



## New method for the immobilization of nitroxyl radical on mesoporous silica



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### ARTICLE INFO

#### Article history:

Received 17 February 2014

Received in revised form 21 September 2014

Accepted 11 October 2014

Available online 18 October 2014

#### Keywords:

SBA-15

MCM-41

TEMPO

DICB

Oxidation

### ABSTRACT

This work reports the covalent attachment of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO) on the mesoporous silicas MCM-41 and SBA-15, by using 1,4-diisocyanatobutane as a binder. The catalysts were characterized by nitrogen adsorption/desorption, XRD, TEM, TGA, DSC and FTIR spectroscopy. Catalytic tests were performed on the liquid phase oxidation of benzyl alcohol and the secondary alcohol isoborneol by using tert-butyl hydroperoxide as oxidant. The catalysts showed good activity and stability in consecutive oxidation experiments with the same catalyst samples.

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### 1. Introduction

Selective oxidation of alcohols to their corresponding aldehydes and ketones is an important transformation in organic synthesis [1]. The conversion of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances and food additives [2]. Aldehydes can also be used as intermediates in organic synthesis such as Aldol, Michael, Cannizzaro and Perkins reactions [3]. Traditional methods for the transformation of alcohols to their corresponding carbonyl compounds generally involve stoichiometric amounts of oxidants such as chromium(VI) reagents, permanganates, or ruthenium(VIII) oxides with considerable drawbacks, such as the use of expensive reagents and volatile organic solvents, and discharge of environmentally pernicious wastes, being contradictory to the principles of Green Chemistry and Sustainable Development [4–6].

Nitroxyl radicals, also known as aminoxyl radicals have been reported to be very effective in the selective oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones with high yields and selectivities [1,2,7–12]. These compounds were first reported by Golubev more than 40 years ago [13].

The immobilization of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) on a variety of organic supports [1,2,9,14–23], inorganic supports [4,7,12,24–30] and ionic liquids confined in the pore system of inorganic supports [31–34] has been widely described.

The immobilization of TEMPO on silica supports has been usually performed by using alkyltrimethoxysilanes [4,7,12,24–30] as binders. In previous works it was reported the successful use of 1,4-diisocyanatobutane (DICB) as linking agent for the immobilization of Schiff base complexes on MCM-41 [35–37]. Isocyanates are known to be very reactive with –OH groups, forming urethane bonds, which are, depending on the diisocyanate used, at least as strong as those obtained with organosilane binders. Diisocyanates show obvious advantages over silyl compounds in the fabrication of oriented zeolite monolayers because the number of such kind of compounds available is higher than that of silyl compounds and the use of diisocyanates has proved to be very effective in preparing oriented zeolites, thanks to the ready formation of urethane linkages between the isocyanates and the surface hydroxyl groups on substrate and zeolite [38]. The present work describes the immobilization of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) on SBA-15 and MCM-41 supports using DICB as linking agent. The catalysts were tested in the liquid phase oxidation of benzyl alcohol and isoborneol, using t-butyl hydroperoxide (TBHP) as oxidant reactant.

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## 2. Experimental

### 2.1. Materials

Pluronic P123, tetraethylorthosilicate (TEOS), 4-hydroxy-TEMPO, nonane, isoborneol and t-butyl hydroperoxide (TBHP) were purchased from Aldrich. Aerosil 200 was obtained from Degussa.

Tetramethylammonium hydroxide (TMAOH), cetyltrimethylammonium bromide (CTMABr), 1,4-diisocyanatobutane (DICB), potassium bromide (KBr), ethyl benzoate and 4-methoxyacetophenone, were obtained from Fluka. Toluene, dichloromethane, t-butyl hydroperoxide, acetonitrile and benzyl alcohol were from Riedel-Haën. Dimethylformamide (DMF) was obtained from May & Baker Ltd. and hydrogen chloride (HCl) came from Panreac.

All solvents and reagents were used without further treatment except for toluene which was distilled and dried with molecular sieves (4 Å).

### 2.2. Synthesis of SBA-15 and MCM-41

SBA-15 was synthesized, according to Gao et al. [39], by using a triblock copolymer as template (Pluronic P123). In a typical synthesis, 2.0 g of Pluronic P123 was dissolved in 60 mL of 2 M aqueous HCl and 15 mL of distilled water under stirring, and then 4.4 g of TEOS was added dropwise to the solution at room temperature. The mixture was stirred for 24 h at 313 K, and then the temperature was raised to 373 K and kept at 373 K for another 24 h in a teflon-lined autoclave. Finally the resulting precipitate was filtered, washed carefully with distilled water, air-dried, and calcined at 773 K in air for 5 h in order to remove the template and obtain the final product SBA-15.

MCM-41 was synthesized according to the method reported by Corma et al. [40]. A reaction gel with a molar composition of 1 SiO<sub>2</sub>:0.18 CTMABr:0.26 TMAOH:27 H<sub>2</sub>O was prepared by suspending 2.6 g of Aerosil 200 in a solution of 28 mmol of TMAOH (97%) in 12.6 mL of water and subsequent addition of 100 mL of a CTMABr (10 mmol) aqueous solution. The mixture was stirred for 1 h, transferred into a Teflon lined autoclave and heated at 413 K for 16 h. The resulting solid was filtered, washed until neutral pH and dried overnight at 393 K. The occluded templates were removed by calcination at 813 K (1 °C/min) for 1 h under a dry nitrogen stream and for 6 h under a stream of dry air.

### 2.3. Immobilization of 4-hydroxy-TEMPO

TEMPO was immobilized on SBA-15 and MCM-41 according to Oliveira et al. [36], by refluxing 3 g of the previously activated mesoporous silica (dried under vacuum at 413 K overnight) in dry toluene (150 mL) with DICB (10.2 mmol) for 24 h after which 4-hydroxy-TEMPO (5.8 mmol) was added and allowed to reflux for another 24 h under argon atmosphere. The unreacted species were removed by washing the solid materials with dry toluene in a Soxhlet apparatus, under argon atmosphere. Finally, the catalytic materials were dried under vacuum.

### 2.4. Characterization

The textural characterization of the materials was obtained from physical adsorption-desorption of nitrogen at 77 K, using a Micromeritics ASAP 2010 V1.01 B instrument. The BET surface area was calculated by using the relative pressure data in the range of 0.04–0.2. The total pore volume,  $V_p$ , was evaluated on the basis of the amount adsorbed at a relative pressure of about 0.99.

Infrared spectra were obtained in transmission mode by using KBr pellets in a Perkin-Elmer FT-IR Spectrum 1000 instrument.

Transmission electron microscopy (TEM) analyses were performed on a Hitachi S-2400 scanning electron microscope, at a current voltage of 25 kV.

The powder X-ray patterns were obtained on a Rigaku Miniflex II Desktop X-ray diffractometer using Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation source (30 kV, 15 mA). Measurements were performed in the 0.5–20  $2\theta$  range. The unit cell parameter,  $a_0$ , was determined by using the (100) ( $a_0 = d_{100} \frac{2\sqrt{3}}{3}$ ) reflection of the materials.

Thermogravimetric analysis (TGA) was performed using a TA Instrument 951 Thermogravimetric Analysis in nitrogen atmosphere at a heating rate of 10 °C/min over the temperature range of 303–1073 K.

Differential Scanning Calorimetry (DSC) was performed using a Calorimeter (Setaram France) model DSC 131 over the temperature range 298–823 K and a signal flow between –100 and +100 mW, with a resolution of  $\pm 0.2 \mu\text{W}$ . The measurements were carried out with a heating rate of 10 °C min<sup>-1</sup> under nitrogen.

### 2.5. Catalytic experiments

The catalytic experiments were carried out in batch reactor (round bottom flask) under magnetic stirring.

#### 2.5.1. Hypochlorite oxidation

For the experiments in which sodium hypochlorite was used as oxidant, the reaction conditions described by Gilhespy et al. [2], were used. In a typical experiment the reactor was loaded with 1-butanol (0.8 M, 30 mL) in dichloromethane, KBr (0.5 M, 5 mL) in water (functioning as co-catalyst), 500 mg of 4-methoxyacetophenone (internal standard) and finally SBA-15/DICB/TEMPO catalyst (200 mg). The reaction mixture was stirred at 273 K overnight before the addition of NaOCl (0.35 M, pH 8.7, 90 mL). Stability tests were performed by running three consecutive experiments at 273 K. After each experiment the catalyst was recovered by filtration, thoroughly washed and used in the next experiment.

#### 2.5.2. Aerobic oxidation at atmospheric pressure

The general procedure for the aerobic oxidation of alcohols was adapted from Ferreira et al. [1]. In a typical experiment the catalyst sample (250 mg), CuCl, as co-catalyst (25 mg) and ethyl benzoate (internal standard), were added to a solution of alcohol (10 mmol) in DMF (25 mL) in a round bottom flask equipped with a condenser. The suspension was stirred at room temperature under the addition of a constant flow rate (100–110 mL min<sup>-1</sup>) of molecular oxygen through a porous glass disk placed at the bottom of the reaction vessel.

#### 2.5.3. Oxidation with H<sub>2</sub>O<sub>2</sub> or TBHP

For the experiments using hydrogen peroxide or tert-butylhydroperoxide as oxidants the reaction conditions reported by Mahdavi et al. [41] were followed. In a typical experiment the reactor was loaded with the catalyst sample (250 mg), CuCl as co-catalyst (25 mg) and ethyl benzoate or nonane (internal standard) added to a solution of alcohol (10 mmol) in DMF or acetonitrile (25 mL), after which 40 mmol of H<sub>2</sub>O<sub>2</sub> or TBHP were added and stirred at room temperature.

Stability tests were carried out by running consecutive experiments with the same catalyst sample, which was recovered by filtration, washed with acetonitrile, ethanol and water and dried before use in the next experiment.

In all the catalytic experiments, sample aliquots were taken regularly and analyzed by GC on a 30 m  $\times$  0.25 mm DB-1 column, from J&W.

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