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Amorphous microporous mixed oxides as selective redox catalysts

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Amorphous microporous homogeneously mixed oxides based on Ti or V in silica can be prepared by an acid catalyzed sol–gel process. The materials have been characterized by TEM, UV, IR and sorption methods. The glasses can be used for the selective epoxidation of alkenes. The catalytic properties are comparable to those of the well known crystalline Ti-containing zeolites TS-1, Ti-MCM-41 and Ti-Beta. Amorphous microporous homogeneously mixed metal oxides seem to be promising new catalytic materials supplementing the well studied selective zeolites.

Keywords: amorphous mixed oxides; microporous oxides; silica; titania; vanadia; selective oxidation; TBHP; epoxidation; heterogeneous catalysis; titania silicate; redox catalysis

Microporous crystalline solids [1] and more specifically Ti-silicalites [2–4] in which transition metals are tetrahedrally-substituted via template-mediated hydrothermal synthesis have remarkable properties in selective oxidation reactions with peroxides as oxidant. Their success as catalysts in new chemical technologies [3] originates from the confinement of the active sites within identical, crystallographically defined microcavities [5]. Unfortunately, this restricted access of organic molecules and oxidantia to the intracrystalline voids and the steric crowding around the active site [6] considerably limits their general applicability. Furthermore, the rigidity of the frameworks narrows the substitution degree that can be reached with Ti [7] and the substitution potential for other catalytically interesting elements such as V, Mo and others.

Although V-substitution in microporous crystalline silicates and aluminophosphates has been claimed [8], severe V-leaching into solution has been reported [9]. Microporous crystalline Ti-silicates with larger pores obtained via the template-mediated hydrothermal synthesis method, invariably showed residual Brønsted acidity [10] and consequently very reduced yields on peroxide basis or in case of octahedral coordination [11] catalytic inertness. Ti-silicates obtained in sol–gel conditions by self-organisation around micelles [12,13] show regular mesopores and a good potential as oxidation catalysts for a wide range of substrate sizes [13]. We succeeded in the synthesis of amorphous mixed oxides with uniform microporosity and wide compositional variability, devoid of Brønsted acidity not associated with the redox-active element. The materials are synthesized by sol–gel processing in the presence of only stoichiometric amounts of water (hydrolysis ratio of 2 [14]) but in absence of any organic templating agent, thus representing major technical advantages over crystallization of substituted molecular sieves. The Ti-substituted materials show good properties as partial oxidation catalysts. The V-substituted materials retain all V and are truly heterogeneous catalysts.

It was shown recently [15] that the synthesis of amorphous microporous silica, alumina, zirconia and titania with narrow pore size distribution requires specific sol–gel processing. We show now that the synthesis of amorphous mixed metal oxide microporous solids is possible when acid catalyzed hydrolysis and condensation of metal alkoxides precursors is slow as a result of the low hydrolysis ratios (water to metal ratio) used, prompting a linear chain growth mechanism to occur. This mechanism, well-known in sol–gel chemistry [16], gives exclusively linear mixed metal oxide chains. During carefully controlled drying and calcination steps, the expulsion of organics is believed to control the porosity of the products.

Thus amorphous microporous titanosilicates were prepared by acid catalyzed copolycondensation of tetraethylorthosilicate [$(EtO)_4Si$] with tetraisopropyltitanate [$(i\text{PrO})_4Ti$]. Typically, to $(46.3 - x)$ mmol of $(EtO)_4Si$, x mmol of $(i\text{PrO})_4Ti$ and 140 mmol of ethanol are mixed in the same order, 2 ml of 8 N HCl are added dropwise with stirring. Hydrolysis, condensation and gelling is conducted at room temperature. After 3 days, the gels are dried by heating to 338 K at a heating rate of 0.1 K/min in dry air at ambient pressure, kept at this temperature for 5 h and then heated at the same rate to the final calcination temperature of 523 K.

The samples will be further denoted as AMM-X_nSi where AMM stands for amorphous microporous metal

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oxide, Si for silica as a base oxide and n for the atom% of the additional oxide X. The porosity of the calcined materials was characterized by nitrogen and argon physisorption. A typical nitrogen adsorption–desorption isotherm for a Ti-rich sample is shown in fig. 1 and compared with that of reference materials. All AMM-Ti$_n$Si (n ranging from 1 to 30) are characterized by a type I isotherm, indicative of microporosity and do not show hysteresis upon desorption. The micropore volume ranges from 0.13 to 0.16 ml/g (depending on x), which is comparable to that of TS-1 (0.16 ml/g). The pore size distribution determined with the Horvath–Kawazoe method [17] is monomodal and narrow (fig. 1), typical for zeolites. The effective pore sizes range from 0.65 to 0.77 nm (depending on x), which is the range of pore diameters of the large pore 12-ring zeolites. Amorphous mesoporous titanosilicates (Ti-MCM-41) [12,13] obtained by self-organisation around an arrangement of micelles in sol–gel conditions and amorphous microporous mixed Ti–Si oxides prepared using a high hydrolysis ratio in absence of catalyst [18] have a different porosity (fig. 1). Mesopores are responsible for capillary condensation and the presence of an hysteresis loop in the nitrogen adsorption–desorption isotherms; micropores and/or monolayer formation on the large internal surfaces are responsible for the strong nitrogen adsorption at low relative pressures.

The amorphous character of the AMM-X$_n$Si materials was verified with X-ray diffraction, high resolution transmission electron microscopy (HR-TEM) and electron diffraction (fig. 2). X-ray analysis of selected areas of various sizes (from 1 μm to 2 nm) showed the materials to have a homogeneous mixed oxide composition, and domain formation to be absent.

The IR transmission spectra of adsorbed pyridine show comparable intensities for AMM-X$_n$Si (X being Ti or V) and TS-1, pointing to a low density of residual Brønsted acid sites. With increasing Ti (or V) content the Brønsted acidity (pyridinium ion vibrations at 1540 cm^{-1}) seems to increase. Similar variations of acidity with titanium content were observed in other amorphous titanosilicates [18], and attributed to octahedral Ti-atoms linked to silicate tetrahedra, the hydroxyl ligands of which have Brønsted acidic properties.

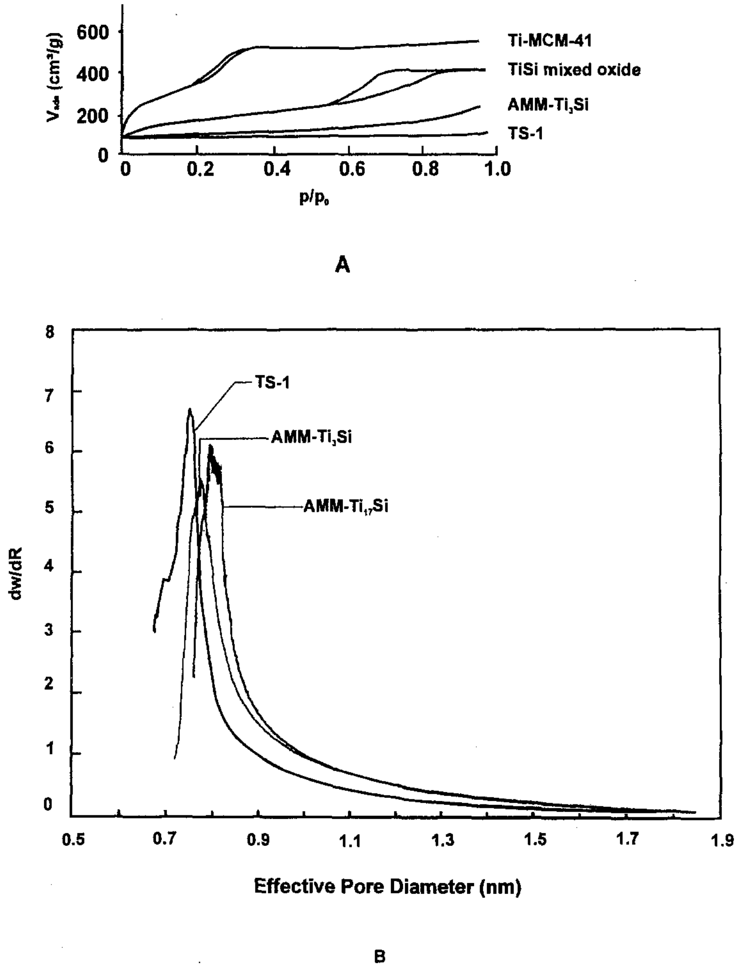

Fig. 1. (A) Nitrogen adsorption–desorption isotherms at 77 K on AMM-Ti$_3$Si and reference titanosilicates (Ti-MCM-41, from ref. [12b]; Ti–Si mixed oxide from ref. [18]). (B) Micropore size distribution in AMM-Ti$_3$Si, AMM-Ti$_{17}$Si and TS-1, determined with argon adsorption at 77 K using the Horvath–Kawazoe [17] method (adapted to a cylindrical pore model and argon–oxygen interaction).

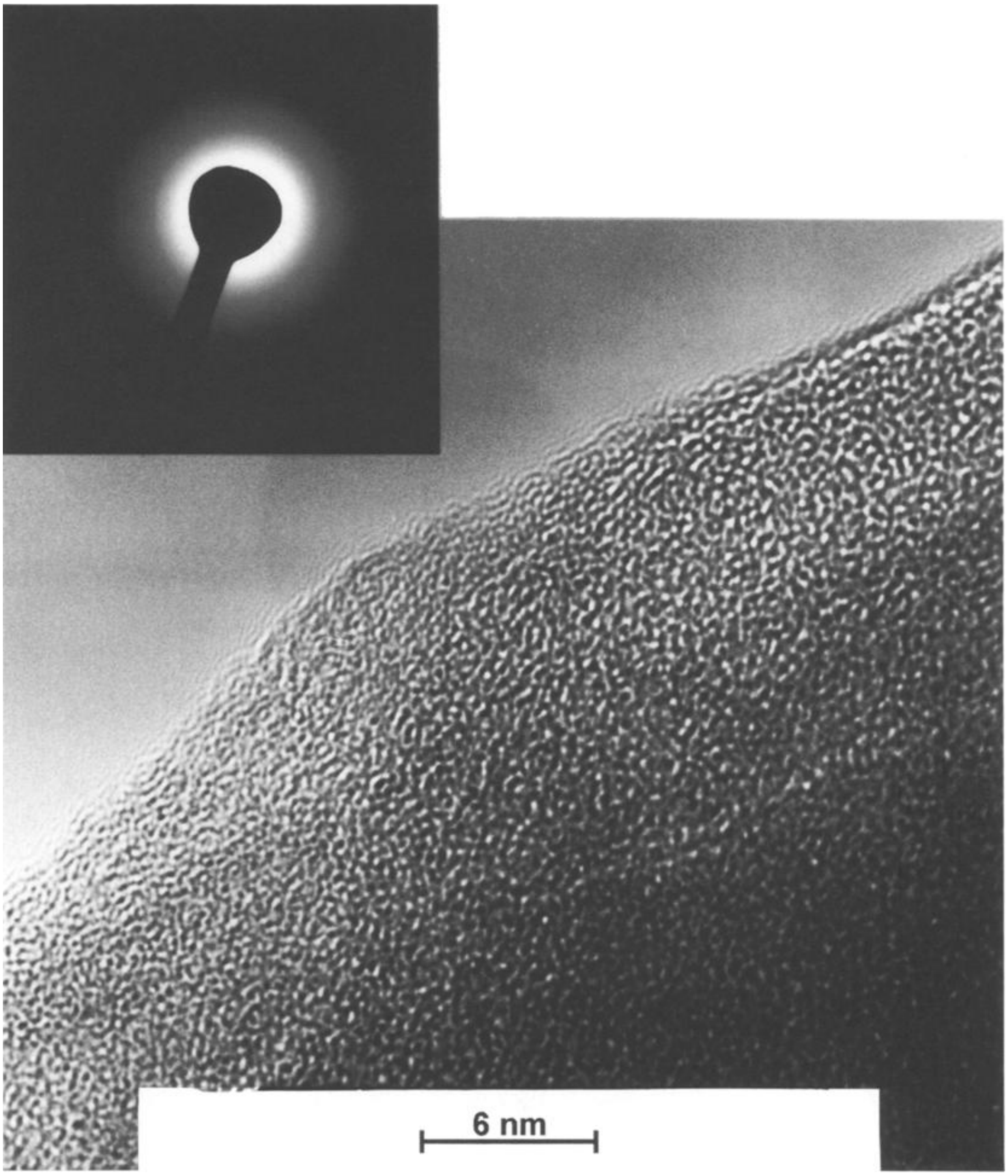

Fig. 2. Representative TEM micrograph at high resolution of AMM-$Ti_{17}Si$ (magnification 1500 k), the insert shows the electron diffraction obtained at magnification 200 k and a camera length of 0.2 m. (NB: figure reduced to 80% of its original size.)

The IR spectra of all AMM-Ti_nSi materials show a lattice vibration around 960 cm^{-1}, which is always present in Ti-silicalites and has been assigned after extensive discussion to tetrahedral titanium atoms substituted into silicate frameworks [1]. Other assignments of this band have also been discussed, such as Si–O defect sites, possibly promoted by Ti in Ti-containing materials, or silanol groups present even in Ti-free materials. In order to avoid spectrum misinterpretations by the latter, the FTIR spectra have been recorded under inert conditions providing SiOH-free surfaces. As a consequence, the intensity of the 960 cm^{-1} band in titanium-containing AMM materials correlates with the titanium content, while pure AMM-Si shows no adsorption in that spectral region. These results are consistent with comparable IR investigations recently published on mesoporous titania–silica mixed oxides, prepared with large efforts, such as titanium-alkoxide chelation, to ensure homogeneous elemental distribution [19–21].

UV–VIS spectroscopy in the DRS mode allows one to probe in more detail the state of titanium in titanosilicates [22]. An optical transition at ca. 48 000 cm^{-1} is assigned to a charge transfer (CT) in tetracoordinated TiO_4. A monomodal shape of the UV-DRS spectra of titania-containing AMM materials as well as of zeolitic Ti–Si materials showing a single adsorption in the high wavenumber region is only observed under dry conditions, while under ambient conditions the isolated titanium tetrahedra are susceptible to water ligand insertions giving rise to an octahedral coordination and a bathochromic shift in the spectrum between 35 000 and 48 000 cm^{-1} [23]. Extra-framework titanium oxides occluded in TS-1 crystals are detected in the 28 000–35 000 cm^{-1} frequency range. The UV–Vis spectra of AMM-Ti$_n$Si materials are compared to literature reference spectra in fig. 3. The CT characteristics of titanium in AMM-Ti$_n$Si materials are comparable to those in crystalline titanosilicates [10,19]. The spectroscopic results clearly indicate the microstructural similarity between AMM-Ti$_n$Si and titanium-containing molecular sieves.

Crystalline microporous titanosilicates catalyze the oxygenation of alkanes to the corresponding alcohols and ketones [2,10,13]. The oxidation rate of cyclohexane with tertiary butylhydroperoxide (*t*BuOOH) on AMM-Ti$_1$Si was found to be comparable to that of samples of Ti-Beta [10] and Ti-MCM-41 [13], synthesized according to methods described by Corma et al. (fig. 4), in terms of Ti-efficiency as well as of long term stability.

Competitive oxygenation reactions of cyclohexane and perdeuterocyclohexane were performed in order to determine the kinetic isotope effect (KIE) and its temperature dependence (from 323 to 353 K). AMM-Ti$_9$Si, TS-1, Ti-Beta and Ti-MCM-41 all exhibit the same KIE (value of 11 at 353 K) and an identical temperature dependence (difference in activation energy of ca. 14 kJ mol^{-1}). Such values suggest that C–H bond activation is rate determining, that the hydrogen transfer complex (probably between a lattice high valent titanium species and the C–H bond of the alkane substrate) is linear and of electrophilic nature [24]. KIE's above 7 are regarded as indication of proton-tunnelling [25], which strengthens the impression, that the active Ti-centers in all materials are of the same nature.

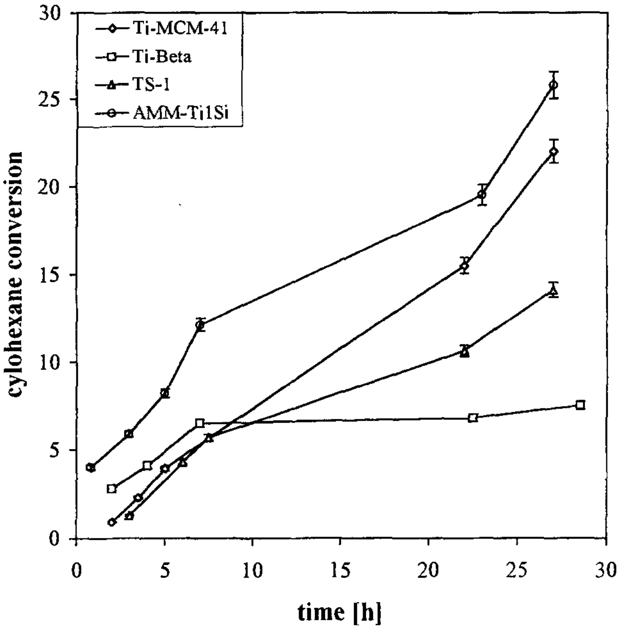

Fig. 4. Cyclohexane conversion with TBHP on different titanium containing oxides against time. (30 mmol cyclohexane, 26.6 mmol tert-butylhydroperoxide (TBHP, 80 wt% in di-tert-butylperoxide), 20 mg of catalyst, $T = 353$ K).

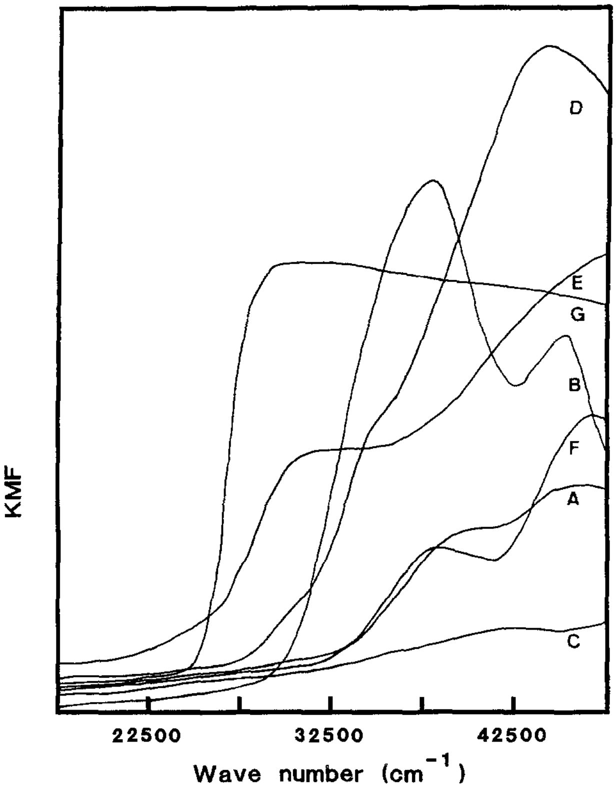

Fig. 3. DRS UV–Vis spectra of hydrated titanosilicates displaying the Kubelka–Munk function against wavenumber: (A) AMM-Ti$_3$Si; (B) AMM-Ti$_9$Si; (C) silicalite-1 (from ref. [22a]); (D) TS-1 (from ref. [22c]); (E) TS-1 with occluded titanium oxide micro-particles (from ref. [22a]); (F) Ti-Beta (from ref. [28]) and (G) anatase (from ref. [22a]).

The AMM-Ti$_n$Si materials are found to be excellent epoxidation catalysts (selectivity > 97%) for alkenes and cycloalkenes with various carbon numbers using *t*BuOOH as oxidizing agent (table 1). With the turnover frequency (TOF, molecules per Ti-site and second) as criterion compared to Ti-Beta, the Ti-atoms in the AMM-Ti$_3$Si are also much more efficiently used (table 1).

Although the experiments have been carried out at different temperatures and the data are derived from initial rates only, the size exclusion effects are clearly demonstrated. An appropriate comparison in terms of active site efficiency has already been demonstrated in fig. 4, underlining the good catalytic properties of the AMM materials when compared to the redox molecular sieves. The peroxide yield is close to quantitative. The activity per Ti-atom of the catalysts, however, decreases with increasing Ti-content (see TOF of the AMM-Ti$_{17}$Si in table 1). It is not clear whether this is due to

Table 1
Turnover frequencies of olefin epoxidations with tert-butylhydroperoxide (TBHP) on various Ti-silicates

Catalyst	Substrate	Reaction time (min)	TOF (mmol olefin/(mol Ti s))
AMM-Ti_4Si [a]	1-hexene	15	17.1
	1-octene	15	8.2
	1-octene	150	7.1
AMM-Ti_9Si	1-octene	150	0.9
AMM-$Ti_{17}Si$	1-octene	15	0.2
Ti-Beta [b]	1-hexene	300	4.0
	1-octene	300	2.1
AMM-$V_{10}Si$ [a]	1-octene	300	3.1

[a] Reaction conditions: 15.8 mmol olefin, 3 mmol TBHP (3m in *i*-octane), $T = 353$ K, catalyst: 50 mg.
[b] Data taken from ref. [10b]: 25.0 mmol olefin, 6.25 mmol TBHP, 10 g acetonitril, $T = 323$ K, catalyst: 300 mg.

increasing Ti–O–Ti presence or just a mass transport problem.

Another remarkable advantage of the AMM-type catalysts over the zeolitic mixed oxides is the substitution potential of these materials also with elements like Ti, V, Mo and others. For example, the AMM-$V_{10}Si$ material also shows a high epoxidation selectivity (> 97%). This result is reproducible with the regenerated catalyst (removed from the mother liquor by centrifugation and washed with acetone prior to a drying in air at 333 K) for a number of reaction cycles. The mother liquor obtained shows no catalytic activity. This has not been reported for V-silicates before. Oxovanadium ions tend to be good catalysts for allylic oxidation, while exchange resin and polymer immobilized vanadyl ions show high epoxidation activity with TBHP [26]. The activity of the V-containing material is with a TOF of 3.1 significantly better than the TOF of 0.2 found for the AMM-Ti_9Si, indicating that stable amorphous vanadium silicates may be alternative materials to the intensively studied Ti-containing catalysts. While the AMM-Ti_nSi materials show only poor activity with H_2O_2 in the presence of water, a significant activity in olefin epoxidation with AMM-V_nSi catalysts using aqueous hydrogen peroxide has been found, as already reported for other amorphous V–Si mixed oxides [27]. Hence, a TOF of 1.9 (mmol epoxide/(mol V s)) is reached in the reaction of 1-octene (1.9 mmol) with aqueous H_2O_2 (8.2 mmol) in tertiary butanol after one hour at 333 K (10 mg of catalyst).

The results presented here show that the AMM materials prepared according to our simple synthesis strategy reveal a high potential in selective oxidation when compared to zeolitic materials or other mixed metal oxides involving expensive or additional, time consuming preparation steps, such as hydrothermal conditions or chelation of the titanium precursors.

All this confirms that the site active for partial oxidation of organic substrates with peroxides found in crystalline microporous Ti-silicates can successfully be mimicked in the amorphous counterparts of the materials. The materials have characteristics that make them excellent substitutes for Ti-Beta and other large pore zeolites, which are more difficult to prepare. Compared to traditional zeolite synthesis, the sol–gel route avoids the use of organic templating agents, that have to be eliminated through calcination and does not require hydrothermal synthesis conditions. In contrast to zeolites, the sol–gel materials are available in a much broader composition range, but with similar pore sizes and porosities.

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