Accepted Manuscript

Research paper

Titanium-Silica Catalyst derived from Defined Metallic Titanium Cluster Precursor: Synthesis and Catalytic Properties in Selective Oxidations

Claudio Evangelisti, Matteo Guidotti, Cristina Tiozzo, Rinaldo Psaro, Nataliya Maksimchuk, Irina Ivanchikova, Alexandr N. Shmakov, Oxana Kholdeeva

 PII:
 \$0020-1693(17)30555-8

 DOI:
 http://dx.doi.org/10.1016/j.ica.2017.06.059

 Reference:
 ICA 17708

To appear in: Inorganica Chimica Acta

Received Date:21 April 2017Revised Date:25 June 2017Accepted Date:27 June 2017



Please cite this article as: C. Evangelisti, M. Guidotti, C. Tiozzo, R. Psaro, N. Maksimchuk, I. Ivanchikova, A.N. Shmakov, O. Kholdeeva, Titanium-Silica Catalyst derived from Defined Metallic Titanium Cluster Precursor: Synthesis and Catalytic Properties in Selective Oxidations, *Inorganica Chimica Acta* (2017), doi: http://dx.doi.org/ 10.1016/j.ica.2017.06.059

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Titanium-Silica Catalyst derived from Defined Metallic Titanium Cluster

Precursor: Synthesis and Catalytic Properties in Selective Oxidations

Claudio Evangelisti^a, Matteo Guidotti^a, Cristina Tiozzo^a, Rinaldo Psaro^a,

Nataliya Maksimchuk^{b,c}, Irina Ivanchikova^b, Alexandr N. Shmakov^{b,c,d}, Oxana Kholdeeva^{b,c}

a Istituto di Scienze e Tecnologie Molecolari (CNR-ISTM), C. Golgi 19, 20133 Milano, Italy b Boreskov Institute of Catalysis, Pr. Lavrentieva 5, Novosibirsk, 630090, Russia c Novosibirsk State University, Pirogova 2, Novosibirsk, 630090, Russia d Budker Institute of Nuclear Physics, Lavrentieva 11, Novosibirsk, 630090, Russia

Abstract

A class of titanium-grafted mesoporous silica catalysts has been designed and prepared starting from molecularly defined metal clusters. The organosol mixture of zerovalent Ti_{13} clusters was impregnated onto the surface of ordered mesoporous silica molecular sieves (MCM-41 and MMM-2) and, after high-temperature calcination, an evenly dispersed non-single-site $Ti(IV)_nO_x$ -like silica-supported catalyst was obtained. The catalytic solids, fully characterized by microscopic, spectroscopic and porosimetric techniques, showed standard performance in the liquid-phase epoxidation of a cyclic alkene, as limonene, but remarkably high selectivity values in the oxidative carboxylation of styrene, with *tert*-butylhydroperoxide and carbon dioxide in the presence of tetrabutylammonium bromide as a cocatalyst. Unprecedented high yields, up to 67%, in styrene carbonate were achieved after 24 h, under solvent-free conditions. The catalysts displayed also a noteworthy stability of the performance to repeated recovery and reuse cycles.

dedicated to Dr. Carlo Mealli

Keywords

Titanium clusters; heterogeneous catalysis; alkene epoxidation; oxidative carboxylation; mesoporous silica

Highlights

- Heterogeneous titanium-grafted silica catalysts obtained from molecularly defined zerovalent Ti₁₃ clusters
- Uniformly dispersed non-single-site titanium oxide-like catalytic sites supported onto ordered mesoporous molecular sieves
- Ti_xO_n-MCM-41 and Ti_xO_n-MMM-2 solids active as oxidation catalysts with *tert*butylhydroperoxide
- Conventional performance in the liquid-phase epoxidation of limonene
- Promising performance and high yields in oxidative carboxylation of styrene with *tert*butylhydroperoxide and carbon dioxide
- Remarkable stability of the catalytically-active sites to repeated recycles under reaction conditions

Graphical Abstract



1. Introduction

The deposition of well-defined metal-containing precursors via post-synthesis techniques onto structured porous inorganic oxides is a versatile and convenient method to prepare heterogeneous catalysts with tailored catalytic performances [1,2,3]. It is possible to select the support with the most suitable characteristics (elemental composition, presence of dopant species, hydrophilic/hydrophobic character, morphology, topology and hydrothermal stability) and the most promising catalytic metal centres in terms of chemical nature, loading, redox properties and/or acidbase character [4]. By this approach, active metal sites can be added to an oxidic porous support by grafting, *i.e.* by irreversible deposition of a precursor metal species (typically an inorganic or organometallic complex) and formation of covalent bonds between the metal centre and the support. As a final result, the metal site presents different chemical features with respect to the pristine precursor species it is derived from, since the chemical surroundings around the metal centre is partially (or totally) modified during the chemical chemisorption of the precursor and, in most cases, during the further final thermal treatment [5,6].

The deposition and grafting strategies have been widely explored for the preparation of titanium-silica catalysts [7,8]. For instance, the catalyst for alkene epoxidation developed by Shell for the styrene monomer-propylene oxide (SMPO) process is considered a milestone in the preparation of grafted titanium(IV)-silica systems and it is obtained by a multistep vapour-phase process by deposition of the titanium precursor (TiCl₄ or an organotitanium compound), heating the obtained material, followed by steaming and silylation [9]. In this case, the Ti(IV)/SiO₂ catalyst is active in epoxidation in the presence of alkylhydroperoxides as oxidants thanks to the formation of site-isolated Ti species on the surface of the support and the increased Lewis acidity of the Ti(IV) sites due to electron withdrawing effect by the siloxy ligands [10]. Since then, an exponential growth of Ti(IV)-silica catalysts obtained via post-synthesis grafting has been observed. Among the most used precursor, one can mention inorganic precursors as well as organometallic complexes

with an increasing level of complexity in order to direct as best the isolation, dispersion and nuclearity expected for the metal sites in the final catalysts: for instance, TiCl₄ [11], Ti(OiPr)₄ [12,13,14], Ti(OBu)₄ [15] or Ti(OEt)₄ [16], TiF₄ [17] or Ti(triethanolaminate)-isopropoxide [18], Ti(η^5 -C₅H₅)₂Cl₂ [19,20], [{Ti(OiPr)₂(OMenth)}₂] and [Ti(OMenth)₄] (OMenth = 1*R*,2*S*,5*R*-(-)-menthoxo) [21], [('BuO)₂Ti{ μ -O₂Si[OSi(O'Bu)₃]₂]₂ [22], [Ti₆(μ ₃-O)₆(μ -O₂CC₆H₄OPh)₆(OEt)₆] [23] or (NH₄)₈[Ti₄(C₆H₄O₇)₄(O₂)₄]·8H₂O [24,25]. These species can be grafted either from solutions in liquid phase or directly from vapour phase onto either ordered (such as MCM-41, MCM-48 and SBA-15 molecular sieves) or non-ordered mesoporous silicas. Alternatively, Ti(IV) species can be introduced into the silica matrix in one step, e.g., by direct synthesis [26] or by evaporation-induced self assembly (EISA) [27]. All these titanium-containing silica systems showed interesting results in selective oxidation reactions, such as the epoxidation of alkenes and unsaturated alcohols [28,29] or oxidative carboxylation of alkenes in the presence of *tert*-butylhydroperoxide (TBHP) [30,31,32], as well as oxidation of substituted phenols to quinones with aqueous hydrogen peroxide (for recent reviews, see ref. 8)

However, to our best knowledge, the use of metallic titanium clusters as precursors to be deposited on silica supports has not been explored yet. In fact, most of the synthetic strategies reported so far aimed at obtaining single-site heterogeneous catalysts in which the Ti centres could be dispersed as evenly as possible, avoiding the formation of titanium oxide-like domains that may be detrimental for the preparation of efficient oxidation catalysts [33]. However, it has been observed in several reports that the site isolation of Ti(IV) atoms is not mandatory to have an effective and selective system and that the formation of nanosized TiO₂ domains at the surface could give rise to good catalysts as well [13,23,24,27,33,34]. For these reasons, in the present work, a multinuclear titanium(0) metallic cluster has been chosen as a starting precursor for the preparation of a mesoporous grafted titanium-silica catalyst to be tested in the selective oxidation of two substrates with different characteristics. The following calcination at high temperature gives rise to the catalytically active Ti(IV) sites with particular properties that are worth to be studied as

heterogeneous catalysts in the liquid-phase epoxidation of cyclic alkenes and in the oxidative carboxylation of styrene, in the presence of carbon dioxide.

2. Experimental

2.1. Materials

All operations involving Ti_n-THF colloidal solution were performed under a dry argon atmosphere with the use of the standard Schlenk techniques. TiCl₄·2THF (97%), THF (puriss. p.a., ACS reagent, RPE \geq 99.9%, distilled under inert atmosphere prior to use), K[BBu₃H] ([®]K-Selectride, 1.0 M in THF solution), (*R*)-(+)-limonene (97%; 98% e.e.), CH₃CN (HPLC grade) and TBHP (5.5 M in *n*-decane solution) were all Aldrich products and used as received. Other reactants were obtained commercially and used without additional purification.

2.2. Synthesis of the siliceous supports

MCM-41 support was prepared as previously reported, by using Aerosil 200 (Degussa) as a silica source and cetyltrimethyl ammonium bromide (CTAB) as a surfactant. The molar ratio of the synthesis mixture was: 1 SiO₂/ 0.1 CTAB, 0.25 NaOH, 20 H₂O. The slurry was maintained at 115°C for 24 h before being filtered, washed, dried at 80°C and calcined at 550°C for 8h.[35].

The mesoporous mesophase MMM-2 silica support was prepared by hydrothermal synthesis under moderately acidic conditions (pH 3.0) following a two-step procedure described previously [36], using sodium silicate as silicon source and cetyltrimethylammonium bromide (CTAB) as a template.

2.3. Preparation of the titanium-silica catalysts

1.0 g of TiCl₄·2THF was added to a three neck flask at 40 mL of THF and the solution was heated up to 40°C. 12 mL of a solution of K[BBu₃H] 1.0 M in THF were added dropwise to the solution,

under stirring. The addition of the borohydride salt was completed in 1 h and, after that, the solution was left under magnetic stirring for the following 30 min. During the reaction the formation of a white solid (KCl) was observed and it was removed by filtration under argon with a D4 fritted glass filter. BBu₃ and THF were removed from the brown filtrate under vacuum (10^{-4} mbar) and the residue was dissolved in 80 mL of THF. The Ti_n-THF colloidal solution was thus stored in refrigerator (-20°C) under inert atmosphere.

1.5 g of the siliceous support (MCM-41 or MMM-2) were pretreated at 150 °C under inert atmosphere for 2.5 h, cooled and then treated in vacuo. The solid was suspended in 20 mL of dry THF under argon atmosphere at 25°C and then 20 mL of the Ti_n -THF solution were added leaving the mixture under stirring for 20 min. After that time, the stirring was then stopped and the colourless supernatant liquid was removed by filtration. The obtained powder was dried under vacuum and then calcined under dry oxygen at 500°C (heating temperature programme 10°C min⁻¹) for 2.5 h.

2.4. Characterisation

The titanium content in the catalysts was analyzed by inductively coupled plasma optical emission spectroscopy ICP-OES (ICAP 6300 Duo, Thermo Fisher Scientific) after mineralization of the sample with a 1:1 aqueous HF/HNO₃ mixture.

Nitrogen adsorption measurements were carried out at 77 K using a NOVA 1200 instrument (Quantachrome) within partial pressure in the range 10^{-4} –1.0. The catalysts were degassed at 150°C for 24 h prior to measurements. Surface areas of the samples were determined by BET analysis of the low-temperature N₂ adsorption data. Pore size distributions were calculated from the adsorption branches of the nitrogen isotherms by means of the regularization procedure, using reference local isotherms calculated in a cylindrical silica pore model, according to the density functional theory (DFT) approach. Special software provided by Quantachrome Corp. was used for this purpose. Mean pore diameters were calculated as mathematical expectation values from these distributions.

Transmission electron microscopy (TEM) analysis were performed by a ZEISS LIBRA200FE microscope equipped with a 200 kV FEG source. Energy-dispersive X-ray spectroscopy (EDS – Oxford INCA Energy TEM 200) and elemental mapping were collected along with HAADF-STEM (high angular annular dark field scanning electron microscopy) images. Powders of the samples were ultrasonically dispersed in isopropyl alcohol and then each suspension were dropped onto a holey carbon coated copper grid (300 mesh) and evaporating the solvent.

XRD measurements were performed with a high-precision X-ray diffractometer mounted on the beamline No. 2 of the VEPP-3 storage ring at the Siberian Synchrotron Radiation Centre (SSRC). The state of titanium in the catalysts was monitored by DR UV-vis spectroscopy under ambient conditions, by using a Shimadzu UV–VIS 2501PC spectrophotometer. FT-Raman spectra (3600-100 cm⁻¹, 300 scans, resolution 4 cm⁻¹, 180° geometry) were recorded using a RFS 100/S spectrometer (Bruker). Excitation of the 1064-nm line was provided by a Nd-YAG laser (100 mW power output).

2.5. Catalytic Studies

GC analyses were carried out on an Agilent 6890 Series; HP-5 column, 30 m - 0.25 mm; FID detector (for limonene oxidation) or a gas chromatograph Tsvet-500 equipped with FID and a quartz capillary column (30 m×0.25 mm) filled with Agilent DB-5MS (for styrene oxidative carboxylation). GC-MS analyses were performed by using an Agilent GC System 7890 interfaced Inert MSD Network 5975C (HP-5MS column 30 m - 0.25 mm - 0.25 μ m). GC peaks were identified by comparison with peaks of genuine samples of reference standards and by means of GC-MS. Oxidation products were quantified by GC using internal standards.

2.5.1. Epoxidation of R-(+)-limonene

The catalyst was pre-treated under dry air at 500°C (heating temperature programme 10°C min⁻¹) for 1 h prior to use. The solid was then cooled down under inert atmosphere. The oxidation

reactions were performed in a 10 mL-glass batch reactor at 90°C under inert atmosphere. To 100 mg of the catalyst, 5 mL of acetonitrile were added and then 0.162 mL (1.0 mmol) of R-(+)-limonene and 0.220 mL (1.1 mmol) of TBHP (5.5 M in *n*-decane solution). The resulting mixture was vigorously stirred (800 rpm). The *n*-decane present as a solvent in the solution of TBHP was used also as internal standard. For each test, conversion of R-(+)-limonene and selectivity to limonene monoepoxide (sum of limonene endocyclic 1,2-epoxide plus exocyclic limonene 8,9-epoxide; Scheme 2) were recorded. Each test was reproduced at least 2 times. Neither significant auto oxidation nor support-catalysed contributions to epoxidation were recorded with titanium-free siliceous supports, limonene conversion being less than 5% with no remarkable epoxide formation. The catalyst was recovered and reused in further catalytic tests after filtration, rinsing with fresh solvent and calcination under dry air at 500°C.

2.5.2. Oxidative carboxylation of styrene

Styrene (0.2 mmol), tetrabutylammonium bromide (TBABr, 0.02 mmol), TBHP (0.3 mmol), the solid catalyst (19-20 mg, corresponding to 0.008 mmol of Ti), biphenyl (internal standard for GC) and acetonitrile (2 mL) were added into a 50 mL high pressure/high temperature stainless steel Parr-4792 reactor with PTFE insert.

For solvent-free conditions, the catalyst loading was 300 mg for Ti_nO_x -MMM-2 (0.11 mmol Ti) at styrene/TBHP/TBABr molar ratio equal to 4.8/7.2/0.48 mmol/mmol. CO₂ was introduced into the reactor, and the pressure was adjusted to 8 bar. The mixture was stirred continuously while the pressure (8 bar) and temperature (70 °C) were kept constant during the reaction. After a specified reaction time (24 or 48 h), the reactor was cooled down by immersion in ice/water bath and depressurized slowly before opening. Each experiment was reproduced at least 2 times.

After the catalytic run, the solid catalyst was separated by filtration and washed with solvent, dried in air at room temperature overnight, calcined under dry air at 350°C for 2 h and at

 510° C for 4 h, and then reused. The catalyst was characterized by DR UV–vis spectroscopy, N₂ adsorption measurements and elemental analysis before and after reuse.

Treatment of Ti_nO_x -MMM-2 with styrene carbonate was carried out in CH_2Cl_2 solution at 70°C. Styrene carbonate (350 mg, 2.1 mmol), Ti_nO_x -MMM-2 catalyst (200 mg, i.e. 0.075 mmol Ti), and CH_2Cl_2 (3 mL) were added into a Parr-4792 reactor with PTFE insert. The mixture was stirred continuously for 24 h, while the temperature (70°C) was kept constant.

SCR

3. Results and discussion

3.1 Preparation and characterization of the titanium-silica catalyst

The titanium(0) cluster precursor was synthesized following a previously reported procedure [37]. Briefly, TiCl₄·2THF was reduced under inert atmosphere with a trialkyl borohydride salt in THF solution leading to organosol titanium clusters. Detailed X-ray absorption spectroscopy (XAS) studies performed on the isolated titanium species revealed the presence of a regular zerovalent Ti₁₃ clusters stabilized by 6 intact THF molecules possibly in the octahedral configuration [38]. The Ti₁₃-THF organosol mixtures were used as precursors of supported titanium species by simple impregnation of the mesoporous silica support at room temperature (25°C). Subsequent exposure to atmospheric air and calcination of the obtained powder gave rise to the Ti_nO_x-silica catalysts (Scheme 1; sketch for MCM-41). The calcination step turned the catalyst from the yellowish-brownish colour of the initial solid into a pure white, suggesting that all of the deposited Ti centres were converted into oxidic Ti(IV) species.

Scheme 1. Preparation sequence for Ti_nO_x-MCM-41



ICP-OES investigations performed on the final Ti_nO_x -silica catalysts revealed a quantitative deposition of the Ti clusters onto the support leading to a titanium metal loading values ranging from 1.9 to 2.1 wt.%, that is always close to the expected value of 2.2 wt.% (Table 1).

In terms of textural properties, the deposition and subsequent calcination of the Ti species onto the siliceous support gives rise to a drastic diminution of specific surface area and pore volume (Table 1). This is consistent with a gradual and remarkable lining of the inner surface of the mesopore channels by the Ti_nO_x moieties. A similar behavior was previously observed with the dry impregnation of titanocene dichloride molecules onto mesoporous silica supports, where a moderate shrinkage of the porosity was observed, although without pore blocking [39,40,41]. In the present case, the species to be deposited is polynuclear, instead of mononuclear (as $Ti(C_5H_5)Cl_2$ was), and the resulting oxidic supported species is accordingly bulkier. For this reason, a more marked decrease in specific surface area and pore volume was recorded, especially for the Ti_xO_n -MCM-41 sample.

Table 1. Textural features and titanium content of the mesoporous silica supports and the related $Ti_n O_x$ -silica catalysts.

Sample	Ti content	S _{BET} ^a	$\mathbf{V}^{\mathbf{b}}$	D ^c
	/ wt.%	$/ m^2 g^{-1}$	/ cm ³ g ⁻¹	/ nm
MCM-41	n.d.	960	0.61	3.7
Ti _x O _n -MCM-41	2.07	260	0.24	3.2
MMM-2	n.d.	940	0.60	3.39
Ti _x O _n -MMM-2	1.90	580	0.28	2.78
	1.90 ^d	36 ^d	0.06^{d}	9.33 ^d

a: S_{BET} . N₂-adsorption BET specific surface area; b: V. total specific pore volume; c: D. average mesopore diameter; d: after 5th catalyst reuse in styrene oxidative carboxylation (reaction conditions as in Tab. 2).

High resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) analysis carried out on both freshly prepared calcined samples (i.e. Ti_xO_n -MCM-41 and Ti_xO_n -MMM-2) indicated the absence of detectable metal oxide aggregates. This suggests the presence of very small size of TiO_x clusters, with sizes ranging from few Ti-O-Ti units up to approx. 0.8 nm (Figure 1). STEM-EDX element maps of some representative grains of the two samples revealed a very high and uniform dispersion of titanium clusters on the mesoporous silica excluding the presence of larger isolated titanium aggregates (Figure 2 and Figure 3). The resulting EDX spectrum showed an elemental compositions very similar to the one recorded by ICP-OES analysis, for the of titanium loading (Ti_xO_n -MCM-41: Si = 97.6 at.%, Ti = 2.4 at.%; Ti_xO_n -MMM-2: Si = 97.1 at.%, Ti = 2.9 at.%). Interestingly, STEM-EDX map of a Ti_n -MCM41 sample, before calcination with air, showed a dispersion of Ti atoms on the silica support that is fully comparable to the one observed on the calcined system, indicating that the calcination step did not affect the size of titanium clusters (Figure S1, *Supplementary Material*).



Figure 1. HR-TEM micrographs of a representative grain of: A) Ti_xO_n -MCM-41 and B) Ti_xO_n -MMM-2.



Figure 2. STEM measurements of Ti_xO_n-MCM-41: A) HAADF image of a catalyst grain; B-C) STEM-EDX mapping of the catalyst showing the titanium dispersion: B) silicon map (red), C) titanium map (blue).



Figure 3. STEM measurements of Ti_xO_n-MMM-2: A) HAADF image of a catalyst grain; B-C) STEM-EDX mapping of the catalyst showing the titanium dispersion: B) silicon map (red),
C) titanium map (blue).

These evidences were further supported by DR UV-vis and Raman spectroscopic techniques. Figure 4 shows the DR UV-vis spectra of the two Ti_nO_x -silica catalysts. The

absence of any characteristic intense absorption around 330-350 nm suggests the absence of TiO_2 anatase microcrystallites [42,43,44]. This observation is also consistent with the absence of the characteristic band at 145 cm⁻¹ in the Raman spectra (Figure S2) [7,45,46] and with the above reported electron microscopy analysis. The DR UV-vis spectra of the two catalysts indeed reveal that the Ti(IV) centres are well dispersed on the surface. Both catalysts show a maximum at ca. 225-230 nm with a shoulder in the range 260-290 nm, which is more pronounced in the spectrum of Ti_nO_x -MCM-41. The former absorption feature can be attributed to oxygen–to–metal charge transfer of distorted tetrahedrally coordinated isolated Ti(IV) sites while the latter is an evidence of octahedrally coordinated titanium centres [47,48,49] and may belong to either 6-coordinated Ti(IV) dimers/small oligomers or hydrated Ti(IV) species is less probable as DR UV-vis spectra are similar after calcination and vacuum treatments (*cf.* Figure S3).



Figure 4. DR UV-vis spectra of Ti_nO_x-catalysts.

3.2 Catalytic Studies

3.2.1 Epoxidation of R-(+)-limonene

The catalytic behaviour of the mesoporous Ti_nO_x -silica systems has been evaluated in the liquidphase epoxidation of limonene (Scheme 2) in the presence of TBHP as an oxidant. Well-dispersed

Ti(IV) sites on mesoporous silica supports are indeed classical good catalysts for the epoxidation of bulky alkenes in the presence of organic hydroperoxides [1,7,8]. For this reason, Ti_nO_x -MCM-41 and Ti_nO_x -MMM-2 were first tested in the epoxidation of a cyclic terpenic olefin. Limonene epoxide is a promising intermediate for the production of polylimonene carbonate and bio-based polymers [50,51] as well as a wide range of products, such as insect repellents [52] or as herbicide components [53].



Scheme 2. Epoxidation of R-(+)-limonene





Figure 5. Curves of conversion (A) and selectivity to monoepoxide (B) for Ti_nO_x -MCM-41 (\blacktriangle and \blacksquare) and Ti_nO_x -MMM-2 (\bullet) catalyst in the liquid-phase epoxidation of (*R*)-(+)-limonene. Conditions: dry CH₃CN solvent; 90°C, 6h, batch reactor; 100 mg catalyst; 1.0 mmol limonene; anhydrous TBHP (1.1 mmol \blacktriangle and \bullet , 2.0 mmol \blacksquare). Blank test: no catalyst (O).

Both catalysts were active in limonene epoxidation and limonene 1,2-epoxide was the main observed product, in particular for short reaction times (Figure 5A and B). As expected, the electron-richer endocyclic C=C bond was epoxidised more readily than the exocyclic one over these systems and this is fully in line with previous observations on Ti-containing mesoporous silicate solids [12,54]. The conversion profiles for Ti_nO_x -MCM-41 and Ti_nO_x -MMM-2 are quite similar, the former being slightly more active at shorter times (1-2 h) and the latter at the end of the tests (Figure 5A). Nevertheless, with an oxidant to alkene molar ratio of 1.1, the conversion values of 34% and 24%, after 1 h of reaction, for Ti_nO_x -MCM-41 and Ti_nO_x -MMM-2, respectively, correspond to specific activities (expressed as moles of converted limonene per mole of Ti in 1 h) of 7.1 h⁻¹ and 6.1 h⁻¹ after 1h. These values are notably lower than the one (21 h⁻¹) recorded, under the

same conditions, over a reference single-site Ti-MCM-41 catalyst obtained by grafting a titanocene dichloride precursor [55]. Considering such modest activity values, any contribution of direct oxidation of TBHP on limonene (in the absence of the catalyst) can be excluded, as shown in the blank test in Figure 5A. The selectivity to limonene monoepoxide, after 1h, on the contrary, was practically the same over Ti_nO_x -MCM-41 and the reference Ti-MCM-41 (73% vs. 75%, respectively), whereas it was remarkably lower (56%) for Ti_nO_x -MMM-2. At longer reaction times, however, the reaction proceeds, but with a non-negligible decrease in selectivity (down to 56% after 6h), a gradual formation of limonene diepoxide (at both 1,2 and 8,9 C=C positions) and the important formation of several by-products with high molecular weight (> 300 g mol⁻¹).

The comparable behaviour of the two catalysts, at least as far as the conversion is concerned, was expected, as the patterns of the DR UV-vis spectra were very similar for the two solids (Figure 4). However, in this set of tests, a new aspect was recorded, with respect to previous observations on previous single-site Ti-silicates: the oxidant efficiency [56] was far lower than usual (< 40%, whereas typical values for TBHP in epoxidation reactions over Ti-silicates are higher than 90%) and TBHP proved thus to be the limiting agent in these tests. Actually, although TBHP was in slight excess (TBHP : alkene = $1.1 : 1 \mod/mol$), no residual oxidant was detected by iodometric evaluation at the end of the 6h of reaction.

In order to circumvent this limitation and to push further the production of limonene epoxide, an additional aliquot of TBHP (1 mmol) was added at the end of the 6h of reaction (Figure S4). A very high limonene conversion value of 96% has been reached over Ti_nO_x -MCM-41, but with a rather low selectivity to the desired monoepoxide, because of the formation of remarkable amounts of side products. So, in the presence of a larger excess of oxidant (TBHP : alkene = 2 : 1 mol/mol), higher conversion values (up to 77% after 6h) were attained over Ti_nO_x -MCM-41.

In specific tests with a radical trap species (hydroquinone in a quasi-equimolar amount with respect to the total Ti sites in the solid catalyst), no inhibition of the epoxidation was observed and

this indicated that the role of a free-radical pathway is limited over these catalysts, under these conditions.



Figure 6. Curves of conversion (A) and selectivity to monoepoxide (B) for Ti_nO_x -MCM-41 catalyst in the liquid-phase epoxidation of (*R*)-(+)-limonene. Conditions: dry CH₃CN solvent; 90°C, 6h,

batch reactor; 100 mg catalyst; 1.0 mmol limonene; 2.0 mmol anhydrous TBHP. Fresh catalyst: 1^{st} run (\blacksquare). Recycled catalyst: 1^{st} recycle (*); 2^{nd} recycle (\Diamond); 3^{rd} recycle (\Box).

The catalyst could also be recycled and a series of tests was performed over Ti_nO_x -MCM-41, as a significant catalyst (Figure 6A and 6B). Interestingly, when Ti_nO_x -MCM-41 was recovered and reused in the second catalytic test (first recycle), it even showed an improved performance with conversions as high as 56 % after 1h (with a TBHP : alkene ratio of 2 : 1 mol/mol) and hence a specific activity of 13 h⁻¹. Such improved performance was kept for the second recycle too. Then, the performance, in terms of conversion and selectivity, started to decrease after the third recycle. The catalyst is therefore able to keep most of its epoxidation capability after the recovery and intermediate re-calcination steps, at least for three catalytic cycles.

3.2.2. Oxidative carboxylation of styrene

Synthesis of cyclic carbonates from olefins and CO₂ through oxidative carboxylation is one of the challenging technologies for the sustainable utilization of CO₂ and production of valuable cyclic organic carbonates [57,58,59,60], which are widely used as a raw material in the synthesis of polycarbonates, fuel additives, electrolyte solvents for lithium batteries, etc. [61]. Recently, some of us have found that one mesoporous titanium-silicate Ti-MMM-E, prepared by evaporation-induced self-assembly, is an efficient heterogeneous catalyst for the one-step oxidative carboxylation of styrenes with TBHP and CO₂, in the presence of TBABr as a cocatalyst, under mild conditions (50-70 °C, 8 bar CO₂) [30]. It was suggested that di(oligo)meric titanium species are more preferable active centers for oxidative carboxylation of alkenes than isolated Ti atoms, although the latter exhibit high activity and selectivity in epoxidation of alkenes with hydroperoxides. This prompted us to evaluate the catalytic performance of elaborated and designed Ti_nO_x-based catalyst for this reaction (Scheme 3).



Scheme 3. Oxidative carboxylation of styrene over Ti-catalysts.

Both of the prepared Ti_nO_x -silica catalysts were active in the oxidative carboxylation of styrene in the presence of TBABr as cocatalyst (Table 2). However, in the absence of TBABr the yield of carbonate was insignificant (Table S1). The results obtained using Ti_nO_x -catalyst are superior to the results previously reported for Ti-MMM-E under the same reaction conditions (24 h at 70 °C): 36 or 41% styrene carbonate (SC) selectivity at 80 or 71% styrene conversion (Table 2; entries 1 and 2) vs. 33% selectivity at 58% conversion (entry 4). After 48 h of reaction, the selectivity to SC and the alkene conversion over Ti_nO_x -MMM-2, *i.e.*, the most efficient catalyst, reached 51 and 81%, respectively (entry 2).

Entry	Catalyst	[Styrene]	Time Styrene		Product selectivity ^a (%)			
		/ M	/h	conversion (%)	BA	SO	BAc	SC
1	Ti _n O _x -MCM-41	0.1	24	80	21	20	21	36
	. O		48	89	13	11	35	40
2	Ti _n O _x -MMM-2	0.1	24	71	21	21	12	41
3			48	81	16	9	20	51
		2.4 ^b	24	94	19	6	4	70
			48	99	14	3	13	68
4	Ti-MMM-E [30]	0.1	24	58	42	25	-	33
5	Ti-MMM-E [30]	2.4 ^b	24	67	16	16	-	67
			48	92	15	10	-	70

Table 2. Styrene oxidative carboxylation with TBHP and CO_2 over Ti_nO_x -silica catalysts.

Conditions: styrene 0.2 mmol, TBHP 0.3 mmol, TBABr 0.02 mmol, Ti_nO_x -catalyst 0.008 mmol Ti, CH₃CN 2 mL, p(CO₂) 8 bar, 70 °C.

^a GC yield based on substrate consumed; ^b Solvent-free conditions: styrene/TBHP/TBABr molar ratio = 1/1.5/0.1, Ti_nO_x-catalyst 0.11 mmol Ti, p(CO₂) 8 bar, 70 °C.

Unlike the reaction catalyzed by Ti-MMM-E, where the only side products were benzaldehyde (BA) and styrene oxide (SO) (entry 4), significant amounts of benzoic acid (BAc) were formed in the presence of Ti_nO_x -silica catalysts. It is worth noting that the oxidation of styrene with TBHP (in the absence of CO₂) over Ti_nO_x -silicates gave BA as the main product (43-62% selectivity), along with SO (32-38%) and BAc (6-10%), at 43-49% alkene conversion after 5 h at 50 °C (Tab. 3). The addition of TBABr to the reaction system promoted the oxidative C=C bond cleavage and led to a slight increase in selectivity of both BA and BAc (Table 3, *cf.* entries 2 and 3). On the other hand, by running the oxidation reaction under CO₂ atmosphere (8 bar), the formation of styrene oxide was favoured (Table S1, entry 1).

Entry	Catalyst	Time	Styrene	Product selectivity ^a (%)		
		/h	conversion (%)	BA	SO	BAc
1	Ti _n O _x -MCM-41	5	43	62	32	6
2	Ti _n O _x -MMM-2	5	49	43	38	10
		24	58	54	28	14
3	Ti _n O _x -MMM-2 + TBABr	5	50	45	32	19
		24	71	24	26	47

Table 3. Styrene oxidation with TBHP over Ti_nO_x-silica catalysts.

Conditions: styrene 0.1 mmol, TBHP 0.15 mmol, Ti_nO_x-catalyst 0.005 mmol Ti, TBABr 0.01 mmol (if any), CH₃CN 1 mL, 50 °C.

^aGC yield based on substrate consumed.

In order to obtain a higher volume yield of the desired carbonate, a larger loading of reactants was used in the reactor. As previously observed over Ti-MMM-E, by increasing the initial concentration of styrene up to solvent-free conditions (*i.e.*, 2.4 M), a high selectivity to SC (70%) was attained at 94 % conversion after 24 h, over Ti_nO_x -MMM-2 (Tab. 2, entry 3). This means that the volume yield of SC can be as high as 0.3 kg L⁻¹ for the reaction mixture. Interestingly, 24 h of

reaction was enough to get the almost complete (94%) conversion of styrene in the presence Ti_nO_{x-} MMM-2, while only 67% conversion was reached over Ti-MMM-E catalyst under the same conditions (Table 2, entry 5). The higher activity of the grafted Ti_nO_x -silica materials is, most likely, due to a better accessibility of titanium active centres in these materials, since all of the Ti sites are exposed on the surface of the catalyst and are not buried within the walls of silicate matrix, as it happens in the case of Ti,Si-materials synthesized via direct synthesis, including EISA technique.

In this case too, an adequate stability of the solid catalysts is a crucial factor for heterogeneous catalysis in liquid phase. The XRD study confirmed the preservation of the MCM-41 ordered structure under turnover conditions of styrene oxidative carboxylation in acetonitrile solution (Figure S5, curves A and B). A slight shift of the XRD reflex is indeed likely due to some shrinkage of the material subjected to turnover conditions and repeated calcinations during the recycling.

A set of recycling tests was carried out on Ti_nO_x -MMM-2. The catalyst was recovered from the reaction mixture after 24 h by simple filtration and then used repeatedly in several consecutive runs under solvent-free conditions. Figure 7 demonstrated that Ti_nO_x -MMM-2 could be reused without notable deterioration of the catalytic properties. After 6 recycles, a total volume yield of SC as high as 1.5 kg L⁻¹ could be achieved.

C



Figure 7. Reuse of Ti_nO_x -MMM-2 in solvent-free styrene oxidative carboxylation. Conditions as in Table 2, entry 3; reaction time 24 h.



Figure 8. DR UV–vis spectra of Ti_nO_x -MMM-2: (A) fresh catalyst, (B)-(D) after one, three and six runs of styrene oxidative carboxylation, respectively. Conditions as in Table 2, entry 3; reaction time 24 h.

In terms of textural properties, a severe loss in specific pore volume was detected after the fifth consecutive recycle of styrene oxidative carboxylation (Table 1). The DR UV-vis spectroscopic analysis showed some changes in the state of the Ti centres after the catalyst reuse (Figure 8). The

observed shift of the absorption apparently suggests that a transformation of di(oligo)meric titanium species into isolated ones takes place. This might be caused by a gradual leaching of titanium during the recycling steps. However, the content of titanium in the solid catalysts remained intact after six reuses (1.9 wt%; Table 1) and really negligible amounts of titanium (1.0 ppm Ti) were found in the liquid-phase reaction mixtures during the recycle tests.

In order to get a deeper insight into the reason for such a change in the state of the active metal along the catalytic reactions, the catalyst was treated with styrene carbonate. The DR UV spectra of Ti_nO_x -MMM-2 material after the first run of oxidative carboxylation of styrene and after the treatment with SC alone are almost identical (Figure S6). Therefore, since no significant leaching of Ti species out of the solid was detected, the Ti_nO_x -like moieties on the silica surface likely undergo a local restructuring of the active sites upon exposure to the polar carbonate products. On the other hand, the reference Ti-MMM-E catalyst showed a gradual agglomeration of the Ti sites upon recycling after the carboxylation of styrene [30], according to a typical process widely observed in other liquid-phase oxidation over titanium-silicate catalysts [7,62]. These data suggest that, although the mesoporous structure of the molecular sieve itself is not fully stable to the hard recycling conditions (especially in repeated solvent-free tests), the chemical environment, the total metal content and the catalytic properties of the Ti(IV) sites are kept and stable even after prolonged reaction periods.

Conclusions

Starting from a molecularly defined zerovalent Ti_{13} cluster, it has been possible to obtain a novel series of titanium oxide-like supported catalysts. The deposition of the metal clusters led to a uniform dispersion and thorough deposition of the Ti sites on the surface of the mesoporous silica molecular sieves. The subsequent calcination transformed the pristine Ti(0) centres into Ti_nO_x catalytically active species with enhanced properties for the selective oxidative conversion of

alkenes. In the presence of TBHP as an oxidant, moderate results were obtained in the liquid-phase epoxidation of limonene. On the other hand, unprecedented high selectivity (up to 70% to styrene carbonate) and total volume yield (up to 1.5 kg L^{-1} of the total reaction mixture) values were achieved in the oxidative carboxylation of styrene with TBHP and CO₂ in the presence of tetrabutylammonium bromide as cocatalyst, under solvent-free conditions.

The obtained solid catalysts showed a remarkable catalytic stability, along repeated recovery and reuse cycles, not only in epoxidation reactions, but also under the harsh conditions of oxidative carboxylation. These highly dispersed and evenly-distributed Ti_nO_x -like catalysts may therefore deserve further attention, since they can also be optimal systems for other Ti(IV)-catalysed transformations by exploiting their potentially enhanced and tunable redox / Lewis-acid / photocatalytic properties.

Acknowledgments

The authors thank Dr. Yu. A. Chesalov, Dr. T. V. Larina and Dr. I. Y. Skobelev for the Raman, DRS UV–vis, and nitrogen adsorption measurements, respectively. This work was conducted within the framework of the budget project No. 0303-2016-0005 for the Boreskov Institute of Catalysis. The research activity was partially supported by the Russian Foundation for Basic Research (grant N 15-33-20225) and the Ministry of Education and Science of the Russian Federation.

Bibliographic References

Titanium-Silica Catalyst derived from Defined Metallic Titanium Cluster

Precursor: Synthesis and Catalytic Properties in Selective Oxidations

Claudio Evangelisti^a, Matteo Guidotti^a, Cristina Tiozzo^a, Rinaldo Psaro^a,

Nataliya Maksimchuk^{b,c}, Irina Ivanchikova^b, Alexandr N. Shmakov^{b,c,d}, Oxana Kholdeeva^{b,c}

Synopsis

A dispersed non-single-site $Ti(IV)_nO_x$ -like silica-supported catalyst was obtained from molecularly defined Ti_{13} metal clusters deposited onto ordered mesoporous silicas. The solids showed standard performance in the liquid-phase epoxidation of limonene, but high selectivity and unprecedented high yields in the oxidative carboxylation of styrene.

[5] C. Louis, M. Che, Anchoring and Grafting of Coordination Metal Complexes onto Oxide Supports, in: Preparation of Solid Catalysts. G. Ertl, H. Knözinger, J. Weitkamp (Eds), Wiley-VCH, (1999) p. 341.

- [6] V. Dal Santo, F. Liguori, C. Pirovano, M. Guidotti, Molecules, 15(6) (2010) 3829-3856.
- [7] O. A. Kholdeeva, in: Liquid Phase Oxidation via Heterogeneous Catalysis, M. G. Clerici, O. A.
- Kholdeeva (Eds.), J. Wiley and Sons (2013), chapter 4, pp. 127–219.
- [8] O. A. Kholdeeva, Catal. Sci. Technol. 4 (2014) 1869–1889.
- [9] R. A. Sheldon, M.C.A. van Vliet, in: Fine Chemicals through Heterogeneous Catalysis, R.A.
- Sheldon, H. van Bekkum (Eds.), Wiley-VCH (2001) p. 473.
- [10] R.A. Sheldon, J. Dakka, Catal. Today 19 (1994) 215.
- [11] K.T. Li, C.C. Lin, P.H. Lin, in: Mechanisms in homogeneous and heterogeneous epoxidation catalysis, S. T. Oyama (Ed.), Elsevier (2008), p. 373.
- [12] C. Cativiela, J. M. Fraile, J. I. Garcia, J. A. Mayoral, J. Mol. Catal. A 112 (1996) 259.
- [13] A. O. Bouh, G. L. Rice, S. L. Scott, J. Am. Chem. Soc. 121 (1999) 7201.
- [14] N. V. Maksimchuk, M. S. Melgunov, J. Mrowiec-Białoń, A.B. Jarzębski, O. A. Kholdeeva, J. Catal., 235 (2005) 175.
- [15] W.S. Ahn, D. H. Lee, J. H. Kim, G. Seo, R. Ryoo, Appl. Catal. A: Gen. 181 (1999) 39.
- [16] Q. Yuan, A. Hagen, F. Roessner, Appl. Catal. A: Gen. 303 (2006) 81.
- [17] E. Jorda, A. Tuel, R. Teisser, J. Kervennal, J. Catal. 175 (1998) 93.
- [18] L. Barrio, J.M. Campos-Martin, M.P. de Frutos-Escrig, J.L.G. Fierro, Micropor. Mesopor. Mater. 113 (2008) 542.
- [19] R.D. Oldroyd, J. M. Thomas, T. Maschmeyer, P.A. MacFaul, D. W. Snelgrove, K.U. Ingold,D.D.M. Wayner, Angew. Chem. Int. Ed., 35 (1996) 2787.
- [20] M. Guidotti, N. Ravasio, R. Psaro, G. Ferraris, G. Moretti, J. Catal., 214 (2003) 242.
- [21] Y. Perez, D.P. Quintanilla, M. Fajardo, I. Sierra, I. del Hierro, J. Mol. Catal. A: Chem. 271 (2007) 227.

[22] R.L. Brutchey, B.V. Mork, D.J. Sirbuly, P. Yang, T. Don Tilley, J. Mol. Catal. A: Chem. 238(2005) 1.

- [23] A. Tuel, L.G. Hubert-Pfalzgraf, J. Catal., 217 (2003) 343.
- [24] N. Mimura, S. Tsubota, K. Murata, K. K. Bando, J. J. Bravo-Suarez, M. Haruta, S. Ted
- Oyama, Catal. Lett., 110 (2006) 47-51.
- [25] C. Pirovano, M. Guidotti, V. Dal Santo, R. Psaro, O. A. Kholdeeva, I. D. Ivanchikova, Catal. Today, 197 (2012) 170-177.
- [26] Z. Wang, K. J. Balkus Jr., Microp. Mesop. Mater., 243 (2017) 76-84.
- [27] I. D. Ivanchikova, M. K. Kovalev, M. S. Mel'gunov, A. N. Shmakov, O. A. Kholdeeva, Catal.
- Sci. Technol. 4 (2014) 200-207.
- [28] P. Ratnasamy, D. Srinivas, H. Knözinger, Adv. Catal., 48 (2004) 1–169.
- [29] M. Guisnet, M. Guidotti, in: Zeolite Chemistry and Catalysis. An integrated Approach and

Tutorial, A. W. Chester, E. G. Derouane (Eds.), ISBN: 978-1-4020-9677-8, Springer (2009), p. 275-347.

- [30] N.V. Maksimchuk, I.D. Ivanchikova, A. B. Ayupov, O.A. Kholdeeva, Appl. Catal. B: Environ.2016, 181, 363–370.
- [31] R. Srivastava, D. Srinivas, P. Ratnasamy, Catal. Lett., 91 (2003) 133–139.
- [32] J. Zhang, Y. Liu, N. Li, H. Wu, X. Li, W. Xie, Z. Zhao, P. Wu, M. He, Chin. J. Catal., 29 (2008) 589–591.
- [33] M. G. Clerici, in: Metal Oxide Catalysis, S.D. Jackson, J. S. J. Hargreaves (Eds.), Wiley-VCH (2009) pp. 705–754.
- [34] O. A. Kholdeeva, I. D. Ivanchikova, M. Guidotti, C.Pirovano, N.Ravasio, M. V. Barmatova, Y.A. Chesalov, Adv. Synth. Catal., 351(2009) 1877 1889.
- [35] M. Guidotti, C. Pirovano, N. Ravasio, B. Lazaro, J. M. Fraile, J. A. Mayoral, B. Coq, A. Galarneau, Green Chem., 2009, 11, 1421–1427.

- [36] O.A. Kholdeeva, M.S. Melgunov, A.N. Shmakov, N.N. Trukhan, V.V. Kriventsov, V.I.
- Zaikovskii, M.E. Malyshev, V.N. Romannikov, Catal. Today 91-92 (2004) 205.
- [37] H. Bonnemann, B. Korall, Angew. Chem. Int. Ed. 31(11) (1992) 1490-1492.
- [38] R. Franke, J. Rothe, J. Pollmann, J. Hormes, H. Bonnemann, W. Brijoux, T. Hindenburg, J.
- Am. Chem. Soc. 118 (1996) 12090-12097.
- [39] J. Jarupatrakorn, T. D. Tilley, J. Am. Chem. Soc., 124 (2002), 8380-8388.
- [40] F. Chiker, J. P. Nogier, F. Launay, J. L. Bonardet, Appl. Catal. A: Gen., 243 (2003) 309-321.
- [41] A. Gallo, C. Tiozzo, R. Psaro, F. Carniato, M. Guidotti, J. Catal. 298 (2013) 77-83.
- [42] Z. Liu, R. J. Davis, J. Phys. Chem., 98 (1994) 1253-1261.
- [43] O.A. Kholdeeva, N.N. Trukhan, Russ. Chem. Rev. 75 (2006) 411.
- [44] H. Shintaku, K. Nakajima, M. Kitano, N. Ichikuni, M. Hara, ACS Catal. 4 (2014) 1198–1204.
- [45] N. N. Trukhan, V. N. Romannikov, A. N. Shmakov, M. P. Vanina, E. A. Paukshtis, V. I.
- Bukhtiyarov, V. V. Kriventsov, I. Y. Danilov, O. A. Kholdeeva, Microp. Mesopor. Mater. 59 (2003) 73.
- [46] X. Gao, I. E. Wachs, Catal, Today, 51 (1999) 233-254.
- [47] A. Carati, C. Flego, E. PrevideMassara, R. Millini, L. Carluccio, W.O. Parker Jr. and G. Bellussi, Microp. Mesop. Mater., 30 (1999) 137.
- [48] E. Gianotti, A. Frache, S. Coluccia, J. M. Thomas, T. Maschmeyer and L. Marchese, J. Mol.Catal. A: Chemical, 204-205 (2003) 483.
- [49] J. M. Fraile, J. I García, J. A. Mayoral, E. Vispe, J. Catal., 233 (2005) 90–99.
- [50] C. M. Byrne, S. D. Allen, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc., 126 (2004) 11404.
- [51] R. C. Jeske, A. M. Diciccio, G. W. Coates, J. Am. Chem. Soc., 129 (2007) 11330.
- [52] R. H. Deboukian, P. J. Weldon, Patent WO2007025197, 2007.
- [53] F. Smith, J. Jankauskas, O. Messerschmidt, Patent WO2006094126, 2006.
- [54] C. Berlini, M. Guidotti, G. Moretti, R. Psaro, N. Ravasio, Catal. Today 60 (2000) 219.

[55] M. Guidotti, N. Ravasio, R. Psaro, G. Ferraris, G. Moretti, J. Catal., 214 (2003) 242.

[56] Oxidant efficiency expressed as the amount of limonene epoxide produced per amount of consumed oxidant.

[57] D. Ballivet-Tkatchenko, A. Dibenedetto, in: Carbon Dioxide as Chemical Feedstock, M.

Aresta (Ed.), Wiley-VCH (2010), chapter 7, p. 169.

- [58] J. Sun, L. Liang, J. Sun, Y. Jiang, K. Lin, X. Xu, R. Wang, Catal. Surv. Asia 15 (2011) 49-54.
- [59] M. Aresta, A. Dibenedetto, A. Angelini, Chem. Rev. 114 (2014) 1709-1742.

[60] M. Aresta, A. Dibenedetto, E. Quaranta, J. Catal. 343 (2016) 2-45.

[61] D.C. Webster, Progress Org. Coatings 47 (2003) 77-86.

[62] J.K.F. Buijink, J.-P. Lange, A.N.R. Bos, A.D. Horton, F.G.M. Niele, in: Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis, S.T. Oyama (Ed.), Elsevier (2008), pp. 356–371.

31