Nanostructured Mesoporous Polyoxometalate and Transition Metal-substituted Polyoxometalate Materials: Applications in Heterogeneous Catalysis

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1. FIANL PUBLISHABLE SUMMARY REPORT

Although the primary polyoxometalate (POM) clusters have attractive properties especially in the fields of acid and oxidation catalysis, they lack significant advantages in various catalytic operations comparable to supported POM catalysts. The low surface area and enormous solubility in polar media are the main limitations of POMs for applications in many heterogeneous catalytic reactions. To overcame these drawbacks and, therefore, to improve the catalytic performance, the POM anions need to dispersed in a high-surface-area nanoporous support. The feature of a mesoporous POM-based framework can incorporate new functionalities, such as high catalytic activity and recyclability. Nanoporous POM-based materials will provide a cost-effective, regenerable catalytic system for environmental remediation processes, including decomposition of pollutant gases, and fine chemical synthesis (e.g. oxidation of hydrocarbon).

The overall objectives of the MESOPOMs project are the synthesis of POM and transmission metal-substituted POM clusters and the design and development of new nanostructured mesoporous POM-based frameworks with well-ordered pore structure and high internal surface area. The evaluation of catalytic activity of these mesostructures in heterogeneous catalysis as “green” method for organic synthesis is also another goal of this project.

During the project life (Sep 1, 2008-Aug 31, 2012) significant progress has been made in synthesis and catalytic applications of mesoporous POM-containing materials. In particular, in the first stage we have studied the chemistry of POM clusters in aqueous and alcoholic solutions. Several POM and TM-POM compounds with different molecular and electronic structure have been synthesized, including $[P(W,Mo)_{12}O_{40}]^{-3}$, $[EMo_6O_{24}H_6]^{4-}$ ($E=Ni^{+2},Co^{+2},Cu^{+2},Zn^{+2}$), $[EMo_6O_{24}H_6]^{-3}$ ($E=Co^{+3},Cr^{+3},Fe^{+3},Co^{+3}$) and $[PMo_{12-n}V_nO_{40}]^{-(n+3)}$ (n=1-4) anions. These POMs were found to be excellent building blocks for the construction of novel mesoporous POM-based catalysts. We employed different soft- or hard-templated ‘nanocasting’ self-assembly approaches to prepare these composite structures and, so far, we achieved in preparing well-ordered mesoporous metal oxide-POM composite frameworks with different architecture of pore structure (pore geometry and pore size) and chemical composition (Al_2O_3, ZrO_2, Co_3O_4, Cr_2O_3), see fig. 1a and 1b.

Significant amount of work has been made on characterization of these materials, including chemical composition, nanoporosity and electronic structure determination. We used a multitude in solution and solid-state techniques provided by the host institution (University of Crete) or through collaborations with other multidisciplinary laboratories. For example, detailed characterization of the prepared materials was accomplished by various state-of-the-art techniques and instrumentation such as small angle X-ray scattering, X-ray diffraction, imaging techniques (TEM, SEM/EDS) X-ray photoelectron spectroscopy, X-ray diffuse scattering (synchrotron radiation), TGA/DSC/DTA, IR and UV/vis spectroscopy and N_2 physisorption.

Substantial progress has been made on catalytic application of prepared materials. As we shown this new class of mesoporous materials have a great implication in various fields of catalysis, including direct

decomposition of nitrous oxide (N_2O) and isopropanol as well as selective epoxidation/oxidation of alkenes and alcohols, showing excellent catalytic activity and stability (see fig. 1c).

The interdisciplinary nature of the project enables the fellow to conduct a number of collaborations with faculty members within the host institution and beyond. So far, results of MESOPOMs research were disseminated through publications in seven high-impact peer refereed journals (at least two further papers are planned for the high-impact journals), including *Chem. Mater.*, *J. Mater. Chem.*, *RSC Adv.* and *Chem. Commun.*, as well as two national and two international conferences. Participating in this project, the fellow was claimed and gained additional funding from other research grants, including the Greek Ministry of Education (ΓΓΕΤ) and Special Account for Research – University of Crete. The main objectives of these projects are highly related to the subjects of MESOPOMs and can enhance or add value to the scientific contribution of this program.

Overall, the MESOPOMs project considerably advanced our knowledge of POM-containing composite materials and has made a significant scientific progress in field of mesoporous composite catalysts.

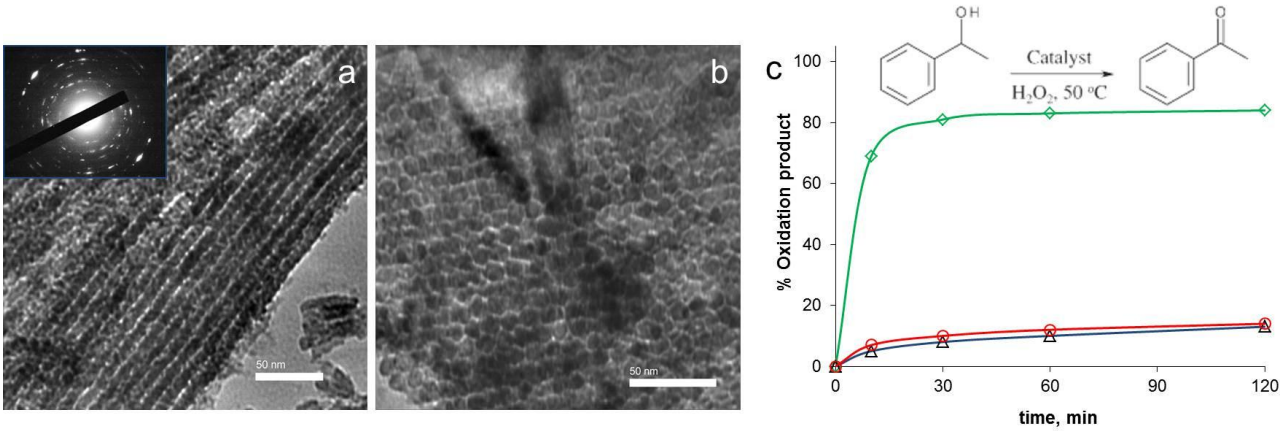

Figure 1. (a and b) Typical TEM images of mesoporous Cr_2O_3 containing on its wall ~38% $H_3PW_{12}O_{40}$ (CrPWA(38)) recorded along the [110] (a) and [001] (b) zone axis. Insets in (a) is the corresponding selected area electron diffraction (SAED) pattern. (c) Time profiles of 1-phenylethanol oxidation over mesoporous Cr_2O_3 (blue) and CrPWA(38) (green) materials and $H_3PW_{12}O_{40}$ compound (red line) (*J. Mater. Chem.* **22**, 6919, 2012).