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Direct immobilisation *versus* covalent attachment of a Mn(III)*salen* complex onto an Al-pillared clay and influence in the catalytic epoxidation of styrene

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Abstract

A Mn(III)*salen* complex was immobilised onto an aluminium-pillared clay (Al-WYO) by three different methodologies: method A (catalyst A2), direct immobilisation of the complex into the Al-WYO; method B (catalyst A4), covalent anchoring through cyanuric chloride (CC); and method C (catalyst A7), covalent attachment onto a 3-aminopropyltriethoxysilane (APTES) modified Al-WYO mediated by CC. All the materials were characterised by XPS and FTIR; the Mn content of the materials with the immobilised complex was determined by AAS.

FTIR and XPS spectra confirmed the organo-functionalisation of Al-WYO and complex immobilisation in the parent and organo-modified Al-PILCs. Direct immobilisation of the complex into the Al-WYO (method A) leads to the highest immobilisation efficiency ($\eta = 37.5\%$) compared with the anchoring procedures using the two spacers, methods B and C, which gave $\eta = 7.4\%$ and 8.7%. Nevertheless, the surface Mn contents are always higher than those obtained by bulk analysis, suggesting that in all materials the complexes are located within the most external pores.

The Mn(III)*salen*-based pillared clays were tested in catalytic epoxidation reaction of styrene using iodosylbenzene as the oxygen source and were reused for several cycles. The catalyst A2 was the best heterogeneous catalyst among the catalysts prepared since it showed similar substrate conversion and styrene epoxide selectivity to the homogeneous counterpart; the heterogeneous catalysts A4 and A7 showed considerably lower values for these parameters. The styrene epoxide yields decrease in the order, $A2 \gg A4 > A7$, which might be associated with some pernicious catalytic activity of the organo-modified supports (A3 and A6). Moreover, A2 could be reused for four times with a slight decrease in its catalytic activity and with almost no leaching of the active phase.

Keywords: Mn(*salen*) complexes; Pillared clays; Immobilisation; Organo-functionalisation; Covalent attachment; Epoxidation

1. Introduction

The oxidation of olefins to the corresponding epoxide derivatives is of great relevance because these products are important and versatile synthetic intermediates for the chemical industry. Recent studies have demonstrated that manganese(III)*salen* complexes in combination with various oxidising agents successfully catalysed this chemical process [1].

One of the most important challenges in homogeneous catalysis is to transform a successful homogeneous catalyst into a heterogeneous catalytic system, due to the intrinsic advantages of catalyst easy separation and recycling and product separation. Particularly, the heterogenisation of [Mn(*salen*)] complexes also efficiently decreases the formation of the catalytic inactive μ-oxo-Mn(IV) dimmers. This is due to the effect of catalyst site isolation and leads to an improvement of the overall catalytic efficiency of the anchored complex when compared to the homogeneous counterpart [2].

Various approaches of immobilisation of Mn(III)*salen* complexes have been reported: complex grafting onto siliceous

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materials [3], clays [4], pillared clays [5], activated carbons [6], encapsulation into the pores of zeolites [7] and anchoring onto organic polymers [8]. The solid matrixes used have their relative advantages and disadvantages. In the case of pillared clays (PILCs), these materials can be prepared from natural expandable clays (such as montmorillonites) as reviewed elsewhere [9]. In terms of porosity, PILCs present wider pores than zeolites, as Y zeolite for instance, but essentially they are still microporous materials, that is, solids with pores less than 2 nm wide [10]. Considering other properties that are also relevant when using inorganic porous materials as matrixes for the immobilisation of metal complexes, such as hydrophobicity, PILCs have intermediate hydrophobic properties, between zeolites and activated carbons [11]. Another relevant feature of this class of materials to the context of the present work is related with their experimental synthesis. These solids can be prepared in experimental conditions which are not chemically aggressive to the Mn(III)*salen* complexes and therefore in some situations the encapsulation of the complexes can be done simultaneously with the PILCs preparation [5b,c].

In this study a [Mn(*salen*X)] complex functionalised with hydroxyl groups in the aldehyde moiety (Scheme 1) was immobilised onto an aluminium-pillared clay, denoted as Al-WYO, by three different methodologies: method A, direct immobilisation of the complex into the Al-WYO; method B, covalent anchoring through cyanuric chloride (CC); and method C, covalent anchoring through CC onto an 3-aminopropyltriethoxysilane (APTES) modified Al-WYO. The catalytic activity of the immobilised [Mn(*salen*X)] complexes was tested in the catalytic epoxidation of styrene using PhIO as the oxygen source. Using three different procedures to heterogenise the [Mn(*salen*X)] complex onto Al-WYO, we aim to evaluate the influence of the type of immobilisation procedure (direct *versus* covalent grafting) in the catalytic activity of the immobilised complex.

2. Experimental

2.1. Solvents and reagents

Cyanuric chloride (CC), 3-aminopropyltriethoxysilane (APTES), styrene and chlorobenzene were from Aldrich. Iodosylbenzene (PhIO) was synthesised according to procedures described in the literature [12]. All solvents were from Merck, except acetonitrile used in catalytic experiments which was from Romil.

2.2. Preparation of materials

2.2.1. Preparation of the aluminium-pillared clay

A montmorillonite from Wyoming (USA) was used as starting material whose structural formula, based on chemical analysis and cation exchange capacity data, is $(Si_{3.91}Al_{0.09})^{IV}(Al_{1.51}Fe_{0.18}Mg_{0.26})^{VI}(1/2Ca,K,Na)_{0.49}$. This smectite has been extensively characterised in a previous report [13]. The pillared interlayered clay based on WYO, denoted as (Al-WYO), was prepared as described detailed elsewhere [14]. Briefly, the clay was pillared with an oligomer solution made from $AlCl_3$ and NaOH. After washing and freeze-drying, the solid was calcined at 350 °C for 2 h after a ramp of 1 °C min^{-1}. The obtained material had a basal spacing (d_{001}) of 1.83 nm and a specific surface area of 270 m^2 g^{-1}.

2.2.2. Functionalisation of Al-WYO with cyanuric chloride (material A3)

The parent material Al-WYO (A1) (0.8 g) was added to a CC saturated solution in dry toluene (50 cm^3) and the resulting mixture was refluxed for 24 h, under inert atmosphere. The solid, A3, was separated by centrifugation, washed with toluene and then with dichloromethane and finally dried overnight at 120 °C, under vacuum.

2.2.3. Functionalisation of Al-WYO with 3-aminopropyltriethoxysilane (material A5)

Al-WYO (A1) (1.0 g) was added to an APTES dry toluene solution (0.3 g, 1.4×10^{-3} mol in 10 cm^3) and the suspension was refluxed for 24 h, under inert atmosphere. The solid, A5, was separated by filtration, Soxhlet extracted with dichloromethane for 48 h and dried overnight at 120 °C in vacuum.

2.2.4. Functionalisation of A5 with CC (material A6)

A suspension of APTES functionalised Al-WYO (A5) (1.0 g) was refluxed for 48 h with a saturated solution of CC in dry toluene (50 cm^3), under inert atmosphere. The solid, A6, was separated by centrifugation, washed with dichloromethane and dried at 120 °C in vacuum for several hours.

2.2.5. Synthesis of [Mn(4-OHsalophen)Cl]

The synthesis and characterisation of the complex [Mn(4-OHsalophen)Cl], chloride-[*N*,*N*′-bis(4-hydroxysalicylaldehyde)phenylenediiminate] manganese(III), was performed by standard methods and has been reported elsewhere [6a].

$MnC_{20}H_{14}N_2O_4Cl$. FAB-HRMS, *m*/*z*: calculated $([MnC_{20}H_{14}N_2O_4–Cl]^+)$ 401.0334, experimental 401.0333. FTIR, $\bar{\upsilon}$/cm^{-1}: 1609 s, 1593 s *versus*, 1576 s, 1546 s, 1497 m, 1435 m, 1374 s, 1327 vw, 1254 s, 1207 s, 1194 s, 1142 m, 1127 m, 986 w, 905 w, 848 m, 806 w, 754 m, 658 m, 609 w, 524 w, 496 m, 405 vw.

2.2.6. Complex immobilisation by method A (material A2)

To A1 (2.0 g) was added a 1×10^{-3} mol dm^{-3} solution of [Mn(4-OHsalophen)Cl] in *N*,*N*′-dimethylformamide and the mixture was refluxed for 30 h. The resulting material, A2, was separated by filtration, Soxhlet extracted with *N*,*N*′-dimethylformamide until colourless washings were obtained, and then finally dried at 120 °C in vacuum for several hours.

2.2.7. Complex immobilisation by method B (material A4)

The CC-functionalised Al-WYO (A3, 0.6 g) was added to 100 cm^3 of a 1×10^{-3} mol dm^{-3} solution of [Mn(4-OHsalophen)Cl] in dry tetrahydrofuran and the mixture was refluxed for 48 h. The resulting material, A4, was separated by centrifugation, washed with ethanol and dried at 120 °C in vacuum for several hours.