

## Characterization and catalytic activity of Mn (salen) immobilized on silica by various strategies

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**Abstract:** Different strategies were applied to prepare supported Mn(salen) on fumed silica and to explore the effect of the interaction nature between the active sites and the surface on the catalytic activity. Direct and multistep grafting methods were used: the silica surface was silylated and the metal complex was modified in order to achieve different metal complex/surface interactions. In the speculated strategy, the covalent binding was provided through a cross linker. The resulting systems were characterized by IR in diffuse reflexion mode (DRIFT), thermogravimetric analysis (TG) and chemical analysis. Then, homogenous and heterogeneous catalysts were used for cyclohexene oxidation with tert-Butyl hydroperoxide (TBHP). Results show that organo-metallic complexes are not totally stable during the immobilization procedure when the surface is previously functionalized. The heterogeneous catalyst efficiency is more dependent on the preparation way rather than on the amount of manganese at the surface. The tested solids showed the absence of important leaching phenomena, regardless of the interaction nature between the active sites and the surface.

**Keywords:** crosslinker, grafting, interaction, Mn(salen), oxidation.

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### I. Introduction

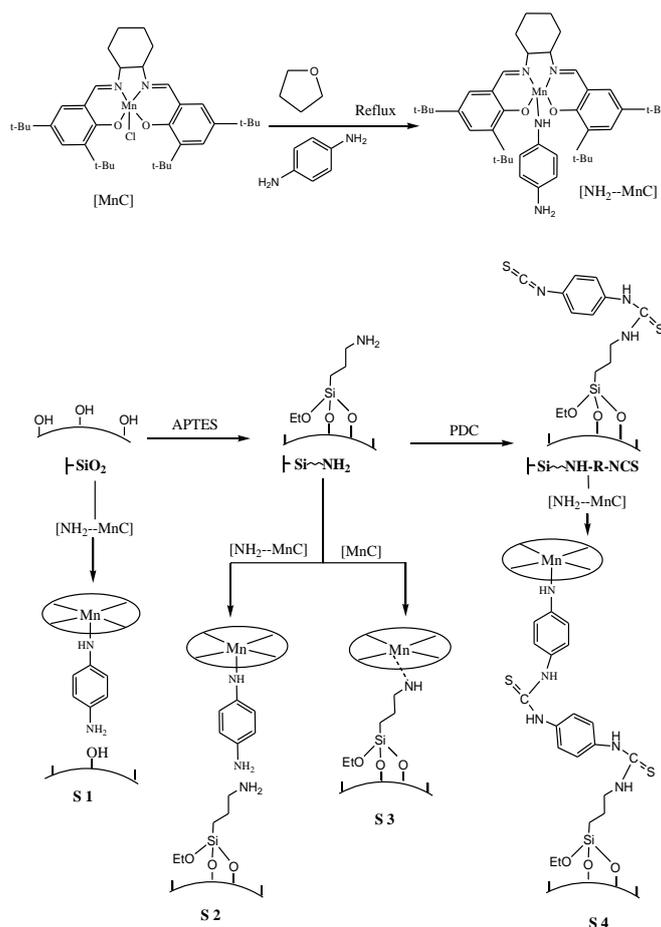
One of the most useful transformations of alkenes is epoxidation. For a selective epoxidation of a broad range of olefins, a great attention has been paid to the development of transition metal-based catalysts, both homogeneous and heterogeneous [1–4]. The main advantages for homogeneously catalyzed reactions are high activity and selectivity at mild reaction conditions. In chemical industries, the heterogeneous catalysts are preferred because the catalyst recovery, from the reaction mixture, is easier. To preserve or enhance the activity and selectivity, the interaction between the active centers and the solid surface must be considered carefully for the solid catalyst. Indeed, the immobilization of the active species can either be achieved by a covalent bond or by non-covalent interactions with the surface. The three main types of non-covalent interactions are hydrogen bonds, ionic bonds, and Van der Waals interactions.

The oxidation reactions catalyzed by the salen-based transition metal complexes have received special attention showing that the choice of an appropriate support is important to provide a successful immobilization strategy [5–7]. Metal-salen complexes have been immobilized on different materials, like zeolites [8–10], silica [11–28], polymers [29–35], carbon materials [36–38] or alumina [39,40]. They can also be immobilized on clays minerals or modified clay minerals [41–48]. The main advantage of the covalent bonding strategy, compared to the other immobilization approaches, is the chemical bonds strength and stability preventing the complex leaching from the support during the catalytic reaction [7,23]. If the host material becomes a ligand for the active metal complex, the terms grafting, axial coordination or apical coordinative bond with metal are used. If the surface groups of the host react with one of the metal complex ligands, the terms tethering or covalent bonding are used. In these cases, some problems such as the active center orientation and the effect of the surface can arise. The use of crosslinkers makes the active site far away from the surface and may prevent these problems [33,49–51]. The aim of this work is to deposit the Mn(salen) complexes on silica surface using different strategies, and to compare the catalytic activities of the resulting materials in an oxidation reaction. The heterogeneity of the catalytic process will be validated for these catalysts. The studied reaction is the oxidation of cyclohexene, in dichloromethane, using tert-Butyl hydroperoxide (TBHP) as oxidant. To avoid having to

suppose a correlation between the catalytic activity and the diffusion phenomena, which can take place in a porous material [14], a non porous support is used here.

On the other hand, when a pure siliceous support is used to graft Mn(salen)Cl catalyst it was demonstrated that the support quickly turned white after a washing with  $\text{CH}_2\text{Cl}_2$ , and no Mn element was detected in the support [19]. Indeed, the  $\text{SiO}_2$  surface is highly hydrophilic which does not favour interaction with the Mn(salen)Cl complex. The  $\text{SiO}_2$  surface is often converted into hydrophobic surface to make specific interaction with the organometallic complex. In this work, an inverse strategy is explored; rather than modifying the  $\text{SiO}_2$  surface, the Mn(salen)Cl is modified by grafting a phenylenediamine [34] to the metal center. This added ligand is hydrophilic and can favour the interaction between Mn complex and the  $\text{SiO}_2$  hydrophilic surface. This simple strategy had not been encountered in the literature. We investigate also a versatile chemistry modification by using the (1,4-phenylenediisothiocyanate) cross-linker (PDC) to achieve covalent binding of Mn(salen) complex. This reaction requires the prior modification of both silica surface and commercialized Mn salen complex. The surface was silylated using 3-aminopropyltriethoxysilane (APTES) [52]. One site of the crosslinker ( $-\text{N}=\text{C}=\text{S}$ ) should react with  $-\text{NH}_2$  groups belonging to the silane groups on the silica surface and the other site should react with the  $-\text{NH}_2$  groups belonging to the aryldiamine Mn(salen) ligand. To the best of our knowledge, this combination has never been reported before.

In fact, generally, the cross linker is used to connect the solid and the complex by reaction with the functional surface groups and a suitable modified salen ligand. Fig. 1 show the different strategies used in this work. The non modified or the modified Mn complexes were deposited on  $\text{SiO}_2$ , APTES/ $\text{SiO}_2$  or PDC/APTES/ $\text{SiO}_2$  surfaces to prepare solid catalysts. The prepared systems, both in homogenous and heterogeneous catalysis, were examined in the cyclohexène oxidation reaction. This reaction was used to estimate the catalytic activity of each prepared solid and thus, correlate the efficiency to the immobilization strategy.



**Fig. 1:** Synthesis of homogeneous aryldiamine modified Jacobsen's catalysts and schematic representation of immobilized Mn(salen) complexes on silica supports methodologies.

## II. Experimental section

### 2.1 Solid preparation

The silica used in this study is fumed silica (Sigma-Aldrich) with a  $390 \text{ m}^2 \text{ g}^{-1}$  specific surface area. The silica surface will be labelled as  $\text{Si-OH}$ . The Mn(III) salen complex (R,R)-(-)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexane diaminomanganese (III) chloride ( $\text{C}_{36}\text{H}_{52}\text{ClMnN}_2\text{O}_2$ ) called (R,R) Jacobsen's catalyst (denoted [MnC]) was purchased from sigma-Aldrich.

Synthesis of modified Mn(III)salen:  $[\text{NH}_2\text{-MnC}]$  ( $\text{C}_{42}\text{H}_{59}\text{MnN}_4\text{O}_2$ ). For the modification of Mn(III) salen, the procedure described by Jing Huang et al. was followed [29,30,34]. Briefly, 1 mmol of Mn(III) salen was mixed with 10 mL of tetrahydrofuran (THF); then 1 mmol of p-phenylene diamine was added. The mixture was kept under stirring and refluxed for 15 h at  $60^\circ\text{C}$ .

Preparation of 3-aminopropyl-modified silica:  $\text{Si-NH}_2$ . In a typical reaction, 8.4 mL of 3-(aminopropyl)-triethoxysilane (APTES) was added to a suspension of silica: 5.0 g in 90 mL of dry toluene. The mixture was stirred at  $60^\circ\text{C}$  for 24 h. The white solid material was filtered, washed in a Soxhlet apparatus with methanol and then dried at  $80^\circ\text{C}$  for 4 h.

Preparation of modified silica with the crosslinker:  $\text{Si-NH-RNCS}$ . 1 g of  $\text{Si-NH}_2$  was treated with a 10.4 mM PDC solution in pyridine/DMF (10%/90%, v/v) for 2 h at room temperature and kept away from light. The solid was washed in DMF then in ethanol and dried overnight at  $75^\circ\text{C}$ .

Immobilization of Mn(III) salen complexes: The immobilization of Mn(III) salen complexes was performed by four different methodologies (Fig. 1). From now on, the  $\text{Si-OH}/[\text{NH}_2\text{-MnC}]$  and the  $\text{Si-NH}_2/[\text{NH}_2\text{-MnC}]$  systems will be symbolized by S1 and S2, respectively. For those systems, the interaction between the surface and the modified complex should be weak. Whereas, the reactions between  $\text{Si-NH}_2$  and [MnC] on one hand, and between  $\text{Si-NH-R-NCS}$  and  $[\text{NH}_2\text{-MnC}]$  on the other hand, should produce covalent interactions and will be symbolized by S3 and S4, respectively. To prepare S1, a mixture of arylamine-modified Mn(III) salen  $[\text{NH}_2\text{-MnC}]$  solution (10 mL) and silica (0.5 g) was stirred at room temperature for 7 h. The material was washed by dichloromethane and dried overnight at  $60^\circ\text{C}$ .

For S2, the arylamine-modified Mn(III) salen  $[\text{NH}_2\text{-MnC}]$  solution (10 mL) and 0.5 g of the  $\text{Si-NH}_2$  were stirred at room temperature for 7 h. The material was washed by dichloromethane and dried overnight at  $60^\circ\text{C}$ . For S3, Mn (salen) (1 mmol) was added to a dispersion of  $\text{Si-NH}_2$  solid (1 g) in dichloromethane (10 mL) and the mixture was stirred during 7 h at room temperature. The catalyst was washed in dichloromethane and dried overnight at  $60^\circ\text{C}$ . Finally, for S4's preparation, the arylamine-modified Mn(III) salen  $[\text{NH}_2\text{-MnC}]$  solution (10 mL) and 0.5 g of the PDC-APTES-modified silica ( $\text{Si-NH-R-NCS}$ ) was stirred at room temperature for 7 h. The material was washed by dichloromethane and dried overnight at  $60^\circ\text{C}$ .

### 2.2 Characterization

Diffuse reflectance IR spectroscopy (DRIFT) was used to follow the evolution of the surface during different steps in the catalyst's preparation. DRIFT measurements were carried out with a Bomem MB 155 infrared spectrum analyzer. For Chemical analysis, the manganese was analysed by ICP using a Horiba Jobin Yvon (Activa) apparatus and the sulfur by an EMIA-V2- 95 Horiba 200V analyzer. TG measurements were performed with SDTQ600 under air flow. Samples were heated starting from room temperature till  $150^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$ , then the temperature was kept constant at  $150^\circ\text{C}$  for 70 min to ensure the removal of strongly physisorbed water and finally samples were heated up to  $800^\circ\text{C}$  and the heating rate was  $5^\circ\text{C min}^{-1}$ . Two temperature ranges were considered. The first one which ranges between room temperature and  $150^\circ\text{C}$  corresponds to moisture departure. The second one which ranges between 150 and  $800^\circ\text{C}$  corresponds to different organic compound decomposition.

### 2.3 Cyclohexene oxidation

The reactions were carried out in a 50 mL-round-bottom flask set with a reflux condenser in 5.0 mL of dichloromethane at  $40^\circ\text{C}$  with constant stirring. The composition of the reaction medium was 0.25 mL of cyclohexene, 0.1 mL of toluene (internal standard) and 0.05 g of heterogeneous catalyst. The oxidant, 0.5 mL of t-BuOOH, was added to the stirred solution under nitrogen. After 24 h, products were collected and analyzed by capillary gas chromatography (Agilent GC). Other experiments using Jacobsen's catalysts [MnC] and  $[\text{NH}_2\text{-MnC}]$  in homogeneous phase were also performed under the same reaction conditions using 0.05 g of each catalyst. Investigation of the heterogeneity and the recyclability was done by filtering off the catalyst after the 24 h reaction and allowing the reaction mixture to continue for 24 h. The recovered catalyst was dried at  $60^\circ\text{C}$  and re-used in the cyclohexene oxidation reaction.

### III. Results and discussion

#### 3.1 Characterization of the materials

The results obtained for all samples by various techniques will be discussed in three stages: spectroscopic, thermal stability and chemical analysis.

##### 3.1.1 FTIR Study

The successful grafting of APTES on the SiO<sub>2</sub> surface was confirmed by DRIFT as shown in Fig. 2. The silylation can be revealed from the disappearance of the band at 3745 cm<sup>-1</sup>, assigned to Si-O-H stretching (Fig 2-a). Drift spectrum of  $\text{---Si}^{\wedge}\text{NH}_2$  (Fig 2-b) exhibits bands at 2933 and 2863 cm<sup>-1</sup> corresponding to the C-H vibration of aliphatic groups [3,54,55]. The bands at 3345 and 3280 cm<sup>-1</sup> are due to the N-H vibration [56,57]. The band at 1273 cm<sup>-1</sup> is possibly due to C-N stretching [58,59]. The bands which appear at 1043 and 801 cm<sup>-1</sup> are attributed to siloxane Si-O-Si stretching [60,61]. While the band at 1190 cm<sup>-1</sup> is probably due to the residual CH<sub>2</sub> in the ethoxy groups (Si-O-CH<sub>2</sub>-CH<sub>3</sub>) [62]. After reaction with the PDC, DRIFT spectrum of the  $\text{---Si}^{\wedge}\text{NH-R-NCS}$  sample evidences the reaction between the surface and the -NCS groups (Fig 2-c). A band at 3029 cm<sup>-1</sup> due to aromatic C-H vibration appears [63], the aliphatic C-H bands (between 1977-1871 cm<sup>-1</sup>) persist and the intensity of  $\nu(\text{NH})$  bands increases. The intensity of the band at 1410 cm<sup>-1</sup> assigned to C-N stretching frequency [64] increases and a band at 1650 cm<sup>-1</sup> due to C=N vibration appears. Finally, bands at 1539 and 1510 cm<sup>-1</sup>, assigned to C=C [16] and C=S vibrations [65] appear. DRIFT Spectra of S1, S2, S3 and S4 are shown in Fig. 3. The region between 1000 and 1350 cm<sup>-1</sup> shows a broad band due to the important number of groups vibrating at this region. In fact, this region is characteristic of both aromatic and aliphatic amines. These groups belong to APTES, PDC and NH<sub>2</sub>--MnC. Fig. 3-a presents the DRIFT spectrum of the S1 system. The band assigned to Si-O-H stretching is still present, but shifts from 3745 to 3735 cm<sup>-1</sup>. This shift is possibly due to the hydrogen bond interaction between the silanol groups and the amine group belonging to [NH<sub>2</sub>-MC] complex. The comparison of the S3 spectrum (Fig 3-c) with the  $\text{---Si}^{\wedge}\text{NH}_2$  one (Fig 2-b), shows the appearance of bands at 1610 and 1538 cm<sup>-1</sup> which can be assigned to C=N and C=C respectively, corresponding to Salen ligand. While the increase of the intensity of the bands corresponding to C-H vibration of aliphatic groups (2800 and 3000 cm<sup>-1</sup>) compared to bands at ~ 3300 cm<sup>-1</sup>, assigned to -NH<sub>2</sub> in the aminopropyl attached groups is observed. This increase is due to the important number of aliphatic groups coming from the Salen ligand. For S1, S2 and S4 samples, the used Mn complex contains both C-H and N-H groups since the Mn complex was previously modified to have an aryldiamine ligand. Concerning the S4 system, the decrease of the band intensity at 1650 cm<sup>-1</sup> assigned above to the C=N vibration, evidences that the free side of the crosslinker has reacted with the amine group belonging to the metal complex.

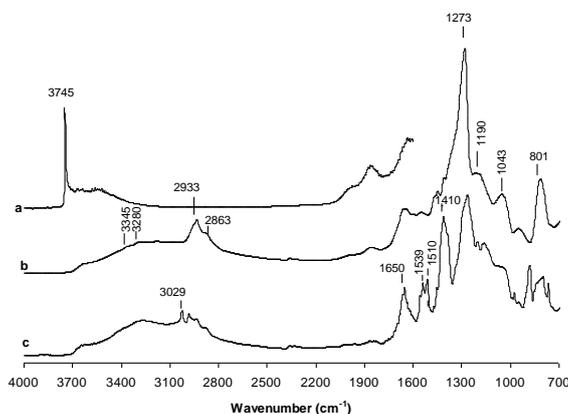


Fig.2: DRIFT spectra of (a) fumed silica, (b)  $\text{---Si}^{\wedge}\text{NH}_2$  and (c)  $\text{---Si}^{\wedge}\text{NH-R-NCS}$ .

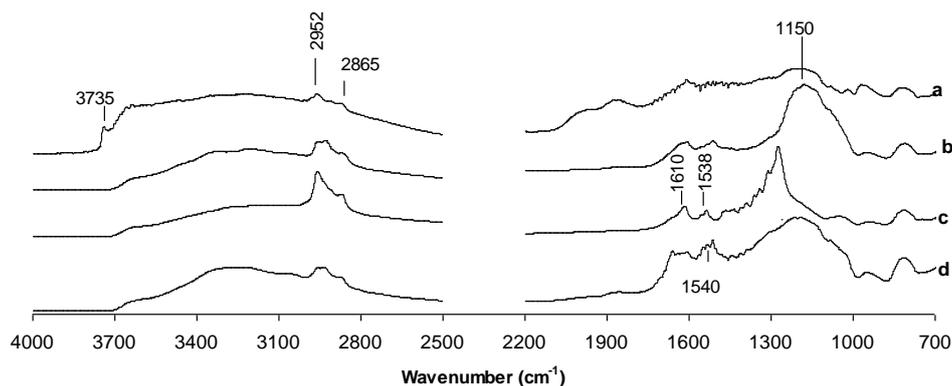


Fig. 3: DRIFT spectra of (a) S1, (b) S2, (c) S3 and (d) S4.

### 3.1.2 Thermal stability study

Fig. 4 shows the TG curves of the  $-\text{Si}^{\wedge}\text{NH}_2$  and  $-\text{Si}^{\wedge}\text{NH-R-NCS}$  samples. Results of the TG measurements are displayed in Table 1. Based on mass losses, it is possible to calculate the grafting amount of APTES at the  $\text{SiO}_2$  surface. Supposing that the APTES molecule was grafted by a bidentate mechanism [39] (DRIFT spectrum shows the persistence of ethoxy groups), APTES on  $\text{SiO}_2$  solid would be  $1.4 \text{ mmol g}^{-1}$ . This value is similar to that found by Luts and Papp [17]. Assuming that the APTES layer at the surface is stable during the reaction with the cross-linker, TG results show that the weight loss due to PDC decomposition is about 4.7 % corresponding to 0.3 mmol of PDC per gram of solid. Since the APTES amount was evaluated above to  $1.4 \text{ mmol g}^{-1}$ , only 21 % of the APTES extremities would have reacted with the crosslinker. Results of the TG measurements displayed in Table 1, indicate that the organic material contents follow the order  $\text{S1} < \text{S2} < \text{S3} < \text{S4}$ . The thermal stability of prepared catalysts can be compared by examining their DTG curves (Fig 5). Between 150 and 600 °C all samples present almost two thermal events corresponding to the loss of different organic fragments. It is not easy to pinpoint the nature of fragment decomposition for each peak. Therefore, we focused on comparing the temperatures of complete decomposition. The decomposition profiles of S1, S2 and S3 samples (Fig 5-a, b and -c respectively) were completed at a temperature lower than 500 °C (470, 480, and 500 °C for S3, S1, and S2, respectively).

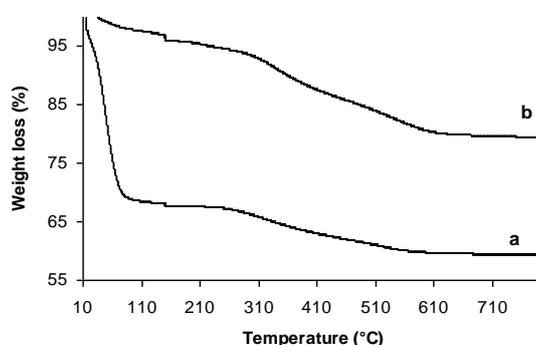


Fig. 4: TG curves of (a)  $-\text{Si}^{\wedge}\text{NH}_2$  and (b)  $-\text{Si}^{\wedge}\text{NH-R-NCS}$ .

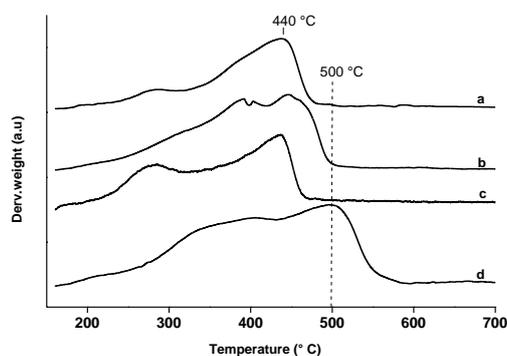


Fig. 5: DTG curves of (a) S1, (b) S2, (c) S3 and (d) S4.

**Table 1:** TG mass loss of different functionalized solids expressed on a dry weight basis (between 150 and 800°C)

Sample	% Mass loss		
	20-150 °C	150-800 °C	150-800 °C*
-Si <sub>3</sub> NH <sub>2</sub>	32.2	8.4	12.4
-Si <sub>3</sub> NH-R-NCS	4.1	16.5	17.2
S1	3.9	10.8	11.2
S2	4.6	21.2	22.2
S3	2.4	21.9	22.4
S4	3.7	20.1	20.9

\* TG mass loss expressed on a dry weight basis

However, for S4 sample, the decomposition was completed upper than 560 °C (Fig 5-d) showing the higher stability of the interaction between the organic and the inorganic materials. This result suggests that, covalent bonds between manganese complex and the functionalized surface have taken place only for the S4 sample, as expected.

### 3.1.3 Chemical analysis

Chemical analysis results of Mn and of C as well as the molar ratio C/Mn present on table 2 show that S1 contains the lowest and S2 the highest amount of manganese. For the S1 sample, the C/Mn ratio equal to 40.2 matches well with the expected value since the formula of the modified Mn(salen) complex is C<sub>42</sub>H<sub>59</sub>MnN<sub>4</sub>O<sub>2</sub> and shows that the Mn(salen) modification has taken place with success. The Mn(salen) modification with the amine ligand seems to create a certain affinity with the hydrophilic SiO<sub>2</sub> surface. This affinity comes more probably from a hydrogen bond interaction between the Si-OH surface groups and the -NH<sub>2</sub> group belonging to [NH<sub>2</sub>--MC] complex like suggested above. For S2 and S4 samples, the C/Mn molar ratio might be higher than 42 and for S3 sample, this ratio might be higher than 36. In fact, carbon comes not only from the organo-metal complex but also from APTES or APTES/PDC organic deposit layers. The results obtained (table 2) clearly show that the structural integrity of the complex does not resist during the interaction with the hydrophobic surface since the C/Mn ratio is lower than 30 for S2, S3 and S4 samples. In previous articles on the topic, immobilized Mn-Salen characterization was done by IR and UV, and aimed exclusively at confirming the complex grafting. XPS was also often used but only for qualitative data and seldom for quantitative data. Unfortunately, the chemical analysis results are not always discussed and authors suppose, implicitly, that the manganese coordination sphere is not affected during the immobilization step. When the Salen ligand is modified, the C/N ratio is always discussed but rarely confronted with the Mn content. When the neat support contains carbon, the system nature does not allow a firm conclusion about the chemical composition of the deposit complex. Inconsistencies in C/Mn and/or N/Mn ratios have nonetheless already been observed for immobilized Mn(salen) [21,23,42,47]. In few cases, the chemical analysis of Mn, C and N match well with speculated system [16,66]. In these later cases, the interaction is via a covalent binding between the salen ligand and the support; the salen ligand was modified to ensure that it can react with the support surface groups. Also, in the case of clay-supported Mn(salen) [43] and of non functionalized alumina supported Mn(salen) [40] the C/N and the N/Mn ratios are consistent with the composition of the complex. In our case, the confrontation between Mn and carbon analysis shows that when the SiO<sub>2</sub> surface is functionalized with organic layers, the [MnC] and [NH<sub>2</sub>--MnC] would have been partially dissociated during their interaction with the surface. The presence of IR bands assigned to the salen ligands show that the organo-metal complex is not completely dissociated and a chemical equilibrium is probably established. A ligand exchange balanced reaction might take place, since the affinity between the surface groups (-NH<sub>2</sub> and -NCS) and the metal center (Mn<sup>3+</sup>) can be important.

**Table 2:** Chemical analysis and Cyclohexene oxidation conversion and selectivities with TBHP in CH<sub>2</sub>Cl<sub>2</sub>

Sample	Chemical analysis (mmol g <sup>-1</sup> )			Molar Ratio C/Mn	Conversion (%)	Selectivity (%)				
	Mn	C	S			ENOL	ENONE	DIOL	EPOX	ONE
S1	0.33	13.27	-	40.2	71.1	27.2	32.4	37.1	3.3	nd
S2	0.96	27.29	-	28.4	54.6	35.9	47.4	14.6	2.1	nd
S3	0.64	12.84	-	20.1	48.4	21.9	31.5	39.3	3.9	3.4
S4	0.65	10.69	0.62	16.5	25.3	36.4	44.0	12.5	2.0	5.1
Mn salen*					89.5	17.3	31.8	45.4	2.1	3.4
NH <sub>2</sub> --Mn salen*					78.2	22.6	42.6	32.7	nd	2.1

\*Homogeneous nd: non detected

The amount of sulphur in S4 sample, obtained by chemical analysis (Table 2), is equal to 0.62 mmol g<sup>-1</sup> corresponding to 0.31 mmol of PDC/g. Note that the amount of PDC in  $[-Si^{NH-R-NCS}]$  estimated by TG is about 0.3 mmol g<sup>-1</sup> (which correspond to 0.6 mmol g<sup>-1</sup> of sulphur). Therefore, first, the reaction between  $[-Si^{NH-R-NCS}]$  and  $[NH_2--MnC]$  seems to have no negative effects on the organic layer. Second, in our S4 speculated system (Fig. 1) each  $-Si^{NH-R-NCS}$  group should react with only one  $[NH_2--MnC]$  complex giving an S/Mn molar ratio equal to 2. The important decrease in C=N vibration bond intensity after adding  $[NH_2--MnC]$ , shows that the PDC free extremity effectively reacted with the complex. But the obtained S/Mn molar ratio equal to 1 show that at least about half of the Manganese is not immobilized via the PDC crosslinker. For this later Mn complex, the structure is not maintained since the total C/Mn ratio is very low. To conclude, the characterization of the prepared catalysts validates only the schematic procedure described for S1 system in Fig. 1. The other studied systems lead to different interactions with silica surface with a partial Mn-Salen complexes alteration.

### 3.2 Catalytic test

The results in the oxidation of cyclohexene over the various catalysts are given in Table 2. In the used reaction conditions, cyclohexene oxidation yielded cyclohexenol, cyclohexenone, cyclohexanone, cyclohexene oxide and cyclohexane diols (Fig. 6). The conversion of the four solid catalysts in the oxidation reaction was high compared to other metal/support systems [67–69] and decreased in the following order: S1 > S2 > S3 > S4. It seems that the higher the complexity of the catalytic system, the lower the activity. This behaviour was observed elsewhere [47], where it was observed that, in the reaction of styrene oxidation, a direct immobilization of a Mn(III)salen complex onto an Al-pillared clay is more efficient than its anchoring through spacers. The conversion of the S1 heterogeneous catalyst reaches 71.1 %. This value is close to the obtained conversion in homogeneous catalyst ( $[NH_2--MnC]$ ) and shows the important reactivity of the active site in S1 sample. The lower conversion of S2, S3 and S4 catalysts, compared to the homogeneous counterparts, is consistent with the partial Mn(salen) dissociation. Establishing a straightforward correlation between the activity of the catalysts and the amount of manganese at the surface is very difficult. However, results present in table 2 show that the higher the C/Mn molar ratio, the higher the activity of the solid catalyst. The C/Mn ratio can very roughly be correlated to the non-dissociated Mn(salen) complex fraction.

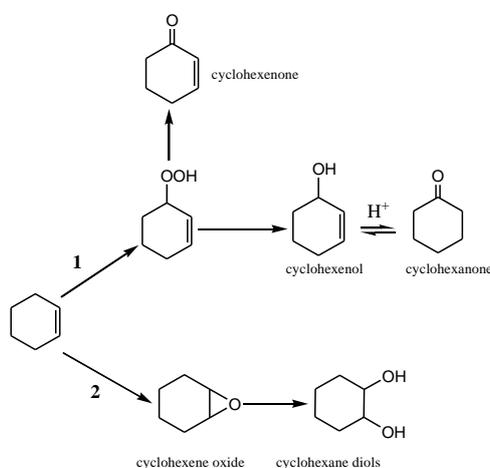


Fig. 6: Oxidative transformation pathways of cyclohexene.

The immobilized Mn(salen) or  $NH_2--Mn(salen)$  seem to be the only active site in the study oxidation reaction. Indeed, the key point in the conversion of cyclohexene, is the reduction of  $L-Mn^{3+}$  to  $L-Mn^{2+}$  and this reduction depends closely on the ligands nature [70]. Therefore, Mn(III) that formed as a result of the Mn(salen) complex dissociation doesn't seem to be active in the cyclohexene oxidation. On the other hand, allylic oxidation (path 1) and ring opening of epoxide (path 2) are the two major paths in oxidation of cyclohexene (Fig. 6). Under the reaction conditions in this study, the amount of products arising from ring opening of epoxide was much less compared to similar systems [40]. The formation of the allylic oxidation products shows the preferential attack of the activated C–H bond over the C=C bond. It has been reported that TBHP as an oxidant promotes the allylic oxidation pathway and epoxidation is minimized [70] and the epoxidation of cyclohexene is inhibited by water [71]. This might be occurring in this work as solid catalysts weren't dehydrated before the catalytic reaction and consequently, they all contain a certain amount of water; TG measurements showed that the amount of water is between 2.4 and 4.6 w% (Table 1). Investigation of the catalytic process heterogeneity shows no appreciable increase in the conversion when the catalyst is removed,

evidencing that no leaching occurred. Moreover, the recovered catalysts show that the activities (Fig. 7) present a small decrease (2-5 %), regardless of the interaction active site/surface nature. Obtained results suggest that the active sites are stable during the catalytic process, regardless of the involved mechanism of their deposition on the surface. To summarize, the studied systems showed that, to avoid the negative effect of the surface and to imitate the homogeneous catalysis, building a complex system that keeps the active sites far away from the surface is not always effective. Better activity was obtained with the systems S1 where the integrity of the Mn(salen) complex was maintained. So, modifying the Mn(salen) complex to create affinity with the SiO<sub>2</sub> surface is a very simple strategy to prepare an active heterogeneous catalysts. Due to their high hydrophilicity, the epoxide selectivity on this system can never be important because of the epoxide transformation to cyclohexene diol even if the oxidant it changed. However, it will be interesting to explore this simply prepared system after the catalysts dehydration or in others oxidation reactions involving chirality to study the effect of this Mn environment on the enantioselectivity of the reaction.

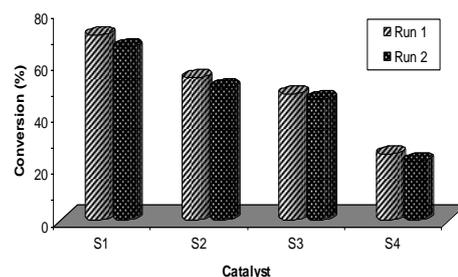


Fig. 7: Selectivity of the cyclohexene oxidation for two runs.

#### IV. Conclusions

In conclusion, we have synthesized a variety of supported catalysts where the Mn(III) salen complexes were immobilized on the surface via different strategies. The surface was used before and after modification by APTES and APTES/PDC molecules. The metal complex was modified to create an Mn(salen) with a ligand containing an amine group. This amine group was sufficient to maintain the NH<sub>2</sub>--Mn(salen) attached to the neat SiO<sub>2</sub> surface during the oxidation reaction. In this paper we have shown a partial Mn(salen) complex dissociation during its deposition at the hydrophobic surfaces. This underlines the necessity of a complete chemical analysis, in addition to spectroscopic data, to gain in-depth understanding of immobilized Mn(salen) systems and their catalytic activities. In fact, there is a paucity of studies dealing with salen-metal complex degradation during the heterogenization process and during the catalytic reaction.

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