

Synthesis and application of Fe^{III}, Ni^{II} and Mn^{II} complexes anchored to HMS as efficient catalysts for cycloalkane oxyfunctionalization



Kelly Machado, Pedro B. Tavares, Gopal S. Mishra*

Laboratory of Materials, Centro de Química-Vila Real (CQ-VR), Department of Chemistry, University of Trás-os-Montes and Alto Douro (UTAD), Vila Real 5001-801, Portugal

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ABSTRACT

Methoxysilane Schiff-base pentacoordinate metal complexes, *i.e.* Fe[Sal(PMeO-Si)DPTA], Ni[Sal(PMeO-Si)DPTA] and Mn[Sal(PMeO-Si)DPTA], were synthesized and single site covalently anchored into the uniform porous texture of HMS (2–10 nm size) *via* condensation process. The correspondent supported catalysts (**4.a**, **4.b** and **4.c**, respectively) were characterized by FT-IR, SEM/EDS, XRD, TG, EPR and AAS analysis. In the catalytic tests, they showed high efficiency in the selective oxidation of cyclohexane using molecular O₂ (overall conversion 40.7% with Cat. **4.a**, 29.5% with Cat. **4.b** and 26.2% with Cat. **4.c**) under relatively mild condition in batch reactor. The Cat. **4.a** system (HMS/**3.a**) exhibits highest TONs *ca.* 4.2 × 10³ with good selectivity *ca.* 70% (48% ketone selectivity). The reaction mechanism involves free radicals, as it was proved by the addition of PPh₃. Finally, these supported catalysts could be reuse up to several catalytic cycles.

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1. Introduction

The activation C–H bond of hydrocarbons with molecular oxygen is an important reaction since several industrial processes are based on this transformation [1–4]. The use of molecular O₂ in the catalysis of alkanes oxidation is much attractive due to its low price, readily availability in atmospheric air as “greener oxidant” [5] and less toxic compared to other oxygen donors: H₂O₂, *t*-BuOOH, *etc.* [6,7]. In particular, Schiff bases ligands are able to stabilize many different metals in various oxidation states [8–11], controlling the performance of metals in a large range of valuable catalytic transformations [12,13]. Nevertheless, homogeneous catalysts must be separated later from the reaction mixture, which is a cost of the process and difficult to recycle. To improve the method, one must immobilize the metal complexes catalysts on solid supports, preventing the requirement for laborious and inefficient extraction processes. The activity of this type of catalyst is mainly dependent upon the structure of complex, surface area of support and substrate polarity which are the requirements for the reactants to be in contact on the active catalyst centre [14]. In the case of using high surface area mesoporous support, the inorganic complexes have been anchored through the interaction between the silanol of the supporting matrix and terminal reactive groups of the complex, yielding supported hybrid catalysts [15–17]. Some such supported

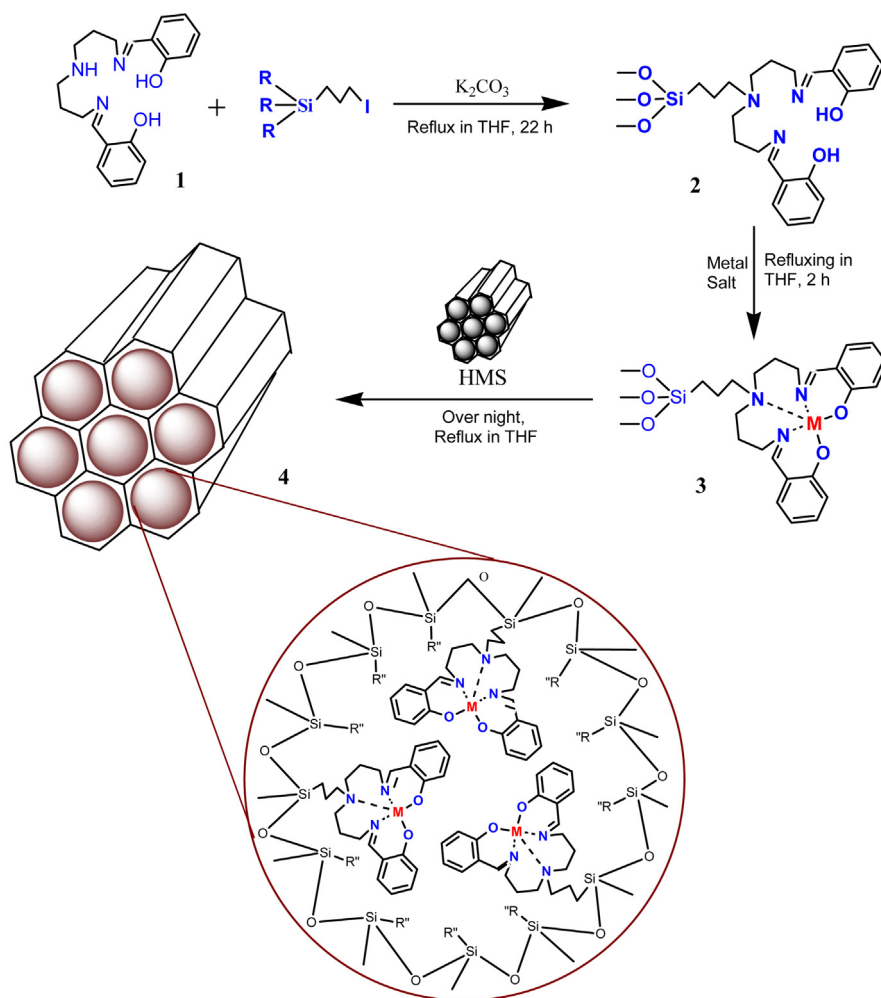
catalysts might be considered, namely due to their easy separation from the product (by simple filtration), the possibility of recycling them and the facility to control and tune the catalyst composition.

For the current process, we have chosen cyclohexane because it oxidizes to alcohol and ketone products, also known as KA oil. These product are further convert to adipic acid and caprolactam, which are the key components for the production of urethane foams, polyamide-6, lubricating additives and nylon-6 [18]. Typically, Co slats have been used in the industrial cyclohexane oxidation either by air O₂ or pure O₂. At temperatures above 423 K low conversions (*ca.* 4%) but 85% selectivity (KA oil) was achieved [19]. This way, industrial cyclohexane oxidation uses inherently inefficient methodology that necessitates repeated recycling of feedstock. The alternative use of peroxides is expensive and is also accompanied by the formation of toxic by-products [20–22]. The establishment of a greener and more effective cyclohexane oxidation process by the using of atmospheric oxygen is therefore a present need.

In past few years, metal cations or often oxides have been incorporated on inorganic materials (*e.g.* zeolites, silica, alumina or aluminophosphates), while promoters have been used to reduce the induction period and to increase the selectivity for the targeted product of cyclohexane [23–25]. Metal-substituted heteropoly compounds (heteropolyoxometalates) catalysts demonstrated good activity towards alkanes oxidation [26]. Re complexes over SiO₂ and Pd–Re over Al₂O₃ have also demonstrated considerably good catalytic activities for the oxidation of cycloalkane [27,28]. The SiO₂ supported di(ethylthio)alkane Pd complexes give 16.2% conversion and 98% selectivity [29]. The Y-type zeolite anchored V and

* Corresponding author. Fax: +351 259350286.

E-mail addresses: mishrags@utad.pt, mishrags@gmail.com (G.S. Mishra).



Scheme 1. Synthesis procedure of Schiff-base trimethoxysilane pentacoordinate metal complexes and single site anchoring into the uniform porous texture of HMS.

Cu salen complex catalysts were applied in the cyclohexane/ H_2O_2 process and achieved 86.6% and 18.1% conversions with V and Cu catalysts, respectively [30]. The Fe and Mn complexes were also tested in the cyclohexane oxidation study and obtained 10.2% conversion with Fe complex and *t*-BuOOH [31]. Previously, we had also prepared same type of pentacoordinate Schiff base ligands of V-complexes over SiO_2 and tested in cyclohexane O_2 oxidation and obtained 36% conversion with 98% product selectivity [32]. Some other maltolato type of V-complexes supported SiO_2 were also applied and obtained relatively low conversion 15% [33]. Alumina supported hetero binuclear macrocyclic Co–V complex and SiO_2 anchored Schiff base Co complexes catalysts have been investigated obtaining 20% conversion in both the cases [34,35]. These results show that the use of non precious metals in catalysts is favourable due to low price, resistance to temperature and light. Its strongly motivate the investigation of low cost catalysts.

Hence, the main target of this study is to synthesize and to apply novel methoxysilane Schiff-base Fe^{III} , Ni^{II} and Mn^{II} complexes for the easy anchoring (without any linker) over hexagonal mesoporous silica (HMS) as heterogeneous catalyst. These catalysts are tested for the gas–liquid oxidation of cyclohexane with molecular O_2 under relatively mild condition to obtain high conversion with product selectivity.

2. Experimental

2.1. General materials and methods

A standard Schlenk technique was used for the synthesis of Fe, Ni and Mn complexes under normal atmospheric conditions. All the chemicals and solvents *i.e.* ethanol (EtOH), *n*-pentane, toluene, diethyl ether (Et_2O), acetonitrile (MeCN), tetrahydrofuran (THF) and cyclohexane (Cy-hx) were from Janssen Chemicals. 3-Idopropyl trimethoxysilane (PMeO-Si), salicylaldehyde (Sal), bis(2,4-pentanedionato)cobalt, bis(aminopropyl)amine (DPTA), potassium carbonate (K_2CO_3), iron chloride anhydrous ($FeCl_3$), nickel acetylacetonate ($C_{10}H_{14}NiO_4$), manganese acetate [$Mn(CH_3COO)_2$], *n*-hydroxyphthalimide (*n*-NIPH) and tetraethylorthosilicate (TOS) were from Sigma–Aldrich and they were used as received.

2.2. Catalyst preparation

Ligand **2** (Scheme 1), Sal(PMeO-Si)DPTA, was prepared as described earlier [32,36], starting from equimolar quantities of bis(salicylideneimino-3-propyl)amine and 3-iodopropyl trimethoxysilane, in THF reflux, in the presence of K_2CO_3 .

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