



# Encapsulation of SALEN- and SALHD-Mn(III) complexes in an Al-pillared clay for bicarbonate-assisted catalytic epoxidation of cyclohexene



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## ABSTRACT

[Mn(3,5-dtSALEN)Cl] (**I**) and [Mn(3,5-dtSALHD)Cl] (**II**) complexes (3,5-dtSALEN = *N,N'*-bis(3,5-di-*tert*-butylsalicylaldehyde)ethylenediamine; 3,5-dtSALHD = *N,N'*-bis-(3,5-di-*tert*-butylsalicylaldehyde)-1,2-cyclohexanediamine) were successfully encapsulated within a natural bentonite by using three preparative approaches: (A) direct adsorption of every metal complex on the previously Al-pillared bentonite, Al-PILC; (B) two-step liquid phase methodology: (i) cationic adsorption of Mn<sup>2+</sup> in Al-PILC by substituting its residual cationic exchange capacity (CEC), followed by (ii) diffusion of either 3,5-dtSALEN or 3,5-dtSALHD ligands, for in-situ generation of the corresponding interlayered metal complexes; and (C) simultaneous pillaring/encapsulation of the complexes on the raw starting clay. The materials were characterized by cationic exchange capacity, X-ray diffraction, atomic absorption, FT-Infrared and UV–vis spectroscopies, and N<sub>2</sub> adsorption at 77 K. The physical encapsulation of the complexes into final materials was proven by spectroscopic analyses. Method C yielded both highest metal incorporation and enhanced basal space on the modified clay. All materials showed to be active catalysts in cyclohexene epoxidation with hydrogen peroxide using acetonitrile as solvent (0.79 atm, 293 K). Addition of sodium bicarbonate as co-catalyst led to enhanced conversion (100%) and selectivity (70%) towards the epoxide in the presence of such a kind of heterogeneized metal-complex catalysts. The catalysts were stable and reusable along at least two catalytic cycles.

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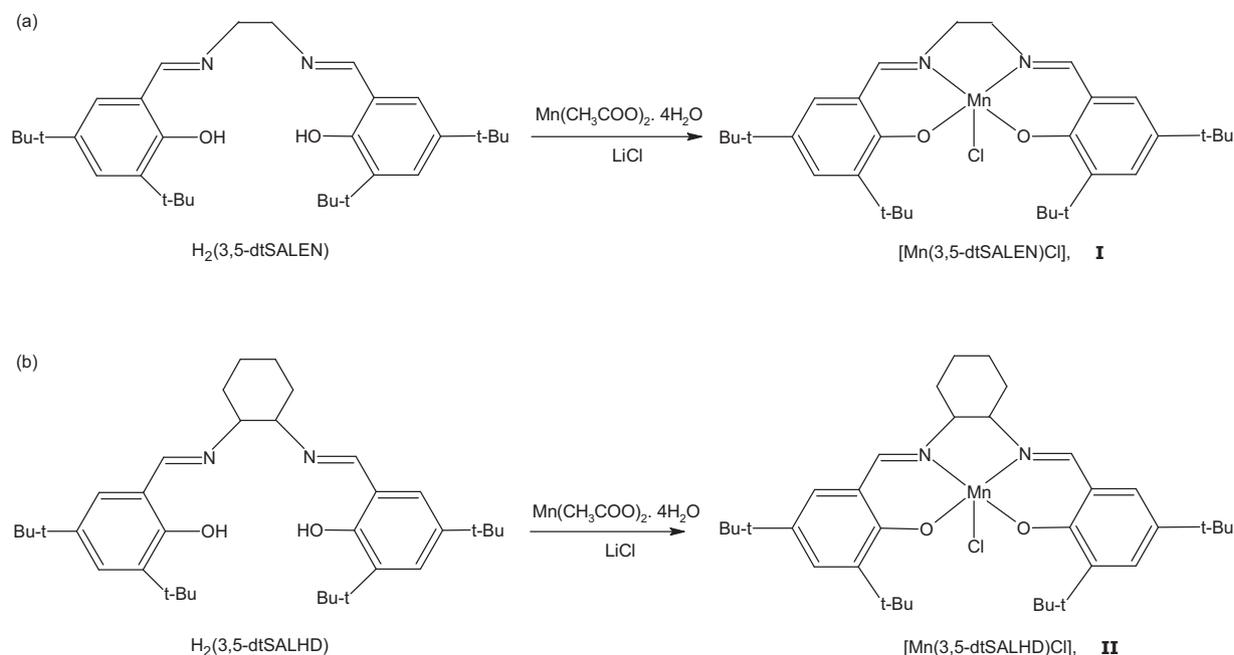
## 1. Introduction

Epoxidations are a class of reactions deserving of great interest since they lead to valuable and versatile intermediates for development of pharmaceutical active compounds [1], fine chemicals, polymers and paints [2–5], among others. Hydrogen peroxide constitutes an environmental-friendly and clean oxidizing agent for this kind of reactions, since it only forms water as by-product, and by its low price and wide availability [1]; however, its use in this reaction has been recognized to be complicated because of its immiscibility in organic solvents [6]. Mn(III) complexes with

Schiff-base ligands displaying coordination environment N<sub>2</sub>O<sub>2</sub>, also so-called SALEN complexes, have been widely reported as soluble and efficient catalysts in olefin epoxidations [7–10].

By this reason, effective immobilization of this type of active agents on solid surfaces shows several advantages, including simpler handling and separation of the products, easy recovery of the solid catalyst from the reaction mixture and lower amount of residues [11,12]. A higher catalytic performance has also been evidenced for such solid catalysts in comparison to the same complexes dissolved, operating under homogeneous conditions; appropriate immobilization allows the isolation of the active centres, preventing inactive dimers of the metal complex of the type  $\mu$ -oxo-Mn(IV) to be formed in the reaction mixture [13]. Thus, heterogeneization of such a type of metal complexes has received much attention in the past few years, the attachment of several

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**Fig. 1.** General sketch employed for preparation of the SALEN–Mn(III) complexes: (a) [*N,N*-bis-(3,5-di-tert-butylsalicylidene)-ethylendiamine]manganese(III) chloride [ $\text{Mn}(3,5\text{-dtSALEN})\text{Cl}$ ] (**I**) and (b) [*N,N*-bis-(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III) chloride [ $\text{Mn}(3,5\text{-dtSALHD})\text{Cl}$ ] (**II**).

Mn complexes on several inorganic surfaces, like silica, mesoporous materials [14–16], activated carbon [17,18] and pillared clays [19–22] has been then reported. It is remarkable that catalysts based on pillared clays have displayed outstanding efficiency in the epoxidation of a variety of olefins [23].

Pillared clays (PILCs) are nanostructured materials very attractive to host metal complexes with catalytic activity. In general terms, these materials are prepared by exchange of the original cations present into the interlayer space of some natural clays by voluminous, highly-charged metal-polycations, mainly Al-based, that upon calcination give rise to pillars of their corresponding oxides. These interlayered species provide final materials with increased thermal stability, specific surface area and pore volume in comparison to the starting mineral [24,25]. PILCs have been successfully prepared from polycations of several metals, as Ti, Zr, Fe, and Cr, among others [26], but the clays pillared with Al (Al-PILCs) have been the most extensively studied [27]; these are prepared by employing the Keggin-like polycation  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ , usually abbreviated as  $[\text{Al}_{13}]^{7+}$ , as interlayering species [28,29]. Therefore, the incorporation and stabilization of SALEN Mn-complexes within the interlayer of Al-PILCs may then efficiently combine in the same catalyst the high catalytic activity displayed by the metal complex with the low cost, excellent textural properties and high resistance to organic solvents featured by the Al-PILCs [13,19,20,30,31]. Various strategies have been assessed in order to confine such a family of metal complexes in clay materials, finding that the final characteristics of the resulting catalysts strongly depend on the experimental procedure used for the incorporation and stabilization of the metal complex into the clay host [19].

Using of  $\text{H}_2\text{O}_2$  as oxidizing agent in catalytic systems where Mn is the active metal leads to competition of their decomposition products for the active centres, driving to deactivation [32]. Besides, it has been also shown that hydrogen peroxide behaves as a more effective oxidizing species in the presence of activators or co-catalysts of the reaction, like NaOH, KOH or  $\text{NaHCO}_3$  [33–35]. Thus, the use of  $\text{NaHCO}_3$  as co-catalyst has been reported to be crucial for achieving good conversions in the presence of Mn-based catalysts [34,36].

Accordingly and taking into account that several methods have been already tested for encapsulation of SALEN complexes in porous matrices like pillared clays, this work was focused to study the direct immobilization of two similar complexes, ( $[\text{Mn}(3,5\text{dtSALEN})\text{Cl}]$ ) and  $[\text{Mn}(3,5\text{dtSALHD})\text{Cl}]$ , having different substituents on the diimine bridge (Fig. 1) within the free channels in the interlayer space of an Al-PILC. Results may be compared to previously reported methods [19]. The effect of the structure and size of the complexes and of the insertion method on the stability and catalytic behaviour of the final functionalized materials have been evaluated in the cyclohexene epoxidation by  $\text{H}_2\text{O}_2$  assisted by  $\text{NaHCO}_3$  as co-catalyst.

## 2. Experimental

### 2.1. Materials

The preparation of the Schiff bases and their corresponding Mn(III) complexes was performed by using 1,2-cyclohexanediamine (98%), manganese chloride tetrahydrate ( $\geq 98\%$ , ACS reagent), ethylenediamine ( $\geq 99.99\%$ , SigmaUltra), manganese acetate tetrahydrate ( $\geq 99\%$ ), absolute ethanol ( $\geq 99.5\%$ , ACS reagent) and *N,N*-dimethylformamide ( $\geq 99\%$ ), all purchased from Sigma–Aldrich®, as well as 3,5-di-tert-butylsalicylaldehyde (99%) from Alfa–Aesar and dichloromethane (99.9%) from Mallinckrodt. The Al-oligomeric solution used to treat the clay was prepared from  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\geq 99\%$ , Sigma–Aldrich) and NaOH ( $\geq 99.8\%$  Mallinckrodt). In the catalytic experiments and the chromatographic analyses, cyclohexene (99.0%, Alfa–Aesar), cyclohexene epoxide (99.0%, Merck), hydrogen peroxide (30% w/w AR, Panreac), acetonitrile (99.0%, Aldrich Chemical), sodium bicarbonate (99.0%, Carlo Erba) and *n*-decane ( $\geq 99.0\%$ , Alfa–Aesar) were used. All reagents were employed as received.

The preparation of the catalysts was made using as starting material a natural bentonite from Valle del Cauca, Colombia, (BVC). Its physicochemical and mineralogical features have been extensively reported elsewhere [37]: cationic exchange capacity, CEC = 89 meq/100 g clay dry basis; elemental composition (w/w%):  $\text{SiO}_2$ , 60.5;  $\text{Al}_2\text{O}_3$ , 24.7;  $\text{Fe}_2\text{O}_3$ , 10.2; MnO, 0.05; MgO, 3.07; CaO,

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