

## **Design of Mesoporous Materials for Alternative Energy Applications: Solar Hydrogen and Dye-Sensitized Solar Cells (DSSCs)**

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The current research work that I am involved includes development of novel porous materials for production of hydrogen using sunlight and producing highly ordered titanium dioxide materials. Porous materials fall into one of three categories: (1) microporous; (2) mesoporous; and (3) macroporous.<sup>1</sup> The microporous materials include porous materials with pores (channels) of less than 2 nm (< 20 Å). An example of microporous materials includes the crystalline zeolite family made of Si, O, and Al. These porous materials currently are extensively used in petroleum refining, which permits greater amounts of crude oil to be converted to high value product(s): gasoline. The second class of porous materials have pore channels between 2-50 nm (20-500 Å), and the mesoporous materials are being studied heavily for applications from partial organic chemistry transformations to various alternative energy uses. The major positive application benefit over crystalline zeolites is the relative easy access of various ions that could be substituted for Si ions in framework from amorphous walls and greater surface area values. The last porous family includes the materials of pores greater than 50 nm (> 500 Å), which are called macroporous. The macroporous materials have been used for application arena, such as: photonic crystals and chromatography columns. Clearly, porous materials have many current and future applications in the areas of catalysis and material science.

The porous material class that the Koodali research group is extensively completing research includes mesoporous materials. As noted previously, the relative easy substitution of ions, such as transition metal ions, of comparable atomic radii in the silica framework work (isomorphous substitution) permits the materials to take on catalytic activity.<sup>1</sup> Also, mesoporous materials made of silica commonly have many defects called silanol groups (Si-OH), which provides another avenue to attaching transition metal ions to the pore walls if the metal ion is too large for isomorphous substitution. The major class of mesoporous materials includes the Mobile Composition of Matter (MCM) family, as shown in Figure 1: (1) MCM-50, (2) MCM-41, and (3) MCM-48. These materials have been previously discovered by the Mobile Oil Company researchers in 1992. The MCM-50 has a lamellar structure similar to graphite. The silica framework occurs in MCM-50 in a two-dimensional (2-D) plane. Due to the 2-D lamellar structure, upon removal of surfactant, the lamellar structure collapses. For most applications, this structure has had limited usefulness due to the pore structure destruction with heating. The second type of material is called MCM-41, and it has a unidirectional honeycomb hexagonal pore structure. In contrast to the MCM-50, the porous nature is retained upon surfactant removal (calcination) in MCM-41. The last material has gained the most interest in the catalysis research community: MCM-48. One of the major limitations in catalytic reactions is mass transfer of reactants and products; however, MCM-48 circumvents this problem with the bi-continuous Ia3d cubic gyroidal structure. The gyroidal structure permits reactants and products to proceed in the three-dimensions (3-D). Therefore, the desired transformations occur at a greater frequency, which is highly desirable in catalytic reactions.

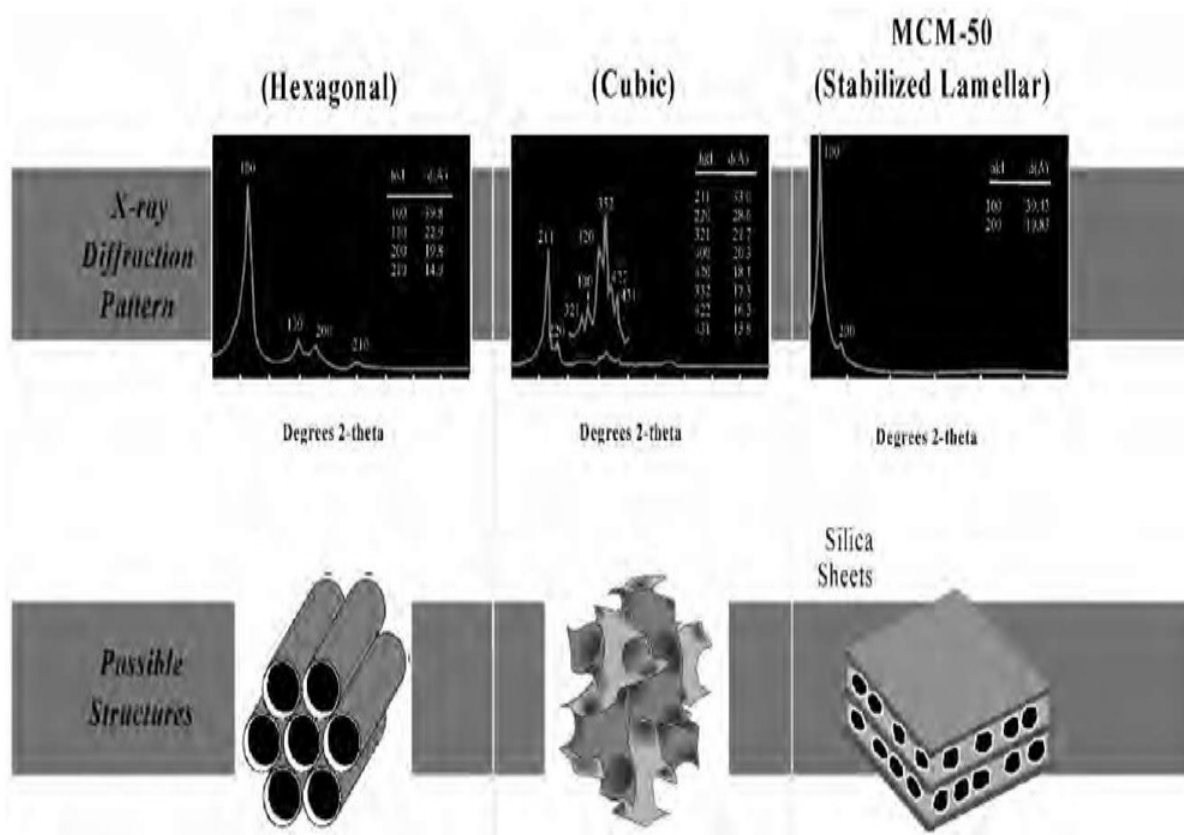
The Koodali group is interested in doping (substituting) transition metal ions in MCM-48 or placing the ions in the pore channels to initiate photocatalytic reactions: water-splitting. The major mechanism for these types of reactions involves ligand-to-metal-charge-transfer (LMCT). For example, in previous research conducted on V-MCM-48 for environmental remediation, the  $O^{2-} \rightarrow V^{5+}$  reaction occurred in the dark, visible, and UV-irradiation to convert acetaldehyde to carbon dioxide and water.<sup>1</sup> The material I have completed work on includes Cr-MCM-48 for solar hydrogen production. Similar to V-MCM-48, the chromium ion is usually in the highest oxidation state ( $Cr^{6+}$ ) and the oxide ligand ( $O^{2-}$ ) donates an electron to the vacant (empty) 3d orbital of chromium. This creates a situation with LMCT at work or in general form: reduction-oxidation chemistry reaction (redox). The ultimate goal of this research includes complete water-splitting under visible light illumination; however, currently, we have been successful with evolving hydrogen using methanol sacrificial reagent under UV-conditions. In addition to studying solar hydrogen production, we have also studied the intermolecular forces that effect the formation of metal-doped MCM-48. In particular, we have systematically studied the role of the chromium salt chosen and

loading on the formation of cubic structure. The type of counter-ion (anion) in the chromium salt has been indicated to dramatically affect the quality of the cubic phase. Additionally, the chromium ion loading is a major factor on the phase formed, be it: cubic, hexagonal, or wormhole (disorder hexagonal). Finally, the long-term aim beyond doping with chromium ion includes development of Cr-Ti-MCM-48 for water-splitting, which may have greater hydrogen evolution rates.

Another project that has begun includes development of hexagonal mesoporous titanium dioxide. Previously, researchers have found that mesoporous TiO<sub>2</sub> has the potential in dye-sensitized solar cells (DSSCs) to capture greater amounts of dye, thereby permitting larger solar cell efficiencies. The major challenge has been retention of the porous network upon heating. We are currently attempting to develop alternative synthetic methods to arrive at stable mesoporous titanium dioxide for DSSCs use. In summary, mesoporous materials have many current and potential applications in solid-state devices, such as battery materials.

## Reference

1. <http://krex.k-state.edu/dspace/handle/2097/4198>



**Figure 1.** Powder XRD diffractograms are shown of hexagonal MCM-41, cubic MCM-48, and lamellar MCM-50.

[http://what-when-how.com/wp-content/uploads/2011/03/tmp25352\\_thumb1.jpg](http://what-when-how.com/wp-content/uploads/2011/03/tmp25352_thumb1.jpg) (Accessed 7/25/2012)