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Palladium–Schiff Base Complexes Encapsulated in Zeolite-Y Host: Functionality Controlled by the Structure of a Guest Complex

Susheela Kumari,[†] Karthik Maddipoti,[†] Bidisa Das,[‡] and Saumi Ray^{*,†}

[†]Birla Institute of Technology and Science, Pilani, Rajasthan 333031, India

[‡]Technical Research Center, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

S Supporting Information

ABSTRACT: A series of palladium complexes of tetradendate Schiff base ligands L1 (N,N'-bis(salicylidene)phenylene-1,3-diamine) and its derivatives L2 and L3 have been synthesized by using the "flexible ligand method" within the supercage of zeolite-Y. These complexes in both their free and encapsulated states have been thoroughly characterized with the help of different characterization tools such as XRD, SEM-EDS, BET, thermal analysis, XPS, IR, and UV-vis spectroscopic studies. All these encapsulated complexes are identified with a dramatic red shift of the d-d transition in their electronic spectra when compared with their free states. Theoretical as well as experimental studies together suggest a substantial modification of the structural parameters of square planar Pd(II)-Schiff base complexes upon encapsulation within the supercage of zeolite-Y. Encapsulated complexes are also subject to show modified catalytic activities toward the Heck reaction. These heterogeneous catalysts can easily be separated from the reaction mixture and reused.



INTRODUCTION

Cross-coupling reactions are of great importance and significance, as these coupling reactions are widely used in organic synthesis for the preparation of natural products, biologically active compounds, conducting polymers, pesticides, pharmaceutical intermediates, and liquid crystals.¹⁻⁵Very commonly, these reactions are catalyzed by palladium based compounds. A number of homogeneous palladium complexes have been reported as efficient catalysts for Heck coupling reactions; however, they certainly have some limitations and disadvantages specifically when separation, purification of the products, thermal stability, and recyclability of catalyst are concerned, and in many cases these catalyst suffer from loss of catalytic activity.^{6,7}In recent years, many researchers are pursuing several techniques such as support of ionic liquids,⁸ immobilized on silica,9 grafted on polymers,10 anchored on activated carbon¹¹ or carbon nanotubes¹² and supported on zeolites¹³ and MCM-41,^{14,15} etc., especially to recover the catalyst successfully.

Among various host materials, zeolite-Y is a well-known microporous crystalline aluminosilicate material with a pore diameter of 7.4 Å and supercage dimension of 12.47 Å. It provides high surface area and excellent chemical stability with quite low toxicity. The specific architecture of the framework makes the zeolite a very attractive host for transition metal complexes, organometallics, organic dyes, and polymer within their voids, which in turn, makes these hybrid systems effective and competent catalysts with size and shape selectivity. Encapsulation of a metal complex inside the porous zeolite definitely enables the coupling between the reactivity of the host complex and the stability, with a specific electronic

environment provided by host materials and ease of separation. It is a unique route for site isolation of the desired catalyst.

Starting from the revolutionary work of Herron,^{16,17} many reports exist in literature encompassing encapsulation of transition metal complexes inside the supercage of zeolite-Y. Vasudevan and co-workers have emphasized the geometries adopted by guest metal complexes upon encapsulation within the cavities of the host framework. From our group we have reported the design of different metal complexes with salen Schiff base ligands inside the zeolite-Y and MCM-41.18-22 Although several reports explore the encapsulation of metal complexes inside zeolite-Y, very few actually focus on investigating the modified catalytic functionality of the encapsulated metal complex, originated from its structural modifications. Recently, we have reported the synthesis of a series of palladium salen complexes inside zeolite-Y. These encapsulated palladium complexes have been perceived to be efficient catalysts for sulfoxidation of methyl phenyl sulfide compared to their neat analogues, and toward the betterment of catalysis, the role of the distorted structure of the encapsulated complexes has been established.²²

The current work deals with the synthesis of encapsulated palladium-Schiff base complexes inside the supercage of zeolite-Y via the "flexible ligand method". This method is found to be appropriate for the encapsulation of palladium salophen complexes, as the salophen ligand having desired flexibility can be introduced into the supercage of zeolite through the channel. Once, the complex formed, it loses the flexibility and thereby becomes immobilized inside the

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Figure 1. Molecular dimensions of palladium complexes.

supercage unless the zeolite framework is destroyed. Encapsulation of these complexes inside the host makes it altogether a heterogeneous catalyst. This is a convenient and efficient route to combine the reactivity of palladium complex with the robustness and stereochemistry of the zeolite framework.

The palladium complexes of interest with the L1, L2, and L3 ligands follow the order of molecular dimension as PdL1 < PdL2 < PdL3, where L1 is N,N'-bis(salicylidene)phenylene-1,3-diamine, L2 is N,N'-bis(5-methoxysalicylidene)phenylene-1,3-diamine, and L3 is N,N'-bis(5-nitrosalicylidene)phenylene-1,3-diamine (given in Figure 1). The metal in three different complexes with different substituents essentially experience the electronic effect differently, along with being subjected to different steric constraints imposed by the topology of the zeolite cavity. The host framework induces the structural modification to the guest complex and alters the electronic, magnetic, and redox properties of the guest metal complex. Therefore, the topology of the host framework has substantial control over the functionality and selectivity of the guest molecule. These hybrid systems are employed as a catalyst for the cross-coupling Heck reaction of bromobenzene with styrene in the presence of sodium carbonate as a base to investigate the steric interaction and electronic effect of the substituent's group attached to the complex.

EXPERIMENTAL SECTION

Materials. The Na-zeolite-Y, salicylaldehyde, 2-hydroxy-5-methoxy benzaldehyde, 2-hydroxy-5-nitro benzaldehyde, 1,3- Phenylenediamine, styrene, and bromobenzene are purchased from Sigma-Aldrich, India. Palladium acetate is purchased from TCI chemicals, India. All the solvents such as methanol, ethanol, acetone, and ether are purchased from SD fine, India.

Synthesis of Ligands and Palladium Complexes. The Schiff bases L1, L2, L3, and corresponding palladium complexes are prepared by following the literature report.²³In a round-bottom flask, 10 mmol of 1,3-phenylenediamine and 20 mmol of salicylaldehyde or its derivatives in ethanol are mixed under constant stirring at 70 °C for 4 h. After the end of the reaction, the yellow solid product is vacuum filtered, washed with ethanol, and finally dried at room temperature (Scheme S1 is given in the Supporting Information (SI)).

To synthesize the palladium–Schiff base complex, the ethanolic solution of the ligand is heated at 80 °C for 30 min and palladium acetate is added in a 1:1 ligand-to-metal molar ratio. The reaction mixture is refluxed for 3 h. The solid palladium–Schiff base complex is washed with ethanol and finally dried. All three palladium complexes are synthesized using the same procedure (Scheme S2 in the Supporting Information).

Preparation of Pd(II) Exchanged Zeolite-Y and Encapsulated Pd(II)–Schiff Base Complexes in Zeolite-Y.¹⁹ Pure zeolite-NaY (10 g) is allowed to react with 0.01 M palladium salt $[Pd(CH_3COO)_2 = 0.224 \text{ g}]$ in 100 mL of distilled water to acquire the required loading level of palladium ions and stirred at room temperature for 24 h. The slurry is filtered, washed repeatedly with water, and then desiccated for 12 h at 150 °C.

The Pd(II) exchanged zeolite-Y is treated with a stoichiometric excess of respective Schiff base ligand. Being a flexible ligand, it diffuses through the channels of the host when the reaction mixture is refluxed for 24 h at 150-200 °C under constant stirring. The color of the solid reaction mass changes from light brown to dark brown. The reaction mass is then recovered and dried at room temperature. The resultant product is further purified by Soxhlet extraction maintaining the sequence of solvents as acetone, methanol, and finally diethyl ether to remove any unreacted ligand and palladium complex adsorbed on the surface of the host. The obtained product is further dried in a muffle furnace at 150 °C for 12 h. The product is allowed to react with 0.01 M NaCl solution to remove the unreacted palladium ions, followed by filtration and washing with distilled water thoroughly until the filtrate is negative for the chloride ion test. Finally, zeolite encapsulated palladium-Schiff base complexes (represented as EPdL1-Y, EPdL2-Y, and EPdL3-Y) are obtained as dark brown powders (Scheme S2 in the Supporting Information).

Catalytic Reaction. A mixture of 0.70 mmol % of catalyst, 10 mL of DMF solvent, 5 mmol of bromobenzene, 10 mmol of styrene, and 1.06 g of base is then refluxed for 20 h at 140 °C under constant stirring. After the completion of the reaction, the catalyst is recovered by filtration and washed with solvents for reuse. The filtrate is collected, and then after centrifugation, the supernatant solution of the reaction mixture is analyzed by FID-GC, using *n*-heptane as the internal standard, to determine the % conversion (Scheme 1). The reaction is monitored by collecting a small amount of the reaction mixture after 1, 4, 8, 12, and 20 h of reaction time.

Scheme 1. Schematic Representation of the Heck Coupling Reaction



RESULTS AND DISCUSSION

Elemental Analysis. The chemical composition of palladium(II)-exchanged zeolite-Y and encapsulated palladium complexes (EPdL1-Y, EPdL2-Y, and EPdL3-Y) are analyzed by the EDX technique. The Si/Al ratio for unit cell $Na_{52}(AlO_2)_{52}(SiO_2)_{140}$, yH_2O of pure zeolite-Y is 2.7. The Si/Al ratio has not been significantly affected during the palladium(II)-exchanged reaction as well as during the process of encapsulation, as the dealumination during encapsulation is minimal. Results obtained from EDX analysis are given in the form of weight % in Table 1 and Figure S1 in the Supporting

Table 1. Concentration of Palladium (wt %) Content in the Different Samples

s. no.	samples	palladium (wt %)	Si/Al ratio
1	Zeolite-Y	-	2.90
2	Pd-Y	0.65	2.79
3	EPdL1-Y	0.38	2.75
4	EPdL2-Y	0.41	2.84
5	EPdL3-Y	0.40	2.80

Information. The concentration of the palladium metal in the encapsulated complexes as compared to palladium(II)-exchanged zeolite-Y is found to be lower. The decrease in palladium content can probably be attributed to the formation of the palladium complex inside the cavity of the host, as leaching of some of the palladium ion during the encapsulation process is commonly observed phenomenon.

X-ray Diffraction and Scanning Electron Microscopy Analysis. The powder X-ray diffraction patterns have been recorded for pure zeolite-Y, palladium(II)-exchanged zeolite-Y, and zeolite encapsulated complexes (presented in Figure 2)



Figure 2. XRD pattern of (a) pure zeolite-Y, (b) Pd-exchanged zeolite-Y, (c) EPdL1-Y, (d) EPdL2-Y, and (e) EPdL3-Y.

with 2θ varying from 8 to 50 to study the crystallinity and the integrity of the host framework and to ensure encapsulation inside the supercage of zeolite-Y. The appearance of very similar XRD patterns for pure zeolite-Y, Pd(II)-Y, and zeolite encapsulated palladium-Schiff base complexes positively indicates that the framework of the host has not undergone any structural modification after encapsulation of the metal complexes inside the cavity and the crystalline nature of host is also not affected.²⁴However, there is an interesting observation with the relative intensities of peaks appearing at 2θ values 10° and 12° corresponding to the planes 220 and 311 respectively. For pure and Pd(II)-Y zeolite samples, the XRD peak at 10° is more intense than the peak at 12°, whereas, for encapsulated metal Schiff base complexes, the relation between intensities is just the reverse, i.e. $I_{220} < I_{311}$. A quite well-established semiempirical fact is that when a large molecule is entrapped within the supercage of zeolite-Y, an intensity reversal of the XRD peaks of pure zeolite at $2\theta = 10^{\circ}$ and 12° takes place.²⁵Our observation is in accordance with this fact. This change in the relative intensities may be related with the rearrangement of randomly coordinated free cations in zeolite-Y.^{26,27} No new peak is detected for Pd(II)-Y as well as for zeolite with encapsulated palladium complexes confirming a low loading level of metal in the host framework.

From scanning electron microscopy analysis, it has been observed that some impurities are present at the surface of the host in the form of complex and unreacted ligand but these impurities have been completely washed from the surface of zeolite-Y by extensive Soxhlet extraction. SEM images are given in Figure 3. After Soxhlet extraction, clear boundaries of the host framework are manifest in the SEM micrograph. This observation further suggests that the crystalline nature of the host is conserved during the encapsulation process.

BET Surface Area Analysis. The BET surface area analysis has been carried out to determine the surface area and pore volume for the pure zeolite-Y and zeolite with encapsulated complexes. The comparative adsorption–desorption isotherms for all encapsulated complexes and zeolite-Y are shown in Figure 4 and the surface area and pore volume data are given in



Figure 3. SEM images (A) EPdL2-Y (before Soxhlet extraction) and (B) EPdL2-Y (after Soxhlet extraction).



Figure 4. BET isotherms for pure zeolite-Y and zeolite encapsulated complexes: (a) pure zeolite-Y and (b) EPdL1-Y, EPdL2-Y, and EPdL3-Y.

Table 2. The pattern of adsorption-desorption isotherms for all the samples are found to be nearly identical (Figure 4),

Table 2. BET Surface Area and Pore Volume of Pure Zeolite Y and Encapsulated Complexes EPdL1-Y, EPdL2-Y, and EPdL3-Y

s. no.	sample	BET surface area (m^2/g)	pore volume (cm ³ /g)
1	Pure zeolite-Y	535	0.3456
2	EPdL1-Y	355	0.2025
3	EPdL2-Y	342	0.1961
4	EPdL3-Y	340	0.1920

suggesting that the host framework remains unaffected during the whole process of encapsulation. However, there exists a considerable difference in the surface area and pore volume of zeolite-Y and all hybrid systems. In all the encapsulated systems, the BET surface area and pore volume are found to be significantly lower in comparison to those for pure zeolite-Y, which directly indicates the presence of the metal complex inside the supercage of zeolite-Y rather than adsorbed on the external surface.^{28,29}All the catalysts have shown type I adsorption–desorption isotherms, which is a characteristic of the microporous material.³⁰ The lowering of BET surface areas and pore volumes for the hybrid systems are largely dependent upon the loading level of metal in zeolites along with the molecular dimension and geometry of the complex encapsulated inside the zeolite supercage.

thermogravimetric analysis have been used in characterization for all neat and encapsulated palladium complexes. The TG/ DTA curves for pure zeolite-Y, free state, and encapsulated PdL3 complexes are presented in Figure 5, and thermal analysis spectra for neat complexes PdL1, PdL2 and corresponding encapsulated complexes are represented in Figure S2 in the Supporting Information. Pure zeolite shows only weight loss due to loss of adsorbed water in the temperature range 70-250 °C. All three neat complexes exhibit sharp weight loss in a single step. There is a sharp decomposition with the highest weight % change at 272 °C for the PdL3 neat complex, and this decomposition corresponds to the loss of the organic moiety of the complex. However, for the corresponding zeolite encapsulated palladium complexes weight loss occurs in two steps. The first step in the temperature range 30-150 °C is certainly due to the desorption of physically adsorbed water molecules from the host framework,³¹ which appears as an endothermic peak in the DTA curve.³² The second step in the wide temperature range 300-800 °C is associated with the decomposition of the organic part of the catalyst as an exothermic phenomenon.³¹The TG/DTA curves show a sharp weight loss occurring for all neat complexes in the exothermic mode,³² but all encapsulated complexes are characterized by a plateau-type plot, indicating slow and continuous weight loss and that the process of decomposition extends toward higher temperature. It is quite apparent that, upon encapsulation, the thermal stability of the complexes is enhanced significantly.³³

Thermal Analysis. Differential thermal analysis and



Figure 5. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results for (A) pure zeolite-Y, (B) PdL3, and (C) EPdL3-Y.



Figure 6. FTIR spectra of (A) pure zeolite-Y, PdL1, and EPdL1Y; (B) zeolite-Y, EPdL1-Y, EPdL2-Y, and EPdL3-Y; and (C) enlarged view in the range of 500 cm⁻¹ to 2000 cm⁻¹ for pure zeolite-Y, EPdL1-Y, EPdL2-Y, and EPdL3-Y.

IR Spectroscopic Study. The FTIR spectral data of ligands, palladium–Schiff base complexes, pure zeolite-Y and zeolite encapsulated palladium complexes are shown in Figure 6 and Table 3 (Figures S3–S4 are given in Supporting

Information). The strong IR peak at 1018 cm⁻¹ of pure zeolite-Y corresponds to the asymmetric stretching vibrations of (Si/Al)O₄ units of host framework. Few important peaks observed at 560, 717, and 786 cm⁻¹, are the signature of T-O bending

Table 3. FTIR Data of Neat and Encapsulated Complexes

s. no.	samples	C=N stretching	C=C stretching	$ u_{\mathrm{C-H}} $ deformation	C–O stretching
1	PdL1	1605	1528,1439	1358	1278
2	EPdL1-Y	1636	1535,1462	1369	1257
3	PdL2	1589	1528,1466	1366	1257
4	EPdL2-Y	1643	1497,1443	1378	1265
5	PdL3	1605	1551,1481	1380	1256
6	EPdL3-Y	1628	1520,1481	1383	1234

mode, double ring and symmetric stretching vibrations respectively.³⁴ In addition, the prominent IR bands appeared at 1643 and 3500 cm⁻¹are assigned to lattice water molecules and surface hydroxylic group, respectively.³⁵All these characteristics IR bands of zeolite-Y remain unaltered after palladium exchange and even after encapsulation reaction, concluding that the host framework maintains its integrity during the whole process of encapsulation of palladium–Schiff base complexes. The IR spectral range of 1200 to1600 cm⁻¹appears to be a suitable range for the study of zeolite encapsulated metal complex as in this range, prominent IR bands of the zeolite are absent. Therefore, the IR peaks observed are only because of the complexes though the intensity of these IR peaks is very weak definitely indicating a low loading level of palladium inside the zeolite cage.

The FT-IR peaks of the ligand, observed as two strong bands at 1612-1620 cm⁻¹ and 1273-1296 cm⁻¹, are attributed to the C=N and C-O stretching vibrations, and these bands are slightly shifted toward lower frequency upon complexation, indicating nitrogen and oxygen coordination inside the cavity of zeolite-Y. The IR spectra of free state palladium complexes show important peaks at 1528, 1439 cm⁻¹(C=C stretch.), 1605 cm⁻¹(C=N stretch.), 1278 cm⁻¹(C-O stretch.), and 1358 cm⁻¹ (ν_{C-H} deformation).²³ Similar IR bands with little shift are also observed in all encapsulated complexes providing indirect evidence for the presence of palladium-Schiff base complexes inside the supercage of the host. Shifts in some characteristics peaks upon encapsulation are attributed to the effect of the host matrix on the metal complex. The shift in ν_{C-H} deformation frequencies obtained in all encapsulated complexes also provides clear evidence for the encapsulation of the metal complex inside the cavity of the host.

X-ray Photoelectron Spectroscopy (XPS). XPS studies also provided explanation regarding the existence of the palladium complex inside the supercage of zeolite-Y. XPS data confirm the relative concentration of elements and their oxidation states in the neat and encapsulated complexes. It is noticed that the XPS signal for palladium metal in the complex is very weak when it is encapsulated, definitely indicating a very low concentration of palladium in the host framework. Observations are in accordance with those obtained from EDX, IR, and UV–vis spectroscopic studies. The XPS measurements are carried out for PdL1 (neat state) as well as EPdL1-Y and EPdL2-Y (encapsulated states). The binding energies (eV) for Pd (3d), C (1s), N (1s), O (1s), Si (2p), Al

(2p), and Na (1s) and XPS spectra of PdL1, EPdL1-Y, and EPdL2-Y are presented in Table 4 and Figure 7 respectively (Figures S5-S6 in the Supporting Information). The binding energies of Pd 3d_{3/2} and Pd 3d_{5/2} confirm the palladium metal present in the +2 oxidation state in all complexes. For the PdL1 complex, these signals appear at 343.6 (Pd $3d_{3/2}$) and 338.2 eV (Pd $3d_{5/2}$),³⁶ whereas, for the encapsulated complexes, these signals are at approximately the same binding energies; for the EPdL1-Y, signals have appeared at 342.4, 337.2 eV, and for EPdL2-Y complex, the signals are observed at 342.5, 336.3 eV with one new XPS signal at a higher binding energy of 347.9 eV. The appearance of the new peak after encapsulation is a mere indication of removal of electron density around the palladium center because of obliteration of the delocalization environment driven by the adaptation of square planar geometry of the encapsulated complexes.^{37–39} For the PdL1 complex, C (1s) XPS signals appear at 286.4 and 284.5 eV corresponding to sp^3 and sp^2 carbon atoms respectively whereas two different type of N (1s) signals appeared, confirming the presence of M–N and C=N species. The O (1s) XPS signal is observed at a binding energy value of 534.0 eV.²⁰ Encapsulated complexes (EPdL1-Y and EPdL2-Y) secure these XPS peaks almost at the identical positions. In both encapsulated complexes, the binding energy signals for Pd (3d), C (1s), N (1s), O (1s), Si (2p), Al (2p) and Na (1s) are observed. The EPdL1-Y system has shown zeolitic Si 2p, Al 2p, and Na 1s signals at 103.2, 75.5, and 1073.3 eV respectively, whereas, in EPdL2-Y, zeolitic signals appear at binding energies at 103.5 eV (Si 2p), 74.8 eV (Al 2p), and 1072.6 eV (Na 1s). The binding energy data of the Pd 3d peak for all encapsulated complexes ensure the successful encapsulation of the palladium-Schiff base complex inside the zeolite-Y.

UV–visible Spectroscopy. The UV–vis spectra of the ligands and free state palladium–Schiff base complexes recorded in $CHCl_3$ have shown a few interesting features (presented in Figure 8; spectral data given in Table 5).

An intense band observed in the UV-vis spectra of the Schiff base ligand in the range 232–278 nm is assigned as the $\pi-\pi^*$ transition, and the $n-\pi^*$ transition is observed in the range 302–375 nm. The lowest energy band appearing at 401–468 nm is identified as a transition involving a metal, i.e. a charge transfer transition or d-d transition. The appearance of lowest energy bands, therefore, strongly supports the formation of the complex.

The solid-state UV-vis spectrum of PdL1 exhibits bands at 200, 246, 308, and 360 nm. The first two bands are assigned as the $\pi-\pi^*$ transition, and the next two bands are originated from the $n-\pi^*$ transition. The peak at 439 nm is assigned as the d-d transition and is blue-shifted to a large extent so that eventually it is merged with charge transfer. This observation is in line with fact that being a 4d transition metal Pd always undergoes large d orbital splitting.⁴⁰

On complexation, metal complexes show these transitions slightly shifted; the $\pi - \pi^*$ transition was observed at 240–245 nm, the $n - \pi^*$ transition was observed at 294–370 nm. The

Table 4. Bindin	g Energy	(eV)	of Neat	and	Enca	psulated	Com	olexes

s. no.	samples	Si (2p)	Al (2p)	Na (1s)	C (1s)	N (1s)	O (1s)	Pd (3d5/2)	Pd (3d3/2)
1	PdL1	-	-	-	286.41, 284.57	400.79, 398.59	534.08	338.24	343.65
2	EPdL1-Y	103.27	70.40, 75.50	1073.31	287.70, 285.08	399.63, 398.49	533.10	337.22	342.40
3	EPdL2-Y	103.53	74.87, 76.30	1072.68	286.37, 285.01	400.84, 399.28	532.92	336.30	342.59, 347.96



Figure 7. (A) XPS survey spectra of PdL1 and encapsulated complexes EPdL1-Y and EPdL2-Y. High resolution XPS signals of Pd (3d) for (B) PdL1, (C) EPdL1-Y, and (D) EPdL2-Y complex.



Figure 8. Solution UV-vis spectra of (A) L1 and PdL1, (B) L2 and PdL2, and (C) L3 and PdL3.

Table 5. Solution UV-visible Data of Ligand and Neat Complexes

s. no.	samples	$\pi - \pi^*$ transitions	$n-\pi^*$ transitions	CT transitions/d–d transitions
1	L1	237, 273	302, 347	-
2	PdL1	245	294, 340	429
3	L2	245, 278	306, 375	-
4	PdL2	240	302, 370	468
5	L3	232, 268	305, 340	-
6	PdL3	241	300, 350	401

presence of similar electronic transitions in the encapsulated states as its neat analogues confirms the complex formation inside the supercage of zeolite-Y quite evidently. However, upon encapsulation inside the zeolite matrix, the d-d transitions are found to be red-shifted clearly indicating a different electronic environment experienced by the square planar complex especially around the metal. The PdL1 complex, simply upon encapsulation, shows the shift of the d-d transition from 439 to 468 nm. Similar observations are found for all three encapsulated palladium complexes (shown in Figure 9 and Table 6), so the structural modification of all the encapsulated complexes must be very alike. The red shift in d-d transition is practically unexpected and hence noteworthy, as it demands an enhanced π -delocalization around the metal center after encapsulation. Encapsulation by some means induces planarity around the central metal atom, thereby, supplementing π -delocalization.

Theoretical Methods. The electronic structure calculations based on Density Functional Theory (DFT) were used to study and analyze the structural and optical properties of the Pd complexes in neat and zeolite encapsulated states. All results presented here are obtained using the GAUSSIAN 09

Table	e 6.	Solid	l-State	UV-visible	Data	of	Neat	and
Enca	psul	ated	Comp	lexes				

s. no.	samples	$\pi - \pi^*$ transitions	$n-\pi^*$ transitions	CT transitions/d-d transitions
1	PdL1	246	308, 360	439
2	EPdL1-Y	259	328, 362	468, 598
3	PdL2	250	301, 386	471
4	EPdL2-Y	252	292, 387	480, 605
5	PdL3	246	309, 375	402
6	EPdL3-Y	256	318, 371	476, 618

suite of *ab initio* quantum chemistry programs.⁴¹ The details of the theoretical methods are included in the Supporting Information (SI).

Structure of Pd-Complexes in Neat and Encapsulated States. We theoretically first studied the free ligands, L1, L2, and L3 (details are presented in SI), and observed that the three aromatic rings in the molecule are not coplanar, but the middle ring of *m*-phenylenediamine is placed at an angle of $40^{\circ}-50^{\circ}$, from the two side rings, depending on the substituents (shown in Figure 10a) and the molecule is flexible and stretched. In the presence of the Pd²⁺ ion, the ligands readily form metal complexes and encompass the metal atom in a half-circular fashion, where the two side rings of the ligand and the metal atom are coplanar, but the middle aromatic ring of the ligand is now bent almost perpendicular to the two terminal aromatic rings (see Figure 10b). The neat PdL1, PdL2, and PdL3 exist as singlet states, without any unpaired electrons; however, there exists higher energy triplet states with two unpaired electrons for all complexes studied. Structural optimizations are carried out for PdL1, PdL2, and PdL3 complexes in the neat singlet states and then in zeolite encapsulated triplet states, and the optimized structures are



Figure 9. Solid state UV-vis spectra of (A) PdL1 and EPdL1-Y, (B) PdL2 and EPdL2-Y, and (C) PdL3 and EPdL3-Y.



Figure 10. (a) Ligand *N*,*N'*-bis(5-methoxysalicylidene)phenylene-1,3-diamine: frontal and side views are shown. The –OMe group is marked by a red circle for L2, which is replaced by $-NO_2$ for L3 and H for L1. (b) The neat, singlet state of the PdL2 complex: frontal and side views are shown. (c) The encapsulated and extracted, triplet state of PdL2 complex: frontal and side views are shown. On the right-hand side, two side views are shown to understand the position of the central ring with respect to the plane of the molecule. The distances d_1 , d_2 , and d_3 are marked on the Pd-complex and are explained in the text. (d) PdL2 complex encapsulated within zeolite pore: two different views are shown.

presented in Figure 10c with the important structural parameters tabulated in Table 7. In the Pd-complex, the central ring itself is no longer completely planar, unlike aromatic rings, but it appears to be somewhat boat-shaped, and a unique structure-property relationship is observed for this class of complexes. To understand the positioning of this ring with respect to the Pd atom we have defined three distance parameters d_1 , d_2 , and d_3 marked in the Figure 10b,c. The encapsulated Pd complexes studied are all triplet, and they are bent longitudinally; thus, the end-to-end distances decrease by ~0.4 Å (see Table 7). The distortion of the encapsulated complexes as a whole, however, affects the positioning of the central out-of-plane ring behind the Pd atom, and the d_1 , d_2 distances now differ and are ~2.80 and ~3.02 Å respectively (Table 7). The shorter distance d_3 is now found to be longer and 2.93 Å. Thus, the whole molecule now resembles a "bowl"

unlike the neat molecules, which indeed were largely planar. Moreover, the central phenylene-1,3-diamine ring is no longer symmetrically placed behind the metal center, and thus Pd–N and N=C distances are different now. The Pd–N distances are 2.07 and 2.13 Å, and the N=C distances are 1.29 and 1.33 Å respectively (Table 7). In contrast, the Pd–O and O–C distances for the singlet and the triplet states are very similar.

Thus, the structural studies show, in the free ground state, PdL1, PdL2, and PdL3 complexes are partially planar with the central aromatic ring aligned almost perpendicular and are diamagnetic and singlet; however, the complexes are deformed and bowl-shaped when encapsulated inside the zeolite pore and the distortion helps to stabilize the triplet state. This, in turn, alters the relative ordering of the molecular orbitals, and consequently, the optical and catalytic properties of the complexes are modified.

Frontier Molecular Orbtials of the Pd-Complexes. To understand the optical properties and related transitions of the Pd-complexes it is imperative to look into the nature of their frontier molecular orbitals. The present study observes that the HOMO for neat PdL1 has a modest Pd d_{xz} character hybridized with the π -bonding character of the ligand, and the LUMO has Pd d_{xy} character hybridized with π -antibonding type orbitals from the central "out-of-plane" aromatic ring of the ligand (Figure S12 in Supporting Information). The HOMO and LUMO energies for PdL1 are -5.55 and -2.67 eV respectively with a HOMO-LUMO energy gap of 2.89 eV. Though HOMO-1 also has some contribution from the Pd d_{yz} orbital, HOMO-2 is comprised primarily of the Pd d_{z^2} orbital. On the other hand, the LUMO+1 orbital has a minimal contribution from Pd d_{yz} while LUMO+2 has a little contribution from the $Pd d_{xv}$ orbital. The nature of the molecular orbitals of similar salen complex has been discussed before in literature.¹⁹⁻²¹A look into the molecular orbitals of PdL2 (Figure S13 in Supporting Information) reveals that the HOMO has a strong contribution from the Pd d_{xz} orbital hybridized with ligand p orbitals, and the LUMO is mainly the Pd d_{xy} orbital similar to the case of PdL1. The HOMO-LUMO gap for PdL2 is 2.59 eV. The HOMO-1 orbital is mainly ligand p with the Pd d_{yz} orbital, and HOMO-2 is the metal d_{r^2} orbital, with contributions from the central ring of the ligand. It is also observed that while LUMO+1 has contributions from the Pd d_{yz} orbital, LUMO+2 and LUMO +4 both have some contributions from the Pd d_{xy} orbital. The molecular orbitals of PdL3 are similar to those of PdL1 and PdL2, and the HOMO is mostly the Pd d_{xz} orbital hybridized with ligand p orbitals and the LUMO is mainly the Pd d_{xy} orbital (Figure S14 in Supporting Information) with the

Table 7. Important Structural Parameters from DFT for Neat and Encapsulated Pd-Comple	exes
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s. no.	bond distances/ angles	PdL1, neat singlet	EPdL1, encapsulated, extracted triplet	PdL2, neat singlet	EPdL2, encapsulated, extracted triplet	PdL3, neat singlet	EPdL3, encapsulated, extracted triplet
1	Pd-O (Å)	2.01	2.01	2.00	2.00	2.01	2.00
2	Pd-N (Å)	2.19	2.06, 2.13	2.19	2.07, 2.13	2.19	2.07, 2.14
3	О-С (Å)	1.29	1.29	1.30	1.30	1.28	1.28
4	N–C(conj) (Å)	1.30	1.29, 1.33	1.30	1.30, 1.33	1.29	1.28, 1.32
5	<o-pd-n< td=""><td>85.9</td><td>88.9</td><td>86.1</td><td>88.0</td><td>85.9</td><td>88.4</td></o-pd-n<>	85.9	88.9	86.1	88.0	85.9	88.4
6	end to end distance (Å)	13.18	12.72	13.74	13.33	13.83	13.53
7	d_1 (Å)	2.91	2.80	2.91	2.80	2.91	2.80
8	d_2 (Å)	2.77	2.93	2.78	2.92	2.79	2.95
9	<i>d</i> ₃ (Å)	2.91	3.02	2.91	3.01	2.91	3.02



Figure 11. Experimental and DFT simulated UV-vis spectra of (A) PdL1, (B) EPdL1-Y, (C) PdL2, and (D) EPdL2-Y complex.

HOMO-LUMO gap being 3.0 eV. The HOMO-1 orbital is mainly ligand p with the Pd d_{yz} orbital, whereas HOMO-2 is the metal d_{z^2} orbital.

The calculated optical spectra for the neat PdL1, PdL2, and PdL3 complexes are given in the Supporting Information, and here we consider only the encapsulated and extracted Pd complexes in triplet states. The molecular orbitals in the triplet states are shown in Figures S15–S17 and comprised of α and β sets, due to the presence of unpaired electrons. In the triplet state, the structural distortion of the complexes means more hybridization with the ligand π orbitals, which makes identification of metal d orbitals difficult. In the triplet state, the HOMO and HOMO-1 are closely placed regarding energies and located in two different halves of the molecule with each exhibiting strong contributions from the Pd d_{xz} orbital. The occupied orbitals are dominated by Pd d_{xz} , d_{yz} , and d_{z^2} orbitals, whereas the unoccupied states are dominated by Pd d_{xy} orbitals. The LUMO is still mainly localized on the Pd d_{xy} orbital, but strong hybridizations ensure that there are more unoccupied orbitals with Pd d_{xy} character. There are inner occupied orbitals with Pd d_{yz} and Pd d_{z^2} character hybridized with ligand p character. A closer look into the TD-DFT spectra (Figure 11 and Figure S10 in Supporting Information) readily reveals that there is an overall shift toward the higher wavelengths, but identification of the individual transitions becomes increasingly difficult because the metal d orbitals are mixed up with the ligand orbitals in a complicated fashion. In the case of neat PdL1, the first prominent peak is around 521 nm (SI, Figure S7), which shifts to 568 nm in the encapsulated EPdL1 case, and this is a HOMO-1 to LUMO transition comprised of the Pd d_{xz} to Pd d_{xy} orbital. In the case of singlet PdL2, we see the first important peak around 545 nm (SI,

Figure S8), which shifts to 594 in the encapsulated triplet case. In the case of EPdL3, important transitions are in the range 550–470 nm. One may note that in the case of EPdL3 the prominent peaks are around 550 nm which were around 495 and 489 nm in the case of PdL3 (SI, Figure S9), indicating a shift toward longer wavelengths upon encapsulation Experimental and DFT simulated UV–vis spectra of PdL1, EPdL1-Y, PdL2, and EPdL2-Y complex are given in Figure 11 for better comparison.

Catalytic Study. All neat and encapsulated palladium-Schiff base complexes have been explored as catalysts for the Heck coupling of bromobenzene with styrene. The results of the Heck reaction are given in Table 8. A calibration curve of bromobenzene is given in the SI (Figure S18). Reaction conditions are optimized using EPdL1-Y as a catalyst by varying the amount of catalyst and temperature. The effect of temperature on the catalytic activity of EPdL1-Y has been studied up to 140 °C. The % conversion of the coupling reaction increased with temperature, but there is no conversion obtained below 70 °C. As the temperature increased from 100 to 140 °C, the conversion increased from 21.3% to 90.8% (Figure S19 in Supporting Information). The effect of the amount of catalyst on the Heck reaction is studied, and excellent conversion occurred with 0.70 mmol % of catalyst. Catalytic data are presented in Supporting Information, Figure S20. All catalytic reactions are monitored by gas chromatography, and % conversion was calculated by using a calibration curve of bromobenzene and *n*-heptane as an internal standard.

By using optimized reaction conditions, all neat and encapsulated complexes containing an electron-donating and -withdrawing substituent have been employed as catalysts. The neat palladium complexes follow the activity order as PdL2 > Table 8. Coupling Reaction between Bromobenzene and Styrene Catalyzed by Palladium Complexes^a

5 mi	Br +	() — 10 mmol	Catalyst, DMF Na₂CO₃	(E)-still	bene
s. no.	catalyst	mmol % of Pd	reaction temp (°C)	% yield of product ^b	TON ^c
1	Zeolite Y	_	140	Nil	-
2	Pd-Y	0.70	140	15.8	122
3	PdL1	0.70	140	56.5	416
4	PdL2	0.70	140	83.6	595
5	PdL3	0.70	140	38.4	281
6	EPdL1-Y	0.70	140	90.0	649
7	EPdL2-Y	0.70	140	39.2	313
8	EPdL3-Y	0.70	140	65.7	474

^{*a*}Reaction conditions: bromobenzene (5 mmol), styrene (10 mmol), Na₂CO₃ (10 mmol), 10 mL of DMF, catalyst, reaction time = 20 h. ^{*b*}Determined by gas chromatography. ^{*c*}Turnover number calculated at the completion of reaction (mol of bromobenzene transformed/mol of palladium metal in catalyst).

PdL1 > PdL3 complex. The PdL2 complex with an electrondonating substituent $(-OCH_3)$ is the most reactive for the Heck coupling, whereas PdL3 with an electron-withdrawing substituent $(-NO_2)$ is the least reactive. The activity order of free state palladium complexes is solely controlled by the electronic effects of the substituent group attached, as expected.⁴² After the encapsulation of the complexes inside the supercage of zeolite-Y, a striking reversal of the reactivity order is observed. Encapsulated palladium complexes follow the order EPdL1-Y > EPdL3-Y > EPdL2-Y; the modified steric environment of the guest complexes imposed by the host zeolite lattice definitely has a significant contribution toward it. New modified functionalities toward the Heck reaction signify the substantial structural changes around the metal center under encapsulation inside the host supercage. The Pd metal center in these complexes with different substituents provides a different electronic environment for catalysis, and additionally on encapsulation they experience differential space constraints, which altogether leads to the modification of the reactivity order. Undoubtedly, the final geometry adopted by the encapsulated complex plays a crucial role. Upon encapsulation, the metal center in the guest complex can have a substantially different electronic charge distribution due to the new adopted structure. The heterogeneous catalyst can easily be separated from the reaction mixture and reused after washing without loss in activity (recyclability of the EPdL1-Y catalyst for Heck coupling is presented in Figure 12).

Correlation between Structural Modification and Modified Functionality. Palladium complexes are usually efficient catalysts for the coupling reactions though they have some limitations, such as difficulties in separation and recovery and thermal instability. However, all these drawbacks of the homogeneous Pd catalyst could be overcome easily by encapsulating these systems within the pore of zeolites, which provide easy separation, high thermal stability, and modified functionality. Hence zeolite encapsulated metal complexes have been studied for various organic transformations.^{22,26,43} Upon encapsulation, the steric and electrostatic constraints provided by the framework of zeolite-Y influence the geometry of the complex and consequently



Figure 12. Recyclability of the EPdL1-Y catalyst for Heck coupling reaction.

modify the electronic, magnetic, and redox properties, and hence striking changes in the functionality of the enclosed metal complex are observed.⁴⁴ The modified functionality for the Heck reaction is an outcome of the modified geometry of the palladium–Schiff base complexes.

The neat palladium–Schiff base complex has a square planar geometry around the central metal; however, the central aromatic ring (*m*-phenylenediamine) exhibits nonplanar arrangement leading to the reduction of π -delocalization. Geometry optimization results directly evidence this. Therefore, [Pd(sal-1,3-phen)] type systems are subject to have a lesser extent of conjugation from the ligand moiety in comparison to their corresponding [Pd(sal-1,2-phen)] complexes.

The electronic contribution of the substituent in the palladium complexes has been analyzed by electronic spectroscopic studies in a series of complexes (PdL1, PdL2, and PdL3). With the increase in the electron-withdrawing character of the substituent attached, as observed in UV-vis spectra, the HOMO-LUMO gap of the neat palladium complex is subject to increase, leading to a hypsochromic shift in absorption spectrum pertaining to the metal. The bathochromic shift is in line with the increase in electron density on the ligand.⁴⁵ An electron-donating group (-OCH₃) enhances π -delocalization and maintains the planarity of the complex whereas an electron-withdrawing group $(-NO_2)$ causes nonplanarity. From electronic spectroscopic studies of the neat complexes, we have found that the d-d transition of the PdL2 complex is red-shifted and the d-d transition of the PdL3 complex is blue-shifted as compared to that of the PdL1 complex. In the present study, comparative catalytic activities of palladium (sal-1,3-phen) complexes are employed as catalysts for the Heck reaction with aryl bromide and styrene in the presence of Na₂CO₃ as the base. Observed catalytic results of neat palladium complexes indicate the reactivity order as PdL2 > PdL1 > PdL3. An electron-donating group $(-OCH_3)$ in the PdL2 complex increases the electron density around the metal center causing the red shift of the band appearing from the metal, and subsequently, the PdL2 complex is most active as a catalyst toward the Heck coupling reaction. The PdL3 complex with an electron-withdrawing group $(-NO_2)$ is the least reactive among all the neat complexes as expected. Our results have been supported by literature reports. Saleem and co-workers have already reported the reactivity of the palladium complexes for the Heck reaction correlated with the HOMO-LUMO energy gap.46 The

palladium complex with a low HOMO-LUMO energy gap shows higher activity toward the Heck reaction.

It has also been reported that the presence of an electronwithdrawing group, the planarity of the salen ligand is disturbed; however, an electron-donating group on the same position maintains the planarity of the complex with substantial electron density on the metal center.⁴⁷ A higher electron density around the metal center facilitates the coupling reactions. Upon encapsulation, the geometry of these palladium-Schiff base complexes is altered significantly due to the space constraint imposed by the topology of zeolite-Y. For all encapsulated complexes (EPdL1-Y, EPdL2-Y, and EPdL3-Y), the charge transfer/d-d transition bands are shifted toward higher wavelength. The optimized geometry of the encapsulated complex obtained from theoretical studies clearly indicates an enhanced planarity and hence enhanced π delocalization induced by the central aromatic ring (mphenylenediamine) as the topology of the zeolite-Y framework enforces the central ring to tilt toward the molecular plane. Consequently, a red shift in charge transfer/d-d transition is observed. Encapsulation of the PdL2-Y complex with the -OCH₃ group obstructs the electron-donating effect to some extent on the other side; zeolite topology imposes planarity to a certain extent. Hence, the effect of the substituent group and electronic effects originating from steric hindrance due to encapsulation oppose each other; therefore, a red shift in the d-d transition is marginal as compared to encapsulated PdL1-Y and PdL3-Y complexes. However, PdL1 and PdL3 complexes when encapsulated in zeolite-Y have shown remarkable improvement in reactivity. The enhanced functionality of these systems are the outcome of the enhanced electron density around the metal thereby causing a significant red shift in the charge transfer/d-d transition. In the case of the encapsulated EPdL3-Y complex, both the electronic effect of the substituent group and that from the distorted geometry function in the same direction cause a much higher red shift. But for the EPdL1-Y complex, only steric factors contribute and the wall of the zeolite supercage enforces the metal complex to adopt the distorted geometry enhancing the electron density around the metal; hence, the reactivity is also enhanced. The functionality of the neat palladium-Schiff base complexes is impacted by the electronic factor of the substituent present on the phenyl ring, and the complexes follow the activity order PdL2 > PdL1 > PdL3. However, after the encapsulation, the activity trend is governed by the electronic effect originated from the substituent as well as steric hindrance. The catalytic activity of the encapsulated complexes follow the order EPdL1-Y > EPdL3-Y > EPdL2-Y. It appears to be an exciting approach to alteration of the HOMO-LUMO energy gap of a guest complex by encapsulation of the complex inside the rigid zeolite supercage, finally leading to advancement in the field of tunable catalysis. The electron density on palladium metal center can be modified in two ways, either by the attachment of different substituent groups on the ligand moiety or by encapsulating the complexes in the cavities of a rigid host framework. Hence, the geometry of these catalysts turns out to be a crucial factor for the enhanced activity toward the Heck reaction.

CONCLUSION

In summary, zeolite encapsulated palladium–Schiff base complexes are synthesized by using the "flexible ligand method" and neat analogues are also studied to compare with their encapsulated states. These complexes are well characterized by the help of different characterization tools such as XRD, SEM-EDS, BET, thermal analysis, XPS, IR, and UV-vis spectroscopic studies. These palladium complexes when employed as catalysts for a Heck coupling reaction, all of them differing significantly from the behavior of their corresponding neat form. The main aim of the present study is to explore the geometry of the palladium complex after encapsulation as well as to rationalize the modified functionality of the systems. The catalytic activity has been explained in terms of the electropositivite character of the metal center. The complex with a less electropositive palladium center showing the lowest energy electronic band red-shifted eventually exhibits higher activity toward the Heck coupling reaction. Interestingly, complexes showing a blue shift in their free state or encapsulated states are less reactive. From detailed comparative experimental and theoretical electronic data and catalysis studies, it can be concluded that the greater the red shifting observed in the d-d transition, the greater the reactivity of palladium complexes toward the Heck coupling reaction. A red shift in the d-d transition for particularly this series of palladium complexes can be produced in two ways, either by addition of a strong electron-donating substituent group on the ligand moiety or by encapsulation in zeolite-Y. Therefore, the geometry of the catalyst complex plays a key role in the Heck coupling reaction for the enhanced activity.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03031.

Physical measurements; schemes for the synthesis of ligands and complexes in both neat and encapsulated state; EDX spectra; TGA and DTA curves; FTIR spectra; high-resolution XPS spectra; theoretical studies; TD-DFT spectra; comparative optical spectra; frontier molecular orbitals; calibration curve of bromobenzene; % conversion of bromobenzene for EPdL1-Y complex with respect to the temperature of reaction and mmol of catalyst (PDF)

AUTHOR INFORMATION

Corresponding Author

E-mail: saumi@pilani.bits-pilani.ac.in.

ORCID 🔍

Bidisa Das: 0000-0001-6002-6390 Saumi Ray: 0000-0002-6893-9634

Notes

The authors declare no competing financial interest.

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