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Mesoporous titanium silicates as catalysts for the liquid-phase selective oxidation of organic compounds †

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Abstract. The data on the synthesis, physicochemical and catalytic properties of mesoporous titanium silicate materials published to date are surveyed. The relationship between the structure of these materials and their catalytic properties in the liquid-phase selective oxidation of organic compounds with peroxides is considered. The emphasis is placed on the problems of stability of mesoporous titanium silicate catalysts and the possibility of their recycling. The bibliography includes 264 references.

I. Introduction

Oxygen-containing organic compounds are important intermediates and products of both base and fine organic syntheses.[1–9] Nearly a quarter of the major chemicals in the modern chemical industry are produced through the catalytic oxidation processes and the share of such processes is constantly increasing.[8,9] Meanwhile, the stoichiometric 'environmentally unfriendly' oxidation of substrates with such agents as manganese or chromium oxides, metal permanganates or bichromates, nitric acid, *etc*., still remains the major route to oxygen-containing products in the fine industrial synthesis.[7,10–17] The stoichiometric oxidation consumes large amounts of expensive and toxic oxidants, which unavoidably gives rise to the problem of hazardous waste utilisation.

However, over the last decade, there has been a marked trend towards replacement of traditional stoichiometric oxidation procedures by catalytic ones, which are substantially more environmentally friendly and cost-effective. Among them, catalytic processes based on the environmentally safe oxidants, such as molecular oxygen and hydrogen peroxide, arouse the greatest interest.[6–25] The active oxygen content in H_2O_2 is 47% and mere water is the only by-product of the H_2O_2 reduction. Although hydrogen peroxide is more expensive than oxygen (100% H_2O_2 costs 0.7 USD per kg),[25] the use of H_2O_2 often proves preferable in small-scale fine organic synthesis. First, the process equimpent required for the oxidation with hydrogen peroxide is less expensive than that for the oxidation with oxygen, since the latter is typically operated at elevated temperatures and pressures.[7–10,26] Second, the processes based on the oxidation with aqueous H_2O_2 are commonly considered to be safer than those utilising oxygen under pressure. The feasibility of the implementation of hydrogen peroxide as an oxidant for a number of large-scale processes, such as caprolactam synthesis (Sumitomo Chemical Co.) or propylene oxidation (BASF and The Dow Chemical Co.) is currently surveyed by leading chemical companies.[25]

Presently, water-soluble metal salts or complexes are dominantly used as catalysts for the liquid-phase oxidation.[4–10,27] However, available catalysts for the selective homogeneous oxidation typically provide high activity and selectivity but low productivity due to the degradation of the catalytic sites in oxidative media. Furthermore, the separation of reaction products from the catalyst and recycling of the latter become a challenging task. Even in the case of two-phase oxidation, *i.e*., when the catalyst is initially present in the aqueous phase, whereas the substrate and product are in an organic medium, contamination of the target product with toxic transition metal derivatives cannot be completely suppressed, since the interaction of the catalyst (or products of its decomposition) with organic components of the reaction mixture (*i.e*., solvent or oxidation products) can yield metal complexes soluble in the organic phase.

The problem of the catalyst separation from the reaction products can be, in principle, solved only by the use of heterogeneous catalytic processes. However, it is known that the liquid-phase oxidation is often accompanied by the leaching of active components from solid catalyst, such that the oxidation process actually proceeds homogeneously in the bulk of the solution and all the above issues related to the product isolation and purification remain.[10,13,16,28–33] Therefore, the development of novel solid catalysts providing the high activity and selectivity simultaneously with the stability against the action of reaction media is one of the most current challenges to the modern liquid-phase catalytic oxidation. The incorporation of tranasition metal ions or their complexes into frameworks or cavities (channels) of ordered micro- and mesoporous materials, *i.e*., the design of so-called redox molecular sieves composed of isolated active sites homogeneously distributed over a solid matrix represents a promising possible route to the solution of this problem.[7–10,13,16,28,29,34–37]

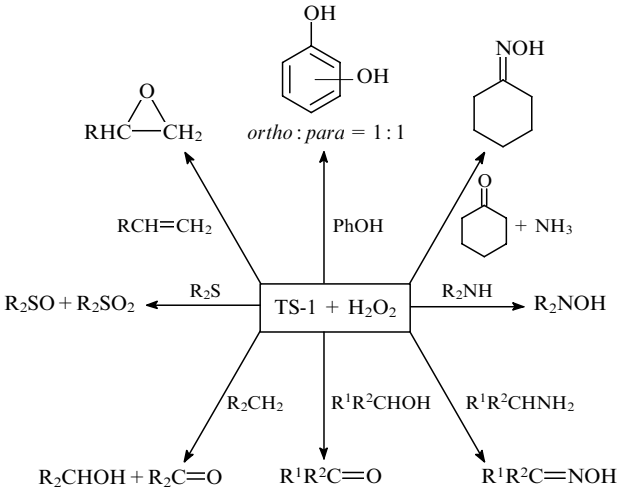
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† The review is dedicated to the memory of V N Romannikov, who stimulated activities on the synthesis and studies of mesostructured silicate and metal-silicate materials at the Institute of Catalysis of the Siberian Branch of the RAS in the end of 1990s.

A real breakthrough in the liquid-phase catalytic oxidation was achieved in the mid-1980s by the Italian company Enichem with the invention of a microporous titanium silicate catalyst TS-1.[38] This catalyst is characterised by the structure of silicalite ZSM-5 (structural type MFI), in which the titanium(IV) ions are isomorphously substituted for a part of silicon atoms. This structure contains a three-dimensional framework of channels with a diameter of 5.3 – 5.6 Å. TS-1 was followed by another microporous titanium silicate catalyst, TS-2 (ZSM-11, structural type MEL, channels of 5.3 – 5.4 Å).[39,40] Presently, TS-1 is still the best catalyst for the heterogeneous liquid-phase oxidation of various classes of organic compounds with aqueous hydrogen peroxide (Scheme 1).[41–49] The oxidation of phenol with hydrogen peroxide over TS-1 was implemented industrially in 1987; using this process, about 10 000 t of hydroquinone and pyrocatechol are produced yearly.[41,45] The main drawback of the microporous titanium silicates is the small size of the pores, which prevents their utilisation for the conversion of large organic molecules. In particular, the system TS-1 – H_2O_2 is an active oxidant only for substrates with a kinetic diameter smaller than 6 Å (which includes unbranched alkanes and olefins, phenols, *etc.*).[41–45] The problem of the selective catalytic oxidation of large organic molecules remains unsolved.

Scheme 1



Over the recent years, several titanium-containing zeolites and disordered titanium silicates with pores larger than in TS-1 have been synthesised, *viz.*, Ti-Beta (6.4 × 7.6 Å),[50,51] Ti-APSO-5 (7.3 × 7.3 Å),[52] Ti-MOR (6.7 × 7.0 Å),[53,54] ITQ-7 (6.1 × 6.5 Å),[55] Ti-MWW (7.1 × 18.2 Å),[56–59] Ti-DMS1 (11.2 Å),[60] *etc.* They were successfully utilised in the catalytic oxidation of some cyclic alkenes and alkanes (*e.g.*, cyclohexene, cyclooctene, norbornene, methylcyclohexane, *etc.*) and unsaturated alcohols,[50–56,59–67] which cannot be oxidised over TS-1. Nevertheless, these catalysts are unable to overcome the problem of oxidation of larger molecules. Furthermore, some of them are sensitive to the action of aqueous hydrogen peroxide.[28,29,31,68]

Over the last decade, a new class of materials, *viz.*, mesoporous silicates containing ions of various transition metals, including titanium, has become in the focus of interest: the number of publications devoted to their synthesis, characterisation and application as oxidation catalysts is rapidly increasing.[32,45,69–91] The specific surface area of such materials can be as high as 1000 $m^2\ g^{-1}$ or even more. Large organic molecules can freely penetrate into the pores of these materials under the conditions of liquid-phase heterogeneous catalysis, in contrast to the pores of microporous materials. The design of such materials takes the first place among the current strategic tasks of fine organic synthesis oriented on the use of hydrogen peroxide.[16]

A number of reviews [32,33,45,74,76–79,81–85,90,91] (not mentioning numerous original papers) devoted to the synthesis and elucidation of the properties of mesoporous metal silicates have recently appeared. The first one was published in 1996.[74,76] In the same year, a detail review devoted to microporous titanium silicates by Notari appeared,[45] which generalised rather scarce experimental data on mesoporous silicate materials available by that time. In 1997, two reviews by Corma [77,78] on the synthesis of mesoporous molecular sieves (including metal silicates) and their applications in catalysis and another review by Schneider and Baiker,[81] who considered mixed titanium – silicon oxides (aerogels), were published.

In the present review, we undertake an attempt to generalise and analyse the experimental results published to date (prior to the beginning of 2005) concerning the synthesis of mesoporous titanium silicates (both structurally ordered and amorphous) and analysis of their physicochemical properties and consider possible applications of these materials as catalysts for the selective liquid-phase oxidations. The emphasis is placed onto the relationship between the physicochemical characteristics of mesoporous titanium silicates and their catalytic properties and onto the problems of their stability and possibility of their recycling.

II. Types of mesoporous titanum silicates and their synthesis

There are two fundamentally different types of mesoporous metal silicate (including titanium silicate) materials, *viz.*, ordered and disordered. The first type includes various mesostructured materials (MMM, MCM-41, MCM-48, HMS, FSM-16, SBA-15, *etc.*), which are often referred to as mesoporous molecular sieves (Fig. 1 *a*). The second type includes amorphous mixed oxides (*i.e.*, aerogels and xerogels) (Fig. 1 *b*). Titanium can be either incorporated into the porous silicate matrix during its synthesis [41,66–77] or grafted onto the surface of a preprepared matrix using the so-called post-synthesis, which means a treatment of a mesoporous silicate with titanium salts or complexes, such as $TiCl_4$, $Ti(OPr^i)_4$, $[(C_5H_5)_2TiCl_2]$, $[Ti_6(\mu_3\text{-}O)_6(\mu\text{-}O_2CC_6H_4OPh)_6.(OEt)_6]$, *etc.*[7,28,92–99]

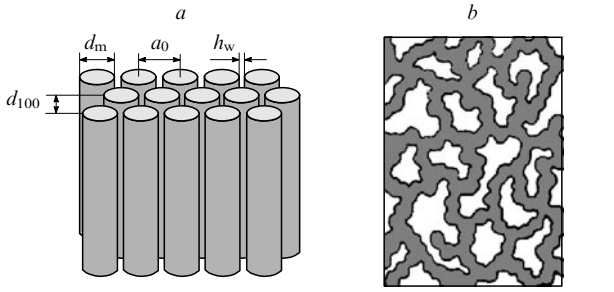


Figure 1. A schematic representation of the structure of a mesostructured material with hexagonally packed cylindrical mesopores (channels) (*a*) and of an aerogel (*b*);
a_0 is the lattice parameter, d_m is the diameter of a mesopore, h_w is the thickness of the silicate wall ($h_w = a_0 - d_m$), d_{100} is the interplanar spacing.

1. Mesostructured titanium silicate materials

Mesostructured silicates are known starting from the early 1990's.[100,101] They represent highly ordered systems produced through the hydrothermal synthesis from inorganic precursors and surfactants.[70–78,82,83,86–91] The mesopores emerging in such materials following the removal of surfactants by calcination or extraction have precisely determined sizes in the nanometre range (typically, from 20 Å to 200 Å) and form channels. The packing of the mesopores can be either hexagonal (MCM-41, HMS, MMM, FSM-16 or SBA-15) (see Fig. 1 *a*), or cubic (MCM-48 or SBA-1) or lamellar (MCM-50), depending on the surfactant : Si ratio and conditions of the hydrothermal synthesis.[74–77,83] The silicate

walls separating the channels of mesopores from each other are amorphous, but nevertheless the structure of these materials is characterised by long-range ordering‡ owing to the ordered arrangement of the hollow channels. The specificity of the structure of these materials is reflected in the terms 'mesophase' or 'mesostructured', which imply long-range ordering (in the distance range from 1 nm to 1000 nm) at the absence of short-range ordering (at the atomic level). This feature distinguish these materials from zeolites that are both short-range and long-range ordered.

Mesoporous mesophase metal silicates (and titanium silicates, in particular) are typically prepared through the hydrothermal synthesis by the crystallisation of a gel containig a source of the structural element (an Si compound), a structure-forming agent (*i.e.*, a surfactant) and a transition metal compound. The crystallisation is often carried out under elevated pressures and temperatures (25–200 °C). The duration of the crystallisation can vary from a few hours to several weeks.

The first report on the synthesis of an ordered mesoporous titanium silicate material, Ti-MCM-41, was published in 1994.[69] Later, several methods for the synthesis of a number of mesostructured titanium silicate materials (*e.g.*, Ti-MCM-41,[69, 70, 72, 77] Ti-MCM-48,[95, 102, 103] Ti-HMS,[73, 87, 104] Ti-MMM,[88, 105, 106] KIT-1,[93] Ti-TUD-1,[107] Ti-MSU-1,[108] Ti-FSM-16,[109] Ti-SBA-15,[95, 96, 99, 110–113] Ti,Al-SBA-15,[114] Ti-SBA-1,[115] Ti-MMM-2,[116] *etc.*) have been elaborated. The basic types of mesostructured titanium silicate materials are summarised in Table 1.

The type of interaction between the inorganic component (I) and the surfactant (S) is the key factor governing the formation of a mesophase material with a specific structure. The following interaction types are possible: electrostatic (S^+I^- or S^-I^+),[76, 77, 82, 83, 88, 104] indirect electrostatic ($S^+A^-I^+$ or $S^-C^+I^-$, where A^- and C^+ are auxillary anions and cations, respectively),[104, 117, 118] hydrogen ($S^0\cdots I^0$)[73, 87, 104, 108] and covalent (S^0-I^0)[119] bonding.

The synthesis of mesostructured silicate and metal silicate materials (MCM-41, MCM-48, MMM, *etc.*) mediated by the electrostatic interactions between cationic surfactants (S^+) and polysilicate anions (I^-), *i.e.*, through the reaction pathway S^+I^-, is realised in alkaline media.[69, 70, 77, 88, 102–106] The first mesostructured silicates of the structural type MCM-41 were synthesised in 1992 by the R&D team of the Mobil company using exactly this method.[100, 101]

Alkyltrimethylammonium halides or hydroxides with the common formula $C_nH_{2n+1}(CH_3)_3NX$ ($n = 12–18$; $X = Cl^-$, Br^-, OH^-) are usually employed as surfactants. The value of n determines the diameter of the resultant mesopores. Trimethylcetylammonium bromide n-$C_{16}H_{33}(CH_3)_3NBr$ is used most frequently giving rise to the mesopores of 3–4 nm. If the reaction pathway S^+I^- is utilised, at least a part of oxygen atoms in the inorganic walls of the material carry a negative charge. In contrast to uncharged SiOH groups, charged SiO^- groups cannot take part in the formation of strong Si–O–Si siloxane bonds through the polycondensation under the hydrothermal treatment, which gives rise to discontinuities within the silicate walls and to a low stability of the materials against hydrolysis.[88, 120] Due to the low hydrolytic stability, such a catalyst degrades structurally during the liquid-phase oxidation thus loosing its activity.[88, 106, 121–126] Attempts aimed at the additional structural stabilisation of the MCM-41 type catalysts with various chemical means (in particular, by addition of water-soluble organic or inorganic salts to the reaction mixture during the synthesis) often resulted in the collapse of the mesostructure and formation of disordered materials (see, for example, Refs 127 and 128).

The thermo- and hydrostability of MCM-41 can be enhanced by an additional hydrothermal treatment of the starting material with water.[129, 130] This procedure, however, leads to an increase in the thickness of the silicate walls (h_w), which is unacceptable for metal silicate catalysts, since a part of active sites can be trapped within the walls and thus become inaccessible for the substrates (see Section III). Alternatively, the stability of the silicate walls towards the reaction (aqueous) medium can be enhanced by their surface silylation with hydrophobic species, such as $(CH_3)_3SiCl$, $(CH_3)_3SiNHSi(CH_3)_3$, *etc.*,[131–138] or by specific doping, for instance, with aluminium.[88] The surface hydrophobicity of Ti-MCM-41 can also be increased by the removal of the template using extraction under supercritical conditions (CO_2 + MeOH).[139] Recently, a micromesoporous titanium silicate Ti-MMM-1, which combines structural motifs of TS-1 and Ti-MCM-41 in one phase, was synthesised using two types of surfactants, *viz.*, tetramethylammonium hydroxide and trimethylcetylammonium bromide on the first and second steps of the synthesis, respectively.[140]

The HMS type mesoporous silicate materials are formed at a pH close to 7 owing to the van der Waals interaction of uncharged surfactants (most typically, amines) with silicate particles (*i.e.*, the interaction type is $S^0\cdots I^0$).[73, 80, 87, 104, 141] The synthesis of Ti-HMS is usually carried out at room temperature.[73, 87, 104] These materials are characterised by larger thickness (and, respectively, by higher strength) of the silicate walls as compared to those synthesised through the reaction pathway S^+I^-. The small size of particles constituting the HMS type materials is responsible for the so-called 'texture mesoporosity'.[73] It has to be stressed, however, that the degree of structural ordering in such materials is rather low.[74, 104, 105]

‡ The long-range ordering can be reliably detected using X-ray diffraction at small angles (less than 6–8 deg), high-resolution electron microscopy and adsorption techniques (see Section III).

Table 1. The main types of mesoporous mesostructured titanium silicate materials.

Material	Surfactant	Lattice type	Mesopore diameter /nm	Wall thickness /nm	Ref.
Ti-MCM-41	$C_{16}H_{33}(CH_3)_3NOH$ or $C_{16}H_{33}(CH_3)_3NBr$	hexagonal	2.9–3.5	1.0–1.5	69, 72, 104
Ti-MMM	$C_{16}H_{33}(CH_3)_3NBr$	"	3.4–3.8	0.8–1.0	88, 106
Ti-MMM-2	$C_{16}H_{33}(CH_3)_3NBr$	"	3.2	1.0	116
Ti-MCM-48	$C_{16}H_{33}(CH_3)_3NBr$	cubic	2.3	–	102, 103
Ti-HMS	$C_{12}H_{25}NH_2$	hexagonal	2.7	1.9	73, 87, 104
Ti-SBA-1	$C_{16}H_{33}(CH_3)_3NBr$	cubic	2.0	–	115
Ti-SBA-15	$(EO)_{20}(PO)_{70}(EO)_{20}$ (see [a])	hexagonal	10.6–10.9	1.6–2.0	110
Ti-MSU-1	$C_{11}H_{23}O(CH_2CH_2O)_{12}H$	"	3.0	–	108
Ti-TUD-1	$(C_2H_5O)_3N$	see [b]	4.5–5.7	2.5–4.0	107

[a] Triblock copolymer polyethylene oxide–polypropylene oxide–polyethylene oxide (Pluronic P123). [b] A disordered three-dimensional framework of mesopores with similar sizes.

Recently, mesoporous silicate materials were synthesised through the reaction pathway $S^0 \cdots I^0$ with polyethylene oxide-based (PEO) oxygen-containing polymers as non-ionogenic surfactants.[108, 142] These surfactants are substantially less expensive than ionogenic alkylammonium salts and non-ionogenic aklylamines and, furthermore, they are non-toxic. Mesoporous titanium silicate Ti-MSU-1 was synthesised by addition of tetraethyl orthosilicate (TEOS) to a solution of amphiphilic surfactant Tergitol 15-S-12 [$C_{11\text{-}15}H_{23\text{-}31}O(CH_2CH_2O)_{12}H$] containing 5% of Ti.[108] The catalyst Ti-MSU-1 possesses a disordered hexagonal-like system of mesopores with a mean diameter of 3.0 nm. An alternative method for the synthesis of Ti-MSU-1 consists of the preparation of an aqueous solution of sodium silicate at pH > 9 followed by its mixing with acidic aqueous solution of non-ionogenic surfactant, *i.e.*, an amphiphilic diblock copolymer A_nB_m (A is a hydrophilic fragment, B is a hydrophobic fragment).§ The required heteroelement is then added to the reaction mixture (at a pH from 4 to 10). The materials obtained by this method are characterised by disordered arrangements of mesopores with similar diameters (from 1.5 nm to 30 nm, depending on the type of the surfactant used) separated from each other by walls with a thickness of >0.5 nm; the specific surface area of these materials is 300–1400 $m^2\ g^{-1}$. Such materials are thermostable but no information on their hydrolytic stability is available.

Mesoporous silicate materials SBA-3 and SBA-15 are synthesised in strongly acidic media at pH $\leqslant$ 1.5 (Refs 75, 104, 118, 143–146) through the reaction pathway $S^+A^-I^+$ using the electrostatic interaction of surfactant cations and uncharged silicon dioxide particles with partly protonated surface silanol groups [*i.e.*, I^+ can be formulated as $H_2O^+Si(OH)_3$] mediated by auxilliary anions ($A^- = Cl^-$ or other anions). Alkylammonium salts,[75, 104, 118] oligomeric alkylpolyethylene oxide with the general formula $C_nH_{2n+1}(EO)_mH$ ($n = 12-18$, $m = 2-25$) and block copolymers of oligomeric polyalkylene oxides $(EO)_n(PO)_m(EO)_p$ ($0 < n < 100$, $5 < m < 150$, $0 \leqslant p < 100$) can be used as surfactants.[118, 142–147] This approach makes it possible to achieve nearly the same degree of ordering of the mesostructure and control over the structural parameters as in the systems produced by the reaction pathway S^+I^-. The resulting materials are characterised by exceptionally high hydrostability,[86, 142–146] since silicon dioxide particles involved into the formation of the mesostructure contain no ionised oxygen atoms that prevent complete polycondensation of siloxane links within the silicate walls.

Therefore, according to the available literature data, the silicate walls of mesoporous mesophase materials, which are stable against the action of water, can be formed only in strongly acidic media. However, the introduction of metal cations (Ti, Al, V, *etc.*) into silicate matrices becomes a problem in these media.[86, 95, 104, 113] In particular, aluminium remains virtually unbound within the silicate walls being present in the forms that are readily leached.[86] The synthesis of Ti-MCM-41,[104] Ti-SBA-15 [113] and Ti-SBA-1 [115] in strongly acidic media requires a large excess of titanium, since its incorporation into the silicate walls is hindered by high solubility of Ti-containing species at this pH.[104] This issue can be overcome only by increasing pH to a value that provides sufficient level of the hydrolysis of dopant transition metal ions. In the majority of cases, this is achieved at a pH from 2.5 to 4.

The first attempt to incorporate titanium into a silicate matrix at a pH of 2.6–3.2 was undertaken in the beginning of 2000 with the synthesis of Ti-SBA-15 using $(EO)_{20}(PO)_{70}(EO)_{20}$ as a surfactant.[110] Recently, a novel mesophase material, Ti-MMM-2, which manifests both thermohydrostability and resistivity to the leaching of the active component (titanium), has been synthesised using this approach with $C_{16}H_{33}(CH_3)_3NBr$ as a surfactant.[116, 148] The Ti-MMM-2 structure is generated in two steps. In the first step, a mixture containing positively charged silicon hydroxy complexes, titanium compounds and a surfactant is prepared while the pH is maintained in the range of 0.5–1.5. In the second step, a certain amount of a basic sodium silicate solution is added to the reaction mixture to increase and maintain the pH to a value in the range from 2.5 to 7.0. Then the mixture is subjected to a hydrothermal treatment.

Recently, two new methods for the synthesis of Ti-SBA-15 have been reported, the first one combines the hydrothermal treatment with the microwave irradiation,[111] the second is based solely on the microwave irradiation.[149, 150] Most frequently, titanium is grafted onto the surface of presynthesised silicate SBA-15 in the post-synthesis step.[95, 96, 99, 111, 112]

In the vast majority of published works, expensive tetraethyl orthosilicate was employed as a source of silicon. In recent years, there have been several reports on the use of less expensive and more available silicon sources, *viz.*, water-soluble inorganic sodium silicates $Na_2Si_2O_5$ and Na_2SiO_3 [106, 110, 116, 142, 144, 145] and 'liquid glass' (28%–30% of SiO_2 and 9%–10% of Na_2O).[121] Alternatively, H_2SiF_6 (Ref. 151) and colloidal dispersions of SiO_2 (Refs 121, 130) can be used. As a titanium source, titanium alkoxides, $Ti(OEt)_4$, $Ti(OPr^i)_4$, $Ti(OBu^n)_4$, and so on were utilised. The hydrolysis of organotitanium derivatives has to be strictly controlled in order to prevent their polymerisation.[152, 153]

Inorganic titanium compounds, *e.g.*, $TiCl_3$,[113] $TiCl_4$, $K_2TiO(C_2O_4)_2$, $(NH_4)_2TiF_6$,[154] $(NH_4)_3[Ti(O_2)F_5]$,[155] $Ti(SO_4)_2$ (Refs 110, 116, 148, 154) have recently started to be used in the synthesis of mesoporous mesophase titanium silicates. However, partial formation of oligomerised particles of titanium oxide was observed in all those cases except for the use of $(NH_4)_3[Ti(O_2)F_5]$ in the synthesis of Ti-MCM-41 [155] and of the system $Ti(SO_4)_2$–H_2SO_4 in the synthesis of Ti-MMM-2.[116] The addition of complex-forming agents (*e.g.*, H_2O_2, acetylacetone, polyalcohols, aminoalcohols, *etc.*) often decelerates the hydrolysis and, respectively, suppresses the undesired polymerisation of titanium species.[107, 113, 145, 153] Additionally, this technique makes it possible to increase the content of titanium in the silicate matrix up to an Si : Ti ratio of 1.9.[153] A synthesis of Ti-MCM-41 from a structure-forming precursor simultaneously containing silicon and titanium, *viz.*, a copolymer of diethoxysiloxane with diethyltitanate $[(C_2H_5O)_2SiO]_n[(C_2H_5O)_2TiO]_m$, has recently been reported.[131]

The question on the formation mechanism of mesoporous mesostructured silicates remains a subject of debate.[74, 76, 77, 82, 83, 88–90, 101] The model of 'liquid crystalline ordering' was one of the first mechanisms proposed.[101] According to this mechanism, surfactant molecules self-assemble first into spherical micelles and then into cylinders. The latter are further arranged to form a hexagonal packing. The resultant 'liquid crystals' are then covered with a shell of inorganic particles.

According to another hypothesis,[156] no ordered phase of 'liquid crystals' is involved. The surfactant molecules assembled into cylinders interact with inorganic particles, which gives rise to the growth of a silicate layer atop the external surface of micelles and only after that the cylinders are arranged into a hexagonal packing.

Nevertheless, the majority of authors adopt the cooperative mechanism, which implies that electrostatic interactions between inorganic ions and surfactant molecules play the key role and govern the morphology of the resultant mesostructure.[157] This mechanism is depicted schematically in Fig. 2. In the first step (Fig. 2 *a*), the ion pairs combining inorganic particles and surfactant molecules are formed due to the electrostatic interactions. In the second step (Fig. 2 *b*), the ion pairs self-assemble into cylindrical micelles. Depending on the conditions, the cylinders are further arranged yielding a hexagonal (Fig. 2 *c*), cubic or lamellar structure. In the last step, the inorganic particles are condensed giving rise to the emergence of a strong framework.

According to an alternative suggestion, the inorganic silicate particles self-assemble into layers separated from each other by

§ Triblock copolymers polyethylene oxide–polypropylene oxide–polyethylene oxide, such as $(EO)_{20}(PO)_{70}(EO)_{20}$ or $(EO)_{20}(PO)_{30}(EO)_{20}$, are most typically used as non-ionogenic surfactants.

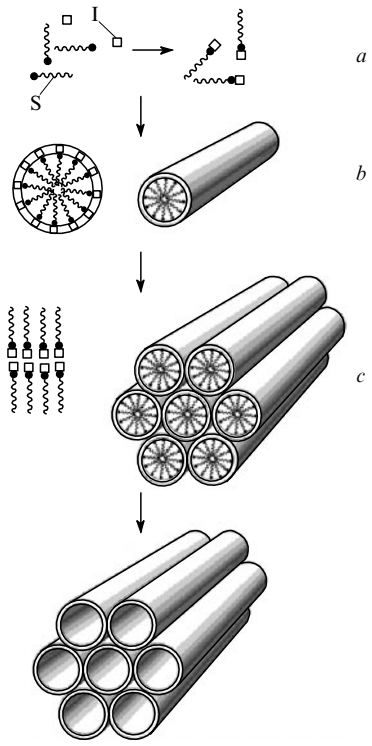


Figure 2. A scheme depicting the cooperative mechanism of the formation of mesostructured silicates;
(*a*–*c*) — see text.

rows of cylindrical micelles formed by the surfactant molecules.[158] Upon ageing, the layers become puckered and undergo cross-linking around the micelles thus yielding a hexagonal packing. Yet another model assumes that layers of surfactant and inorganic silicate particles are initially formed in the synthesis of MCM-41.[159] In the course of the polymerisation of silicate particles, the charge density is redistributed, which gives rise to the contortion of the layers and transformation of the lamellar mesostructure into the hexagonal one. However, the detailed consideration of modern concepts concerning the mechanisms of the mesostructure formation lies beyond the scope of the present review.

2. Amorphous mesoporous mixed oxides TiO_2-SiO_2

Amorphous mixed oxides TiO_2-SiO_2 (*i.e.*, aerogels and xerogels) represent another important class of mesoporous titanium silicate materials.[81, 84, 85, 160–172] In terms of the structure, aerogels and xerogels can be described as long chains composed of primary silica particles (globules) touching each other only in a few points (see Fig. 1 *b*).[173] Aerogels are characterised by a mean pore size of >100 Å, whereas the mean pore size of xerogels is 5–20 Å. The typical specific surface area of xerogels is 300–700 $m^2\ g^{-1}$. Aerogels manifest larger specific surface areas ($>1000\ m^2\ g^{-1}$) and simultaneously very high porosity (the specific volume of pores can be as high as 3–3.5 $cm^3\ g^{-1}$).

Mixed oxides TiO_2-SiO_2 are routinely prepared by the sol–gel technology[81, 173–175] that includes five major steps: (1) hydrolysis of silicon and titanium alkoxides, (2) polycondensation of alkoxides and growth of sol particles, (3) sol aggregation into an alcogel network, (4) gel ageing and (5) drying. The significant difference between the hydrolysis rates of silicon and titanium alkoxides makes certain problems in the preparation of materials with a homogeneous distribution of titanium ions over the silicon sol–gel matrix. These difficulties can be overcome by the utilisation of prehydrolised TEOS[84, 160, 161, 171] or tetramethyl orthosilicate (TMOS), which is more reactive towards hydrolysis, or by modification of titanium tetraisopropoxide with peroxide or chelating agents, such as acetylacetone, cyclohexane-1,4-diol, *etc.*[164, 165, 167–171, 176]

Aerogels are produced from alcogels by their drying under the conditions of a gradual increase in the temperature and solvent vapour pressure up to supercritical values. This results in the elimination of the 'liquid–vapour' interface and the related reduction of capillary pressure, which under the normal drying conditions in narrow pores can reach values equivalent to hundreds atmospheres and thus decrease the initial volume of the gel several-fold. The supercritical drying can be classified into high-temperature and low-temperature ones.[81, 163, 167] In the former case, alcohols are used as solvents, whereas CO_2 is utilised in the latter case. The drying under the supercritical conditions makes it possible to avoid significant structural modifications of the starting alcogel. Xerogels are produced by the ordinary thermal drying of alcogels.

Prior to the 1980s, mixed oxides TiO_2-SiO_2 were synthesised with the use of either acidic or basic catalysis. The use of basic catalysts gives rise to gels composed of large particles with wide pores between them, whereas, finely structured gels composed of small particles separated from each other by narrow pores are formed under the conditions of acid catalysis. The latter structure is extremely fragile and breaks down to a significant extent even upon drying in supercritical CO_2. As a result, the specific volume of pores in aerogels prepared with the use of acidic catalysts typically does not exceed 1 $cm^3\ g^{-1}$.[168]

In 1982, a new convenient method for the control over the structure of synthetic silica gels was suggested. It employs a two-step sol–gel procedure with the subsequent utilisation of acidic and basic (amine) catalysts in the first (partial hydrolysis and condensation) and second (polycondensation) steps, respectively.[177] This synthetic scheme enables stricter control over the structure of the resultant gel. In the first step, the chain-length distribution of alkoxide oligomers can be efficiently adjusted and various forms of particles can be deliberately generated (from active monomers to virtually completely condensed colloidal particles). In the second step, further growth of particles generated and the gel formation process can be finely tuned. The use of basic catalysts in this step provides more efficient polycondensation and enhances both the strength of the resultant material and its porosity. This technique was successfully applied to the synthesis of mixed aerogels TiO_2-SiO_2 affording materials with the specific pore volume of 2 $cm^3\ g^{-1}$.[178, 179] As has been established recently,[126, 180, 181] a partial or complete replacement of traditional silicon alkoxides by less expensive ethyl silicate-40 (ES-40, the commercially available form of ethoxypolysiloxane; acidic hydrolysis of ES-40 yields low-molecular-weight polysilicate hydroxide[174]) enables the preparation of aerogels TiO_2-SiO_2 with the specific pore volume as high as 3 $cm^3\ g^{-1}$.

A substantial drawback of mixed oxides (primarily, of aerogels) is the collapse of their porous structure under the action of polar solvents (water, in particular). As has been demosntrated in a number of studies, the surface hydrophobisation of aerogels or the introduction of hydrophobic additives during the sol–gel synthesis often increases their activity and stability towards the reaction media.[182–187] Methods for the production of composite mesoporous materials utilising presynthesised TS-1 as a component for the subsequent step of the sol–gel synthesis[188] are currently under development.

III. Methods of physicochemical characterisation of mesoporous titanium silicates

1. X-Ray diffraction

X-Ray diffraction (XRD) gives valuable information in studies of the hydrothermostability of mesostructured titanium silicates.[88, 110, 116, 121, 125] XRD patterns of mesostructured materials, such as Ti-MCM-41, Ti-MMM, Ti-HMS and Ti-SBA-15, which are characterised by the hexagonal packing of cylindrical (or hexagonal prismatic) mesopores, reveal an intense peak (100)

and three weaker reflections, (110), (200) and (210).[72, 77, 83, 86, 87] These reflections are indexed in a hexagonal lattice with the unit cell parameter given by $a_0 = 2d_{100}/\sqrt{3}$. Owing to the high degree of structural order in the mesoporous mesophase materials, the lattice parameter a_0 is constant. For the mesostructured systems under consideration this means that the diffraction patterns reveal narrow peaks with full widths at half maximum ($w_{h/2}$) of $(0.07-0.09)^\circ$ 2θ, which is close to the instrumental broadening. According to the experimental finding, the structure of Ti-MMM is more ordered than that of Ti-MCM-41 and Ti-HMS, as described in the literature.[104–106] The peaks observed in the XRD pattern of Ti-MMM are substantially narrower with $w_{h/2} = (0.08-0.18)^\circ$ 2θ and have symmetrical shapes. Meanwhile, the widths of the (100) reflection are $w_{h/2} = (0.40-0.70)^\circ$ 2θ and $> 0.50^\circ$ 2θ for Ti-MCM-41 and Ti-HMS, respectively; in the latter case, only one reflection is observed in the pattern, whereas the former also reveal feebly marked (110), (200) and (210) peaks (Fig. 3).[75, 104]

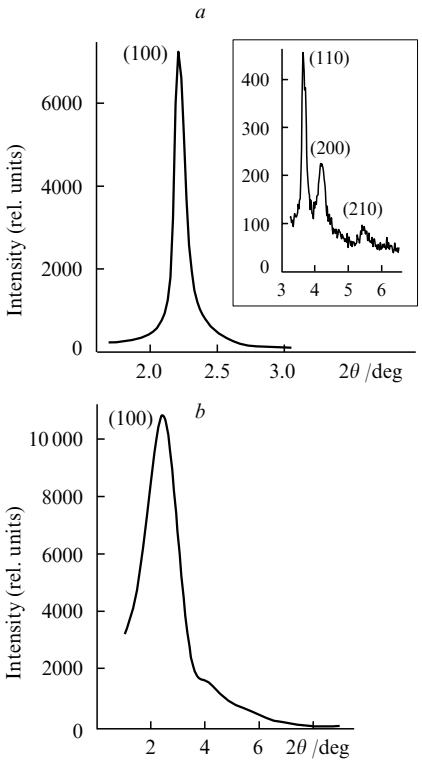


Figure 3. The X-ray diffraction patterns of the mesostructured titanium silicates Ti-MMM (*a*) and Ti-HMS (*b*).[104, 105]

It was estbalished that the lattice parameters of calcined ordered titanium silicates (TS-1, Ti-ZSM-48, Ti-MCM-41 and Ti-HMS) linearly increase with an increase in the titanium content (up to 2%–2.5%).[35, 45, 87, 104] This experimental fact can be rationalised assuming that the substitution of titanium for silicon is isomorphous. Since the ionic radius of titanium is larger than that of silicon, the substitution should give rise to a dilatation of the unit cell. Based on this observation, it was concluded [189] that the maximum titanium content, which can be accomodated in the TS-1 silicate matrix, is 2.5 mass %. A further increase in the titanium content does not result in a lattice dilatation, which indicates the appearance of non-structural titanium in TS-1. An increase in the titanium content in Ti-MMM and Ti-MCM-41 above 3 mass% gives rise to a significant loss in their structural order, which is manifested in the broadening of peaks in the XRD patterns.[88, 105, 190] It is of note that this is not accompanied by any noticeable changes in the lattice parameter a_0.[125]

A recently developed method of structure simulation based on the quantitative analysis of intensities of diffraction reflections made it possible to recover the electron density distribution maps for a number of hexagonal mesostructured materials and reveal important information on the shape of the mesopores, the thickness and electronic structure of the silicate walls and the structure–chemical composition relation for these materials.[88, 120, 191]

Mixed oxides TiO_2-SiO_2 are amorphous as regards X-ray diffraction due to the both lack of short- and long-range order.

2. Low-temperature nitrogen adsorption

Low-temperature (at 77 K) N_2 adsorption gives quantitative information concerning the texture of titanium silicate mesoporous materials, including specific surface area (A_m), specific volume (V_m) and mean diameter of the mesopores (d_m). The cylindrical shape of the mesopores in titanium silicates Ti-MCM-41, Ti-MMM, Ti-HMS and Ti-SBA-15 determines a characteristic shape of the adsorption isotherm,[73, 74, 77, 83, 192] which is classified as type IV according to the IUPAC nomenclature (Fig. 4). Assuming zero scatter in the pore diameters, the range of pressures $\Delta(P/P_0)$, at which the capillary condensation should occur upon nitrogen adsorption, is rather narrow (0.06–0.08). Exactly these small values of $\Delta(P/P_0)$ are typical of type Ti-MMM materials (Fig. 4*a*), which fully supports the higher degree of their ordering as compared to, for instance, Ti-HMS, where $\Delta(P/P_0) > 0.2$ (Fig. 4*b*).[105, 106] The strict constancy of the diameters of all cylindrical mesopores along their lengths requires the adsorption and desorbtion curves of nitrogen adsorption isotherms to be identical, at least, for $d_m \leqslant 4.5$ nm.[88, 193] Investigations into the N_2 adsorption demonstrated that the texture porosity of Ti-HMS is substantially higher than that of Ti-MCM-41. In particular, the specific volumes of mesopores (with a diameter of 10–30 nm) between fine particles of Ti-HMS and Ti-MCM-41 are 1.11 and 0.03 $cm^3\ g^{-1}$, respectively.[73]

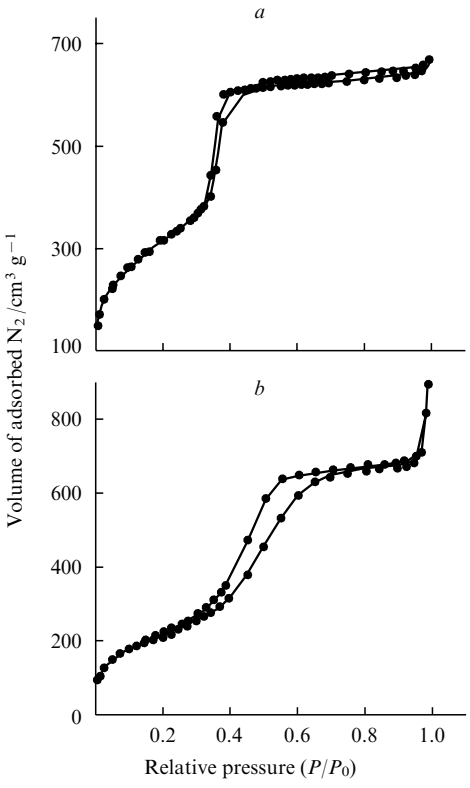


Figure 4. The isotherms of N_2 adsorption on the mesostructured titanium silicates Ti-MMM (*a*) and Ti-HMS (*b*).[105]

Most typically, aerogels (they also manifest the type IV adsorption isotherms) do not contain micropores, whereas both micro- and mesopores are usually present in xerogels. Most frequently, xerogels manifest the type I isotherms. In order to estimate the texture parameters of mixed oxides TiO_2-SiO_2 (including aerogels and mesoporous xerogels), which are characterised by a broad size distribution of pores (Fig. 5), a modification of the Kelvin equation is normally applied, which takes into account the thickness of the multilayer of adsorbed molecules (it is the so-called BJH, or Barrett–Joyner–Halenda, method). This calculation, however, neglects pores smaller than 17 Å.[84]

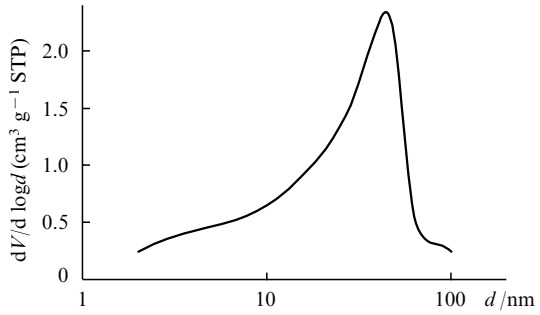


Figure 5. The size distribution of pores in the aerogel TiO_2-SiO_2 (20% TiO_2) calculated from the desorption part of the N_2 adsorption isotherm (273 K, 1 atm).[164]
STP is standart temperature and pressure.

The BJH method is employed by the majority of authors for the calculation of texture parameters of mesostructured titanium silicates. Nevertheless, Fenelonov *et al.*[194] proposed a more accurate method for estimating the specific surface area, volume and size of the mesopores in such materials based on the combined structural and adsorption approach. It assumes that the following relations are held for a hexagonal (honeycomb) structure:

$$a_0 = d_m + h_w,$$
$$d_m = a_0(\varepsilon_m)^{1/2},$$

where ε_m is the porosity determined from the specific area of mesopores and real density (ρ) according to the equation

$$\varepsilon_m = \frac{V_m\rho}{1 + V_m\rho}.$$

The specific volume of mesopores can be estimated from the nitrogen adsorption isotherms measured at 77 K by standard procedures. For the determination of the specific volume V_m, external surface area (A_{ext}) and total surface area (A_Σ), the widely adopted comparison method is utilised.[194] The specific surface area of mesopores (A_m) is calculated by the equation

$$A_m = A_\Sigma - A_{ext}.$$

Table 2 lists the values of the texture parameters of four titanium silicates, *viz.*, Ti-HMS, Ti-MMM, Ti-MMM-2 and Ti-SBA-15 with the hexagonal packing of the mesopores, determined by the method described above. These results unambiguously indicate that the degree of structural ordering decreases along the series Ti-SBA-15 ~ Ti-MMM > Ti-MMM-2 > Ti-HMS. It was found that the size of the mesopores and the thickness of the silicate walls in Ti-SBA-15 are substantially larger than those in Ti-MMM and Ti-MMM-2. The thickness of the walls in Ti-MCM-41 increases with an increase in the titanium content.[195]

3. Water adsorption

The adsorption and, consequently, catalytic properties of titanium silicates (*i.e.*, their activities and selectivities) as well as their stability against reaction media are determined to a large extent by their surface structures. According to the published data,[45, 74, 77, 87, 101, 196, 197] microporous TS-1 possesses a hydrophobic surface, in contrast to mesoporous materials, such as Ti-MCM-41, Ti-HMS, *etc.*, which are characterised by hydrophilic surfaces owing to the presence of a large amount of the SiOH groups. Several types of such groups can occur on the surface of mesostructured silicates, in particular, free, H-bonded and coupled ones.[198] Only free and coupled SiOH groups are active towards the silylation upon hydrophobisation.

The surface hydrophobicity (or hydrophilicity) of titanium silicates can be evaluated using thermogravimetry by measuring mass losses due to water removal from the surface upon controlled heating.[133, 134] Another modification of the thermogravimetric analysis consists of masuring the mass gain by evacuated or calcined samples in air with a certain humidity.[132] According to this method, the ability of mesoporous materials to absorb water decreases in the series aerogel TiO_2-SiO_2 > Ti-MMM-2 > xerogel TiO_2-SiO_2 > Ti-SBA-15 > Ti-MMM ≫ hydrophobised aerogel TiO_2-SiO_2 (Fig. 6). The saturation of identical

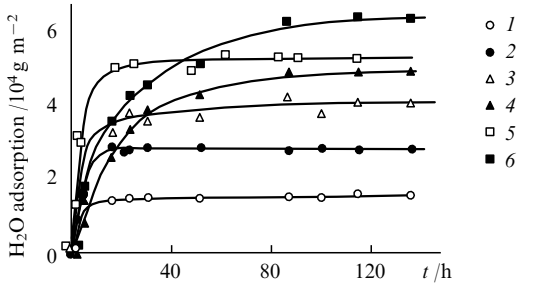


Figure 6. The kinetics of water adsorption on mesoporous titanium silicates (20 °C, relative humidity of 100%).[132]
(*1*) Hydrophobised aerogel TiO_2-SiO_2, (*2*) Ti-MMM, (*3*) Ti-SBA-15, (*4*) xerogel TiO_2-SiO_2, (*5*) Ti-MMM-2, (*6*) aerogel TiO_2-SiO_2.

Table 2. Structural and texture parameters of selected titanium silicate materials calculated from the results of the combined structural-adsorption method.[194]

Material	Ti content (mass %) (Si : Ti ratio)	pH [a]	Texture parameters					Structural parameters		Ref.
			A_m /m² g⁻¹	A_{ext} /m² g⁻¹	V_m /cm³ g⁻¹	d_m /nm	h_w /nm	a_0 /nm	$w_{h/2}$ /deg 2θ	
Ti-HMS	2.60 (30)	7.0	627	170	0.89	–	–	–	>0.5	105
Ti-MMM-2	1.67 (46)	3.0	1147	51	0.74	3.2	1.0	4.2	0.36	116
Ti-MMM	1.53 (49)	9.0	1059	53	0.91	3.8	0.8	4.6	0.078	105
Ti-SBA-15	2.05 (38)	3.2	573	30	1.34	10.6	1.7	12.2	0.054	110

[a] pH of the reaction mixture during the synthesis.

cylindrical pores with water proceeds faster and thus the adsorption equilibrium is established over a shorter time.

4. ^{29}Si NMR with the magic-angle spinning

The ^{29}Si nuclear magnetic resonance spectroscopy with line narrowing by the magic-angle spinning (NMR-MAS) provides important supplementary information on the structure of walls in titanium silicates, in particular, on their surface hydrophobicity (hydrophilicity) and the degree of polymerisation of siloxane links (including the possibility of the real-time synthesis monitoring).[77, 83, 84, 104, 118, 130, 134, 138, 179, 197, 199] Despite some ambiguities in the deconvolution of overlapping signals in the ^{29}Si NMR-MAS spectra into single components, this technique makes it possible to quantify the number Q^n of sites with specific coordination types, *i.e.*, $Si(OSi)_n(OH)_{4-n}$ ($n = 2-4$) in silicates (Fig. 7). The ratio between Q^n values depends on the degree of condensation of silicon in the silicate walls, which, in turn, is a function of the material preparation procedure. Using this technique, it was demonstrated that fluorides promote the polymerisation of silicon compounds; the addition of fluorides into the reaction mixture during the synthesis enables the preparation of materials with a higher degree of condensation. In particular, in the case of SBA-15, the ratios $Q^3:Q^4$ are 0.34–0.62 and 0.74–0.78 in the presence and in the absence of fluorides, respectively.[199] The solid-state ^{29}Si NMR-MAS was used to establish that the silicate M41S undergoes a structural change under the conditions of hydrothermal treatment such that the degree of polymerisation of siloxane links in the walls increases.[130] The ^{29}Si NMR-MAS technique is widely applied to quantify the degree of surface silylation of mesostructured materials after their hydrophobisation.[134, 138, 186, 200]

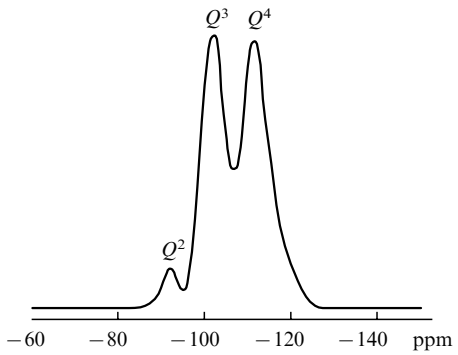


Figure 7. The ^{29}Si NMR-MAS spectrum of the titanium silicate Ti-MCM-41 (2.0% Ti).[104]

Similar ratios of Q^n were found for mixed oxides with a low titanium content synthesised by the traditional method in an acidic medium with TEOS as a silicon source[201, 202] and by the two-step method (see Section II) from ES-40.[181] Meanwhile, smaller Q^4 and larger Q^2 and Q^3 were determined by ^{29}Si NMR-MAS for the TiO_2-SiO_2 samples prepared by the two-step method from TEOS.[179] Based on these results, it was concluded that the utilisation of ES-40 in the synthesis of mixed oxides TiO_2-SiO_2 increases the degree of silicon self-condensation (which correlates with the number of sites with the coordination type Q^4). It was found that the proportion of Q^4 relative to Q^3 in mixed oxides TiO_2-SiO_2 increases by approximately 20% (from 40% to 60%) with an increase in the titanium content, while the number of sites with the coordination type Q^2 remains virtually constant ($< 10\%$).[181] A similar effect was observed by other authors,[104, 200] which allowed them to conclude that the introduction of a small amount of titanium increases the degree of silicon condensation. However, if the titanium content exceeds a certain critical value, the degree of silicon condensation decreases and the respective signals in the ^{29}Si NMR-MAS spectra become broader.[200]

5. Electron microscopy

Scanning electron microsopy (SEM), transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) are used for the elucidation of the texture and morphological properties of titanium silicates, including the size and shape of particles and pores. As has been established, the particles of Ti-HMS and Ti-MCM-41 are characterised by different morphologies. The former represent small spherical particles with a diameter of 0.2–0.3 μm.[74] Electron micrographs of Ti-MMM (Fig. 8 *a*), Ti-HMS and Ti-MCM-41 (Ref. 73) samples clearly reveal a long-range-ordered porous structure with a hexagonal packing of identical mesopores. In contrast, a micrograph of Ti-MMM-2 (Fig. 8 *b*)[116] reveals domains of ordered mesopores, the degree of their ordering being substantially lower than that in Ti-MMM.

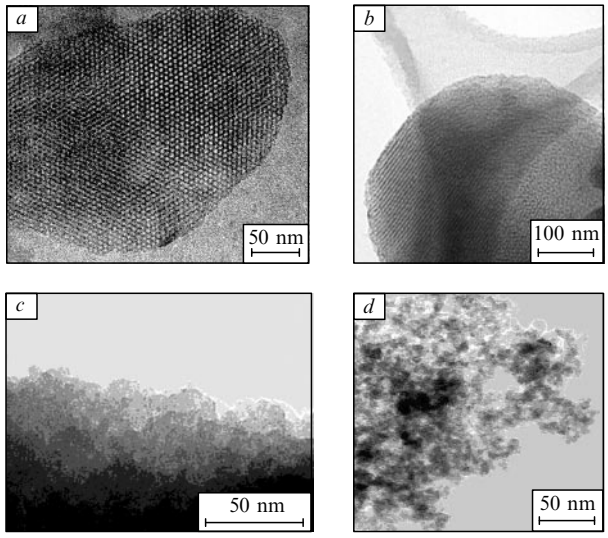


Figure 8. The electron micrographs of Ti-MMM (*a*), Ti-MMM-2 (*b*), xerogel TiO_2-SiO_2 (*c*) and aerogel TiO_2-SiO_2 (*d*).[116, 181]

Microdomains of crystalline TiO_2 smaller than 1–2 nm in mixed titana–silica, which are invisible for X-ray diffraction, can be identified using HREM.[81, 183, 203] According to TEM, samples of aerogels TiO_2-SiO_2 with the titanium content of 2 mass % – 17 mass % represent porous aggregates of interconnected amorphous particles (Fig. 8 *d*).[81, 181, 203] The size of primary aerogel particles is 3–5 nm and their shape is close to spherical. The size of primary SiO_2 particles in xerogels TiO_2-SiO_2 is virtually the same as in aerogels, but the xerogels are characterised by a significantly denser packing of the primary particles within the aggregates, which gives rise to a substantial contraction of the interparticle distance (Fig. 8 *c*). Furthermore, the morphology of particles resemble a 'crumbled glass'.[81, 181, 203, 204] According to SEM, the use of a combined method for the preparation of mixed oxides TiO_2-SiO_2 involving suspending a mixed sol in an organic solvent (decanol or hexane) followed by its gelation affords spherical particles with a mean diameter of 50 μm.[171]

6. Diffuse reflectance optical spectroscopy

Diffuse reflectance ultraviolet (DRUV) spectroscopy is the simplest method for the determination of the electronic state of Ti(IV) ions in a solid silicate matrix. The charge transfer from a ligand X ($X = HO^-$, SiO^- or TiO^-) to a vacant d-orbital of the Ti^{4+} ions (ligand-to-metal charge transfer, LMCT) can be calculated from

the optical electronegativities (χ_{opt}) of the ligand X and the Ti^{4+} ion:

$$Ti^{4+}|O^{2-} + h\nu \longrightarrow Ti^{3+}|O^{-},$$

$$\nu = 30000\,[\chi_{opt}(X) - \chi_{opt}(Ti)].$$

With an increase in the coordination number of Ti(IV) from 4 to 6, the value of χ_{opt}(Ti) increases from 1.85 to 2.05.[84] Therefore, in the case of Ti(IV) ions in the octahedral environment, the LMCT band should be red-shifted with respect to Ti(IV) ions in the tetrahedral environment.

According to numerous literature data,[45, 68, 74, 77, 84, 87, 104, 197] the band position in the DRUV spectra of titanium silicates depends, in addition to the coordination number of Ti(IV), on the proximity of other titanium ions, *i.e.*, on the degree of dispersion of the titanium ions over the silicate matrix. The band at 205–208 nm observed in the spectrum of evacuated TS-1 is assigned to isolated titanium ions in the tetrahedral coordination environment.[41, 45, 197, 205, 206] A treatment of TS-1 with water vapour or ammonia gives rise to an increase in the Ti coordination number, which is manifested in a reversible red-shift of the spectral maximum to 210–225 nm.[68, 207, 208] The DRUV spectra of mesoporous titanium silicates with the titanium content below 2.5% typically reveal a main peak centred at 220–230 nm sometimes with a shoulder at 250–280 nm.[74, 77, 84, 87] Table 3 summarises the literature data on the DRUV spectra of TS-1, Ti-MCM-41, Ti-MMM-2, mixed oxides TiO_2-SiO_2 and anatase (TiO_2). The band centred at 220–230 nm in the spectra of mesoporous titanium silicates is usually attributed to isolated Ti(IV) ions in the penta coordinated, octahedral (Refs 45, 72, 74, 77, 110, 116, 207, 208) or distorted tetrahedral coordination environment.[104, 107, 209] This assignment is supported by the fact that there is no substantial blue-shift of the band upon the thermal dehydration of Ti-MCM-41 and Ti-HMS.[104] Since the bands corresponding to octahedral Ti(IV) in anatase and rutile are observed at 310–330 nm and 400 nm, respectively,[45, 84, 197] the red-shift of the main band to this region or emergence of a shoulder in the spectra of titanium silicates is typically interpreted as clusterisation of octahedrally coordinated titanium ions due to the formation of the Ti–O–Ti bonds.[41, 68, 77, 110, 167, 205, 209, 210] This interpretation agrees with the red-shift of the main band observed with an increase in the titanium content.[87, 105, 106] Meanwhile, taking into account that the intensity of the band at 270 nm is reduced upon the thermal dehydration or evacuation of titanium silicates, it can be attributed to isolated titanium ions in a highly hydrated or distorted octahedral environment.[68, 87, 104, 207, 211]

Table 3. Spectral parameters of selected titanium silicates.

Material	Parameter (method)			Ref.
	position of the maximum of the LMCT band /nm (DRUV)	pre-edge peak intensity (%) (XANES)	the everage Ti–O bond length /Å (EXAFS)	
TS-1	205–208	75	1.80–1.81	45
TiO_2-SiO_2	220–240	58–75[a] (32)[b]	1.81–1.82	84, 181
Ti-MCM-41	220–230	77[a] (33)[b]	1.81	77
Ti-MMM-2	221	(30)[b]	–	116
Anatase	310–330	< 5	1.94	45

[a] Data for evacuated samples. [b] Data for the samples in air.

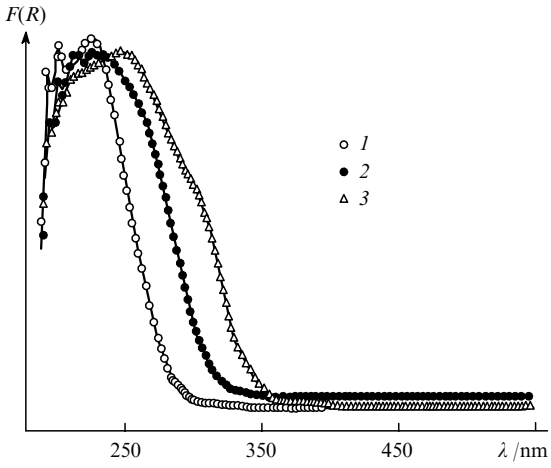


Figure 9. The DRUV spectra of mesoporous titanium silicates with similar titanium loadings.[11, 125, 126]
(*1*) Ti-MMM (1.89% Ti), (*2*) aerogel TiO_2-SiO_2 (1.68% Ti), (*3*) Ti-SBA-15 (2.05% Ti).

Figure 9 compares the DRUV spectra of Ti-MMM, aerogels TiO_2-SiO_2 and Ti-SBA-15 with similar titanium contents.¶ According to the spectral assignment described above, Ti-MMM and the aerogel contain isolated titanium ions with the coordination numbers of 4, 5 and/or 6. In the case of Ti-SBA-15, the band is red-shifted and broadened. Taking into account that the spectrum does not change after calcination of the sample, this indicates the presence of clusterised titanium ions.[110]

7. XANES and EXAFS

XANES spectroscopy (X-ray Absorption Near-Edge Structure) is substantially more expensive than DRUV, and thus it is utilised less frequently. Nevertheless, it gives important supplementary information on the coordination environment of titanium in titanium silicates. XANES spectra at the Ti K-edge of both ordered titanium silicates, such as TS-1,[45, 197, 207] Ti-Beta,[45] Ti-MCM-41,[72, 77, 92, 212, 213] Ti-HMS[104] and Ti-MMM-2,[116] and amorphous mixed oxides TiO_2-SiO_2[84, 181, 214, 215] containing only finely dispersed titanium ions reveal a distinct pre-edge peak (due to the electronic transition $1s \rightarrow 3d$) with the intensity strongly dependent on the degree of hydration of titanium ions (*i.e.*, on their coordination numbers). Dehydrated titanium ions in the tetrahedral coordination environment give rise to the pre-edge peak with an intensity of ~75%–80% of the X-ray absorption edge jump and the full width at half maximum of ~1.5 eV. Meanwhile, the pre-edge peak with the intensity of ~30% corresponds to penta(hexa) coordinated titanium ions, which are formed in the reaction of tetrahedral titanium ions with water.[45, 77, 92, 104, 197, 200, 207] The XANES spectra of rutile and anatase manifest three weak pre-edge peaks, which thus correspond to clusterised octahedral titanium ions.[45, 197, 214] Therefore, if a XANES spectrum of a mesoporous titanium silicate material manifests these three weak peaks, then it might be concluded that the sample contains clusterised octahedral titanium ions.[110, 214, 216, 217] Figure 10 depicts the XANES spectra of mesoporous titanium silicates Ti-MMM-2 and Ti-SBA-15 and of aerogel TiO_2-SiO_2. The shape and intensity of the pre-edge peaks in the spectra of Ti-MMM-2 and aerogel indicate the presence of isolated penta(hexa) coordinated Ti(IV) ions in these samples, whereas Ti-SBA-15 undoubtedly contains oligomerised titanium ions. Therefore, the XANES results are fully consistent

¶ The DRUV spectra are given in the Kubelka–Munk units $F(R) = (1-R)^2/2R$ (R is the reflectivity index).

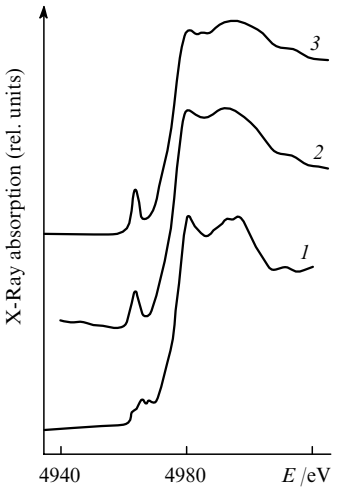


Figure 10. The XANES spectra of mesoporous titanium silicates measured in air.[110, 116, 190]
(*1*) Ti-SBA-15 (2.05% Ti), (*2*) Ti-MMM-2 (1.68% Ti), (*3*) aerogel TiO_2-SiO_2 (3.68% Ti).

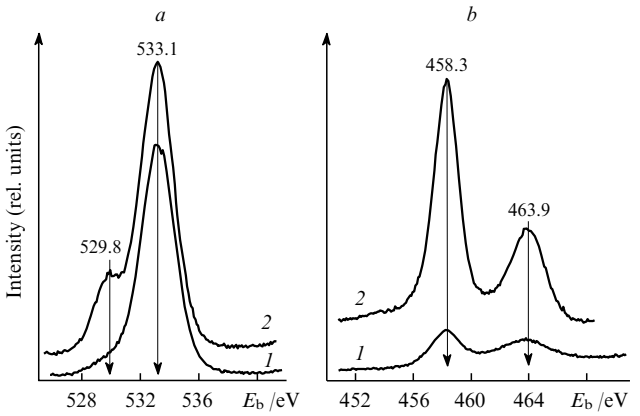


Figure 11. The XPS spectra of the mesoporous titanium silicate Ti-SBA-15 with the Ti loading of 2.05% (*1*) and 7.17% (*2*).[110]
(*a*) O(1s) core-level photoemission line, (*b*) Ti(2p) core-level photoemission line.

with the aforementioned DRUV spectral data.[110, 116, 181] According to Table 3, the intensity of the pre-edge peak in the XANES spectra of Ti-MCM-41 and mixed oxides TiO_2-SiO_2 increases upon evacuation, which implies that the titanium ions are present in the samples dominantly in the isolated octahedral sites under atmospheric conditions but are converted into the tetrahedral state upon complete dehydration.[77, 84, 104, 214]

The elucidation of titanium silicates by means of EXAFS spectroscopy (Extended X-Ray Absorption Fine Structure) reveals information on the number of oxygen atoms and Ti–O bond lengths in the first coordination sphere of the titanium ions and on distances between the titanium ions and second-coordination-shell neighbours. According to EXAFS results, the mean Ti–O bond lengths are 1.79–1.84 Å, 1.89–1.91 Å and 1.94–2.06 Å for tetra-, penta- and hexa-coordinated titanium ions, respectively.[72, 84, 218]

8. X-Ray photoelectron spectroscopy

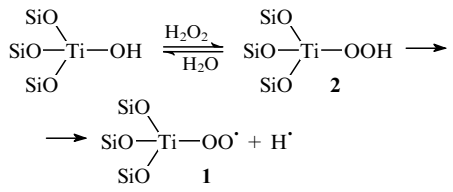
Using X-ray photoelectron spectroscopy (XPS), the electronic state of elements and chemical composition of the near-surface layer of catalysts with a thickness of up to 4–5 nm can be probed. The Ti(2p), Si(2p) and O(1s) core-level photoemission lines in titanium silicates have been studied by several authors.[74, 84, 197] The absence of the Ti(2p) component at a binding energy of 457.4 eV typical of Ti^{3+} ions in the XPS spectra indicates that titanium is present exclusively as Ti^{4+} ions. The Ti(2p) core-level photoemission line shows up in the spectra as a spin–orbit doublet $Ti(2p_{3/2})/Ti(2p_{1/2})$ (Fig. 11). The exact position of the $Ti(2p_{3/2})$ photoemission line is indicative of the coordination environment of the titanium ions. The photoemission line in a binding energy range of E_b = 458.4–458.6 eV is commonly attributed to titanium in the octahedral coordination (as in TiO_2), whereas the line at 459.9–460.2 eV is assigned to isolated titanium ions with the tetrahedral coordination (Refs 45, 72, 74, 84, 197, 219, 220). The XPS spectra of Ti-MCM-41 and Ti-HMS reveal a photoemission line centred at E_b = 459.9 eV,[74] whereas the main component in the spectrum of TS-1 is located at E_b = 460.2 eV.[45] In the case of a catalyst Ti-SBA-15 (with 2.05–7.17 mass % of Ti), the $Ti(2p_{3/2})$ photoemission line is located at 458.3 eV, which is consistent with the octahedral environment of Ti(IV) ions similar to that in anatase (see Fig. 9).[45, 74, 96] As a rule, XPS data fully agree with the DRUV spectral results.[96, 110] A quantitative analysis of intensities of the $Ti(2p_{3/2})$ and Si(2p) core-level photoemission lines yields the Ti : Si atomic ratio on the surface of titanium silicate catalysts.[84, 110, 197, 219]

As for O(1s) core-level photoemission lines, the peak at E_b = 532.9–533.3 eV is attributed to the silicon-bound oxygen atoms, since the oxygen line of SiO_2 appears exactly at this position.[221, 222] In TiO_2, the respective line is observed at E_b = 529.8–530.0 eV and thus this region is attributed to the titanium-bound oxygen atoms.[45, 74, 221, 222] In the XPS spectra of mixed oxides TiO_2-SiO_2, in addition to the two above lines at E_b = 530.6 eV (which corresponds to the Ti–O–Ti bonds) and 532.7 eV (which corresponds to the Si–O–Si bonds), the third line at an intermediate binding energy (531.4 eV) is observed, which is thus assigned to the Ti–O–Si bonds.[219] The disappearance of this line upon calcination of the samples at 1000 °C is interpreted as a structural transformation of the sample giving rise to TiO_2 agglomerates.

9. Electron spin resonance spectroscopy

Electron spin resonance (ESR) spectroscopy is widely used for the detection and elucidation of properties of paramagnetic transition metal ions incorporated into molecular sieves. Capabilities of this method as regards titanium silicates are limited, since the titanium ions are characterised by the oxidation state 4+ and thus are diamagnetic. Structural information concerning Ti ions can be obtained after reduction of titanium silicate samples with CO, H_2, UV- or γ-radiation, *i.e.*, when the diamagnetic Ti(IV) ions are converted into the paramagnetic Ti(III) ions. This ESR-based approach was utilised to confirm the isomorphous substitution of Ti(IV) for Si(IV) in TS-1.[223, 224] The ESR spectrum of TS-1 reduced by carbon monoxide manifests an axially symmetric signal with a split $g_\parallel$-component $[(g_\parallel)_1 = 1.98,\ (g_\parallel)_2 = 1.97]$ and $g = 1.913$ attributable to titanium(III) in the axially distorted tetrahedral coordination. This means that its precursor, *i.e.*, titanium(IV) ions, were also located in tetrahedral sites.[223] So far, there have been only a few ESR studies on the state of titanium ions in mesoporous titanium silicates.[225, 226] In particular, the ESR spectrum of γ-irradiated Ti-MCM-41 reveals, in addition to the aforementioned axial signal of tetrahedral titanium ions, an axial signal characterised by values of $g_\parallel = 1.898$ and $g_\perp = 1.967$ typical of Ti(III) in the distorted octahedral environment.[225]

The ESR technique is widely utilised in structural studies of catalytically active particles in particular, of Ti superoxide radicals **1**,[207, 226–229] which are generated from titanium peroxo complexes **2**.[227]



In particular, titanium silicate TS-1 in the presence of H_2O_2 produces an intense anisotropic ESR signal with the following parameters of the g-tensor: $g_{xx} = 2.0030$, $g_{yy} = 2.0099$ and $g_{zz} = 2.0238$. This signal is attributed to superoxotitanium species $Ti(O_2^{\bullet})$.[207] The interaction of TS-1, Ti-Beta, Ti-MCM-41 and amorphous TiO_2-SiO_2 with aqueous H_2O_2 yields two types of superoxotitanium species (*viz.*, **A** and **B**).[228,229] The superoxo particles **A** ($g_{xx} = 2.0023$, $g_{yy} = 2.0090$, $g_{zz} = 2.0266$) and **B** ($g_{xx} = 2.0023$, $g_{yy} = 2.0090$, $g_{zz} = 2.0238$) are characterised by rhombic g-tensors. It was suggested that the type **A** particles are produced from $(SiO)_4Ti$ species localised inside the silicate walls, whereas the type **B** particles are formed from $(SiO)_3Ti(OH)$ species localised on the external surfaces of the walls. The fraction of the type **A** species decreases in the series TS-1 > Ti-Beta > amorphous TiO_2-SiO_2, whereas the fraction of the type **B** species decreases in the series Ti-MCM-41 > amorphous TiO_2–SiO_2 > Ti-Beta > TS-1. It was proposed that the type **A** species are involved in the selective oxidation of styrene to the respective epoxide.

10. Raman spectroscopy

The Raman spectra of mesoporous silicate TS-1, which contains only isomorphously substituted isolated titanium ions within the silicate walls, reveal vibrational bands at 799–828 cm^{-1}, 467 cm^{-1}, 375 cm^{-1} and 290 cm^{-1}.[197] An increase in the titanium content gives rise to the appearance of four new bands at 140–145 cm^{-1} (it is the most intense band; its detection limit as regards TiO_2 is 0.05 mass %), 386–400, 513–516 and 637–639 cm^{-1}. These bands are attributed to non-structural titanium; likely, they can be interpreted as the initial stage of anatase formation.[45,74,84,109,197,230,231] Apparently, Raman spectroscopy is one of the most sensitive techniques that enables detection of early stages of the emergence of TiO_2 crystallites in mesoporous titanium silicates.[110,111] In particular, the Raman spectrum of Ti-SBA-15 with Ti contents 7.17 mass % manifests an intense peak at 145 cm^{-1} (Fig. 12). Meanwhile, neither X-ray diffraction nor electron microscopy give any evidence of the emergence of the TiO_2 phase in this sample.[110]

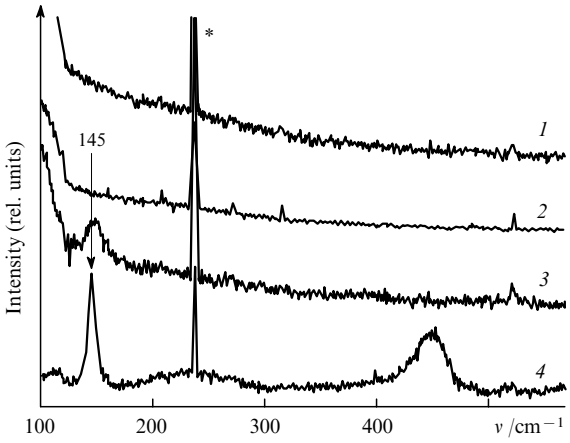


Figure 12. The Raman spectra of mesoporous titanium silicates.[110] (*1*) Ti-MMM (1.89% Ti), (*2*) Ti-SBA-15 (2.05% Ti), (*3*) Ti-SBA-15 (7.17% Ti), (*4*) TiO_2 (anatase). The * mark corresponds to plasma excitation.

11. IR spectroscopy

There are two most informative regions in the IR spectra of titanium silicates: 3200–3800 cm^{-1} and 950–970 cm^{-1}. Two peaks at 3728–3748 cm^{-1} (narrow) and 3222–3540 cm^{-1} (broad) are observed in the region of stretching vibrations of the O–H groups.[132,197,220] These bands are attributed to vibrations of the free and H-bonded silanol Si–OH groups, respectively.

The band at 960 cm^{-1} observed in titanium-containing zeolites is often assigned to the Ti–O–Ti bonds sites,[45,197,206] an increase in its intensity with an increase in the titanium content in TS-1 is interpreted as a manifestation of titanium trapping in the silicate walls. However, in the case of mesoporous mesophase titanium silicates, the assignment of this band to the Ti–O–Ti bonds is not ambiguous, since spectra of metal-free mesoporous silicates reveal a band in the same region ascribed to Si–O vibrations of the Si–O–R groups.[45,72,74,77] Notwithstanding, the intensity ratios of the bands at 960 cm^{-1} and 800 cm^{-1} (the latter is attributed to symmetrical stretching vibrations of the SiO_4 groups) in the spectra of mesostructured titanium silicates is substantially larger than in their titanium-free analogues.[74]

In the case of mixed oxides TiO_2-SiO_2, the relative degree of dispersion of titanium over a silicate matrix $D_{(Ti-O-Si)}$ can be estimated on the semiquantitative level by analysing the intensity distributions of deconvoluted spectral components at 940–960 cm^{-1} (vibrations of the Ti–O–Si groups) and 1210 cm^{-1} (vibrations of the Si–O–Si groups).[81,164,179,181] Using this technique, it was demonstrated that the level of titanium dispersion decreases with an increase in its content in the mixed oxides.

12. IR spectroscopy of adsorbed CO molecules

The accessibility of active titanium sites for reagents is one of the most important parameter of mesoporous titanium silicate catalysts. Since the typical size of nanopores lies in the nanometre range, the diffusion hindrances to the transport of reagents towards the active sites can be quite decisively ruled out, however a part of the sites can appear trapped inside the silicate walls and thus become inaccessible for reagents. In this regards, the thickness of the silicate walls is an important characteristics of mesostructured titanium silicates. It is known that the wall thickness depends on the preparation procedure. For instance, the walls in Ti-MMM and Ti-MMM-2 are only 0.8–1.0 nm thick,[87,116,125] which approximately corresponds to the size of two SiO_4 tetrahedra (the size of an SiO_4 tetrahedron is ~0.4 nm).[173] This means that all titanium sites in these materials should be accessible for reagents. Meanwhile, in the case of Ti-SBA-15, the wall thickness is already 1.5–2.0 nm[110] and thus a part of titanium sites can be located inside the walls and become inaccessible for reagents. Presently, there are no direct methods to strictly quantify the accessibility of titanium sites for reagents; however, this parameter can be estimated on a qualitative level using IR spectroscopy of adsorbed CO molecules.[110] Three types of bands are observed in the IR spectra of adsorbed CO molecules, *viz.*, at 2135 cm^{-1} (attributed to physisorbed CO), 2153 cm^{-1} (CO forming complexes with the silanol groups)[232] and 2179 cm^{-1} (CO interacting with the Ti cations localised on the surface of the silicate matrix).[233,234]

This method was applied to a comparative analysis of Ti-MMM and Ti-SBA-15. It turned out that the band centred at 2179 cm^{-1} in the spectrum of Ti-SBA-15 is substantially less intense than that in Ti-MMM (Fig. 13), *i.e.*, the concentration of surface titanium ions accessible for reagents is lower in this sample.[110] As has been established in a similar way, aerogels TiO_2-SiO_2 are characterised by a larger amount of surface Ti ions than xerogels TiO_2-SiO_2.[181,204]

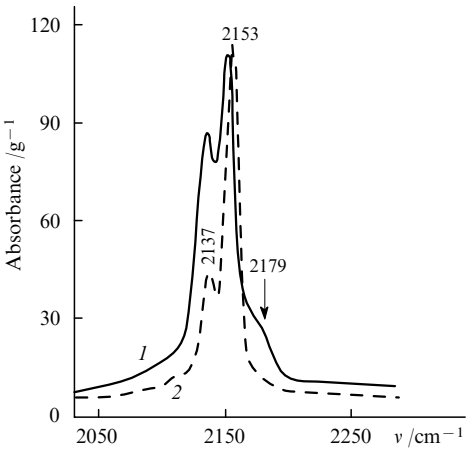


Figure 13. The IR spectra of CO adsorbed on mesoporous titanium silicates at 100 K (the region of C–O vibrations).[110]
(*1*) Ti-MMM (1.89% Ti), (*2*) Ti-SBA-15 (2.05% Ti).

IV. Catalytic properties

Numerous reports on the use of mesostructured titanium silicates and mixed oxides TiO_2-SiO_2 as catalysts for the selective liquid-phase oxidation of organic substrates have appeared over the last decade. Selected examples of such reactions are given in Table 4. The oxidation of non-functionalised and substituted alkenes, organic sulfides and alkylphenols has been studied most thoroughly. These reactions assisted by mesoporous titanium silicates are considered in more detail below. The problems concerning the efficiency of oxidant utilisation and the stability of catalysts under the reaction conditions, including the possibility of their recycling, are also discussed.

1. Oxidation of alkenes

Mesoporous titanium silicate Ti-MCM-41 has proven to be an efficient catalyst for the selective epoxidation of alkenes with aqueous hydrogen peroxide or alkyl hydroperoxides. Ti-MCM-41 is less active than TS-1 with respect to the oxidation of small molecules with hydrogen peroxide under similar conditions, which is explained by its higher hydrophilicity that prevents efficient adsorption of non-polar substrates.[45, 69, 72, 77] Furthermore, some reactions easily realisable with TS-1 (in particular, propylene epoxidation, oxidation of linear alkanes and primary amines) are virtually impossible over Ti-MCM-41 and Ti-HMS.[74, 254, 255] On the other hand, a clear advantage of Ti-MCM-41 and other mesoporous titanium silicates is that they are capable of catalysing the oxidation of bulky organic molecules, which cannot penetrate into the pores of microporous catalysts. In particular, only linear alkenes are efficiently oxidised over TS-1, whereas the majority of mesoporous titanium silicates activiely catalyse the oxidation of cyclohexene (typically yielding the respective epoxides and/or diols as primary products).[105–107, 122, 134, 137, 151, 166–168, 179, 182–185, 212, 235] The introduction of aluminium into the structure of SBA-15 with subsequent titanium deposition enables the deep oxidation of cyclohexene into adipic acid in a 88% yield at a 96% substrate conversion.[114]

Another advantage of Ti-MCM-41 and other mesoporous titanium silicates over microporous titanium silicates consists of the possible use of relatively large organic hydroperoxides as oxidants.[41, 69, 72, 77, 78, 81, 166–168, 182–185, 200, 236, 238, 245–253] For instance, mesoporous titanium silicate Ti-MCM-41 manifested higher activity towards the oxidation of α-terpineol and norbornene with *tert*-butyl hydroperoxide as compared to zeolite Ti-Beta [72, 236] (Table 5). If alkyl hydroperoxides are used as oxidants, titanium silicate catalysts provide higher selectivity of the epoxidation and manifest higher stability, although the oxidation rate is, as a rule, lower than in the case of the oxidation with H_2O_2.[122] In some cases, mesoporous titanium silicates

Table 4. Reactions of the liquid-phase selective oxidation of organic compounds with peroxides catalysed by mesoporous titanium silicates.

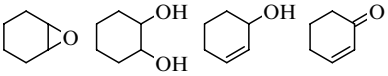
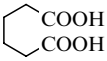
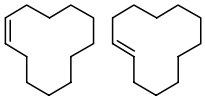
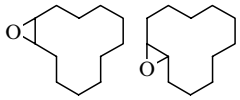
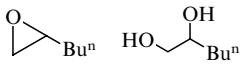
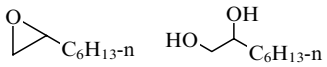
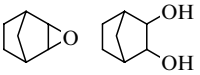
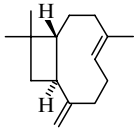
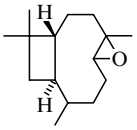
Substrate	Major products	Oxidant	Catalyst	Ref.
		H_2O_2	Ti-HMS	235
		H_2O_2, Bu^{t}OOH	Ti-MCM-41	72, 122
		H_2O_2	Ti-MCM-48	134
		H_2O_2	Ti-MMM	105, 106
		Bu^{t}OOH	Ti-TUD-1	107
		Bu^{t}OOH	TiO_2-SiO_2	166–168, 182–185
		Bu^{t}OOH	Ti,Al-SBA-15	114
		H_2O_2, Bu^{t}OOH	Ti-MCM-48, Ti-MCM-41	103, 121
		ROOH,[a] H_2O_2	TiO_2-SiO_2	166, 167
		H_2O_2, Bu^{t}OOH	Ti-MCM-41	69, 72
		Bu^{t}OOH	TiO_2-SiO_2	183, 200
		Bu^{t}OOH	TiO_2-SiO_2	124, 200
		H_2O_2, Bu^{t}OOH	Ti-MCM-41	72, 236
		Bu^{t}OOH	TiO_2-SiO_2	166, 167
		H_2O_2	Ti-MMM	105
		Ti-MMM	Ti-MMM-2	116

Table 4 (continued).

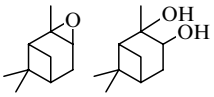
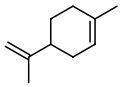
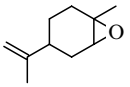
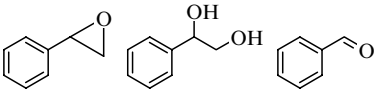
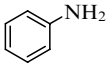
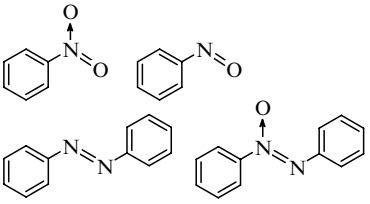
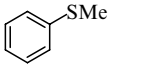
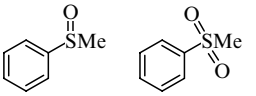
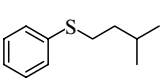
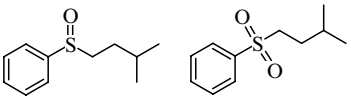
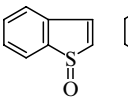
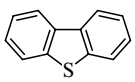
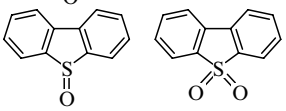
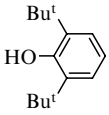
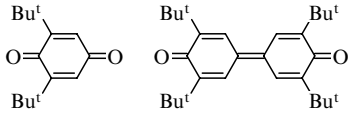
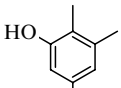
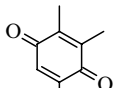
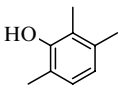
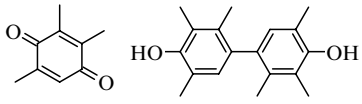
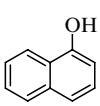
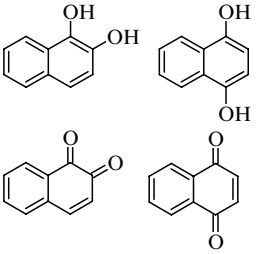
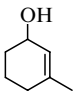
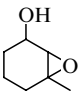
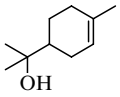
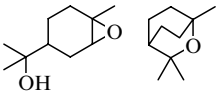
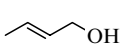
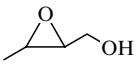
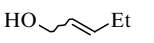
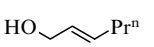
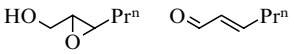
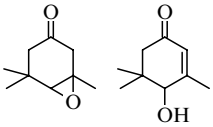
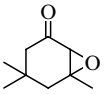
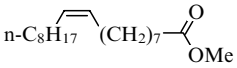
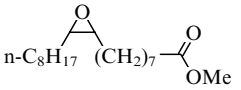
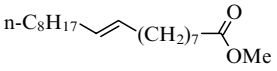
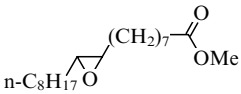
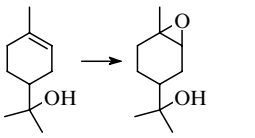
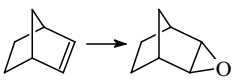
Substrate	Major products	Oxidant	Catalyst	Ref.
		H_2O_2, Bu^tOOH	Ti-HMS, Ti-MCM-41	237
		Bu^tOOH Bu^tOOH	TiO_2-SiO_2 Ti-MCM-41	166, 203 238
		H_2O_2	Ti-MCM-41, Ti-HMS Ti-MCM-48	104 102
		H_2O_2, Bu^tOOH	Ti-MCM-41, Ti-HMS Ti-SBA-15	235, 239 87
		H_2O_2	Ti-MCM-41 Ti-MMM Ti-MMM-2	240 105, 106 116
		H_2O_2	Ti-MCM-41	240
		H_2O_2	Ti-HMS	241
		H_2O_2	Ti-HMS	241
		H_2O_2	Ti-MCM-41, Ti-HMS	73, 104
		H_2O_2	Ti-HMA	242
		H_2O_2	Ti-MCM-41 Ti-MMM Ti-MMM-2 Ti-SBA-15 TiO_2-SiO_2	243 125, 126 116 99, 110 126, 181
		H_2O_2, Bu^tOOH	Ti-MCM-41	244
		Bu^tOOH	TiO_2-SiO_2	183–185, 245–247
		Bu^tOOH	TiO_2-SiO_2	248

Table 4 (continued).

Substrate	Major products	Oxidant	Catalyst	Ref.
		Bu^tOOH	Ti-MCM-41	72, 236, 238
			TiO_2-SiO_2	245, 249
		Bu^tOOH	Ti-MCM-41	250
		H_2O_2	Ti-MCM-41, Ti-MCM-48	134
		Bu^tOOH	TiO_2-SiO_2	185, 251
		Bu^tOOH	TiO_2-SiO_2	249, 252
		Bu^tOOH	TiO_2-SiO_2	168, 203
		Bu^tOOH	Ti-MCM-41	253
		Bu^tOOH	Ti-MCM-41	253
		H_2O_2	Ti-MCM-41, Ti-HMS	104
			Ti-MCM-48	102

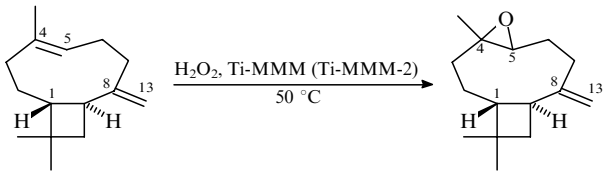
[a] R is cumyl.

Table 5. The performance of titanium silicate catalysts in the oxidation of α-terpineol and norbornene with *tert*-butyl hydroperoxide.[72, 236]

Catalyst						
	reaction time /h	yield (%)		reaction duration /h	yield (%)	
		epoxide	other		epoxide	alcohol
Ti-MCM-41	8	32	9	11	42	6
Ti-Beta	8	8	6	11	18	13

prepared by the deposition of titanium onto a silicate matrix in the post-synthesis step demosntrated higher activities than Ti-MCM-41, which can be due to the higher accessibility of titanium sites in the supported catalysts.[87, 107, 238]

A naturally occurring terpene, (−)-caryophyllene can be oxidised with hydrogen peroxide over Ti-MMM or Ti-MMM-2 to 4,5-monoepoxide derivative with a selectivity of 70% – 80% at an alkene conversion of 70% – 75% in 4 h.[105, 116] It is of note that no reaction is observed in the presence of TS-1.[116]



The oxidation of α-pinene with *tert*-butyl hydroperoxide over Ti-HMS or Ti-MCM-41 yields the respective epoxide with 100% selectivity, although the substrate conversion does not exceed 11%.[237] The epoxide ring can be opened to afford the respective diol using Ti-MCM-41 modified with acid sites (by doping with Al, Fe or B).[237] The oxidation of styrene with hydrogen peroxide catalysed by titanium silicates, such as Ti-MCM-48, Ti-MCM-41 or Ti-HMS, proceeds with the cleavage of the C=C bond to yield benzaldehyde with a selectivity of 77% – 85% at a substrate conversion of 10% – 28%.[102, 104] The catalyst Ti-MCM-48, which contains a three-dimensional framework of cylindrical mesopores, manifested higher activity than Ti-MCM-41 towards the oxidation of a number of higher alkenes with hydrogen peroxide.[103, 134]

MCM-41 modified with titanium in the post-synthesis step is more active than Ti-MCM-41 towards the oxidation of unsaturated terpenic alcohols. The difference in their activities is smaller in the case of alcohols with the OH group located closer to the C=C double bond.[238] Supported titanium catalysts MCM-41 manifest high activity and selectivity in the epoxidation of methyl esters of unsaturated fatty acids with *tert*-butyl hydroperoxide and, furthermore, the epoxidation proceeds stereospecifically.[251] In the case of Ti-MCM-41, the difference in the oxidation rates of *E*- and *Z*-isomers is substantially smaller than with $Ti-SiO_2$,

which is probably due to the higher accessibility of channels present in MCM-41 for the *E*-isomer (methyl elaidate) as compared to the *Z*-isomer (methyl oleate).

The catalytic propertis of mixed oxides TiO_2-SiO_2 are best studied by the example of the epoxidation of olefines and oxidation of unsaturated alcohols and ketones with alkyl hydroperoxides (see Table 4). Aerogels synthesised by the low-temperature supercritical drying are more active than both xerogels and aerogels prepared by the high-temperature supercritical drying.[167] The use of aqueous H_2O_2 as an oxidant leads to the titanium leaching from the silicate matrix and the collapse of the porous structure. Therefore, organic hydroperoxide in non-aqueous solvents should preferably be used.[167]

In a number of cases, it was possible to improve the selectivity of epoxidation by surface hydrophobisation of mixed oxides and mesostructured titanium silicates (Table 6). The hydrophobisation was accomplished by the surface silylation with hydrophobic reagents [131–134] or by the introduction of hydrophobic modificators directly into the silicate matrix during its synthesis.[182–185] It was shown that the porous structure and activity of hydrophobised mesoporous titanium silicates is better sustained after several cycles of operation. Although hydrophobisation generally decreases the surface of mesopores and often decreases their diameter as well, hydrophobised catalysts exhibit improved activity and selectivity of the oxidation of alkenes and alkanes with respect to their non-hydrophobised precursors.[131, 133, 134, 182, 184, 187] In addition, the efficiency of H_2O_2 (Refs 131, 134 and 182) and alkyl hydroperoxide utilisation is enhanced.[133]

Table 6. The effects of the surface hydrophobisation on the performance of titanium silicate catalysts in the epoxidation of cyclohexene.

Catalyst	Reaction time /h	Oxidant	Cyclohexene conversion (%)	Epoxide selectivity [a] (%)	Ref.
Aerogel TiO_2-SiO_2	2	Bu^tOOH	18	80	184
Hydrophobised aerogel TiO_2-SiO_2 (see [b])	2	Bu^tOOH	33	94	184
Ti-MCM-41	0.5	Bu^tOOH	63	91	133
Hydrophobised Ti-MCM-41 [c]	0.5	Bu^tOOH	87	99	133
Ti-MCM-41	3	H_2O_2	0.72	0	134
Hydrophobised Ti-MCM-41 [d]	3	H_2O_2	13	14	134

[a] Based on the substrate. [b] The aerogel was modified with phenyl groups during the sol–gel synthesis. [c] The surface of Ti-MCM-41 was silylated with $(CH_3)_3SiNHSi(CH_3)_3$. [d] The surface of Ti-MCM-41 was silylated with $(CH_3)_3SiCl$.

The selectivity of epoxidation in the oxidation of unsaturated alcohols, in particular, cyclohexenol, with *tert*-butyl hydroperoxide in the presence of aerogel TiO_2-SiO_2 was substantially improved by the surface modification of the catalyst with amine and 3-acetoxypropyl groups either during the sol–gel synthesis [245, 246] or by addition of an amine directly into the reaction mixture.[248] The type of the modificator affects the ratio of *cis*- and *trans*-epoxides among the reaction products.

Numerous literature data indicate that the catalytic activity of mesoporous titanium silicates in the alkene oxidation reactions is mainly determined by the state and accessibility of titanium sites. However, it can also be affected by other factors, such as size and shape of crystallites (particles), concentration of surface defects, surface hydrophobicity/hydrophilicity and acid–base properties, concentration of dopant ions, and so on.[73, 84, 104, 179] As in the case of titanium-containing zeolites (TS-1, Ti-Beta, *etc.*),[67, 256] the activity of mesoporous titanium silicates is likely to be strongly affected by the presence of sodium ions therein. The coordination number of titanium ions in the initial catalyst plays no decisive role in the catalytic properties of titanium silicates as regards oxidation with hydrogen peroxide, since tetra-coordinated titanium is unavoidably converted into penta- and hexa-coordinated species in the presence of water (see Sections III.6 and III.7).[99, 116] Meanwhile, in the case of oxidation with alkyl hydroperoxides in non-polar solvents, titanium silicates originally containing tetra-coordinated titanium can manifest higher activity as compared to titanium silicates comprising titanium ions with the coordination numbers of 5 and 6.[77, 84, 85] So far, no direct experimental evidence have been obtained that ordered titanium silicates are more active in the oxidation of alkenes and unsaturated alcohols than amorphous mesoporous titanium silicates with a similar titanium loading (provided that titanium is uniformly distributed over the matrix).[98, 249, 257]

2. Oxidation of thioethers

Mesostructured titanium silicates Ti-MCM-41, Ti-HMS, Ti-MMM and Ti-MMM-2 are efficient catalysts of the oxidation of bulky organic sulfides to the respective sulfoxides and sulfones.[70, 71, 77, 105, 106, 116, 240, 241] For the oxidation of methyl phenyl sulfide, the activity of titanium silicate catalysts decreases in the series Ti-MMM ~ Ti-MMM-2 ≫ Ti-SBA-15 > TS-1,[110, 116] the maximum selectivity of the sulfoxide formation is 76% at the 100% substrate conversion. The activity of TS-1 rapidly decreases in the following series of substrates: dimethyl sulfide ≫ diethyl sulfide > methyl phenyl sulfide > ethyl phenyl sulfide ≫ diphenyl sulfide (for the latter substrate, the conversion is nearly zero).[258] Type Ti-Beta zeolites are more active than Ti-MCM-41 in the oxidation of methylphenyl sulfide, whereas the reversed series of activities is observed for bulkier sulfides, *e.g.*, for isopentyl phenyl sulfide.[240]

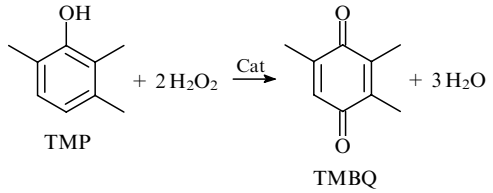
The catalyst Ti-HMS manifested a high activity in the oxidation of benzo- and dibenzothiophenes with hydrogen peroxide;[241] these reactions are considered as a prospective method for the removal of sulfur-containing compounds from motor fuels alternative to the hydrodesulfurisation.

3. Oxidation of substituted phenols

Mesoporous titanium silicates are efficient catalysts of the oxidation of sterically hindered phenols, such as 2,6-di-*tert*-butylphenol, 2,3,5-trimethylphenol, 2,3,6-trimethylphenol, *etc.*, with hydrogen peroxide to quinones and diquinones (Refs 73–75, 77, 99, 104, 116, 125, 126, 146, 148, 149). According to the experimental results, Ti-HMS is more catalytically active than Ti-MCM-41 towards the liquid-phase oxidation of methyl methacrylate, styrene and 2,6-di-*tert*-butylphenol.[73, 104] It is of note that the difference in the activities of the catalysts becomes more distinct in the case of bulkier phenols. Probably, this is partly due to the higher texture mesoporosity of Ti-HMS, which facilitates the free transport of bulky substrates.[73, 104]

According to the recently published results, the oxidation of 2,3,5-trimethylphenol with hydrogen peroxide over microporous Ti-APO-5 [259] and mesoporous Ti-HMA [242] affords 2,3,5-trimethyl-1,4-benzoquinone (which is an intermediate of the vitamin E synthesis) in yields of 85% and 58%, respectively. However, the authors gave no evidence of the heterogeneity of the process and the lack of titanium leaching. In general, the problem of titanium leaching from solid matrices and of structural degradation of the catalysts in the course of oxidation is not adequately addressed by many authors, although it represents the main factor restricting wide practical application of titanium-containing catalysts. The oxidation of 2,3,6-trimethylphenol (TMP) with hydrogen peroxide and *tert*-butyl hydroperoxide has been comprehensively studied [110, 116, 125, 126] in the presence of diverse mesoporous titanium silicates, including mixed oxides

TiO_2-SiO_2 (both aerogels and xerogels), Ti-MMM, Ti-MMM-2 and Ti-SBA-15.



A new method for the synthesis of 2,3,6-trimethyl-1,4-benzoquinone (TMBQ) by the oxidation of TMP with hydrogen peroxide in the presence of mesoporous titanium-containing catalysts has been elaborated recently, which provided a selectivity as high as 98% at the 100% TMP conversion.[180] The main by-product of this reaction is 2,2′,3,3′,6,6′-hexamethyl-4,4′-biphenol; its yield increases with a decrease in temperature of the reaction mixture and an increase in the [TMP]:[Ti] ratio. No further substrate conversion occurs after withdrawal of the catalyst by the rapid filtration of the reaction mixture (Fig. 14). This, coupled with the results of the chemical analysis, gives strong evidence that the oxidation proceeds exclusively on the catalyst surface and that there is no noticeable leaching of Ti(IV) from the silicate matrix.[125, 126]

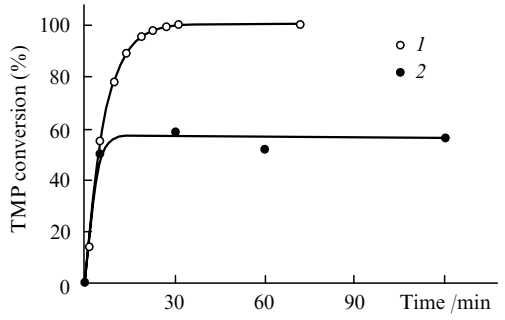
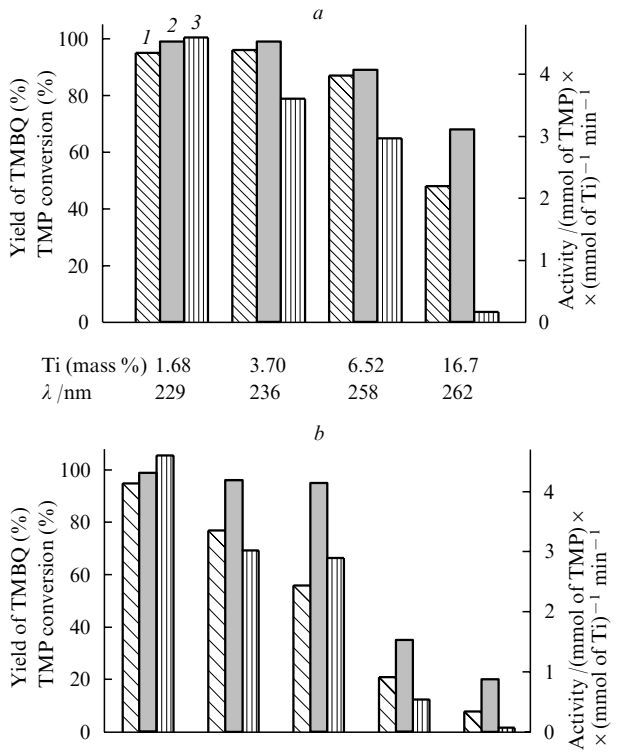


Figure 14. The kinetics of TMP oxidation with hydrogen peroxide in the presence of Ti-MMM.[125]
Reaction conditions: 0.1 mol litre^{-1} of TMP, 0.7 mol litre^{-1} of H_2O_2, 1.3×10^{-2} mmol of Ti, 3 ml of MeCN, 80 °C;
(*1*) without filtration, (*2*) the catalyst is removed by filtration in 5 min after the start of the reaction.



Ti (mass %)	1.68	3.70	6.52	16.7
λ /nm	229	236	258	262

Catalyst	Aero-gel Ti-Si	Ti-MMM (Ti-MMM-2)	Xerogel Ti-Si	Ti-SBA-15	TS-1
Ti (mass %)	1.68	1.15	1.44	2.05	2.54
λ_{max} /nm	229	218	216	247	204
V_m /cm^3 g^{-1}	3.03	0.91	0.21	0.62	–
d_m /nm	15.9	3.79	2.96	9.33	0.56
E_a /kJ mol^{-1}	81	60	29	–	–

Figure 15. The performance of aerogels TiO_2-SiO_2 with various titanium loadings (*a*) and different mesoporous titanium silicates with similar titanium concentrations (*b*) in the catalytic oxidation of 2,3,6-trimethylphenol with hydrogen peroxide.[110, 116, 125, 126, 181]
Reaction conditions: 0.1 mol litre^{-1} of TMP, 0.013 mmol of Ti, 0.35 mol litre^{-1} of H_2O_2, 3 ml of MeCN, 80 °C;
(*1*) the yield of TMBQ, (*2*) the conversion of TMP in 20 min after the start of the reaction, (*3*) the activity.

The activity of different types of mesoporous titanium silicates (aerogel TiO_2-SiO_2, xerogel TiO_2-SiO_2, Ti-MMM, Ti-MMM-2 and Ti-SBA-15) towards the oxidation of TMP per active catalytic site decreases with an increase in the titanium loading of the catalysts (Fig. 15*a*). This dependence can be rationalised taking into account that the level of dispersion of titanium over the silicate matrix decreases with an increase in the titanium loading, which gives rise to the formation of less reactive Ti–O–Ti bonds, as evidenced by the red-shift of the absorption band in the DRUV spectra. As has been already stated above, the degree of dispersion of titanium is one of the main parameters determining the catalytic activity of titanium silicates: the higher the degree of dispersion, the higher the activity (Refs 77, 84, 125, 126, 167, 168, 203).

The activity of catalysts with similar concentrations of titanium decrease in the following series: aerogel TiO_2-SiO_2 > Ti-MMM ~ Ti-MMM-2 > xerogel TiO_2-SiO_2 ≫ Ti-SBA-15 > TS-1. This activity series correlates well with the size of mesopores in the respective materials and also with the apparent activation energies of the reaction (E_a).[125, 181, 260] In particular, the activation energies are 81 kJ mol^{-1} and 60 kJ mol^{-1} over the aerogel TiO_2-SiO_2 and Ti-MMM catalysts, respectively. Therefore, the oxidation of TMP with hydrogen peroxide in the presence of these catalysts proceeds in the kinetic regime and is not limited by diffusion processes. In the case of the xerogel TiO_2-SiO_2, which is characterised by substantially smaller pores, the activation energy is E_a = 29 kJ mol^{-1}, which is rather typical of diffusion limited processes.[260] Ti-SBA-15 represents an exception to this correlation, since its activity is substantially lower as compared to other mesoporous titanium silicates despite the large size of the mesopores therein. Probably, this is due to both the low degree of titanium dispersion and large thickness of the silicate walls in this material, which is in accord with the IR spectral analysis of adsorbed CO molecules (see Section III.12).[110] It is important to note that the structural ordering of mesoporous titanium silicates does not correlate with their activities. For instance, Ti-HMS is more active than Ti-MCM-41,[104] whereas Ti-MMM-2 and Ti-MMM manifest similar activities,[116] although Ti-MCM-41 and Ti-MMM are more structurally ordered than Ti-HMS and Ti-MMM-2, respectively.

4. The efficiency of H_2O_2 utilisation

The activity of mesoporous titanium silicate catalysts in the oxidation correlates with the rates of H_2O_2 decomposition in the absence of organic substrates: aerogel TiO_2-SiO_2 >

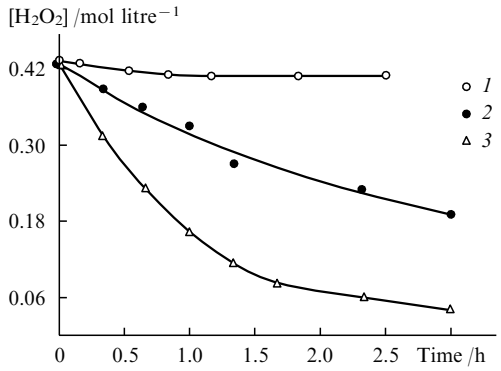


Figure 16. The kinetics of decomposition of H_2O_2 in the presence of Ti-SBA-15 (*1*), Ti-MMM (*2*) and aerogel TiO_2-SiO_2 (*3*).[204]
Reaction conditions: 1.29 mmol of H_2O_2, 0.013 mmol of Ti, 3 ml of MeCN, 80 °C.

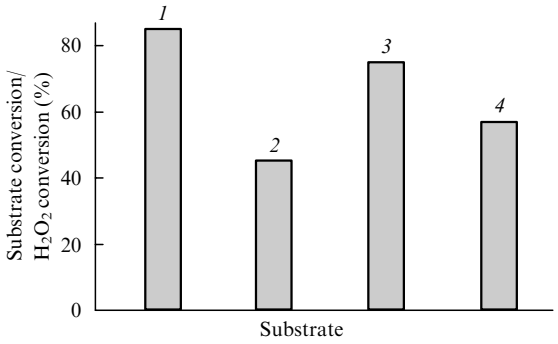


Figure 17. The efficiency of H_2O_2 utilisation in the oxidation of various organic substrates over Ti-MMM.[204]
Substrates: (*1*) methylphenylsulfide (20 °C), (*2*) cyclohexene (50 °C), (*3*) caryophyllene (50 °C), (*4*) 2,3,6-trimethylphenol (80 °C).

Ti-MMM > Ti-SBA-15 (Fig. 16).[204] The efficiency of hydrogen peroxide utilisation (H_2O_2 selectivity) can be estimated as the ratio of the rates of H_2O_2 consumption by the target oxidation of an organic substrate and the concomitant non-productive decomposition of H_2O_2 over the catalyst. Since this ratio clearly depends on the substrate type and/or reaction conditions, the efficiency of H_2O_2 utilisation is also a function of these parameters (Fig. 17). The more active the substrate, the higher the efficiency of H_2O_2 utilisation. In particular, the efficiencies of H_2O_2 utilisation are 45% and 75% in the oxidation of cyclohexene and more nucleophilic caryophyllene, respectively.

The H_2O_2 selectivity is an important parameter of a catalytic process. In order to improve the efficiency of H_2O_2 utilisation, large-scale industrial oxidation processes of petrochemical synthesis are usually accomplished with a large excess of an organic substrate (which is typically less expensive than the oxidant). In contrast, substrates often appear more expensive than oxidants in fine chemical synthesis processes, such that it appears more cost-effective to use an excess of H_2O_2 (which partly decomposes non-productively) in order to enhance the substrate conversion and minimise the costs of product isolation and purification.[26,47] In certain cases, the efficiency of H_2O_2 utilisation can be improved by the surface hydrophobisation of mesoporous titanium silicates.[131,133,134,182]

5. The problem of stability of titanium silicate catalysts

As has been mentioned above, the leaching of the active component and consequent loss of activity of catalysts is one of the most serious problems in the practical use of liquid-phase catalytic oxidation with aqueous H_2O_2. The stability of titanium silicates against the titanium leaching depends both on the properties of the titanium silicate itself (the degree of dispersion of titanium over the silicate matrix, thickness of the silicate walls, surface hydrophobicity, *etc.*) and the reaction conditions (solvent type, H_2O_2 concentration, temperature, composition of the reaction products, *etc.*).[124] In particular, titanium is leached from Ti-MCM-41 [122,250] and mixed oxides TiO_2-SiO_2,[167,203] if methanol is used as a solvent. Meanwhile, aerogels and xerogels TiO_2-SiO_2 and Ti-MMM proved stable against the titanium leaching in acetonitrile media.[105,106,125,126] Notwithstanding, the activity of the catalysts decreased substantially upon recycling, despite the lack of titanium leaching.

According to the systematic investigations into the factors affecting the stable functioning of mesoporous titanium silicate catalysts upon repetitive use, the main reason for the loss of activity of Ti-MMM catalysts and mixed oxides TiO_2-SiO_2 is the negative impact of water (or aqueous hydrogen peroxide) on the hydrophilic surface of the catalysts.[106,110,125,126] As has been established by small-angle X-ray diffraction and N_2 adsorption, the structure of Ti-MMM degrades as a result of treatment with water (Fig. 18). The structural decomposition of Ti-MCM-41 in

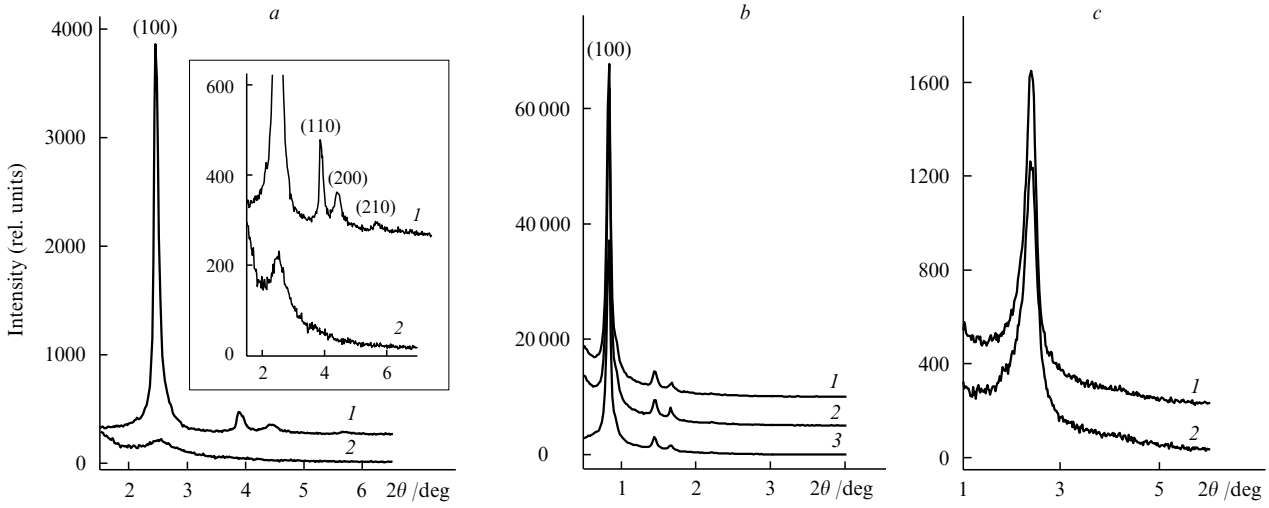


Figure 18. X-Ray diffraction patterns of Ti-MMM (*a*), Ti-SBA-15 (*b*) and Ti-MMM-2 (*c*) before (*1*) and after their treatment with H_2O (*2*) or with 30% aqueous H_2O_2 in MeCN (*3*).[110,116,125]

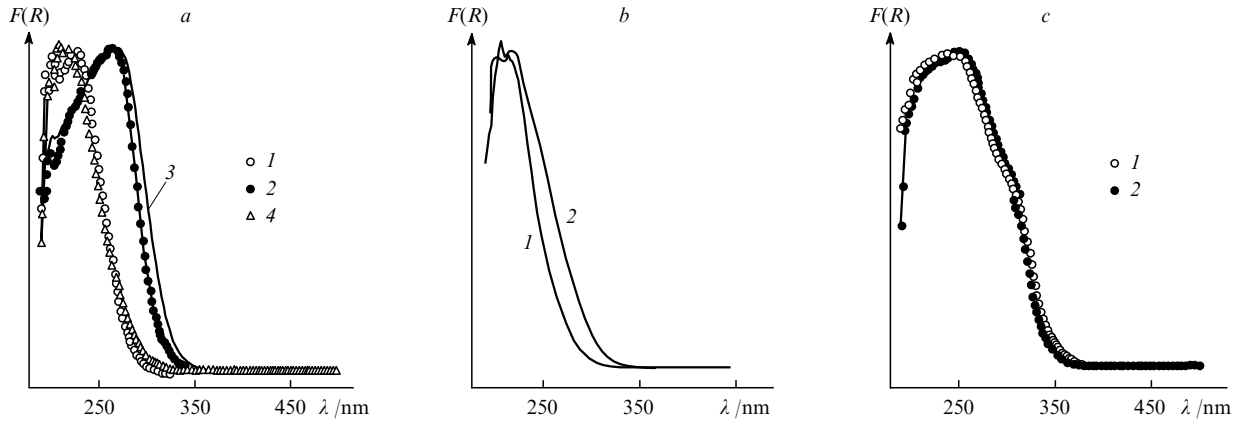


Figure 19. The DRUV spectra of Ti-MMM (1.89% Ti) (*a*),[125] Ti-MMM-2 (1.67% Ti) (*b*)[116] and Ti-SBA-15 (2.05% Ti) (*c*).[110]
(*1*) Prior to treatment, (*2*) after the treatment with 30% aqueous H_2O_2 in MeCN, (*3*) after the second treatment with the same solution, (*4*) after the treatment with a 74% solution of H_2O_2 in MeCN.
Treatment conditions: 1.3×10^{-2} mmol of Ti, 0.35 mol litre^{-1} of H_2O_2, 3 ml of MeCN, 80 °C, 1 h.

the course of phenol hydroxylation [123] and upon its treatment with water vapour was revealed by X-ray diffraction.[121] In the case of mixed oxides TiO_2-SiO_2, a decrease in the specific surface area and volume of the mesopores was detected following their treatment with a 30% solution of H_2O_2 in MeCN.[126] The collapse of the porous structure gives rise to 'oligomerised' forms of titanium, which are inert in the oxidation, as evidenced by the irreversible red-shift of the band in the DRUV spectra of Ti-MMM and mixed oxides TiO_2-SiO_2 after their treatment with H_2O_2 in MeCN (Fig. 19). The emergence of 'oligomerised' forms of titanium was also registered by DRUV spectroscopy in zeolites Ti-Beta and Ti-MWW after several catalytic cycles,[53, 68] although Ti-MWW exhibited slightly higher stability against the hydrogen peroxide action than Ti-Beta. A similar conclusion on the conversion of isolated titanium ions into 'oligomeric' agglomerates in the course of the oxidation with H_2O_2 was derived from the comparative analysis of the XANES spectra of Ti-MCM-41 before and after the reaction.[123, 212]

A decrease in the water concentration in the oxidation of TMP increases the catalyst stability but gives rise to an overall loss of its activity (Fig. 20). The surface hydrophobisation of titanium silicate catalysts gives rise to similar effects.[204] Although a decrease in water concentration in the reaction mixture has a positive effect on the oxidation of non-polar substrates (*e.g.*, alkenes), the efficient oxidation of polar substrates requires a certain amount of H_2O. Water is involved in the formation of the Ti–OH bonds manifesting high reactivity towards H_2O_2,[261, 262] thus promoting the generation of active oxidising species, *viz.*, titanium hydroperoxo complexes.[43, 45, 263] As has been established recently,[264] water also promotes the adsorption of H_2O_2 on titanium sites in TS-1.

In contrast to Ti-MMM, Ti-MMM-2 and Ti-SBA-15 synthesised in weakly acidic media can be considered as hydrothermostable materials. According to the X-ray diffraction data, no structural changes with Ti-MMM-2 and Ti-SBA-15 are observed after their boiling in water for several hours (see Fig. 18). The DRUV spectrum of Ti-SBA-15 does not change at all after treatment with 30% aqueous of H_2O_2 in acetonitrile at 80 °C. In the case of Ti-MMM-2, the DRUV band is only insignificantly broadened, although its position remains constant (see Fig. 19). Furthermore, the DRUV spectrum of Ti-MMM-2 reveals no changes, if hydrogen peroxide treatment is performed at a lower temperature (*e.g.*, at 20 °C), which implies that the initial state of the titanium ions in the samples is not affected. The state of the titanium ions in Ti-MMM-2 also remains unaffected after treatment with boiling water, in contrast to, for example, Ti-MMM [125]

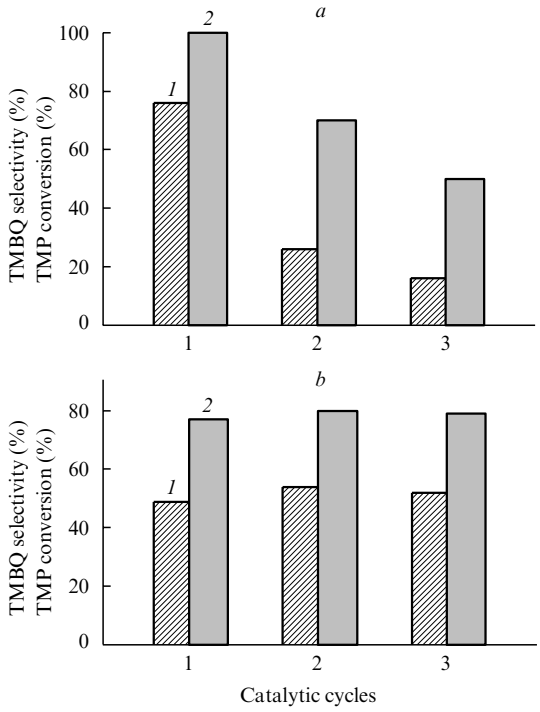


Figure 20. The performance of Ti-MMM (1.89% Ti) in the oxidation of 2,3,6-trimethylphenol with 30% (*a*) and 84% (*b*) aqueous solutions of H_2O_2.[125]
For the reaction conditions, see caption to Fig. 15.
(*1*) TMBQ selectivity, (*2*) TMP conversion in 30 min (*a*) and in 100 min (*b*) after the start of the reaction.

and Ti-TUD-1,[107] which exhibit red-shifts of the respective bands in the DRUV spectra. In contrast to Ti-SBA-15, the silicate walls in Ti-MMM-2 are sufficiently thin and titanium is smoothly dispersed over the matrix. These factors are responsible for the high catalytic activity of this material, which is comparable to that of hydrolytically unstable Ti-MMM in the first catalytic cycle. The structural stability provides the steadiness of the catalytic properties of the material. In contrast to Ti-MMM, Ti-MMM-2 can be repeatedly used in the reaction without significant losses of activity (Fig. 21), which makes it a promising catalyst for the oxidation of large organic molecules.

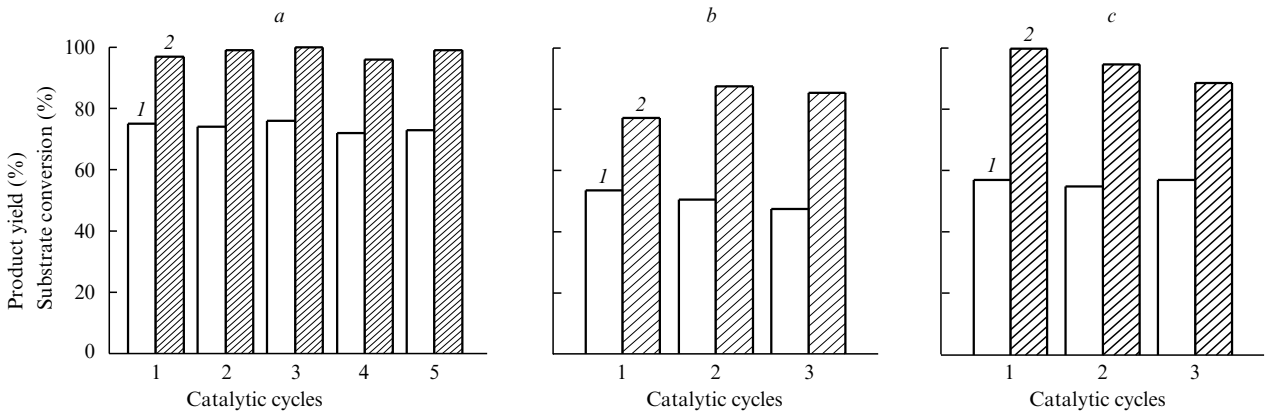


Figure 21. The performance of Ti-MMM-2 (1.67% Ti) in the oxidation reactions of methyl phenyl sulfide to the respective sulfoxide (*a*), of caryophyllene to the respective epoxide (*b*) and of 2,3,6-trimethylphenol to 2,3,6-trimethyl-1,4-benzoquinone (*c*) with hydrogen peroxide.[116]
Reaction conditions: (*a*) 0.1 mol litre^{-1} of MeSPh, 0.12 mol litre^{-1} of H_2O_2, 6×10^{-3} mmol of Ti, MeCN, 20 °C; (*b*) 0.1 mol litre^{-1} of caryophyllene, 0.11 mol litre^{-1} of H_2O_2, 6×10^{-3} mmol of Ti, MeCN, 50 °C; (*c*) see caption to Fig. 15.
(*1*) The product yield, (*2*) substrate conversion in 35 min (*a*), 4 h (*b*) and 30 min (*c*) after the start of the reaction.

V. Conclusion

A large number of mesoporous titanium silicates, both ordered and amorphous, have been synthesised over the last decade and reliable procedures of their detail structural characterisation using a combination of physicochemical instrumental methods have been elaborated. The use of small-angle X-ray diffraction, electron microscopy and low-temperature nitrogen adsorption gives valuable insights into the real structure of these materials (including such parameters as the size, shape and packing type of the mesopores, degree of ordering, thickness of the silicate walls, particle size, and so on). The degree of surface hydrophobicity/hydrophilicity of titanium silicate materials can be assessed using the gravimetric analysis of water adsorption/desorption or ^{29}Si NMR-MAS spectroscopy. The combined application of spectroscopic techniques (DRUV, XANES, IR, Raman, XPS, ESR, and some others) sheds light upon the structure of active titanium sites in the catalysts (*i.e.*, the coordination environment and degree of their dispersion over the silicate matrix). IR spectroscopy of adsorbed CO molecules gives qualitative comparative information on the accessibility of titanium ions in various materials, however methods for the quantitative analysis of this parameter are yet to be developed.

Mesoporous titanium silicates are promising catalysts for the oxidation of large organic molecules with peroxides owing to the suitable pore size and high specific surface area. Using such catalysts, the selective oxidation of different classes of organic substrates has been successfully implemented, in particular, the oxidation of alkenes to epoxides and diols, of unsaturated alcohols, ketones and esters to epoxides, of organic sulfides to sulfoxides and sulfones, of alkylphenols to quinones and dibenzoquinones, *etc*. It has to be stressed that both the characteristics of specific catalysts (titanium loading, concentration of dopant ions, thickness of the silicate walls, specific surface area, diameter and specific volume of mesopores, *etc*.) and the reaction conditions have to be taken into account in the comparative analysis of the literature data on the catalytic activities of different types of mesoporous titanium silicates in the oxidation reactions. All available information obtained by the set of physicochemical instrumental techniques should be consistently analysed in order to understand the differences in the activities of specific catalysts.

Systematic investigations into the mutual relationships between the structural, texture and catalytic properties of mesoporous mixed oxides TiO_2-SiO_2 and mesostructured titanium silicates established that it is the degree of dispersion (isolation) of titanium ions over the silicate matrix and the accessibility of the active titanium sites for reagents, which is in turn determined by the size of pores and the thickness of the silicate walls, that are the key factors governing their activity as catalysts. In contrast, the coordination number of titanium ions is apparently of low importance in the case of the oxidation with aqueous hydrogen peroxide, since tetrahedral titanium ions are effectively converted into penta- and hexa-coordinated species in the presence of water. So far, there have been no direct experimental evidence that ordered mesoporous titanium silicates are any superior to amorphous titanium silicates with similar titanium loadings in terms of the catalytic activity. The surface acid – base properties of titanium silicates strongly affect their activity and selectivity towards certain reactions. The systematic investigations into this phenomenon can shed light upon the origin of the selectivity manifested by mesoporous titanium silicates in the oxidation of various classes of organic substrates.

For the majority of presently known mesoporous titanium silicates, the problem of their stability against hydrolysis is a very urgent question, which restricts wide practical applications of these materials to the liquid-phase oxidation of different substrates with aqueous hydrogen peroxide. The surface hydrophobisation is a promising means to improve upon the structural stability of the catalysts. Hydrophobised catalysts manifest higher activity towards the oxidation of non-polar and weakly polar compounds (*e.g.*, alkanes and alkenes) than their non-hydrophobised precursors. The reverse trend is observed for the oxidation of polar substrates (*e.g.*, alkylphenol or naphthols). A substantial progress in solving the problem of the hydrolytic instability of mesoporous titanium silicates has been made with the synthesis of a thermohydrostable catalyst Ti-MMM-2, which compares well with Ti-MCM-41 and Ti-MMM in terms of activity but is, unlike them, stable against the action of water.

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References

1. R A Sheldon, J K Kochi *Metal-Catalyzed Oxidations of Organic Compounds* (New York: Academic Press, 1981)
2. A Mortreux, F Petit (Eds) *Industrial Applications of Homogeneous Catalysis* (Dordrecht: Reidel, 1988)
3. G W Parshall, S D Ittel, in *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes* (2nd Ed.) (New York: Wiley-Interscience, 1992) p. 151

4. J Haber, in *Handbook of Heterogeneous Catalysis* Vol. 2 (Eds G Ertl, H Knozinger, J Weitkamp) (Weinheim: VCH, 1997) p. 2253
5. A E Shilov, G B Shul'pin *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes* (Ed. B R James) (Dordrecht: Kluwer Academic, 2000)
6. G-J Brink, I W C E Arends, R A Sheldon *Science* **287** 1636 (2000)
7. J H Clark, C N Rhodes *Clean Syntheses Using Porous Inorganic Solid Catalysts and Supported Reagents* (Cambridge: Royal Society of Chemistry, 2000)
8. G Centi, F Cavani, F Trifirro *Selective Oxidation by Heterogeneous Catalysis* (New York: Kluwer Academic, Plenum, 2001)
9. I T Horvath (Ed.) *Encyclopedia of Catalysis* Vol. 6 (New York: Wiley-Interscience, 2003)
10. R A Sheldon *Chem. Ind.* 903 (1992)
11. R A Sheldon, J Dakka *Catal. Today* **19** 215 (1994)
12. G Centi, M Misono *Catal. Today* **41** 287 (1998)
13. R A Sheldon, R S Downing *Appl. Catal. A* **189** 163 (1999)
14. J S Rafelt, J H Clark *Catal. Today* **57** 33 (2000)
15. W F Hölderich *Catal. Today* **62** 115 (2000)
16. W R Sanderson *Pure Appl. Chem.* **72** 1289 (2000)
17. B M Choudary, M L Kantam, P L Santhi *Catal. Today* **57** 17 (2000)
18. I I Moiseev *J. Mol. Catal. A: Chem.* **127** 1 (1997)
19. K Sato, M Aoki, R Noyori *Science* **281** 1646 (1998)
20. C W Jones *Applications of Hydrogen Peroxide and Derivatives* (Cambridge: Royal Society of Chemistry, 1999)
21. W Adam (Ed.) *Peroxide Chemistry* (Weinheim: Wiley-VCH, 2000)
22. D Mandelli, M C A van Vliet, R A Sheldon, U Schuchardt *Appl. Catal. A* **219** 209 (2001)
23. G Centi, S Perathoner *Catal. Today* **77** 287 (2003)
24. G Grigoropoulou, J H Clark, J A Elings *Green Chem.* **5** 1 (2003)
25. R Noyori, M Aoki, K Sato *Chem. Commun.* 1977 (2003)
26. G Strukul (Ed.) *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* (Dordrecht, Boston: Kluwer Academic, 1992)
27. J Hagen *Industrial Catalysis: a Practical Approach* (Weinheim: Wiley-VCH, 1999)
28. R A Sheldon *Stud. Surf. Sci. Catal.* **110** 151 (1997)
29. H E B Lempers, R A Sheldon *J. Catal.* **175** 62 (1998)
30. E F Murphy, T Mallat, A Baiker *Catal. Today* **57** 115 (2000)
31. I W C E Arends, R A Sheldon *Appl. Catal. A* **212** 175 (2001)
32. M Ziolek *Catal. Today* **90** 145 (2004)
33. D T On, D Desplantier-Giscard, C Danumah, S Kaliaguine *Appl. Catal. A* **222** 299 (2001)
34. *Catal Today* **19** (Spec. Issue) (1994)
35. G Bellussi, M S Rigutto *Stud. Surf. Sci. Catal.* **85** 177 (1994)
36. M Hartmann, L Kewvan *Chem. Rev.* **99** 635 (1999)
37. N V Chukanov, I V Pekov, R K Rastsvetaeva *Usp. Khim.* **73** 227 (2004) [*Russ. Chem. Rev.* **73** 205 (2004)]
38. US P. 4410501; *Chem. Abstr.* **95** 206272 (1983); US P. 4701428; *Chem. Abstr.* **106** 158282 (1987)
39. Bel. P. 1001038; *Chem. Abstr.* **111** 184844 (1989)
40. J S Reddy, R Kumar *J. Catal.* **130** 440 (1991)
41. B Notari *Stud. Surf. Sci. Catal.* **37** 413 (1988)
42. G Bellussi, A Carati, M G Clerici, G Maddinelli, R Millini *J. Catal.* **133** 220 (1992)
43. M G Clerici, P Ingallina *J. Catal.* **140** 71 (1993)
44. F Maspero, U Romano *J. Catal.* **146** 476 (1994)
45. B Notari *Adv. Catal.* **41** 253 (1996)
46. R J Saxton *Top. Catal.* **9** 43 (1999)
47. M G Clerici *Top. Catal.* **13** 373 (2000)
48. D R C Huybrechts, L De Bruycker, P A Jacobs *Nature (London)* **345** 240 (1990)
49. J S Reddy, P A Jacobs *Catal. Lett.* **37** 213 (1996)
50. M A Camblor, A Corma, J Perez-Pariente *Zeolites* **13** 82 (1993)
51. T Tatsumi, Q H Xia, N Jappar *Chem. Lett.* 677 (1997)
52. A Tuel *Zeolites* **15** 236 (1995)
53. G J Kim, B R Cho, J H Kim *Catal. Lett.* **22** 259 (1993)
54. P Wu, T Komatsu, T Yashima *J. Phys. Chem.* **100** 10316 (1996)
55. M Díaz-Cabañas, L A Villaescusa, M A Camblor *Chem. Commun.* 761 (2000)
56. P Wu, T Tatsumi *Chem. Commun.* 897 (2001)
57. P Wu, T Tatsumi, T Komatsu, T Yashima *J. Catal.* **202** 245 (2001)
58. P Wu, T Tatsumi *J. Catal.* **214** 317 (2003)
59. P Wu, T Tatsumi *Catal. Surv. Asia* **8** 137 (2004)
60. A Bhaumik, S Samanta, N K Mal *Microporous Mesoporous Mater.* **68** 29 (2004)
61. A Corma, M A Camblor, P Esteve, A Martinez, J P Pariente *J. Catal.* **145** 151 (1994)
62. V Hulea, E Dumitriu, F Patcas, R Ropot, P Graffin, P Moreau *Appl. Catal. A* **170** 169 (1998)
63. J C van der Waal, M S Rigutto, H van Bekkum *Appl. Catal. A* **167** 331 (1998)
64. E G Derouane, G J Hutchings, W F Mbafor, S M Roberts *New J. Chem.* 797 (1998)
65. S Krijnen, P Sanchez, B T F Jakobs, J H C van Hooff *Microporous Mesoporous Mater.* **31** 163 (1999)
66. W Adam, A Corma, T I Reddy, M Renz *J. Org. Chem.* **62** 3631 (1997)
67. M Ogura, S Nakata, E Kikuchi, M Matsukata *J. Catal.* **199** 41 (2001)
68. A Carati, C Flego, E P Massara, R Millini, L Carluccio, G Bellussi *Microporous Mesoporous Mater.* **30** 137 (1999)
69. A Corma, M T Navarro, J Perez-Pariente *J. Chem. Soc., Chem. Commun.* 147 (1994)
70. Eur. P. 0655278A1; *Chem. Abstr.* **122** 171252 (1995)
71. US P. 5783167; *Chem. Abstr.* **129** 148780 (1998)
72. T Blasco, A Corma, M T Navarro, J P Pariente *J. Catal.* **156** 65 (1995)
73. P T Tanev, M Chibwe, T J Pinnavaia *Nature (London)* **368** 321 (1994)
74. A Sayari *Chem. Mater.* **8** 1840 (1996)
75. P T Tanev, T J Pinnavaia *Chem. Mater.* **8** 2068 (1996)
76. D M Antonelli, J Y Ying *Curr. Opin. Colloid Interf. Sci.* **1** 523 (1996)
77. A Corma *Chem. Rev.* **97** 2373 (1997)
78. A Corma *Top. Catal.* **4** 249 (1997)
79. T Maschmeyer *Curr. Opin. Solid State Mater. Sci.* **3** 71 (1998)
80. US P. 5855864; *Chem. Abstr.* **128** 142332 (1999)
81. M Schneider, A Baiker *Catal. Today* **35** 339 (1997)
82. J Y Ying, C P Mehnert, M S Wong *Angew. Chem., Int. Ed.* **38** 56 (1999)
83. S Biz, M L Ocelli *Catal. Rev.-Sci. Eng.* **40** 329 (1998)
84. X Gao, I E Wachs *Catal. Today* **51** 233 (1999)
85. M Dusi, T Mallat, A Baiker *Catal. Rev. Sci. Eng.* **42** 213 (2000)
86. Y H Yue, A Gedeon, J-L Bonardet, N Melosh, J-B D'Espinose, J Fraissard *Chem. Commun.* 1967 (1999)
87. A Tuel *Microporous Mesoporous Mater.* **27** 151 (1999)
88. V N Romannikov, S D Kirik, L A Solov'ev, A N Shmakov, A Yu Derevyankin, V B Fenelonov, O A Kholdeeva, O B Lapina, E A Paukshtis *Kinet. Katal.* **42** 938 (2001) [a]
89. V B Fenelonov *Khim. Zhizn* (11) 8 (2001)
90. P Selvam, S K Bhatia, C G Sonwane *Ind. Eng. Chem. Res.* **40** 3237 (2001)
91. D E De Vos, M Dams, B F Sels, P A Jacobs *Chem. Rev.* **102** 3615 (2002)
92. T Maschmeyer, F Rey, G Sankar, J M Thomas *Nature (London)* **378** 159 (1995)
93. W S Ahn, D H Lee, J H Kim, G Seo, R Ryoo *Appl. Catal. A* **181** 39 (1999)
94. C Cativiela, J M Fraile, J I Garcia, J A Mayoral *J. Mol. Catal. A: Chem.* **112** 259 (1996)
95. M S Morey, S O'Brien, S Schwarz, G D Stucky *Chem. Mater.* **12** 898 (2000)
96. Z Luan, L Kevan *Microporous Mesoporous Mater.* **44–45** 337 (2001)
97. J M Fraile, J I Garcia, J A Mayoral, E Vispe *J. Catal.* **189** 40 (2000)
98. J M Fraile, J I Garcia, J A Mayoral, E Vispe, D R Brown, M Naderi *Chem. Commun.* 1510 (2001)
99. A Tuel, L G Hubert-Pfalzgraf *J. Catal.* **217** 343 (2003)
100. C T Kresge, M E Leonowicz, W J Roth, J C Vartuli, J S Beck *Nature (London)* **359** 710 (1992)
101. J S Beck, J C Vartuli, W J Roth, M E Leonowicz, C T Kresge, K D Schmitt, C T Chu, D H Olson, E W Sheppard, S B McCullen, B Higgens, J L Schlenker *J. Am. Chem. Soc.* **114** 10834 (1992)
102. W Zhang, T J Pinnavaia *Catal. Lett.* **38** 261 (1996)

103. K A Koyano, T Tatsumi *J. Chem. Soc., Chem. Commun.* 145 (1996)
104. W Zhang, M Fröba, J Wang, P T Tanev, J Wong, T J Pinnavaia *J. Am. Chem. Soc.* **118** 9164 (1996)
105. O A Kholdeeva, A Yu Derevyankin, A N Shmakov, N N Trukhan, E A Paukshtis, A Tuel, V N Romannikov *J. Mol. Catal. A: Chem.* **158** 417 (2000)
106. N N Trukhan, A Yu Derevyankin, A N Shmakov, E A Paukshtis, O A Kholdeeva, V N Romannikov *Microporous Mesoporous Mater.* **44 – 45** 603 (2001)
107. Z Shan, J C Jansen, L Marchese, T Maschmeyer *Microporous Mesoporous Mater.* **48** 181 (2001)
108. S A Bagshaw, E Pouzet, T J Pinnavaia *Science* **269** 1242 (1995)
109. B J Aronson, C F Blanford, A Stein *Chem. Mater.* **9** 2842 (1997)
110. N N Trukhan, V N Romannikov, A N Shmakov, M P Vanina, E A Paukshtis, V I Bukhtiyarov, V V Kriventsov, I Yu Danilov, O A Kholdeeva *Microporous Mesoporous Mater.* **59** 73 (2003)
111. B L Newalkar, J Olanrewaju, S Komarneni *Chem. Mater.* **13** 552 (2001)
112. F Chiker, J-F Nogier, F Launay, J-L Bonardet *Appl. Catal. A* **243** 309 (2003)
113. Y Chen, Y Huang, J Xiu, X Han, X Bao *Appl. Catal. A* **273** 185 (2004)
114. F Chiker, G Lapisardi, F Launay, J-F Nogier, J-L Bonardet *Catal. Commun.* **5** 247 (2004)
115. D Ji, T Ren, L Yan, J Suo *Mater. Lett.* **57** 4474 (2003)
116. O A Kholdeeva, M S Melgunov, A N Shmakov, N N Trukhan, V V Kriventsov, V I Zaikovskii, V N Romannikov *Catal. Today* **91 – 92** 205 (2004)
117. Q Huo, R Leon, P M Petroff, G D Stucky *Science* **268** 1324 (1995)
118. Q Huo, D I Margolese, U Ciesla, P Feng, T E Gier, P Sieger, R Leon, P M Petroff, F Schüth, G D Stucky *Nature (London)* **368** 317 (1994)
119. D M Antonelli, J Y Ying *Angew. Chem., Int. Ed.* **35** 426 (1996)
120. V B Fenelonov, A Yu Derevyankin, S D Kirik, L A Solovyov, A N Shmakov, J-L Bonardet, A Gedeon, V N Romannikov *Microporous Mesoporous Mater.* **44 – 45** 33 (2001)
121. K A Koyano, T Tatsumi *Microporous Mater.* **10** 259 (1997)
122. L Y Chen, G K Chuah, S Jaenicke *Catal. Lett.* **50** 107 (1998)
123. C H Rhee, J S Lee *Catal. Lett.* **40** 261 (1996)
124. Y Deng, C Lettmann, W F Maier *Appl. Catal. A* **214** 31 (2001)
125. N N Trukhan, V N Romannikov, E A Paukshtis, A N Shmakov, O A Kholdeeva *J. Catal.* **202** 110 (2001)
126. O A Kholdeeva, N N Trukhan, M P Vanina, V N Romannikov, V N Parmon, J Mrowiec-Bialon, A B Jarzebski *Catal. Today* **75** 203 (2002)
127. US P. 5958368; *Chem. Abstr.* **131** 230626 (1999)
128. S Noda Pérez, E Moreno, C A Henriques, S Valange, Z Gabelica, J L F Monteiro *Microporous Mesoporous Mater.* **41** 137 (2000)
129. R Mokaya *Chem. Commun.* 933 (2001)
130. L Chen, T Horiuchi, T Mori, K Maeda *J. Phys. Chem. B* **103** 1216 (1999)
131. M B D'Amore, S Schwarz *Chem. Commun.* 121 (1999)
132. X S Zhao, G Q Lu *J. Phys. Chem. B* **102** 1556 (1998)
133. A Corma, M Domine, J A Gaona, J L Jorda, M T Navarro, F Rey, J Perez-Pariente, J Tsuji, B McCulloch, L T Neneth *Chem. Commun.* 2211 (1998)
134. T Tatsumi, K K Koyano, N Igarashi *Chem. Commun.* 325 (1998)
135. A Bhaumik, T Tatsumi *J. Catal.* **189** 31 (2000)
136. K A Koyano, T Tatsumi, Y Tanaka, S Nakata *J. Phys. Chem. B* **101** 9436 (1997)
137. J Bu, H-K Rhee *Catal. Lett.* **65** 141 (2000)
138. M L Peña, V Dellarocca, F Rey, A Corma, S Coluccia, L Marchese *Microporous Mesoporous Mater.* **44 – 45** 345 (2001)
139. M Chatterjee, H Hayashi, M Saito *Microporous Mesoporous Mater.* **57** 143 (2003)
140. R H P R Poladi, C C Landry *Microporous Mesoporous Mater.* **52** 11 (2002)
141. P T Tanev, T J Pinnavaia *Science* **267** 865 (1995)
142. US P. 2001043901; *Chem. Abstr.* **135** 332956 (2001)
143. D Zhao, Q Huo, J Feng, B F Chmelka, G D Stucky *J. Am. Chem. Soc.* **120** 6024 (1998)
144. J M Kim, G D Stucky *Chem. Commun.* 1159 (2000)
145. S-S Kim, T R Pauly, T J Pinnavaia *Chem. Commun.* 1661 (2000)
146. US P. 6391278; *Chem. Abstr.* **128** 142332 (2002)
147. S A Bagshaw *Chem. Commun.* 1785 (1999)
148. Russ. P. 2229930; *Byull. Izobret.* (16) (2004)
149. A Belhekar, M Agashe, H Soni, S Sathaye, N Jacob, J Thundamadathil *Bull. Chem. Soc. Jpn.* **73** 2605 (2000)
150. K-K Kang, C-H Park, W-S Ahn *Catal. Lett.* **59** 45 (1999)
151. W-S Ahn, N-K Kim, S-Y Jeong *Catal. Today* **68** 83 (2001)
152. A Thangaraj, S Sivasanker *J. Chem. Soc., Chem. Commun.* 123 (1992)
153. J E Haskouri, S Cabrera, M Gutierrez, A Beltran-Porter, D Beltran-Porter, M D Marcos, P Amoros *Chem. Commun.* 309 (2001)
154. Y Luo, G Z Lu, Y L Guo, Y S Wang *Catal. Commun.* **3** 129 (2002)
155. T E W Nieyen, J P M Niederer, T Gjervan, W F Hölderich *Microporous Mesoporous Mater.* **21** 67 (1998)
156. C-Y Chen, S L Burkett, H-X Li, M E Davis *Microporous Mater.* **2** 27 (1993)
157. A Firouzi, D Kumar, L M Bull, T Besier, P Sieger, Q Huo, S A Walker, J A Zasadzinski, C Glinka, J Nicol, D Magnolese, G D Stucky, B F Chmelka *Science* **267** 1138 (1995)
158. A Steel, S W Carr, M W Anderson *J. Chem. Soc., Chem. Commun.* 1571 (1994)
159. A Monnier, F Schüth, Q Huo, D Kumar, D Magnolese, R S Maxwell, G D Stucky, M Krishnamurty, P Petroff, A Firouzi, M Janicke, B F Chmelka *Science* **261** 1299 (1993)
160. J B Miller, S T Johnston, E I Ko *J. Catal.* **150** 311 (1994)
161. J B Miller, E I Ko *J. Catal.* **159** 58 (1996)
162. G M Pajonk *Catal. Today* **35** 319 (1997)
163. M Schneider, A Baiker *Catal. Rev. Sci. Eng.* **37** 515 (1995)
164. D C M Dutoit, M Schneider, A Baiker *J. Catal.* **153** 165 (1995)
165. US P. 5935895; *Chem. Abstr.* **125** 36299 (1999)
166. R Hutter, D C M Dutoit, T Mallat, M Schneider, A Baiker *J. Chem. Soc., Chem. Commun.* 163 (1995)
167. R Hutter, T Mallat, A Baiker *J. Catal.* **153** 177 (1995)
168. D C Dutoit, M Schneider, R Hutter, A Baiker *J. Catal.* **161** 651 (1996)
169. D C Dutoit, U Göbel, M Schneider, A Baiker *J. Catal.* **164** 433 (1996)
170. L Delattre, F Babonneau *Chem. Mater.* **9** 2385 (1997)
171. F Garbassi, L Balducci *Microporous Mesoporous Mater.* **47** 51 (2001)
172. S Hu, R J Willey, B Notari *J. Catal.* **220** 240 (2003)
173. R K Iler *The Chemistry of Silica : Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica* (New York: Wiley, 1979)
174. C J Brinker, G W Scherer *Sol–Gel Science — the Physics and Chemistry of Sol–Gel Processing* (San Diego: Academic Press, 1990)
175. R D Gonzalez, T Lopez, R Gomes *Catal. Today* **35** 293 (1997)
176. F Mizukami, S Niwa, M Toba, T Tsuchiya, K Shimizu, S Imai, J Imamura, in *Preparation of Catalysts IV* (Eds B Delmon, P Grange, P A Jacobs, G Ponselet) (Amsterdam: Elsevier, 1987) p. 45
177. C J Brinker, K D Keefer, D W Schaefer, C S Ashley *J. Non-Cryst. Solids* **48** 47 (1982)
178. C A Müller, M Schneider, T Mallat, A Baiker *J. Catal.* **192** 448 (2000)
179. C Beck, T Mallat, T Bürgi, A Baiker *J. Catal.* **204** 428 (2001)
180. Russ. P. 2196764; *Byull. Izobret.* (2) (2003)
181. J Mrowiec-Bialon, A B Jarzebski, O A Kholdeeva, N N Trukhan, V I Zaikovski, V V Kriventsov, Z Olejniczak *Appl. Catal. A* **273** 47 (2004)
182. F Figueras, H Kochkar *Catal. Lett.* **59** 79 (1999)
183. C A Müller, M Maciejewski, T Mallat, A Baiker *J. Catal.* **184** 280 (1999)
184. C A Müller, R Deck, T Mallat, A Baiker *Top. Catal.* **11/12** 369 (2000)
185. C A Müller, M Schneider, T Mallat, A Baiker *J. Catal.* **189** 221 (2000)

186. J L Sotelo, R VanGrieken, C Martos *Chem. Commun.* 549 (1999)
187. Y Deng, W F Maier *J. Catal.* **199** 115 (2001)
188. Eur. P. 0791558A1; *Chem. Abstr.* **127** 207681 (1997)
189. R Millini, E P Massara, G Perego, G Bellussi *J. Catal.* **137** 497 (1992)
190. C H Rhee, J S Lee *Catal. Today* **38** 213 (1997)
191. L A Solovyov, S D Kirik, A N Shmakov, V N Romannikov *Microporous Mesoporous Mater.* **44 – 45** 17 (2001)
192. S A Bagshaw *Stud. Surf. Sci. Catal.* **117** 381 (1998)
193. E G Kodenev, A N Shmakov, A Yu Derevyankin, A V Nosov, V N Romannikov *Izv. Akad. Nauk, Ser. Khim.* 1685 (2000) [b]
194. V B Fenelonov, V N Romannikov, A Yu Derevyankin *Microporous Mesoporous Mater.* **28** 57 (1999)
195. M D Alba, A I Becerro, J Klinowski *Faraday Trans.* 849 (1996)
196. R S Drago, S C Dias, J M McGilvray, A L M L Mateus *J. Phys. Chem. B* **102** 1508 (1998)
197. G N Vayssilov *Catal. Rev. Sci. Eng.* **39** (3) 209 (1997)
198. X S Zhao, G Q Lu, A J Whittaker, G J Millar, H Y Zhu *J. Phys. Chem. B* **101** 6525 (1997)
199. P Schmidt-Winkel, P Yang, D I Margolese, B F Chmelka, G D Stucky *Adv. Mater.* **11** 303 (1999)
200. K Kosuge, P S Singh *J. Phys. Chem. B* **103** 3563 (1999)
201. P J Rainho, J Rocha, L D Carlos, R M Almeida *J. Mater. Res.* **16** 2369 (2001)
202. D M Pickup, G Mountjoy, G W Wallidge, R Anderson, J M Cole, R J Newport, M E Smith *J. Mater. Chem.* **9** 1299 (1999)
203. R Hutter, T Mallat, A Baiker *J. Catal.* **157** 665 (1995)
204. N N Trukhan, Candidate Thesis in Chemical Sciences, Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2003
205. G Petrini, A Cesana, G De Alberti, F Genoni, G Leofanti, M Paclovan, G Paparatto, P Rofia *Stud. Surf. Sci. Catal.* **68** 761 (1991)
206. M R Boccuti, K M Rao, A Zecchina, V Leofanti, G Petrini *Stud. Surf. Sci. Catal.* **48** 133 (1989)
207. E Geobaldo, S Bordiga, A Zeccina, E Giamello, G Leofanti, G Petrini *Catal. Lett.* **16** 109 (1992)
208. S Bordiga, S Coluccia, C Lamberti, L Marchese, A Zecchina, F Boscherini, F Buffa, F Genoni, G Leofanti, G Petrini, G Vlaic *J. Phys. Chem.* **98** 4125 (1994)
209. L Marchese, E Gianotti, V Dellarocca, T Maschmeyer, F Rey, S Coluccia, J M Thomas *Phys. Chem. Chem. Phys.* **1** 585 (1999)
210. S Klein, S Thorimbert, W F Maier *J. Catal.* **163** 476 (1996)
211. J Weitkamp, S Ernst, E Roland, G F Thiele *Stud. Surf. Sci. Catal.* **105** 763 (1997)
212. A Hagen, K Schueler, F Roessner *Microporous Mesoporous Mater.* **51** 23 (2002)
213. M D Alba, Z Luan, J Klinowski *J. Phys. Chem.* **100** 2178 (1996)
214. Z Liu, R J Davis *J. Phys. Chem.* **98** 1253 (1994)
215. V V Kriventsov, D I Kochubey, M V Tsodikov, J A Navio, G M Restrepo, M Macias *Nucl. Instrum Methods A* **470** 347 (2001)
216. F Farges, G E Brown Jr, J J Rehr *Phys. Rev. B* **56** 1809 (1997)
217. A Muñoz-Paez, P Malet *Appl. Surf. Sci.* **56** 873 (1992)
218. S Pei, G W Zajac, J A Kaduk, J Faber, B I Boyanov, D Duck, D Fazzini, T I Morrison, D S Yang *Catal. Lett.* **21** 333 (1993)
219. G M Ingo, S Dire, F Babonneau *Appl. Surf. Sci.* **70/71** 230 (1993)
220. B M Weckhuysen, P van der Voort, G Catana (Eds) *Spectroscopy of Transition Metal Ions on Surfaces* (Leuven: Leuven University Press, 2000)
221. C D Wagner, W M Riggs, L E Davis, J F Moulder, G E Muilenberg *Handbook of X-ray Photoelectron Spectroscopy* (Eden Praier: Perkin-Elmer, 1979)
222. J Willey, in *Practical Surface Analysis, Auger and X-ray Photoelectron Spectroscopy* Vol. 1 (2nd Ed.) (Eds D Briggs, M P Seah) (Chichester: Wiley, 1990)
223. A Tuel, J Diab, P Gelin, M Dufaux, J-F Dutel, Y B Taarit *J. Mol. Catal.* **63** 95 (1990)
224. A Ghorbel, A Tuel, E Jorda, Y B Taarit, C Naccache *Stud. Surf. Sci. Catal.* **97** 471 (1995)
225. A M Prakash, H M Sung-Suh, L Kevan *J. Phys. Chem.* **102** 857 (1998)
226. K Chaudhari, R Bal, D Srinivas, A J Chandwadkar, S Sivasanker *Microporous Mesoporous Mater.* **50** 209 (2001)
227. L Bonoldi, C Busetto, A Congiu, G Marra, G Ranghino, M Salvalaggio, G Spano, E Giamello *Spectrochim. Acta, Part A* **58** 1143 (2002)
228. K Chaudhari, D Srinivas, P Ratnasamy *J. Catal.* **203** 25 (2001)
229. D Srinivas, P Manikandan, S C Laha, R Kumar, P Ratnasamy *J. Catal.* **217** 160 (2003)
230. M Schraml-Marth, K L Walther, A Wokaun, B E Handy, A Baiker *J. Non-Cryst. Solids* **143** 93 (1992)
231. J M Miller, L J Lakshmi *J. Phys. Chem. B* **102** 6465 (1998)
232. H Knözinger, S Huber *J. Chem. Soc., Faraday Trans.* 2047 (1998)
233. D V Kozlov, E A Paukshtis, E N Savinov *Appl. Catal. B* **24** L7 (2000)
234. A Fernandez, J Leyrer, A R Gonzalez-Elipe, G Munuera, H Knozinger *J. Catal.* **112** 489 (1988)
235. M Besson, M C Bonnet, P Gallezot, I Tkatchenko, A Tuel *Catal. Today* **51** 547 (1999)
236. A Corma, M T Navarro, J Perez-Pariente, F Sanchez *Stud. Surf. Sci. Catal.* **84** 69 (1994)
237. D T On, M P Kapoor, P N Joshi, L Bonneviot, S Kaliaguine *Catal. Lett.* **44** 171 (1997)
238. C Berlini, M Guidotti, G Moretti, R Psaro, N Ravasio *Catal. Today* **60** 219 (2000)
239. S Gontier, A Tuel *J. Catal.* **157** 124 (1995)
240. A Corma, M Iglesias, F Sanchez *Catal. Lett.* **39** 153 (1996)
241. V Hulea, F Fajula, J Bousquet *J. Catal.* **198** 179 (2001)
242. S K Mohapatra, F Hussain, P Selvam *Catal. Commun.* **4** 57 (2003)
243. A Sorokin, A Tuel *Catal. Today* **57** 45 (2000)
244. S C Laha, R Kumar *Microporous Mesoporous Mater.* **53** 163 (2002)
245. C A Muller, M Schneider, A Gisler, T Mallat, A Baker *Catal. Lett.* **64** 9 (2000)
246. A Gisler, C A Muller, M Schneider, T Mallat, A Baker *Stud. Surf. Sci. Catal.* **130** 1637 (2000)
247. M Dusi, T Mallat, A Baiker *J. Catal.* **173** 423 (1998)
248. M Dusi, T Mallat, A Baiker *J. Catal.* **187** 191 (1999)
249. C Berlini, G Ferraris, M Guidotti, G Moretti, R Psaro, N Ravasio *Microporous Mesoporous Mater.* **44 – 45** 595 (2001)
250. L J Davis, P McMorn, D Bethell, P C B Page, F King, F E Hancock, G J Hutchings *J. Mol. Catal. A: Chem.* **165** 243 (2001)
251. R Hutter, T Mallat, A Peterhans, A Baiker *J. Catal.* **172** 427 (1997)
252. R Hutter, T Mallat, A Peterhans, A Baiker *J. Mol. Catal. A: Chem.* **138** 241 (1999)
253. M Guidotti, N Ravasio, R Psaro, E Gianotti, L Marchese, S Coluccia *Green Chem.* **5** 421 (2003)
254. L Y Chen, G K Chuah, S Jaenicke *J. Mol. Catal. A: Chem.* **132** 281 (1998)
255. J S Reddy, A Sayari *Appl. Catal. A* **128** 231 (1995)
256. C B Khow, M E Davis *J. Catal.* **151** 77 (1995)
257. M Guidotti, N Ravasio, R Psaro, G Ferraris, G Moretti *J. Catal.* **214** 242 (2003)
258. R S Reddy, J S Reddy, R Kumar, P Kumar *J. Chem. Soc., Chem. Commun.* 84 (1992)
259. R J Mahalingam, P Selvam *Chem. Lett.* 455 (1999)
260. N N Trukhan, O A Kholdeeva *Kinet. Katal.* **44** 378 (2003) [a]
261. O A Kholdeeva, G M Maksimov, R I Maksimovskaya, L A Kovaleva, M A Fedotov, V A Grigoriev, C L Hill *Inorg. Chem.* **39** 3828 (2000)
262. O A Kholdeeva, T A Trubitsina, G M Maksimov, A V Golovin, R I Maksimovskaya *Inorg. Chem.* **44** 1635 (2005)
263. M G Clerici *Appl. Catal.* **68** 249 (1991)
264. F Bonino, A Damin, G Ricchiardi, M Ricci, G Spano, R D'Aloisio, A Zecchina, C Lamberti, C Prestipino, S Bordiga *J. Phys. Chem. B* **108** 3573 (2004)

[a] — *Kinet. Catal. (Engl. Transl.)*
[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*