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Metal organic frameworks as solid promoters for aerobic autoxidations

Amarajothi Dhakshinamoorthy^{a,b,*}, Abdullah M. Asiri^c, José Raúl Herance^d,
Hermenegildo Garcia^{b,c,*}

^a School of Chemistry, Madurai Kamaraj University, Tamil Nadu, 625 021, India

^b Instituto de Tecnología Química CSIC-UPV, Av. De los Naranjos s/n, 46022, Valencia, Spain

^c Centre of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

^d Vall d'Hebron Research Institute (VHIR)-CIBBIM-Nanomedicine, Passeig de la Vall d'Hebron 119-129, Barcelona, Spain

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ABSTRACT

This manuscript illustrates the activity of MIL-101(M) (M = Cr, Fe) (MIL: Matériaux Institut Lavoisier) as solid promoter of aerobic oxygenations of organic compounds, including benzylic hydrocarbons and alcohols, sulfur-containing condensed heterocycles and thiols. MIL-101(M) (M = Cr, Fe) has been selected due to its high structural stability, open porosity and adequate composition that make the solid recoverable and reusable without observing any decrease in its ability to promote the reactions. Available kinetic data indicates that these oxygenation reactions occur through a radical-chain mechanism with a long-propagation chain. Comparison with homogeneous radical initiators shows that MIL-101 can be more selective towards the wanted products, a fact that has been interpreted assuming that the reaction takes place inside the pores of this metal organic framework.

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1. Autoxidations

Oxygenations are reactions in which one or more oxygen atoms become incorporated to a substrate [1–3]. Aerobic oxygenations using molecular oxygen are important reactions from the industrial point of view, mainly for conversion of hydrocarbons [4] into oxygenated products, such as oxidation of alkylaromatics to aromatic aldehydes, acids and anhydrides, the conversion of aliphatic hydrocarbons to mixtures of the corresponding alcohols and ketones and epoxidations of alkenes, among other many reactions [1,2]. There are several possible reaction mechanisms for the reaction of organic compounds with molecular oxygen, including those that involve the intermediacy of highly reactive singlet oxygen or those occurring through electron transfer, generating initially superoxide. However, one of the most general reaction mechanisms involves the reaction of ground state, triplet molecular oxygen with carbon centered organic radicals. This general oxygenation mecha-

nism is known as “autoxidation” [5], since it can occur upon storage of virtually any organic compound provided that some radicals are spontaneously generated, either thermally or photochemically. Autoxidations occur through chain-reaction mechanisms, in which there is an initiation step in which the carbon centered radical is generated, but the reaction rate depends on the propagation steps [2]. Scheme 1 illustrates the steps of this type of oxygenation reactions of organic substrates.

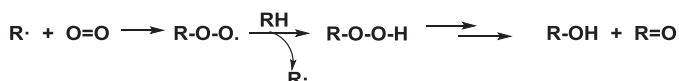
Autoxidation is a very general reaction for organic compounds, even saturated hydrocarbons, that does not really require the action of any catalyst, but most appropriately, of an initiator generating carbon centered radicals. The reason for this is that the propagation steps do not require any catalyst, since the reaction of carbon centered radicals with molecular oxygen is a barrierless reaction that occurs at diffuse-controlled rate and, then, hydroperoxyl radicals abstract a H atom from C–H bonds almost without any activation energy [6]. However, autoxidation occurs after the generation of carbon centered radicals and this process requires either radical initiators, i.e. a primary radical for instance the one generated in azobis(isobutyronitrile) (AIBN) by thermolysis, or a solid material able to induce the formation of radicals. This is really the role that is played by some metal ions in autoxidation reactions [7]. In the present manuscript, it will be commented that also

* Corresponding authors at: Instituto Universitario de Tecnología Química CSIC-UPV, Universitat Politècnica de Valencia, Av. de los Naranjos s/n, 46022 Valencia, Spain.

E-mail addresses: admgu@qim.upv.es (A. Dhakshinamoorthy), hgarcia@qim.upv.es (H. Garcia).

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**Scheme 1.** Steps of autoxidations of organic substrate.

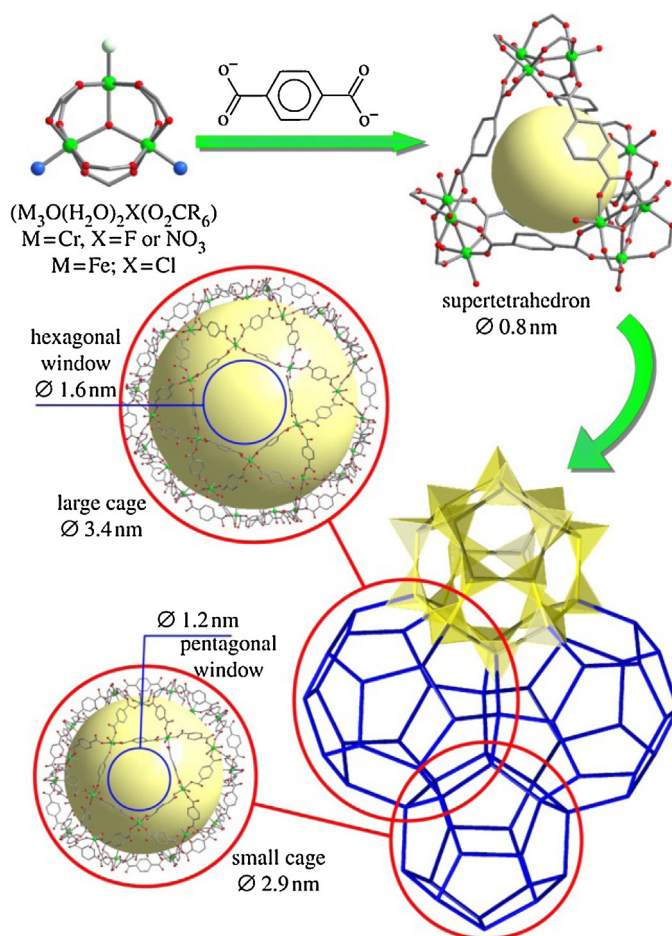
metal-organic frameworks (MOFs) can be considered as solid promoters of aerobic autoxidations of different types of organic compounds with a high efficiency and selectivity different from that found for homogeneous phase autoxidations.

The ability of MOFs to promote aerobic oxidations originates from the presence of a large content of transition metals in the composition of these materials, as well as their large surface area and porosity [8–10]. In other words, the same features that have made MOFs among the preferred solid catalysts are also responsible for their ability to promote autoxidations through the intermediacy of carbon centered radicals.

2. MIL-101(Cr or Fe)

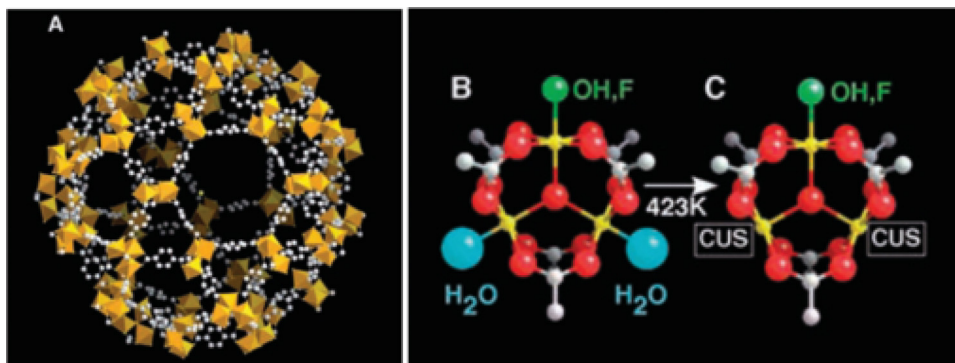
Specially, in the present manuscript, we have made ample use of a particular MOF structure, namely, MIL-101 [11], as solid promoter to carry out the aerobic oxidation of organic compounds. In MIL-101, the metallic nodal positions of the framework are constituted by three trivalent transition metal cations (generally Cr^{3+} or Fe^{3+}) connected through a $\mu_3\text{-O}$ atom and each metal ion of these trimeric units are connected with two 1,4-benzenedicarboxylate (BDC) linkers. There is an additional coordination position that defines an octahedron around each of the metal ions. One third of these additional positions are occupied by a halogen (Cl^- for Fe^{3+} and F^- for Cr^{3+}) and the other two thirds are occupied by solvent molecules (either DMF or H_2O) [11–13]. By means of evacuation and thermal pretreatment, it is possible to remove the solvent molecules present in MIL-101 leaving free coordination positions around metal ions (Fig. 1) that are assumed to be the active sites in most of Lewis acid catalyzed and oxidation reactions [13,14].

Four of these trimeric $\text{M}_3^{3+}\text{-}\mu_3\text{O}$ metallic nodes arrange with terephthalate linkers in such a way that they define super tetrahedra of about 0.8 nm dimension. The arrangement of these super tetrahedra determines the formation of two types of cages in MIL-101, one smaller (2.9 nm diameter) with pentagonal windows (1.2 nm opening) and other larger (3.4 nm dimension) accessible through hexagonal windows (1.6 nm pore opening). Fig. 2 illustrates the key structural building blocks and the geometry of pores in MIL-101. This structural arrangement makes MIL-101 a highly porous material with a large surface area that can be above $2000 \text{ m}^2/\text{g}$ [11]. One important feature of MIL-101 that has made this particular MOF one of the preferred solid catalysts is its high thermal and chemical

**Fig. 2.** Schematic representation of key structural building blocks and the geometry of pores in MIL-101.

stability that makes this material compatible with a broad range of reagents and conditions [15].

In the present contribution, it will be commented the results on the aerobic oxidation through C-centered radicals of benzylic hydrocarbons, aromatic sulfur containing compounds as well as alcohols promoted by MOFs. The key point of our study has been to show that selectivity of aerobic oxidations promoted by MIL-101 is different from analogous autoxidations in homogeneous phase promoted either by soluble radical initiators in solution or by dissolved transition metal ions. This difference in selectivity is proposed to derive from the fact that the reaction occurs inside the pores and

**Fig. 1.** (A) Perspective view of the large mesoporous cages of MIL-101(Cr) with hexagonal windows; (B) a chromium trimer building unit of MIL-101(Cr) coordinated to water molecules and (C) generation of coordinatively unsaturated sites (CUS) from chromium trimers of MIL-101(Cr) by vacuum treatment at 423 K. Figure taken with permission from ref [13].

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