst as well as the substrate on the rate of reaction was studied. The catalyst showed an excellent recycling efficiency over six cycles without leaching of metal from the polymer support.

1. Introduction

Catalytic reduction of organic compounds is an important process in the laboratory and industry and continues to be a subject of active research. Methods based on catalytic hydrogenation in homogeneous and heterogeneous media are commonly adopted for the hydrogenation of organic compounds. Transition metal complexes are reported to be powerful catalysts for organic transformations [1]. Studies have revealed that the complexes of platinum group metals such as palladium, platinum and rhodium are effective catalysts for hydrogenation of nitro compounds, aldehydes and Schiff bases [2,3].

In the recent past, there has been an increasing interest in developing environmental friendly greener processes which are also economically viable. Heterogeneous catalysts can be used in fluidized and packed bed reactor where recycling is easy. This becomes more significant when noble metals are used as catalysts. Highly

inert and thermally stable materials like silica, alumina, carbon or polymers are used as supports [4–16]. Polymer supports have several advantages as they can be functionalised with different types of ligands and the functionalised polymer supports can form stable complexes with different metals suitable for various organic transformations. Catalysts can be tailor made for reactions.

Earlier researchers have reported the hydrogenation of Schiff bases like benzylideneaniline using transition metal complexes as catalysts under high pressure and temperature [1,17]. In the present work, chloromethylated polystyrene beads (PS-DVB) were functionalised with imidazole to create an environment analogous to those in active homogeneous catalysts. Palladium chloride was anchored on to the functionalised beads and was used for hydrogenation of benzylideneaniline and few of its para derivatives.
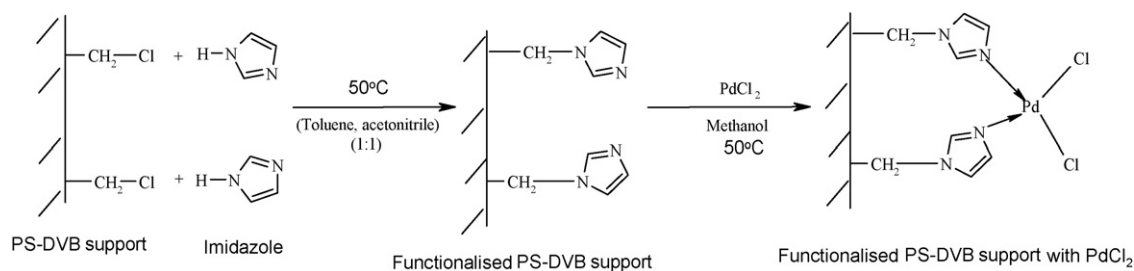
2. Experimental

2.1. Materials, methods and equipment

PS-DVB with 6.5% cross-linking was obtained as a gift by Thermax India Ltd., Pune, India. Palladium chloride was procured from Arora Matthey Ltd., India. Benzylideneaniline and its derivatives were prepared as per the literature method [18]. All the solvents were purified before use. The IR spectra were recorded using a Shimadzu FTIR-8500S spectrometer and far IR spectra by using a PerkinElmer, Spectrum 1000, FTIR spectrometer. Surface area was

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Scheme 1. Preparation of the polymer-supported palladium-imidazole catalyst.

measured using a Nova 1000 instrument in nitrogen atmosphere. TGA studies were carried out using a PerkinElmer, Diamond instrument under inert atmosphere. Scanning electron micrographs were recorded on a Leica S440i. HPLC studies were recorded using a Shimadzu Prominence, 2A with C18 column and UV detector. GC–MS were recorded with a Shimadzu GC–MS instrument. C, H and N analyses were carried out using Finnegan Eager 300 and a Elementar Vario EL III, Carlo Erba 1108, at SAIF, Cochin, CDRI, Lucknow. Palladium content was determined using a GBC, Avanta PM, atomic absorption spectrophotometer and chloride content by Volhard's method. Photoelectron spectra were recorded on a ESCA-3000 electron spectrometer, equipped with a hemispherical electron analyzer using the Al K$_\alpha$ radiation (1486.6 eV) X-ray source. The neat complex Pd(Imz)$_2$Cl$_2$ (Imz = imidazole) was prepared according to a literature method [19].

2.2. Preparation of the polymer-supported palladium-imidazole catalyst

Functionalisation of PS-DVB with imidazole was carried out by treating PS-DVB with imidazole, in a mixture of 1:1 toluene and acetonitrile on a hot water bath maintained at 50 °C for 60 h [6,14]. The functionalised beads were filtered and washed by Soxhlet extraction using ethanol as a solvent. The beads were treated with ethanolic solution of palladium chloride for 10 h during which the beads colour changed to buff [2]. Beads were finally washed by Soxhlet extraction using ethanol and dried (Scheme 1). The catalyst was activated by treating with methanolic solution of sodium borohydride, washed several times with methanol and vacuum-dried.

2.3. Hydrogenation procedure

All the reactions were carried out using ethanol as a solvent at 596 mmHg hydrogen pressure in a glass reactor. In a typical experiment, the catalyst was added along with the solvent into the reactor, flushed with hydrogen and evacuated. A known quantity of the substrate was injected and the system was opened to hydrogen gas burette. The reaction was monitored by hydrogen uptake at different intervals of time. The reaction mixture was then filtered, evaporated to dryness and the resulting solid was recrystallized. Products obtained were identified using HPLC, IR spectra and GC–MS. A blank reaction was also carried out for all the substrates without using the catalyst.

Table 2
Elemental analysis of polymer support and polymer bound catalyst.

	% C	% H	% N	% Pd
A	69.50	5.78	–	–
B	62.92	5.21	8.80	–
C	50.60	4.78	6.52	10.03
D	52.13	5.06	6.22	9.95
E	53.9	4.87	5.00	9.86

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. Surface area and porosity of the catalyst

Surface area and porosity of the catalyst influences the activity of the catalyst. Bulk density is also an important pre-requisite to be fulfilled by a catalyst. High bulk density facilitates the efficient use of reactor volume and therefore is economical. Surface area, pore volume and pore diameter determined by BET method is tabulated along with apparent bulk density in Table 1. Decrease in surface area, pore volume and pore diameter after functionalisation and activation of the catalyst was observed which may be attributed to the blocking in pores of the polymer-support. Increase in bulk density is due to the functionalisation and anchoring of the metal salt on the support.

3.1.2. Swelling studies

Swelling studies on the polymer support and the catalyst in various solvents were carried out at room temperature. Though the swelling was found to be maximum in DMF, the reactions were carried out in ethanol as the solubility of hydrogen is maximum in ethanol [20–23].

3.1.3. Elemental analysis

Elemental analysis for A, B, C, D and E were carried out and the data are tabulated in Table 2. Decrease in chloride content and the presence of nitrogen in B determined the extent of functionalisation of A. Changes were also observed after treatment of the functionalised beads with palladium chloride and treating it with sodium borohydride. Amount of metal was determined by stripping the bound metal from the support and analyzed using atomic absorption spectrophotometer. Palladium content remained almost unchanged even after recycling the catalyst for six cycles.
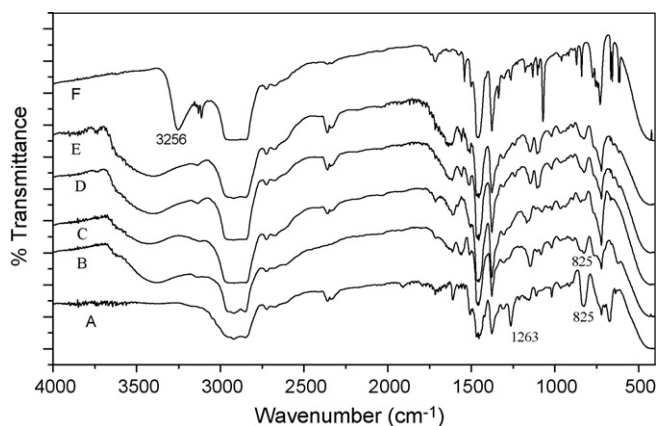
Table 1
Physical properties of polymer-support and polymer bound catalyst.

	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	Pore diameter (Å)	Apparent bulk density (g cm^{-3})
A	0.0421	28.24	59.67	0.323
B	0.0299	20.16	59.48	0.439
C	0.0335	21.81	61.41	0.505
D	0.0344	23.39	58.91	0.489
E	0.0397	25.19	62.66	0.475

Fig. 1. IR-spectra of A, B, C, D, E and F.

3.1.4. Infrared spectral studies

The IR spectra of A, B, C, D, E and F were recorded in nujol and a comparative study was made (Fig. 1). PS-DVB exhibits a peak at 1263 cm^{-1} attributed to –CH$_2$Cl (Spectrum A) and imidazole exhibited υ_{N-H} around 3124 cm^{-1}. The later peak was not found after functionalisation of the polymer indicating that hydrogen of (N–H) imidazole is lost consequent to functionalisation and it is bonded to the polymer support through nitrogen [11]. Decrease in intensity of band at 825 cm^{-1} corresponding to υ_{C-Cl} of A further support the bonding of imidazole with A (Spectrum B) [24]. The sharp absorbance due to υ_{N-H} of palladium-imidazole complex at 3256 cm^{-1} in the spectrum F has not been observed after attachment of the complex with the polymer support [25]. This further confirms the bonding of complex with the polymer support. No change in the spectral features was observed after activation of catalyst with sodium borohydride or after recycling the catalyst over six cycles (Spectra D and E, respectively). A high intense absorption band at 312 cm^{-1} in the far-IR spectrum recorded for D has been assigned to Pd-Cl stretching.

3.1.5. SEM and TGA studies

Scanning electron micrographs of A and D were taken to study the surface of the polymer support and the catalyst. Change in morphology of the activated catalyst surface was observed when compared with the support. The scanning electron micrographs are depicted in Fig. 2a and b.

Thermal stability of the support and the catalyst was studied by TGA–DTA analyses in an inert atmosphere with heating rate of 10 °C/min up to 500 °C for A, B, C, D and E. The TGA–DTA curve for D is shown in Fig. 3. The weight loss observed around 100 °C could be due to the moisture content. No significant weight loss has been observed till 254 °C.

3.1.6. XPS studies

The oxidation state of the metal in the catalyst was ascertained by carrying out XPS studies (Fig. 4). Spectrum of C revealed the presence of palladium in a +2 oxidation state with binding energies 338.0 eV (3d$_{5/2}$) and 343.3 eV (3d$_{3/2}$). After treating the anchored catalyst with sodium borohydride (Spectrum D) it exhibited one minor peak at 335.3 eV (3d$_{5/2}$) along with two major peaks at 338 eV (3d$_{5/2}$) and 343.3 eV (3d$_{3/2}$) indicating the presence of small amount of palladium in zero oxidation state [5,26,27]. After recycling the catalyst for six times its XPS was taken in which broadening of 3d$_{5/2}$ peak was observed (Spectrum E) which could be due to increase in the concentration of palladium in zero oxidation state on recycling.
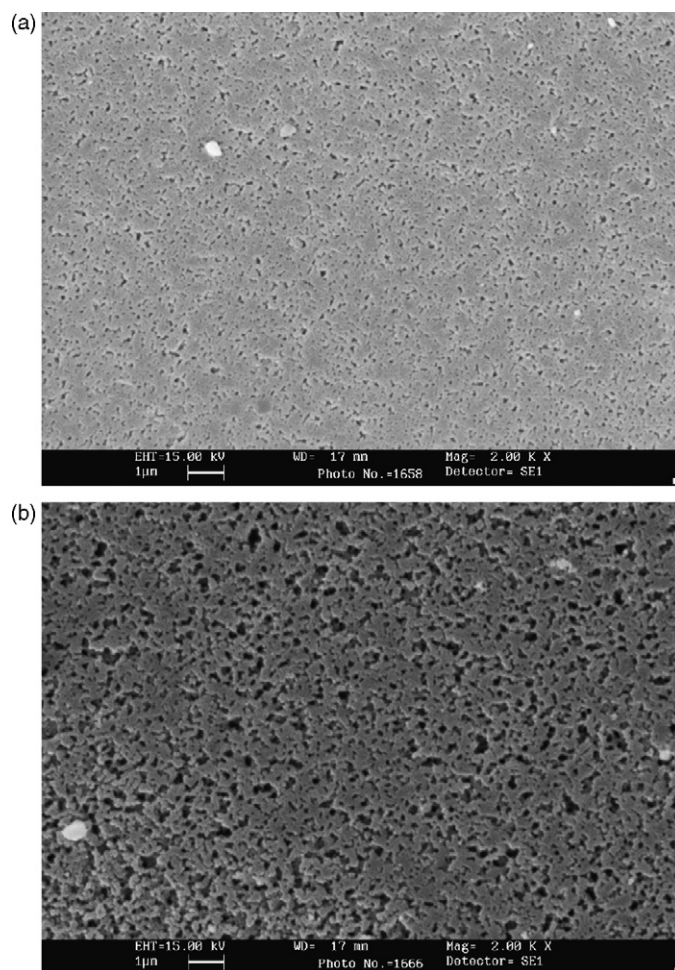

Fig. 2. (a) Scanning electron micrograph of A. (b) Scanning electron micrograph of D.

3.2. Hydrogenation reaction

Palladium-imidazole complex, Pd(Imz)$_2$Cl$_2$, in ethanol was used as catalyst for hydrogenation of benzylideneaniline to N-benzylaniline but the attempt was unsuccessful since it resulted in the separation of metal from the solution during the course of the reaction. Hence the polymer-supported palladium-imidazole catalyst was synthesized and used for the reduction of benzylideneaniline and its derivatives. It was found that during the reaction
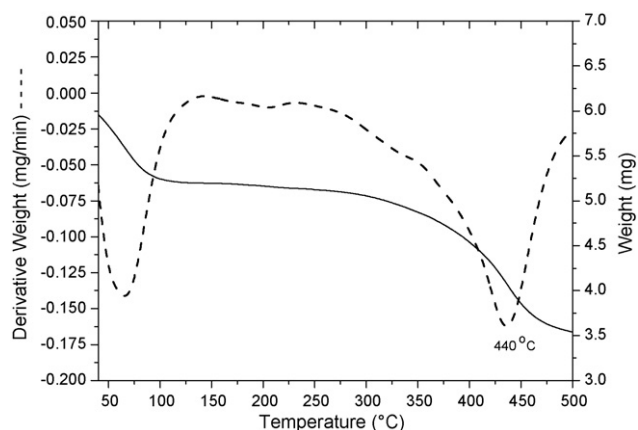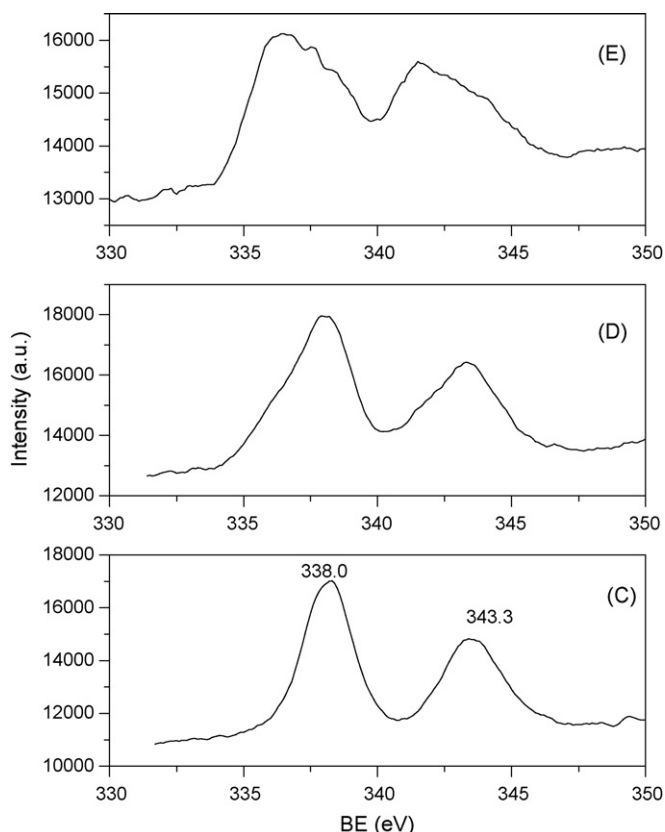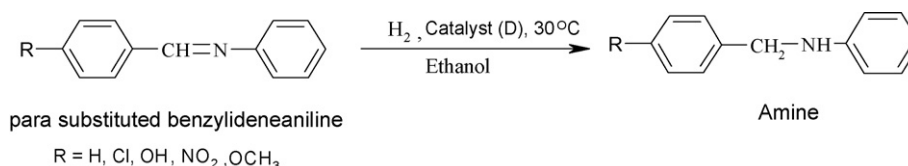

Fig. 3. TGA-DTA curves of D.

Fig. 4. XPS spectra of C, D and E.

Fig. 5. Dependency of rate of hydrogenation on [catalyst].

3.3. Kinetic studies

The kinetics of hydrogenation of the benzylideneanilines were studied by following the hydrogen uptake at 596 mmHg hydrogen pressure. The rate of hydrogenation was calculated from the slope after plotting the volume of hydrogen uptake by the substrate as a function of time. The dependency of the rate on variables like catalyst, substrate concentration and temperature was studied in detail for all the substrates.

3.3.1. Effect of catalyst concentration

The influence of catalyst concentration on the rate of hydrogenation was carried out over a range of 14.8×10^{-4} to 20.72×10^{-3} mol dm^{-3} Pd at constant substrate concentration of 33.3×10^{-3} mol dm^{-3} at a temperature of 30 °C with 596 mmHg hydrogen pressure using ethanol as solvent [18]. The plot of log(initial rate) against log[Catalyst] in the range of 14.8×10^{-4} to 7.4×10^{-3} mol dm^{-3} Pd is depicted in Fig. 5. Order of the reaction determined from the slope of the plot showed that all the substrates followed fractional order kinetics. However, the range of concentration in which the catalyst follows the fractional order on the rate is not the same for all the substrates. This may be due to change in structure of the substrate molecules. As the rate of hydrogenation of hydroxyl derivative is close to that of chloro derivative the same has not been included in the plot.

Above 7.4×10^{-3} mol dm^{-3} Pd concentration, initial rate was found to be independent of catalyst concentration and it followed zero order kinetics indicating that for the substrate 4×10^{-3} mol dm^{-3} Pd is sufficient to hydrogenate and higher concentration of catalyst may not be required. Hence the rate becomes independent of catalyst concentration.

3.3.2. Effect of substrate concentration

The influence of substrate concentration on the rate of the reaction was studied in the range of 33.0×10^{-4} to 13.3×10^{-2} mol dm^{-3} of substrate at 30 °C and at 596 mmHg hydrogen pressure with a constant catalyst concentration of

metal does not leach out from the polymer support and was found to be intact even after recycling for six times. All reactions were conducted in ethanol at 596 mmHg of hydrogen pressure. Since the activity of the activated catalyst (D) was more compared to palladium chloride anchored catalyst (C), the activated catalyst was used for hydrogenation reactions. [5,17]. The products were identified by HPLC, IR and GC–MS. To determine the effect of substitution at the para position of benzylideneaniline on hydrogenation, few derivatives with –NO$_2$, –Cl, –OH and –MeO groups were chosen. Earlier studies have shown that the introduction of substituents at para position of the amine ring of the benzylideneaniline has very little effect on the hydrogenation rate. In our studies it has been observed that the insertion of substituents on to the para position of aldehyde ring of benzylideneaniline reduced the activation energy markedly [28] (Scheme 2).

When p-nitrobenzylideneniline was used as the substrate, both C=N and nitro group were hydrogenated simultaneously and the catalyst does not show selectivity towards C=N. Hence the effect of nitro group substitution on the rate could not be determined. Similar observation was made by Arthur Roe and Montgonery [18].

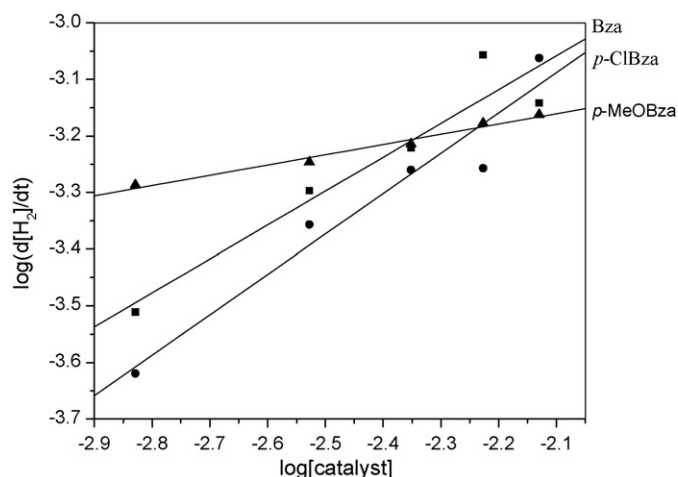**Scheme 2.** Hydrogenation of substituted benzylideneanilines.

Fig. 6. Dependency of rate of hydrogenation on [substrate].

Scheme 3. Probable mechanism of hydrogenation.

59.2×10^{-4} mol dm^{-3} Pd for all the substrates in ethanol [18]. The plot of log(initial rate) against log[substrate] is given in Fig. 6. Order of the reaction in this concentration range for all the substrates was found to follow fractional order. However, the range of concentration where the substrate follows a fractional order on the rate is not the same for all the substrates. This may be due to structural changes in substrate molecules and coordinating ability of the catalyst towards different derivatives.

In the range 33.3×10^{-3} to 66.6×10^{-3} mol dm^{-3} substrate concentration, the initial rate was independent and followed zero order [9]. This could be attributed to the fact that as the catalyst concentration is constant, all the catalyst would have been used and no catalyst is available for higher concentration of the substrate.

Based on the results obtained, a probable mechanism is proposed for the hydrogenation reaction (Scheme 3). The polymer bound catalyst binds reversibly with the substrate. In the slow step, the π-complex reacts with hydrogen to form a dihydrido complex which finally gives the amine.

A rate law derived for the above mechanism is given in Eq. (1):

$$\text{rate} = Kk_1 \frac{[C]_{\text{total}}}{1 + K[S]_{\text{unreacted}}} \times \frac{[S]_{\text{total}}}{1 + K[C]_{\text{unreacted}}}[H_2] \qquad (1)$$

where $[C]_{\text{total}}$ is the total concentration of catalyst initially taken, $[C]_{\text{unreacted}}$ is the concentration of unreacted catalyst at equilibrium, $[S]_{\text{total}}$ is the total concentration of substrate, $[S]_{\text{unreacted}}$ is the concentration of unreacted substrate at equilibrium. K is the equilibrium constant for reversible reaction and k_1 is the velocity constant for the rate determining step. All the reactions were carried out at a constant hydrogen pressure of 596 mm of Hg. Therefore, Eq. (1) reduces to

$$\text{rate} = Kk_1 \frac{[C]_{\text{total}}}{1 + K[S]_{\text{unreacted}}} \times \frac{[S]_{\text{total}}}{1 + K[C]_{\text{unreacted}}}$$

This equation explains that at low concentration, the reaction follows fractional order with respect to catalyst and substrate concentration, but at higher concentration the rate is independent of both.

3.3.3. Dependency of the rate on temperature

Rate of hydrogenation reactions for all the substrates were studied in the range of 30–45 °C with a constant catalyst concentration of 59.2×10^{-4} mol dm^{-3} Pd, substrate concentration of 33.3×10^{-3} mol dm^{-3} in ethanol at 596 mmHg pressure of hydrogen. The rate of the reaction was found to be dependent on temperature (T) of the system. Values of activation energy, activation entropy were calculated from the slope of Arrhenius plot
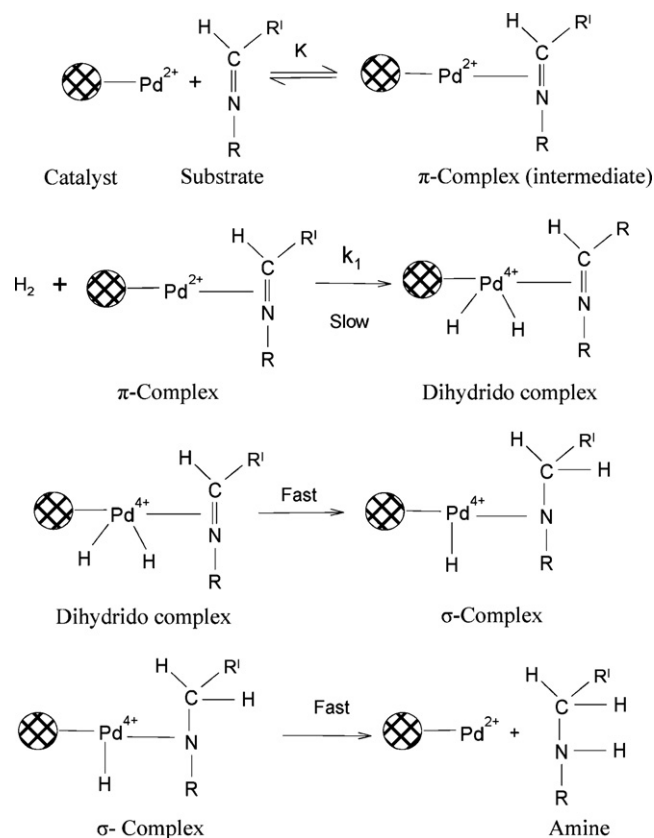
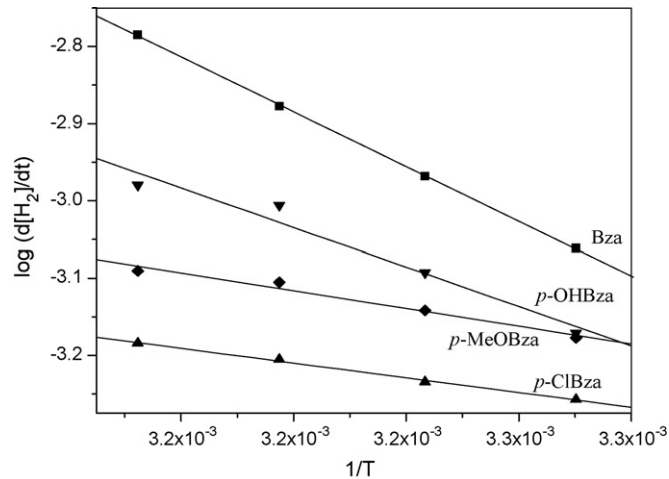**Fig. 7.** Effect of temperature: Arrhenius plot.

of log(initial rate) against $1/T$ (Fig. 7). The results are tabulated in Table 3. Results revealed that activation energy decreased after substituting –NO$_2$, –OH, –Cl and –MeO groups on to the para position of aldehydes ring of benzylideneaniline [28]. Lower activation

Table 3
Activation energy, activation entropy values for hydrogenation.

	Bza	p-NO$_2$Bza	p-ClBza	p-OHBza	p-MeOBza
Activation energy (kJ/mol)	34	31	9	24	12
Activation entropy (J/K mol)	−200	−212	−286	−233	−276

Table 4
Percentage conversion of various benzylideneanilines with supported palladium-imidazole complex catalyst.

Substrates	Products	Time (min)	Percentage conversion[a]	
			Fresh catalyst	After six recycles
Bza	N-Benzylaniline	60	72	67
p-ClBza	N-(4-Chlorobenzyl)aniline	100	88	84
p-MeOBza	N-(4-Methoxybenzyl)aniline	80	78	71
p-NO$_2$Bza	4-Aminobenzylaniline	100	97	83
p-OHBza	4-(Anilinomethyl)phenol	60	97	97

[a] Conversion based on the HPLC analysis.

energy also indicates higher activity of the catalyst. The lower activation entropy indicates that the substrate molecules are bonded to the catalyst surface and they have lost all translational degrees of freedom and probably gained only three vibrational degrees of freedom. Further, activation of the substrate with the catalyst may be due to localization of the substrate on the catalyst surface and this localized interaction may be necessary for the hydrogenation reaction since a double bond (C=N) involved is in the middle of the substrate molecule.

3.3.4. Effect of substituents

Effect of substituents on the rate of hydrogenation of benzylideneaniline was studied by varying the para substituents with different groups like –OH, –MeO, and –Cl [29]. It was observed that the rate of hydrogenation was slower upon substitution with these groups. When log(initial rate) was plotted against Hammett substituent constant (σ_{para}) it was a straight line with the slope of −0.99 (Fig. 8) indicates that the substituents do not have significant effect on the rate of the reaction.

4. Recycling efficiency of the catalyst

In order to test metal leaching from the catalyst, metal estimation was carried out at the end of first cycle and at the end of sixth cycle of the reaction. Percentage of metal in the catalyst remained constant in both the cases. Metal estimation for the reaction mixture was also carried out to make sure that there is no loss of metal from the catalyst. From this it is evident that there is no leaching of metal from the catalyst.

Recycling ability of the catalyst was studied by carrying out reactions over six cycles at a constant catalyst concentration of $59.2 \times 10^{-4}\,mol\,dm^{-3}$ Pd, substrate concentration of

$33.3 \times 10^{-3}\,mol\,dm^{-3}$ and temperature 30 °C with 596 mmHg of hydrogen pressure. The initial rate remained almost constant for over six cycles without any loss in efficiency of the catalyst.

Percentage conversion of the substrates for fresh and recycled catalyst is presented in Table 4. In the case of p-NO$_2$Bza, catalyst did not show selectivity towards C=N as both C=N and nitro group were hydrogenated simultaneously.

5. Conclusion

Polymer-supported palladium-imidazole complex could be used for hydrogenation of C=N group at ambient temperature and pressure to synthesize corresponding amines. The catalyst was found to be stable up to 250 °C as determined by TGA–DTA analysis.

It can be concluded from the Hammett plot, that the substituents in para position of benzaldehyde ring of benzylideneaniline do not have significant effect on rate of hydrogenation. However, the substitution at the para position reduces the activation energy. The catalyst has an excellent recycling efficiency over six cycles without leaching of metal from the polymer-support.

Fig. 8. Hammett plot: effect of para substituents on the initial rate of hydrogenation.

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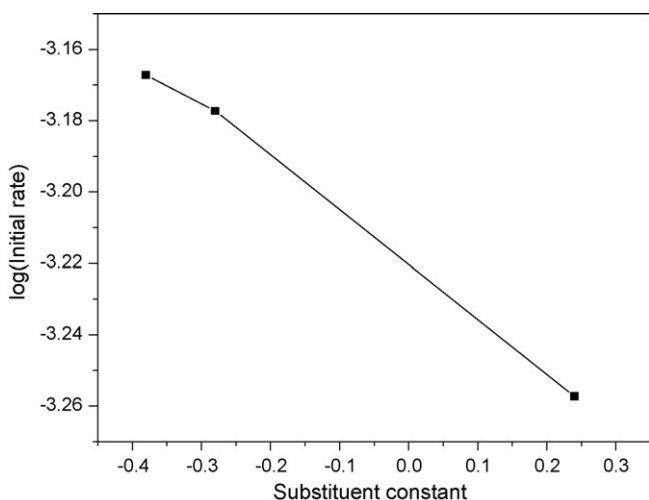[18] A. Roe, J.A. Montgonery, J Am. Chem. Soc. 75 (1953) 910–912.

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