



Silica immobilized salicylaldimine Cu(II) and Co(II) complexes as catalysts in cyclohexene oxidation: A comparative study of support effects

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ABSTRACT

Unsubstituted and tertiary-butyl substituted salicylaldimine complexes of Cu(II) and Co(II) immobilized on silica supports (MCM-41, SBA-15 and Davisil 710) were tested as catalysts for cyclohexene oxidation using hydrogen peroxide as an oxidant under an oxygen atmosphere. The effect of the nature of the salicylaldimine ligand and the type of support were investigated. Allylic species were isolated as the major products with cyclohexene-epoxide produced as a by-product in only some instances. Product selectivity was found to be greatly influenced by the nature of the support material.

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1. Introduction

Recently, more environmentally friendly processes for the oxidation of hydrocarbons to produce oxygenates (alcohols, aldehydes, ketones, acids, etc.) have become extremely important and have increasingly been applied industrially. One way of achieving this has been by combining the important features of homogeneous and heterogeneous catalysis. This can be achieved by immobilizing the catalysts on inorganic supports thereby creating a heterogeneous-like catalyst. Several of the published articles in this field have reported systems with very good selectivity but these have largely been based on iron porphyrin catalysts [1–3]. There are not many examples of immobilized salicylaldimine complexes of Cu(II) and Co(II) anchored on mesoporous and amorphous supports, although Koner et al. reported the immobilization of copper on MCM-41 [4]. However in this example the ligand was first anchored on the surface of the support followed by subsequent complexation of the metal. This system was used to oxidize cyclohexene using tertiary-butyl hydroperoxide as an oxidant to produce epoxidation products with good selectivity and yields. Baiker et al. also reported the incorporation of M(salen) type complexes into silica aero and xerogels using sol–gel techniques [5]. The material was however not tested as catalysts instead a detailed description of the characterization of these inorganic/organic hybrid materials is given in this article. Earlier work by Ratsanamy has also concentrated on the use of

zeolite-immobilized salen complexes as catalysts in phenol hydroxylation and oxidation of para-xylene [6]. Canali and Sherrington in a review reported on the preparation of immobilization of chiral complexes containing salen ligands [7]. These systems were found to be applicable as catalysts in a range of organic transformations.

Das and Clark [8] and Park et al. [9] reported the immobilization of Co(III) onto carboxylic acid functionalized HMS and SBA-15 mesoporous silica. In these systems the cobalt cation was found to be weakly bound to the surface carboxylic acid groups resulting in metal leaching occurring. In a 2006 publication Mukherjee et al. reported on copper complexes immobilized on organically modified amorphous silica as catalysts in the oxidation of alkenes using different oxidants such as dilute aqueous hydrogen peroxide and tertiary-butyl hydroperoxide under ambient conditions [10].

A recently published paper reported a one-pot synthesis of a cobalt salen catalyst immobilized on silica produced by a sol–gel process using tetraethylorthosilicate (TEOS) in the presence of the salen complex. When employed in the oxidation of cyclohexene, the catalyst yielded both allylic and epoxidation products with 2-cyclohexen-1-one as the major product followed by small amounts of cyclohexene oxide and 1,2-cyclohexanediol as by-products [11]. Luo and Lin also reported silica-supported Co and Mn salicylaldimine complexes in the oxidation styrene and found both systems more reactive than analogous homogeneous complexes [12]. An interesting variation in immobilizing catalytically active copper complexes is the report by Corma et al. in which they describe the use of metal–organic frameworks as catalyst supports [13]. The latter paper however deals with the oxidation of tetralin and not cyclohexene which is the focus of our work.

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In this paper we report the use of unsubstituted and tertiary-butyl substituted salicylaldimine Cu(II) and Co(II) complexes supported on mesoporous and amorphous supports as catalysts in cyclohexene oxidation using molecular oxygen and hydrogen peroxide as oxidants. The effect of the substituents present on the salicylaldimine ring as well as the nature of the support on the catalytic activity is also discussed.

2. Experimental

2.1. Materials

All the chemicals were obtained from Sigma–Aldrich Ltd. unless otherwise mentioned. The solvents ethanol, dichloro-methane and toluene were purchased from Kimix Ltd., South Africa and were dried using appropriate drying agents. Amorphous silica gel (Davisil, Grade 710) was obtained from Sigma–Aldrich.

2.2. Techniques

^1H NMR spectra were recorded in CDCl_3 using a Varian XR200 spectrometer. Sample signals are relative to the resonance of residual protons in the solvent. Chemical analysis for cobalt, nickel and copper was performed using atomic absorption spectroscopy on a Pye Unicam 9100 atomic absorption spectrophotometer. Powder X-ray diffraction patterns were recorded on a Bruker-AXS diffractometer using a $\text{Cu K}\alpha$ radiation ($\lambda = 1.5409 \text{ \AA}$) and a graphite monochromator at Ithemba Laboratories, Somerset West, South Africa. The samples were scanned in the 2θ range of $2\text{--}10^\circ$, with $\Delta 2\theta = 0.01$. Diffused reflectance FTIR spectra were recorded using a Perkin-Elmer Paragon 1000 PC spectrometer. The BET surface area was analysed using a Tristar 3000 Micromeritics Surface Area and Porosity Analyzer at the Chemical Engineering Department of the University of Cape Town, South Africa. Prior to the measurement, the samples were initially degassed at 90°C for 1 h and then heated to 165°C over 1 h under N_2 at a pressure of 70 bar.

2.3. General synthesis of ligands, **L1** and **L2**

The synthetic procedure for salicylaldimine ligands (**L1** and **L2**) followed the method previously described in the literature [14–16]. The ligands were synthesized by condensation of 3-aminopropyl triethoxysilane with salicylaldehyde to produce (**L1**) and 3,5-ditertiarybutyl-salicylaldehyde to produce (**L2**). Thus for example 3-aminopropyl triethoxysilane (5 mmol) was dissolved in dry ethanol (5 ml). To this was added a solution of the salicylaldehyde (5 mmol) in ethanol (5 ml). The mixture was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure yielding the product as a yellow oil. Both products obtained were stored under vacuum since these ligands tend to undergo hydrolysis over time if left in air at room temperature.

2.3.1. Characterization data, **L1**

^1H NMR (CDCl_3) $\delta = 0.73$ (t, $^3J_{\text{H,H}} = 8.4 \text{ Hz}$, 2H, Si- CH_2), 1.27 (t, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 9H, Si-O CH_2CH_3), 1.87 (t, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 2H, NCH_2), 3.63 (m, 2H, NCH_2CH_2), 3.88 (q, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 6H, Si-O CH_2), 6.95 (m, 2H, Ar), 7.18 (m, 2H, Ar), 8.36 (s, 1H, N **CH**). IR (cm^{-1} , neat between NaCl plates): 1632 ($\nu_{\text{C=N}}$), 1280 ($\nu_{\text{C-O}}$), 1582–1342 ($\nu_{\text{C=C}}$), 1186–1094 ($\nu_{\text{Si-O}}$).

2.3.2. Characterization data, **L2**

^1H NMR (CDCl_3) $\delta = 0.78$ (t, $^3J_{\text{H,H}} = 8.4 \text{ Hz}$, 2H, Si- CH_2), 1.26 (t, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 9H, Si-O CH_2CH_3), 1.31 (s, CCH_3), 1.44 (s, CCH_3), 1.90 (t, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 2H, NCH_2), 3.61 (m, 2H, NCH_2CH_2), 3.88 (q, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 6H, Si-O CH_2), 7.09 (d, 2H, Ar), 7.37 (d, 2H, Ar), 8.35 (s,

1H, N **CH**). IR (cm^{-1} , neat between NaCl plates): 1630 ($\nu_{\text{C=N}}$), 1250 ($\nu_{\text{C-O}}$), 1596–1342 ($\nu_{\text{C=C}}$), 1120–1078 ($\nu_{\text{Si-O}}$).

2.4. Complex formation

The preparation of **Complexes 1–4** was performed using the method described previously for other salicylaldimine complexes [17]. Thus the appropriate ligand (1.54 mmol) was reacted with either copper(II) acetate monohydrate or Co(II) acetate tetrahydrate (0.77 mmol) in dry ethanol (5 ml) as the solvent. The crude **Complex 1** was obtained as an oily residue. The product was isolated by triturating the oily residue with acetonitrile at low temperature (-5°C) to obtain a green solid.

IR (cm^{-1} , recorded as KBr pellet): 1610 ($\nu_{\text{C=N}}$), 1124–1066 ($\nu_{\text{Si-O}}$), 1172 ($\nu_{\text{C-O}}$). Anal. calc. (%) for $\text{C}_{32}\text{H}_{52}\text{CuN}_2\text{O}_8\text{Si}_2$: C, 53.94; H, 7.36; N, 3.93. Found (%): C, 53.74; H, 7.18; N, 3.43.

Similarly **Complex 2** was also isolated as a dark green solid. IR (cm^{-1} , recorded as KBr pellet): 1618 ($\nu_{\text{C=N}}$), 1134–1066 ($\nu_{\text{Si-O}}$), 1172 ($\nu_{\text{C-O}}$). Anal. calc. (%) for $\text{C}_{32}\text{H}_{52}\text{CoN}_2\text{O}_8\text{Si}_2$: C, 54.30; H, 7.40; N, 3.96. Found (%): C, 53.94; H, 7.19; N, 3.23.

Complex 3 was isolated as a dark brown solid. IR (cm^{-1} , KBr pellet): 1622 ($\nu_{\text{C=N}}$), 1124–1038 ($\nu_{\text{Si-O}}$), 1194 ($\nu_{\text{C-O}}$). Anal. calc. (%) for $\text{C}_{48}\text{H}_{84}\text{CuN}_2\text{O}_8\text{Si}_2$: C, 61.53; H, 9.04; N, 2.99. Found (%): C, 61.01; H, 9.64; N, 2.29.

Complex 4 was isolated as a yellow orange solid. IR (cm^{-1} , recorded as KBr pellets): 1608 ($\nu_{\text{C=N}}$), 1132–1026 ($\nu_{\text{Si-O}}$), 1192 ($\nu_{\text{C-O}}$). Anal. calc. (%) for $\text{C}_{48}\text{H}_{84}\text{CoN}_2\text{O}_8\text{Si}_2$: C, 61.84; H, 9.08; N, 3.00. Found (%): C, 61.22; H, 9.59; N, 2.18.

2.5. Synthesis of mesoporous silica supports

The mesoporous silica supports MCM-41 and SBA-15 were prepared according to a synthetic route reported previously [18,19].

2.6. Immobilization of complexes onto inorganic silica supports

2.6.1. Preparation of immobilized catalyst

The immobilization of all the complexes was done as illustrated below using the copper system on Davisil 710 (amorphous silica) as an example.

The bis-(propyltriethoxysalicylaldimine) Cu(II) complex, **Complex 1** (0.10 g) was added to a slurry of 1.0 g of commercial silica gel, Davisil 710 in dry toluene (10 ml) in a 100 ml round bottom flask. The mixture was refluxed under a nitrogen atmosphere at 110°C for 24 h. The solution was filtered using gravity filtration, washed with several portions of toluene followed by dichloromethane (20 ml) to remove any unreacted metal complex. The dark green powder was dried under vacuum for 24 h. The product was stored in a nitrogen-purged glove box until further use.

2.7. Oxidation of cyclohexene

A Radley's Discovery Technologies 12 Place Heated Carousel Reaction Station fitted with a reflux unit as well as a gas distribution system was used to perform cyclohexene oxidation reactions in 45 ml glass reactors. In a typical reaction the catalyst (0.01 mmol of metal used) and cyclohexene (10 mmol) were transferred to the glass reaction vessel followed by 3 ml of acetonitrile. It should be noted that the level of metal concentration was kept at 0.01 mmol for all reactions irrespective of the metal loading on the catalyst support. Thus different masses of catalyst material were employed for the different catalysts. The temperature was set at 60°C while stirring the solution. When the desired temperature was reached, a 30% hydrogen peroxide solution (10 mmol) was added to the stirred solution. The reaction was allowed to proceed for 5 h after which a 1 ml of sample was withdrawn from the reactor. The reaction

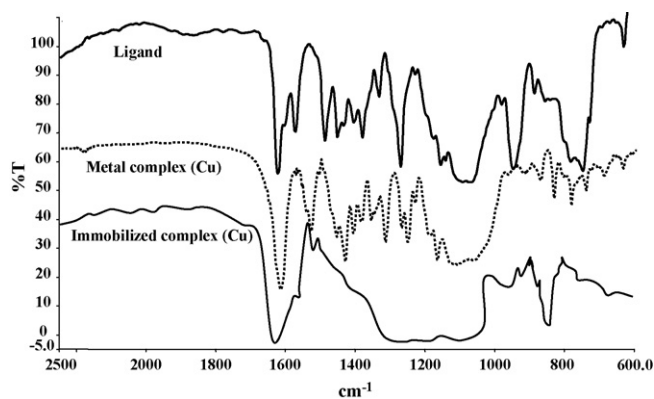


Fig. 1. FTIR spectra of the ligand, a metal complex and an immobilized catalyst.

range of supported catalysts prepared is illustrated in Table 1 while the preparative route to immobilized catalysts is illustrated in Scheme 1.

3.1. Physicochemical characterization

IR spectroscopy studies show that the $\nu(\text{C}=\text{N})$ band for the ligands shifts to lower wavenumbers for the metal complexes. Thus in the case of the copper **Complex 1**, the shift is from 1632 cm^{-1} in the free ligand to about 1620 cm^{-1} in the complex. The $\nu(\text{C}=\text{N})$ band is also observed in the immobilized catalysts although in this case it is much weaker. $\nu(\text{Si}-\text{O})$ vibrations were also observed in the range $1186\text{--}1094\text{ cm}^{-1}$ for the ligand. These shift to slightly lower wavenumbers for the metal complexes and occur in the region $1134\text{--}1066\text{ cm}^{-1}$. Typical IR spectra are shown in Fig. 1. The metal complexes were also characterized by ESI mass spectrometry, which confirms the identity of the complexes.

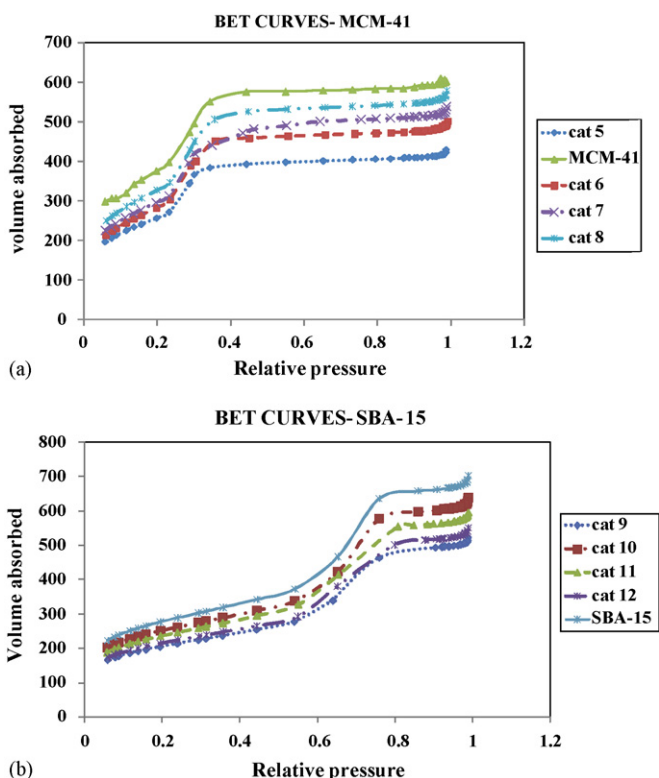


Fig. 2. (a) Nitrogen adsorption isotherm of MCM-41. (b) Immobilized catalysts and SBA-15 (right) immobilized catalysts.

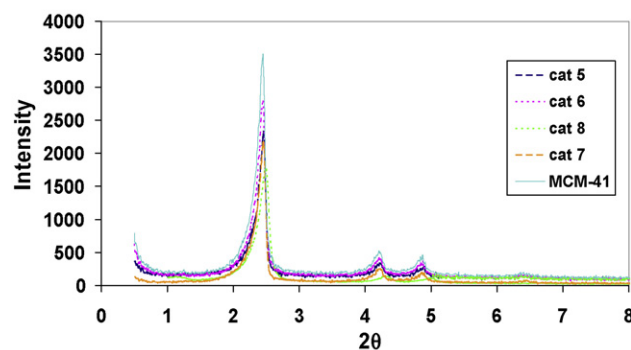


Fig. 3. XRD plots of MCM-41 immobilized catalysts.

Atomic absorption spectroscopy was used to determine the metal loading for each of the immobilized catalyst (see Table 1). The metal loading of these immobilized systems differs with respect to the type of metal used, the nature of the support and the type of ligand employed. From the results in Table 1, it can be seen that the Davisil immobilized systems have slightly higher metal loading than both the MCM-41 and SBA-15 immobilized systems irrespective of the type of metal used. This is probably due to the fact that the Davisil 710 support is uncalcined while both the MCM-41 and SBA-15 supports were calcined prior to the immobilization of the metal complexes. The calcination of the support would reduce the number of silanol groups on the surface of the material. This would lead to less of the complex being anchored. It can also be seen that in most cases the extent of immobilization of the cobalt complexes is lower than for the copper systems irrespective of the type of silica support used. The exception being the Co complexes which have ^tBu substituents on the salicylaldimine ligands. This is most likely due to differences in the solubility of the complexes in the solvent used during the immobilization process. The copper complexes generally show higher solubility in toluene, the solvent used to disperse the metal complexes onto the support material.

The immobilized catalysts were also characterized by BET surface area analysis. Both the native support materials as well as the post-immobilized materials were subjected to surface area analysis. In all cases the BET surface analysis of the native supports as well as the immobilized catalysts shows adsorption isotherms that resemble TYPE IV plots which are typical of mesoporous materials. In both the MCM-41 and SBA-15 systems, the immobilized catalysts show surface areas which are marginally lower than that of the native supports. Thus immobilization of the catalysts on the supports does not have a significant impact on the surface area of the catalytic materials. On the whole the surface area for MCM-41 systems is higher than their SBA-15 counterparts. Thus, for example,

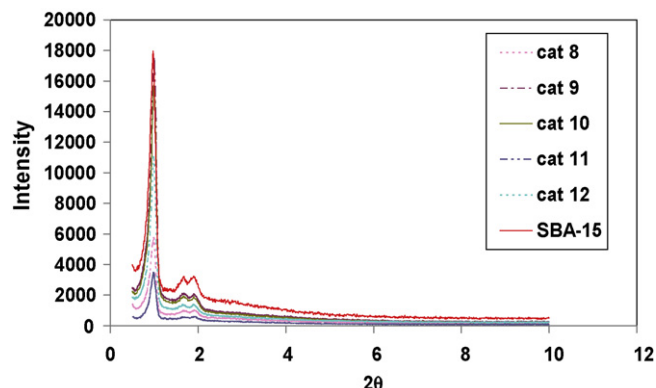


Fig. 4. XRD plots of SBA-15 immobilized catalysts.

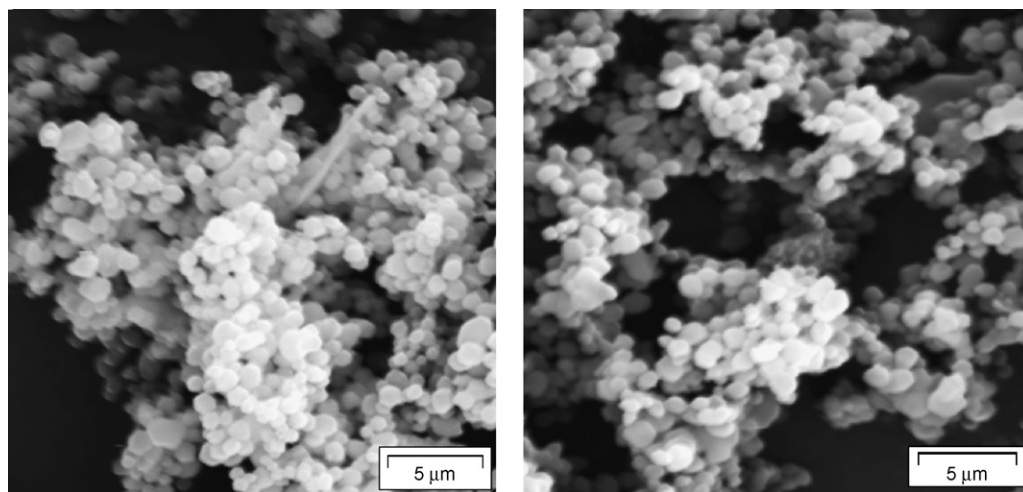


Fig. 5. SEM micrographs of pure MCM-41 (left) and immobilized catalyst on MCM-41 (right).

the surface area for MCM-41 based catalysts ranges from 1190.10 to 928.35 m²/g and for those supported on SBA-15, the BET surface area ranges from 943.30 to 842.93 m²/g. For both the MCM-41 and SBA-15 based materials, the copper complexes having the unsubstituted salicylaldehyde as a ligand showed the lowest surface area. From the results it can also be seen that the cobalt based systems have slightly higher surface areas. This appears to be closely related to the degree of immobilization of the metal complex. The higher the metal loading on the support, the lower the surface area (Fig. 2).

Nitrogen adsorption measurements suggest that native SBA-15 has a larger average pore size than the native MCM-41 as the capillary condensation of SBA-15 occurs at higher relative pressures ($P/P_0 = 0.6–0.85$) than MCM-41 catalysts ($P/P_0 = 0.25–0.6$). This confirms to what was previously reported in the literature [19–21]. The BET average pore diameters of the SBA-15 and MCM-41 immobilized catalysts also differ, with average pore diameter of SBA-15 immobilized catalysts ranging from 43.4 to 44.40 Å whereas for MCM-41 immobilized catalysts, average pore diameter as determined via BET calculations ranges from 28.53 to 30.90 Å. Very little change in pore sizes is observed after immobilization.

3.1.1. XRD studies

The supported catalysts were also studied by XRD. This reveals that the supports essentially retain their crystallinity after immobilization of the metal complexes. Representative XRD plots for both the MCM-41 and SBA-15 systems are shown in Figs. 3 and 4. In the case of the MCM systems it can be seen that post immobilization, we still observe peaks at 2θ values of 2.5°, 4.2°, 4.8° and 6.6°. Similarly SBA-15 shows three peaks at 2θ values of 1°, 1.7° and 1.9° indicating that the mesoporous structure is maintained after immobilization. No XRD studies were carried out on the Davisil 710 based systems, since these are amorphous materials.

Scanning electron microscopy was also used to study the morphology of the immobilized catalyst systems. The SEM scans of MCM-41 materials show that they consist of spherical particles (Fig. 5). The shape of the support is retained after immobilization with the different metal complexes. The nature of the complexes does not have any significant impact on the morphology. A similar result is obtained for SBA-15 systems. The SBA-15 systems however show elongated tubes (Fig. 6) as opposed to spherical particles of MCM-41.

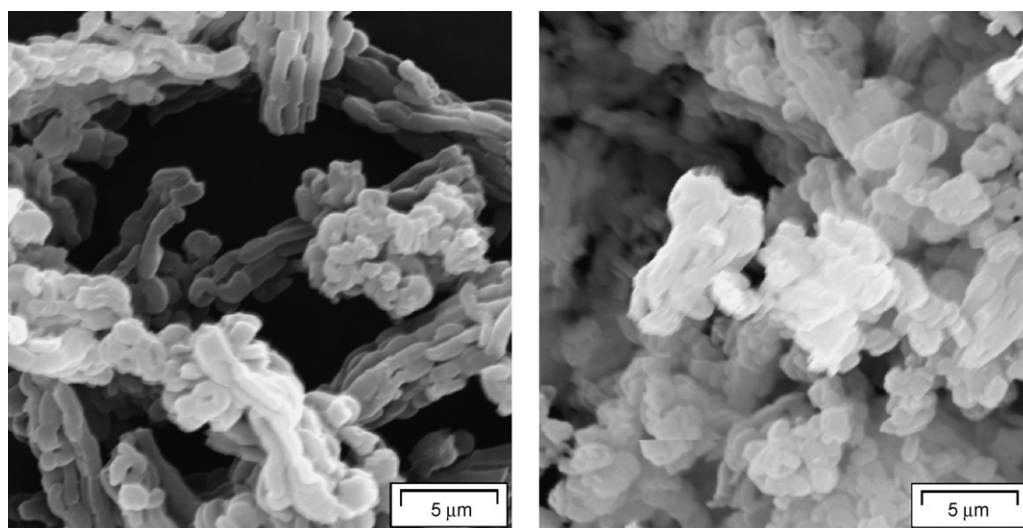
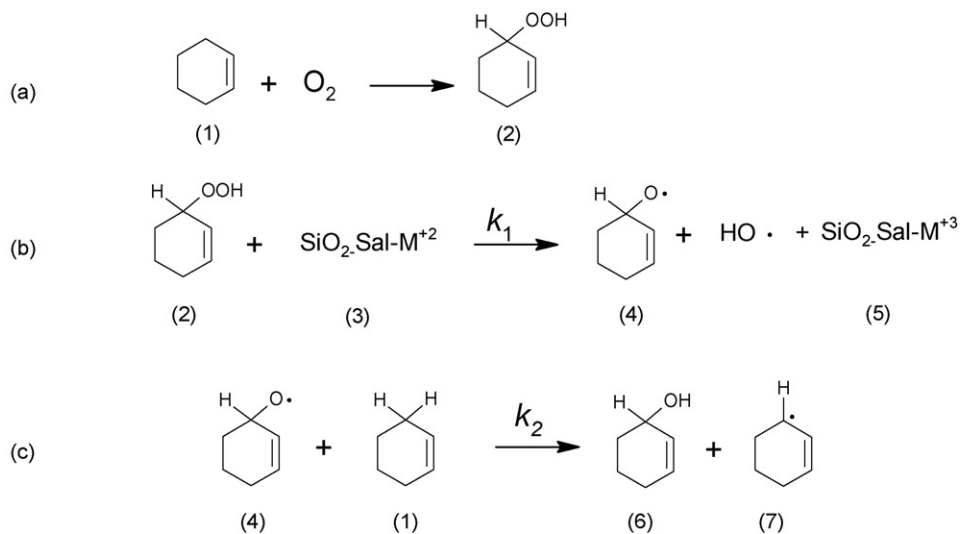
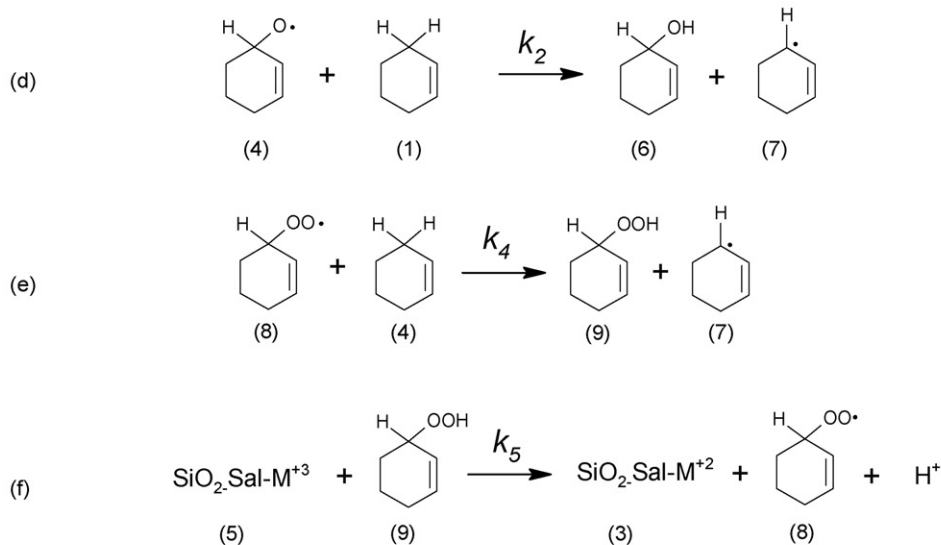


Fig. 6. SEM micrographs of pure SBA-15 (left) and immobilized catalyst on SBA-15 (right).

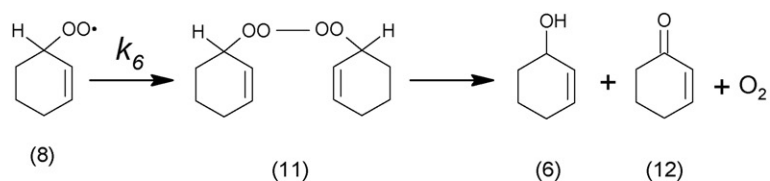
Initiation



Propagation



Termination



Scheme 2. Possible reaction pathway for the oxidation of cyclohexene.

3.2. Catalytic activity

Oxidation of cyclohexene using the various immobilized catalysts (catalysts **1–12**) was investigated in acetonitrile as solvent at 60 °C. In all cases the metal concentration was maintained at a level of 2×10^{-3} M irrespective of the metal loading of the various immobilized catalysts. H₂O₂ under an atmosphere of molecular oxygen was used as the oxidant. Attempted catalysis in the absence

of both H₂O₂ and oxygen shows no conversion of the alkene substrate. Reactions carried out using only H₂O₂ as the oxidant showed remarkably reduced oxidation activity although it was greater than using just pure oxygen. However using a combination of the two oxidants gives the best activity results. The fact that better results were obtained with H₂O₂ than with pure oxygen would suggest that the oxidation proceeds largely via a free radical auto-oxidation process and that the allylic oxidation pathway

Table 2

Cyclohexene oxidation results using 30% hydrogen peroxide as an oxidant and molecular oxygen as a co-oxidant.

Catalysts	%Conversion	Oxide	Alcohol	Ketone	Diol
1	64	0	45	46	9
2	83	0	54	46	0
3	60	0	56	44	0
4	50	0	0	100	0
5	43	0	45	55	0
6	41	0	0	100	0
7	47	0	44	56	0
8	45	0	0	56	0
9	53	0	47	49	7
10	54	0	40	49	11
11	84	1	46	48	5
12	55	0	35	55	10

is favoured. The role of the immobilized salicyaldimine complexes is to mediate the decomposition of the hydrogen peroxide via a one electron redox cycle. The proposed mechanism is outlined in Scheme 2.

The auto-oxidation free radical pathway was confirmed by the addition of the radical trap hydroquinone. Addition of 15 mg of the radical trap leads to very low conversion (~5%) of the cyclohexene after 18 h of reaction. If amounts in excess of 20 mg are added we observe no reaction at all. This result is in line what is expected for reactions proceeding via free radical auto-oxidation processes [22].

All catalysts evaluated were found to be active in the oxidation of cyclohexene with conversions varying between 41% and 84% depending on the nature of the catalyst. The performance of the various catalysts is summarized in Table 2.

3.2.1. The effect of the nature of metal on activity

In the case of the unsubstituted salicyaldimine catalysts, the cobalt complexes generally exhibit slightly higher activity than the copper complexes irrespective of the support used. The situation is reversed for the ^tBu substituted salicyaldimine catalysts where the copper catalysts have a greater activity than its cobalt analogues. The electron releasing tertiary-butyl substituents increases the reduction potential of Cu²⁺ thus making it a better oxidizing agent (Figs. 7 and 8).

3.2.2. The effect of substituents on activity

In general tertiary-butyl systems tend to be more active than the unsubstituted analogues. This is most likely due to the fact that the bulky tertiary-butyl group hinders catalyst deactivation by preventing aggregation of the active metal sites via μ -oxo dimer formation. The above trend is observed for both the cobalt and copper systems. It should also be noted that in the case of the copper systems, the

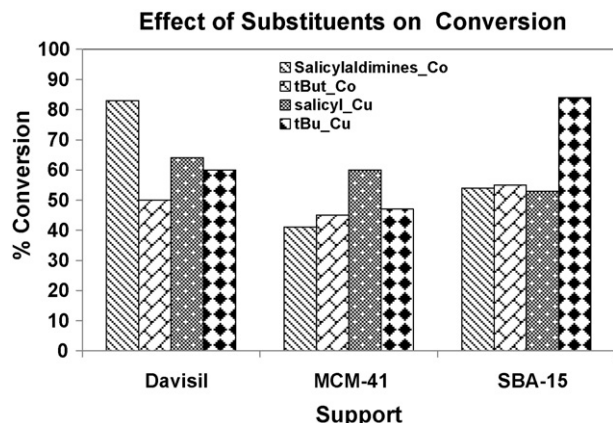


Fig. 7. Catalyst activity for the various supported catalysts.

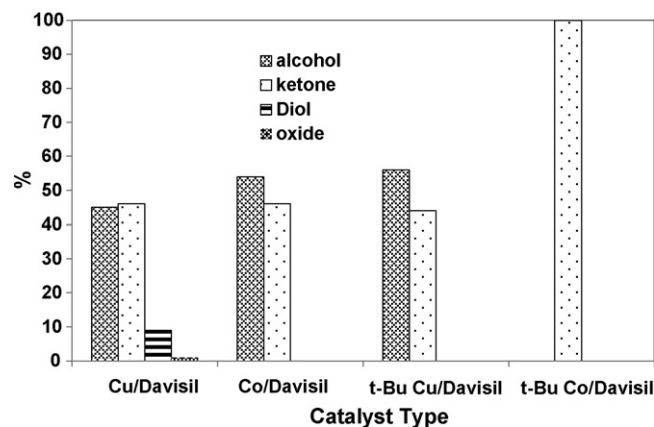


Fig. 8. Selectivity Davisil based catalysts.

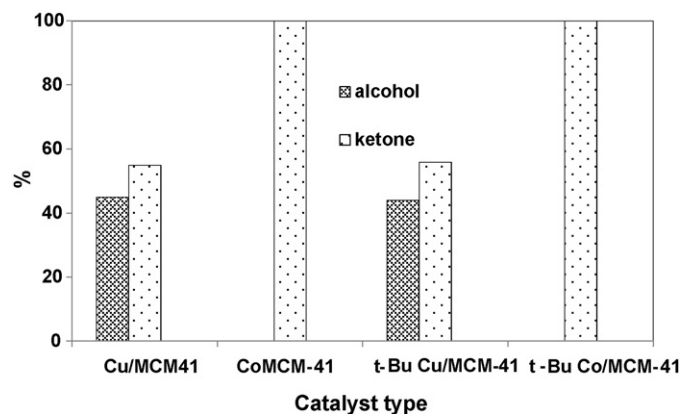


Fig. 9. Selectivity MCM-41 based catalysts.

difference in activity between the substituted and unsubstituted salicyaldimine systems is not very great Fig. 7.

3.2.3. The effect of support material on activity

The nature of the support greatly impacts the overall oxidation activity. Thus it can be seen from Fig. 7 that for the unsubstituted salicyaldimine catalyst the complexes supported on Davisil 710 show the highest activity, followed by SBA-15 and then MCM-41. This is probably due to the fact that in the case of the Davisil 710, the active sites are exposed on the surface of the support while for both MCM-41 and SBA-15 a substantial amount of the active centres

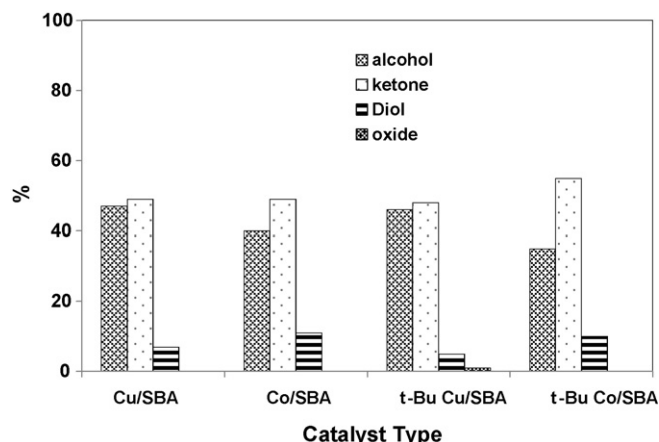


Fig. 10. Selectivity SBA-15 based catalysts.

are encapsulated within the pores of the support material. Another possibility could be differences in surface polarity of the different supports. Hermans et al., for example, showed that surface polarity played a significant role in catalyst stability. They found that silica with high polarity as a result of a high concentration of surface hydroxyls leads to facile catalyst deactivation [23]. Davisil 710 has a surface area of between 475 and 560 m²/g while MCM-14 has a surface of 1050 m²/g and SBA-15 ~950 m²/g. One would expect that high surface area supports would have higher concentrations of surface hydroxyl groups and thus higher polarity. If this is indeed the case then the Davisil silica would be expected to have the lowest concentration of surface hydroxyls and thus to be least prone to catalyst deactivation. This in turn would lead to a higher overall activity. Indeed this what is observed for the Davisil 710 systems which show the highest activity.

3.3. Selectivity

All catalysts evaluated to favour the formation of allylic oxidation products. Only in two instances were traces of epoxide detected. The preponderance of 2-cyclohexen-1-ol and 2-cyclohexen-1-one indicates that the reaction proceeds via the allylic oxidation pathway as opposed to the direct oxidation of the alkene double bond. A similar observation was made recently by Park et al. when using a Co(cyclam) functionalized SBA-15 catalyst [24]. However in their case cyclohexen-1-hydroperoxide was found to be the major product. In none of our reactions do we observe any formation of the hydroperoxide. The preponderance of allylic oxidation products and the absence of cyclohexene-oxide as a product are most likely due to the fact that reaction takes place via a radical auto-oxidation mechanism.

3.3.1. Effect of substituent on selectivity

When looking at the Davisil supported catalysts (Fig. 8), it can be seen that the substituents on the salicylaldimine ring have very little effect on the selectivity of the copper catalysts, with almost equal amounts of the alcohol and ketone being formed. In the case of the cobalt catalysts the ^tBu substituents have a dramatic effect on selectivity. In this case the substituted catalysts form exclusively the ketone. It appears that the ^tBu substituted Co system has a higher oxidation propensity than its unsubstituted analogue. This is most likely due to the electronic influence of the ^tBu substituent.

When examining the MCM-41 catalysts (Fig. 9), we once again observe that the copper catalysts are not greatly impacted by the substituents on the salicylaldimine ring. As found for the Davisil 710 systems, the cobalt catalyst, which contains a ^tBu substituent once again give the ketone exclusively. A similar situation is observed for the SBA-15 systems (Fig. 10) where the substituent essentially plays a greater role in the cobalt catalysts. Once more the substituted cobalt catalyst produces more of the ketone.

3.3.2. Effect of the support material on selectivity

The mesoporous silicas show a different behaviour when examining the selectivity. MCM-41 tends to favour ketone formation over the alcohol. SBA-15 on the other hand leads to higher levels of the alcohol being formed, although in all cases there is still a slightly higher level of the ketone. SBA-15 is also the only support on which diol formation is observed. The SBA-15 support has much larger pore sizes than the other supports and this allows it to accommodate the more bulky diol molecule within the pores. Diol formation is thought to be the result of hydrolysis of the corresponding epoxide which can also be accommodated within the pores of the SBA-15 support. Traces of the epoxide are observed in some of the reactions using the SBA-15 catalysts.

3.3.3. Effect of the metal on selectivity

From Table 2 it is clear that the cobalt catalysts generally favour the formation of the ketone. This is most obvious in the case of the MCM-41 catalysts, where both the unsubstituted and ^tBu substituted catalyst produce exclusively the ketone. Cobalt is well known for its ability to oxidize alcohols to carbonyl derivatives [25–27]. Thus it can easily oxidize the alcohol to the corresponding ketone. The copper catalysts on the other hand generally produce almost equal amounts of the alcohol and ketone.

4. Conclusion

The functionalized salicylaldimine ligands and catalysts were successfully characterized. These catalysts were successfully immobilized on different supports (MCM-41, SBA-15 and Davisil silica gel). These catalysts were tested for cyclohexene oxidation. The immobilized catalysts tested in this paper tend to favour allylic products irrespective of the substituent on the ligand and type of support used. From the results it is clear that the nature of the support plays a significant role in the selectivity observed. SBA-15 with its large pore sizes is the only support that can facilitate the formation of 1,2-hexanediol. The nature of the metal also plays a role in product selectivity with the cobalt catalysts favouring the production of cyclohexanone as opposed to the alcohol.

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