Metal modified MCM-41 materials prepared at room temperature with varied transition metal and metalloids sources: Evaluation of oxidation and acid ability in liquid phase catalytic systems

S. Karakoulia[1*], C. Michailof[1], A. Marianou[1], M. Sountourlis[2], A. Lappas[1]

1 Chemical Process and Energy Resources Institute, CERTH, GR 57001, 6th km Charilaou-Thermis, Thessaloniki, Greece; 2 Newenergy S.A., Paralimni, GR 62100, Serres, Greece
**Corresponding author: matoula@cperi.certh.gr*

Since the disclosure of mesostructured materials by Mobil a remarkable effort has been devoted to their preparation and a variety of synthesis procedures has been proposed that can lead to materials with different structural and catalytic properties [1]. Incorporation of aluminium into silica framework, either by direct synthesis or post-synthesis grafting, which generates acid active sites, usually results in a decrease in the quality of the pore structure compared with the pure silica grades, the extent of which depends on the synthesis pathways.

An alternative procedure, based on that developed for pure silica grades [2], is proposed here for a synthesis of pure or metal modified mesoporous silicas (M-MCM-41) by using tetraethoxysilane (TEOS), hexadecyltrimethylammonium bromide (CTAB)under mild conditions with high porosity characteristics and well-ordered mesopore hexagonal pore structure. The main advantages of the method are excellent reproducibility, easy preparation of large batches and flexibility in using different type of heteroatoms for the partial incorporation in silica framework allowing thus the preparation of metal modified MCM-41 materials with catalytic capability. Oxidation or/and acid mesoporous catalysts were generated by incorporating metals such as Al, Sn, Ga, Mn, Ni, Cu, Cr, Fe and Zr, Modification with heteropolyacids ($H_3[P(W_3O_{10})_4]\cdot xH_2O$ or $H_4[Si(W_3O_{10})_4]\cdot xH_2O$) in some cases was also performed in order to enhance Brönsted acidity. All synthesized materials were fully characterized with the following techniques: ICP-OES, XRD, SEM, N_2 porosimetry, TPD and in-situ pyFTIR.

Selected mesoporous silicas with oxidation incorporated metals (ca. Ni, Cu, Mn, Fe) were tested in glucose conversion in terms of yield and selectivity for glucaric acid synthesis showing promising heterogenous catalytic performance. Activity of the acid M-MCM-41 catalysts (were M: Al, Sn, Ga, Zr) with or without heteropolyacids, was tested via acidification of refinery soapstocks and their conversion to esters in presence of glycerine in order to assess the potential of using soapstock and glycerine as alternative biodiesel feedstock or as feedstock for the synthesis of high-added value chemicals respectively.

References

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