Mesoporous TiO₂ materials have been prepared by an aerosol process, which leverages on the acetic acid-mediated sol-gel chemistry and on the evaporation-induced self-assembly phenomenon to obtain materials with high specific surface area and large mesoporous volume. The obtained spherical particles are calcined to release the porosity. It is shown that the mesoscopic order can be preserved when the calcination is carried out at relatively low temperature (375 °C and below). Harsher calcination conditions lead to the progressive destruction of the mesostructured, concomitant with a progressive drop of textural properties and with the crystallization of larger anatase domains. The mesoporous TiO₂ material calcined at 350 °C (specific surface area = 260 m².g⁻¹; pore volume = 0.36 cm³·g⁻¹; mean pore diameter = 5.4 nm) was selected as a promising support for preformed RuO₂ nanoparticles, and subsequently annealed in air. It is shown that the presence of RuO₂ nanoparticles and subsequent annealing provoke further intense modification of the texture and crystallinity of the TiO₂ materials. In addition to a drop in the textural parameters, a RuO₂-mediated crystallization of rutile TiO₂ is highlighted at temperature as low as 250 °C. After an in situ reduction in H₂, the catalysts containing TiO₂ rutile and relatively small RuO₂ crystals showed the highest activity in the methanation of CO₂.
Aerosol-assisted sol-gel synthesis of mesoporous TiO$_2$ materials, and their use as support for Ru-based methanation catalysts

Ara Kim,$^{a,b}$ Clément Sanchez,$^b$ Bernard Haye$^b$, Cedric Boissiere,$^b$ Capucine Sassoye,$^{b,*}$ Damien P. Debecker$^{a,*}$

$^a$ Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Place Louis Pasteur, 1, box L4.01.09, 1348 Louvain-La-Neuve, Belgium. E-mail: damien.debecker@uclouvain.be

$^b$ Sorbonne Universités, UPMC Université Paris, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 Place Jussieu, 75252 Paris Cedex, France. E-mail: capucine.sassoye@upmc.fr
Abstract

Mesoporous TiO$_2$ materials have been prepared by an aerosol process, which leverages on the acetic acid-mediated sol-gel chemistry and on the evaporation-induced self-assembly phenomenon to obtain materials with high specific surface area and large mesoporous volume. The obtained spherical particles are calcined to release the porosity. It is shown that the mesoscopic order can be preserved when the calcination is carried out at relatively low temperature (375 °C and below). Harsher calcination conditions lead to the progressive destruction of the mesostructured, concomitant with a progressive drop of textural properties and with the crystallization of larger anatase domains. The mesoporous TiO$_2$ material calcined at 350°C (specific surface area = 260 m$^2$.g$^{-1}$; pore volume = 0.36 cm$^3$.g$^{-1}$; mean pore diameter = 5.4 nm) was selected as a promising support for preformed RuO$_2$ nanoparticles, and subsequently annealed in air. It is shown that the presence of RuO$_2$ nanoparticles and subsequent annealing provoke further intense modification of the texture and crystallinity of the TiO$_2$ materials. In addition to a drop in the textural parameters, a RuO$_2$-mediated crystallization of rutile TiO$_2$ is highlighted at temperature as low as 250°C. After an in situ reduction in H$_2$, the catalysts containing TiO$_2$ rutile and relatively small RuO$_2$ crystals showed the highest activity in the methanation of CO$_2$.

Keywords

Mesoporous TiO$_2$, aerosol, spray drying, CO$_2$ hydrogenation, RuO$_2$ nanoparticles, methanation
1. Introduction

Considering the impact of human activities on the atmospheric CO\(_2\) levels and the related effects on climate change, the need to curve our net CO\(_2\) emissions is pressing [1]. The catalytic hydrogenation of CO\(_2\) towards methane, also called the Sabbatier reaction or methanation, is currently being intensely investigated as a suitable way to activate CO\(_2\), turning a waste into a fuel (at the cost of H\(_2\) which must be produced using renewable energy) [2-6]. Heterogeneous catalysts based on Ni, Ru, Pd, Co, Rh, Fe, etc.[7-14] exhibit CO\(_2\) methanation activity, but Ru is known to be the most active at mild temperature.[3, 15, 16] For such reactions, the nature of the support is crucial, and TiO\(_2\) materials have been identified as best supports for Ru.

Recently, it was shown that the crystalline structure of the titania support plays a decisive role in the formation of a highly active Ru/TiO\(_2\) methanation catalyst, and this was explained by studying the active phase-support interaction in the RuO\(_2\)-TiO\(_2\) system during calcination.[17, 18] On the one hand, RuO\(_2\) does not disperse on anatase TiO\(_2\) and segregates in the form of large chunks with low activity. On the other hand, RuO\(_2\) forms a dispersed epitaxial layer on rutile TiO\(_2\) favoring a high Ru dispersion and high activity [19]. Thus, the nature of the active phase-support interactions, governed by the TiO\(_2\) support crystallinity, dictates the catalytically active metallic Ru-species obtained after in situ reduction. The best catalytic activity is obtained when a non-sintering rutile TiO\(_2\) is used as a support.[17, 20] Such materials, however typically have low specific surface area, which limit the amount of Ru that can dispersed. This prompted us to explore mesoporous and amorphous TiO\(_2\) with high surface area as a support for Ru-based methanation catalysts.

Sol-gel chemistry is recognized as a powerful toolbox for the preparation of such solids, often allowing to respond to strict specifications in terms of texture, composition, homogeneity, surface chemistry, etc. [21-25]. Yet, the design and synthesis of mesoporous transition metal oxides is not as extensively studied as silica-based mesostructured materials [26] for their synthesis is more difficult to control. This is attributed to the different sol-gel condensation kinetics of silicate and non-silicate precursors [27]. Many metal oxide precursors are highly reactive toward water due to coordination expansion and rapid condensation [28]. As a consequence, several strategies are developed for the stabilization of inorganic precursor in solution including the use of reactivity-modifiers that are complexing agents [28-30] or the use of non-hydrolytic conditions [31-33]. A successful strategy based on the use of acetic acid has been demonstrated by Doeuff et al. [30] and Fan et al. [28] In the starting alkoxide solution containing acetic acid, hydrochloric acid, and ethanol (AcHE system), the strong acid (HCl)
serves as a catalyst for the esterification of acetic acid with ethanol to produce water. It was
demonstrated that the acetate ligands are directly bonded to the metal cores of metal alkoxide
in a bidentate and bridging fashion to form stable, nanometer-sized metal oxo-acetate particles
[34], which slows down the hydrolysis process, thereby increasing the time of gelation.

The aerosol-assisted sol-gel process (AASG) [35], integrates (i) sol-gel chemistry, (ii)
aerosol spray handling and (iii) evaporation-induced self-assembly. It has been proposed as a
simple, continuous and rapid mode of production of high surface area-nanostructured materials
with well-defined pore size and controllable texture [35-37]. This has proven highly effective
for the preparation of a wide range of oxide and mixed oxide catalysts [38-47]. In this process,
a stable solution of precursors and surfactants is atomized into droplets (aerosol) and processed
by contact with a drying gas. Upon solvent evaporation, surfactant molecules form micelles and
reactive precursors polycondense to form a solid inorganic network. Porosity is then released
through a thermal treatment step designed as to remove the organic template.

In the present study, we synthesize mesoporous TiO$_2$ with high surface area, using the
coupling of acetic acid mediated sol-gel chemistry with aerosol-assisted self-assembly process,
as proposed by Stucky et al.[34]. The effect of calcination on the properties of the obtained
mesostructured TiO$_2$ was studied by characterizing the solid with series of techniques. One of
the resulting mesoporous TiO$_2$ with preserved mesostructured was used as a support for
preformed RuO$_2$ nanoparticles [48] and then calcined and reduced to be tested in the catalytic
CO$_2$ methanation.

2. Experimental

2.1. Preparation of mesoporous TiO$_2$ by the aerosol-assisted sol-gel process

The synthesis of mesoporous TiO$_2$ via aerosol-assisted self-assembly process was
adapted from Stucky et al. [34]. The setup for the aerosol-assisted self-assembly process is
illustrated in Figure 1. An aerosol generator from TSI (model 9306) was employed; a pump
was used to carry the aerosol towards the collection of dried powder.

The precursor solution was prepared by dissolving Titanium (IV) butoxide precursor,
acetic acid, and hydrochloric acid (37 wt.%) in ethanol. The molar ratio of the components was
Ti(OBu)$_4$ : acetic acid : HCl : EtOH : F127 = 1 : 4 : 1.2 : 40 : 0.01 (water from concentrated
HCl gives metal to water ratio of 1 to 4). To form nanometer-sized stable metal oxo-acetate
precursor particles, amphiphilic block copolymer F127 (EO$_{106}$PO$_{70}$EO$_{106}$, Mw=12000 gmol$^{-1}$)
was added after stirring for 2 h. The solution was stirred vigorously for at least one more hour to obtain a clear solution and transferred to a closed container attached to the aerosol generator. During the aerosol spray process, the aerosol droplets were allowed to dry and start the surfactant-directed assembly gradually across the heating zone at 400 °C inside a 1 m-long quartz tube with a diameter of 8 cm. The dried powder was collected on a membrane filter with pore size of 0.2 µm. The gas flow was kept constant within the drying zone throughout the process with an oil bubbler, which also gave an indication of the pressure drop increase throughout the process. The collected powder was carefully spread out in a shallow crucible(s) as a thin layer and calcined at various calcination temperatures (325, 350, 375, 400, 425, or 450 °C) for 5 h with 1 °C/min heating rate in static air to remove the surfactant and release the mesoporosity. The obtained titania materials are denoted as “TiX”, where X represents the calcination temperature, in °C (Table 1).

![Figure 1. Schematic of the aerosol process [35]. The precursor solution is sucked up through a capillary and atomized using compressed air. The aerosol mist is carried through a tubular furnace where solvent evaporation, surfactant self-assembly, and TiO₂ polycondensation occur. The dried particles are collected on an absolute filter. Air enters the system via the atomizer and via the bubbler (filled with glycerol) which is used to ensure a constant pressure in the system and as an indicator for the build-up of the cake in the filter.]

2.2. Preparation of the Ru/TiO₂ methanation catalysts

To prepare Ru-based catalysts, mesoporous TiO₂ samples were impregnated with pre-synthesized RuO₂ nanoparticles, as detailed below.

The preparation of the aqueous colloidal suspension of 2 nm RuO₂ by reaction of RuCl₃ with H₂O₂ is described elsewhere [48, 49]. This suspension had a Ru concentration 0.007 M. First, certain amount (2 g to 12 g) of mesoporous TiO₂ was added to a calculated volume of RuO₂ nanoparticles colloidal suspension to yield 2.2 wt. % of Ru in the final catalyst, then the mixture was put in an ultrasonic bath for 30 minutes operating at 40 kHz at room temperature. This step was introduced in attempt to separate agglomerated mesoporous spheres as well as to favor the diffusion of RuO₂ nanoparticles inside the pores. Then, water was evaporated by
rotary evaporation under vacuum at 50 °C. The resulting dried powder was annealed at various temperatures (350, 450, 550, or 650 °C) for 4 h with heating ramp of 10 °C/min. The obtained catalysts are denoted “TiXRuY”, where X corresponds to the temperature of calcination for the titania support and where Y represents the annealing temperature after RuO$_2$ nanoparticles deposition (Table 1).

### Table 1. List of the samples, denotation and thermal treatments applied, and their textural properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination$^a$ T (°C)</th>
<th>Annealing$^b$ T (°C)</th>
<th>SSA$_{BET}$ (m².g⁻¹)</th>
<th>D$_p$ (nm)</th>
<th>V$_p$ (cm³.g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supports</td>
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<td></td>
<td></td>
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<tr>
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<td>5.4</td>
<td>0.43</td>
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<tr>
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</tr>
<tr>
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<td>210</td>
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<tr>
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<td>400</td>
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<td>160</td>
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</tr>
<tr>
<td>Ti425</td>
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<td>130</td>
<td>6.8</td>
<td>0.22</td>
</tr>
<tr>
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<td>N/A</td>
<td>130</td>
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<td>0.23</td>
</tr>
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<td>350</td>
<td>166</td>
<td>6.7</td>
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<tr>
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<td>350</td>
<td>600</td>
<td>29</td>
<td>17.7</td>
<td>0.13</td>
</tr>
</tbody>
</table>

$^a$ Performed to remove the surfactant and release the mesoporosity from TiO$_2$ support  
$^b$ Performed to anneal RuO$_2$ nanoparticles on the TiO$_2$ support. Such annealing before reduction is needed to get high methanation activity.[18]

### 2.3. Characterization

The specific surface area of the catalysts was obtained by nitrogen adsorption–desorption isotherm collected at −196 °C on a BELSORB-mini II (BEL Japan, Inc.). The samples were outgassed for overnight at 140 °C prior to the analysis. Specific surface area ($S_{BET}$) was calculated applying the Brunauer-Emmet-Teller (BET) method for N$_2$ relative pressure in range of 0.05 < $P/P_0$ < 0.30. Total pore volume (V$_p$) was measured at $P/P_0 \sim 0.98$. Pore size distribution was determined by the Barret-Joyner-Halenda (BJH) method.

Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai 120 Twin microscope, operating at 120 kV and equipped with a GatanOrius CCD numeric camera. The samples were prepared by ultrasonic dispersion of the powders in water and a droplet of the dispersion was then placed onto a carbon-coated copper grid.

High-resolution analysis (HR-TEM) images were obtained by using a JEOL JEM 2010 microscope, operating at 200 kV and equipped with a Gatan camera. The samples were
prepared by embedding of the powders in epoxy resin (Araldite 502) and ultra-thin section of 80nm were sliced with a UC7 Leica ultra-microtome.

X-ray diffraction (XRD) measurements were performed using Cu Kα radiation in a Bruker D8 Advance diffractometer equipped with a Lynx eye detector. The 20 diffractograms were recorded between 24–50° with a step size of 0.04° and a step time of 20 s/step. The ICDD-PDF2 database was used to identify the crystalline phases. When possible, TiO₂ and RuO₂ XRD peaks were deconvoluted, using WinPLOTR 2014 [50]. The Scherrer equation was used to calculate the crystallite size of particles [51]. The same sample holder was used, with similar quantities of powder and similar packing. This allows us to compare the diffraction peaks surfaces over temperature and obtain a relevant estimation of the quantity evolution of each crystalline phase.

SAXS experiment was carried out with Rigaku's S-MAX3000 3-pinhole SAXS camera with X-ray source (high brilliance MiCroMax-002) with Copper anode (λ_CuKα = 1.54056 Å). The scattering radiation was collected on 2D Multiwire Area Detector (gas detector) with sample-to-detector distance of 1469 mm.

H₂-TPR experiments were performed for 100 mg of each catalyst after in situ purging under inert gas (Ar) at 140 °C for one hour. The analysis was carried out under 2.5 v/v % H₂ diluted in inert gases (2.5: 82.5: 15 v/v % H₂: He: Ar) in stream of 20 mL.min⁻¹ from 20 °C to 500 °C using a 5 °C min⁻¹ temperature ramp. H₂ consumption and H₂O production were measured simultaneously via a quadrupole mass spectrometer QMC 311 (Balzers) coupled in line with the reactor.

The weight percentages of Ru and Ti inside the catalysts were measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) on an ICAP 6500 from Thermo Scientific.

H₂ chemisorption at 100 °C was used to measure the exposed Ru atoms using ASAP 2010C apparatus from Micrometrics. Catalyst weight between 150 – 200 mg was loaded into a Pyrex tube, and subsequently degassed in He at 150 °C for 30 min. After evacuation, the sample was reduced in pure H₂ at 200 °C for 2 h (same as in situ reduction for methanation) followed by purging with He at 100 °C for 1h and adsorption of H₂. Two isotherms were measured in the range of 0.08-95 kPa. The first accounts for reversible and irreversible chemisorption. The H₂ was evacuated in vacuum at 200 °C for ~ 2 h as the sample was being cooled down to 100 °C to desorb reversibly adsorbed H₂. The second isotherm was then measured which accounts only for the reversibly adsorbed H₂. The subtraction of the linear part of the two isotherms gave the total amount of irreversibly adsorbed (chemisorbed) H₂. The amount of surface Ru atoms was
calculated from the amount of chemisorbed H\textsubscript{2} assuming that the chemisorption stoichiometry is H:Ru = 1 [52, 53]. Dispersion is defined as surface Ru atoms divided by total Ru atoms in the catalyst.

Infrared spectroscopy was performed on Single reflection horizontal ATR accessory from Brucker, diamond crystal plate equipped with high pressure QuickLock. The spectra was recorded with 100 scans between 400 and 4000 cm\textsuperscript{-1} with a resolution of 4 cm\textsuperscript{-1}.

2.4. CO\textsubscript{2} methanation

200 mg of catalyst with particle size between 100 and 315 µm was loaded in a continuous flow fixed bed reactor and reduced in situ at 200 °C for 2 h under 30 ml/min of H\textsubscript{2} prior to the catalytic reaction. The reaction was carried out at 1 atm in the temperature range of 50 to 200 °C under reaction mixture of 20 ml/min (CO\textsubscript{2} (10 vol. %), H\textsubscript{2} (40 vol. %) diluted in He). Each temperature was maintained for 52 min (+ 5 min of temperature increment) (account for 3 GC injections). The exit gases were quantified using a gas chromatograph (Varian CP3800), equipped with Hayesep Q, Molsieve 5A, and CP-Sil-5CB columns. The separated gases were detected with a flame ionization detector (CH\textsubscript{4}) and a thermal conductivity detector (CO and CO\textsubscript{2}). Analysis parameters were set as to allow an analysis each 19 min and to obtain measurements accurate within about 1 % (relative) for the methane production rate (mole of methane produced per gram of catalyst per second). All transfer lines were maintained at 110 °C to avoid water condensation.

3. Results and discussion

3.1. Preparation of pure mesoporous TiO\textsubscript{2} with tunable texture and structure

Through such “Type IIIc” aerosol process [35] a fresh TiO\textsubscript{2} powder was produced in a continuous mode. The spherical shape of the particles (Figure 2) is a reminiscence of the liquid droplets from which the particles originate. When the calcination temperature is relatively low (e.g. Ti350), the particle surface appeared smooth and the mesostructure was clearly visible, with uniform pore size of ~5 nm. The pores were in close-packing down to the core of the particles. On the other hand, when the calcination is relatively high (e.g. Ti450) the growth of TiO\textsubscript{2} grains is observed, together with the partial destruction of the mesostructure. Yet, the global shape of the aerosol droplets was fairly well-preserved.
Figure 2. TEM image of Ti350 (top) and Ti450 (bottom); the inset shows a zoomed-in image of Ti350 showing the pore size of 5 nm.

The porosity is generated by the presence of a structure-directing triblock copolymer (F127) which undergoes evaporation-induced self-assembly during the aerosol processing, generating micelles around which the inorganic polycondensation takes place [35]. The removal of the surfactant is needed to obtain mesoporous TiO$_2$ spheres. This is, however, a delicate process due to the amorphous nature of the initially obtained mesostructured TiO$_2$ spheres by the aerosol process. Due to the replacement of hydrolysable alkoxy groups by acetate groups, the degree of cross-linking of the metal gel network as well as the density of the gel network is
lower than that of bulk TiO$_2$ materials with a pure oxide framework \[28\]. As a result, the fresh mesostructured TiO$_2$ is less-condensed and sustaining the mesoscopic order after removal of the organic template by thermal treatment requires a strategic approach.

The decomposition of pure F127 was analyzed by TGA (Figure S1). F127 was mostly decomposed before 400 °C and almost completely decomposed at 600 °C. The fresh mesostructured TiO$_2$ material was analyzed under two different conditions: (i) up to 600 °C with a heating rate of 5 °C/min and (ii) up to 350 °C with a heating rate of 1 °C/min followed by a plateau at 350°C for 10 hours, same as the calcination condition. The decomposition temperature of F127 was slightly shifted towards lower temperature with a decreased heating rate. When the fresh sample was heated up to 350 °C with 1 °C/min and kept at 350 °C for 10 hours, further weight loss was observed only during the first 4.5 hours of the dwell (Fig. S1). This shows that a calcination duration of 5 hours is enough to remove the organic template at maximum at a given calcination temperature. The total weight loss of the fresh sample was about 60 % which is consistent with the composition of non-volatile organic components of the sol that was used in the aerosol-assisted sol-gel process.

FTIR-ATR analysis was performed on selected samples: pure F127, fresh TiO$_2$, Ti350, Ti375, Ti425, and Ti450 (Figure 3). Expectedly, the stretching vibration of C-H and C-O-C of PEO and PPO blocks at 2880 cm$^{-1}$ and 1105 cm$^{-1}$ was detected in the fresh TiO$_2$ aerosols\[54\]. The removal of F127 after calcination at 350 °C and higher temperatures was confirmed, as these bands disappeared. The very weak peak observed at 2980 cm$^{-1}$ on all samples is related to C-H asymmetric stretching \[55\] and can be attributed to the presence of organic residues or carbon impurities. The broad band around 3300 cm$^{-1}$ and 1630 cm$^{-1}$ are assigned to stretching and bending vibration modes of adsorbed water molecules \[56\]. For calcined materials, the broad band centered around 715 cm$^{-1}$ and the weak band at 410 cm$^{-1}$ are associated to Ti-O-Ti vibrations \[56, 57\]. These bands, however, are slightly shifted towards higher wavenumber (at 790 cm$^{-1}$ and 440 cm$^{-1}$) when the support was calcined at 350°C only (Ti350). The peak around 800 cm$^{-1}$ is assigned to Ti-O vibration, where the oxygen atom is in the non-binding condition \[58\]. This can be associated with the lower degree of TiO$_2$ lattice formation after calcination at 350 °C compared to higher temperature-calcined samples \[56, 59\].
Calcination of the support had a dramatic impact on the textural properties of the obtained mesoporous TiO$_2$ (Table 1). At 325°C, the specific surface area and the total pore volume reached 310 m$^2$.g$^{-1}$ and 0.43 cm$^3$.g$^{-1}$ respectively, which is remarkable for pure TiO$_2$ materials.[34, 39] The specific surface area (SSA) decreased linearly with increasing calcination temperature between 325°C and 425°C (Figure 4). At 450°C however, the SSA did not decrease further. The pore volume followed the same trend (Figure 4).

The N$_2$ physisorption isotherms of all samples belong to type IV [60], with a characteristic hysteresis associated with the presence of open mesopores (Figure 5). The shape of the hysteresis loops corresponds to H2 type (asymmetrical with a steeper desorption branch than the adsorption branch) characteristic of restrictions within the porous network. With increasing calcination temperature, N$_2$ desorption appears at higher partial pressure and is less steep, which is most probably meaning less defined pore size and shape or interconnectivity of pores [61]. So, the observed modification of the isotherms are consistent with the fact that channel-like pores created by the removal of calibrated micelles cylinders are progressively replaced by pores formed as the interstices between TiO$_2$ crystals.

Pore size distribution was centered around 3-5 nm for the support calcined at relatively low temperature (Figure 5). This size is consistent with the expected size of the micelles formed
by F127 [47]. The pore size distribution started to become broader and to shift to larger size after calcination at 400°C and higher, consistent with a progressive disruption of the mesoscopic order when calcination temperature increases.

**Figure 4.** Specific surface area (top) and total pore volume (bottom) of the mesoporous TiO$_2$ supports as a function of the calcination temperature.
Figure 5. $N_2$ physisorption analyses: (top) $N_2$-physisorption isotherms and (bottom) BJH pore size distribution of Ti325 (●), Ti350 (▲), Ti375 (■), Ti400 (★), Ti425 (♦), and Ti450 (★). Adsorption isotherms are plotted in black and desorption isotherms are plotted in grey.

XRD analysis revealed the onset of anatase phase already starting at the calcination temperature of 350 °C (Figure 6). The crystal growth is more pronounced as the calcination temperature increases. This confirms that the amorphous mesoporous walls are progressively being converted into aggregates of growing anatase crystallites.
Figure 6. XRD patterns of (a) Ti325, (b) Ti350, (c) Ti400, (d) Ti375, (e) Ti425, and (f) Ti450. Black dots indicate anatase TiO$_2$ crystal planes; black dot (●) indicates anatase TiO$_2$ phase.

From SAXS analysis, a correlation peak which indicates the mesoscopic order in the sample was found in the case of the fresh and 350 °C calcined samples (Figure S2). The d-spacing, which corresponds to the distance between the repeating unit, pore-to-pore or wall-to-wall distance in this case, was calculated ($d = 2\pi/q$) to be 11.4 nm and 8.4 nm for the fresh sample and Ti350, respectively. The decrease in the d-spacing after calcination is attributed to the shrinkage due to the densification of the TiO$_2$ network. Based on the pore diameter observed by TEM and N$_2$ physisorption analysis for Ti350 (approximately 5 nm), the TiO$_2$ wall thickness is estimated to be 3 to 4 nm. On the other hand, no correlation peak was observed after calcination at 375 °C and higher. This further indicates the destruction of the mesostructure due to the growth of anatase phase.

Overall, the employed aerosol-assisted sol-gel process led to spherical TiO$_2$ particles with mesopores released by the efficient removal of the surfactant. The calcination temperature can be seen as a tool to tune both the textural properties and the crystallinity of the support. In the following, the mesoporous TiO$_2$ material obtained after calcination at 350 °C (Ti350) was chosen as a starting support since it maintained the mesostructure with high specific surface area and well-defined pore size, without significant crystal growth after calcination.
3.2. RuO₂/TiO₂ catalysts prepared by the impregnation of RuO₂ NP onto mesoporous TiO₂

Ti350 was impregnated with a suspension of ~2 nm sized RuO₂ nanoparticles [48, 62] so as to reach a loading of 2.2 wt.% of Ru (the experimental Ru loading was between 2.0 and 2.3 wt., as verified by ICP-AES on selected catalysts; not shown). The catalyst was further annealed at different temperatures under static air.

Clearly, the introduction of Ru species combined with further annealing affected the texture of the starting mesoporous TiO₂, even when the annealing temperature of the catalysts was the same as the calcination temperature of the pure mesoporous TiO₂ (Table 1 and Figure 7). As expected, the surface area and the pore volume decreased with higher annealing temperatures, whereas the average pore diameter was increased which indicates the progressive destruction of the mesoscopic order. All catalysts presented type IV isotherms characteristic of mesoporous materials, maintaining the shape of the hysteresis loop.

![Figure 7](image-url)  
**Figure 7.** N₂ isotherms of Ti350 (●), Ti350Ru350 (▲), Ti350Ru450 (■), Ti350Ru550 (★), and Ti350Ru650 (♦). Adsorption isotherm is in black and desorption isotherm is in grey.

The XRD patterns of the catalysts annealed at different temperatures are presented in Figure 8 and the XRD peaks were deconvoluted using WinPlotR software to obtain precise positions and widths of TiO₂ and RuO₂ phases in between 34 and 42 in 2theta (Fig. S3 and Table S1). While the bare support calcined at 350°C showed only weak signals of anatase TiO₂, further crystallization and growth of this anatase phase is observed upon annealing in the presence of Ru species. Interestingly, the (110) and (101) peaks of rutile TiO₂ (ICDD 00-021-1276) were also detected starting at the very low 250°C annealing temperature. Looking at the
evolution of the amount of each phase as a function of annealing temperature (Figure S4) it appears that rutile TiO$_2$ and anatase TiO$_2$ both increase from 250 to 450°C, indicating that the crystallization of the amorphous TiO$_2$ solid takes place during annealing. Rutile TiO$_2$ amount further increase over 450°, while the anatase amount reaches a maximum at 450°C and then decreases, showing the anatase to rutile transition at high temperature [63, 64]. In fact, amorphous TiO$_2$ [65, 66] or anatase or brookite [67] phases are known to undergo a non-reversible phase transition towards rutile when heated at high temperature, rutile TiO$_2$ being the thermodynamic phase. This solid-solid transition usually occurs between 400 to 700°C, depending on several criterions such as particle size, purity, atmosphere, etc. Here, the amorphous to rutile TiO$_2$ transition starts as low as 250°C, which is to our knowledge unprecedented. It clearly appears to be triggered by the presence of RuO$_2$ nanoparticles, because the rutile TiO$_2$ phase did not form when bare Ti350 was further annealed at 550 °C, in the same condition as Ti350Ru550 (XRD pattern not shown). It should be noted that the 2nm impregnated RuO$_2$ nanoparticles are already crystalline from start [48], yet their size prevent any diffraction phenomena to occur. Sintering at higher temperature is responsible for RuO$_2$ peak appearance.
Interestingly, at low annealing temperature, the (110) TiO\(_2\) rutile peaks appears shifted towards high angles, while the (101) peaks are shifted towards low angles (as compared to the reference for rutile TiO\(_2\)). Rutile TiO\(_2\) peaks are thus closer to the RuO\(_2\) peak positions. In the meantime, RuO\(_2\) peaks are distinguished from 450°C (Figure S3); their positions are perfectly centered on the known ICDD 01-070-2662 RuO\(_2\) reference. As the annealing temperature increases, the positions of RuO\(_2\) peaks remained constant while the positions of rutile TiO\(_2\) peaks, evolved towards the expected positions of rutile TiO\(_2\) (Figure 9). This phenomenon is a proof that the rutile TiO\(_2\) is seeded by the impregnated 2 nm RuO\(_2\) nanoparticles. In fact, Rutile TiO\(_2\) has already been reported to crystallize from anatase at 350°, in the presence of RuO\(_2\) [18]. The degree of mismatch between ICDD 01-070-2662 RuO\(_2\) and ICDD 00-021-1276 rutile TiO\(_2\) of 1.8% for (110) and 2.7% for (101), largely below the generally accepted 5% authorized limit for epitaxial growth. Thus, the growth of rutile TiO\(_2\) layer was also reported to be promoted by using RuO\(_2\) as a seed layer [68, 69] for the fabrication of RuO\(_2\)-TiO\(_2\) films, using the epitaxial match between the rutile RuO\(_2\) and rutile TiO\(_2\). This epitaxial relation between (101) TiO\(_2\) and (101) RuO\(_2\) becomes weaker as the size of the particles increases (and surface decrease) with increasing annealing temperature. The Scherrer calculations confirmed the growth of RuO\(_2\) crystallites with increased annealing temperature; 29 nm (450°C), 38 nm (550°C), to 68 nm (650°C) for (110) RuO\(_2\) and 13 nm (450°C), 12 nm (550°C), to 22 nm (650°C) for (101) RuO\(_2\).
**Figure 9.** Difference between 101 and 110 peak positions for (a) rutile RuO$_2$ and (b) rutile TiO$_2$. The grey lines represent the expected value based on ICDD 01-070-2662 for RuO$_2$ and ICDD 00-021-1276 for TiO$_2$. Peak surfaces (c) of 101 TiO$_2$ anatase (blue), 110 TiO$_2$ rutile (grey) and 110 RuO$_2$ (red). The complete XRD data set (peak position and width after deconvolution) is available in Table S1.

HR-TEM was performed on Ultra-thin sections of spent Ru350Ti350 samples. This way, Ru species are reduced, which allows a better Ru/TiO$_2$ contrast and thus easier detection. The location of Ru species allows us to define the location of RuO$_2$ since it has already been established that no Ru species migration occurs during reduction or methanation [18]. Ru is clearly detected inside the spheres, proving that RuO$_2$ nanoparticles had indeed the possibility to diffuse inside the mesoporous network of the support during impregnation (Figure 10). A certain accumulation of Ru nanoparticles is also noticed forming domains of about 40 nm wide in which higher concentration of small Ru nanoparticles ranging from 2 to 5 nm are visible. This shows that a partial but limited sintering of RuO$_2$ could not be avoided. This can be related to previous observations where RuO$_2$ would highly sinter in presence of anatase [18]. Upon annealing at higher temperature (Ru350Ti450) the HRTEM images showed that the Ru species are always present within the TiO$_2$ support, and not separated from the TiO$_2$ microspheres (Figure 10). Rutile TiO$_2$ phase was observed in close proximity to Ru species, as expected from X-Ray analysis. The size of Ru aggregates observed in HR-TEM is in accordance with the RuO$_2$ size estimated from Scherrer calculations.
Figure 10. HRTEM performed on Ultra-thin sections of spent catalysts. (top) Ru350Ti350: red arrows show isolated Ru nanoparticles (larger aggregates are clearly visible, see also
inset). (bottom) Ti350Ru450: the inset shows a zoomed image showing the crystal planes of rutile TiO$_2$ close to the Ru aggregates.

FTIR-ATR analysis after RuO$_2$ deposition and further annealing is shown in Figure S5. The weak bands in the 800 – 400 cm$^{-1}$ range became more prevalent for the further annealed catalysts compared to Ti350. Specifically, the maxima of the peaks at 790 cm$^{-1}$ and 440 cm$^{-1}$ shifted towards lower wavenumber, which can be attributed to the strengthening of the TiO$_2$ network [56, 59].

TPR experiments were carried out on selected samples after RuO$_2$ deposition. The shape of the reduction profile was different depending on the annealing temperature (Figure S6). A small reduction peak was observed around 125 °C for Ti350Ru350 suggesting that some residual Ru$^{3+}$ species from the colloidal suspension may still be present after annealing at 350 °C [70]. The main reduction event occurred at higher temperature and tended to shift towards higher temperatures with higher annealing temperature. This can be attributed to a lower reducibility of the larger RuO$_2$ particles detected by XRD.

3.3. CO$_2$ methanation

The catalysts were activated in situ in a pure hydrogen feed at 200 °C before being tested in the CO$_2$ methanation reaction up to 200 °C. The N$_2$ physisorption analysis after in situ reduction and methanation reaction showed that the textural properties remained unchanged (not shown). For all catalysts discussed here, the selectivity to methane was 100%, as classically observed with Ru-based catalysts at 200°C or lower [18]. The absence of external and internal diffusion limitations was verified (see ESI and Fig S7). Also, the reaction conditions were set as to obtain relatively low conversion levels, far away from the thermodynamic equilibrium, ensuring that the reported rates correspond to the intrinsic specific activity. The methane production rates is expressed as µmol of methane produced per gram of catalyst and per second.

For the catalysts annealed at various temperatures the methanation production rate is relatively low after annealing at 350°C but reached its maximum after annealing at 450 °C, and decreased after annealing at 550 °C or higher temperature (Figure 11). The most active catalyst (Ti350Ru450) reached a methane production rate of about 2.1 µmol of methane per gram of catalyst and per second. Comparing with other catalysts with the same Ru loading and tested in the same conditions, this is slightly lower than the rate reported when a non-sintering rutile-TiO$_2$ support was used (3.5 µmol$_{\text{CH}_4}$ g$_{\text{cat}}^{-1}$ s$^{-1}$ [17]) but in the same order as the rates reported for Ru/TiO$_2$ prepared Degussa-P25 as a support (2.6 µmol$_{\text{CH}_4}$ g$_{\text{cat}}^{-1}$ s$^{-1}$ [18]).
Several parameters determine the final stability and activity of Ru/TiO$_2$ methanation catalysts: crystalline structure (of the support and of the ruthenia phase), sintering (support or/and ruthenia), migration of RuO$_2$ species towards rutile TiO$_2$, phases stabilization, modification of porosity or surface accessibility, dispersion or aggregation of the active phase, phase transition, etc. For non-sintering TiO$_2$ supports, rutile TiO$_2$ was shown to be the most effective support to prepare highly active Ru/TiO$_2$ methanation catalysts [18]. The strong epitaxy link between TiO$_2$ rutile and RuO$_2$ lead to the best RuO$_2$ dispersion on TiO$_2$ surface, and thus after reduction, to well dispersed Ru particles. In the case of mixtures between anatase and rutile, it is the amount of accessible rutile that drives the activity. Here we show that it is possible to trigger TiO$_2$ rutile crystallization, benefitting from the seeding action of RuO$_2$ nanoparticles and keeping a mesoporous material. The increase of activity between 350°C and 450°C annealing can be seen as the consequence of the increase in the amount of rutile TiO$_2$ particles. Unfortunately, with further heating, a strong decrease in porosity is provoked by a heavier TiO$_2$ and RuO$_2$ sintering, which appear to limit the catalytic activity.

![Figure 11. Comparison of methane production rates of Ru/TiO$_2$ catalysts prepared by impregnation RuO$_2$ nanoparticles on the mesoporous TiO$_2$ calcined at 350°C and after annealing at various temperatures.](image)

4. Conclusion
Mesostructured TiO\textsubscript{2} materials were successfully synthesized via an aerosol-assisted sol-gel process. The resulting TiO\textsubscript{2} powders could be obtained with a good control on the textural properties upon removal of the organic template. Crystallization of amorphous TiO\textsubscript{2} to crystalline anatase phase was inevitable especially after calcination at 350 °C and higher temperatures. These modifications resulted in significant textural modifications that are controllable to a certain extent. The mesoscopic order was maintained after calcination at 350 °C with well-defined pore size of 5 nm and specific surface area of 260 m\textsuperscript{2}.g\textsuperscript{-1}. It was however progressively disrupted when higher calcination temperature were used.

The 350°C-calcined mesoporous TiO\textsubscript{2} support was used as support for RuO\textsubscript{2} nanoparticles to serve as a catalyst containing 2.2 wt. % Ru for CO\textsubscript{2} methanation. Ru-species were found inside the pores of TiO\textsubscript{2} support after in situ reduction and reaction, showing that a simple impregnation of the mesoporous support with an aqueous suspension of RuO\textsubscript{2} nanoparticles is suitable. The annealing of the partially oxidized Ru-species was found to be an important activation step as the catalytic activity was at its maximum when annealed at 450 °C. The RuO\textsubscript{2} nanoparticles promoted further modifications of the low crystalline TiO\textsubscript{2} support materials during annealing. On the one hand, the growth of the rutile TiO\textsubscript{2} phase was triggered at annealing temperature as low as 250 °C, due to the close structural similarities of RuO\textsubscript{2} and rutile TiO\textsubscript{2} (epitaxy). On the other hand, the amorphous materials is mainly crystallized in the anatase phase, which favors the buildup of large RuO\textsubscript{2} aggregates. Globally, these catalysts did not outcompete the reference prepared from non-sintering rutile TiO\textsubscript{2} supports. This study allows us to observe the beneficial role of rutile TiO\textsubscript{2} structure to stabilize RuO\textsubscript{2}, maintain good dispersion, and trigger high catalytic activity.

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References
Aerosol-assisted sol-gel synthesis of mesoporous TiO$_2$ materials, and their use as support for Ru-based methanation catalysts

Ara Kim,$^{a,b}$ Clément Sanchez,$^b$ Bernard Haye$^b$, Cedric Boissiere,$^b$ Capucine Sassoye,$^{b,*}$ Damien P. Debecker$^{a,*}$

$^a$ Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Place Louis Pasteur, 1, box L4.01.09, 1348 Louvain-La-Neuve, Belgium. E-mail: damien.debecker@uclouvain.be

$^b$ Sorbonne Universités, UPMC Université Paris, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 Place Jussieu, 75252 Paris Cedex, France. E-mail: capucine.sassoye@upmc.fr
Figure S1. (top) TGA curves showing sample weight loss for F127 with heating rate of 10 °C/min (black), fresh mesoporous TiO$_2$ with a heating rate of 5 °C/min up to 600 °C (grey) and fresh mesoporous TiO$_2$ with a heating rate of 1 °C/min up to 350 °C, followed by a 10 h dwell at this temperature (lighter grey). (bottom) TGA curves showing sample weight loss as a function of time of analysis, from a fresh mesoporous TiO$_2$ sample with heating rate of 1 °C/min up to 350°C, followed by a 10h dwell at this temperature.
Figure S2. SAXS patterns of (a) fresh sample, (b) Ti350, (c) Ti375, (d) Ti400, (e) Ti425, and (f) Ti450. The wave vector, q, is defined as $(4\pi \sin \theta) / \lambda$, where $2\theta$ is the scattering angle.
Figure S3. XRD analyses. Deconvoluted RuO$_2$ (◇), rutile TiO$_2$ (▲), anatase TiO$_2$ (●) peaks in the 2θ range of 34° – 42°; (a) Ti350Ru450, (b) Ti350Ru550, (c) Ti350Ru650. Black dotted lines indicate theoretical (101) TiO$_2$ peak position. The deconvolution of the (110) and (101) RuO$_2$ peaks was only possible after annealing at 450 °C and higher temperatures. (d) Zoom of the XRD patterns of Ti350 (black), Ti350Ru250 (green), Ti350Ru350 (blue), Ti350Ru450 (purple), Ti350Ru550 (pink) and Ti350Ru650 (red).
Figure S4. Evolution of the amount of crystalline (▲) rutile TiO₂, (●) anatase TiO₂ and (●) RuO₂ as a function of the annealing temperature. The surface of the diffraction peaks is taken as an indicator of the amount of crystalline phase.
**Figure S5.** FTIR-ATR spectra of (a) F127, (b) fresh mesostructured sample, and 5x amplified spectra of (c) Ti350, (d) Ti350Ru350, (e) Ti350Ru400, and (f) Ti350Ru450; dotted lines are guide to the eyes.

**Figure S6.** H$_2$-TPR of (a) Ti350Ru350, (b) Ti350Ru450, and (c) Ti350Ru500.
Validation of the activity measurements (diffusional limitations, equilibrium)

It is important to verify that the levels of activity correspond to the intrinsic activity of the catalysts and are not biased by physical (diffusion) or thermodynamic limitations.

Activation energy (Ea) was always ~15 kcal/mol for non porous catalysts [1] and also here in the case of mesoporous supports. Thus, internal diffusion limitation can be excluded (lower activation energies – typically half of Ea from chemical kinetics – would be expected in such case). Also, external limitations are avoided by selecting a relatively small particles size (and also lower activation energies (< 5 kcal/mol) are expected in such case). Catalysts are systematically ground and sieved in the 100-315 µm range which is suitable in the conditions used here to consider that external diffusional limitations are unlikely.[2]

In order to examine whether the activity is not underestimated by thermodynamic limitations – i.e. when approaching the equilibrium, the turnover slows down – a catalytic test was repeated with half the mass used for the initial catalytic test for Ti350Ru350. In these conditions, CO₂ conversion was exactly divided by two. In other words, the specific activity (or rate) was the same (Figure S2). This clarifies that the reported levels of activity truly correspond to intrinsic activity levels and are not biased by thermodynamic limitation. The equilibrium at 200 °C corresponds to ~ 100 % CO₂ conversion, while the rate measured here at 200 °C corresponds to 12.6 % (200 mg catalyst) and 6.7 % (100 mg catalyst) conversion.

![Figure S7](image.png)

**Figure S7.** Comparison of methane production rates of Ti350Ru350 tested with different mass; 200 mg (●) and 100 mg (▲).
**Table S1.** Position (2θ) and width (FWHM) for the main TiO$_2$ and RuO$_2$ peaks obtained after deconvolution. Data expressed in °.

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