Activated amorphous TiO2 coated into periodic mesoporous-

organosilicate channels as a new binary photocatalyst for regeneration of

carbonyl compounds from oximes under the sunlight irradiation

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Experimental

PMO-ICS Synthesis

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer template $(EO_{20}PO_{70}EO_{20}, Pluronic P123 \text{ from BASF})$, tetraethoxysilane (TEOS from Fluka), tris[3-(trimethoxysilyl)propyl]isocyanurate (Aldrich) and Titanium tetraisopropoxide (TTIP, Ti(OPr^{*i*})₄ from Fluka) were used without additional purification.

The synthesis of PMO-ICS has been achieved using known procedure described by Jaroniec and his co-workers¹ In a typical preparation, 4.0 g of Pluronic P123 (Aldrich, average Mw \cong 5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution. Then 0.01 mol (6.159 g) of tris[3-trimethoxysilyl)propyl]isocyanurate (ICS, Aldrich) and 0.03 mol (6.24 g) tetraethoxysilane (TEOS) was added into that solution. This mixture was stirred in the constant rate at room for 24 h. The mixture was aged at 100 °C for 48 h without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water (100 ml of 95% ethanol and 4 ml of 12 M HCl) using a soxhelet apparatus for 72 h to remove the surfactant molecules. It was dried in air at 100 °C overnight.

Preparation of the Catalysts

The preparation of PICS-Ti catalysts was achieved according to the known procedure described by Dai *et.al.*² The resulting PMO-ICS was loaded into a predried two-neck reflux flask sealed with a rubber septum. Subsequently, 9 ml of anhydrous super dry Toluene and 3.4 mmol of $Ti(OPr^i)_4$ were transferred into the bottle through a syringe. The solution was refluxed at 110 °C for 1 h (for the growth of the first layer of titania). The multilayer (for more titan loading) of titanium oxide on PMO-ICS can be prepared by the iteration of the above procedure. The final product was washed several times with anhydrous ethanol and DI water and dried at 75 °C overnight.

General experimental procedure for deoximation reaction using photocatalytic system

A mixture of alcohol (0.01 mmol) and Catalyst (0.025g) in dry CH₃CN (12 ml) was prepared in a two-necked flask. One neck is for the oxygen inlet and outlet and the other is equipped with a short-side head for O_2 bladder. The flask was then evacuated and refilled with pure oxygen. The reaction mixture was stirred under the oxygen atmosphere (1 atm. for the indicated time in Table 2 of the manuscript) while the reactor was placed outdoor, in the sunlight irradiation between 10 am to 4 pm (May to July 2011, in daily room temperature and sunlight intensity between $80-10\times10^3$ Lux that have been measured by LX-1108 (Lutron) type luxmeter.). Because of supporting the oxygen bladder during the irradiation, it was covered with aluminum foil. After completion of the reaction, the catalyst was filtered off and the reaction mixture was analyzed with a VARIAN Gas Chromatograph (CP-3800).

After the reaction of acetophenone oxime, the catalyst was filtered by centrifuging, stirred in 1:1 CH₃CN: CH₃OH for 24 hours and then dried in the oven at 75°C and denoted as PICS-Ti (45B).

R ₂		NOH	OH PICS-Ti (45)		R ₂		
		R_1	D ₂ , CH ₃ CN, Su	unlight	$\stackrel{2}{\longrightarrow} \stackrel{1}{=} \stackrel{1}{R_1}$		
	R'_3	·			R ₃	·	
Entry	R.	R.	R.	Time	Yield	Daily Temp.	
Lifti y	R1	\mathbf{R}_2	R ₃	[h]	$[\%]^{a}$	range [°C]	
1 ^b	Me	Н	Н	15	6	25-35	
2	Н	Н	Н	3	11	29-35	
3	Н	Н	Н	7	95	29-35	
4	Н	Cl	Н	10	93	27-33	
5	Н	Me	Н	6	97	24-33	
6	Me	Н	Н	2	100	23-32	
$7^{\rm c}$	Me	Н	Н	4	100	33-39	
8	Me	Me	Н	1	100	35-39	
9	Me	OCH ₃	Н	1	100	27-33	
10	Me	OCH ₃	OCH_3	1	100	27-33	
11	Me	Cl	Н	3	5	26-35	
12	Me	Cl	Н	6	100	26-35	
13	Me	Н	Br	6	100	22-35	
14	Me	Ph	Н	1:30	100	38-40	
15	Et	Н	Н	4	100	20-32	
16	Ph	Н	Н	6	100	25-35	
17	2-pyridy	2-pyridyl acetophenone oxime			100	27-37	
19 ^d	Me	H	Н	1	23	28-35	
20^{d}	Me	Н	Н	10	92	28-35	
21 ^e	Me	н	Н	10	7	27-35	

Table S1. Regeneration of carbonyl compounds from oximes under the sunlight irradiation using PICS-Ti (45).

^a GC yield, Reaction condition: oxime (20 mg), catalyst (25 mg), 12 ml dry CH₃CN, O₂ atmosphere (1 atm.), daily sunlight (10 am-4 pm, sunlight intensity between 80-10×10³ Lux). ^b in the dark, ^c in the presence of 10 mg of the catalyst, ^d 25 mg SBA-15 having 45% TiO₂ loading as photocatalyst. ^e with 25 mg of pure amorphous TiO₂ as photocatalyst.

Table S2. Recycling reactions of PICS-Ti (45) in deoximation reaction of acetophenone oxime in sunlight irradiation.

Run	1	2	3	4	5
Time	8	8	9	10	10
Acetophenone yield (%) ^a	99	99	99	97	96

^a GC yield, Reaction condition: oxime (20 mg), catalyst (25 mg), 12 ml dry CH₃CN, O₂ atmosphere (1 atm.), daily sunlight (10 am-4 pm, sunlight intensity between $80-10 \times 10^3$ Lux).



Electron microscopy

Samples were prepared by dispersing the powder over a carbon coated copper grid. Images were collected on Titan Krios microscope operated at 300kV using a Gatan Ultrascan 4kx4k CCD camera.

Energy-filtering transmission electron microscopy (EFTEM) was performed at 300kV using a Gatan image filter (GIF).

For electron tomography (ET), data collection was done at an electron dose of approximately 1500 electrons/Å2 per tomogram at a nominal magnification of 75k corresponding to a pixel size of 1.2Å. A total of 10 tilt series were taken using the FEI software in the angular range between -70° and +70° at 1° increment. Previously, individual images at a much higher dose in order to verify that no electron beam damage occurs.

The Ti map was calculated using the jump ratio technique, in which an image recorded using electrons at the energy of the maximum of the absorption peak is divided by an image recorded just before the ionization energy.

Reconstruction of 3D volumes was done using the IMOD software suite.³ Three dimensional rendering was done using Chimera.⁴



Fig. S1 Infrared Spectrum of PMO-ICS and PICS-Ti (45)

The IR spectrum of PMO-ICS indicates the CH-stretching mode at 2940 cm⁻¹ and the mode of amidic carbonyl groups related to incorporation of isocyanurate substitution at 1679 cm⁻¹ as well comparatively long peak of Si-O-Si bindings. Remaining of these modes after insertion of titania in the reflux of toluene, certified the appropriate stability of the based PMO-ICS framework in this conditions. Because of there is just a thin layer of titania merging into PMO walls, the mode of Ti-O-Si that must be clear at about 930-970 cm⁻¹, could not be recognized. However, more perturbation of the silica's absorption at 1076 cm⁻¹ and the existing of a more broadening peak above 3000 cm⁻¹ obviously demonstrate the incorporation of titania and further hydrophilic character of the catalyst than the organosilica framework.



Fig. S2 Infrared Spectrum of PICS-Ti (45B)

The peak on 1676.9 cm⁻¹ in the infrared spectrum of PICS-Ti (45B), obviously confirmed the stability of amidic carbonyl groups in isocyanurate substitution in the PMO structure after the deoximation reaction in the sunlight. Moreovere, The TEM image (Fig. S7) and CHN analysis (Table S2 in ESI⁺) could also verify the stability of the material (ICS group) after the reaction.



Fig. S3. XRD patterns of the PMO-ICS and PICS-Ti (45) sample.



Fig. S4 BJH plots of PMO-ICS, PICS (45), PICS (45B)

BJH diagram shows the formation of some new pores (inset) more than 10 diameters in the PICS (45B) that related to vacancies produced due to a little segregation produced in the titania domain.



Fig. S5 N₂ adsorption-desorption of PMO-ICS (•), PICS-Ti (45) (♦) and PICS-Ti (45B) (▲).



Fig. S6 DTG and TGA curves for the PICS-Ti (45)

The incorporation of isocyanurate substitutes was proved with IR, TGA and elemental analysis. Thermogravimetric analysis of PMO-ICS-Ti (45) showed about 550°C thermal stability for organics which have been incorporated into the silica and ~22.3 percent weight lose that is so close to the ratio of tris[3-(trimethoxysilyl)propyl]isocyanurate precursor (25%) has been used in the preparation of the PMO framework.

Table S3. Comparison of the theoretical and experimental values of the nitrogen and carbon content for PMO-ICS and PICS-Ti (45).

Sample	Predicted on the basis of the gel composition used in the synthesis		Estimat elementa	N/C ratio	
	C%	N%	C%	N%	
PMO-ICS	24.45	7.13	26	7.3	0.28
PICS-Ti (45)	14.91	4.35	9.2	2.4	0.26
PICS-Ti (45R)			8.4	2.1	0.25

The values of N% and C% were calculated by using the molecular weight (MW) of the incorporated part of ICS into the PMO structure, i.e., MW of ICS without $CH_3O_{1/2}$ groups. For TEOS, the molecular weight of TEOS without $C_2H_5O_{1/2}$ groups was used. For PICS-Ti (45), MW is calculated with sum of PMO-ICS plus 45% titan which has incorporated into that. No correction was made to account for silanol groups. Also, it was assumed that all alkoxy groups were hydrolyzed.



Fig. S7 EFTEM images of (a) PMO-ICS (b) PICS-Ti (45) and (c) PICS-Ti (45B).







Fig. S9 Electron tomography of PICS-Ti material. A) projection image. B) 1 nm slice through the reconstructed tomogram. C) surface representation at a high threshold level of an area of the reconstructed tomogarm viewd along the long axis of the particle. D,E) the same as in C rotated 45° and 90° respectively. The green tubes represent the Si/Ti rods of the material fitted to the 3D reconstruction. F) Model representing the structure of the material.

This mesoporous composite material played an amazing role after insertion of titania as an efficient binary photocatalyst which has activated amorphous TiO_2 on its organosilica framework.



Fig. S10 UV-visible absorption spectra of (a) PICS-Ti (45), (b) SBA-15 (45), (c) PMO-ICS, (d) Degussa P25 and (e) Isocyanuric acid.

References

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The¹H-NMR (400 MHz, CDCl₃- d_I), ¹³C-NMR (100 MHz, CDCl₃- d_I) spectra for the oximes are as follows:









The ¹³C-NMR and ¹H- spectra of benzaldehyde oxime





The ¹³C-NMR and ¹H- spectra of 1-(2-Pyridinyl)-1-ethanone oxime





The ¹³C-NMR and ¹H- spectra of 1-(3-bromophenyl)ethanone oxime





The ¹³C-NMR and ¹H- spectra of 1-(4-chlorophenyl)ethanone oxime





The ¹³C-NMR and ¹H- spectra of 4-chlorobenzaldehyde oxime





The ¹³C-NMR and ¹H- spectra of 4-methylbenzaldehyde oxime





The ¹³C-NMR and ¹H- spectra of 1-(4-methoxyphenyl)ethanone oxime





The ¹³C-NMR and ¹H- spectra of 1-(3,4-dimethoxyphenyl)ethanone oxime





The ¹³C-NMR and ¹H- spectra of benzophenone oxime





The ¹³C-NMR and ¹H- spectra of propiophenone oxime





The ¹³C-NMR and ¹H- spectra of 4-phenylacetophenone oxime

