

**EXECUTIVE SUMMARY OF RESEARCH  
PROJECTS FUNDED BY THE UNIVERSITY GRANTS  
COMMISSION, NEW DELHI**

**1. Title of the Major Research Project**

Synthesis, characterization and catalytic applications of metal complex functionalized silica-based mesoporous solids

**2. Name of the Principal Investigator**

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**3. Number and date of Sanction letter**

F. No. 43-168/2014(SR) dt. 15/6/2015

**4. Duration of the Project**

01/07/2015 to 30/06/2018

**5. Total outlay of the Project**

Rs. 14,21,899/- (sanctioned); Rs. 12,54,970/- (received till date)

**6. Brief introduction**

Many chemical transformations would not seem to be happened in our world without catalysts. Catalysts are essential in the living systems. For obvious reasons it has become indispensable in a wide range of industrial reactions also. However, the study of these systems can offer much more: it can change our understanding of fundamental chemical concepts and at times compelled us to rethink the rules of the chemical world. Research in this area moving very fast: many catalytic reactions now appeared to be trivial to the chemists that were remained previously unachievable. In search for environmentally benign catalytic system, porous matrices have been used to design new types efficient catalysts in this project. Performance of the newly designed catalytic systems was found to be excellent in many industrially important reactions. Solid catalysts can be separated easily from reaction mixture and can be reused in several cycles with minimum loss of activity. They are capable to cut down the pollution level and energy consumption in catalytic process will be much lower than the conventional processes. In essence the broad objective of this project is very much in line with the modern outlook of the chemical research for development of the clean technology that is extremely necessary for a sustainable growth of the society.

**7. Objectives**

1. To prepare mesoporous silica/silica alumina based framework solids which have potential to act as catalyst
2. To study the various heterogeneous catalytic reactions by employing the prepared materials
3. To achieve selectivity of the products in catalytic reactions by tuning the pore size of the framework solids and electronic properties of the metal centers

**8. Outputs**

### ***Key findings***

Highly porous and robust mesoporous silica, SBA-15 has been subjected to post-synthesis modification for the anchoring of copper through Schiff base moiety formation using the silicon alkoxide route. The hybrid porous material has been fully characterized by powder-XRD, electronic spectra, EPR, thermogravimetric analysis, N<sub>2</sub> sorption measurements, and TEM and SEM/EDS studies. The efficiency of the catalyst has been assessed in the O-arylation reaction using various substituted phenols and nitroarenes in heterogeneous conditions. The catalytic coupling reaction efficiently produces unsymmetrical diaryl ethers. The impressive capability to activate substrates having electron-donating or electron-withdrawing substituents and to have a high turnover frequency in the catalytic reactions made the catalyst highly desirable.

A novel heterogeneous catalyst using mesoporous silica have been developed for synthesis of some important unsymmetrical N,N-diarylated imidazolium compounds via a facile procedure. Single catalyst can activate consecutively two step of N- and N-arylation of imidazoles and some of its congeners. Simplicity of the method and outstanding character of the catalyst facilitates the reaction to go smoothly encompassing a broad range of functional groups. The catalyst is resistant to leaching under the reaction condition. Both the arylation can be undertaken in open flask reaction which makes the procedures easily accessible for synthesis of a variety of important compounds.

Besides, in our subsequent attempt we have been successful in synthesizing a series of copper- and alkaline-earth metal based multidimensional metal-organic frameworks, {[CuMg(pdc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O]<sub>n</sub>} (1), [CuCa(pdc)<sub>2</sub>]<sub>n</sub> (2), [CuSr(pdc)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (3), and {[CuBa(pdc)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>·H<sub>2</sub>O]<sub>n</sub>} (4), where H<sub>2</sub>Pdc = pyridine-2,5-dicarboxylic acid, through hydrothermal route. Two different metals act as the active center to catalyze two kinds of reactions, *viz.*, olefin to its epoxide followed by epoxide ring opening to afford the corresponding vicinal diol in a sequential manner. Framework compounds act as multifunctional catalysts, where copper acts as an active center for epoxidation of olefins and, subsequently, alkaline-earth metals act as active centers for epoxide ring-opening reactions, in tandem, to afford vicinal diol. With an increase in the size of the alkaline-earth metals, the diol formation rate from epoxides rapidly enhanced because of the increase of the open metal sites. Frameworks behaved as heterogeneous catalysts and can easily be recovered and reused without significant catalyst deactivation due to either leaching of the active species or degradation of the structure.

### ***Knowledge creation***

1. S. Das, S. Koner et al. Heterogeneous sequential N-arylation of N-heterocycles over copper anchored mesoporous silica catalyst, *Appl. Catal. A: Gen.* **513**, 53–66 (2016).

2. T. Maity, S. Bhunia et al., Heterogeneous O-arylation of nitro-arenes with substituted phenols over copper immobilized mesoporous silica catalyst, *RSC Adv.* **6**, 33380 - 33386 (2016).
3. D. Saha, D. K. Hazra, T. Maity and S. Koner, Heterometallic MOFs that Catalyze Two Different Reactions Sequentially, *Inorg. Chem.* **55**, 5729–5731 (2016).
4. D. Saha, S. Gayen, S. Koner, Cu(II)/Cu(II)-Mg(II) Containing Pyridine-2,5-dicarboxylate Frameworks: Synthesis, Structural Diversity, Inter-conversion and Heterogeneous Catalytic Epoxidation, *Polyhedron* **146**, 93–98 (2018).

### ***Capacity building***

PhD- 1 (registered)