

# Amorphous Microporous Mixed Oxides, New Selective Catalysts with Chemo- and Shape-Selective Properties

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The increasing economical and ecological demands on chemical processes have led to a growing need for more selective heterogeneous catalysts. Selectivity based on hindered diffusion of molecules of different polarity or size in micropores, the so called shape selectivity, is 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 catalyzed copolycondensation 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 centers 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-8materials is shown below:



<i>catalytic centers</i>	<i>polarity modifier</i>	<i>microporous matrix</i>	<i>Amorphous Microporous Mixed oxide (AMM)</i>
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The materials are denoted as AMM-M<sub>x</sub>M', 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%. A typical pore size distribution and a high resolution TEM-micrograph (AMM-Ti<sub>3</sub>Si = 3 % titania in 97 % silica) are shown in Figure 1.

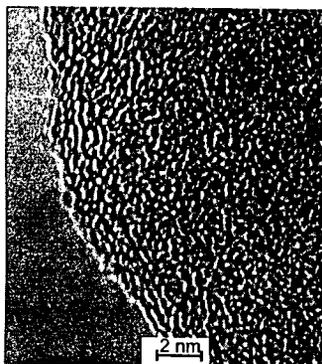
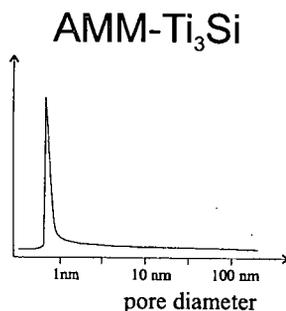


Fig. 1: Pore size distribution (Horvat-Kawazoe-method) and TEM-micrograph of a typical AMM-catalyst.

Rheological studies show a simultaneous increase in elasticity and viscosity under these sol-gel conditions indicative of a linear chain growth in the polycondensation process [2]. The porosity of these amorphous materials has been shown to be stable up to 800 °C. Diffuse reflectance IR, XANES [3] and diffuse reflectance UV [4] provide evidence for homogeneity and atomic isolation of the Ti-centers in AMM-Ti<sub>x</sub>Si at Ti-concentrations < 5%. PFG-NMR studies on hydrophobic and hydrophilic AMM-Si-materials with small molecules show diffusion rates comparable to those observed in Y-zeolites. It was found, that the diffusion of unpolar molecules like hydrocarbons is not affected by the surface polarity, while the diffusion of polar molecules like water and butanol is strongly hindered in hydrophilic AMM-Si, while both molecules are not observable in the hydrophobic AMM-M<sup>n</sup>Si<sub>x</sub>Si [5].

In general, AMM-materials can be described as catalysts prepared to contain isolated catalytically active centers in the shape selective environment of micropores. The lack of inherent limitations with respect to chemical composition and pore size makes AMM-materials versatile catalyst for many uses. AMM-materials have already shown promising properties as selective heterogeneous catalysts in a variety of applications:

**Hydrocracking:** Decane hydrocracking is an established test reaction for the precise assignment of pore structure and pore architecture of zeolites [6]. After impregnation with 0.5 % Pt, AMM-Ti<sub>3</sub>Si, AMM-Ti<sub>17</sub>Si and AMM-V<sub>10</sub>Si have been exposed to the decane hydrocracking test under standard pore conditions. The product distribution positioned the Ti-containing AMMs in the range of large pore zeolites, while the AMM-V<sub>10</sub>Si is positioned in the zeolite free range between the medium-pore 10-ring zeolites and the large pore 12-ring zeolites. The test furthermore identifies the AMM-materials as having a tubular pore system lacking larger cavities and pore intersections [7]. These results showed for the first time shape selective properties of amorphous materials. Therefore shape selective properties are not associated with crystallinity, but only with a small pore size and a narrow pores size distribution.

**Redox-catalysis with organic hydroperoxides:** With TBHP as oxidizing agent AMM-Ti<sub>3</sub>Si catalyzes the selective epoxidation of alkenes. With linear and cyclic olefins, the rate of epoxidation decreases rapidly with increasing number of carbon atoms [7]. A similar decrease in the rate of epoxidation of alkenes with TS-1 has been ascribed to molecular shape selectivity [8]. AMM-V<sub>x</sub>Si and AMM-Ti<sub>x</sub>Si can selectively oxidize olefins and saturated hydrocarbons [9]. Like other crystalline and amorphous Ti-silicates the catalysts are deactivated during epoxidation reactions by product inhibition, caused by pore- or surface blocking with the alcohol formed from the hydroperoxide. The catalysts are not active with hydrogen peroxide as oxidant.

**Redox-catalysis with hydrogen peroxide:** Due to unconnected surface coordination sites highly porous oxides are rich in surface hydroxyl groups and thus highly hydrophilic. By copolycondensation of increasing amounts of Me-Si(OEt)<sub>3</sub> with Si(OEt)<sub>4</sub> and 1% (iPrO)<sub>4</sub>Ti a series of AMM-materials with increasing hydrophobicity was prepared. The most hydrophobic materials (AMM-Ti<sub>1</sub><sup>M</sup>Si<sub>45</sub>Si) show several interesting properties. The catalysts do not deactivate during epoxidation reactions and they can be reused. They can be used with hydrogen peroxide as oxidant. In fact, with H<sub>2</sub>O<sub>2</sub> these hydrophobic amorphous microporous Ti-Si-oxides show comparable activities as Ti-containing zeolites for a wide range of selective oxidation reactions, such as ammoxidation, oxidation of alcohols, and oxidations of saturated hydrocarbons [11].

**Acid catalyzed etherification and esterification reactions:** Solid acid catalysts are of increasing importance as potential replacement of homogeneous acid catalysts in the production of fine and bulk chemicals. AMM-Sn<sub>2</sub>Si with low Sn-content have been found to be very active and selective mild acid catalysts. The catalysts are Lewis-acidic, no evidence for Brønsted acidity was obtained by IR-studies. The catalysts showed excellent catalytic activities for esterification reactions of pentaerythritol with stearic acid and for the formation of t-butylethers [12].

**Oxidative dimerization of propene with air:** Oxidative coupling of propene with air in the gas phase under selective formation of 1,5-hexadiene has been reported with diene selectivities peaking at 60 % at propene conversions far below 10 %. With AMM-In<sub>3</sub>Si at 560 °C under continuous gas phase flow conditions propene (23 % conversion) is selectively converted with air to 1,5-hexadiene (selectivity 84 %). The unusual selectivity is attributed to the presence of isolated In-centers (confirmed by EXAFS-studies) in the shape selective environment of the

micropores [13]. With AMM-Cu<sub>6</sub>Si at 370 °C acrolein is formed with a remarkable selectivity of 93 % at a propene conversion of 10 % [14].

**Selective Oxidation of toluene to benzaldehyde with air:** In a gas phase flow reaction at continuous reaction conditions AMM-Mn<sub>3</sub>Si selectively oxidizes toluene to benzaldehyde with air (normal pressure, 450 °C, toluene conversion 5 %, selectivity 83 %). EXAFS investigations identify the Mn as isolated centers of oxidation state II [15].

**Selective aromatic alkylation:** The isopropylation of naphthalene and biphenyl have been investigated with various AMM-catalysts. The AMM-Al<sub>3</sub>Si materials show the most promising activity. After deactivation of external acid sites, AMM-Al<sub>3</sub>Si exhibits highly selective alkylation behaviour. In the gas phase at continuous flow conditions at 250 °C 4,4'-diisopropylbiphenyl is formed directly from biphenyl with a selectivity of 61 % at a biphenyl conversion of over 7 %. At identical reaction conditions a H-Mordenite reaches 73 % selectivity. Isopropylation of naphthalene at unoptimized conditions at a conversion of 46 % produces only mono and diisopropynaphthalene (ratio 2:1), the latter consists to 44.5 % of the 2,7- and to 50 % of the 2,6-isomer. This shows that AMM-catalysts can be modified to become selective dialkylation catalysts comparable to the best zeolites [16].

**Microporous catalyst membranes:** Another promising area is the application of catalytic membranes as a means to improve the selectivity of heterogeneously catalyzed reactions. The combination of permselectivity with catalysis opens a new field of reaction engineering and reactor design [17]. Due to the preparation process, which passes through a sol, thin AMM-catalyst films can be prepared by dip-coating [18]. With the use of proper support membranes, thin catalyst membranes have been prepared, characterized and applied in various heterogeneously catalyzed reactions. Poison resistant catalysis has been achieved in the hydrogenation of fatty esters by dosing the hydrogen through a microporous AMM-Pt<sub>3</sub>Ti membrane catalyst. Addition of well known poison molecules like tetrahydroacridine or quinoline in equimolar amounts have no effect on the rate of hydrogenation, since the poison molecules are too large to penetrate the micropores of the membrane containing the catalytically active sites [19]. A higher turnover frequency (TOF) in the membrane relative to the batch reactor was noted. In a more detailed study of the rate of hydrogenation of 1-octene in the batch reactor relative to the membrane reactor, this higher TOF could be confirmed. It was shown, that comparable TOFs in the membrane reactor and in the batch reactor are obtained, when the hydrogen is dosed through the liquid sitting on top of the catalyst membrane, while the TOF increases by a factor of 10 when hydrogen is dosed through the catalyst membrane to the alkene containing solution. By competition experiments it is shown, that the normally occurring competitive adsorption of alkene and hydrogen on the Pt-sites does not seem to occur, when hydrogen is dosed through the membrane [20]. In another investigation a new way to prevent secondary reactions has been demonstrated. The basic scheme is to pass a solution of two reactants through a catalytically active microporous membrane. When the pores are so narrow, that molecular passing of reactants is hindered or inhibited during the diffusion through the pores (single file diffusion), secondary reactions cannot take place as long as the concentration of the limiting reactant does not allow a second reaction to occur. The action of the micropores is to provide a defined reaction zone and to completely prevent backmixing of the products formed with the reactants. With AMM-Pt<sub>3</sub>Ti-membranes at proper reaction conditions 1,3-hexadiene can be hydrogenated selectively to monoenes at conversions of up to 40 %. At 20 % conversion 2-hexyne is selectively hydrogenated to cis-2-hexene. In both reactions no n-hexane formation is detectable. However, when the hydrogen pressure is increased (increases the hydrogen concentration in the solution and the pores) n-hexane formation occurs. The same AMM-Pt<sub>3</sub>Ti-catalysts is completely unselective in the batch reactor at identical reaction conditions [21]. The prevention of back-mixing by microporous catalyst membranes is a new means to avoid secondary reactions.

Clearly, amorphous microporous mixed oxides are a promising class of selective heterogeneous catalysts, ready and waiting for technical applications.

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