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Peroxidative oxidation of cyclic and linear hexane catalysed by supported iron complexes under mild and sustainable conditions

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ABSTRACT

The development of economical heterogeneous catalysts based on first row transition metal complexes that work under mild and sustainable reaction conditions in the activation of C—H bonds is very important. Herein, commercially available iron(II) and iron(III) acetylacetonate were immobilised onto amine functionalised economical and environmentally acceptable solid porous supports: hexagonal mesoporous silica and activated carbon. The materials prepared by this very simple and straightforward methodology were characterised by elemental analysis, ICP-AES, FTIR, isotherms of adsorption at 77 K and thermogravimetry. It showed that both porous materials were conveniently functionalised with amine groups and that the iron metal complexes could be effectively anchored onto these materials. The immobilised iron salts were active as heterogeneous catalysts in the oxidation of cyclohexane and n-hexane at room temperature with hydrogen peroxide, giving the respective alcohols and ketones. They could also be recycled at least two times without loss of catalytic activity in the oxidation of cyclohexane. In the oxidation of n-hexane this was only true for the anchored Fe(II) salts. In the oxidation of cyclohexane, both iron salts are more active heterogeneous catalysts anchored onto the activated carbons than onto the hexagonal mesoporous silicas. The opposite is observed in the oxidation of n-hexane. The heterogeneous catalysts reported herein are economical and work under mild reaction conditions and thus could be valuable for the improvement of the sustainability and environmental impact of processes currently used in industry.

1. Introduction

The main oxidised products of cyclohexane are of great industrial significance. A large amount of cyclohexanol and cyclohexanone is produced worldwide, mostly to be used as precursors to the manufacture of added-value products, such as Nylon-6 and Nylon-6,6 [1,2]. Industrially, the reaction is performed using a cobalt(II) naphthenate catalyst at 160 °C and 15 bar, yielding 4% conversion into oxidised products with 80% selectivity towards cyclohexanol and cyclohexanone [2,3].

Terminally oxidised hydrocarbons are also interesting feedstocks for the chemical and pharmaceutical industry. The regioselective oxidation of only the terminal methyl groups in alkanes is however a challenging task [4,5]. The synthesis of these functionalised compounds by C—H oxidation requires severe conditions and non-toxic oxidants and metals. An ideal method would yield only the desired oxidised products, with 100% conversion of

the substrate, using green oxidants, like oxygen or hydrogen peroxide (H_2O_2), non-toxic solvents, like acetonitrile, and highly active and reusable catalyst, in mild conditions. H_2O_2 simply produces water as by-product and the controlled partial oxidation is easier to achieve than with molecular oxygen and air [4].

Enzymes are the state-of-the-art in alkane oxidation. Cytochrome P-450 and many other metallo-enzymes are capable of performing the hydroxylation of alkanes [6]. Therefore, in the past years there has been an interest in modelling such enzyme active sites and manufacture catalysts that mimic this oxidation. Catalysis by transition-metal complexes is however a favourable route to the selective functionalisation of alkanes under mild conditions, since they are cheap and easy to produce, particularly the Schiff base ones, and enzymes are expensive and easily deactivated [6].

The active centre of Cytochrome P-450 is iron which forms complexes with molecular oxygen in haemoglobin and myoglobin [5]. Hence iron-containing catalysts are of high potential interest, especially because iron is cheap, widespread in nature and essential for the human body. Chemoselectivity plays however a major role in these reactions, thanks to potential non-selective Fenton or Gif-type chemistry [2]. We have found that Fe(III) complexes with N_2O_2 Schiff base complexes were the most efficient homogeneous

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catalysts, among other studied first-row transition metal complexes, in the oxidation of cyclohexane and n-hexane using H_2O_2 at room temperature [7]. As previously reported [8] nitric acid (in 10 mol%) was found to have a promoting effect in the reaction [7].

Heterogeneous catalysts however prevent the obstacles that commonly occur in homogeneously catalysed systems. Anchoring a homogeneous catalyst onto solid supports makes the separation from the reaction media easy, preventing therefore the use of laborious and inefficient extraction processes, thus allowing the reuse of the catalyst in more catalytic cycles [9–12]. The high selectivity of transition metal homogeneous catalysts is hence combined with the heterogeneous catalysts advantages.

In terms of industrial application the use of economical porous supports is also very important. Relatively to conventional mesoporous silicas prepared by electrostatic assembly pathways, hexagonal mesoporous silicas (HMS) are prepared by using economic alkylamines as templates [13]. Consequently, they present more extensively cross-linked frameworks, besides of thicker framework walls, which contribute to superior thermal stability upon calcination in air. HMS also possesses smaller particles sizes, along with defects in channel packing, which yields complementary textural mesoporosity providing better access to the framework-confined mesopores in liquid phase catalysis [14]. Their surface silanol groups can be functionalised using derivatizing agents, such as (3-aminopropyl)triethoxysilane (APTES), allowing the chemical attachment of the homogeneous catalyst through Schiff condensation of the free amine group [9,10].

Activated carbons (AC) are porous carbon materials that possess several advantages over the inorganic porous solids, such as hydrophobic nature of their surfaces, high specific surface area, large pore volumes, chemical inertness and good mechanical stability [15]. Its tunable surface chemistry rich in oxygen functional groups also allows for wider strategies of homogeneous catalyst anchoring than the inorganic solids [16].

In this work, we anchored $[Fe(acac)_n]$ (n = 2, 3) complexes onto solid supports (AC and HMS) functionalised with APTES, through Schiff condensation between the carbonyl groups of the acetylacetonate ligands and the APTES amine. These materials were used as heterogeneous catalysts for the oxidation of cyclohexane and n-hexane under mild conditions using hydrogen peroxide as oxidant and nitric acid as co-oxidant.

2. Experimental

2.1. Materials and solvents

The reagents were used as received; tetraethoxysilane, 1-octylamine, (3-aminopropyl)triethoxysilane (APTES), dry toluene, iron(II) acetylacetonate, iron(III) acetylacetonate, cyclohexane, chlorobenzene, hydrogen peroxide 30 wt% in water, nitric acid and triphenylphosphine were purchased from Sigma–Aldrich. Dichloromethane and acetonitrile were HPLC grade and from Romil company. n-Hexane was from Fisher Scientific. For the FTIR potassium bromide was used spectroscopic grade and from Sigma–Aldrich.

The starting carbon material was a NORIT ROX 0.8 activated carbon (rodlike pellets with 0.8 mm diameter and 5 mm length). This material has a pore volume of 0.695 $cm^3 g^{-1}$, as determined by porosimetry (corresponding to meso- and macropores), an ash content of 2.6% (w/w), an iodine number of 1000 and mercury and helium densities of 0.666 and 2.11 $g\,cm^{-3}$, respectively. The activated carbon was purified by Soxhlet extraction with 2 M HCl for 6 h, washed with deionised water until pH 6–7 and then dried in an oven at 150 °C for 13 h under vacuum.

2.2. Synthesis of hexagonal mesoporous silica (HMS)

The HMS was synthesised according to procedures described in the literature [9,13]; tetraethoxysilane (37.0 mL, 0.166 mol) was added to a stirred solution of ethanol (88.1 mL, 1.51 mol), water (88.5 mL, 4.91 mol) and 1-octylamine (7.4 mL, 0.0448 mol). The mixture was stirred at room temperature for 24 h. The obtained precipitate was vacuum filtered, washed with deionised water (100 mL) and ethanol (100 mL). In order to remove the template (1-octylamine), the precipitate was calcined at 600 °C for 24 h.

HMS: elemental analysis (%) C 0.81 H 0.00 N 0.02.
AC: elemental analysis (%) C 88.68 H 0.24 N 0.47.

2.3. Functionalisation of the HMS or AC with APTES

The functionalisation of both porous materials was performed according to procedures described in the literature [9–12]; a mixture of calcined HMS or dried AC (5.0 g) in dry toluene (50.0 mL) and (3-aminopropyl)triethoxysilane (15.0 mmol, 3.5 mL) was refluxed for 24 h (pH of the APTES in toluene solution was 10). The material was vacuum filtered, washed with toluene (3× 50 mL) and refluxed in toluene for 6 h. The material was dried overnight in an oven at 100 °C. These materials will be referred as APTES@HMS or APTES@AC.

APTES@HMS: elemental analysis (%) C 7.52 H 1.45 N 1.93, loading APTES 1.38 $mmol\,g^{-1}$.
APTES@AC: elemental analysis (%) C 85.77 H 1.66 N 1.19, loading APTES 0.85 $mmol\,g^{-1}$ and ICP-AES Si 2.27%, loading APTES 0.81 $mmol\,g^{-1}$.

2.4. Anchoring of iron(III) acetylacetonate onto amine-functionalised HMS or AC

The HMS or AC functionalised with APTES (2.0 g) was added to 100 mL of a solution of $[Fe(acac)_3]$ (0.352 g, 996 μmol) in dichloromethane, and the mixture was refluxed for 24 h. The resulting material was extensively washed with dichloromethane and then refluxed with dichloromethane for 6 h and dried overnight in an oven at 60 °C. These materials will be referred as $[Fe(acac)_3]$APTES@HMS or $[Fe(acac)_3]$APTES@AC.

$[Fe(acac)_3]$APTES@HMS: elemental analysis (%) C 9.49 H 2.04 N 1.84; ICP-AES Fe 1.2%, loading Fe 215 $μmol\,g^{-1}$.
$[Fe(acac)_3]$APTES@AC: elemental analysis (%) C 85.62 H 1.46 N 1.19, loading APTES 0.85 $mmol\,g^{-1}$; ICP-AES (%) Fe 0.18 Si 2.11, loading Fe 32 $μmol\,g^{-1}$ and APTES 0.75 $mmol\,g^{-1}$.

2.5. Anchoring of iron(II) acetylacetonate onto amine-functionalised HMS or AC

A solution of iron(II) acetylacetonate (0.127 g. 498 μmol) in dichloromethane (100 mL) was refluxed with amine-functionalised HMS or AC (1.0 g) for 24 h. The solid was vacuum filtered, washed with dichloromethane (3× 20 mL), and then refluxed with dichloromethane for 6 h. Finally, the solid was dried overnight in an oven at 60 °C. These materials will be referred as $[Fe(acac)_2]$APTES@HMS or $[Fe(acac)_2]$APTES@AC.

$[Fe(acac)_2]$APTES@HMS: elemental analysis (%) C 9.74 H 2.60 N 2.86; ICP-AES Fe 1.38%, loading Fe 247 $μmol\,g^{-1}$.
$[Fe(acac)_2]$APTES@AC: elemental analysis (%) C 82.21 H 0.96 N 1.32, loading APTES 0.94 $mmol\,g^{-1}$; ICP-AES (%) Fe 0.77 Si 2.38, loading Fe 138 $μmol\,g^{-1}$ and APTES 0.85 $mmol\,g^{-1}$.