

## **Report of the work done**

### **i. Brief objective of the project**

- To synthesize acidic ILs by one pot synthesis route.
- Characterization of a synthesized ILs using spectroscopic method.
- To synthesize Ionic Liquid functionalized Mesoporous materials.
- 3D structure of acidic ILs by single crystal X-ray diffraction method.
- Single crystals of optimum size are grown by different solution methods.
- In parallel the ab-initio MO energy calculations carried out using Gaussian 09 software to correlate theoretical and experimental results.
- To study the biological response of the said molecules.

**ii. Work done so far and results achieved**

**a) Definition of the problem handled:**

The present proposal mainly deals with the synthesis and 3D-structural characterization of acidic ILs by using single crystal X-ray diffractometer. All the acidic ILs will be also characterized by spectroscopic methods especially FTIR, NMR techniques and Mass spectrometry. These ILs shall be tested as a catalyst for various organic reactions. In order to check other possible applications of ILs, the full structural characterization is mandatory.

Non bonded intermolecular interactions like  $\pi$ - $\pi$ , C- H...  $\pi$  , C- H...O in addition to nonconventional forces will be investigated to understand the role of these interactions in molecular structure and its function.



**b) Methodology adopted:**

**Preparation of Ionic liquids: (N,N-dimethyl benzimidazolium iodide):**

Normally, di-alkylation of imidazolium based ionic liquids was carried out in either multiple steps or by taking mono substituted imidazolium derivatives. Both these methods are not viable in terms of economical as well as environmental point of view. In view of this, we have developed a single step, one pot synthetic route in which di-alkylation of benzimidazole was carried out using dimethyl iodide in basic medium. As the methodology adopted is new, and the melting points of this kind of Ionic liquids are lower it is essential to know the exact structure of this molecule. In order to know the exact structure, in addition to normal spectroscopic analysis, single crystal method serves the purpose in better way.

Single crystals of optimum size are the necessary prerequisite for single crystal X-ray diffraction work. Out of many, the most friendly method 'slow evaporation technique' will be adopted to grow the optimum size crystal of ILs. Once the single crystals are grown intensity data will be collected to analysis its 3D structure, to explore the non – bonded intermolecular interactions which play an important role in the stability of the structure. Once the structure is established, its function can be correlated and if required structure can be modified as desired to improve the function of specific ILs. In parallel with it, ab-initio Mo energy and DFT calculations will be carried out using Gaussian 09 software, to obtain molecular geometry, HOMO- LUMO energy, single point energy, Mullikan charges and vibrational spectroscopy. The computed data will be compared with the experimental results. Biological response of the molecules will be tested using the laminar set up with different primary bacteria.

**Preparation of Mesoporous materials:**

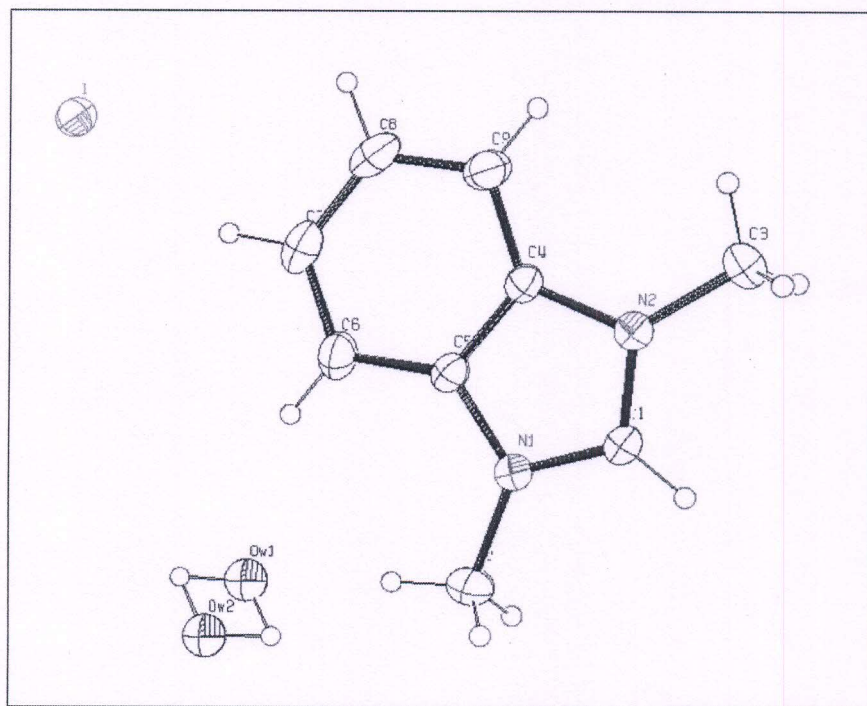
The metal doped titania ( $\text{TiO}_2$ ) and silica ( $\text{SiO}_2$ ), Ionic Liquid functionalized Mesoporous materials, were prepared by using sol – gel method in which amphiphilic block copolymers are used as a templating agent. The as prepared material contains polymer domain surrounded by metal oxides. The resultant sols were aged for a day at  $120\text{ }^\circ\text{C}$  in vacuum oven and then in order to remove templating agent, they were calcined at  $450\text{ }^\circ\text{C}$  (with a heating ramp  $2\text{ }^\circ\text{C}/\text{min}$ ). Alternatively, the templating agent can be removed by hot ethanol rinsing method at  $80\text{ }^\circ\text{C}$ . The thin films of the same material were prepared on glass substrate by EISA (Evaporation Induced Self Assembly) method using dip coating unit under controlled humidity and temperature.



**c) Detailed work (including prominent figure/data)**

**Synthesis of 1,3-dimethylbenzimidazolium iodide:-**

Methyl iodide and 1H-Benzimidazole were heated to 70 °C in THF (30ml) for 14h, after which time the THF was decanted off; the oil that was formed was washed with a further 10ml of THF. The oil was taken up in dichloromethane (DCM) (40ml) and  $\text{KHCO}_3$  was added along with ca.5ml of water. The DCM was removed in vacuo, the remaining oil taken up in THF (10ml) and a further 1 equivalent of methyl iodide added. After the solution was heated to 70 °C for 18h, then cooled and the THF was decanted off the reaction mass. The product was washed with ether and dried to leave fine crystals of the product. The final product was characterized by IR, NMR and Mass spectroscopy. To obtain 3D structure of the title molecule, optimized single crystals have been grown by slow evaporation method. Crystallographic data are collected on a Bruker APEX-II CCD diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71703 \text{ \AA}$ ) at  $T = 296.15 \text{ K}$ .



**Figure 1 ORTEP diagram of N,N-dimethyl benzimidazolium of iodide**

The title compound, 1,3-Dimethyl-3H-benzimidazol-1-ium iodide monohydrate,  $C_9H_{13}N_2IO$ , crystallizes in monoclinic system with space group  $P2_1/c$  and  $Z = 4$  with one molecule of  $[C_9H_{11}N_2]^+$ ,  $I^-$  having one  $H_2O$  molecule in the asymmetric unit. The lattice parameters are  $a = 8.9323(4)$ ,  $b = 7.1654(3)$ ,  $c = 17.6425(8)$  Å and  $\beta = 101.432(2)^\circ$ . The crystal structure is solved by direct method and refined by full- matrix least square technique on  $F^2$ , using WinGX program. The structure has been refined to a final  $R = 0.0352$  for the observed structure factor with  $I \geq 2\sigma(I)$ . The stability of the title compound is due to the network of  $\pi$ - $\pi$ , C-H...O and O-H...I hydrogen bond interactions. ORTEP diagram of the title molecule showing 50% probability displacement ellipsoids with numbering scheme is shown in figure 1.

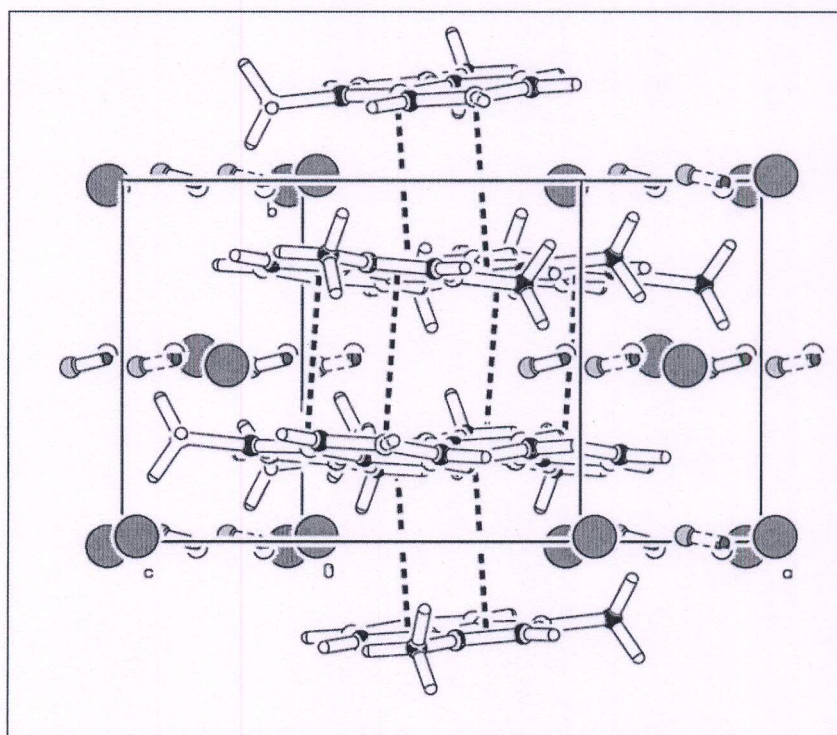


Figure 2  $\pi$ - $\pi$  interaction between molecules



The title compound, 1-amido alkyl naphthol derivative ( $C_{20}H_{19}NO_3$ ), crystallizes in monoclinic space group  $P2_1/n$  with  $Z=4$ . The crystallographic parameters are  $a=10.5268(5)$ ,  $b=13.7438(7)$ ,  $c=11.4453(6)\text{\AA}$  and  $\beta=96.180(1)^\circ$ . The structure has been refined to a final  $R=0.0421$  for the 3805 observed reflection with  $I \geq 2\sigma(I)$ . The intermolecular interactions of  $\pi$ - $\pi$ ,  $C-H\cdots\pi$  and  $O-H\cdots O$  hydrogen bond interactions are observed in the title molecule and additionally weak but significant intra  $N-H\cdots F$  and  $C-H\cdots O$  interactions observed to contribute to the stability of the structure. ORTEP diagram of the title molecule showing 50% probability displacement ellipsoids with numbering scheme is shown below. The final product was characterized by IR, NMR and Mass spectroscopy. To obtain 3D structure of the title molecule, optimized single crystals have been grown by slow evaporation method. Crystallographic data are collected on a Bruker APEX-II CCD diffractometer with graphite monochromated  $MoK\alpha$  radiation ( $\lambda=0.71703\text{\AA}$ ) at  $T=296.15\text{ K}$ .

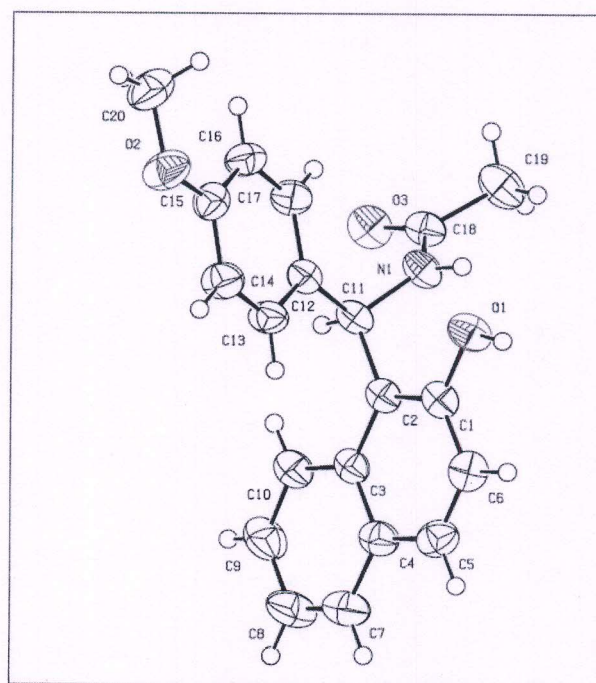


Figure 3 ORTEP diagram of  $C_{20}H_{19}NO_3$

The title compound, a significant benzimidazole derivative ( $C_7H_6N_2$ ), crystallizes in orthorhombic space group  $Pna2_1$  with  $Z=4$ . The crystallographic parameters are  $a=13.4905(4)$ ,  $b=6.8083(2)$ ,  $c=6.9396(2)$  Å. The structure has been refined to a final  $R=0.0276$  for the 1031 observed reflection with  $I \geq 2\sigma(I)$ . The intermolecular interactions of  $\pi$ - $\pi$ ,  $C-H \cdots \pi$  and  $N-H \cdots N$  hydrogen bond interactions are observed in the title compound. ORTEP diagram of the title molecule showing 50% probability displacement ellipsoids with numbering scheme is shown below. The final product was characterized by IR, NMR and Mass spectroscopy. To obtain 3D structure of the title molecule, optimized single crystals have been grown by slow evaporation method. Crystallographic data are collected on a Bruker APEX-II CCD diffractometer with graphite monochromated  $MoK\alpha$  radiation ( $\lambda=0.71703$  Å) at  $T=296.15$  K.

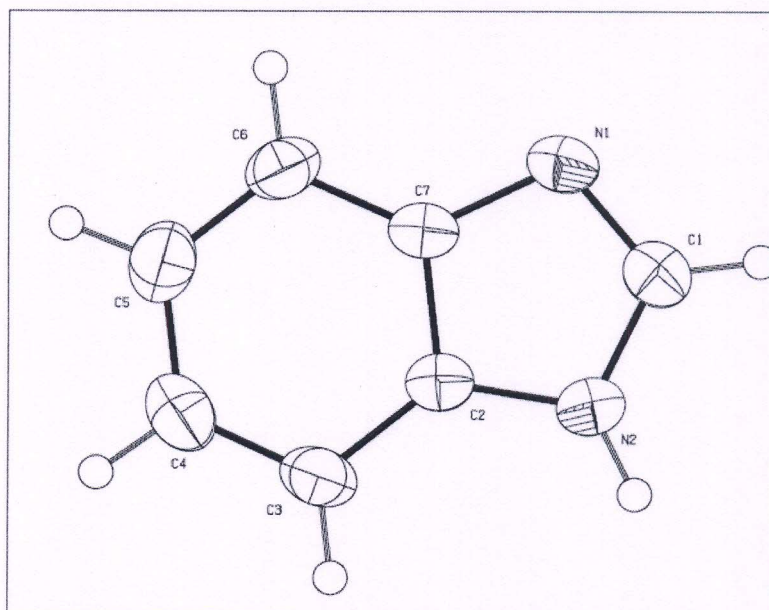


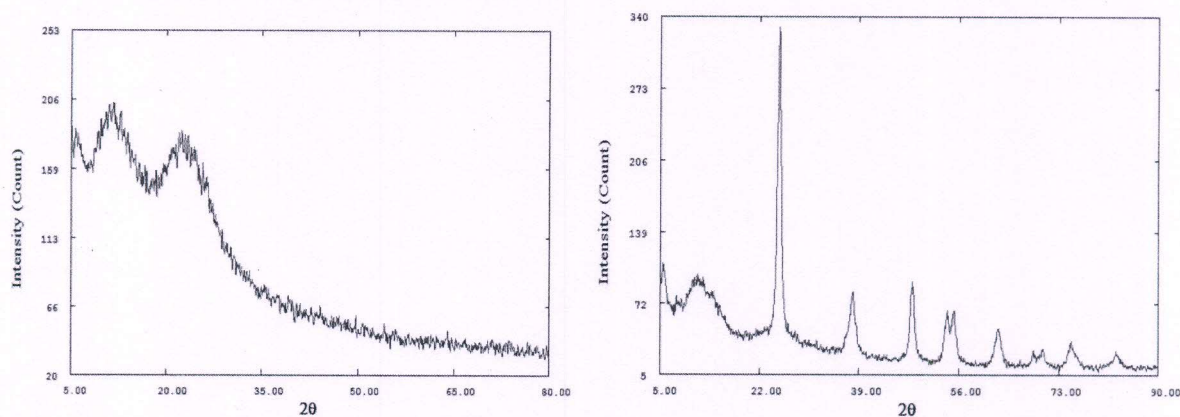
Figure 4 ORTEP diagram  $C_7H_6N_2$



## Ionic Liquid functionalized Mesoporous materials:

### Fe/TiO<sub>2</sub> and Fe/SiO<sub>2</sub>

**Fe doped Silica-** Mesoporous doped silica were synthesized using a prehydrolyzed solution containing TEOS (tetraethoxysilane), ethanol and hydrochloric acid was stirred for an hour. A second solution prepared by dissolving the Fe-P123 surfactant mixture in ethanol under acidic conditions, was then added to the former one. The resultant was then kept for ageing for one day under humid atmosphere and then under atmospheric conditions for self evaporation of solvent which was then dried, grounded to form fine yellow colored free flowing powder. The final doped silica was rinsed in ethanol for 2h at 80°C to remove surfactant and then dried under at 80°C for 2 days. The synthesized Fe/SiO<sub>2</sub> were then characterized using XRD, BET, TEM, SEM, EDS and DLS measurements.



**Figure 5** XRD pattern of Fe-doped silica (left side) and titania (right side)

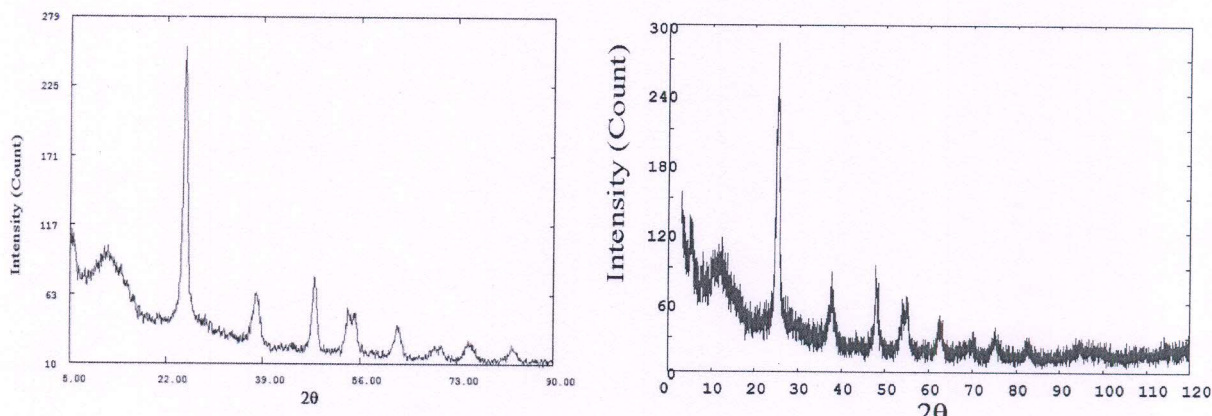
**Fe doped Titania-** Mesoporous doped titania were synthesized from Ti(iPrO)<sub>4</sub> (Titanium tetraisopropoxide) to which HCl is added with constant stirring at 0°C and after completion of addition continued to stir for 30min at room temperature. A second solution prepared by dissolving the Fe-P123 surfactant mixture in ethanol under acidic conditions, was then added to the former one. The resultant was then kept for ageing for one day under humid atmosphere and then under atmospheric conditions for self evaporation of solvent which was then dried. The crude sticky material was then calcined at 450°C for 3.30h at a heating rate of 2°C/min to obtain a fine Fe/TiO<sub>2</sub> powder which was further characterized using XRD, BET, TEM, SEM, EDS and DLS measurements.



### Pd/TiO<sub>2</sub> and Pd/SiO<sub>2</sub>

**Pd doped TiO<sub>2</sub>-** Ordered mesoporous Pd/TiO<sub>2</sub> materials were synthesized through a simple sol-gel process in the presence of triblock polymer P123 as structure directing agent. To homogeneously distribute Pd nanoparticles into the Titania framework, we utilized multicomponent assembly approach where surfactant, titania and Pd were assembled in an one-step process. The molar ratios of each reagent in the starting solutions were fixed at TiO<sub>2</sub>/P123/C<sub>2</sub>H<sub>5</sub>OH/HCl. In particular, pre weigh HCl was added dropwise to Ti(iPrO)<sub>4</sub> in at 30 °C under stirring and after completion of addition the reaction mass was allowed to stir further for 2h at room temperature. On the other hand, the calculated amount of Pd(OAc)<sub>2</sub> was added to P123 ethanolic solution and stirred vigorously. The as-made mesostructured hybrids were calcined at 450°C in air for 3h at a heating rate of 3°C/min to remove surfactant and to obtain highly ordered mesostructured Pd/TiO<sub>2</sub>.

**Pd doped SiO<sub>2</sub>-** Mesoporous doped silica were synthesized using a prehydrolyzed solution containing TEOS (tetraethoxysilane), ethanol and hydrochloric acid was stirred for an hour. A second solution prepared by dissolving the Pd(OAc)<sub>2</sub> in P123 surfactant in ethanol under acidic conditions, was then added to the former one. The resultant was then kept for ageing for one day under humid atmosphere and then under atmospheric conditions for self evaporation of solvent which was then dried, grounded to form fine light grey colored free flowing powder. The final doped silica was rinsed in ethanol for 2h at 80°C to remove surfactant and then dried under at 80°C for 2 days. The synthesized Pd/SiO<sub>2</sub> were then characterized using XRD, BET, TEM, SEM, EDS and DLS measurements.



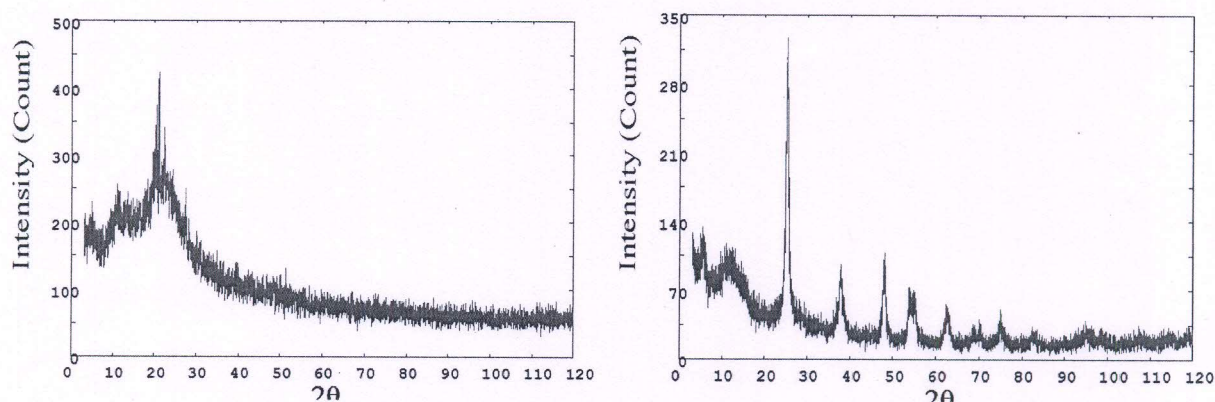
**Figure 6** XRD pattern of Pd-doped silica (left side) and titania (right side)



### Ni/TiO<sub>2</sub> and Ni/SiO<sub>2</sub>-

**Ni doped Silica-** Mesoporous doped silica was synthesized using a pre-hydrolyzed solution containing TEOS (tetraethoxysilane), ethanol and hydrochloric acid was stirred for an hour. A second solution prepared by dissolving the Ni(OAc)<sub>2</sub> and P123 surfactant in ethanol under acidic conditions, was then added to the former one. The resultant was then kept for ageing for one day under humid atmosphere and then under atmospheric conditions for self evaporation of solvent which was then dried, grounded to form fine light green colored free flowing powder. The final doped silica was rinsed in ethanol for 2h at 80°C to remove surfactant and then dried under at 80°C for 2 days. The synthesized Ni/SiO<sub>2</sub> were then characterized using XRD, BET, TEM, SEM, EDS and DLS measurements.

**Ni doped Titania-** Mesoporous doped titania were synthesized from Ti(iPrO)<sub>4</sub> (Titanium tetraisopropoxide) to which HCl is added with constant stirring at 0°C and after completion of addition continued to stir for 30min at room temperature. A second solution prepared by dissolving the Ni(OAc)<sub>2</sub> and P123 surfactant in ethanol under acidic conditions, was then added to the former one. The resultant was then kept for ageing for one day under humid atmosphere and then under atmospheric conditions for self evaporation of solvent which was then dried. The crude sticky material was then calcined at 450°C for 3.30h at a heating rate of 2°C/min to obtain a fine Ni/TiO<sub>2</sub> powder which was further characterized using XRD, BET, TEM, SEM, EDS and DLS measurements.



**Figure 7** XRD pattern of Ni-doped silica (left side) and titania (right side)



**d) Results and conclusion:**

- As proposed, a few IL materials have been synthesized successfully and characterized fully. As expected in one of the IL, ionic iodine has gone into the lattice with one water molecule in it.
- But synthesis of IL with  $\text{H}_2\text{SO}_4$  in it could not be obtained.
- Ab initio calculations are yet to be carried out.
- Antimicrobial study is also planned to be carried out.

**e) Details of the publications(including conference presentation)**

Research paper entitled "Synthesis & Molecular structure of 1,3-Dimethyl-3H-benzimidazol-1-ium iodide monohydrate" by Urmila H Patel, Sahaj A. Gandhi, Saurabh S. Soni, Deepali Kotadia has been presented in "41st National Seminar on Crystallography" on October 8-10, 2012 at CAS in Crystallography and Biophysics, University of Madras, Chennai in poster presentation category.

1. One pot synthesis of N,N-dimethyl imidazolium iodide and their catalytical activity in preparation of 1-amidoalkyl naphthols

D. A. Kotadia, Sahaj Gandhi, U. H. Patel, S. S. Soni

J. Molecular Catalysis A (Under Preparation)

2. A3 coupling reactions catalyzed by Fe-doped metal nanoparticles under microwave irradiation

D. A. Kotadia, Sahaj Gandhi, U. H. Patel, S. S. Soni

Advanced Synthesis and Catalysis 2013 (Under Preparation)