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MESOPOROUS MOLECULAR SIEVES FOR THE SYNTHESIS OF FINE CHEMICALS

Catalysis by ordered mesoporous molecular sieves offers new possibilities for transformations of bulky organic molecules and in the synthesis of various chemical specialties.
Tailoring of their pore sizes and surface areas makes them particularly attractive as catalysts or supports for active species. Examples of some condensation, redox and C-C bond forming reactions are provided in this short account.

While zeolite-based catalysts represent one of the most important groups of inorganic crystalline materials with a large number of industrial applications [1-3], the first successful synthesis of mesoporous molecular sieves has opened a new era of investigating the properties of these materials particularly with emphasis to catalysis. The breakthrough in the synthesis of materials with pore dimensions from 2 to 25 nm started a very fruitful period of their research [4-6]. Although, industrial applications of mesoporous molecular sieves are still rather limited, these materials show a great potential for transformations of large organic molecules whether used as catalysts or supports for catalytically active phases [7].

The objective of this short contribution is to highlight some examples of synthesis of fine chemicals, which mesoporous molecular sieves are able to catalyze and to stress the advantages of these materials for potential applications.

Catalysis by Mesoporous Molecular Sieves

While siliceous mesoporous molecular sieves (see Fig. 1 - TEM picture) exhibit very rarely catalytic activity in reactions like e.g. Beckmann re-arrangement, after their modification with heteroatoms, metal oxides or organometallic complexes they can be

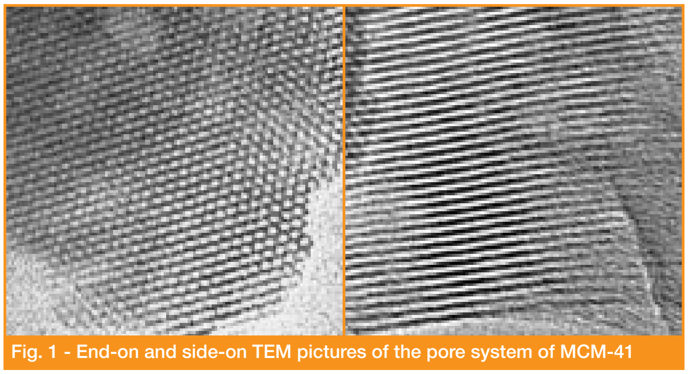
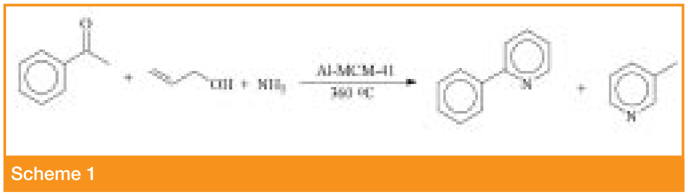
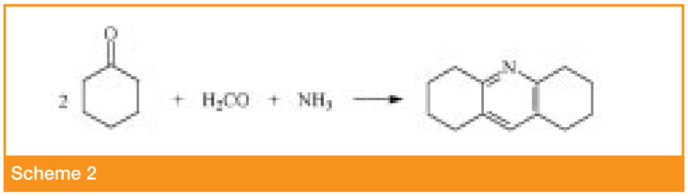


Fig. 1 - End-on and side-on TEM pictures of the pore system of MCM-41



Scheme 1



Scheme 2

used as highly active and usually also selective catalysts, not only for the synthesis of various petrochemicals but also for preparation of different chemical specialties.

In acid catalysis Al-MCM-41 catalyzes condensation reactions of a mixture of acetophenone, allyl alcohol and ammonia at 360 °C in a fixed bed reactor. 2-Phenylpyridine is formed in a good yield with a major side product 3-methylpyridine (β-picoline). The best results were obtained with the MCM-41 catalyst: 67.1% selectivity at 99.7% conversion (Scheme 1).

In a similar way mesoporous material Al-MCM-41 catalyzes the one-pot synthesis of octahydroacridine from the low cost compounds cyclohexanone, formaldehyde and ammonia. Presumably 1-aminocyclohexene and 2-hydroxymethylcyclohexanone are the intermediates (Scheme 2). At the surface of siliceous MCM-41 thiol groups can be oxidized to sulfonic acid [8], which proved to be excellent catalyst for esterification of glycerol with lauric and oleic acids. Schematic representation of the surface of MCM-41 with thiol groups is given in Figure 2.

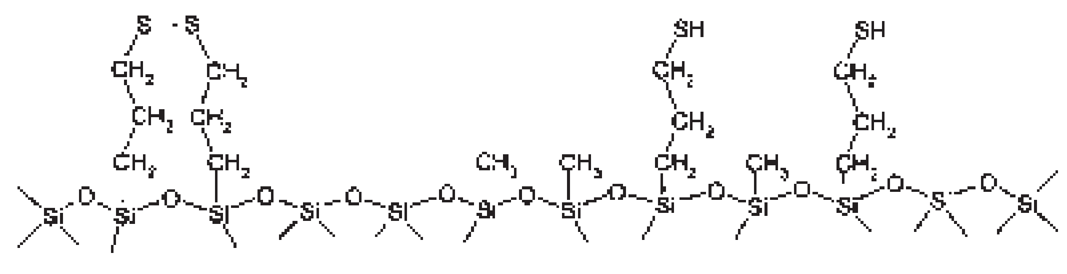


Fig. 2

In this reaction a decrease in the pore size from 1.4 to 1.0 nm diminished substantially the rate of the reaction and the selectivity to monolaurin product.

Incorporation of other metals into the structure of mesoporous molecular sieves can provide highly active and selective oxidation catalysts. Titanium containing MCM-41 is an interesting oxidation catalyst for epoxidation of double bond in bulky compounds however TS-1 is still more active for small molecules.

Zirconium MCM-41 was described as a suitable catalyst for Meerwein-Ponndorf-Verley reduction of bulky ketones with alcohols via hydrogen-transfer reaction. Zirconocene dichloride served as a precursor for the formation of the active species [9]. Zr-MCM-41 or Mn-MCM-41 was also active in oxidation of *trans*-stilbene to *trans*-stilbene oxide in a liquid phase [10].

Recently, Corma *et al.* [11] described the modification of MCM-41 with tin. This catalyst exhibits high activity and almost 100% selectivity in Baeyer-Villiger oxidation of cyclic lactones to respective ketones. The Sn-MCM-41 catalyst is tolerant to other functional

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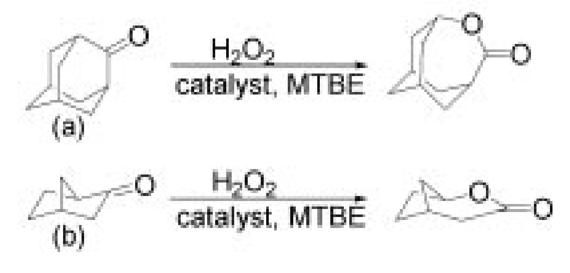

Scheme 3

groups of the cyclic ketone (Scheme 3).

Probably the most attractive area for application of mesoporous molecular sieves as supports is heterogenization of organometallic catalysts, which are extremely active and selective in homogeneous phase. Proper immobilization or anchoring can stabilize them to the support and benefit from their high intrinsic activity enhanced by the advantages of the heterogeneous system. Critical issue of immobilization of catalysts is the possibility of their leaching to the liquid phase. Filtration of the catalysts at reaction temperature has been suggested to prove the stability of the catalysts without adsorption of leached species.

Enzyme catalysts like trypsin were immobilized on MCM-41, MCM-48 or SBA-15 [12]. Silica based MCM-41 functionalized by thiol groups seemed to increase the interaction with the enzyme molecule and prevent the leaching compared with a pure silica material. The activity of this catalysts achieved 84% of the activity of free trypsin in hydrolysis of N-α-DL-arginine-4-nitroanilide.

Palladium based catalysts immobilized on the surface of mesoporous silicas or organosilicas are active catalysts in C-C bond formation like Heck and Suzuki reaction between arylhalides and arylboronic acids or olefins [13].

Conclusions and Outlook

Novel catalysts based on mesoporous molecular sieves are definitely very interesting materials and numerous laboratories around the world are focused on their synthesis, characterization and catalytic testing. Although some of them have already been identified as excellent catalysts with even better performance compared with conventional catalysts, their price and certain "conservatism" of producers limit up-to-now their industrial applications.

In the case of acid catalysis, the attempts to synthesize strong acidic mesoporous molecular sieves are still not successful however medium acid sites of Lewis type can be applied for transformations of bulky compounds. With regard to that mesoporous molecular sieves are very promising catalysts for acid, base as well as redox reactions, whenever transformations of molecules not entering microporous zeolites are required.

Finally, we personally believe that earlier or later mesoporous molecular sieve based catalysts will be applied in an industrial scale especially in the synthesis of compounds with high added values.

Setacci molecolari mesoporosi per la sintesi di fine chemicals RIASSUNTO

La catalisi tramite setacci molecolari mesoporosi ordinati offre nuove possibilità per la trasformazione di molecole organiche grezze e per la sintesi di varie specialità chimiche. La possibilità di regolare le dimensioni dei pori e delle aree superficiali li rende particolarmente versatili sia come catalizzatori sia come supporti per specie attive. In questo breve articolo vengono riportati alcuni esempi di reazioni di condensazione, ossido-riduzione e formazione del legame C-C.