

# Improving Catalytic Activity by Synergic Effect between Base and Acid Pairs in Hierarchically Porous Chitosan@Titania Nanoreactors

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## **1. Typical chitosan@titania preparation procedure:**

### **1.1. Synthesis of native chitosan microspheres (M0).**

An aqueous solution of chitosan was obtained by dissolving 1g of chitosan in 100 mL of a solution of acetic acid ( $0.055 \text{ mol L}^{-1}$ ) corresponding to a stoichiometric amount of acid with respect to the amount of  $\text{NH}_2$  functions. Total dissolution was obtained under stirring over one night at room temperature. This solution was dropped into a NaOH solution (4N) through a 0.8 mm gauge syringe needle providing gelified chitosan microspheres. The chitosan beads were stored in the alkaline solution for 2 h and then dehydrated by immersion successively in a series of ethanol–water baths containing more and more ethanol until 100% ethanol bath. (These beads called alcogels were directly used for the synthesis of **M1H**, **M2H** and **M3H**). The native microspheres were then dried under supercritical  $\text{CO}_2$  conditions (74 bar,  $31.5 \text{ }^\circ\text{C}$ ) in a Polaron 3100 apparatus to lead to **M0**. The chitosan aerogel beads present a porous network featuring high surface area and large pore diameter as determined by nitrogen sorption measurements (see section 2.1. Nitrogen adsorption measurements: entry 1).

### **1.2. Synthesis of chitosan@titania hybrid aerogel microspheres. (M1H, M2H and M3H).**

The titania solution was prepared with titanium alcoxide source  $\text{Ti}(\text{acac})_2(\text{OiPr})_2$  (for preparation of **M1H**),  $\text{Ti}(\text{OiPr})_4$  (for **M2H**) or  $\text{Ti}(\text{O}i\text{Bu})_4$  (for **M3H**) and isopropanol ( $\text{Ti:iPrOH}$  ) 1:10). The beads of chitosan swelled in ethanol (250 mg) were suspended in the titania solution (4 mmol) at room temperature for 48 h. The microspheres were washed first with isopropanol twice and then with ethanol. The hybrid microspheres were dried by supercritical  $\text{CO}_2$  leading aerogel microsphere materials. The obtained materials present a porous network featuring high surface area and large pore diameter as determined by nitrogen sorption measurements (see section 2.1. Nitrogen adsorption measurements: entries2-4).

### 1.3. Synthesis of chitosan@titania hybrid xerogels (M1Hxero).

The difference between the aerogel microspheres and the xerogel microspheres consists simply in their drying method. For xerogels, after immersing the beads of chitosan in the titania solution at room temperature for 48 hours, the microspheres were washed twice with ethanol and dried in air overnight. Complete solvent evaporation was achieved by drying beads in an oven at 50°C for 2 hours. By this treatment, significant shrinkage occurs and, as suspected, nitrogen adsorption measurements did not show a valuable porosity.

### 1.4. Preparation of titanium dioxide microsphere.

The resulting chitosan@titania aerogels **M1H**, **M2H** and **M3H** were subjected to calcinations under air for 6 hours at 550°C (rate : 20°C/ min) in order to remove the organic template giving thus a pure titanium inorganic oxides **M1**, **M2** and **M3**, respectively. Under calcination, the beads shrink due to the space lost by polymeric organic phase removal. But interestingly, highly surface materials are obtained (entries 5-7). Titanium crystallizes leading to Anatase form of TiO<sub>2</sub> identified by X-ray diffraction analysis (not shown).

## 2. Textural characterization.

### 2.1. Nitrogen adsorption measurements.

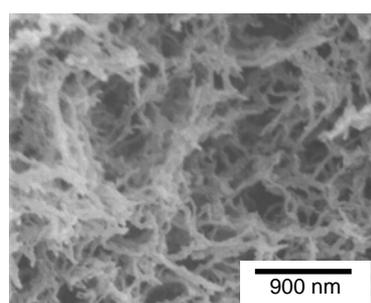
Entry	material	Titanium precursor	% TiO <sub>2</sub> *	S <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )	V (cm <sup>3</sup> .g <sup>-1</sup> )	Pore diameter** (Å)	C	size (Å)***
1	<b>M0</b>	-----	0	120	0.34	85	142	----
2	<b>M1H</b>	Ti(acac) <sub>2</sub> (OiPr) <sub>2</sub>	25	480	1.86	112	70	---
3	<b>M2H</b>	Ti(OiPr) <sub>4</sub>	29	450	1.29	50	58	---
4	<b>M3H</b>	Ti(OBu) <sub>4</sub>	25	370	0.94	110	63	---
5	<b>M1</b>	Ti(acac) <sub>2</sub> (OiPr) <sub>2</sub>	100	308	0.87	108	94	78
6	<b>M2</b>	Ti(OiPr) <sub>4</sub>	100	274	0.62	96	112	80
7	<b>M3</b>	Ti(OBu) <sub>4</sub>	100	266	0.93	112	106	81

\* From TGA. \*\* From BJH (nitrogen adsorption). \*\*\* XRD.

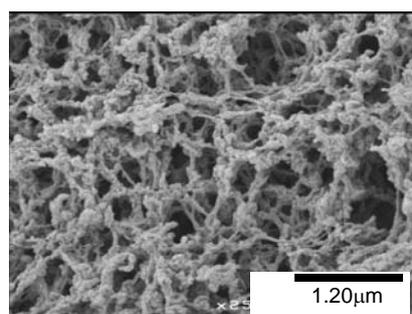
## 2.2. Scanning electronic microscopy (SEM) analysis.

It is notable that all the described aerogel based materials (chitosan **M0**, hybrid chitosan@titania **M1H**, **M2H** and **M3H**, and the calcined materials TiO<sub>2</sub> (**M1**, **M2** and **M3**) feature similar textural properties (fibrous and macroporous network) as evidenced by nitrogen adsorption measurements and SEM. This is very important to mention because it permit to rule out the influence of diffusion and mass transfer during catalysis. Hence, the enhancement of the catalytic activity of chitosan@titania **M1H**, **M2H** and **M3H** (compared to **M0** and titanium dioxide **M1**) can be mainly attributed to the cohabitation of basic functions (amino groups) and acidic functions (nanotitania) in their framework.

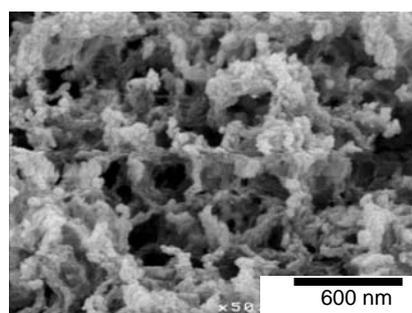
SEM of **M0**, **M2H** and **M2** are given for comparison.



**M0**



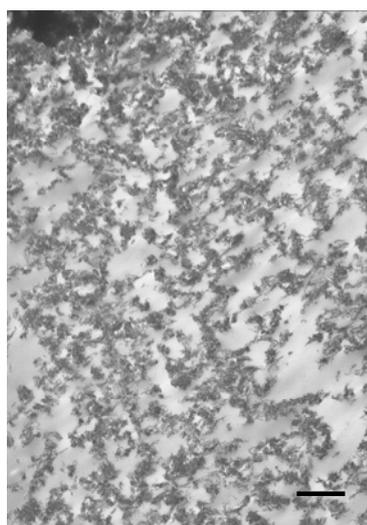
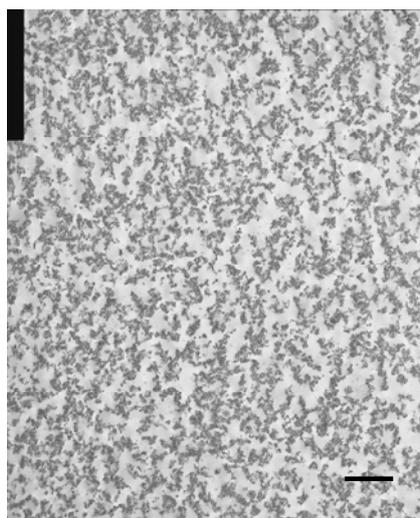
**M2H**



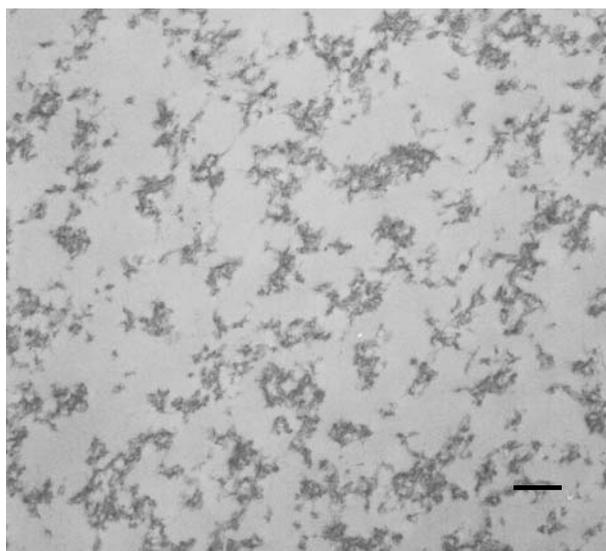
**M2**

### 2.3. Transmission electronic microscopy (TEM) analysis.

The three aerogel hybrid materials **M1H**, **M2H** and **M3H** showed a good dispersion of titanium nanoclusters in chitosan matrix. No bulk material or aggregate which may indicate a phase separation formation was observed. This is mainly due to the ability of chitosan to control mineral growth of titanium dioxide.



a) TEM of **M1H** : scale bar : 800 nm, b) TEM of **M2H** : scale bar : 400 nm



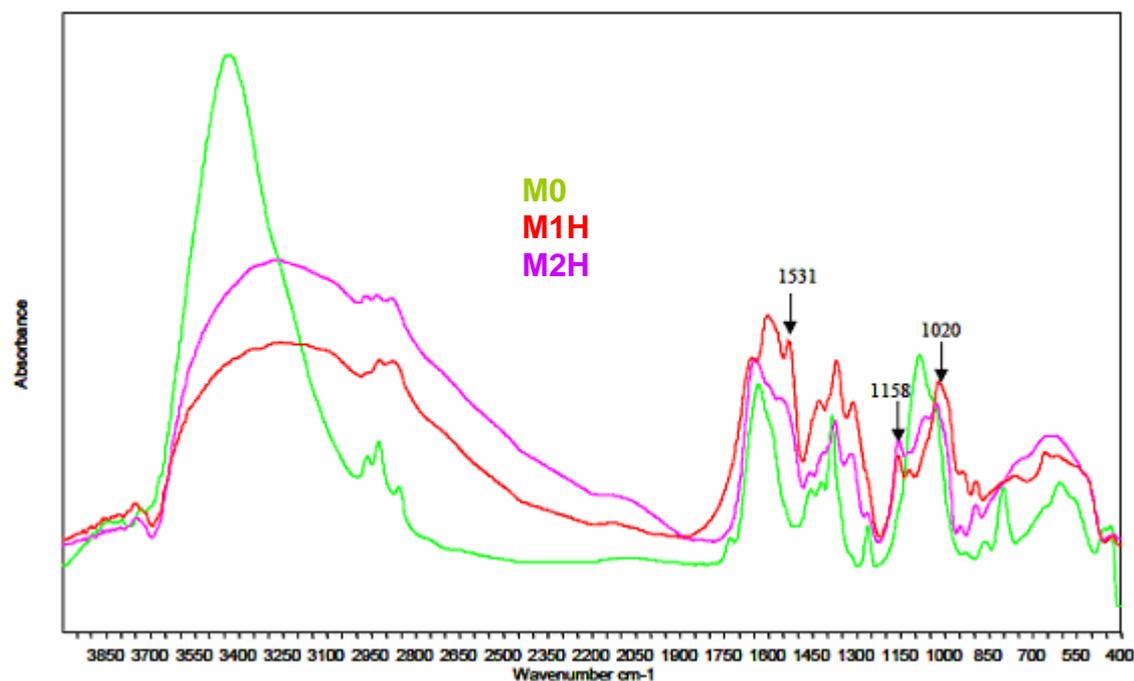
TEM of **M3H** : scale bar : 500 nm

### 3. Structural characterization of M1H, M2H and M3H.

Structural composition of the hybrid microspheres was investigated by DRIFT,  $^{13}\text{C}$  MAS NMR, DRUV and X-ray photoelectron spectroscopy (XPS) analysis.

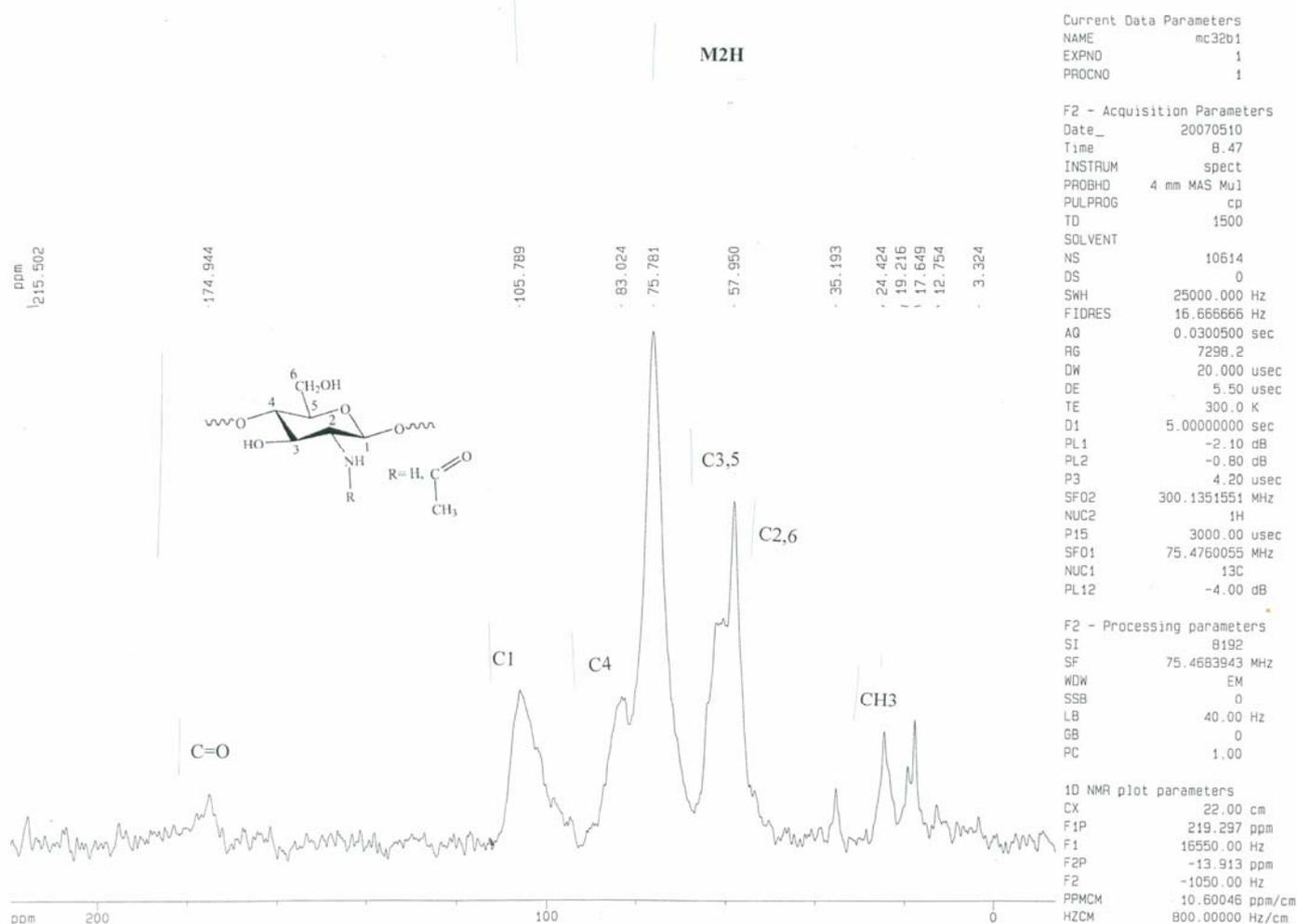
#### 3.1. DRIFT analysis.

DRIFT analyses were performed on a pellet obtained by grinding one bead of material and mixing it with KBr. The results revealed the characteristic bands of polymeric chitosan (comparison of native beads **M0** and hybrid beads **M1H** or **M2H**); a broad and unstructured absorption at  $3700\text{-}3000\text{ cm}^{-1}$  due to the overlap of OH and NH stretching vibration bands is observed. Characteristic bands of  $\text{CH}_2$  and  $\text{CH}_3$  are also observed at  $2950\text{ cm}^{-1}$ . Deformation of  $\text{NH}_2$  and NH are also shown around  $1600\text{ cm}^{-1}$ . New bands were also observed at  $1020$  and  $1158\text{ cm}^{-1}$  and can be assigned to C-O-Ti.<sup>1</sup> The broad band below  $800\text{ cm}^{-1}$  is consistent with the formation of titanium clusters.<sup>2</sup>



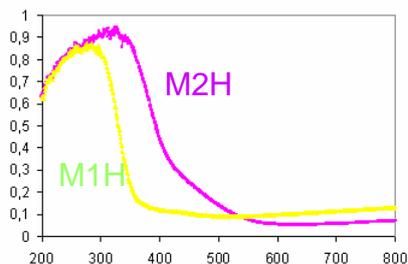
### 3.2. $^{13}\text{C}$ NMR.

Solid state carbon NMR of the three hybrids was performed and compared with the literature data of polymeric chitosan. Both spectra of the three hybrids exhibited two peaks around 24 to 26 and 174 ppm, which can be assigned to methyl and carbonyl groups, respectively. Peaks at 55, 75, 82 and 105 ppm can be assigned to  $\text{C}_{2,6}$ ,  $\text{C}_{3,5}$ ,  $\text{C}_4$  and  $\text{C}_1$ , respectively. An NMR spectrum of **M2H** was shown as example.



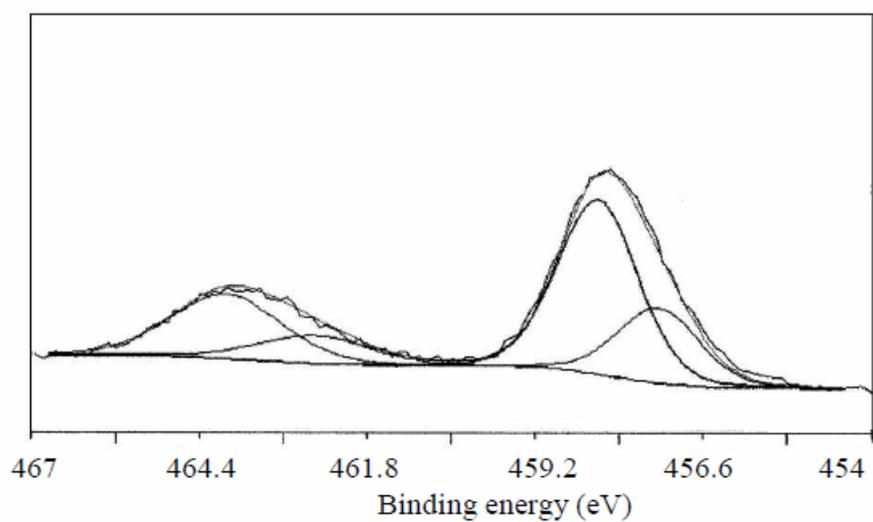
### 3.3. DRUV analysis.

DRUV analysis of the materials shows a broad adsorption at 312 nm (**M1H**); 280nm (**M2H**) and 285 nm (**M3H**). This adsorption is consistent with an incipient oligomerisation of Ti(IV) species.<sup>3</sup> DRUV of **M1H** and **M2H** are given as example.

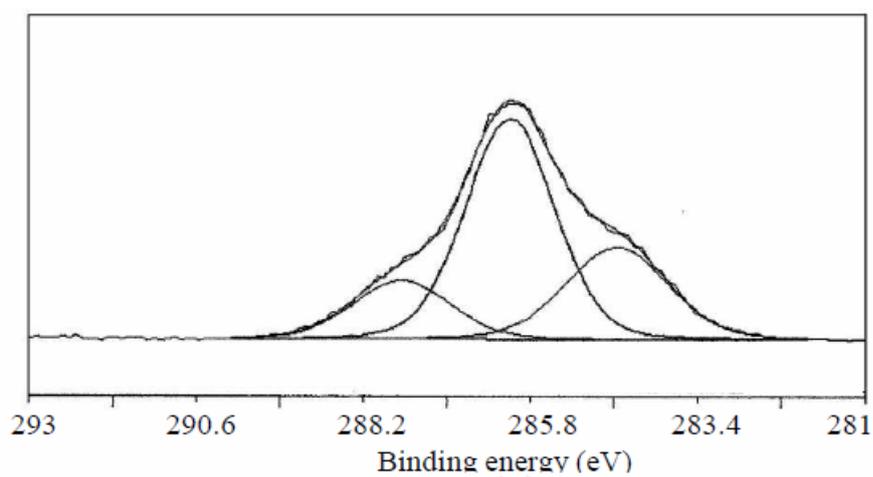


### 3.4. XPS of M1H, M2H and M3H.

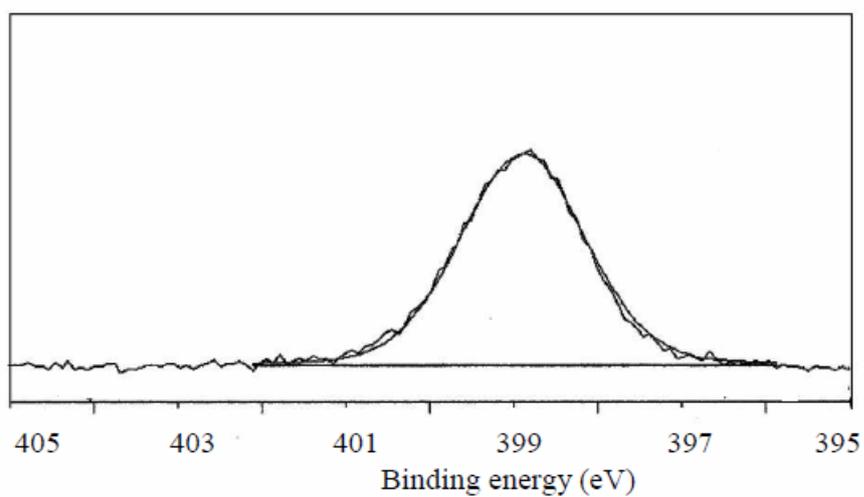
XPS analysis is an efficient tool to better elucidate the nature of chemical species present both at the surface and in the whole of the materials. Grinding the samples and their analysis allow us to provide additional information about the distribution of titanium species across the microspheres. First, it was found that the percent of inorganic titanium clusters was slightly more important (by ~ 7%) at the surface than in the bulk. The presence of absorption peaks at 458.3 eV, 458.5 eV and 458.4 eV for **M1H**, **M2H** and **M3H**, respectively confirms the presence of titanium oligomeric clusters inside the beads matrices.<sup>4</sup> Characteristic adsorption of CH<sub>3</sub> and CH<sub>2</sub> (at 286.6) and of NH<sub>2</sub> (399 eV) are also shown.<sup>4</sup> Spectra recorded for **M1H** are given as example.



XPS spectra of titanium Ti 2p for **MIH**.



XPS spectra of carbon C1s of **MIH**.



XPS spectra of nitrogen N1s (NH<sub>2</sub>) of **MIH**.

## 4. Stability of the materials.

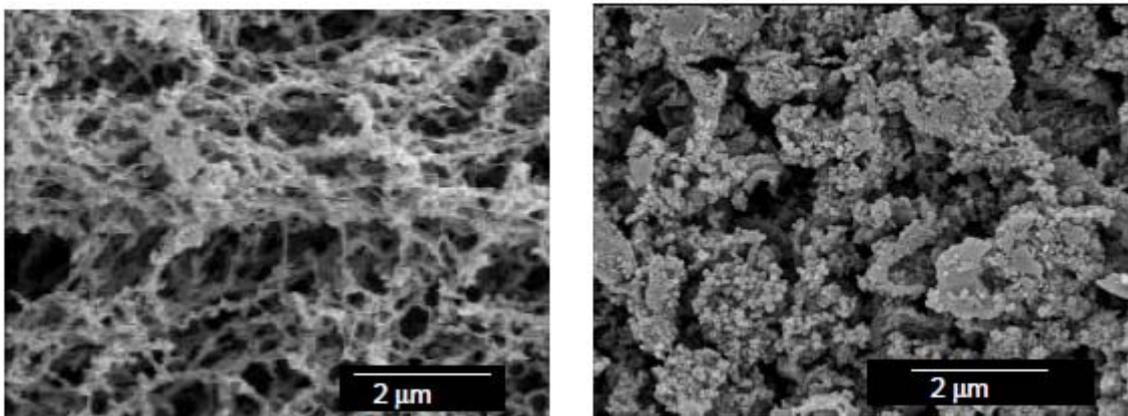
The stability of chitosan@titania hybrids was assessed by means of SEM, TGA and nitrogen sorption analysis. For comparison purposes, the stability of the native chitosan **M0** and chitosan@silica hybrid (ref **9b** in the manuscript) was also evaluated.

### 4.1. Stability under basic conditions.

20 mg of the material were immersed in 20 mL of basic solution (NaOH, 0.1 N) and the mixing was ensured by rotation of the flask around its horizontal axis on a Heidolph Reax2 stirrer for 1 h. Then, the beads were washed several times with distilled water until pH 7. This aqueous solution was then exchanged with 10%, 30%, 50%, 70%, 90% and 100% of ethanol. Ethanol was exchanged again by CO<sub>2</sub> and the obtained samples were then dried under supercritical conditions (74 bar, 31.5°C) in a Polaron 3100 apparatus.

Morphology: the morphology of the three hybrids **M1H**, **M2H** and **M3H** was preserved, whereas the size of the native chitosan **M0** bead was significantly reduced. For chitosan@silica, crumbling of the material was observed due to the dissolution of silica under basic conditions (TGA analysis shows a loss of 16% of the initial amount of silica inorganic oxide).

Texture: examination by SEM of the network of all tested materials revealed that only chitosan@titania hybrid stands to harsh basic conditions. The fibrous network of the materials was maintained (SEM, see below). In contrast, significant evolution and alteration was detected in the case of native chitosan **M0** and chitosan@silica hybrid.



SEM of (left) **M1H** after treatment under basic conditions showing the fibrous texture of the material. (right) chitosan@silica after treatment under basic conditions showing a collapse of the network and the apparition of some aggregates.

#### **4.2. Stability under acidic conditions.**

20 mg of the material are immersed in 20 mL of acidic solution (AcOH, 0.1 N) and the mixing was ensured by rotation of the flask around its horizontal axis on a Heidolph Reax2 stirrer for 1 h. Then, the beads were removed and washed several times until pH 7. This aqueous solution was exchanged with 10%, 30%, 50%, 70%, 90% and 100% of ethanol. Ethanol was exchanged again by CO<sub>2</sub> and the samples are dried under super critical conditions (74 bar, 31.5 °C) in a Polaron 3100 apparatus.

Morphology: native chitosan **M0** and chitosan@silica were completely dissolved (chitosan is soluble under acidic conditions). By contrast, chitosan@titania materials **M1H**, **M2H** and **M3H** were found to be stable and no significant damage was detected. This indicates that chitosan fibres are fossilized (or replicated) by titanium inorganic oxides, which prevents their dissolution.

Texture: SEM analysis corroborated these observations. The fibrous network of the three materials was maintained (photos not shown).

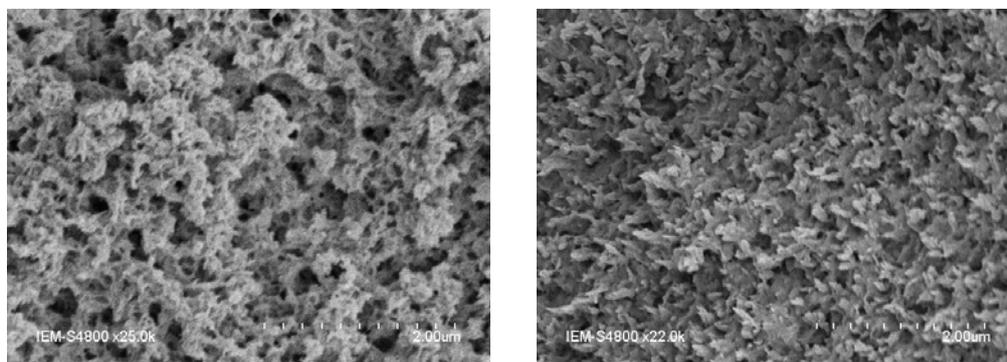
#### **4.3. Stability under hydrothermal conditions.**

20 mg of the materials were introduced in a flask containing 20 mL of distilled water and the solution was refluxed at 100°C for 1 h. The heater was stopped and the solution was cooled to

room temperature and left for one hour more. The solution was exchanged with ethanol, liquid CO<sub>2</sub> and then dried under supercritical conditions (74 bar, 31.5 °C) in a Polaron 3100 apparatus.

Morphology: native chitosan **M0** beads are totally damaged because of the lower stability of organic polymer. In contrast, the three hybrids **M1H**, **M2H** and **M3H** retain their morphology.

Texture: as expected, native chitosan was completely collapsed because of the lower stability of organic polymers. By contrast, the fibrous network is still present in the case of the hybrid chitosan@titania materials (see photos).



SEM of (left) **M1H** after thermal treatment showing the fibrous texture of the material. (right) chitosan **M0** after thermal treatment: the fibres are damaged which induce the collapse of the structure.

Porosity: the table reports the surface areas, obtained from nitrogen adsorption, of the tested materials before and after treatment. A significant decrease in the surface area of native chitosan **M0** and chitosan@silica is observed. The surface area of chitosan@titania decreases slightly but the porous structure is still present due to their stability enhancement.

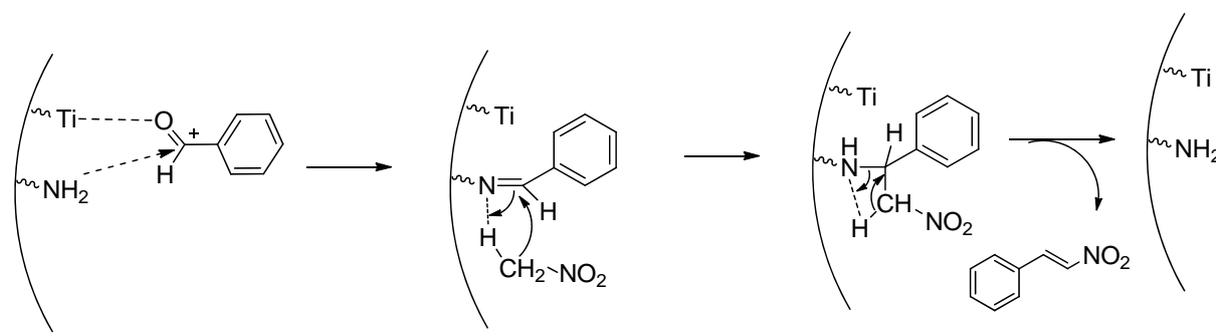
Materials	$S_{BET}$ before treatment (cm <sup>3</sup> /g)	$S_{BET}$ after acid treatment (cm <sup>3</sup> /g)	$S_{BET}$ after basic treatment (cm <sup>3</sup> /g)	$S_{BET}$ after thermal treatment (cm <sup>3</sup> /g)
<b>M0</b>	120	0	22	3
<b>M1H</b>	480	429	435	362
<b>M2H</b>	450	398	412	402
<b>M3H</b>	370	n.a	n.a	324
chitosan@silica	157	70	84	n.a

n.a = not available.

## 5. Catalytic tests.

All catalysis experiments were carried out under inert atmospheres (under nitrogen). Before catalysis, the used materials were introduced in a flask and activated at 50°C under vacuum for 1 hour and the flask was then purged with nitrogen and kept in an inert atmosphere. The solvents and reactants were added at room temperature and the zero time of reaction was taken when the temperature reached the value indicated in each table (80°C for Henry reaction and 80 or 120°C for jasminaldehyde synthesis). The reagents and the products amounts were determined by GC analysis (FID, HP5,  $T_{inj} = 250^{\circ}\text{C}$ ,  $T_{det} = 275^{\circ}\text{C}$ , oven 50-250°C,  $15^{\circ}\text{C min}^{-1}$ ) with dodecane as external standard according to a calibration curve established with authentic samples.

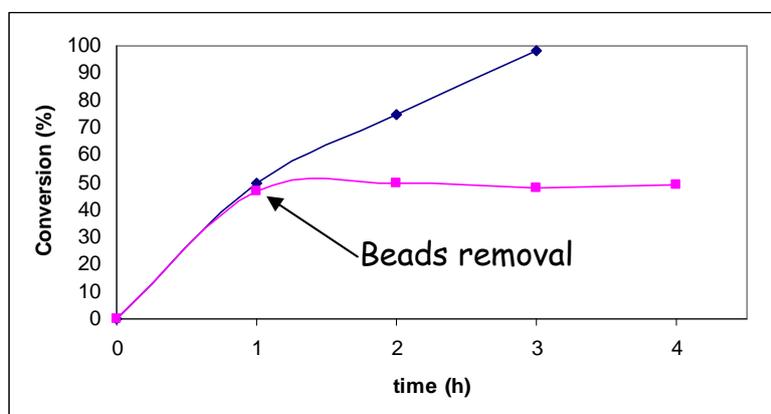
## 6. Reaction mechanism for Henry reaction.



Suggested imine catalytic mechanism for the production of the dehydrated product for the Henry reaction (with nitromethane) catalyzed by amines on chitosan@titania. Both the imine formation step and the attack of the nucleophile on the imine are known to be acid catalyzed.

## 7. Hot filtration tests.

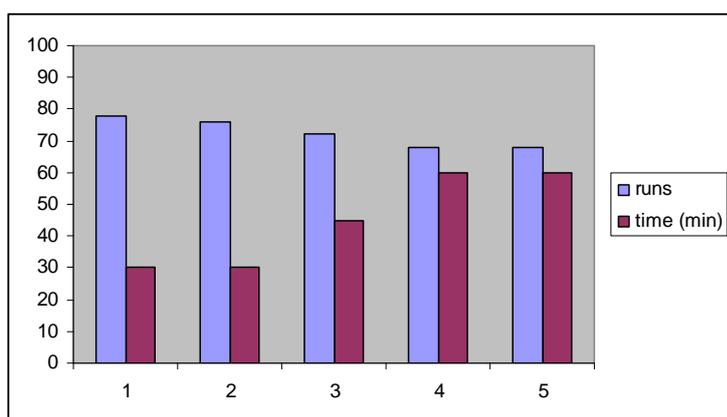
In the reaction of nitromethane with 4-methoxybenzaldehyde (table 1 in the manuscript), no more methoxybenzaldehyde conversion was further observed even during extended time after removal of the **M1H** beads by hot filtration. This indicates that no (or negligible) leaching occurred.



## 8. Recycling of the catalysts.

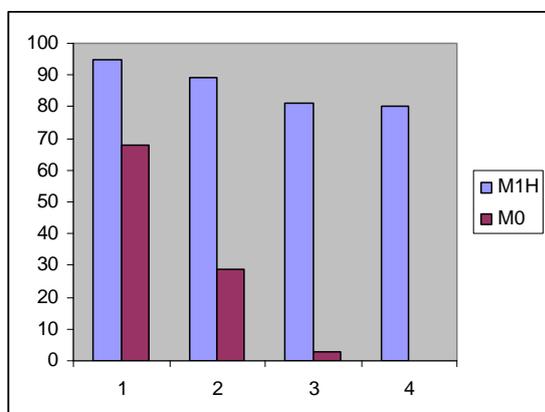
### 8.1. Michael addition.

The recycling of the catalyst **M1H** was tested in Michael addition of ethyl cyanoacetate with methyl vinyl ketone. Based on the conversion, only a slight decrease in the activity was observed after five runs.



### 8.2. Henry reaction.

To demonstrate the stability gained by mineralization of chitosan microspheres by titanium inorganic oxide, the recycling of **M1H** was studied in Henry reaction and compared to the recovery of native chitosan **M0**. Whereas native chitosan deactivated easily with only 3% of conversion in the third run, only a slight decrease in the activity of chitosan@titania **M1H** was observed with up to 80% during the fourth run.



## References.

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