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#### Zeolite Encapsulated Ni(II) Schiff-Base Complexes: Improved Catalysis and Site Isolation

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#### Abstract

Two series of zeolite encapsulated Ni(II) Schiff-base complexes e.g., {Ni(II) sal-1,2-phen and Ni(II) sal-1,3phen series} have been synthesized in neat and encapsulated states and characterized by different characterization techniques such as XRD, SEM-EDS, BET, thermal analysis, XPS, IR, UV–vis spectroscopy and magnetic studies. UV–vis spectroscopy, XPS and magnetic studies all together reveal the structural modification of the guest complex and thereby, adaptation of electron density around the metal center upon encapsulation. However, encapsulation imposes structural alterations for these two series differently and hence, introduces a certain level of proficiency to these Ni(II) complexes as catalysts for phenol oxidation reaction. However, analysis of catalytic data emphasizes upon site isolation as a major governing factor for the improved reactivity over the modified electron density around the metal center of phenol oxidation when heterogeneous mode of catalysis is concerned.

#### Introduction

Over the last few decades, the transition metal Schiff-base complexes have been widely reported as homogenous catalysts though there are few challenges associated with homogenous catalysis such as separation, reusability and thermal stability of the catalysts. To overcome these disadvantages, heterogenization of metal Schiff-base complexes has been attempted by immobilizing and encapsulating these homogeneous metal complex catalysts in the cavities of organic and inorganic supporting materials.<sup>1-3</sup> Among the all-supporting materials, special mention to zeolites as zeolites indeed, have considerably unique framework-architecture, thermal stability and ion exchange capability.<sup>4, 5</sup> The structures of zeolites are well-ordered with the building blocks organized in a regular array to form a three-dimensional framework with regular cavities. These are very stable in various media and show a large surface area.<sup>6</sup>

Research on oxidation of phenol in the presence of a clean oxidant such as  $H_2O_2$  is of great importance due to its industrial applications. Less than 60% concentrated  $H_2O_2$  is recognized as clean and green oxidizing agent amongst various oxidants.<sup>7, 8</sup> Product of phenol oxidation such as catechol and hydroquinone have many important applications as antioxidant, polymerization inhibitor, photographic film developer, medicines and in organic synthesis etc.<sup>9, 10</sup>

The study of the zeolite encapsulated metal complexes and their catalytic activities even has real significance because of their applications in a variety of fields. Industrial processes are fundamentally challenged by the recyclability while employing the soluble metal complexes as catalysts because of the difficulties associated with their recovery and separation from the reaction mixture.<sup>11</sup> Due to size and shape constraints provided by the zeolite walls, encapsulation approach can really improve the product selectivity and the lifetime of the guest complex.<sup>12</sup> A metal complex once encapsulated in zeolites, is marked by steric constraint imposed by the topology of zeolite framework and also be in isolation from the other metal complex.<sup>13</sup> The molecular dimension of the guest metal complex once, is comparable with that of zeolitic cavities e.g., supercage in case of zeolite –Y, the complex may suffer from strong sterically constrained environment imposed by the topology

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of zeolite-Y.<sup>14</sup> These steric and electrostatic environment induced by the architecture of zeolite framework control the geometry of the guest metal complex and consequently imply changes in magnetic, electronic and redox properties of the metal complex.<sup>15</sup> These modified properties thereby lead to change the catalytic activity of encapsulated metal complex. Subsequent possibility will be, the guest molecule inside the cage may show exciting properties that are not observed under free-state conditions. All these anticipations and few findings encourage many researcher to explore the catalytic properties of the encapsulated metal complexes inside the supercage of zeolite-Y.<sup>16-18</sup>

Encapsulation of metal complexes inside the zeolite supercage can be achieved by either using template synthesis method or flexible ligand approach based on the size and nature of the ligand chosen. In both the cases, once the metal complex is formed within the supercage of zeolite, it is too large and rigid to leak out from the supercage through the channels. Detailed Characterizations can only establish the successful encapsulation of the guest metal complexes within the zeolite supercages. Syntheses of transition metal Schiffbase complexes inside the supercage of zeolite have achieved major attention because of their exciting contribution in catalysis. Zeolite encapsulated metal complexes reported till now primarily find their applications in heterogeneous catalysis<sup>19-21</sup> like shape-selective epoxidation of alkenes<sup>22</sup>, oxidation of styrene and cyclohexene<sup>23</sup> and phenol oxidation<sup>24</sup>.

In the current report, a typical approximately square planar nickel complex of selection e.g., NiL2 has endto-end distance calculated as 17.08 Å to encapsulate in the supercage of zeolite -Y with diameter of 12.47 Å. However, the spherical supercage of zeolite can still host small reactant molecules like phenol, hydrogen peroxide etc. even after encapsulating this complex with slight deviated geometry (shown in the figure S1 in Supporting Information). Hence, such encapsulated systems can be potential catalysts for phenol hydroxylation reaction. There are only few reports available in the literature which emphasize to study the correlation existing between altered geometry of encapsulated metal complex and their modified catalytic activity. Therefore, we aim to investigate the effect of structural modifications of the zeolite encapsulated Ni(II) salophen complexes on their catalytic activity, and hence have synthesized zeolite

encapsulated Ni(II) Schiff-base complexes with two different series of salophen ligand (sal-1,2-phen and sal-1,3-phen) having H, -OCH<sub>3</sub>, -NO<sub>2</sub> substituent groups, as shown in Figure 1.

This report discusses the syntheses of zeolite encapsulated Ni(II) Schiff-base complexes and their reactivity towards hydroxylation of phenol. In the current study, in addition to the syntheses, detailed characterization and reactivity have been scrutinized for the encapsulated nickel salophen complexes to perceive the effect of zeolite framework on the geometry, electronic and magnetic properties, and catalytic activity of guest nickel complexes.

#### Figure 1



Figure 1. Schematic representation of synthesized nickel (II) Schiff-base complexes.

#### **Results and Discussions**

In the present work, we have synthesized six nickel–Schiff base complexes (two different series of salophen ligand; sal-1,2-phen and sal-1,3-phen) encapsulated in zeolite Y as well as in the free-state. To synthesize the ligands, 1,2-phenylenediamine or 1,3-phenylenediamine and salicylaldehyde or its derivatives are used as precursor molecules and to synthesize free-state complexes, an equimolar ratio of

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the Schiff-base ligand and nickel acetate in ethanol are refluxed at 80 °C for 3 h. Encapsulated Ni(II) Schiff-base complexes are synthesized from Ni-exchanged zeolite-Y by using 'flexible ligand method' following the reported literature .<sup>25, 26</sup> These systems are employed as catalysts for the phenol hydroxylation reaction to study the steric and electronic effect of different substituent on their reactivity upon encapsulation. Detailed experimental section part is given in the Supporting Information.

#### **Elemental Analysis**

Energy-dispersive X-ray spectroscopy (EDX) technique confirms the presence of the different elements in the encapsulated nickel systems and Ni(II) exchanged zeolite Y along with their weight% (data provided in Table 1). Elemental analysis indicates the Si to Al weight% ratio of parent zeolite-Y as 2.7corresponding to the unit cell formula as Na<sub>52</sub>(AlO<sub>2</sub>)<sub>52</sub>(SiO<sub>2</sub>)<sub>140</sub>. yH<sub>2</sub>O. The Si/Al ratio has changed marginally during metal exchange reaction and encapsulation process, which indeed confirms the nominal dealumination during the whole process of encapsulation. The amount of nickel metal in all Soxhlet extracted encapsulated systems is found to be less as compared to that in Ni (II) exchanged zeolite -Y. The reduction in the nickel concentration during the formation of complex inside the supercage of zeolite Y is an indirect evidence of complex formation inside. This observation therefore, proves that Soxhlet extraction has successfully removed the complexes that are formed on the surface, leading into the overall reduction of Ni content as compared to the parent Ni-exchanged zeolite.

Table 1. Concentration of nickel (wt %) content in the different Samples.

S.No.	Samples	Nickel (wt%)	Si/ Al ratio
1	Zeolite-Y	-	2.79
2	Ni-Y	2.13	2.79
3	ENiL1-Y	0.52	2.78
4	ENiL2-Y	0.54	2.79
5	ENiL3-Y	0.45	2.78
6	ENiL1'-Y	0.55	2.79
7	ENiL2'-Y	0.56	2.78

8	ENiL3'-Y	0.42	2.79

#### X-ray Diffraction (XRD) studies

To prove crystallinity and integrity of zeolite framework after encapsulation processes, we have performed powder X-ray diffraction (PXRD) analysis for zeolite-NaY, Ni (II) exchanged zeolite-NaY and all zeolite samples having encapsulated Ni(II) complexes (XRD patterns presented in Supporting Information Figure S2). Nearly identical XRD patterns certainly confirm the retention of crystalline structure of zeolite during the process of encapsulation of Ni(II) Schiff-base complexes.<sup>27</sup> Only difference is apparent in the intensities of the diffractions at (220) and (311) planes appearing at 20 of 10° and 12°, respectively. The initial intensity relationship of  $I_{220} > I_{311}$  observed for the parent zeolite-Y and Ni(II) exchanged zeolite-Y goes for intensity reversal as  $I_{220} < I_{311}$  for the all encapsulated systems. Such observations already has been notified and empirically correlated only with the presence of large molecule inside the supercage of zeolite-Y.<sup>16, 18, 28-30</sup> It is never observed when complex formation takes place on the surface of the host framework.<sup>18, 31</sup> Thereby, the successful encapsulation of Ni(II) Schiffbase complexes inside the cavity of host framework is proven consequentially

#### Scanning Electron Microscopy (SEM)

The Ni(II) Schiff-base complexes have been synthesized inside the supercage of zeolite Y by using 'flexible ligand method'. However, target synthesis of complex only inside the supercage is practically not viable as some of these complex molecules definitely get synthesized on the host framework or some ligand molecules may remain unreacted. Therefore, Soxhlet extraction becomes mandatory till the solvent becomes colourless to remove the uncoordinated ligand molecules and complexes adsorbed on surface of the host framework. The surface morphology of the host framework is studied by scanning electron micrographs for all these zeolite samples before and after Soxhlet extraction (SE micrographs of zeolite with encapsulated NiL1 complex presented in Figure 2). Before Soxhlet extraction, surface adsorbed

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species are clearly visible on host framework; however, are entirely removed after the extraction. Thereby, boundaries of the zeolite particles are clearly evident for Soxhlet extracted samples and the final pale color of the encapsulated complex is an indication for the encapsulation of metal complex inside the cavity of host.

#### Figure 2



**Figure 2.** SE micrograph of the encapsulated NiL1 in zeolite Y, (A) and (B) (before Soxhlet extraction), (C) and (D) (after Soxhlet extraction).

BET surface area analysis

The surface parameters estimated from the low-temperature nitrogen adsorption are given in Table 2. N<sub>2</sub> adsorption-desorption isotherms obtained from BET analysis for pure zeolite-Y and encapsulated Ni(II) Schiff-base complexes (ENiL1-Y and ENiL1'-Y) presented in Figure 3 and it shows typically type I isotherm indicating the microporous nature of the samples.<sup>32, 33</sup> Values of  $S_{BET}$  and  $S_t$  are close to each other for the samples which indicate the correct choice of standard t curves used in pore analysis and also the absence of the ultra-micropores in these materials. The  $S_{BET}$  values are larger than analogies of  $S_{ext}$ (external surface area) by ~ 10% for the materials indicating the porous nature of these samples. However, the decrease in microporous volume ( $V_{mic}$ ) in ENiL1-Y by 49% and for ENiL1'-Y by 39% as compared to the parent zeolite Y, must be accredited to the large volume of the complex. Significant lowering in BET surface area and pore volume of pure zeolite-Y after undergoing the process of encapsulation certainly suggest that Ni(II) Schiff-base complex is present inside the inner space of zeolite, i.e., supercage rather than on the surface.<sup>16, 34</sup> The reduction in the BET surface area and pore volume of zeolite-Y during encapsulation depends on the loading level of metal along with the molecular dimension of the complex inside the cavities of zeolite framework. The extent of micro porosity decreases from parent zeolite Y to encapsulated systems.

#### Figure 3



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 **Figure 3.** BET isotherms for pure zeolite-Y and zeolite encapsulated complexes: (A) pure zeolite-Y, (B) ENiL1-Y and ENiL1'-Y.

 Table 2. BET surface area and pore volume of pure zeolite Y and encapsulated nickel complexes
 (ENiL1-Y and ENiL1'-Y).

S.No.	Sample	S <sub>BET</sub>	$S_{t}$	S <sub>ext</sub>	Smicro	$S_{ m wide}$	$V_{ m p}$	V <sub>micro</sub>	V <sub>wide</sub>
		$(m^2/g)$	$(m^2/g)$	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)
1	Pure zeolite Y	535	530	51	460	74	0.595	0.345	0.25
2	ENiL1-Y	320	312	32	256	66	0.362	0.190	0.172
3	ENiL1'-Y	328	320	33	261	59	0.382	0.211	0.171

*Note:*  $S_{\text{BET}}$ : total surface area by using BET method;  $S_t$ : specific surface area determined from  $V_{1-}$ t plots;  $S_{\text{ext}}$ : external surface area of micropores;  $S_{micro}$ : surface area of microspores;  $S_{\text{wid}}$ : surface area of wide pores;  $V_p$ : total pore volume;  $V_{\text{micro}}$ : volume of micropores;  $V_{\text{wide}}$ : volume of wide pores.

#### X-ray Photoelectron Spectroscopy analysis (XPS)

The X-ray Photoelectron Spectroscopy (XPS) analysis for free state (NiL1 and NiL1') and encapsulated nickel complexes (ENiL1-Y, ENiL2-Y, ENiL1'-Y and ENiL2'-Y) furnishes the relative concentration of elements and their chemical states in the samples. It indicates the presence of C, N, O and Ni(II) in their relevant chemical states in all the complexes and also Si, Al and Na in the encapsulated systems. XPS spectra are shown in Figure 4, Figure S6-S11 in Supporting Information (SI). From the comparison of XPS signal intensity of Ni 2p level, the fact emerged is that the encapsulated systems have quite a low concentration of nickel ions than the free state complexes, which is just in line with the EDX, FTIR (Figure S3 & Table S1 in Supporting Information), thermo-gravimetric (TGA) analysis (in Supporting Information) and UV-vis results. Survey spectra of the nickel complexes presented in Supporting Information Figure S5, indicates the presence of Ni, C, N and O in free as well as in encapsulated states.

The presence of Ni<sup>+2</sup> is confirmed by the Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub> peaks appearing at binding energies of 856.24 and 873.59 eV, respectively, for NiL1. The observed binding energy for Ni(II) is lower than the usually Ni(II) holding octahedral geometry and moreover, the absence of any shakeup satellite peak beyond 878 eV confirms the square planar geometry of nickel complex.<sup>24</sup> However, a distinct difference exists in the deconvoluted spectra of Ni2p of NiL1 and NiL1' complexes. The  $2p_{3/2}$  and  $2p_{1/2}$  peaks of Ni(II) in NiL1' are observed at the binding energies of 856.24 and 873.77 eV, respectively, along with two shakeup satellite broad peaks at the binding energies of 861.63 and 879.70 eV, respectively. This indicates the disturbed environment of the square planar geometry around the metal center and is in agreement with our previously reported theoretical results.<sup>35</sup>

In case of encapsulated system ENiL1-Y, the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks of Ni(II) appear at the binding energies of 856.24 and 873.42 eV, respectively. Two shakeup satellite peaks at the binding energies of 862.35 and 882.07 eV are the indicatives of the change in the coordination geometry of Ni(II) in the entrapped form. Encapsulated ENiL1'-Y system does not recommend any significant change of its geometry under encapsulation.

The C(1s) XPS peaks are broad and intense for all the complexes, which is further deconvoluted into two peaks at the binding energies of 285.41 and 287.02 eV, confirming the presence of two different type of carbon atoms (sp<sup>3</sup> and sp<sup>2</sup> types) in the samples. The O(1s) and N(1s) XPS traces are also found at the expected binding energies according to literature.<sup>16, 36</sup> For encapsulated system ENiL1-Y, the Si(2p), Al(2p) and Na(1s) appear at the binding energies of 103.27, 74.93 and 1072.85 eV respectively. All the encapsulated systems like ENiL2-Y and ENiL1'-Y show the same type of XPS spectra with the presence of Si(2p), Al(2p) and Na(1s) signals. The presence of Ni2p<sub>3/2</sub>, Ni2p<sub>1/2</sub>, C(1s), N(1s), O(1s), Si(2p), Al(2p) and Na(1s) XPS signals for the encapsulated nickel complexes are just in accordance with the signals observed for free state nickel complexe (presented in Table 3) demonstrating the formation of the complex within the supercage of zeolite Y.

Figure 4

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**Figure 4.** High resolution XPS signals of Ni (2p) for (A) NiL1, (B) NiL1', (C) ENiL1-Y and (D) ENiL1'-Y complex.

Table 3. Binding energy (eV) of neat and encapsulated complexes.

S. No	Samples	Si (2p)	Al (2p)	Na (1s)	C (1s)	N(1s)	O (1s)	Ni	Ni
								(2p <sub>3/2</sub> )	$(2p_{1/2})$
1.	NiL1	-	-	-	285.41,	400.38	532.37	856.24	873.59
					287.02				
2.	NiL1'	-	-	-	285.22,	399.69	532.29	856.24,	873.77,
					287.08			861.63	879.70
3.	ENiL1-Y	103.27	74.93	1072.85	285.41,	400.46	532.52	856.24,	873.42,
					287.20			862.35	882.07

4.	ENiL2-Y	103.05	74.82	1072.91	285.14,	399.80	532.56	855.22,	873.07,
					287.20			861.28	881.55
5.	ENiL1'-Y	103.28	74.90	1072.84	285.36,	400.44	532.51	856.67,	875.31,
					287.22			863.00	881.75
6.	ENiL2'-Y	103.04	74.88	1072.78	285.38,	399.24	532.54	855.21,	872.95,
					287.06			861.26	881.35

#### UV-vis/Diffuse Reflectance Spectroscopy (UV-vis/ DRS)

The electronic spectroscopic studies always remain very informative to comprehend the geometry and reactivity of such host-guest systems. The electronic spectra of the Schiff-base ligands and free state Ni(II) complexes are recorded in CHCl<sub>3</sub> (shown in Figure 5, Figure S12 in Supporting Information (SI) with summary of data presented in Table 4). The nickel salophen complex (NiL1) shows four intense bands. The bands at 260, 294 and 379 nm are assigned as intra-ligand  $\pi$ - $\pi$ \* transition and n- $\pi$ \* transitions. However, the absorption band at 483 nm is either charge transfer or d-d transitions involving the metal center, which strongly supports the complex formation as this band is absent in the spectrum of the corresponding ligand (L1).

#### Figure 5



**Figure 5.** Solution UV-vis spectra of (A) L1 and NiL1, (B) L2 and NiL2 and (C) L1' and NiL1' and (D) L2' and NiL2'.

Table 4. 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	272, 283	335, 364	-
2	NiL1	260, 294	360, 379	483
3	L2	246, 275	350, 378	-
4	NiL2	260, 298	365, 385	514

5	L3	240, 271	308, 364	-
6	NiL3	246, 274	310, 372	480
7	L1′	273, 298	345	
8	NiL1′	276, 302	323, 350	437
9	L2′	244, 279	302, 375	
10	NiL2′	245, 281	301, 380	443
11	L3′	268	305, 338	
12	NiL3'	269	302, 343	432

The DRS / solid state UV-vis spectra and spectral data of free state and encapsulated Ni(II) Schiff-base complexes are presented in Figure 6 and Table 5. The transition originated from the metal of NiL2 complex is red shifted and that of NiL3 is blue shifted as compared to those of NiL1 complex. This is well understood as NiL2 complex has strong electron donating groups (-OCH<sub>3</sub> groups) and NiL3 is having strong electron withdrawing groups (-NO<sub>2</sub> groups) in the ligand moiety. Another interesting observation is that the lowest energy transition, indeed originated from the metal of NiL1, is found to be red shifted in comparison to that of NiL1' complex directing to the fact that L series of ligands provide more electron density around the metal as compared to L' series.

The comparison of the UV-vis study of the free state NiL1 complex with those of the encapsulated ENiL1-Y complex unfolds the blue shift of the lowest energy band originated from the metal upon encapsulation, whereas the sane transition is red shifted in case of ENiL1'-Y complex. Encapsulation enforces metal related transition for all L series complexes to undergo blue shifts however, all L' series of Ni(II) complexes are showing red shift. This phenomenon is undoubtedly the consequence of geometrical modification of metal complexes after encapsulation and is pointing towards the fact that L and L' series promote two different and nearly opposing kinds of structural modifications. Red shift in metal related

 transition for encapsulated Ni(II) Schiff-base complexes suggests enhanced  $\pi$ -delocalization around the metal and blue shifts indicate the interrupted  $\pi$ -delocalization.

Figure 6



**Figure 6.** Solid state UV-vis spectra of (A) NiL1 and ENiL1-Y, (B) NiL2 and ENiL2-Y, (C) NiL3 and ENiL3-Y, (D) NiL1' and ENiL1'-Y, (E) NiL2' and ENiL2'-Y and (F) NiL3' and ENiL3'-Y.

Table 5. Solid-state UV-visible data of neat and	encapsulated complexes.
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S. No	Samples	$\pi$ — $\pi^*$ transitions	n—π <sup>*</sup> transitions	CT transitions / d-d transitions
1	NiL1	255	320, 378	487, 580
2	ENiL1-Y	252	335, 380	448, 556
3	NiL2	250	298, 386	526, 578
4	ENiL2-Y	230	302, 362	509, 580

5	NiL3	250	316, 386	439, 469
6	ENiL3-Y	260	322, 372	464, 496
7	NiL1′	243	298, 387	440
8	ENiL1'-Y	245	284, 380	474, 596
9	NiL2'	243	285,	407, 468
10	ENiL2'-Y	248	294, 392	515, 608
11	NiL3'	254	297, 386	445
12	ENiL3'-Y	232	349	480, 615

#### Magnetic study

To know the effect of the host framework specifically on the geometry of guest complex, magnetic measurements have been carried out for the Ni(II) complexes in both their neat and encapsulated states by using a SQUID magnetometer. The molar susceptibility ( $\chi_M$ ) vs. temperature (T) K for both the neat and encapsulated states are presented in Figure 7. In neat state, the Ni(II) in NiL1 and NiL1' are diamagnetic in nature and the magnetic moment appears to be close to zero (ranging from 0.43–0.46µ<sub>B</sub>). The nature of molar susceptibility ( $\chi_M$ ) vs. temperature (T) K (shown Figure 7) confirms the diamagnetic behavior of NiL1 manifesting planarity around the Ni(II) center. However, the case is different for NiL1' complex as it exhibits paramagnetism to a certain extent. These results are in agreement with the XPS observations and previously reported theoretical studies as well,<sup>35</sup> which once again identifies NiL1' complex with devoid of planarity to a greater extent as compared to NiL1 system.

Encapsulated Ni(II) Schiff-base complexes are demonstrating improved magnetization that is certainly from the guest complexes as zeolite host is diamagnetic in nature.<sup>37, 38</sup> The most plausible reason could be the distortion that these salophen complexes undergo upon encapsulation to be accommodated inside the supercage. These geometric modifications subsequently, reshuffles the ordering of molecular energy levels and thereby alters the electronic environment around the metal center.

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All the encapsulated systems show an enhanced magnetism and encapsulated complexes of L' series exhibit higher magnetization than that of the encapsulated nickel complexes of L series probably because of the geometry of the complexes in L' series is fundamentally non-planar in their free states. With an increase of molecular dimension, the extent of non-planarity increases on encapsulation and thereby the magnetization. Both the series exhibit a very similar trend of enhancement of magnetization along with the increasing order of the molecular dimension of the complexes. Magnetism is maximum for ENiL3'-Y than ENiL2'-Y and then is for ENiL1'-Y complex. Zeolite encapsulated ENiL3'-Y complex shows the highest magnetic moment among all the encapsulated Ni(II) Schiff-base complexes (2.85µ<sub>B</sub> at room temperature).

Figure 7



**Figure 7**. Molar susceptibility vs. temperature plots in the range of 5 K – 300 K of the complexes in free and encapsulated states (A) NiL1, ENiL1-Y and ENiL2-Y and (B) NiL1', ENiL1'-Y, ENiL2'-Y and ENiL3'-Y.

#### **Catalytic Study**

All free-state and encapsulated nickel complexes have been employed for the phenol oxidation reaction (shown in Scheme 1). Observed catalysis results of all the complexes are shown in Table 6. The reaction

conditions have been standardized with respect to encapsulated nickel salophen complex, ENiL1-Y, with the varied amount of catalyst and at different reaction temperatures (Catalytic data given in Supporting Information Figure S14-S15). The utilization efficiency of  $H_2O_2$  is found to be around 65% under the optimized reaction condition for four different encapsulated systems (data are presented in Table S2 in Supporting Information). All catalytic reactions are monitored by gas chromatography and % conversion calculated by using a calibration curve of phenol with bromobenzene as an internal standard (Figure S13 in Supporting Information).

Scheme 1



#### Scheme 1: Hydroxylation of phenol in the presence of catalyst and H<sub>2</sub>O<sub>2</sub>.

A plausible mechanism for the phenol oxidation reaction catalyzed by Ni(II) Schiff-base complexes is shown in Scheme 2. A reactive species (NiL--H<sub>2</sub>O<sub>2</sub>) is first generated as intermediate by the attack of H<sub>2</sub>O<sub>2</sub> on the Ni(II) complex followed by a quick generation of NiL\*S (shown in the Scheme 2) species. Finally, the catechol formation takes place by the transfer of oxygen from H<sub>2</sub>O<sub>2</sub> to phenol with the simultaneous release of water molecule.<sup>39</sup>

#### Scheme 2

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Scheme 2: A Plausible mechanism for the conversion of phenol to catechol in the presence of nickel salophen complex and  $H_2O_2$  (adapted from Ref.<sup>39</sup>).

All the complexes under encapsulation exhibit quite enhanced catalytic activities as compared to their corresponding free states. Both free and encapsulated state complexes are more selective towards the formation of catechol over hydroquinone. However, free state complexes are marginally more selective for the catechol formation over the corresponding encapsulated states. Heterogeneous catalyst (ENiL2-Y) has been recycled five times without significant loss in catalytic activity (Recyclability for the ENiL2-Y catalyst is presented in Figure 8). Performances of these catalysts have been also compared with other related catalysts reported in literature and are summarized in table S3 in Supporting Information. The direct comparison is not very straight-forward as the parameters of interest could be many. In terms of the parameters like amount of the catalyst used, time taken and % conversion, the catalyst of interest for the current study, ENiL2-Y competes well with other such catalysts.

# Table 6. Oxidation of phenol by nickel exchanged zeolite Y and neat and encapsulated nickel salophen complexes in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant.

S.	Samples	$Ni^{+2}$ in catalyst (mmol) <sup>[a]</sup>	% Conversion	TON <sup>[b]</sup>	Sel	ectivity
NO		(IIIII0I)		-	Catechol	Hydroquinone
1	Zeolite-Y	-	2	-	80	20
2	Ni-Y	0.01814	14	47.5	78	22
3	NiL1	0.06701	10	9.1	81	19
4	ENiL1-Y	0.00443	37	514.6	75	25
5	NiL1′	0.06701	24	22.0	78	22
6	ENiL1'-Y	0.00468	32	421.4	74	26
7	NiL2	0.05772	5	5.3	95	5
8	ENiL2-Y	0.00460	43	576.1	72	28
9	NiL2'	0.05772	15	16.0	80	20
10	ENiL2'-Y	0.00477	39	503.8	76	24
11	NiL3	0.05399	13	14.8	90	10
12	ENiL3-Y	0.00383	33	531.0	78	22
13	NiL3'	0.05399	18	20.5	82	18
14	ENiL3'-Y	0.00357	30	517.8	77	23

Reaction conditions: Phenol (0.58 g, 6.16 mmol),  $H_2O_2$  (2.54 ml (30%), acetonitrile 2 ml, temperature 80 °C, catalyst (0.05 g for encapsulated complexes and 0.025 g for neat complexes), Reaction time-6 h.

WF

 [a] mmol of Ni atom calculated in 0.025 g for neat complexes and 0.05 g for encapsulated complexes). [b] TON (turn over number): Turnover number calculated at the completion of reaction (mmol of phenol transformed / mmol of nickel metal in catalyst).

### Figure 8



Figure 8. Recyclability of the ENiL2-Y catalyst for phenol hydroxylation reaction.

## Structural modification and modified functionality

It is quite remarkable to note that the reactivity in terms of turn over numbers (TON) of all encapsulated complexes along with the Ni(II) exchanged zeolite Y are considerably higher than the all free state nickel complexes. A metal center in a complex, encapsulated inside the supercage of zeolite is categorized by isolation from the other metal centers by the host lattice and it has much lower mobility. Therefore, to achieve the desired reactivity, required reactive sites are much lesser inside the cavities, yielding higher TON.

To achieve the comparable and variable molecular dimensions of the transition metal Schiff-base complexes with that of the zeolite cavity and hence modified reactivity, attaching different substituents to

the salophen Schiff-base ligand moiety could be a viable option. In this report, with encapsulation, structural and functional modifications of two different series of Ni(II) salophen complexes have been studied in detail. Free-state Ni(II) sal-1,2-phen systems exhibit more planarity around metal center whereas the other series {Ni(II) sal-1,3-phen } show the typical arrangement of the central phenyl ring (Figure 9) yielding a certain extent of non-planarity.<sup>35</sup> An interesting observation emerging from the electronic spectroscopic studies of both series is associated with the metal-related transition; the transition for NiL1 complex (a complex of Ni(II) sal-1,2-phen series) appears at 487 nm whereas that for NiL1' complex (a complex of Ni(II) sal-1,3-phen series) appears at 440 nm. These observations actually support disrupted  $\pi$  delocalization around the metal for NiL1' system, as studied previously.<sup>35</sup>

Figure 9



**Figure 9.** Representation of middle phenyl ring arrangement in both {Ni(II) sal-1,2-phen} and {Ni(II) sal-1,3-phen} complexes.

Magnetic studies also clearly indicate the extent of non-planarity around nickel metal center in [Ni(II) sal 1,3 phen] complexes (see Figure 7). Planar electron–rich metal center becomes less susceptible for the nucleophilic attack of  $H_2O_2$ . Therefore, being more non-planar, the [Ni(II) sal-1,3-phen] systems show enhanced reactivity towards phenol oxidation as compared to the corresponding [Ni(II) sal-1,2-phen] systems. Apart from electronic and magnetic studies, XPS studies also indicate nickel center as more electropositive in NiL1' complex as compared to that in NiL1 complex and more electropositive metal

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center acts as a more efficient receptive center for the nucleophilic attack of hydrogen peroxide. With the same line of argument, the free-state NiL3' complex with  $-NO_2$  group attached is found to be the most active catalyst for the phenol oxidation reaction (plausible mechanism for phenol oxidation shown in Scheme 2). In another series, NiL3 complex is most reactive however, though it is still less reactive as compared to the NiL3' complex.

All the encapsulated nickel complexes exhibit much higher reactivity in comparison to their neat analogues. At this point, it is quite interesting to note that Ni-exchanged zeolite shows better reactivity as compared to all the free-state complexes (Catalysis Table 6). Substantial reactivity of Ni-exchanged zeolite indeed identifies the Ni(II) center is the catalytic center and active site isolation in the supercage of zeolite-Y as a major driving factor for enhancing the reactivity. Encapsulation of Ni(II) salophen systems inside the cavities of zeolite-Y primarily introduce site isolation and with an extent of distortion, it makes the metal center further electropositive and subsequently more reactive. Interestingly, encapsulated L series complexes are found with more improvement in the reactivity than corresponding complexes of L' series. Once encapsulated, encapsulation indeed provides site isolation very similarly for both the series. Therefore, the marginal difference in the reactivity is by and large controlled by the different structural modifications that these two series undergo upon encapsulation. Encapsulation enforces non-planar central benzene ring in free-state Ni complexes of L' series for improved planarity. Typically, encapsulated complexes of L' series encounter more enhancement of electron density on the metal center as compared to L series complexes.<sup>35</sup> These structural modifications, well-supported by the electronic spectroscopic data, controls the catalytic activities marginally here. All encapsulated [Ni(II) sal-1,3-phen] systems show a red shift in metal-related transition as compared to their free-state analogues whereas all [Ni(II) sal-1,2-phen] systems show a blue shift of the same transition upon encapsulation. Therefore, the performance of the encapsulated catalysts is governed by the major crucial factor like active site isolation, though the electronic factor of the substituent groups, the steric constraint imposed by the host framework

also contribute towards a catalytic activity. The overall comparative studies indeed, validate the mechanism of the phenol oxidation reaction.

The most striking result is observed for the NiL2 system. Encapsulated NiL2 complex manifests maximum reactivity for the phenol oxidation reaction whereas its neat state is least reactive amongst all entries in Table 6. On encapsulation, the TON of NiL2 complex increases from 5.3 to 576.1. In the free-state NiL2 complex, electron-donating character of the substituent –OCH<sub>3</sub> group prevails to make the catalyst least efficient in the lot. The electropositive character of the nickel metal increases due to non-planarity induced by steric constraint inside the host cavity. Finally, the addition of large substituent such as -OCH<sub>3</sub> group on salophen ligand moiety enhances the molecular dimension of the complex significantly, resulting in higher degree of non-planarity when encapsulated within the supercage. Subsequently, the nickel center becomes more electron deficient, resulting in amazingly higher reactivity. XPS analysis of encapsulated systems confirms the enhanced electropositive character of the nickel metal center (Figure 4C).

A very recent literature report states that in -situ generation of uniform peroxo species permit an unusual non-radical reaction mechanism for the oxidation reaction in the presence of  $H_2O_2$  as an oxidant in the zeolite framework. These species play a crucial role for the superior reactivity of catalysts towards  $H_2O_2$  based hydroxylation.<sup>40</sup> Active and stable M-OOH species is generated inside the supercage of zeolite-Y and formation of M-OOH species is identified as the rate-determining step for the  $H_2O_2$  based oxidation reaction.<sup>41</sup> Phenol is then actually adsorbed on the surface of zeolite, but not at the catalytic metal center to finally be oxidized. Zeolite walls eventually make phenol coming to the close proximity of the catalytic center which facilitates the complexes encapsulated in zeolite -Y for the styrene oxidation reaction.<sup>25, 42</sup> The enhancement of the catalytic activity of these encapsulated complexes are mainly controlled by the steric constraints that the complexes undergo on encapsulation. Structure of the catalyst and subsequently, electronic distribution becomes the decisive factor as styrene gets attached to the

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59 60 catalytic metal center and hence site isolation is not so important for that matter. Phenol oxidation reaction however, is facilitated via site isolation and hence is fundamentally following different mechanistic pathways from styrene oxidation.

#### Conclusion

Two small series of Ni(II) Schiff-base complexes [Ni(II) sal-1,2-phen and Ni(II) sal-1,3-phen series] have been synthesized in neat as well as in encapsulated states. All the systems are successfully characterized by the help of several spectroscopic techniques such as XRD, SEM-EDS, BET, XPS, IR, UV-vis studies and thermal analysis, magnetic studies and further employed as catalysts for the oxidation of phenol in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant. The electronic behavior of the neat and encapsulated systems is analyzed with the help of UV-vis and XPS studies. The complexes of [Ni(II) sal-1,3-phen] series are proven to have non-planarity in their free states and as a result, the formation of more electropositive nickel center becomes the basis of the marginally better reactivity towards phenol oxidation as compared to the [Ni(II) sal-1,2-phen] series. Zeolite supercage imposes notable space constraints when the guest complex has comparable molecular dimensions with that of the supercage. Hence, the efficiency of the catalysts is improved. The plausible driving factors for the betterment of reactivity of the complexes could be the altered coordination environment around the metal center as well as isolation of active sites inside the cavities of zeolite. The comparative analysis actually concludes that the phenol oxidation reaction is rather facilitated due to the site isolation phenomenon imparted by the heterogeneous catalysis.

#### Acknowledgements

The authors are thankful to the DST-FIST, Department of Chemistry and Department of Physics, BITS Pilani, for the instrumental facility. They also thank MNIT Jaipur, for the XPS measurements.

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# "For Table of Contents Only"

# Zeolite Encapsulated Ni(II) Schiff-Base Complexes: Improved Catalysis and Site Isolation

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# Highlighting the novelty of work

Site isolation and distorted geometry of zeolite encapsulated complex govern the improved catalysis for phenol hydroxylation reaction.