Catalytic hydroxylation of phenol using immobilized late transition metal salicylaldimine complexes

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Abstract

Immobilized late transition metal complexes based on salicylaldimine ligands were used as catalysts in the wet air hydroxylation of phenol in the presence of hydrogen peroxide. Three metals, viz. cobalt, nickel and copper, and two different kinds of supports, namely, amorphous silica and mesoporous MCM-41, were employed. The effect of pH on the hydroxylation process was also investigated. It was observed that the regioselectivity of the hydroxylation process strongly depends on the kind of support employed.
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1. Introduction

Catechol and hydroquinone have a very wide range of applications, ranging from pharmaceuticals to polymers, photographic and agrochemical materials. Wet air oxidation of phenol is a well-known synthetic route to produce these dihydroxybenzenes. Most of the common techniques for wet oxidation of phenol involve the use of hydrogen peroxide as an oxidant. The advantage of hydrogen peroxide over other potential oxidants is its relative stability. In addition, hydrogen peroxide is a relatively strong oxidant.

Examples of homogeneous processes known to produce dihydroxybenzenes are the Rhône-Poulenc process [1], where the oxidation of phenol is catalyzed by strong mineral acids, or the Hamilton process [2], where Fenton reagent is used as a catalyst. These processes, being homogeneous in nature, face difficulties with continuous operation, catalyst recovery and separation. The use of heterogeneous catalysts can eliminate such difficulties. Titanium silicate (TS-1), which is a titanium containing zeolite, is one of such heterogeneous catalysts [3]. One of the advantages of TS-1 is higher para selectivity, which is attributed to the

shape selectivity of the catalyst [4–10]. Another advantage of this catalyst is the higher phenol conversion and the low amount of tar formation. However, the difficult preparative method for TS-1 makes it a less desirable option for phenol hydroxylation. Several other heterogeneous systems have been tried for the hydroxylation of phenol. These include metals encapsulated within zeolites [11–21] and metals encapsulated in pillared clays [22]. Several metals, such as iron, cobalt, nickel and copper have been tried as catalysts in the phenol hydroxylation processes. All of the above-mentioned heterogeneous systems involve the physical absorption of metal salts or metal complexes on the inorganic support.

In this paper we report on salicylaldimine complexes of cobalt, nickel and copper chemically immobilized on two different kinds of materials, namely, amorphous silica and mesoporous MCM-41. These systems were evaluated as catalysts in phenol hydroxylation over a range of pH values. The effect of the nature of the support on catalyst performance was also evaluated.

2. Experimental

2.1. Materials

All the chemicals were procured from Sigma–Aldrich Ltd. unless otherwise mentioned. The solvents ethanol, dichloro-

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methane and toluene were procured from Kimix Ltd., South Africa and were dried using appropriate drying agents. Amorphous silica gel (Davisil, Grade 710) was procured from Sigma–Aldrich. MCM-41 was synthesized using a reported method [23] employing tetraethylorthosilicate as the starting material and cetyltrimethylammonium bromide as the template.

2.2. Techniques

^{1}H 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 Cu Kα radiation ($\lambda = 1.5409$ Å) and a graphite monochromator at Ithemba Laboratories, Somerset West, South Africa. The samples were scanned in the 2θ range of 2–10°, 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 analyzed 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 degassed at 90 °C for 1 h and ramped to 165 °C over 1 h at a pressure of 70 bar. The analysis bath was kept at 77 K. Analysis of the catalysis products was carried out on a HP 1090 Liquid Chromatograph. A ZORBAX® SB-C18 column of dimension 4.6 mm × 150 mm was used to analyze the residual phenol, and the resulting catechol and hydroquinone in the reaction mixture. The mobile phase used was a mixture of 0.1% formic acid solution and acetonitrile.

2.3. Synthesis of the salicylaldiminato complex

Synthesis of the ligand was performed using a reported method with slight modifications [24,25]. Aminopropyl triethoxysilane (2.21 g, 10 mmol), dissolved in 10 mL of dry ethanol, was added to salicylaldehyde (1.22 g, 10 mmol). To it 30 mL dry ethanol was added. The resulting mixture was refluxed for 2 h. The solvent was removed in *vacuo*. The resulting viscose orange oil was dissolved in dichloromethane and washed with two 10 mL portions of water. The organic layer was separated and then dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off and the solvent was removed to obtain the salicylaldimine ligand (A). Yield = 68%. ^{1}H NMR (CDCl$_3$) $\delta = 0.68$ (t, $^3J_{H,H} = 8.4$ Hz, 2H, Si–CH_2), 1.23 (t, $^3J_{H,H} = 7.0$ Hz, 9H, Si–OCH$_2$CH_3), 1.82 (t, $^3J_{H,H} = 7.0$ Hz, 2H, NCH_2), 3.627 (m, 2H, NCH$_2$CH_2), 3.82 (q, $^3J_{H,H} = 7.0$ Hz, 6H, Si–OCH_2), 6.93 (m, 2H, Ar), 7.29 (m, 2H, Ar), 8.33 (s, 1H, N=CH). IR (cm^{-1}, chloroform) 1637 (ν C=N), 1267 (ν C–O), 1475 (δ CH$_{3\,as}$), 1380 (δ CH$_{3\,s}$). The cobalt, nickel and the copper salicylaldimine complexes were prepared using a reported method [24].

2.4. Immobilization of the metal complexes

The solid supports (MCM-41 and amorphous silica, Davisil 710) were degassed under vacuum at 100 °C overnight prior to use. The solid support (1.0 g) was transferred into a 100 mL round bottomed flask and to it 100 mg (∼0.14 mmol) of the salicylaldimine complex followed by dry toluene (20 mL) were added. The slurry was refluxed for 4 h. At the end of the refluxing period, the solid was filtered and washed repeatedly first with toluene (5× 20 mL) followed by copious amounts of dichloromethane until the washing were completely colourless. The solids obtained were collected and dried under vacuum at room temperature for 10 h [26]. The metal loading of the various immobilized catalysts was determined using Atomic-Absorption Spectroscopy.

2.5. Phenol hydroxylation experiments

Batch reactions were carried out using a Radley's Discovery Technologies 12 place Heated Carousel Reaction Station fitted with a Reflux unit as well as a gas distribution system. The reactions were performed in 45 mL glass reactors using deionized water buffered at the appropriate pH as a solvent. Requisite amounts of the catalyst giving 0.01 mmol metal, was added to the glass reactor, followed by 1 mmol of phenol and 10 mL of the buffered solvent, which had previously been saturated with oxygen. The resulting mixture was stirred at 110 °C for 15 min under an oxygen blanket, after which 1 mmol of 6% H$_2$O$_2$ was added to the solution. The reaction was allowed to continue for 6 h at 110 °C under a constant flow of oxygen. After completion of the reaction, the products formed were analyzed by HPLC after diluting the sample a 100 times with deionized water. Samples were filtered through a nylon syringe filter membrane of 0.45 μm, thickness prior to injection onto the HPLC column.

3. Result and discussion

In the current study, the effect of two different types of support systems were investigated, viz. amorphous silica (Davisil 710) and mesoporous MCM-41 using three different metal salicylaldimine complexes, namely, cobalt, nickel and copper (Table 1, Scheme 1). Liquid phase hydroxylations of phenol were carried out in conjunction with H$_2$O$_2$ at a controlled pH (2–6 range). The pH of the reaction medium was controlled by using appropriate buffer solutions.

Table 1
Catalyst code and the metal content

Catalyst code	Metal	Inorganic support	Metal (wt%)
Im1	Cu	MCM-41	0.28
Im2	Co	MCM-41	0.64
Im3	Ni	MCM-41	0.58
Im4	Cu	Silica	0.40
Im5	Co	Silica	1.05
Im6	Ni	Silica	1.01
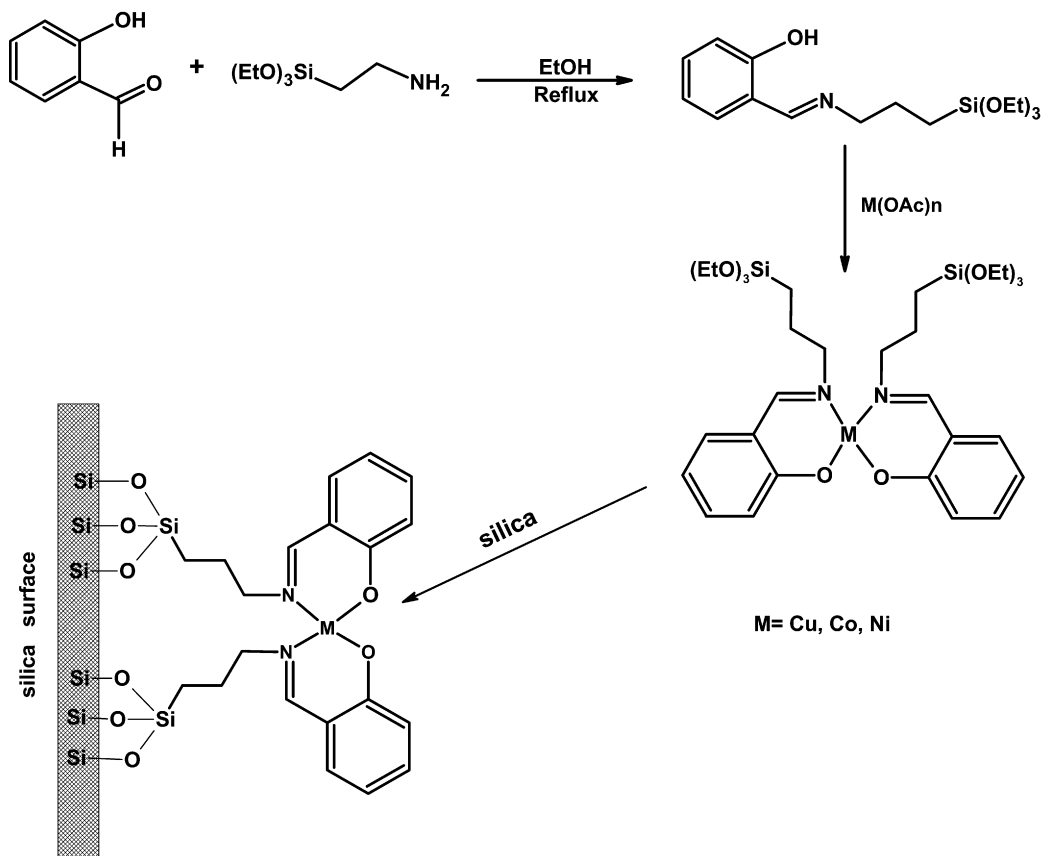
Scheme 1. Synthetic route of the supported salicylaldimine complex.

3.1. Physicochemical characterization

The infrared spectrum of the free ligand (before complexation) shows a band at 1637 cm^{-1}, which can be attributed to the C=N stretching frequency of the imine group. The diffused reflectance FTIR of the silica supported and the MCM-41 supported catalysts are shown in Figs. 1 and 2. In all cases a sharp band around 1625 cm^{-1} appeared, which was assigned to the C=N stretching frequency of the complexed ligand [25].

X-ray diffraction analysis of the synthetic MCM-41 revealed high degree of crystallinity of the material (Fig. 3). The X-ray diffraction pattern of the material after supporting of the metal complex also showed high degree of crystallinity.

Table 2 summarizes the BET surface area and the average pore size of the pure MCM-41 and that of the three MCM-41
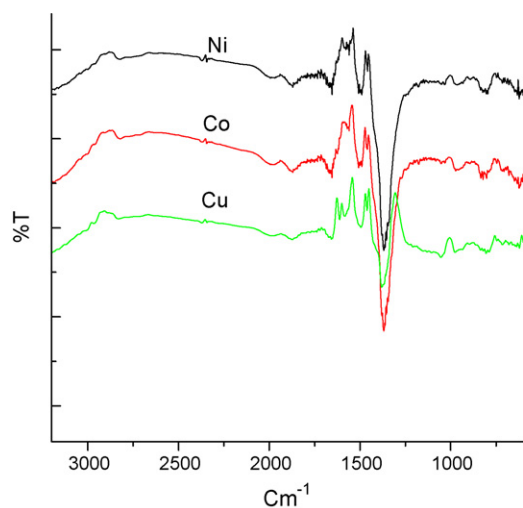

Fig. 1. Diffused reflectance FTIR spectra of the silica (Davisil 710) supported salicylaldimine complexes.
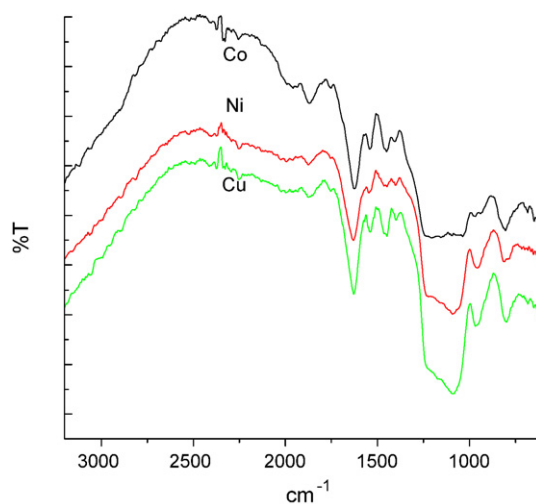

Fig. 2. Diffused reflectance FTIR spectra of the MCM-41 supported salicylaldimine complexes.
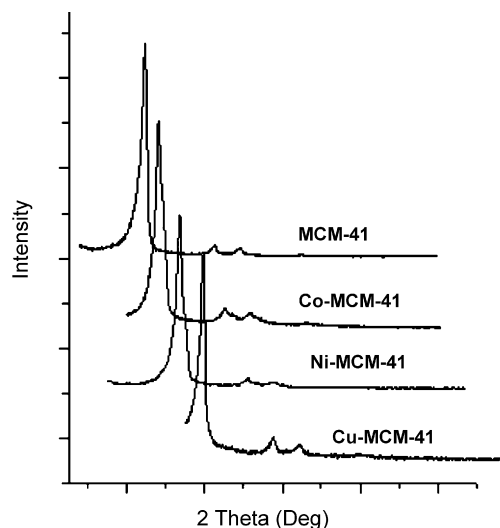
Fig. 3. X-ray diffraction pattern of MCM-41 compared to that of the MCM-41 supported catalysts.

Table 2
Surface area analysis of the MCM-41 supported catalysts

Sample	Surface area (BET, m^2/g)	Adsorption average pore diameter (BET, Å)
MCM-41	1050	28.43
Im1	1011	28.30
Im2	996	29.82
Im3	1029	28.23

Table 3
Hydroxylation of phenol in MCM-41 supported catalyst

Entry	Sample	pH	% phenol consumed	TOF[a]	HQ:CAT[b]
1	**Im1**	2	53.3	8.88	HQ[c]
2	**Im1**	3	49.9	8.32	3.08
3	**Im1**	4	54.5	9.09	3.11
4	**Im1**	5	66.0	11.0	4.11
5	**Im1**	6	76.0	12.67	3.14
6	**Im2**	2	56.2	9.37	2.70
7	**Im2**	3	47.4	7.90	2.16
8	**Im2**	4	36.9	6.15	1.91
9	**Im2**	5	26.2	4.37	1.47
10	**Im2**	6	38	6.33	3.90
11	**Im3**	2	39.3	6.55	HQ
12	**Im3**	3	53.4	8.9	6.11
13	**Im3**	4	45.4	7.57	2.92
14	**Im3**	5	45.1	7.52	4.50
15	**Im3**	6	53.6	8.93	5.85

[a] (moles phenol consumed)/(moles metal) h.
[b] HQ, hydroquinone; CAT, catechol.
[c] Only hydroquinone is formed.

supported catalysts. The N_2 adsorption isotherm of MCM-41 shown in Fig. 4 corresponds to a type IV adsorption isotherm suggesting mesoporosity [27]. The surface areas and the average pore diameters of the immobilized catalysts are comparable to that of the native MCM-41 indicating that the high surface area framework of the support is retained after immobilization of the metal complexes on its surface.

Determination of the metal content of the supported catalysts revealed that the metal loading for the catalysts immobilized on amorphous silica were always greater than those on the MCM-41 (Table 1). This is expected, as the metal complexes were
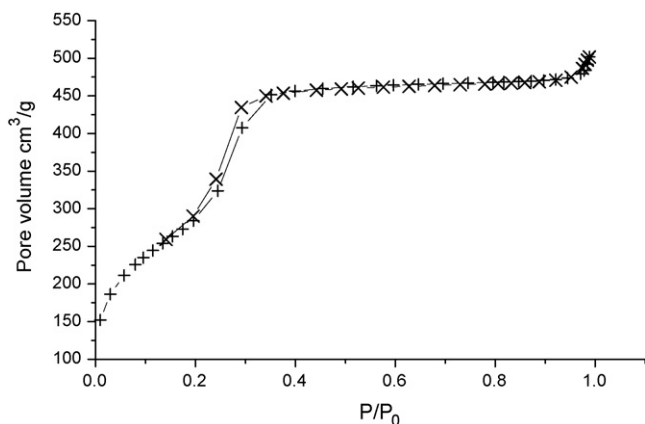
anchored to the surface by reacting to the free hydroxyl groups present on the support surface. Also the free hydroxyls available on the surface of the amorphous silica should be higher than that available on the surface of MCM-41, as MCM-41 was calcined at 550 °C, which led to a substantial depletion of the free hydroxyl groups. No such calcination was performed in case of the amorphous silica support. It was also observed that the loading of the cobalt and the nickel catalysts were much higher than that of the copper catalysts in both the silica and the MCM-41 supported materials. This might be due to the differences in the solubility of the metal complexes which are used as precursors for the immobilized catalysts. It is expected that the difference in solubility would be important during the immobilization process.

3.2. Hydroxylation of phenol

Phenol hydroxylations using all six catalysts (**Im1–Im6**) were carried out in buffered solutions over a pH range of 2–6. In each case a phenol:metal ratio of 100:1 was employed. A 6% H_2O_2 solution was used as a co-oxidant at a phenol:H_2O_2 ratio of 1:1. In all experiments the molar amount of the metal used, was kept constant at 0.01 mmol. Products were analyzed using HPLC and results are tabulated in Table 3 (for MCM-41 supported catalysts) and Table 4 (for amorphous silica supported catalysts). Other than hydroquinone and catechol as hydroxylation products there is also formation of small amount of benzoquinone in some cases.

3.2.1. Effect of pH on the phenol conversion

In the case of the amorphous silica supported catalysts (Table 4, Fig. 5), the copper systems outperformed the catalysts based on the other two metals. This is the case over the whole range of pH values evaluated. The highest phenol conversion is obtained using the copper supported system at pH 2. The copper catalyst system shows a slow decrease in activity from pH

Fig. 4. N_2 adsorption isotherm of MCM-41.

Table 4
Hydroxylation of phenol in amorphous silica (Davisil 710) supported catalysts

Entry	Sample	pH	% phenol consumed	TOF[a]	HQ:CAT[b]
16	**Im4**	2	62.5	10.42	0.81
17	**Im4**	3	51.4	8.57	0.89
18	**Im4**	4	45.2	7.54	0.89
19	**Im4**	5	40.0	6.67	0.88
20	**Im4**	6	47.8	7.96	0.76
21	**Im5**	2	2.2	0.37	CAT[c]
22	**Im5**	3	27.9	4.65	0.45
23	**Im5**	4	9.7	1.61	0.39
24	**Im5**	5	10.1	1.69	0.34
25	**Im5**	6	11.4	1.89	CAT
26	**Im6**	2	19.3	3.22	0.48
27	**Im6**	3	43.2	7.21	0.49
28	**Im6**	4	16.0	2.67	0.48
29	**Im6**	5	6.8	1.13	CAT
30	**Im6**	6	0.0	0.0	–

[a] (moles phenol consumed)/(moles metal) h.

[b] HQ, hydroquinone; CAT, catechol.

[c] Only catechol is formed.

2 to 6. The other two metals, Co and Ni show optimum activity around pH 3, with nickel having a slightly higher activity than cobalt. The former however, is still less active than copper at the corresponding pH. As was the case for copper, both the nickel and cobalt systems showed a drop-off in activity as pH is increased above 3. The decrease in activity with increasing pH is more dramatic for the nickel system with the catalyst being either completely inactive or showing very low activity at higher pH. Similar pH effects have previously been observed where it was shown that alkaline pH leads to catalyst deactivation [28]. It appears that acidic media favors metal-assisted decomposition of H_2O_2 to the hydroxyl radical, which is an important step in the hydroxylation of phenol [14,29]. In the case of cobalt, the effect of pH is not as dramatic, with fairly similar conversions obtained at a number of different pH values.
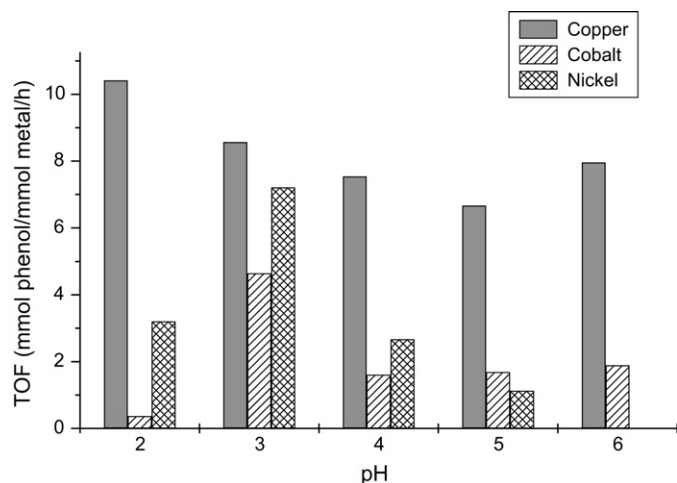

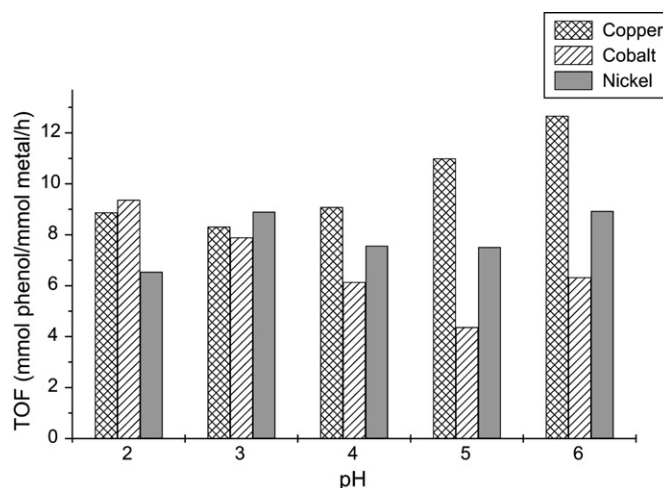Fig. 5. Effect of pH on catalytic activity of catalysts immobilized on silica Davisil 710.

Fig. 6. Effect of pH on catalytic activity of catalysts immobilized on MCM-41.

In the case of the MCM-41 supported catalysts, we see a completely different picture (Table 3, Fig. 6). There is in general a higher catalytic activity than is the case using the analogous amorphous silica for the all the metal systems. Liu et al. reported a similar enhancement in the catalytic activity in case of MCM-41 supported iron(II)-8-quinolinol catalyst when compared to the homogeneous counterpart [14]. The reason for this was attributed to either the high localized concentration of the substrate in the channels of MCM-41 or distortion of the iron(II) complexes by the pore wall of the MCM-41. Similar conclusions can also be drawn in our case. Recently Wang et al. reported hydroxylation of phenol by copper-containing SBA-15, and they observed that the catalytic activity of the catalyst is 17.5% higher when the copper is within the framework of the support, when compared to the extra-framework Cu(II) supported on SBA-15 [29].

Considering the MCM-41 supported copper catalyst (**Im1**), the activity increases as the pH increases from 2 to 6, the highest activity being at pH 6. In the case of the cobalt (**Im2)** and the nickel (**Im3**) catalysts the activity is consistently high over the pH range 2–6. Thus it can be observed that the pH has much less dramatic effect on the activity of the catalyst in case of the MCM-41 supported systems.

3.2.2. Formation of hydroquinone and catechol as the hydroxylation products

The pH of the reaction medium also impacts on the ratio of catechol to hydroquinone produced. In the case of the amorphous silica supported copper system (**Im4**), the ratio of catechol to hydroquinone varies between 1.12:1 and 1.32:1 over the pH range examined (Table 4). It is clear that the change in pH does not have a dramatic influence on the catechol:hydroquinone ratio for the copper system. The effect of pH on the catechol:hydroquinone ratio is more pronounced for both the amorphous silica immobilized cobalt (**Im5**) and nickel catalyst (**Im6**) systems. Catechol is the more preferred product in both of the systems, the highest catechol:hydroquinone ratio is obtained at pH 4. In the case of the cobalt system there is an overall decrease in the hydroquinone level in the reaction

mixture. This culminates in the exclusive production of only catechol at pH 6. A similar situation is observed for the nickel catalyst where the selectivity to catechol is 100% at pH 5. It must however be pointed out that the level of conversion at pH 5 and above is lower than that at a more acidic pH. This is in fact a general observation that the selectivity to catechol is much higher at lower phenol conversion.

In the case of the MCM-41 supported systems we see a dramatic change in the relative proportion of hydroquinone and catechol in the products (Table 3). In all cases hydroquinone is the predominant product. The relative proportion of hydroquinone is higher in case of the nickel catalyst (**Im3**) followed by the copper catalyst (**Im1**) and the cobalt catalyst (**Im2**). Thus there is a clear demonstration of the regioselectivity in this case. Also worth noting is the fact that the hydroquinone:catechol ratio is less sensitive to the overall activity, if compared to the amorphous silica supported systems. We propose that in case of the amorphous silica supported systems, where the organometallic complexes are probably anchored largely on the surface, there is no shape selectivity. In such a situation catechol, which is the kinetically preferred product, is predominantly formed. However, due to its unique channel-like structure, MCM-41 can impart regioselectivity on the hydroxylation product, giving rise to a higher proportion of hydroquinone. Similar observations were reported previously by Sobczak et al. [13], where MCM-41 containing niobium in the framework and extra-framework copper, have been found to show high para selectivity for phenol hydroxylation. These authors proposed that the Nb$^+$ species in the skeleton chemisorbed the phenol via the oxygen of the OH group. Partial leaching of copper causes homolytic decomposition of the H_2O_2 forming $^\bullet$OH radical which can attack the phenol only in the *para* position due to steric reasons and the phenol hydroxylation selectivity observed.

A close examination of the results reveals that in general the copper catalysts (**Im1** and **Im4**) preferably form hydroquinone over catechol, whereas the cobalt catalysts (**Im2** and **Im5**) preferentially yield catechol over hydroquinone. However, it will not be appropriate to conclude that the cobalt catalyst prefers *ortho*-hydroxylation and the copper catalyst *para*-hydroxylation, since there are other simultaneous oxidation processes undergoing, namely, the formation of benzoquinones. The rate of formation of these under particular reaction conditions, also determine the final concentration of hydroquinone and catechol.

4. Conclusions

Salicylaldiminato complexes of cobalt, nickel and copper were immobilized onto amorphous silica and mesoporous MCM-41 and their efficacies towards hydroxylation of phenol were examined. The MCM-41 supported catalysts have higher activity for phenol conversion than the amorphous silica systems probably because of the higher surface area of the support, resulting in a higher concentration of catalytically active sites. The amorphous silica immobilized catalysts are more sensitive to pH changes in the reaction medium, with the nickel catalyst

being the most sensitive and the copper catalyst being the least sensitive among the three. Also the amorphous silica supported catalysts shows a predominance of catechol as the product while the reverse is observed in the case of the MCM-41 immobilized catalysts. This can be attributed to the shape selectivity of the products formed inside the porous channels of MCM-41.

References

[1] P. Maggioni, US Patent 3, 914, 322 (1975).
[2] G.A. Hamilton, J.P. Friedman, P.M. Campbell, J. Am. Chem. Soc. 88 (1966) 5266–5268.
[3] J.A. Martens, P. Buskens, P.A. Jacobs, A.V.D. Pol, J.H.C. van Hooff, C. Ferrini, H.W. Kouwenhoven, P.J. Kooyman, H. van Bekkum, Appl. Catal. A 99 (1993) 71–84.
[4] U. Wilkenhöner, G. Langhendries, F. van Laar, G.V. Baron, D.W. Gammon, P.A. Jacobs, E.V. Steen, J. Catal. 203 (2001) 201–212.
[5] H. Liu, G. Lu, Y. Guo, Y. Guo, J. Wang, Chem. Eng. J. 116 (2006) 179–186.
[6] T. Yokoi, P. Wu, T. Tatsumi, Catal. Commun. 4 (2003) 11–15.
[7] H. Liu, G. Lu, Y. Guo, Y. Guo, Appl. Catal. A 293 (2005) 153–161.
[8] A. Thangaraj, R. Kumar, P. Ratnasami, J. Catal. 131 (1991) 294–297.
[9] J.S. Reddy, S. Sivasankar, P. Ratnasamy, J. Mol. Catal. 71 (1992) 373–381.
[10] A. Tuel, Y.B. Taarit, Appl. Catal. A 102 (1993) 69–77.
[11] J.S. Choi, S.S. Yoon, S.H. Jang, W.S. Ahn, Catal. Today 111 (2006) 280–287.
[12] M. Trejda, M. Zoilek, Catal. Today 101 (2005) 109–116.
[13] I. Sobczak, M. Ziolek, M. Renn, P. Decyk, I. Nowak, M. Daturi, J.C. Lavalley, Micropor. Mesopor. Mater. 74 (2004) 23–36.
[14] C. Liu, Y. Shan, X. Yang, X. Ye, Y. Wu, J. Catal. 168 (1997) 35–41.
[15] L. Noreno-Franco, I. Harnandez-Perez, J. Aguilar-Pliego, A. Maubert-Franco, Catal. Today 75 (2002) 189–195.
[16] A.L. Villa, C.A. Caro, C.M. de Correa, J. Mol. Catal. A 228 (2005) 233–240.
[17] S.S. Shevade, R. Raja, A.N. Kotasthane, Appl. Catal. A 178 (1999) 243–249.
[18] A. Ribera, I.W.C.E. Arends, S. De Vries, J. Péres-Ramírez, R.A. Sheldon, J. Catal. 195 (2000) 287–297.
[19] J.N. Park, J. Wang, K.Y. Choi, W.Y. Dong, S.I. Hong, C.W. Lee, J. Mol. Catal. A 247 (2006) 73–79.
[20] S. Seelan, A.K. Sinha, Appl. Catal. A 238 (2003) 201–209.
[21] M.R. Maurya, S.J.J. Titinchi, S. Chand, Catal. Lett. 89 (2003) 219–227.
[22] M. Kurian, S. Sugunan, Chem. Eng. J. 115 (2006) 139–146.
[23] Q. Chai, W.Y. Lin, F. Xiao, W. Pang, X. Chen, B. Zou, Micropor. Mesopor. Mater. 32 (1999) 1–15.
[24] I.C. Chisem, J. Rafelt, M.T. Shieh, J. Chisem, J.H. Clark, R. Jachuck, D. Macquarrie, C. Ramshaw, K. Scott, Chem. Commun. (1998) 1949–1950.
[25] U.G. Singh, R.T. Williams, K.R. Hallam, G.C. Allen, J. Solid State Chem. 178 (2005) 3405–3413.
[26] S.I. Mostafa, S. Ikeda, B. Ohtani, J. Mol. Catal. A 225 (2005) 181–188.
[27] S. Brunauer, L.S. Deming, W.E. Deming, E. Teller, J. Am. Chem. Soc. 62 (1940) 1723–1732.
[28] A. Dubey, V. Rives, S. Kannan, J. Mol. Catal. A 181 (2002) 151–160.
[29] L. Wang, A. Kong, B. Chen, H. Ding, Y. Shan, M. He, J. Mol. Catal. A 230 (2005) 143–150.