



Generating and optimizing the catalytic activity in UiO-66 for aerobic oxidation of alkenes by post-synthetic exchange Ti atoms combined with ligand substitution

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ABSTRACT

The catalytic activity for the aerobic epoxidation of cyclooctene of UiO-66 has been introduced by post-synthetic ion exchange of Zr^{4+} by Ti^{4+} at the nodes and the performance optimized by nitro substitution in the terephthalate ligand. In this way a TON value of 16,600 (1660 considering Zr + Ti content) was achieved, comparing favorably with the highest catalytic activity reported in homogeneous for the same reaction (10,000 for $\gamma\text{-SiW}_{10}(\text{Fe}^{3+}(\text{OH}_2)_2\text{O}_{58})$). Kinetic studies have shown that the most likely reactive oxygen species involved in the oxidation is superoxide, with hydroxyl radicals also contributing to the reaction. UiO-66($Zr_{5.4}Ti_{0.6}$)-NO₂ is stable under catalytic conditions, being used six times without any change in the conversion temporal profile and in the X-ray diffractogram. The scope of UiO-66($Zr_{5.4}Ti_{0.6}$)-NO₂ promoted aerobic oxidation of alkenes was expanded by including smaller rings cycloalkenes, as well as acyclic and aryl conjugated alkenes.

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1. Introduction

Transition metals have general catalytic activity to promote aerobic oxidations of hydrocarbons through different mechanisms, some of them involving reactive oxygen species [1–3]. While the use of oxygen as terminal oxidant, rather than peroxides or other oxidizing reagents, is very appealing due to availability, greenness and sustainability of the process, the lack of product selectivity limits, in most of the cases, the applicability of aerobic oxidations [3–9].

Metal-organic frameworks (MOFs) are crystalline porous solids whose lattices are constituted by nodes of metal ions or clusters of metal ions, most frequently transition metals, coordinated by rigid bi- or multidentate organic linkers [10–13]. Due to the high metal content, high surface area and high porosity, among other properties, MOFs are attracting much current interest as heterogeneous catalysts to promote organic reactions, including aerobic

Abbreviations: MOF, metal-organic framework; TON, turnover number.

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oxidations [7,14–23]. As solid catalysts, MOFs offer various possibilities to introduce the catalytic activity by changing the nature of the metal ion [24–27] and also subsequent optimization by introducing substituents on the organic linker that are able to control the electronic density of the active metal sites by inductive effects [28–30]. Following the pioneer work of de Vos [30], we and others [28,29,31–33] have shown that the activity of a given MOFs can be increased over one order of magnitude in Lewis or Brønsted acid catalyzed reactions [29] and some oxidations [28] by introducing electron withdrawing substituents on the aromatic ring of the terephthalate linker in MIL-101 [28,29,31] and UiO-66 [30,32,33].

Continuing with this line of research aimed at exploiting the catalytic activity of MOFs, it would be of interest to create active sites in otherwise inactive MOFs by ion exchange at the nodes and, subsequently, optimization of their performance by substitution on the terephthalate linker [34–36]. In this regard, Li and coworkers have shown that it is possible to replace in UiO-66 (Zr) a certain percentage up to about 30% of Zr^{4+} metal ions by Ti^{4+} ions by post-synthetic modification of parent UiO-66(Zr) with $TiCl_4(\text{THF})_2$ through ion exchange [37]. This strategy has been used, for instance, to increase the photocatalytic activity of parent UiO-66(Zr) for CO₂ reduction by introducing Ti^{4+} acting as electron relay between photoexcited terephthalate ligand and Zr^{4+} [38].

To check this concept, and considering the known activity of Ti^{4+} grafted on mesoporous silicas and zeolites as oxidation catalysts, particularly in the presence of peroxides as oxidizing reagents, but also using oxygen as terminal oxidant [39–45], in the present study we have focused on the reactivity of alkenes, particularly, cycloalkenes, to form the corresponding epoxide or allylic ol/one mixtures. The novelty of our study derives from the consideration that, as it will be described below, UiO-66(Zr) is devoid of any significant activity in the aerobic oxidation of cycloalkenes, but by applying known chemistry in the field of zeolites and aluminum silicates grafting Ti^{4+} it is possible to introduce active sites to promote this aerobic oxidation. Furthermore, it will be shown that the activity of UiO-66(Zr, Ti) can be increased by a factor of 8 when NO_2 is present on the terephthalate linker. In the area of Ti catalysts grafted on micro- and mesoporous materials, it was found that isolated titanium sites are active sites for epoxidation [43,46,47] and similar isolated Ti^{4+} sites can be easily obtained in UiO-66 by appropriate post-synthetic partial exchange Zr^{4+} by Ti^{4+} ion. Therefore, up to now, the combination of the flexibility of MOFs to exchange metal ions and introduce substituents in the organic linker has not been combined with the concept derived from Ti-containing zeolites of site isolated Ti atoms.

Although recent reports have confirmed incorporation of Ti in UiO-66 they have proposed that it occurs at defective sites where linkers are vacant through Ti attachment rather than ion exchanged [48].

2. Experimental section

2.1. Materials

All the reagents and solvents used in this work were of analytical or HPLC grade and supplied by Merck.

2.2. Catalyst preparation

Isostructural UiO-66(Zr)-X (X: H, NO_2 and NH_2) were prepared following reported procedures [32,37,49,50]. Briefly, the corresponding terephthalic acid derivative (1 mmol) and ZrCl_4 (1 mmol) were added to a Teflon-lined autoclave containing dimethylformamide (3 mL). The system was heated at the corresponding temperature for the required period of time (Table 1). After this time, the system was cooled down to room temperature and the resulting precipitate was first washed under stirring with DMF (40 mL) for 2 h (3 times) and, then, the solid was washed with methanol in a Soxhlet system for 12 h. Finally, the solid was dried in an oven at 100 °C for 24 h.

The three UiO-66-X (X: NH_2 , H and NO_2) solids were further submitted to Zr^{4+} exchange using different percentages of Ti^{4+} following reported procedures [37,51]. Briefly, UiO-66-X (X: NH_2 , H and NO_2) solids (200 mg) were suspended in anhydrous DMF (5 mL) and magnetically stirred for 96 h at 120 °C with freshly prepared $\text{TiCl}_4(\text{THF})_2$ complex. $\text{TiCl}_4(\text{THF})_2$ is prepared immediately prior to its use by mixing TiCl_4 (2.9 mL) in anhydrous dichloroethane (50 mL) with 8.6 mL of THF in 100 mL of anhydrous *n*-hexane.

Table 1
Temperature and time employed for the preparation of UiO-66-X (X: NH_2 , H and NO_2) solids [32].

X	Temperature (°C)	Reaction time (h)
NH_2	100	24
H	220	12
NO_2	220	24

2.3. Catalyst characterization

Powder X-ray diffraction (PXRD) patterns of UiO-66(Zr Ti)-X (X: NH_2 , H and NO_2) materials were recorded on a Philips XPert diffractometer equipped with a graphite monochromator (40 kV and 45 mA) employing Ni filtered $\text{Cu K}\alpha$ radiation. ATR-FTIR spectra of UiO-66(Zr, Ti)-X materials were collected at 20 °C using a Bruker Tensor27 instrument. Previously, the solid samples were heated in an oven (100 °C for 20 h) to remove physisorbed water. N_2 adsorption isotherms were recorded at 77 K using a Micromeritics ASAP 2010 instrument. Thermogravimetric measurements were performed on a TGA/SDTA851e Mettler Toledo station. Scanning electron microscopy (SEM, Zeiss instrument, AURIGA Compact) having incorporated a EDX detector has been employed to determine the morphology of the solid samples and obtain the element mapping of selected areas, respectively. The EDX detector has a limit of detection of about 1 wt%. X-ray photoelectron (XP) spectra were collected on a SPECS spectrometer with a MCD-9 detector using a monochromatic Al ($K\alpha = 1486.6$ eV) X-ray source. Spectra deconvolution was performed with the CASA software using the C 1s peak at 284.4 eV as binding energy [52].

The metal content (Zr and/or Ti) of solid samples have been determined by ICP-OES analysis. Previously, the solid samples (5 mg) were digested using a HNO_3 aqueous solution (3 M, 30 mL) at 80 °C for 12 h. Then, the filtered aqueous samples were analyzed by ICP-OES [37].

FTIR spectra of CO adsorption were recorded in a Nexus 8700 FTIR spectrophotometer using an IR cell allowing *in situ* treatments at controlled temperature, from -176 °C to 500 °C, and connected to a high vacuum system with gas dosing facility. For CO adsorption measurements the samples were pressed into self-supported wafers and treated under vacuum (10^{-6} mbar) at 150 °C for 2 h. After activation, the wafers were cooled down to -176 °C under dynamic vacuum, followed by CO dosing at increasing pressure (0.4–6 mbar). IR spectra were collected after each dosage. All IR spectra corresponding to CO adsorption measurement have been normalized to the weight of the IR wafer.

2.3.1. Catalytic experiments

Briefly, the required amount of UiO-66(Zr Ti)-X (X: NH_2 , H and NO_2) employed as catalyst (0.016 mmol of total metal Zr + Ti) was introduced into a reactor vessel (5 mL). Subsequently, the olefin reagent (2 mmol) dissolved in CH_3CN (2.5 mL) was added to the vessel. The system was pressurized with O_2 at the required value at room temperature (i.e. 5 or 2 atm). The reactions were carried out under 600 rpm magnetic stirring to ensure that the process is under kinetic control.

Catalyst reusability was studied for the most active sample (UiO-66($\text{Zr}_{5.4}\text{Ti}_{0.6}$)- NO_2). At the end of the reaction, the solid catalyst was recovered by filtration (Nylon membrane, 0.2 μm) and transferred to a round-bottom flask (50 mL) and washed under magnetic stirring with ethanol (20 mL) at 80 °C for 2 h. This procedure was repeated three times. The washed, used solid catalyst was recovered by filtration (Nylon membrane, 0.2 μm) and dried in an oven at 100 °C for 24 h. Before the new catalytic cycle, the solid catalyst was activated at 150 °C under vacuum for 16 h.

Selective radical quenching experiments were carried out following the general reaction procedure described above, but with the addition of radical quenchers (20 mol% with respect to the substrate). In particular, dimethylsulfoxide (DMSO) [53–56] or *p*-benzoquinone [53,54,56,57] were added as selective hydroxyl or superoxide/hydroperoxyl radical scavengers, respectively.

Activation energy for cyclooctene was estimated according the Arrhenius law by plotting the natural logarithm of the initial reaction rate of cyclooctene disappearance versus the reciprocal of the absolute temperature, fitting the experimental points to the best

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