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# Photo-epoxidation of cyclohexene, cyclooctene and 1-octene with molecular oxygen catalyzed by dichloro dioxo-(4,4'-dicarboxylato-2,2'-bipyridine) molybdenum<sup>(VI)</sup> grafted on mesoporous TiO<sub>2</sub>



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## ABSTRACT

The photo-assisted oxygen transfer to cyclohexene, cyclooctene and 1-octene was investigated using molecular O<sub>2</sub> as a primary oxidant with a dichloro-dioxo-(4,4'-dicarboxylato-2,2'-bipyridine) molybdenum<sup>(VI)</sup> complex grafted on the surface of mesoporous TiO<sub>2</sub> supports exhibiting different textural properties. Such mesoporous titania samples were prepared following a hydrothermal treatment (HT) and through an original procedure under supercritical CO<sub>2</sub> (SC) conditions. Non porous TiO<sub>2</sub> Degussa P-25 was also used for comparison purposes. The porosity of the titania supports, as well as the amount and dispersion of the covalently anchored dioxo Mo<sup>(VI)</sup> complex were shown to strongly influence the resulting photo-catalytic properties. A particular attention was also devoted to the stability of the grafted catalysts by performing long-term epoxidation experiments. The new hybrid Mo<sup>(VI)</sup>-derivatized mesoporous SC TiO<sub>2</sub> catalyst proved to be the most efficient in the photo-assisted oxygen transfer to various alkenes. Additionally, the high stability of such catalyst was ascertained by recycling studies.

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## 1. Introduction

Traditional oxidation reactions based on stoichiometric oxidants tend to produce waste side products generating a negative environmental impact [1]. In this respect, the use of environmentally friendly oxidants such as molecular oxygen is a more attractive and challenging option in order to generate oxygenates without formation of by-products [2–4].

Epoxidation of alkenes is a suitable route prime of importance for the preparation of relevant industrial intermediates [5]. Epoxides are versatile and reactive compounds for the synthesis of fine

chemicals, pharmaceuticals, agrochemical products, epoxy paints and dyes [6,7]. However, the production of epoxide compounds is still a big issue because several side reactions can take place, such as oxidation in the allylic positions, ring opening of the epoxides or complete oxidation to CO<sub>2</sub> [8]. Furthermore, the epoxidation of terminal olefins such as 1-octene is difficult and therefore requires long time reaction [9]. Traditionally, epoxides are prepared by partial oxidation of alkenes using “exotic” oxidants like iodosylbenzene, hypochlorite or organic hydroperoxides [10]. Hydrogen peroxide or *t*-butyl hydroperoxide (TBHP) are known as efficient oxidants [11] with the assistance of homogeneous transition metal-based catalysts [12–14]. The epoxidation of ethylene and propylene was recently reported with molecular oxygen or air as a primary oxidant with a heterogeneous silver catalyst [15,16]. However, the reaction conditions are rather severe and risky. Thus, the development of catalytic systems that use molecular oxygen or air in mild

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conditions remains a challenging target [17]. In previous studies [18–21], we have reported on the selective production of organic oxygenated compounds by Oxygen Atom Transfer (OAT) reactions, using O<sub>2</sub> as the primary oxidant, with a dioxoMo(VI) complex grafted on a commercial TiO<sub>2</sub> (MoO<sub>2</sub>L/TiO<sub>2</sub>) and UV–vis irradiation.

Here, the photo-assisted oxygen transfer to cyclohexene, cyclooctene and 1-octene was investigated on new grounds with a dichloro-dioxo-(4,4'-dicarboxylato-2,2'-bipyridine)-Mo<sup>(VI)</sup> complex (labelled as Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy) grafted on the surface of various mesoporous titania powders. Two different TiO<sub>2</sub> synthesis routes were explored with the aim of highlighting the influence of the porosity on the dispersion of the Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy complex, and hence, on the resulting photo-catalytic properties. High surface area mesoporous TiO<sub>2</sub> supports with anatase walls were prepared following a CTAB-assisted hydrothermal process, as well as by a sol-gel route under supercritical carbon dioxide (SC CO<sub>2</sub>). As a non-toxic and environmentally benign green solvent, SC CO<sub>2</sub> exhibits many unique features and great versatility in materials processing and synthesis. Such characteristics allow for a better control of the nanoarchitecture and the textural properties of the resulting materials [22].

Several complementary techniques, including XRD, nitrogen sorption isotherm, Raman, ATR-FTIR, UV–vis and <sup>13</sup>C CP-MAS NMR spectroscopies were used to characterize the parent mesoporous TiO<sub>2</sub> supports and the Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy grafted counterparts. Finally, the stability of these hybrid catalysts was evaluated after long-term photo-epoxidation experiments (56 h).

## 2. Experimental

### 2.1. Materials

All chemical reagents were purchased and used without further purification unless otherwise specified. All solvents were thoroughly degassed prior to use. Acetonitrile was distilled and kept under argon. Cetyltrimethylammonium bromide (CTAB) and HCl (37%) were purchased from Acros, while ethanol (absolute for analysis) and NaOH were obtained from Aldrich. Titanium oxide (Degussa-P25) with a specific area of 50 m<sup>2</sup> g<sup>-1</sup> and a crystalline structure composed of 80% anatase and 20% rutile was used for comparison. All supports were dehydrated at 60 °C under 5 × 10<sup>-4</sup> mbar for 48 h prior to the anchoring procedure.

### 2.2. Catalysts synthesis

#### 2.2.1. CTAB-assisted hydrothermal route

The hydrothermal preparation route of the mesoporous TiO<sub>2</sub> was based on the following procedure. An aqueous solution of titanium sulphate (1.1402 g) was first prepared and added to a CTAB ethanolic solution under stirring. The molar ratio of Ti(SO<sub>4</sub>)<sub>2</sub>:CTAB is 1:0.12. The resulting mixture was then aged at room temperature for 12 h before being transferred to an autoclave at 100 °C for 72 h. After the hydrothermal treatment, the solid was recovered by centrifugation, washed with water and ethanol, dried at 120 °C and then calcined at 400 °C in air for 6 h with a heating rate of 2 °C min<sup>-1</sup> [23]. The TiO<sub>2</sub> sample was labelled as TiO<sub>2</sub> (HT-400).

#### 2.2.2. SC CO<sub>2</sub>-assisted sol-gel route

This procedure consists in the elaboration of mesoporous TiO<sub>2</sub> by a sol-gel route under supercritical CO<sub>2</sub> through hydrolysis-condensation of titanium tetraisopropoxide at 150 °C under 30 MPa. Briefly, titanium tetraisopropoxide was introduced into the reactor prior to the injection of CO<sub>2</sub>. As soon as the desired reaction was reached, an excess of water was added under supercritical conditions. The alcohol formed through hydrolysis as well as the

excess of precursor were separated from the reaction medium during the CO<sub>2</sub> expansion. The TiO<sub>2</sub> sample synthesized under SC CO<sub>2</sub> was referred to as TiO<sub>2</sub> (SC-150).

#### 2.2.3. Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy grafting procedure

The covalent grafting of the dichloro-dioxo-(4,4'-dicarboxylato-2,2'-bipyridine)-Mo<sup>(VI)</sup> complex on the surface of both dehydrated titania supports was carried out according to the following procedure. Hexamethyldisilazane was added to a benzene suspension of TiO<sub>2</sub>, stirred 24 h at room temperature, filtered, washed thoroughly with benzene and dried under vacuum. A benzene suspension of freshly prepared trimethylsilylated TiO<sub>2</sub> was then added to a benzene suspension of 2,2'-bipyridyl-4,4'-dicarboxylic acid, stirred 72 h at room temperature, filtered and thoroughly washed with benzene. Finally, a THF suspension of MoO<sub>2</sub>Cl<sub>2</sub> was added to a benzene suspension of the previously obtained solid, stirred 4 h at room temperature and the excess of solvent evaporated. The solid product was then washed with acetonitrile and dried at room temperature [20]. The dioxo Mo<sup>(VI)</sup> grafted titania samples were designated as follows: Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy/TiO<sub>2</sub>(HT-400), Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy/TiO<sub>2</sub>(SC-150) and Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy/TiO<sub>2</sub>(P-25), where the label in brackets stands for the titania support prepared under hydrothermal treatment, supercritical conditions and the reference Degussa TiO<sub>2</sub>, respectively.

### 2.3. Catalysts characterization

The TiO<sub>2</sub> supports and the grafted catalysts were characterized by powder X-ray diffraction (XRD) using a Bruker AXS D8 Advance DaVinci geometry with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 30 mA. The diffraction patterns were recorded in the  $2\theta$  value range of 20–70° (with a step size of 0.01° and a step time of 0.4 s) for wide-angle analysis and at  $2\theta = 2$ –10° for low-angle analysis. Nitrogen adsorption/desorption isotherms at 77 K were measured on a Micromeritics Tristar 3000 apparatus at –196 °C. Before analysis, the samples were degassed under vacuum at 150 °C for 12 h. The specific surface area was determined from the linear part (0–0.23 P/P<sub>0</sub>) of the BET plot. The total pore volume was measured from the isotherms at P/P<sub>0</sub> = 0.95 and the mean pore diameter was determined by the BJH method applied to the adsorption branch. Raman analysis of both supports and catalysts was carried out on a LabRAM HR800UV HORIBA Jobin Yvon spectrometer with a BxRFM microscope, equipped with a CCD detector and an internal HeNe laser (632.81 nm) and an external Ar laser (514.532 nm). All grafted Mo<sup>(VI)</sup>Cl<sub>2</sub>O<sub>2</sub>Bipy/TiO<sub>2</sub> catalysts were characterized by attenuated total reflectance (ATR FT-IR) spectroscopy on a Perkin Elmer spectrometer and <sup>13</sup>C CP-MAS NMR spectroscopy on a Bruker Avance-400 MHz NMR spectrometer equipped with a 4 mm magic angle spinning (MAS) probe head for solids. The CP technique was applied during Magic Angle Spinning (MAS) of the rotor at 10 kHz. A ramped 1H-pulse starting at 100% power and decreasing until 50% was used during contact time (2 ms) in order to circumvent Hartmann–Hahn mismatches. In order to obtain a good signal-to-noise ratio in <sup>13</sup>C CPMAS experiment, 2048 scans were accumulated using a delay of 2 s. The <sup>13</sup>C chemical shifts were referenced to tetramethylsilane and calibrated with the adamantane signal set at 38.48 ppm [24]. Diffuse reflectance spectra (200–700 nm) were measured on a Cary 5000 Varian spectrophotometer. The amount of grafted complex was determined by thermo gravimetric analyses (TGA) under N<sub>2</sub> atmosphere between 30 and 900 °C with a 10 °C min<sup>-1</sup> heating ramp using a SDT-Q600 apparatus. Molybdenum elemental analysis was carried out with a Thermo S4 atomic absorption spectrophotometer (AAS), after acid digestion of the samples.

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