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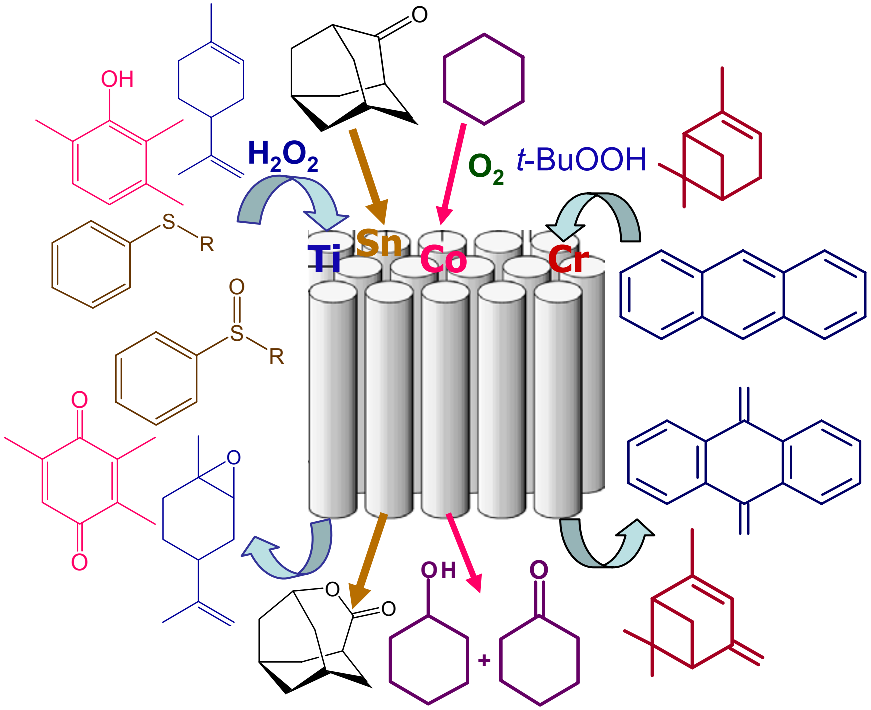
H$_2$O$_2$
Ti
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ARTICLE TYPE

Recent developments in liquid-phase selective oxidation using environmentally benign oxidants and mesoporous metal-silicates

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This *Perspective* article surveys recent advances in the synthesis of mesoporous transition-metal-containing silicate materials and their use for the liquid-phase selective oxidation of organic compounds (alkanes, alkenes, aromatics, S-compounds, etc.) with environmentally friendly oxidants – molecular oxygen, hydrogen peroxide and organic hydroperoxides. A selection of the most relevant results reported thus far in the literature is provided, with particular attention paid to the issues of the nature of catalysis, catalyst stability and reusability. Approaches elaborated in recent years to create hydrothermally stable mesoporous metal-silicates are considered, and the scope and limitations of such catalysts in liquid-phase oxidations are discussed.

Introduction

The selective catalytic oxidation of organic compounds with atomically efficient, cheap and readily available oxidants is the most economic and ecological route to a wide variety of valuable oxygen-containing products and intermediates of organic synthesis.[1–3] While the bulk chemicals industry widely exploits both homogeneous and heterogeneous catalysts, most fine chemicals manufactures still employ stoichiometric oxidations with hazardous reagents such as $K_2Cr_2O_7$, $KMnO_4$, $Pb(OAc)_4$, HNO_3 and others, thereby producing enormous quantities of waste.[1] Heterogeneous catalysis offers clear benefits of ease of catalyst separation and recycling and amenability to continuous processing and thus better meets the requirements of sustainable chemistry, which has become one of the greatest scientific challenges of our time.[3,4] The development of green and sustainable technologies based on the use of heterogeneous catalysts and atomically efficient and clean oxidants – O_2 and H_2O_2 – has become a widely accepted strategy of the modern chemical industry.[1–6] However, progress in this direction is obstructed by the limited number of efficient, leaching-tolerant solid catalysts suitable for operation in liquid phase.[5–8] The creation of highly active, selective, stable and recyclable heterogeneous catalysts would have a major impact in industrial applications as well as in fundamental research.

In recent years, a great scientific effort was made on the development of methods for the synthesis of mesoporous materials (according to the IUPAC definition, these are materials with pore diameters in the range of 20–500 Å).[9–13] The interest in such materials in the catalytic community was stimulated by their potential advantage in transformations of large molecules that meets the demands of the fine chemical industry[4–8,14] and production of fuel from biomass.[15] While microporous zeolites can serve as effective catalysts for reactions of small molecules, they suffer from mass transfer limitations when reactants with sizes comparable with the pore dimensions have to be employed.

Several approaches have been suggested for elaboration of mesoporous silica[†] materials containing catalytically active transition-metal ions as a part of the solid structure. Among them are the sol–gel technique that allows the preparation of mixed oxides (aerogels and xerogels) comprising catalytically active MO_n species dispersed at the molecular level within the main silicon oxide matrix,[16–18] various methods leading to hierarchical micro-mesoporous zeolite structures,[10,19] grafting transition-metal molecular precursors onto the surface of mesoporous silicas,[4,20–22] and finally, the surfactant-templating methodology that, since the discovery of the M41S family of molecular sieves by researchers at Mobil Oil Corporation in the early 1990s,[23] has been widely used for the preparation of ordered mesoporous metal-silicates. Various aspects of such materials including synthetic routes, formation mechanisms, surface modification, characterization, and applications have been covered by the extensive review literature.[9,11–14,16,17,19,21,22,24,25]

Following the critical target of creating a mesoporous analogue of the titanium-silicalite TS-1, the catalyst developed by the *Eni* group that had already found application in three industrial processes,[3,5] a great deal of research work was devoted to the synthesis of mesoporous titanium-silicates and assessment of their catalytic performances.[17–20,22,24,25] Significant progress has been also achieved in the incorporation of many other metals (M = Zr, Ce, V, Nb, Cr, Mo, W, Mn, Fe, Co, etc.) into mesoporous silica matrixes. In this *Perspective* we review the current state of the mesoporous metal-silicates research from the standpoint of their relevance to heterogeneous liquid-phase selective oxidation catalysis. Our aim was to give the most relevant examples of their application in the synthesis of oxygenated compounds, with a special focus on the critical issues of the catalyst stability and reusability, and the nature of catalysis.

General Synthetic Approaches

Based on the structural features of silica matrixes, all the diversity of mesoporous metal-silicates can be divided into two fundamentally different classes, namely, non-ordered materials and ordered ones.

Non-ordered mixed oxides

Conventional sol-gel synthesis. X-ray amorphous mixed oxides of silicon and transition metals are most often obtained by the conventional sol-gel technique.[16,17] The goodness of mixing (i.e., homogeneity throughout the bulk on a molecular scale) strongly affects catalytic properties of mixed oxides. Since reactivities of silicon and transition metal alkoxides in hydrolysis/condensation reactions differ significantly, special measures are required to suppress the formation of M–O–M bonds in the resulting alkogels and to avoid segregation of active metal into a metal-oxide phase. Strategies that allow the relative precursor reactivity to be adjusted include pre-hydrolysis of tetraethyl orthosilicate (TEOS), employment of a more reactive silicon precursor, viz., tetramethyl orthosilicate (TMOS), and/or addition of metal complexing agents such as peroxides, alkoxyalcohols, aminoalcohols, β-diketones, β-ketoesters, carboxylic and phosphonic acids.[16,17,26] However, even with these precautions, the upper limit for the amount of a foreign metal oxide that can be introduced with a good homogeneity into a silica matrix (without emergence of an MO_n phase) typically does not exceed 20 mol%.

Evaporative drying of alkogels leads to xerogels, whereas supercritical drying (SCD) enables the production of aerogels (Figure 1). Major advantages of aerogels are their mesoporosity and high specific surface area, which makes it possible to increase the number of active sites per gram of material and to use the internal surface without diffusion limitation. However, small particles and the low density of aerogels cause difficulties with their handling and separation from reaction mixtures. Low hydrothermal and mechanical stabilities are other drawbacks. By contrast, conventional xerogels suffer from diffusion limitations but are more resistant to crumbling and moisture.

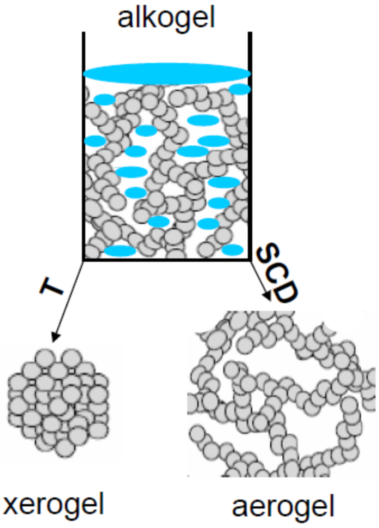

Fig. 1 Effect of alkogel drying method on the texture of mixed oxides and schematic representation of xerogel and aerogel.

Nonhydrolytic sol-gel synthesis. Various approaches have been suggested to create materials that would combine the benefits of both aerogels and xerogels but would not display their shortcomings. In particular, nonhydrolytic sol-gel synthesis[18] which is based on the etherolysis and condensation reactions (Eqs. 1 and 2; X = Si or M) offers a simple and efficient route to mesoporous xerogels with homogeneous distribution of metal.

$$\text{X–Cl} + \text{iPr}_2\text{O} \rightarrow \text{X–OiPr} + \text{iPrCl} \qquad (1)$$

$$\text{X–Cl} + \text{X–OiPr} \rightarrow \text{X–O–X} + \text{iPrCl} \qquad (2)$$

The high degree of condensation of nonhydrolytic gels prevents complete pore collapse during the evaporation of solvent, and xerogels containing 6–9 mol% of Ti exhibit pore volumes up to 2.5 $cm^3\ g^{-1}$, usually associated with aerogels.[18]

Thermolytic molecular precursor method. An advanced alternative to the sol-gel method is based on the use of single-source molecular precursors that possess a defined ratio of elements to be incorporated into the target material and provide a low-temperature, kinetically controlled pathway to homogeneous, mixed-metal-oxide materials.[22] Upon heating the oxygen-rich molecular precursors eliminate isobutylene and water to give materials with well-defined stoichiometries, e.g.:

$$\text{M[OSi(O}^t\text{Bu)}_3]_4 \xrightarrow{\Delta} \text{MO}_2{\cdot}4\text{SiO}_2 + 12\ \text{CH}_2\text{=CMe}_2 + 6\ \text{H}_2\text{O}$$

The dimeric molecular precursor $[(^t\text{BuO})_2\text{Ti}\{\mu\text{-O}_2\text{Si[OSi(O}^t\text{Bu)}_3]_2\}]_2$ was synthesized by silanolysis of $\text{Ti(O}^t\text{Bu)}_4$ with $\text{(HO)}_2\text{Si[OSi(O}^t\text{Bu)}_3]_2$ and used for the preparation of titania–silica ($\text{TiO}_2{\cdot}3\text{SiO}_2$).[27] The solution phase thermolysis of $(^i\text{PrO})_2\text{Ta[OSi(O}^t\text{Bu)}_3]_3$ prepared *via* silanolysis of $\text{Ta(O}^i\text{Pr)}_5$ with $(^t\text{BuO})_3\text{SiOH}$ in nonpolar media afforded xerogel $\text{Ta}_2\text{O}_5{\cdot}6\text{SiO}_2$.[28].

Ordered metal-silicates

Ordered mesoporous silicas (also called mesostructured silicates) are synthesized using supramolecular assemblies of surfactants as templates for inorganic precursors.[9–13,23] Mesopores emerging after removal of templates by calcination or extraction have calibrated sizes in the nanometre range and form a system of channels (two examples are given in Figure 2). The surface areas of mesopores normally attain 600–1400 $m^2\ g^{-1}$, while pore volumes are in the range of 0.6–2.5 $cm^3\ g^{-1}$. The size and shape of the pore channels strongly depend on the size and nature of the surfactant as well as the synthesis conditions. The silica walls that separate the channels are amorphous. The peculiarity of such structures is reflected in the terms “mesophase” and “mesostructure” which imply existence of long-range ordering

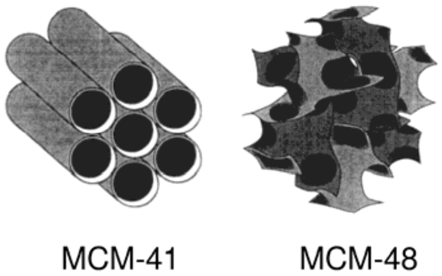

Fig. 2 Schematic representation of two mesostructured silicas.

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Table 1 Main types of mesostructured silicates.

Material	Medium	Template	Silica source	Structure	D, [a] nm	h_W, [b] nm	Key refs.
MCM-41	Basic	Alkyltrimethylammonium salts [c]	Sodium silicate	Hexagonal	2–4	1–1.2	23, 30
			Fumed silica				30
			Colloidal silica				31a
			TEOS, TMOS				30, 31b
MCM-48	Basic	Alkyltrimethylammonium salts	TEOS, TMOS	Cubic	2–4	1	23, 32
		Gemini surfactants [d]	Fumed silica				30
FSM-16	Basic	Alkyltrimethylammonium salts	Layered silicate ($NaHSi_2O_5$)	Hexagonal	2–3	1	43
KIT-1	Basic	Alkyltrimethylammonium salts + sodium salts of organic acids	Sodium silicate	Wormhole	3–4	1.1–1.3	42
HMS	Neutral	Primary amines C_8-C_{18}	TEOS	Wormhole	2–4	1.1–2.7	33
MSU-X	Neutral	Poly(ethylene oxides) [e]	TEOS, TMOS	Wormhole	2–6	1–2.5	34a
MSU-H		$EO_{20}PO_{70}EO_{20}$	Sodium silicate	Hexagonal	8–11		34b
MSU-G		Neutral gemini surfactants [f]	TEOS	Vesicle-like	2.7–4	2–3	35
TUD-1	Neutral	$(HOCH_2CH_2)_3N$	TEOS	Foam-like	2.5–25		39
COK-12	Near neutr. [g]	$EO_{20}PO_{70}EO_{20}$	Sodium silicate	Hexagonal	4.5–6.5	4–5	40
MMM-2	Weak acidic [h]	Alkyltrimethylammonium salts	Sodium silicate	Hexagonal	3–4	1–1.2	41
SBA-1	Acidic	Alkyltrimethylammonium salts Gemini surfactants	TEOS	Hexagonal	2–4	1–1.3	36
SBA-3	Acidic	Alkyltrimethylammonium salts	TEOS	Hexagonal	2–4	1–1.3	36
SBA-15	Acidic	Triblok copolymers	TEOS, TMOS	Hexagonal	4–12	3–6	37
		$EO_nPO_mEO_p$ [i]	Sodium silicate				30, 37c
SBA-16	Acidic	$C_{12}H_{25}EO_{23}$ or $EO_{106}PO_{70}EO_{106}$	TEOS	Cubic	4.5–6.5		30, 37b
			Sodium silicate				37c
MCF	Acidic	$EO_{20}PO_{70}EO_{20}$ + swelling agent [j]	TEOS	Cellular foam-like	10–15 [k]		30, 38

[a] Mesopore diameter; [b] silica wall thickness; [c] $(C_nH_{2n+1}(CH_3)_3NX$, where X = Cl, Br, OH/Cl and n = 8–18; [d] $[C_mH_{2m+1}(CH_3)_2N–C_sH_{2s}–N(CH_3)_2C_nH_{2n+1}]_2Br$, where m and n = 16–18 and s = 2–12; [e] $C_nH_{2n+1}EO_m$, n = 11–18, m = 9–25; [f] $C_nH_{2n+1}NH(CH_2)_2NH_2$, n = 10–14; [g] citric acid – citrate buffer pH 5–6.5; [h] two-step synthesis, pH 2.5–4 at the second step; [i] $0 < n < 100$, $5 < m < 150$, $0 \le p < 100$; [j] mesitylene (1,3,5-trimethylbenzene) most commonly used; [k] cage entrances (BJH, desorption branch), size of cages (adsorption branch) is 20–30 nm..

and lack of short-range ordering (at the atomic level). Accordingly, each type of mesostructure reveals a specific XRD pattern in the range of low angles and no high angle distinctive peaks. These structural features distinguish mesostructured materials from zeolites, crystalline materials that possess both types of ordering. Therefore, mesostructured materials occupy an intermediate position between zeolites and amorphous mixed oxides.

The type of interaction between inorganic component and surfactant depends on both the nature of template and synthesis conditions (first of all, pH) and is a crucial factor that governs the formation of a specific mesostructure.[9–13,23,29–43] Verified receipts for the synthesis of selected relevant materials of the MCM, SBA, MSU and other families have been surveyed in the review paper of Meynen *et al.*[30] and the book recently published by Zhao and co-workers.[13] For each material, a basic set of characteristics (N_2 sorption, XRD, TEM, SEM, NMR, etc.) and alternative synthesis setups were provided.

In Table 1, we present the main types of mesostructured silicates which have been mentioned in the literature in relation with liquid-phase oxidation catalysis. Since the use of expensive organosilicas limits synthesis of mesostructured materials on a large, industrial scale, procedures based on less expensive and more available inorganic precursors such as water-soluble sodium silicates,[23,30,34b,37c,40–42] colloidal and fumed silicas,[30,31a] and layered silicates[43] have been developed. The state-of-the-art in the synthesis and characterization of transition-metal-containing mesoporous silicates has been recently reviewed,[25] and below we just give some important notes.

Incorporation of a foreign metal into silica framework requires interaction of a metal precursor with Si–OH groups in the synthesis gel. The incorporation level strongly depends on the nature of the metal source and synthesis route.[24,25] Basic and neutral conditions usually facilitate the incorporation process through partial hydrolysis of the metal precursor and its condensation with silanols, although precautions are required to suppress the formation of M–O–M bonds and segregation of a metal-oxide phase.[31a,33a,44] On the contrary, strongly acidic medium disfavours metal inclusion into silica framework.[31a,45] The reactivity of metal precursors can be tuned by adjusting pH of the synthesis[41a,46] and by using complexing agents.[45a,47] In some cases, template plays the role of ligand that regulates the metal hydrolysis rate.[39,47b] The isolated state of metal within a silica matrix can be realized when the Si/M molar ratio in the calcined material exceeds 30.[25] In general, inclusion of metal ions with radii close to that of Si^{IV} (e.g. Ti^{IV}) occurs more readily than incorporation of larger ions. Substitution of M^{IV} for Si^{IV} is more favourable than of metal ions for which compensation of excessive positive or negative charge is required. Inclusion of Cr^{VI}, Mo^{VI} and W^{VI} is additionally complicated by their polynuclear anionic nature preserved in a wide range of pH, and typically the level of incorporation is low for these metals.

Post-synthesis modification

Alternatively to the direct synthesis, transition metal species can be grafted onto the surface of prefabricated silica using various post-synthesis methodologies. Wet impregnation and chemical vapour deposition (CVD) are the most widely used techniques.[48] More sophisticated approaches employ tools of surface organometallic chemistry.[4,21,22,49–52] To avoid hydrolysis, polymerization and deactivation of the metal precursor, most of post-synthesis techniques operate under anhydrous inert conditions.

Grafting of a mononuclear metal precursor can result in the formation of monopodal ($\equiv$Si–O)–M–$(L)_n$, bipodal $(\equiv Si{-}O)_2$–M–$(L)_{n-1}$, or tripodal $(\equiv Si{-}O)_3$–M–$(L)_{n-2}$ species.[21,50] The podality depends not only on the surface density of silanols on the support, but also on the surface geometry and the nature of the metal precursor. Figure 3 gives examples of reactions (some of them can involve multiple steps) leading to the formation of tripodally bound Ti^{IV} species. After calcination, such species transform to tripodal $(\equiv Si{-}O)_3$–Ti–OH sites. Bulky organometallic precursors are employed to favour the formation of isolated metal sites.[49-52] However, di(oligo)merization of the metal species may occur at high metal loadings (typically > 0.25 atom/nm^2).

Mesostructured silicates are considered as feasible supports owing to their spatially ordered architecture with tunable pore sizes and narrow pore-size distributions. Their high surface areas and pore volumes may allow a higher accommodation capacity of metal precursors with respect to conventional silicas. However, commercial amorphous silicas are by far cheaper and more available, usually possess higher thermal and mechanical stabilities and often enable the preparation of catalysts with the catalytic performance comparable or even superior to that of ordered materials. Therefore, the choice of the silica support depends on the specific catalytic reaction and the intended objectives.

A characteristic feature of grafted metal-silicates is high accessibility of metal centers, which may result in a higher catalytic activity compared to metal-silicates prepared by direct synthesis. However, the higher exposure to reactants may also result in worse stability of the catalyst toward metal leaching (this problem will be discussed later).

Organic–inorganic hybrid materials

Considerable efforts were made to incorporate organic moieties within inorganic silica frameworks to tune the surface properties and the catalytic performance and stability. Synthetic approaches to hybrid organic–inorganic materials have been comprehensively reviewed in the literature.[13,53] Since the hydrophilic nature of mesoporous silicates is detrimental for selective oxidation of hydrocarbons, surface silylation can often improve the adsorption and catalytic properties.[48a,54] Alternatively, an organic functionality can be introduced during the direct sol-gel synthesis *via* co-condensation of TEOS (TMOS) and organotrialkoxy silanes, $RSi(OEt)_3$.[17c,55] The nonhydrolytic sol-gel route allows preparation of hybrid titania–silica xerogels using low cost precursors ($TiCl_4$, $SiCl_4$ and $MeSiCl_3$) and routine evaporative drying technique.[56]

Transition-metal-containing mesostructured organosilicas can be prepared by co-condensation of TEOS, $RSi(OEt)_3$ (R = methyl, vinyl, phenyl, etc.) and metal source in the presence of various surfactants.[57] Organic–inorganic hybrid materials having organic moieties as molecularly bridging ligands in the framework position referred to by the name periodic mesoporous organosilicas (PMO) are obtained from the hydrolysis and condensation of silsesquioxane precursors $(OR)_3Si{-}R_1{-}Si(OR)_3$ (R_1 = $-CH_2-$, $-(CH_2)_2-$, $-C_6H_5-$, etc.) using surfactants as templates.[53] Transition metals (Ti, Cr and Nb) have been successfully incorporated within the framework of such PMO materials.[58]

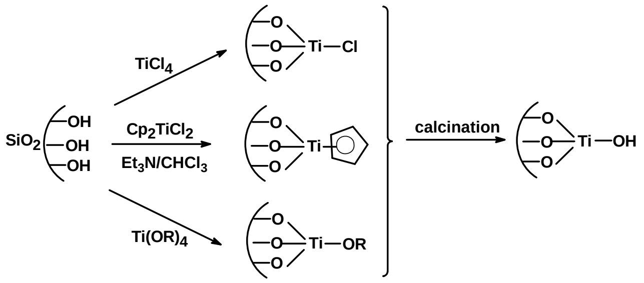


Fig. 3 Examples of Ti(IV) grafting on to silica surface.

Core–shell composites

Sophisticated catalysts of the so-called core–shell morphology, consisting of a magnetic silica core and mesoporous titanium-silicate shell, have been prepared using a combination of different synthetic methodologies.[59] Mori *et al.* prepared a composite Fe*x*O*y*@Ti-HMS *via* coating as-synthesized iron oxide nanoparticles with an amorphous silica layer followed by the sol-gel polymerization using TEOS, $Ti(^iPrO)_4$, and dodecylamine as surfactant.[59a] Another composite material designated as Ti-SMCMS (solid magnetic core–mesoporous shell) was synthesized following the general scheme depicted in Figure 4 (ODTAB stands for octadecyltrimethylammonium bromide).[59b]

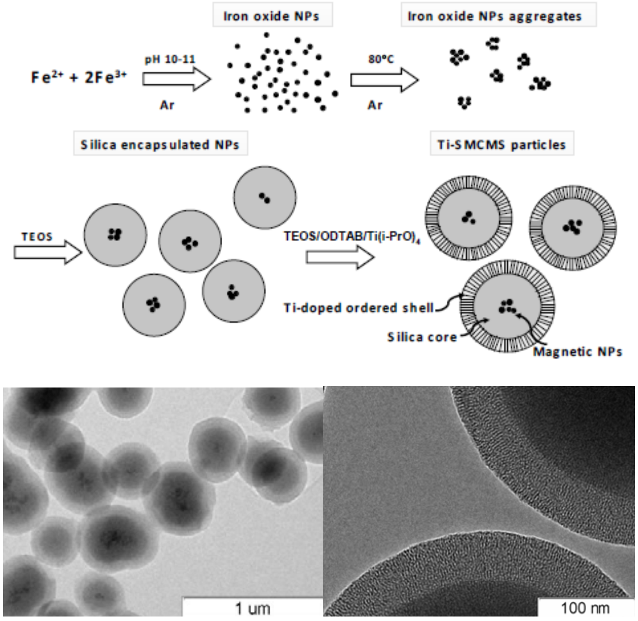


Fig. 4 The general scheme for the synthesis of Ti-SMCMS and its representative TEM micrographs (elaborated from ref. 59b).

In Ti-SMCMS, superparamagnetic nanoparticles are embedded into a nonporous silica core and are completely protected from the reaction medium. An ordered mesoporous titanium-doped silica shell has quasi parallel channels oriented perpendicularly to the core surface (Figure 4). Such composite catalysts can be easily separated from reaction mixtures using an external magnet.[59b]

Recently, a new type of core–shell catalysts, in which a uniform SiO_2 core supporting Pd NPs was covered with a Ti-containing mesoporous silica shell (Pd/SiO_2@TiMSS) was reported.[59c,59d] Although the inner Pd NPs are located at the boundary of the core–shell structure, reactants can penetrate to the Pd NPs through the mesoporous shell, which enables H_2O_2 production from H_2 and O_2 at Pd sites followed by H_2O_2 activation over isolated Ti sites and oxidation of organic substrates within the mesopores in one-pot reaction.

Catalytic applications

Since the first syntheses of mesoporous metal-silicates at the early 1990s a huge number of research papers devoted to evaluation of their catalytic properties in liquid-phase oxidation has been published. In this *Perspective*, we aimed at considering, first of all, the catalytic systems, for which the nature of catalysis (true heterogeneous *vs.* homogeneous due to active species leached into solution) was investigated following the methodology suggested by Sheldon and co-workers that involves filtering the catalyst at the reaction temperature before completion of the reaction and testing the filtrate for activity (the so-called *hot filtration test*).[7] Only deadlock of the reaction in the filtrate unambiguously proves true heterogeneous nature of catalysis.

Oxidation of alkanes

The selective catalytic oxidation of alkanes is a demanding task because their oxidation products are desirable potential feedstocks for the chemical industry. In particular, the oxidation of cyclohexane (CH) into a mixture of cyclohexanone (K) and cyclohexanol (A), the so-called K-A oil, is a key process in the manufacture of Nylon-6 and Nylon-6,6.[60]

The oxidation of CH with molecular oxygen (air) over mesoporous metal-silicate catalysts was extensively explored.[61–66] Table 2 presents a short summary on the results published in the literature. The sponge-like material Co-TUD-1 was shown to be an active and selective catalyst for the aerobic oxidation of CH using traces of cyclohexyl hydroperoxide (CHHP) as initiator.[61] The catalyst with Si/Co = 100 containing isolated Co atoms displayed the highest activity. Under continuous semi-batch reactor conditions, CH conversion attained 5–6% after 6 h and the selectivity to the mono-oxygenated products (mostly A and K) was 87%, which compares well with the homogeneous industrial process.[60] Co-TUD-1 revealed stable activity over a period of one week in the decomposition of CHHP and produced A and K with excellent selectivity. No cobalt leaching was found (the detection limit was 0.1 ppm) but slow deactivation of Co-TUD-1 occurred, which was attributed to the rather crude feed.[61]

Table 2 Oxidation of CH with O_2 over mesoporous metal-silicates.

Catalyst	Conv., %	Select. K + A, %	K/A	Leaching	Ref.
Co-TUD-1	5–6	87	0.64	no	61
Co-HMS	11	79	1.5	[a]	62
Al-HMS	10	92	1.8	no	62
CoPh-HMS	9–10	74	1.5	[a]	63
Bi-MCM-41	12–17	91–94	3.5[b]	no	64
Cr-MCM-48	7	93	2.9	[a]	65
Cr-PMO	7	94	2.6	[a]	65
Hybrid Cr-Si	8	92	2.1	no/yes[c]	66

[a] Hot filtration test and elemental analysis data for the filtrate were not provided; [b] strongly depended on metal content; [c] depended on CH conversion.

Among M-HMS catalysts, Al-HMS revealed the best performance, behaved as true heterogeneous catalyst, did not suffer from leaching and showed stable catalytic properties for 5 reuses.[62] For Bi-MCM-41, the K/A ratio strongly depended on the Bi content and hot filtration tests corroborated true heterogeneous nature of the catalysis over Bi-MCM-41.[64]

With the periodic mesoporous organosilica Cr-PMO, the selectivity to K-A oil achieved 94% at CH conversion of 7%.[65] The catalyst was recyclable with a slight change in the selectivity. The main by-products were CHHP and adipic acid. Similar results in conversion and selectivity were obtained with Cr-MCM-48[65] and another Cr-containing organic–inorganic hybrid material.[66] The hot filtration experiments performed after 2 and 6 hours demonstrated that catalysis was mostly heterogeneous at low conversions but then became homogeneous due to the formation of acids that accelerated leaching of the active chromium species.[66]

Oxidation of CH with alkylhydroperoxides and hydrogen peroxide were widely explored.[60] Schuchardt *et al.* reviewed the catalytic systems reported for CH oxidation, with particular attention to the issue of metal leaching.[67] Besides Ti-MCM-41, all metal-silicates suffered leaching, and the observed catalytic activity was mainly due to homogeneous species. The lower activity and H_2O_2 efficiency of Ti-MCM-41 relative to TS-1 was attributed to the hydrophilic environment of Ti centers, which disfavours CH adsorption within pores and, oppositely, favours adsorption and subsequent unproductive decomposition of the oxidant.

Ce-containing (5.9 wt%) amorphous silicas with average pore diameters of about 3.3 nm were found to be efficient catalysts for CH oxidation with *tert*-butyl hydroperoxide (TBHP).[68] CH conversions up to 12% were obtained in acetone as solvent; the only identified products were K, A and CHHP. A hot filtration test indicated heterogeneous nature of the catalysis. Among the family of M-TUD-1 (M = Ti, Co, Fe, Cr and Cu; Si/M = 100) the highest CH conversions (10–14%) were attained with Co, Cr and Cu; however, only for Co-TUD-1, no metal leaching occurred and catalysis was true heterogeneous.[69] The overall K + A selectivity was 92% (K/A = 6) at ca. 10% substrate conversion.

Cr-PMO exhibited superior catalytic activities and selectivities than conventional Cr-MCM-41 in CH oxidations with aqueous H_2O_2 and non-aqueous TBHP.[58b] The major products of the reaction over Cr-PMO using TBHP were K and A (K/A > 5 after 5 h) along with trace amounts of CHHP and cyclohexyl-*tert*-butylperether. The conversion of CH was 4% in the absence of solvent and increased to 12% in acetone. Whereas hot filtration tests revealed substantial chromium leaching and homogeneous nature of catalysis in the case of H_2O_2, catalysis was principally heterogeneous with TBHP, at least at the initial stage of the reaction. The higher catalytic activity and stability of Cr-PMO relative to Cr-MCM-41 were attributed to the improved hydrophobicity of the former and its complementary textural and structural features that facilitate adsorption of the reactants close to the active Cr sites.[58b]

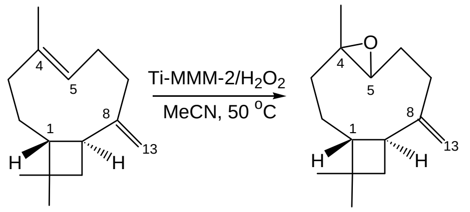
Oxidations of acyclic alkanes over mesoporous metal-silicates are relatively scarce. Tatsumi *et al.* demonstrated that trimethylsilylation of Ti-MCM-41 and Ti-MCM-48 improves both the catalytic activity and H_2O_2 efficiency in the solvent-free oxidation of hexane, but the achievable level of conversion remained very low (< 0.2%).[54a] The mixed-phase catalyst Ti-MMM-1 prepared using two templates, cetyltrimethylammonium bromide (CTAB) and tetrapropylammonium bromide (TPABr), was more active and selective than Ti-MCM-41 or TS-1 in the oxidation of CH and *n*-octane with H_2O_2 in acetone.[70] Unfortunately, no catalyst recycling and leaching tests were provided for Ti-MMM-1.

The hydrothermally stable catalyst Ti-MMM-2 synthesized under weak acidic conditions[41a] was examined in the oxidation of a range of alkanes (cyclooctane, *n*-heptane, *n*-octane, *iso*-octane, methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexane) by H_2O_2 in acetonitrile.[71] The selectivity parameters C(1):C(2):C(3):C(4), which reflect the relative reactivities of hydrogen atoms at carbons 1, 2, 3 and 4 of the *n*-heptane or *n*-octane chain, differed significantly for Ti-MMM-2 and TS-1 (1:5.2:4.5:4.4 *vs.* 1:80:62:59 for *n*-octane). The bond-selectivity parameters 1°:2° in the oxidation of 2,2,4-trimetylpentane and methylcyclohexane by H_2O_2 over Ti-MMM-2 were close to the parameters found for homogeneous systems that oxidize alkanes with the participation of hydroxyl radicals. Accordingly, the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes proceeded non-stereoselectively to give a mixture of *cis*- and *trans*-isomeric alcohols. The reactions stopped completely after removal of the catalyst by hot filtration, thus indicating true heterogeneous nature of the catalysis.[71]

Alkene epoxidation

Epoxides are key intermediates in the manufacture of a wide variety of valuable products. The TiO_2-on-SiO_2 catalyst developed by Shell forms the basis of the commercial POSM process for propylene epoxidation with ethylbenzene hydroperoxide (EBHP).[1,48a,72] This catalyst is prepared in a multistep gas phase process by grafting a Ti precursor onto silica. However, the Shell catalyst is rapidly deactivated by water, which renders it unsuitable for oxidations with aqueous H_2O_2. This limitation has been overcome by the creation of the hydrophobic titanium-silicalite TS-1 by the ENI group.[73] Micropores of TS-1 allow efficient transformations of linear alkenes but not of cyclic and branched ones. In 1994, Corma *et al.* first applied a mesostructured titanium-silicate, Ti-MCM-41, for epoxidation of alkenes.[44a] Although its activity in H_2O_2-based epoxidation of small linear molecules was lower than activity of TS-1 (9% *vs.* 49% conversion of hexene-1),[44b] the advantage of Ti-MCM-41 was manifested by its ability to epoxidize large molecules (e.g. norbornene and α-terpineol) and to use bulky organic hydroperoxides as oxidants.

Subsequent studies demonstrated that mesoporous titanium-silicates are more active than TS-1 in the oxidation of cyclic alkenes with H_2O_2.[41a,44,48d,54a,74] The oxidation of cyclododecene (*cis*/*trans* = 75/25) over Ti-MCM-48 produced selectively cyclododecene oxide (*cis*/*trans* = 58/42) with higher turnovers than Ti-MCM-41, which was attributed to the three-dimensional structure of Ti-MCM-48.[44c] (–)-Caryophyllene, a component of clove oil, was oxidized with H_2O_2 (1 equiv.) over Ti-MMM-2 to give 4,5-monoepoxide (a food and cosmetics stabilizer approved by FDA) with 52% yield at 75% conversion.[41a] Over TS-1, only 5% yield of this product was found. Stable catalytic performance of Ti-MMM-2 was observed in several reuses.



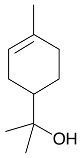
A controlled drop-wise addition of H_2O_2 allowed excellent selectivity (>98%) and fairly good yields (44–63%) of cyclohexene epoxide to be obtained even for substrates with reactive allylic H atoms (e.g. cyclohexene and limonene).[75] The slow addition of H_2O_2 is crucial to minimize its unproductive decomposition and to keep the local concentration of water as low as possible, thus suppressing the formation of allylic oxidation products and hydrolysis of epoxides to diols.

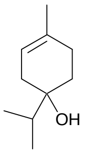
Irrespective of the alkene nature, high epoxide yields can be reached using mesoporous titanium-silicates (both amorphous and ordered) with alkylhydroperoxides as oxidants.[17,18,39,49,55,74,76] A comparison of the catalytic performance of TiO_2–SiO_2 aerogels with some other types of titanium-silicate catalysts can be found in the review of Baiker and co-workers.[17b] In general, their catalytic behaviour resembles that of the Shell TiO_2-on-SiO_2 catalyst. The advantage of aerogels could be the possibility of the higher titanium loading with a good Ti dispersion, which might ensure higher catalyst productivity. However, low hydrothermal and mechanical stabilities of aerogels restrict their use in liquid-phase oxidations.

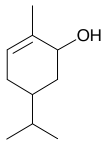
Nearly quantitative yield of cyclohexene epoxide was obtained using cumyl hydroperoxide (CHP) and Ti/SBA-15 prepared by CVD.[48f] Importantly, the reaction performed in the absence of any solvent and at substrate to oxidant molar ratio of 100/11 led to an epoxide yield > 90%. (*R*)-limonene and α-pinene produced epoxides with 97 and 91% yields and 93 and 96% hydroperoxide efficiencies, respectively.[48e] With both TBHP and CHP, no leaching of titanium and very little change of catalytic activity was observed after four successive recycles. Grafted Ti/MCM-41 demonstrated high selectivity in epoxidation of cyclohexene and pinene with TBHP.[49] Although one could expect a higher activity for the grafted Ti catalysts than for catalysts prepared by direct synthesis due to a better accessibility of Ti centres in the former, the activities appeared to be similar when the turnover frequency (TOF) values of Ti/MCM-41 were compared with Ti-MCM-41[49] or Ti-TUD-1.[39]

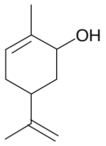
Unsaturated alcoholic terpenes such as α-terpineol, terpinen-4-ol, carvotanacetol, isopulegol, and carveol were epoxidized with

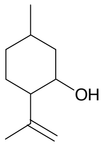
TBHP over silica-grafted Ti-catalysts.[51a] Conversions up to 90% and good epoxide selectivities (60–80%) were achieved in polar aprotic solvents. A 100% diastereoselectivity was observed in epoxidation of the homoallylic and bishomoallylic substrates, α-terpineol and terpinen-4-ol.


α-terpineol

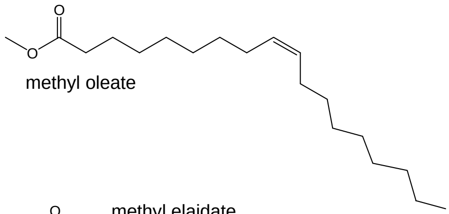

terpinen-4-ol

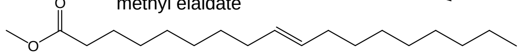

carvotanacetol


carveol


isopulegol

Grafted Ti-containing silicas showed promising results in the TBHP-based epoxidation of C_{18} unsaturated fatty acid methyl esters (FAMEs) and their mixtures obtained from high-oleic sunflower, castor, coriander, and soy-bean oils.[77] Epoxidation proceeded stereoselectively to give only *cis*-epoxide from (*Z*)-isomer (methyl oleate) and *trans*-epoxide from (*E*)-isomer (methyl elaidate). Over nonporous Ti/SiO_2, (*Z*)-isomer reacted four times faster than (*E*)-isomer but the difference in the epoxidation rates decreased over mesoporous Ti/SiO_2 and especially Ti/MCM-41, suggesting that (*E*)-isomer could fit inside the channels of Ti-MCM-41 more easily than (*Z*)-isomer.

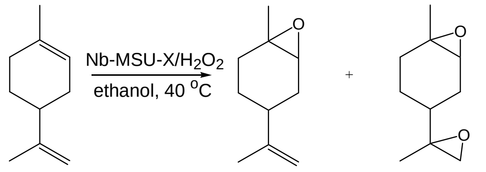

methyl oleate


methyl elaidate

Recent studies demonstrated a comparable behaviour of Ti/MCM-41, Ti/MCM-48 and Ti/SiO_2, in terms of conversion and selectivity, in epoxidation of methyl oleate with H_2O_2, notwithstanding the morphology and textural properties of the silica support.[78] A slow addition of H_2O_2 under optimal reaction conditions led to 91% epoxide yield with a high stereoselectivity (80%) towards *cis*-epoxide.

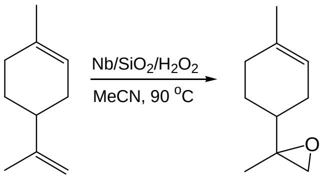
Surface hydrophobization often leads to improvement of the catalytic performance of titanium-silicates in alkene epoxidation.[48a,54,55b] Silylated Ti-TUD-1 was significantly more selective in epoxidation of 1-octene with CHP than unsilylated one.[54c] Moreover, it worked even with electron-poor olefins, e.g. *p-tert*-butylphenylallyl ether gave epoxide with 87% selectivity. Organically modified Ti-SBA-15 revealed a correlation between the catalytic activity in epoxidation of 1-octene with TBHP and the length of the alkyl chain.[54d] Improved efficiency of the oxidant utilization was observed and recycling tests indicated high stability of the catalysts. Mesoporous hybrid titania–silica xerogels prepared by the non-hydrolytic sol–gel route showed practically complete conversion (>98%) of cyclohexene to its epoxide after only 30 min at 90 ºC with CHP as oxidant.[56] The high activity was due to a large amount of incorporated hydrophobic methyl groups (6 CH_3 for 10 Si atoms). Ethane bridged hybrid Ti-HMM gave α-pinene epoxide with more than 99% selectivity at 23% substrate conversion and displayed up to 50% hydrogen peroxide efficiency.[58a] On the other hand, epoxidation of α-terpineol occurred more readily over nonsilylated Ti-MCM-41 than over silylated one although the latter was more active in epoxidation of limonene.[54e]

A few highly selective and true heterogeneous epoxidations have been reported for mesoporous silicas containing metals other than titanium, e.g. Nb,[51d,51e,79] Ta,[28,52d] W,[80], Mn,[81] and Co.[82] Niobium-containing MSU-X efficiently catalyzed the selective oxidation of several terpenes and terpenoids (limonene, geraniol, α-terpineol) with 1 equiv. of H_2O_2.[79a] In the oxidation of limonene, the selectivity for endocyclic 1,2-epoxide was *ca.* 100% at the beginning of the reaction but then dropped to 70% due to the formation of diepoxide.



limonene endocyclic epoxide diepoxide

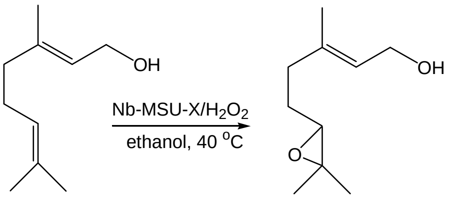
The oxidation was not stereoselective and gave a nearly 1:1 mixture of *cis*- and *trans*-limonene oxides. No allylic oxidation products, carveol and carvone, formed, indicating heterolytic oxidation mechanism. Nb/SiO_2 catalysts synthesised by post-synthesis modification of a commercial silica, starting from niobocene dichloride through solventless organometallic precursor dry impregnation or liquid-phase grafting technique revealed high activity, nearly 98% chemoselectivity and an unexpected regioselectivity towards epoxidation of the less electron-rich exocyclic C=C double bond.[51d] With TBHP, the reaction was slow and produced mainly endocyclic epoxide.



exocyclic epoxide

The Nb/SiO_2 materials were resistant to leaching, recyclable, active and selective catalysts in the production of the epoxidized FAMEs using aqueous H_2O_2.[79b] Nb-PMO was also found to be an efficient catalyst for the epoxidation of methyl oleate.[58c]

The oxidation of geraniol over Nb-MSU-X produced 6,7-epoxygeraniol (98%) and practically no 2,3-epoxygeraniol and 2,3:6,7-diepoxygeraniol, thus discriminating the role of the hydroxyl group in the epoxidation reaction.[79a]

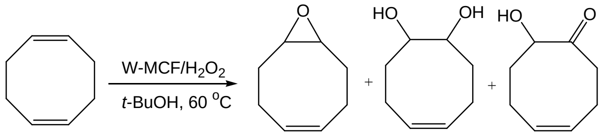


geraniol 6,7-epoxygeraniol

On the contrary, $Nb_2O_5–SiO_2$[83a] and $WO_3–SiO_2$[83b] mixed oxides favoured epoxidation of the 2,3-double bond in geraniol.

Silica-grafted Ta(V) complexes catalyzed cyclohexene and cyclooctene oxidation with H_2O_2 in acetonitrile with 90–95% selectivity to epoxide and diol at 10% substrate conversion.[52d] The catalysts revealed TOF values of 2.3 min^{-1}, unaffected by surface density until 0.25 Ta/nm^2, indicating the single-site character of the active centers. Grafted Ta/SBA-15 catalysts prepared by the thermolytic molecular precursor method were also highly active.[28]

In the epoxidation of cycloocta-1,5-diene with 50% H_2O_2, W-MCF revealed a greater selectivity to monoepoxide (93–96%) and TOF values than W-containing SBA-15 and MCM-41, demonstrating advantages of the ultra-large pores and the unique 3D cell-window structure of the MCF materials.[80].



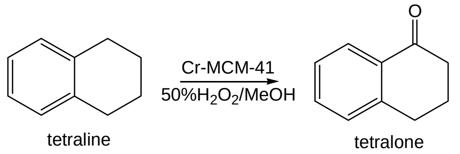
No appreciable loss of the activity and selectivity was observed for five reuses, and no tungsten was determined in the filtrate. The efficiency of H_2O_2 utilization was close to 50% for both the fresh and recycled W-MCF. The activity of 10%WO_3/MCF prepared by impregnation was several times lower.

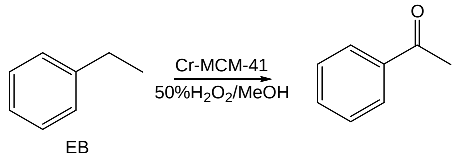
The catalytic activity of Mn-TUD-1 in epoxidation of styrene or *trans*-stilbene with TBHP strongly depended on the fraction of isolated Mn^{3+} sites in the framework.[81] With acetonitrile as solvent, Mn-TUD-1 (Si/Mn = 100) produced epoxides with 61–66% selectivity at 54–77% conversion and TOF 555–880 min^{-1}. Benzaldehyde was the main by-product. The catalyst revealed high stability toward manganese leaching. Co-TUD-1 showed high conversion (92% after 10 h) and selectivity (91%) toward *trans*-stilbene oxide in the oxidation of *trans*-stilbene with molecular oxygen (1 atm) in dimethylformamide.[82] Conversion and selectivity were similar for fresh and recycled catalyst. Microwave-assisted reaction reduced the reaction time from 10 to 2 h, keeping high selectivity.

Allylic and benzylic oxidations

Allylic and benzylic oxidations produce α,β-unsaturated ketones and alcohols, which serve as valuable intermediates for the fine chemicals industry.[1,84] Chromium catalysts are well-known for this type of organic transformations. Allylic oxidation of cyclohexene with 70% TBHP over Cr-MCM-41 and Cr-MCM-48 in chlorobenzene produced 2-cyclohexen-1-one as the major product.[85] After an initial loss of non-framework chromium species in the first run, no further metal leaching was noticed. Catalyst washing with successive portions of acidified ferrous sulphate solution resulted in the material with the amount of Cr similar to that determined in the recycled catalyst (0.8–1.0 wt. %). The filtrate obtained from the calcined catalyst after 2 h of the reaction showed a considerable activity (*ca.* 12–15%), indicating the presence of chromium in solution. However, the filtrate obtained from the washed catalyst revealed no chromium and showed negligible activity, suggesting heterogeneous nature of the catalysis.

Cr-MCM-41 was highly active in the allylic and benzylic oxidation of alkenes with 50% H_2O_2 and produced enones as the main products at reasonable conversions.[86] Ethylbenzene (EB) and tetraline gave acetophenone and tetralone, respectively, with *ca.* 100% selectivity at 85–87% conversion.

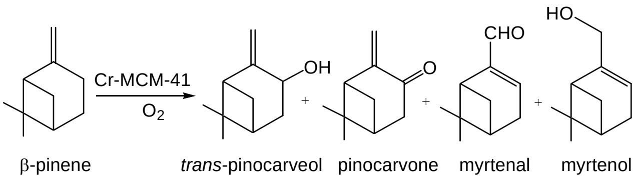




The oxidation of C5–C7 cycloolefins to α,β-unsaturated ketones was effectively realized with 1 atm of molecular oxygen under mild (70 ºC) solvent-free conditions using Cr-MCM-41 as catalyst.[87] Cyclohexene was converted to cyclohexenone with 71% selectivity at 52% conversion, which is comparable with the results acquired over Cr-MCM-41 using TBHP as oxidant and chlorobenzene as solvent.[85b] A gradual decrease in the substrate conversion was observed after catalyst recycling, which was attributed to leaching of loosely bound chromium species. Indeed, elemental analysis determined loss of *ca.* 0.3–0.4 wt% of Cr in the recycled catalyst. According to ICP–AES, leaching of the active metal stopped in the subsequent reuses, and catalysis was supposed to be heterogeneous based on filtration experiments.

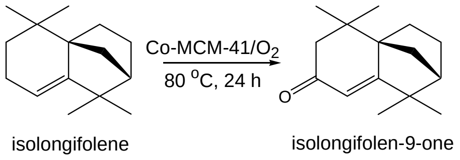
The allylic oxidation of terpenes, the low cost renewable feedstock for a wide variety of fragrances, flavours, medicines, and agrochemicals, has attracted significant attention. Cr-SBA-15 was used for the oxidation of α-pinene with TBHP in chlorobenzene.[88] Substrate conversion achieved 92% after 24 h with verbenone selectivity 88%, but leaching of chromium was substantial. However, ICP-AES analysis showed that Cr leaching from Cr-SBA-15 practically stopped after the third run.

The aerobic oxidation of a range of monoterpenic alkenes over chromium-silicate catalysts was studied under mild solvent-free conditions.[89] Oxygenated monoterpenoids relevant for the flavour and fragrance industry were obtained with total selectivities of 75–92% at 30–40% substrate conversions. Importantly, their separation is often not necessary as the mixtures themselves show attractive organoleptic properties and can be used in fragrance compositions. The oxidation of β-pinene led almost exclusively to allylic mono-oxygenated derivatives with a total selectivity of 92%.[89] A silica–chromia catalyst prepared by the conventional sol–gel method showed activity comparable with Cr-MCM-41 but lower selectivity.

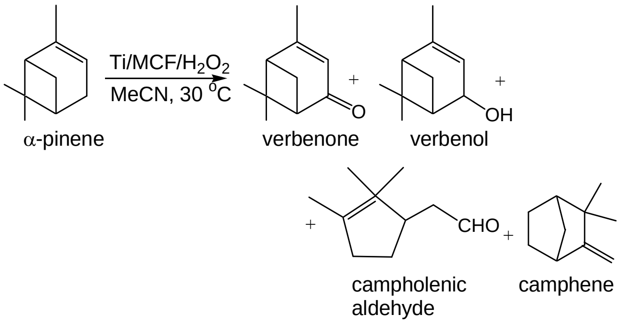


In the presence of chromium-silicates, limonene and α-pinene demonstrated a stronger preference to allylic oxidation over epoxidation.[89] The catalysts could be easily recovered and reused (TON = 222 after three cycles) without regeneration. To control metal leaching, Cr-MCM-41 was removed at the reaction temperature after 0.5 h and the solution was allowed to react further. Only trace amount of products were detected in the filtrate, suggesting heterogeneous nature of catalysis, at least, at the initial stage of the reaction.

An efficient process for the aerobic oxidation of isolongifolene, one of the most available sesquiterpenes, has been developed using Co-MCM-41 as catalyst.[90] Isolongifolen-9-one, a compound widely used in the perfume industry, was produced with 81% yield under mild solvent-free conditions. A hot filtration test indicated true heterogeneous nature of catalysis, and the catalyst was reused without loss of activity and selectivity.



Catalytic properties of various mesoporous silica materials containing Ti^{IV}, Zr^{IV} and Fe^{III} were assessed in the allylic oxidation of α-pinene with 30% H_2O_2.[48d] The activity decreased in the order Ti/MCF (prepared by post-modification) > Ti-MMM-2 > Zr/MCF > TiO_2–SiO_2 > Fe-MMM-2. The major oxidation products were verbenol, verbenone and campholenic aldehyde. Camphene, the product of α-pinene rearrangement, also formed.



Under optimized conditions (MeCN, 30 °C) the selectivity to the sum of verbenol and verbenone reached the maximum of 80–82% at 8–15% conversion and then decreased due to overoxidation/polymerization processes. Although some loss of activity was observed for Ti/MCF after recycling, calcination at 550 °C or evacuation at 200 °C allowed the catalytic properties to be restored, indicating reversibility of the deactivation process (Figure 5). The α-pinene oxidation over Ti/MCF was a true heterogeneous process, as verified by hot filtration tests.[48d]

Production of quinones

The oxidation of bulky phenols was one of the first reactions accomplished using mesoporous titanium-silicate catalysts. Pinnavaia's group first reported the oxidation of 2,6-di-*tert*-butylphenol (DTBP) to a mixture of corresponding *p*-benzoquinone (*p*-BQ) and diphenoquinone (DPQ) with aqueous H_2O_2 over Ti-HMS and Ti-MCM-41.[31a,33a] Catalysts prepared by grafting metal precursors on to the surface of MCM-41, KIT-1, MCM-48 or HMS also revealed activity in the H_2O_2-based oxidation of DTBP.[91] Metal leaching was detected for all grafted HMS catalysts: V/HMS (22 wt%) >> Zr/HMS (3 wt%) > Ti/HMS (2 wt%). A significant contribution of homogeneous catalysis was established for V/HMS and Zr/HMS. Leaching of V was observed in DTBP oxidation with both H_2O_2 and TBHP for V-HMS prepared by direct synthesis.[92]

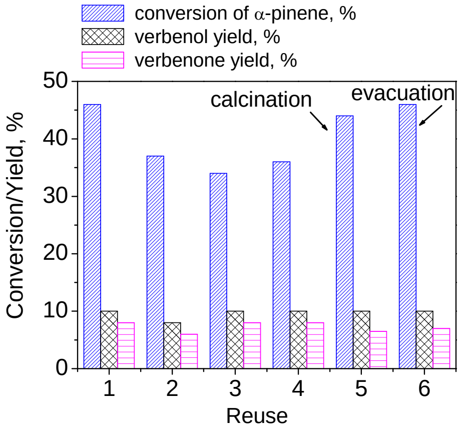
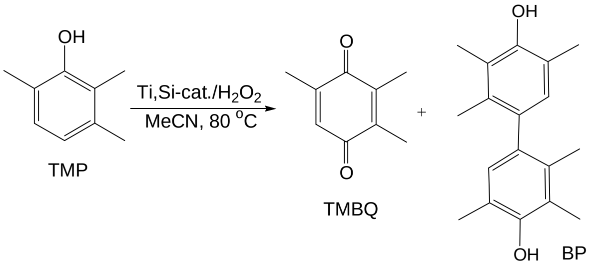


Fig. 5 Re-use and regeneration of Ti/MCF in α-pinene oxidation with H_2O_2. Reaction conditions: 0.1 mmol α- pinene, 0.12 mmol H_2O_2, 14 mg catalyst, 1 mL MeCN, 30 °C, 5 h (elaborated from ref. 48d).

Two groups independently found that oxidation of 2,3,6-trimethylphenol (TMP) with H_2O_2 over mesostructured titanium-silicates, Ti-MCM-41 and Ti-MMM, leads to trimethyl-*p*-benzoquinone (TMBQ, vitamin E key intermediate) with the selectivity of 77–82% at substrate conversion close to 100%.[93,94]. The major by-product of this reaction was 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol (BP).[94]



When Ti^{VI} was replaced by V^{V} or TBHP was used instead of H_2O_2, the yield of TMBQ reduced significantly.[94] As verified by hot filtration tests shown in Figure 6, a substantial contribution of homogeneous catalysis due to leached vanadium species was observed for V-MMM while catalysis was true heterogeneous over Ti-MMM.

TiO_2–SiO_2 aerogels appeared to be very selective catalysts for TMP oxidation with H_2O_2.[95] TMBQ yield attained 95–98% after 0.5 h at 80 °C for samples containing 4–7 wt% of Ti. Selectivities in TMBQ up to 98% were also reported for TiO_2 nanoparticles monodispersed on SBA-15.[96] A nearly quantitative yield of TMBQ was achieved using Ti(IV) grafted on commercial mesoporous silicas.[97]. A correlation between TMBQ selectivity

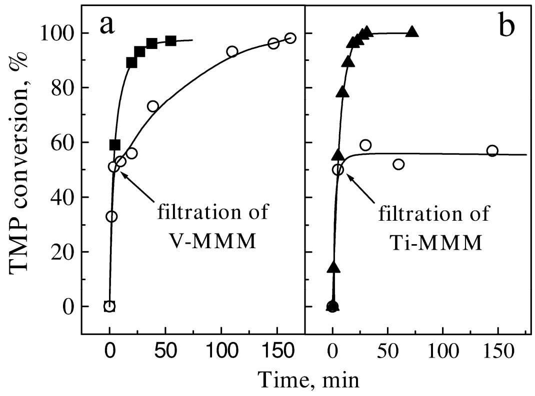


Fig. 6 Hot filtration test for TMP oxidation with (a) TBHP over V-MMM and (b) H_2O_2 over Ti-MMM. Reproduced from ref. 94 with permission of Elsevier; Copyright 2001.

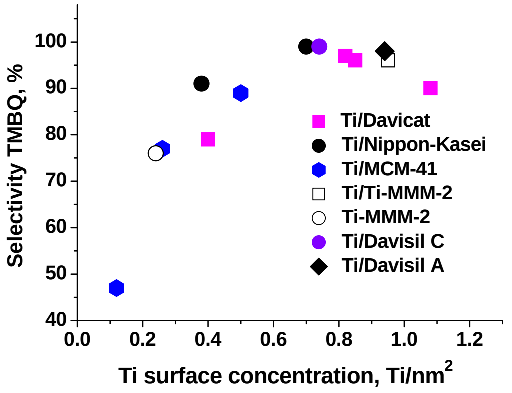


Fig. 7 TMBQ selectivity *versus* Ti surface concentration for silica-grafted Ti catalysts. Adapted from ref. 97b.

and Ti surface concentration has been hypothesized.[97c] The existence of such correlation was confirmed through evaluation of a series of grafted Ti catalysts (Figure 7).[97b]

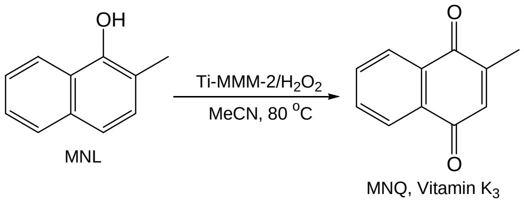
Catalysts with a Ti coverage below 0.6 Ti/nm^2, which possess a large fraction of isolated Ti sites (maximum at 210–230 nm in DRS UV), produced a mixture of TMBQ and BP. Mesoporous silicas with Ti surface concentration in the range of 0.7–1.0 Ti/nm^2 have been identified as optimal catalysts for the selective transformation of alkylphenols to *p*-benzoquinones.[97b] The use of di-/tetranuclear titanium precursors for grafting allowed TMBQ selectivity as high as 96–99% to be reached even at low Ti loadings.[97b] It was concluded that the key point to achieve excellent quinone selectivity is the presence of Ti dimers or subnanometer-size clusters within silica mesopores. Such species show a characteristic broad DRS UV absorption in the range of 240–290 nm. On the other hand, the absence of anatase-like microcrystallites, which are manifested at 330 nm in DRS UV and at 140 cm^{-1} in Raman spectra, is indispensable for both the catalyst activity and selectivity.[98]

Although structural ordering of mesoporous silica had a very little effect on the catalytic performance, mesoporosity itself was crucial. When titanium was grafted onto nonporous Aerosil, TMBQ selectivity reached only 47% in spite of the optimal density of Ti centers (0.85 Ti/nm^2).[97c] A large increase in mesopore diameter from 2.6 nm (Ti/MCM-41) to 15.4 nm (Ti/SiO_2 Davicat) produced no effect on the reaction rate, indicating that diffusion limitations do not play a primary role in the oxidation of TMP over catalysts with mesopores larger than 2.6 nm.

A gradual loss of the catalytic activity and selectivity was observed for the silica-grafted Ti catalysts after few reuses due to progressive agglomeration of Ti species on the silica surface caused by a cooperative effect of water and H_2O_2. Only the use of concentrated (70%) H_2O_2 as oxidant allowed the recycling behaviour to be improved.[97b] Surface silylation enhanced stability, but the catalyst activity dramatically decreased.[97c] Mesoporous titanium-silicates prepared by evaporation induced self assembly (EISA) methodology combined excellent TMBQ selectivity with fairly good stability and demonstrated superior recycling performance in TMP oxidation with 30% H_2O_2.[99] Efficiency of the oxidant utilization was in the range of 54–57%.

Microporous TS-1 showed very little activity in TMP oxidation (only 7% conversion *vs.* 100% over mesoporous titanium-silicates).[41a] An ordered mesoporous titanosilicate, MTS-9, prepared through the assembly of preformed TS-1 nanoclusters with triblock copolymers in a strongly acidic media was reported to be significantly more active than TS-1, Ti-MCM-41 or Ti-HMS.[24d,100] Trimethylhydroquinone (TMHQ) rather than TMBQ was identified as the main product, at least at TMP conversions below 20%.

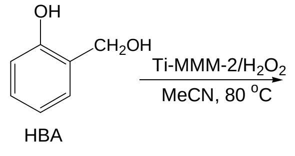
The oxidation of 2-methylnaphthol (MNL) to 2-methyl-1,4-naphthoquinone (MNQ, menadione or vitamin K$_3$) with the yield of 78% was accomplished using 30% H_2O_2 and the hydrothermally stable Ti-MMM-2 catalyst.[101]



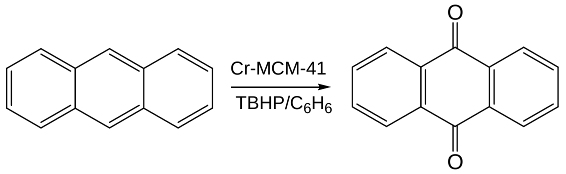
The main by-products were C–C coupling dimers, 4,4'-di(2-methyl-1-naphthol) and 4,4'-di(2-methyl-1-naphthoquinone).[101c] The formation of naphthoxyl radical intermediates during the oxidation process was confirmed by EPR spin-trapping technique. Ti- and Nb-SBA-15[102] along with Nb_2O_5–SiO_2 mixed oxides[103] also catalysed this reaction.

Menadione is currently produced in industry *via* the stoichiometric oxidation of 2-methylnaphthaline (MN) by carcinogenic chromium(VI) oxide with 40–50% yields, isomeric 6-MNQ being one of the main by-products.[101b] MNQ selectivity as high as 90% at 66% substrate conversion was claimed for MN oxidation with H_2O_2 over Ti-MCM-41.[104] Surprisingly, 6-MNQ was not found among the oxidation products.

The oxidation of 2-allylphenol and phenols bearing alcohol functional groups over Ti-MMM-2 produced *p*-benzoquinones with good to moderate yields keeping the other oxidizable sites intact.[105] For example, 2-hydroxybenzyl alcohol (HBA), which could be alternatively converted to salicylaldehyde, gave 2-hydroxymethyl-*p*-BQ in a 74% yield.



The oxidation of anthracene with TBHP was studied using various M-MCM-41 catalysts.[106] Cr-MCM-41 with 0.46 wt% of Cr revealed the best catalytic performance and produced 9,10-anthraquinone (AQ) with *ca.* 98% selectivity at 79% conversion after 20 h at 80ºC.

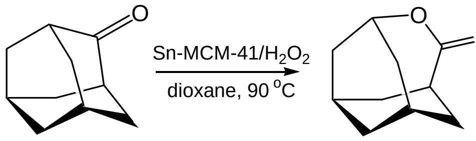


The yields of AQ were nearly constant during four reuses, and hot filtration tests proved the heterogeneous nature of the catalysis.[106] A 90% yield of AQ was reported for the anthracene oxidation with TBHP over Ti-HMS (Si/Ti = 30).[107]

Baeyer–Villiger Oxidation

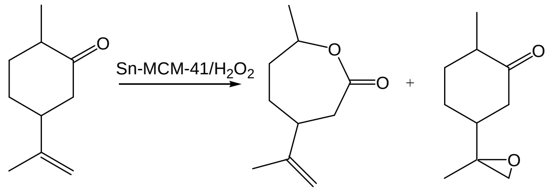
The Baeyer–Villiger (BV) oxidation is one of the most important transformations in synthetic organic chemistry.[108] Solid catalysts can promote *in situ* formation of peroxy acids from sacrificial aldehydes and molecular oxygen. Fe-MCM-41 exhibited high activity in the BV oxidation of cyclic ketones to lactones using O_2 and benzaldehyde.[109] Conversion of cyclohexanone to ε-caprolactone attained 85% with 78% selectivity without appreciable loss in activity and selectivity for four recycles. No Fe leaching was detected and hot filtration test verified the true heterogeneous nature of the catalysis over Fe-MCM-41. Under identical experimental conditions, the catalytic activity of Fe-MCM-48 was superior to that of Fe-MCM-41, which was attributed to the three-dimensional mesopore system of MCM-48.[110] The catalysts showed good reusability, and no iron leaching was detected for samples with Fe loadings below 1 wt%.

Since the use of sacrificial aldehyde leads to the formation of a carboxylic acid by-product in a stoichiometric amount, the aldehyde/O_2 system is less attractive for industry than “clean” oxidants, such as H_2O_2 that produces water as the sole by-product. Tin-containing mesostructured silicates were intensively studied by the group of Corma in BV oxidations with H_2O_2.[111] In the oxidation of cyclohexanone, catalysts prepared by direct synthesis and post-synthesis, Sn-MCM-41[111a] and Sn/MCM-41,[111b] respectively, were intrinsically less active than zeolite Sn-Beta. The activity of Sn-MCM-41 strongly depended on the Sn loading (TOF 23 and 13 h^{-1} for samples with 1 and 2% SnO_2) but, irrespective of the metal content, the selectivity to lactone attained 94–97%.[111a] With a bulkier substrate, adamantanone, both Sn-MCM-41 and Sn/MCM-41 showed activities comparable with Sn-Beta.[111c] The oxidation of adamantanone over Sn-MCM-41 showed complete substrate conversion after 6 h in dioxane and produced lactone as the sole product (>99% selectivity) with H_2O_2 efficiency of more than 90%.[111a]

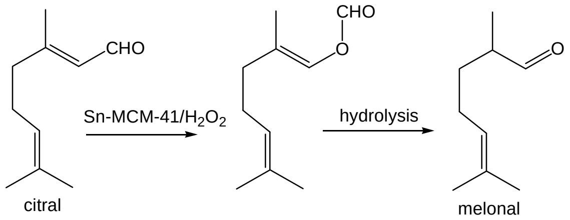


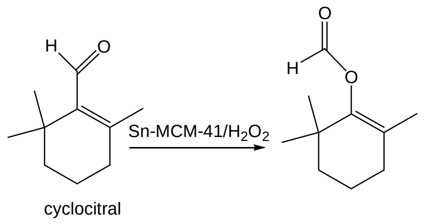
To check a possible contribution of the homogeneous reaction, Sn-MCM-41 was removed from the reaction mixture at *ca.* 70% conversion.[111a] The reaction in the filtrate stopped, suggesting that the active species was present on the catalyst surface. Yet, it was demonstrated that homogeneous Sn species is about one order of magnitude less active than Sn incorporated into MCM-41. Nevertheless, some loss of activity was observed for Sn-MCM-41 after recycling, most likely, due to lactone remaining adsorbed within the catalyst pores. Indeed, the catalytic activity was restored after calcination or extraction with methanol.

Using tin-silicates, unsaturated ketones can be oxidized with good chemoselectivity to unsaturated lactones,[111a,111b] which is not possible with peroxy acids or Ti-containing catalysts that are highly active in the epoxidation reaction. Over Sn-MCM-41, dihydrocarvone gave 68% of lactone, just 18% of epoxide, and no epoxylactone.



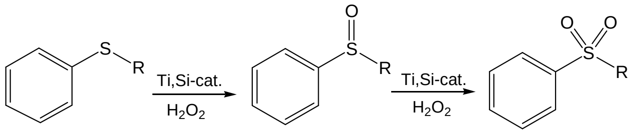
Citral, a common compound in the fragrance industry, was oxidized chemoselectively with 50% H_2O_2 over Sn-Beta or Sn-MCM-41 to produce, after hydrolysis, the fragrance melonal.[111d] Sn-Beta was more active than Sn-MCM-41. On the contrary, with cyclocitral as substrate, Sn-Beta showed only 43% conversion and 36% selectivity while Sn-MCM-41 converted 90% of cyclocitral into the formate ester with 100% selectivity.





Oxidation of thioethers

The oxidation of thioethers to sulfoxides and sulfones over mesoporous titanium-silicates was first described by Corma’s group.[112] While zeolite Ti-Beta was more active than Ti-MCM-41 in the oxidation of methyl phenyl sulfide (MPS) with both H_2O_2 and TBHP, an opposite trend was observed for a more bulky substrate, isopentyl phenyl sulfide.



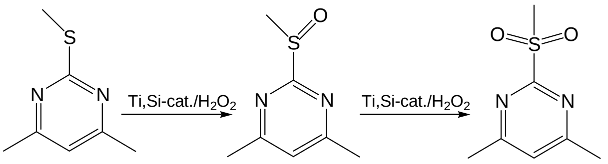
Another MCM-41-type catalyst, Ti-MMM, was highly active in MPS oxidation with H_2O_2 at room temperature.[113] The substrate conversion attained 99% after 15 min, and the selectivity to sulfoxide was 76% in MeCN or MeOH. The molar ratio of products changed in acetone where sulfone predominated over sulfoxide. In the range of Ti loadings 1–2.5 wt% the value of TOF was constant, indicating the uniformity of Ti active centers. The oxidant efficiency was 90%. V-MMM showed 98% MPS conversion after 4 min with 82% selectivity to sulfoxide, but practically all vanadium leached into solution.[113] With nonaqueous TBHP, no metal leaching occurred but the reaction was much slower and the sulfoxide selectivity was poor.

Although catalysis was true heterogeneous, a progressive loss of activity occurred after recycling of Ti-MMM in H_2O_2-based MPS oxidation because of low hydrothermal stability of this catalyst.[113] The hydrothermally stable Ti-MMM-2 showed the activity and selectivity close to Ti-MMM but demonstrated an excellent recycling behaviour (Figure 8).[41a] Magnetic composite Ti-SMCMS (see Fig. 4) demonstrated similar activity and selectivity and could be separated from the reaction mixture by means of an external magnet.[59b]

The core–shell architecture Pd/SiO_2@TiMSS, consisting of Pd NP-supported SiO_2 core and a Ti-containing mesoporous silica shell offerred an efficient route to one-pot oxidation of thioethers in the presence of H_2 and O_2.[59c,59d] The selectivity to methyl phenyl sulfoxide attained 87% while efficiency of H_2O_2 utilization reached 65%. No reaction was observed for either SiO_2@TiMSS without Pd NPs or Pd/SiO_2@MSS without Ti.

Ti-containing MCM-41 catalyzed asymmetric oxidation of sulfides with H_2O_2 in the presence of optically active tartaric acid (TA).[114] The chemical and optical yields of methyl 4-methylphenyl sulfoxide reached 54% and 30% *ee*, respectively, in dichloromethane at a TA/Ti ratio of 2 at 0 ºC and 72 h reaction time. The enantiomeric excess gradually increased during the reaction course due to contribution of kinetic resolution in the subsequent oxidation of sulfoxide to sulfone. The titanium content in the filtrate after the reaction was below the detection limit (ppb order).

Sulfoxidation of 4,6-dimethyl-2-methylthiopyrimidine with H_2O_2 was performed using Ti-SBA-15 and Ti-Ge-MCM-41 catalysts (Si/Ti = 44–66) in dioxane, ethanol and ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) and triflate ([emim][OTf]).[115]



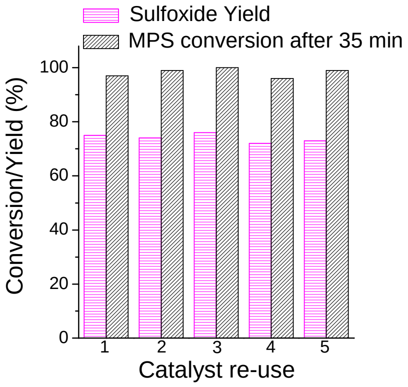


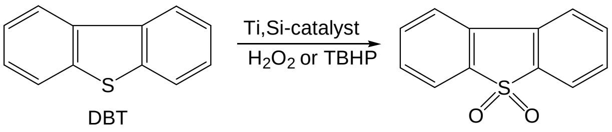
Fig. 8 Recycling of Ti-MMM-2 in sulfoxidation of MPS with H_2O_2 in MeCN (elaborated from ref. 41a).

The reaction in ionic liquids showed superior selectivity of sulfoxidation (83–93% at 100% substrate conversion) compared with the molecular solvents (58–75%). A significant increase in the catalyst stability was found in the ionic liquids both in terms of recycling activity and titanium leaching.

Oxidative desulfurization

Environmental regulations have been introduced in many countries to reduce the sulfur content in fuel to ultralow levels (10 ppm). Existing hydrodesulfurization (HDS) processes require severe processing conditions to remove the last 100 ppm of sulfur which are constituted mainly from bulky benzothiophenes. The oxidative desulfurization (ODS) is not cost competitive with HDS, but it may be useful to remove these last ppm of sulfur until the level fixed by environmental legislations.

Hulea *et al.* compared the catalytic activity of TS-1, Ti-Beta and Ti-HMS in the oxidation of thiophene derivatives with H_2O_2.[116] While TS-1 was inactive in the oxidation of bulky polyaromatic compounds like benzothiophene (BT) and dibenzothiophene (DBT) because of restricted access of the reactants into the micropores, these substrates could be readily oxidized at 60 ºC over Ti-Beta and Ti-HMS. In the case of BT, the activity of Ti-Beta was higher than the activity of Ti-HMS but, on the contrary, Ti-Beta was slightly less active than Ti-HMS with more bulky DBT. The oxidation of kerosene (1310 ppm sulfur) with H_2O_2 was explored at 70ºC. The oxidant efficiency was *ca*. 90 and 80% and the removal of sulfur achieved 94 and 85.5% for Ti-Beta and Ti-HMS, respectively.



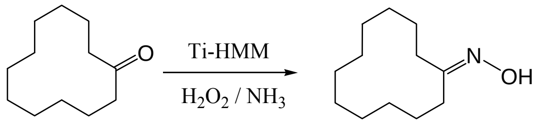
Catalytic properties of various metal-containing molecular sieves, including Ti-MCM-41, were evaluated in the oxidative desulfurization of model sulfur-containing compounds dissolved in *n*-heptane with TBHP as oxidant.[117] The best catalysts were then studied for the ODS of simulated and industrial diesels (40–300 ppm of sulfur) in a continuous fixed-bed reactor. Calcined Ti-MCM-41 was more active, did not leach Ti and deactivated more slowly than other catalysts. Even the most difficult compound, 4,6-dimethyl dibenzothiophene (DMDBT), was completely oxidized to sulfone. The amount of adsorbed sulfone was strongly reduced by decreasing the polarity of Ti-MCM-41 by silylation, with the corresponding increase in catalyst activity and lifetime. Deactivated catalysts could be regenerated by washing with methanol.

Efficient removal of BT, DBT and DMDBT was achieved through oxidation with 70% H_2O_2 over a grafted Ti/SiO_2 catalyst.[118] Both BT and DBT were easily oxidized to sulfones, but the reaction with DMDBT was slow, presumably, because of the steric hindrance. The catalysts were reused four times in the reaction with DBT without loss of activity. The H_2O_2 efficiency was *ca*. 80%. The oxidation of S-containing compounds present in a commercial kerosene fraction (1291 ppm) was carried out by applying optimal conditions established using DBT. After 5 min, the remaining sulfur concentration was below 250 ppm, while after 15 min it was below 10 ppm (sulfur removal >99%).

Mesoporous TiO_2–SiO_2 xerogels prepared by the non-hydrolytic sol–gel method showed excellent catalytic performances in the oxidation of bulky sulfides and thiophenes with H_2O_2.[18] Even DMDBT, the less reactive molecule, could be effectively oxidized. H_2O_2 efficiency was more than 98%. Anhydrous TBHP (5.5 M in decane) and 70% aqueous TBHP produced similar results. The catalysts were stable under the operating conditions. Only a minor increase in DBT conversion (2%) was observed in the filtrate after catalyst removal by hot filtration at 35% conversion.

Ammoximation

Ketone ammoximation is a key step in the production of caprolactam.[119a] The ethane bridged hybrid mesoporous material Ti-HMM was less active in the ammoximation of cyclohexanone with aqueous H_2O_2 and NH_3 relative to conventional TS-1.[119b] However, with more bulky cyclododecanone, its catalytic performance was superior to that of TS-1 or Ti-MCM-41 (Table 3). Calcination increased the activity of Ti-HMM but did not affect the selectivity.



It should be noted, however, that ammoximation, in principle, may not require large mesopores to accomplish conversions of bulky substrates. It had been proved that, over TS-1, hydroxylamine is formed within the micropores and then it desorbs and reacts non-catalytically with ketone in the bulk solution to form oxime.[73c,119a,119c]

Table 3 Ammoximation of cyclododecanone over titanium-silicates.

Catalyst	Si/Ti	Conversion, %	Oxime selectivity, %
Ti-HMM	26	42	100
Ti-HMM-calc.	24.5	73	100
TS-1	27	0.8	100
Ti-MCM-41	48	No reaction	

Reaction conditions: substrate, 0.01 mol; substrate/H_2O_2/NH_3 = 1/1.25/2.5; catalyst, 20 wt.%; 10 mL *tert*-butanol; 80 ºC, 8 h (adapted from ref. 119b)

Stability

Deactivation processes

Deactivation of metal-silicate catalysts can be caused by mechanical, thermal and hydrothermal treatments as well as by interaction with the reaction mixture that, in turn, may result in poisoning or fouling and/or induce irreversible transformations of active metal sites, viz., their aggregation on the surface and leaching into solution.

Poisoning is caused by chemisorption of reaction products or impurities from feed that possess a strong affinity to the catalytic site. In case of poisoning, the catalyst activity can be partially or totally restored by various treatments such as calcination, extraction and washing. Thus in alkene epoxidation over grafted titanium-silicates with TBHP, glycol by-products poisoned Ti active sites, but calcination allowed the catalytic properties to be restored.[75b] Fouling (surface coverage by carbonaceous species that block the connection between the active sites and the reaction mixture) is less pronounced for mesoporous silicates than for microporous zeolites.[120] However, if this phenomenon takes place, the use of materials with open three-dimensional ordered (MCM-48, SBA-1, SBA-16) or worm-like (KIT-1, MSU-X) structures may be advantageous as compared with one-dimensional channel systems (MCM-41, HMS, MMM). Evidently, the use of larger pores materials (SBA-15, SBA-16, MCF or MSU-H) is preferable. Catalyst regeneration by calcination is possible, provided it has a sufficient thermal stability.

Mechanical degradation includes phenomena, such as crushing, attrition, friction and/or erosion of the catalyst particles, which may affect negatively the catalytic performance and shorten the catalyst lifetime. Mechanical stability is a crucial issue for materials that have to be shaped into beads or pellets for use in a catalytic reactor. Typically, it decreases in the order: silicagels (xerogels) > mesostructured silicas > aerogels. Ordered mesoporous silicates with a lower initial pore volume and thicker walls are generally more stable.[9] Mechanical stabilities of a wide range of mesoporous materials (MCM-41, MCM-48, HMS, FSM-16, KIT-1, PCH, and SBA-15) were studied by XRD and nitrogen adsorption.[121] All materials collapsed at a maximum pelletizing pressure of 450 MPa. Ball milling caused destruction of Ti-MCM-41 accompanied by blocking of the channels but did not affect the local environment around Ti centers.[122] A 2–3 fold improvement of the mechanical stability of MCM-48 was observed after its silylation, indicating a relation between mechanical and hydrolytic stability.[123] Although mechanical stability of mesostructured silicas is inferior to that of alumina, silica gels and zeolites, it is more than sufficient to withstand typical treatments such as pressing and molding.

Thermal degradation is induced by high temperatures in dry air that leads to a decrease in surface area and a partial or even total collapse of the porous structure which, in turn, may result in sintering of the active component, its entrapment inside the reorganized support and loss of accessibility. Thermal degradation can arise during the catalyst activation, pre-treatment or regeneration steps. Thermal stability of mesostructured silicates strongly depends on the silica wall thickness and silica precursor used in the synthesis.[9,29c,43,121–124] By comparing hexagonal mesostructures with similar wall thicknesses, the following stability trend was found: KIT-1 (colloid silica), MCM-41 (fumed silica) > FSM16 (layered silicate) > MCM-41 (TEOS), HMS (TEOS).[121] The M41S materials prepared from fumed silica were stable to at least 850 °C whereas materials prepared with TEOS completely collapsed at 750 °C. Among TEOS-derived materials, SBA-15 showed much higher stability than HMS and MCM-41 due to the thicker pore walls in SBA-15 (see Table 1). The thermal stability of Ti-MCM-41 was practically unaffected by the metal content ($5 \leq Si/Ti \leq 100$).[124] The complete collapse of the ordered structure occurred only at 1100 ºC while for the pure silica MCM-41 it started at 1000 ºC. Tetracoordinated titanium incorporated in the walls remained stable up to 873 ºC. In general, the thermal stability of mesoporous metal-silicate catalysts is sufficient, at least, for fine chemicals synthesis, as most materials can resist temperatures up to 700 ºC, which is enough for catalysts activation and regeneration by calcinations.

A weakness of most mesoporous silicates is low hydrothermal stability (the resistance to the combined effect of water/steam and temperature).[9–13,24,29,42,121,125–127] Mesostructured silicates subjected to a mild hydrothermal treatment at 400 °C with 25% steam at 1 atm pressure revealed the hydrothermal stability trend different from the thermal stability: KIT-1 > SBA-15 > MCM-48 (fumed silica and TEOS), PCH > FSM-16, MCM-41 (fumed silica and TEOS), HMS.[121] While SBA-15 and KIT-1 could even withstand a more severe test, the structure of the other materials was completely collapsed under the rather mild steaming conditions. For silicates with comparable wall thicknesses, the structural degradation was less pronounced for cubic MCM-48 than for hexagonal mesostructures HMS, MCM-41, and FSM-16. In general, increasing the thickness of silica walls and the degree of silica polymerization enhance the hydrothermal stability.[121,127] Though, a direct correlation between the degree of silica polymerization (the value of Q_4/Q_3 in ^{29}Si MAS NMR spectra)[‡] and the hydrothermal stability was not always found.[128] Some materials, e.g. COK-12 and MMM-2, revealed a fairly good hydrothermal stability although they have a moderate degree of silica polymerization (Q_4/Q_3 = 1.5–1.8).[40,41] Moreover, MMM-2 possesses thin silica walls (1–1.2 nm). Some authors assumed that the main reason for the low hydrothermal stability of ordered mesoporous silicates is a high ratio of strained siloxane bonds in amorphous silica walls as compared to crystalline walls of zeolites.[126,129] The strained bonds are first subjected to hydrolysis followed by the formation of local defects during calcinations. Strategies that allow increasing hydrothermal stability of mesoporous silicates will be discussed below.

Interaction with the reaction mixture can produce a strong deactivation effect on mesoporous metal-silicate catalysts. Water causes not only hydrolysis of Si–O–Si bonds and collapse of the porous structure (the process described above) but may also hydrolyze Si–O–M bonds, inducing the formation of extra-framework metal oxide species and metal leaching into solution.

Leaching is serious problem of solid catalysts in liquid-phase oxidation and is attributed to strong complexing and solvolytic properties of oxidants and/or polar products with –OH, $–NH_2$ or –COOH groups, especially, in a chelate form (polyols, dicarboxylic acids, etc.).[7] Thus in the epoxidation of crotyl alcohol over titanium-silicates, gradual Ti leaching was caused by the reaction by-product, 1,2,3-butanetriol.[130] Cr-containing catalysts started to loose the active metal as cyclohexane conversion increased and carboxylic acids appeared among the oxidation products.[57b] The combination of water and hydrogen peroxide, a strong complexing agent, is particularly detrimental for metal-silicates.[74,94,95,122,131] Agglomeration and leaching of active metal can be minimized to ensure a good catalyst reusability if H_2O_2 is added drop-wise to the reaction mixture[75] or 30% H_2O_2 is replaced with a more concentrated one[94,97] or anhydrous alkylhydroperoxide is used as oxidant.[39,74,76,131,132] Solvent may also affect metal leaching. In methanol, H_2O_2-based oxidations are typically accompanied by titanium leaching.[74,132] With acetonitrile as solvent, Ti leaching may not occur but gradual oligomerization of Ti centers on the surface leads to irreversible catalyst deactivation.[94,95,122,131] Similar regularities were observed for mesoporous Fe-[46d] and Ce-silicates.[133]

Along with experimental conditions and the nature of reactants/products, structural and geometrical factors as well as the nature and state of active metal may strongly affect stability of catalysts toward leaching. Metals such as V, Cr and Mo are especially liable to leaching. Generally, metal cations incorporated in the silica framework are more resistant to leaching than grafted species, which are more exposed to reactants.

Solving problem of hydrothermal stability

Since hydrothermal stability is one of the main critical parameters for practical applications of mesoporous silicates, enormous efforts were made to improve it either by adjusting the synthesis procedure or by post-synthesis manipulations. All methods were directed to increase the thickness of silica walls, degree of silica polymerization and/or local order within the silica walls. Ryoo and Kim found that pH adjustment of the reaction mixture with acetic acid to keep pH *ca.* 11 led to MCM-41 materials stable up to 700 ºC in humid air.[126a] Edler and White revealed that resistance to moisture is favoured by long aging of the dry, template containing MCM-41 prior to calcination.[129a] Increasing crystallization temperature and adding small amounts of fluoride ions allowed a considerable improvement of the hydrothermal stability of MCM-48.[134] Furthermore, stability could be increased by the addition of inorganic salts or organic additives during the synthesis.[42,128a,135] Hydrothermal stability of MCM-41 and MCM-48 was also enhanced by post-synthesis restructuring through additional hydrothermal treatments of the material before removal of the surfactant.[128b,136] Mokaya suggested restructuring *via* a route that involves the use of calcined MCM-41 as a silica source for secondary synthesis.[129b] The remarkable stability achieved was rationalized by a combination of thicker pore walls, higher silica condensation, and less strained silica framework.

A breakthrough in solving the problem of hydrothermal stability was related to the synthesis of SBA-15, the material with extremely thick silica walls (see Table 1).[37] The presence of micropores in the walls can be an additional factor that ensures good hydrothermal stability.[137] No structural degradation of SBA-15 was observed after treatment in boiling water for 48 h.[37b] However, after 10 days of a similar treatment, a significant loss of the structural ordering was observed for both SBA-15 and SBA-16.[138]

Ultrastable MSU-G resisted calcination at 1000 °C and hydrothermal treatment with boiling water at 100 °C for 150 h while other mesostructured silicas with benchmarked hydrothermal stabilities such as KIT-1 and SBA-15 became X-ray amorphous and lost mesoporosity in 50 h when subjected to equivalent treatments.[35] The high hydrothermal stability of MSU-G was explained by the thick silica walls (2.5 nm) and unusually high degree of silica polymerization (Q_4/Q_3 = 6.2–7.1). The specific hierarchical structure of MSU-G with wormhole-like mesopores arranged between undulated silica sheets of the multilamellar vesicles may also account for the unprecedented hydrothermal stability.

Incorporation of metal heteroatoms into silicate frameworks often leads to enhancement of the hydrothermal stability.[139]. Studies by ^{29}Si MAS NMR revealed that titanium incorporation promotes cross linking of the SBA-15 framework.[45b] However, the effect of heterometal on the catalyst resistance to water may strongly depend on the Si/M ratio.[139] Thus stability of Cr-MCM-48 in boiling water was improved with increasing Cr content until Si/Cr = 50 (the catalyst maintained its mesoporous structure after refluxing in boiling water for 36 h) but then it decreased.[139c]

Since the poor stability of mesostructured silicates is ascribed to the amorphous nature of their walls, attempts were undertaken toward zeolitization of the walls. Partial recrystallization of the amorphous walls into zeolitic domains was induced by impregnation of MCM-41 with TPAOH followed by a hydrothermal treatment.[140] An approach that seems to be the most useful for the preparation of metal-silicate catalysts involves the assembly of zeolite seeds or protozeolite clusters in mesoporous frameworks.[19,100,141] A number of hierarchical micro/mesoporous materials have been prepared using pre-synthesized TS-1 as a component for the subsequent step in the synthesis of a mesostructured material.[70,100,139b,142] Alternatively, the walls of mesoporous silica can be coated with zeolitic nanoclusters/nanoparticles.[143]

Incorporation of nonpolar organic groups either during synthesis or *via* post-synthesis silylation is widely used to improve hydrothermal stability of mesoporous catalysts. Whereas the structure of Ti-MCM-41 was almost completely destroyed upon exposure to moisture over saturated aqueous solution of NH_4Cl for 3 days, silylated Ti-MCM-41 and Ti-MCM-48 kept their structures intact for 30 days.[54a] Mesoporous organosilicas PMO-SBA-15 and PMO-SBA-16 exhibited unprecedented hydrothermal stability for as long as 60 days without any loss of structural integrity, as confirmed by SAXS, nitrogen adsorption, TEM, SEM, and ^{29}Si MAS NMR techniques.[138] The superior hydrothermal stability of the hybrid PMO materials relative to SBA-15 and SBA-16 was attributed to a blend of thick pore walls, enhanced polymerization degree of siloxane bonds, and highly hydrophobic nature of the organosilica framework.

Hydrothermally stable catalysts: realities and limitations

Although hydrothermal stability of a silicate matrix does not give a full warranty that no catalyst deactivation would occur on account of a synergistic attack at M–O–Si bonds by H_2O_2 and H_2O molecules, the catalysts based on hydrothermally stable silicates, e.g. Ti-containing MSU-G,[76a] SBA-15,[54b,98] SBA-16,[76b] MCF,[48d] TUD-1,[39] and MMM-2,[41a] are certainly less prone to the deactivation processes than catalysts having low hydrothermal stability. Indeed, Ti-SBA-15 demonstrated much better resistance against titanium leaching than Ti-MCM-41.[54b] No loss of active metal took place for Ti-MSU-G, but the isolated Ti centers were more stable toward clusterization with TBHP than with aqueous H_2O_2.[76a] While TiO_2–SiO_2 aerogels[95a] and mesostructured Ti-MMM[94,113] lost their activity already after the first run, Ti-MMM-2 demonstrated fairly good reusability in H_2O_2-based oxidations.[41a,101a] After treatment with boiled water or 30% H_2O_2 in MeCN solution followed by drying and calcination, the position of DR UV–vis maximum (205–210 nm) of Ti-MMM-2 remained unchanged, indicating a relative stability of the tetrahedrally coordinated Ti centers toward oligomerization. Meanwhile, in the oxidation of cyclohexene to adipic acid, where higher concentrations of hydrogen peroxide were employed, a gradual transformation of isolated Ti centres to extra-framework TiO_2 species led to irreversible catalyst deactivation.[133] Furthermore, titanium leaching into solution happened at high conversions due to interaction of the Ti sites with adipic acid. Therefore, high concentrations of H_2O_2 and formation of highly polar products, in particular, dicarboxylic acids is a serious limitation for catalytic applications of even hydrothermally stable metal-silicates, let alone unstable ones.

So far, not all metal-silicates that had been claimed as hydrothermally stable ones have been tested as catalysts in liquid-phase oxidations. For some materials, the catalytic activity in the first run only was reported and compared with conventional catalysts, like TS-1 and Ti-MCM-41, while neither recycling performance nor leaching tests nor the state of active metal after catalysis were addressed. Therefore, a reliable conclusion on their utility for liquid-phase oxidation catalysis would be possible only after further studies.

Conclusions and future perspectives

Twenty years have passed since the first syntheses of mesoporous metal-silicates were accomplished. During these years the synthetic methodologies have been greatly expanded and improved, and a wide range of transition metal ions have been successfully incorporated into silica frameworks. From the very beginning, mesoporous metal-silicates were expected to show advantages relative to microporous zeolites in the oxidation of sterically demanding substrates, and in this *Perspective* we tried to demonstrate the success of this concept. In the oxidation of small molecules, however, mesoporous catalysts revealed intrinsically lower activities than TS-1 or Ti-Beta, most likely due to the presence of a large number of silanols on the surface, which promotes adsorption of water at the expense of nonpolar substrates. Some reactions easily realizable over TS-1 with H_2O_2 (e.g. propylene epoxidation, oxygenation of linear alkanes and primary amines) are practically impossible over hydrophilic mesoporous titanium-silicates. On the contrary, a variety of oxidations with bulky alkylhydroperoxides have become possible with mesoporous metal-silicates.

Surface hydrophobization has a positive effect on the oxidation of nonpolar or low polar molecules, but a hydrophilic environment of mesoporous silicas may offer advantages for substrates with intermediate polarity and bearing functional groups that interact with the catalyst active site, e.g. phenols and allylic alcohols.

Catalysis by titanium incorporated into silica matrix remains the most developed area although interesting catalytic applications have been found for mesoporous silicates containing other metals, e.g. Cr, Co, Fe, Mn, Ce, Sn, Nb, and W. Several studies demonstrated that the catalytic performances of ordered metal-silicates are often fully comparable (in terms of conversion, activity and selectivity) to M-containing amorphous silicas, provided the state and accessibility of active sites are similar.[51b,51c,78,97b,144]

A great progress has been achieved in the development of hydrothermally stable materials and solving the problem of metal leaching, which broadens applications of mesoporous metal-silicates in liquid-phase processes, including oxidations with aqueous H_2O_2. However, some restrictions still exist with regards to the operation conditions and specific oxidation reactions. Even hydrothermally stable metal-silicates should be used with a caution, because the formation of highly polar products or an improper choice of solvent, oxidant concentration or other parameters can be potentially detrimental for the catalysts.

At the moment, it is not always easy to conclude which types of catalysts are superior in terms of activity, selectivity and stability because direct comparative studies are still a rare case while the reaction conditions used by different groups may differ significantly. An exchange of samples within the scientific community would favour further progress in the development of new efficient catalytic materials and their diversification. In addition, more contacts between “synthetic” and “catalytic” groups would get benefits for both of them and would facilitate discovery of new approaches and finding of new solutions.

The present state-of-the-art of the field allows one to suggest that synthesis of fine chemicals is the most suitable area for application of mesoporous metal-silicate catalysts which could potentially form a basis for new advanced oxidation technologies. In the future, such clean and sustainable technologies should replace the existing stoichiometric processes that employ hazardous reactants and produce toxic waste. The beneficial use of mesoporous metal-silicates in liquid-phase oxidation catalysis will mainly depend on the progress made in both tailoring the surface chemistry of these materials and overcoming the operation and economical obstacles, such as the cost of catalyst relatively to the cost of products, catalyst life-time, and possibility of regeneration.

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Notes and references

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† The terms “silica” and “silicate” are interchangeably used in the literature related to mesoporous materials.

‡ The ratio between sites with a specific coordination, viz. $Si(OSi)_n(OH)_{4-n}$ (Q_n, n = 3 and 4). In ^{29}Si MAS NMR spectra: Q_4 peak (*ca.* –110 ppm) and Q_3 peak (*ca.* –100 ppm).

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