

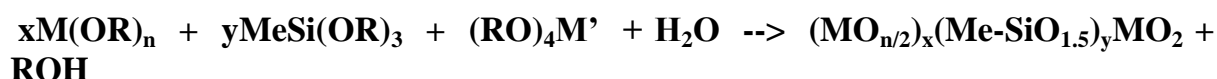
CATALYTIC SYSTEMS FOR HYDROCARBON OXIDATION AND NEW MONOMER PRODUCTION

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ABSTRACT

The increasing economical and ecological demands on chemical processes lead to a growing need for more selective processes. Since 90 % of chemical processes involve a heterogeneous catalyst, research concentrates on more selective heterogeneous catalysts. The area of most promising applications is presently selective oxidation of hydrocarbons, where emphasis is put on the development of selective catalysts capable of using air or H₂O₂ as oxidant. The most challenging target molecules are here new monomer production processes for polymer chemistry. Selectivity based on hindered diffusion of molecules of different polarity or size in micropores, the so called shape selectivity, is the key to the success of zeolites [1]. However, fundamental limitations with respect to chemical composition and pore architecture restrict general applications of these catalysts. Amorphous microporous mixed oxides (AMM) are promising new materials, whose catalytic properties can be controlled during a one-step preparation procedure of the sol-gel-type. By acid catalysed co-polycondensation of an alkoxide of Si, Zr, Al or Ti with a soluble derivative of a catalytically active element, such as Mn, Mo, V, Ti, Sn, In, Cu, Fe, Cr, atomically distributed active centres in the oxide matrix can be obtained. In the absence of any template, the reaction conditions followed by drying and calzining provides a highly porous mixed oxide with a narrow pore size distribution around 0.6-0.9 nm. The surface polarity of such an oxide can be controlled by the addition of alkoxides containing a nonhydrolyzable alkylgroup, such a methyltriethoxysilane, to the copolycondensation reaction. The basic reaction for silica based AMM-materials is shown below:



catalytic *polarity* *microporous* *Amorphous Microporous*
Mixed

centers *modifier* *matrix (M'=Si, Ti, Zr)* *oxide*
(AMM)

The materials are denoted as AMM-M_xM', where M' stands for the base oxide and x for the atom% of the additional oxide M. After proper calzination, these materials remain amorphous and have a porosity of 10-35%. AMM catalysts have shown promising activity and selectivity for the selective oxidation of hydrocarbons to lead to products such as acrolein, phenol, styrene, 1,5-hexadiene, benzaldehyde, epoxides, and others. Concepts and results are reviewed.

Another approach to improve the selectivity of heterogeneously catalysed reactions is the combination of catalytic activity with the permselectivity of inorganic membranes used in membrane reactors. Despite intensive efforts over the past few years, convincing demonstrations of such effects have been rare. Thin film membranes prepared from our

AMM-catalysts have been used successfully in hydrogenation reactions, where poisoning effects could be prevented and high hydrogenation selectivities have been observed. The concept of the suppression of secondary reactions by microporous catalyst membranes is introduced. Membrane preparation, characterisation and reactions in comparison to appropriate control experiments are presented.

The need for new materials and catalysts has never been satisfied by conventional methods. Combinatorial chemistry applied to the discovery of new materials and catalysts must and will provide many new lead structures, which has already been demonstrated by pioneers in the field. The concept of combinatorial chemistry for the search of new materials will be introduced. The reliable synthesis of combinatorial libraries, the efficient identification of desired properties, the efficient detailed characterisation of the materials followed by the synthesis of identified new library materials on the laboratory scale are among the most important targets of present research in the field. The potential strength of combinatorial chemistry is the discovery of new catalysts for selected applications, such as selective oxidation. We have been engaged in the development of new catalysts by combinatorial approaches. The development of emissivity corrected IR-thermography provides a powerful and reliable tool for the recording of reaction energies on libraries based on microscopic amounts of materials (50-100 μg). Library preparation by hydrothermal synthesis as well as by sol-gel-processes has been up-scaled from 40 component libraries to libraries containing 750 materials. Here robotics had to overcome several hurdles. Direct library characterisation by automated microdiffraction and X-ray fluorescence allow the reliable identification of the materials prepared. In-situ IR-thermography allows identifying with excellent spatial resolution the temperature dependent catalytic activity of the materials.