Catalytic hydroxylation of phenol over ternary hydrotalcites containing Cu, Ni and Al

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Abstract

Liquid phase catalytic hydroxylation of phenol was carried out over ternary hydrotalcites containing copper, nickel and aluminum using hydrogen peroxide as oxidant. The influence of various reaction parameters, namely, substrate:catalyst ratio, substrate:oxidant ratio, nature of oxidant, solvent, pH, time-on-stream, reaction temperature and calcination temperature on the activity and selectivity for the "sought for" reaction, were studied. The catalysts were synthesized by the coprecipitation technique using metal nitrates and a NaOH/Na$_2$CO$_3$ mixture. Hydroxylation of phenol over these catalysts resulted mainly in the formation of catechol and hydroquinone. Among the catalysts studied, CuNiAl3-5 ((Cu + Ni)/Al = 3.0; Cu/Ni = 5.0) and CuNiAl2-1 ((Cu + Ni)/Al = 2.0; Cu/Ni = 1.0) showed maximum activity with a catechol:hydroquinone ratio close to 1.6. An increase in the substrate:catalyst ratio enhanced the conversion of phenol over these catalysts. With respect to the influence of reaction temperature, the conversion increased up to 65 °C and decreased when the temperature was further increased. Oxidants other than H$_2$O$_2$ and solvents other than water have not showed measurable conversion of phenol. Time-on-stream studies indicated that around 90% of conversion of phenol was achieved in 10 min and longer reaction time did not significantly enhance the conversion. Among the calcined samples studied, that calcined at 800 °C showed a maximum activity for phenol hydroxylation; however, the activities of calcined catalysts were lower than those of fresh hydrotalcites. The observed variation in the activity may be attributed to the copper concentration, especially those present on the surface. A reaction pathway involving hydroxy radical is proposed for the formation of dihydroxybenzenes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ternary hydrotalcites; Phenol hydroxylation; Selective oxidation; X-ray diffraction

1. Introduction

Hydrotalcite-like compounds, otherwise referred as anionic clays or double layered hydroxides, are a class of layered materials receiving an increasing attention in recent years owing to their diverse applications, namely, ion-exchangers [1,2], catalysts [3–5],

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catalyst supports [6] and polymer additives [7]. Structurally, they can be perceived by starting with the brucite (Mg(OH)$_2$) lattice wherein a partial substitution of Mg^{2+} by a trivalent cation, say Al^{3+}, occurs, and the resulting excess positive charge generated is compensated by anions, usually carbonate, occupying the interlayers. Synthesis of these materials having transition metal ions, especially copper, in the sheets is of particular interest owing to their selective oxidation behavior, efficiently exploited for various redox-mediated catalytic transformations. Trifirò and coworkers [8] have used calcined Cu–Co–Zn–Cr

hydrotalcites in the synthesis of methanol from CO and H_2 and attributed the observed high activity and selectivity of methanol over these catalysts to the synergetic effect between copper and cobalt. Zhu et al. [9] have carried out hydroxylation of phenol over copper containing hydrotalcite-like compounds using H_2O_2 as oxidant and showed $CuAlCO_3$-HT with Cu/Al atomic ratio of 3.0 efficiently oxidized phenol and gave high yields of diphenols under appropriate reaction conditions. Very recently, Alejandre et al. [10] have synthesized Cu–Al mixed oxides through hydrotalcite-like precursors and tested them for oxidation of phenol aqueous solutions in a trickle-bed reactor using air as an oxidant. Phenol conversion decreased continuously over time for the samples calcined at lower temperature (400 °C), while it reached a steady activity plateau in the range 55–65% conversion for those catalysts calcined at higher temperature (800 °C). In our recent paper [11], we have disclosed the detailed physicochemical characterization of hydrotalcites having different amounts of copper, nickel and aluminum and concluded that the nature of the phase obtained, crystallinity of HT-like phase formed and the thermal behavior of these materials were significantly influenced by the nature and concentration of the different metals present in the sheets. In the present paper, we report a systematic activity studies on selective hydroxylation of phenol over these materials using hydrogen peroxide as an oxidant. The choice of this reaction is well documented, as the products of this reaction have a wide range of applications [12] and heterogeneous hydroxylation using H_2O_2 has shown an increasing impetus with the advent of discovery of metallosilicates [13].

2. Experimental

The samples were synthesized by coprecipitation under low supersaturation employing metal nitrates as precursors and $NaOH/Na_2CO_3$ as precipitants. Detailed synthetic methodology of these samples is given in our earlier work [11]. Samples will be designated in this paper as CuNiAla-b where "a" is the $(Cu + Ni)/Al$ atomic composition and "b" the Cu/Ni atomic ratio. Powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D500 instrument, using Cu Kα radiation and equipped with AT diffract

software. The crystalline phases were identified by comparing with the JCPDS files [14]. Specific surface area assessment and pore-size analysis was carried out in a Gemini instrument from Micromeritics. The sample was previously degassed in flowing nitrogen at 150 °C for 2 h in order to remove physisorbed water in a FlowPrep 060 apparatus (Micromeritics), and the data were analyzed using published software [15].

Hydroxylation of phenol was carried out in a two-neck glass reactor (50 ml) fitted with a condenser and a septum. Hydrogen peroxide (30%, w/v) was added through the septum at once to the magnetically stirred solution of phenol containing catalyst kept at the desired reaction temperature. The course of the reaction was monitored by taking periodically small samples (0.05 cm^3) which were analyzed by gas chromatography (GC) fitted with OV-17 packed column (2 m × 4 mm i.d.) using flame ionization detector. To avoid the possible reaction of H_2O_2 in the injection port of the GC, we have chemically decomposed H_2O_2, assuming its presence in the system. Quantification was done after considering the response factors of reactants and products, whose retention times were determined using authentic samples, derived using standard mixtures containing both of them. The conversion of phenol was also measured for the reactions carried out with high substrate:catalyst ratios, by adding an external standard, here o-cresol, which showed a variation of 5–10% (than obtained through direct analysis) probably due to tar formation, depending on the nature of catalysts.

3. Results and discussion

The PXRD of these samples, except CuNiAl1-1, showed a single phase typical of hydrotalcite-like material intercalated with carbonate anion, exhibiting harmonics close to $2\theta = 11°$, $24°$ and $35°$ characteristic of 3R packing of the layers. The peaks in the diffraction pattern of the Cu-rich sample CuNiAl3-5 was relatively broad especially for higher-order reflections, indicating the incompatibility of copper in a regular octahedral network of the hydrotalcite lattice. The PXRD pattern of CuNiAl1-1 showed a broad and ill-defined HT-like phase with additional peaks around $2\theta = 18.3°$ and $20.5°$, ascribed to $Al(OH)_3$, gibbsite (JCPDS file 12-0460). Detailed physicochemical

Table 1
Composition, specific surface area and phenol hydroxylation activity of various catalysts studied

Catalyst[a]	Composition	Conversion (%)	Product distribution (wt.%)			Selectivity[b] (%)	S_{BET}[c] (m^2/g)
			Cat	HQ	Cat/HQ		
CuNiAl1-1	NA[d]	14.8	9.5	5.3	1.8	29.6	
CuNiAl2-1	$[Ni_{0.30}Cu_{0.38}Al_{0.32}(OH)_2](CO_3)_{0.16} \cdot 1.23H_2O$	22.6	14.6	8.0	1.8	45.2	105
CuNiAl3-1	$[Ni_{0.39}Cu_{0.36}Al_{0.25}(OH)_2](CO_3)_{0.13} \cdot 1.27H_2O$	17.3	11.2	6.1	1.8	34.6	77
CuNiAl4-1	$[Ni_{0.37}Cu_{0.44}Al_{0.19}(OH)_2](CO_3)_{0.10} \cdot 1.13H_2O$	17.7	11.1	6.6	1.7	35.4	50
CuNiAl3-5	$[Ni_{0.14}Cu_{0.61}Al_{0.25}(OH)_2](CO_3)_{0.13} \cdot 0.96H_2O$	23.7	14.1	9.6	1.5	47.4	89
CuNiAl3-0.2	$[Ni_{0.64}Cu_{0.12}Al_{0.24}(OH)_2](CO_3)_{0.12} \cdot 1.03H_2O$	10.7	8.2	2.5	3.3	21.4	87

[a] Phenol: 1.0 g; phenol/H_2O_2 (mol): 2.0; catalyst: 10 mg; solvent (water): 10 ml; temperature: 65 °C; time: 2 h; pH = 5.0.
[b] Selectivity of H_2O_2 calculated on the basis of dihydroxybenzenes formed.
[c] Specific surface area.
[d] Not applicable as it has impurity phase along with HT-like phase.

characterization of these compounds has been already reported [11].

3.1. Effect of different metal ion concentration

Table 1 summarizes the activity of various catalysts studied for phenol hydroxylation. On all catalysts, catechol and hydroquinone were formed as the major products. It is clear that among the catalysts studied, CuNiAl1-1 showed poor activity indicating the influence of phase purity. Among the catalysts studied, CuNiAl3-5 and CuNiAl2-1 showed the maximum conversion, with nearly 50% H_2O_2 selectivity, and were selected for further investigations. We attribute this high activity to the large concentration of copper in the former, while a larger specific surface area of the later catalyst. This is further substantiated taking into account that a decrease in the copper concentration of the catalyst having a similar $(Cu + Ni)/Al$ atomic composition decreased the activity. Further, variation in the copper concentration affected the product distribution: hydroquinone is more favored for the catalyst having higher copper concentration, while catechol is favored for the catalyst having lesser copper concentration. Comparison of CuNiAl2-1 and CuNiAl3-1 indicated that, although they have nearly similar copper concentrations, the activity of the former is higher owing to its larger specific surface area (Table 1). Phenol hydroxylation over pure NiAl hydrotalcite did not result in measurable conversion corroborating the necessity of copper in driving the reaction. These results substantiate that copper is the active center involved in the hydroxylation reaction, whose surface concentration controls the overall activity and selectivity of the reaction.

3.2. Effect of the substrate:catalyst ratio

An interesting observation was noted, when the substrate:catalyst ratio was increased, giving rise to high conversion of phenol, as illustrated in Fig. 1 for CuNiAl3-5. We presume this result is due to the spontaneous formation of coke (reaction mixture turned dark black), at high catalyst concentration, obtained through consecutive reactions of the primary products (which also consumes hydrogen peroxide). To verify, we have estimated the coke formed for the reaction having substrate:catalyst ratio of 10:1 and observed around 0.2–0.3 g of coke per gram of catalyst (calculated after taking due consideration of weight loss due
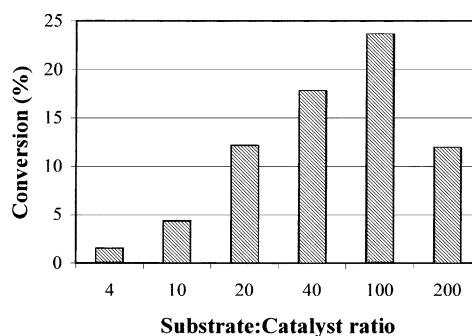

Fig. 1. Variation of conversion of phenol with the substrate:catalyst ratio (phenol: 1 g; solvent (water): 10 ml; phenol/H_2O_2 (mol): 2.0; temperature: 65 °C; time: 24 h; pH = 5.0).

to catalyst upon calcination in air). We believe, once coke is formed in the reaction, it masks the active centers of the catalyst thereby inhibiting the access of the reactant molecule to further undergo the reaction. This is similar to the observation by Figueras and coworkers [16] for faujastes, who reported that the yield of dihydroxybenzenes was unaffected by the mass of the catalyst for FAU 15 (Si/Al = 15), while it continuously decreased with an increase in the mass for FAU 2.5 (Si/Al = 2.5). They claimed that dealumination results in an enhancement of both acidity and mesoporosity facilitating the diffusion of primary products and in turn preventing consecutive reactions. However, such an increase in the activity was noted to a certain extent and decreased with further increase in the ratio (more than 100). This could probably be due to the decrease in the number of available active centers for the reaction. A similar observation was noted for the other catalysts as well. An optimum substrate:catalyst ratio of 100 was selected for further studies.

3.3. Effect of the reaction temperature

Phenol hydroxylation reaction was carried out over these two catalysts with substrate:catalyst ratio of 100 in the temperature range 30–90 °C (Table 2). The conversion increased markedly with an increase in the reaction temperature up to 65 °C, with a stronger influence for CuNiAl3-5. Furthermore, the catechol/hydroquinone (Cat/HQ) ratio decreased for CuNiAl3-5 with an increase in reaction temperature,

in other words, facilitating the formation of hydroquinone. A further rise in the reaction temperature decreased the conversion of phenol and could be ascribed to the competitive thermal decomposition of H_2O_2 at higher temperature without being involved in the desired reaction. The decrease in the conversion was also more evident for CuNiAl3-5 than for CuNiAl2-1. The presence of an optimum concentration of nickel may render stability to the catalyst in sustaining the activity even with subtle variations in the reaction conditions. It is well-known that oxidation activity of nickel catalysts is relatively poorer than that of copper containing catalysts, but they possess a longer catalyst life [17]. These results suggest that although copper is the active center involved in the hydroxylation reaction, the possible variation of the geometric and/or electronic environment around copper in these catalysts discriminates the overall course of the reaction.

3.4. Effect of the reaction medium and oxidant

In order to study the influence of the reaction medium on phenol hydroxylation, the reaction was performed in various solvents (other than water), namely acetone, acetonitrile, t-butanol, THF and DMF. On both catalysts, none of the solvents other than water showed measurable conversion. This fact (water behaves as a good solvent for this reaction over these catalysts) is beneficial in both industrial and environmental perspectives. We believe that the proximity of the hydroxylating agent and the substrate molecule on

Table 2
Effect of the reaction temperature for phenol hydroxylation over CuNiAl3-5 and CuNiAl2-1 catalysts (conditions as in Table 1)

Catalyst	Temperature (°C)	Conversion (%)	Product distribution (wt.%)			H_2O_2 selectivity (%)
			Cat	HQ	Cat/HQ	
CuNiAl3-5	30	4.3	2.7	1.6	1.6	8.6
	50	16.0	9.7	6.3	1.5	32
	65	23.7	14.1	9.6	1.4	47.4
	80	21.2	12.6	8.6	1.5	42.4
	90	17.4	10.5	6.9	1.5	34.8
CuNiAl2-1	30	7.4	4.3	3.1	1.4	14.6
	50	21.9	14.2	7.7	1.8	43.6
	65	22.6	14.6	8.0	1.8	45.2
	80	20.4	12.4	8.0	1.5	40.8
	90	20.6	12.3	8.3	1.5	41.0

or near the active catalyst site is essential for driving the reaction. In water, both phenol and H_2O_2 dissolve simultaneously and approach the active center, thereby generating hydroxy radicals, thought to be the active species involved in the hydroxylation reaction. Moreover, such an electrophile is easier produced and stabilized in water than in organic solvents. Possibly, the lack of a hydroxylated nature for the other organic solvents may be responsible for the non-occurrence of this reaction. Furthermore, the reaction was carried out using different oxidants other than H_2O_2, namely oxygen, air and *t*-butylhydroperoxide. None of these oxidants hydroxylated phenol to a significant extent under similar reaction conditions, possibly due to the lack of generation of the active oxidant species and the solubility problems associated with the reactant and the oxidant.

3.5. Effect of pH of the reaction medium

Table 3 summarizes the effect of pH on the hydroxylation reaction using water as solvent. No significant difference in the activity was observed between pH = 5.0 (which is the pH of the medium without any adjustment) and pH = 7.0. This is in contrast to the results reported by Zhu et al. [9] for copper containing hydrotalcites who claimed a maximum conversion at pH = 7.0, while at other pH a decrease or a lack of activity was observed. The higher activity at pH = 5.0 could possibly be due to a better stabilization of the hydroxy radical. Further, when we measured the pH after the reaction, a decrease by one unit was observed (pH = 4.0), possibly due to generation of organic acids, which might have been formed through consecutive oxidation of dihydroxybenzene. However,
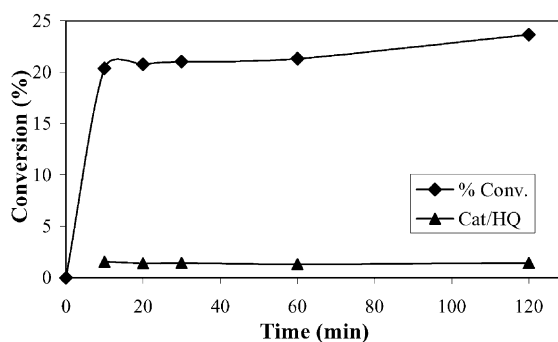

Fig. 2. Effect of reaction time on the phenol conversion and Cat/HQ ratio for CuNiAl3-5 (conditions as given in Fig. 1).

a careful ^{1}H NMR study of the reaction mixture was done, which did not reveal proton corresponding to organic acids. Further, for our samples also at pH = 9.0, no activity was observed. This could be due to generation of HO^- species, which would approach the active center thereby inhibiting the adsorption of hydrogen peroxide, and in turn affecting the generation of hydroxy radicals.

3.6. Effect of the reaction time

Fig. 2 shows the variation in the conversion of phenol over CuNiAl3-5 at different time intervals. It is clear from the figure that around 90% of the conversion was achieved in the first 10 min, while a further increase in the reaction time did not significantly enhance the conversion. This is in contrast to the behavior of many zeolite based catalysts, which either showed a progressive growth in the conversion of phenol or exhibited an induction time [18].

Table 3
Influence of the pH of the reaction medium for phenol hydroxylation over CuNiAl3-5 and CuNiAl2-1 catalysts (conditions as in Table 1)

Catalyst	Temperature (°C)	pH	Conversion (%)	Product distribution (wt.%)			H_2O_2 selectivity (%)
				Cat	HQ	Cat/HQ	
CuNiAl3-5	65	5	23.7	14.1	9.6	1.4	47.4
	65	7	19.2	12.1	7.1	1.7	38.4
	65	9	0	0	0	–	0
CuNiAl2-1	80	5	20.4	12.4	8.0	1.5	40.6
	80	7	20.2	12.3	7.9	1.5	40.5
	80	9	0	0	0	–	0

No significant variation in the Cat/HQ ratio was observed with the reaction time, suggesting the lack of inter-conversion and/or consecutive reactions. In one of our experiments, we filtered the catalyst after 30 min of reaction and monitored the progress of the reaction in the absence of catalyst. This was done to verify whether leaching of metal ions had occurred by H_2O_2 into the aqueous phase during the reaction, which can by themselves act as active homogeneous centers. However, no change in the conversion of phenol with time was observed after filtering the catalyst, confirming the non-leaching of metal ions from the HT-like lattice. This is further supported by PXRD results, which showed no significant change in the crystallinity of the HT-like phase after the reaction.

3.7. Effect of the substrate:oxidant ratio

Variation of the substrate:oxidant ratio indicated that the conversion increased with a decrease in the ratio for both the catalysts, whose values are summarized in Table 4. Further, the increase in the conversion is nearly proportional to the increase in H_2O_2 concentration for both catalysts, maintaining similar selectivity for dihydroxybenzenes, corroborating the fact that the added H_2O_2 is essentially used for the desired hydroxylation reaction and not for the undesired consecutive reactions. In addition, a continuous increase in the Cat/HQ ratio was observed for these catalysts with a decrease in this ratio, indicating the preferential formation of catechol at higher H_2O_2 concentration. CuNiAl3-5 exhibited a maximum activity yielding 61% conversion of phenol with Cat/HQ ratio of 1.7 at 80 °C employing 1:2 substrate:oxidant ratio.
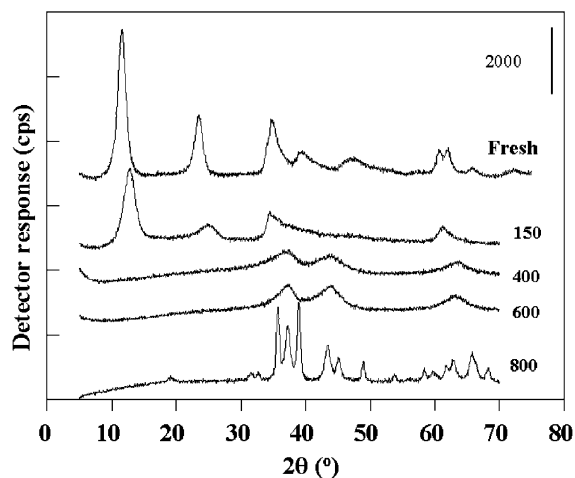

Fig. 3. PXRD patterns of CuNiAl2-1 calcined at different temperatures for 2 h.

The activity of this catalyst is comparable to that of some titanium based zeolite catalysts reported in the literature [19] indicating a promising role of HT-based catalysts for commercial exploitation.

3.8. Effect of the calcination temperature

Calcination of these materials results in non-stoichiometric mixed metal oxides whose phase and crystallinity are influenced by their precursor chemical composition and the calcination temperature. Fig. 3 shows the PXRD patterns of CuNiAl2-1 calcined at different temperatures. It is clear that calcination at 400 °C leads to the destruction of the HT-like network, giving rise to a diffuse amorphous pattern

Table 4
Influence of the substrate:oxidant ratio for phenol hydroxylation over CuNiAl3-5 and CuNiAl2-1 catalysts (conditions as in Table 1)

Catalyst	Substrate:oxidant ratio	Conversion (%)	Product distribution (wt.%)			H_2O_2 selectivity (%)
			Cat	HQ	Cat/HQ	
CuNiAl3-5	3:1	13.8	7.5	6.3	1.2	41.2
	2:1	21.2	12.6	8.6	1.5	42.1
	1:1	41.4	25.6	15.8	1.6	41.0
	1:2	60.9	38.8	22.1	1.7	30.5
CuNiAl2-1	3:1	11.4	6.7	4.7	1.4	36.5
	2:1	20.2	12.3	7.9	1.5	40.3
	1:1	40.3	25.0	15.3	1.6	39.8
	1:2	55.8	35.6	20.2	1.7	27.9

with three peaks recorded close to 2.42, 2.07 and 1.47 Å, positions coincident with the main diffraction maxima of bunsenite (NiO, JCPDS file 4-0835). An increase in the calcination temperature up to 700 °C enhanced the crystallinity of M(II)–O phases, as evidenced by the sharpening of these peaks. In our case, no peak was recorded which could be ascribed to Al containing phases. This is not unexpected, as usually at 400–500 °C, only diffraction peaks of divalent metal oxides are recorded, whose peak positions do not match with pure metal oxides, this being generally attributed to dissolution of Al^{3+} cations in the M(II)–O matrix. When the calcination temperature is further increased, say at 800 °C, crystallization of the $M^{II}Al_2O_4$ spinel occurred along with NiO. In addition, sharper maxima whose positions were coincident with those of ternorite (CuO, JCPDS file 5-0661) were also observed. However, the concentration of these phases varied, as evidenced from the relative intensities of the corresponding maxima, in relation with the content of the different metal ions in the parent HT-like lattice. Accordingly, for CuNiAl2-1, the main diffraction maxima recorded corresponded to the spinel with a weak CuO phase, while the reverse was observed for CuNiAl3-5.

Hydroxylation of phenol was carried out over hydrotalcites calcined at different temperatures yielding the results summarized in Table 5. CuNiAl3-5 calcined at 150, 400 and 600 °C showed a similar conversion (∼12%) while the sample calcined at 800 °C exhibited a higher conversion (18%). In the case of CuNiAl2-1, a continuous increase in the conversion with an increase in the calcination temperature was observed. The higher activity of the high temperature

calcined catalysts (800 °C) could be due to the inherent activity of spinel phase, which crystallizes around this temperature, in mediating the reaction. Further, no significant difference in the activity of these high temperature calcined catalysts was observed, confirming the stable activity of the spinel phase. Furthermore, the specific surface areas of these catalysts were nearly the same, validating the above observation. Fig. 4 shows the variation in the BET specific surface area of these samples with the calcination temperature. An increase in the specific surface area was observed with an increase in the calcination temperature up to 400 °C for the CuNiAl2-1, while nearly similar specific surface areas were observed for CuNiAl3-5 up to 600 °C. The observed activity trends exhibited by these catalysts could possibly be correlated to the variation in their specific surface areas. The influence of the specific surface area of the mixed metal oxides as well the stability of the spinel phase in the oxidation of aqueous solution of phenol has been emphasized earlier [17]. However, the conversion observed for the calcined catalysts is lower than that observed for pure hydrotalcites. This could possibly be due to the crystal phase transformation coupled with the loss in the specific surface area.

If one were to consider the mechanism of hydroxylation reaction over these materials, similar to Fenton's reaction, hydroxy radicals could participate as an electrophile in this reaction. The hydroxy radical may be generated through oxidation of Cu^{2+} ions in the HT-lattice by H_2O_2, which subsequently attack at *ortho* and *para* positions of phenol resulting in the desired dihydroxybenzenes, respectively, catechol and hydroquinone. To verify the participation of the

Table 5
Influence of the calcination temperature for phenol hydroxylation over CuNiAl3-5 and CuNiAl2-1 catalysts (conditions as in Table 1)

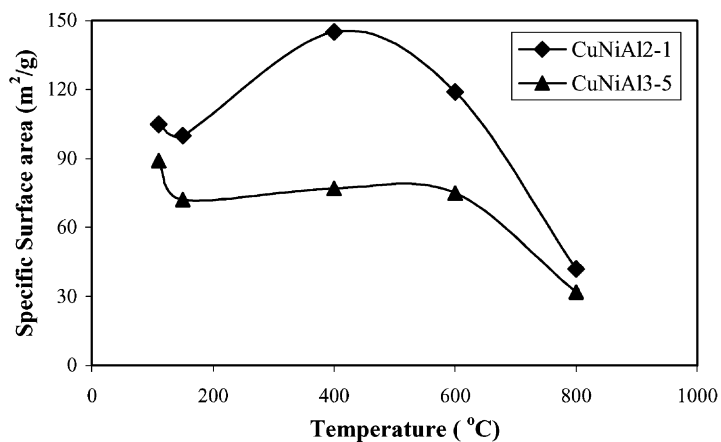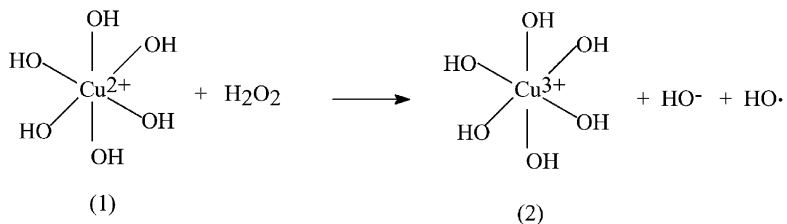| Catalyst	Calcination temperature (°C)	Conversion (%)	Product distribution (wt.%)			H_2O_2 selectivity (%)
			Cat	HQ	Cat/HQ	
CuNiAl3-5	150	13.3	6.6	6.7	1.0	26.8
	400	12.0	5.1	6.9	0.7	24.0
	600	10.4	4.3	6.1	0.7	20.8
	800	18.4	10.9	7.5	1.5	36.0
CuNiAl2-1	150	10.4	5.9	4.5	1.3	20.8
	400	12.8	7.2	5.6	1.3	25.5
	600	15.6	8.4	7.2	1.2	31.2
	800	18.9	11.0	7.9	1.4	36.6

Fig. 4. Variation of BET surface area of CuNiAl2-1 and CuNiAl3-5 with the calcination temperature.

Generation of electrophile

(1)   (2)

Attack of electrophile

Attack at *o*-position

Catechol

Attack at *p*-position

Hydroquinone
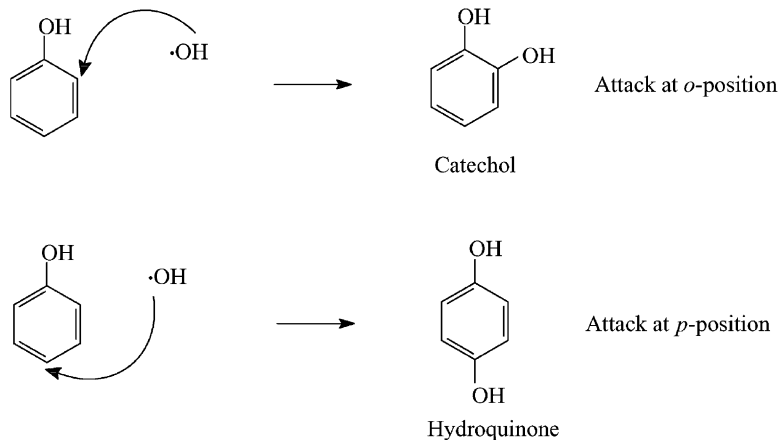
Regeneration of active site

$$H_2O_2 \ + \ \cdot OH \longrightarrow HO_2 \cdot \ + \ H_2O$$

$$(2) \ + \ HO_2 \cdot \longrightarrow (1) \ + \ O_2 \ + H^+$$
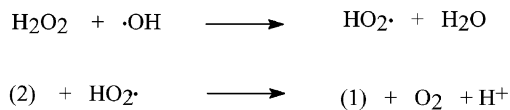
Scheme 1. Reaction pathway for dihydroxybenzenes in phenol hydroxylation over CuNiAl hydrotalcites.
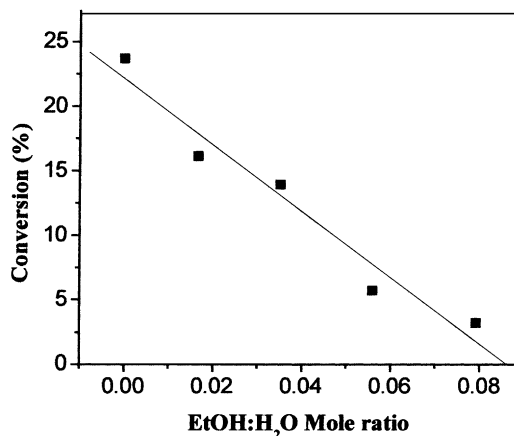
Fig. 5. Plot of variation in the conversion of phenol with EtOH:H$_2$O mole ratio for CuNiAl3-5.

hydroxy radical, the effect of the added alcohol, which is a well-known scavenger for the hydroxy radical [20], on the conversion of phenol was monitored for CuNiAl3-5, as elucidated in Fig. 5. A nearly linear plot showing a decreasing conversion with an increase in ethanol concentration was observed, confirming the participation. A further increase in the concentration of ethanol leads to a complete drop in the activity. Possible reaction pathways for the hydroxylation reaction over these catalysts are summarized in Scheme 1. It can be assumed that a structural arrangement of the substrate molecule and of the active oxidant species on the catalyst surface along with residence time of the hydroxylated products control the overall activity and selectivity of this reaction.

4. Conclusions

The hydroxylation of phenol was carried out over Cu, Ni and Al containing hydrotalcites with varying atomic composition. The influence of various reaction parameters such as substrate:catalyst ratio, substrate:oxidant ratio, temperature, oxidant, pH, solvent and effect of calcination were studied. An increase in the conversion was observed with an increase in copper concentration, and between the catalysts having similar copper concentrations, that with higher specific surface area yielded better activity. More than 90% of the conversion was achieved in 10 min of reaction time, and catechol and hydroquinone were observed as the major products. An increase in the substrate:catalyst ratio interestingly enhanced the conversion of phenol over these catalysts. Oxidants other than H$_2$O$_2$ and solvents different of water did not yield measurable conversion of phenol. Among the samples calcined at different temperatures, that calcined at 800 °C showed the maximum activity, although the activities of these samples were less than those of the fresh hydrotalcites. Among the catalysts, CuNiAl3-5 exhibited a maximum activity, yielding 61% conversion of phenol with Cat/HQ ratio of 1.7 at 80 °C using a 1:2 substrate:oxidant ratio, comparable to many transition metal containing molecular sieves. Electrophilic attack of hydroxy radical is proposed to be the reaction pathway for the formation of dihydroxybenzenes over these catalysts.

Acknowledgements

References

[1] F. Trifirò, A. Vaccari, in: J.L. Atwood, J.E.D. Dasvies, D.D. MacNicol, F. Vogtle, J.-M. Lehn, G. Alberti, T. Bein (Eds.), Comprehensive Supramolecular Chemistry, Solid State Supramolecular Chemistry: Two and Three-dimensional Inorganic Networks, Vol. 7, Pergamon Press, Oxford, 1996, p. 251.

[2] V. Rives, M.A. Ulibarri, Coordin. Chem. Rev. 181 (1999) 61.

[3] D. Tichit, A. Vaccari (Eds.), Recent Catalytic Applications of Hydrotalcite-type Anionic Clays, Appl. Clay Sci. 13 (1998) 311.

[4] B. Sels, D. DeVos, M. Buntinx, F. Pierard, A.K. Meshmaeker, P. Jacobs, Nature 400 (1999) 855.

[5] J.S. Valente, F. Figueras, M. Gravelle, P. Kumbhar, J. Lopez, J.-P. Besse, J. Catal. 189 (2000) 370.

[6] S. Narayanan, K. Krishna, Appl. Catal. A 174 (1998) 221.

[7] J.C.A. Engels, European Patent 248 492 (1987), to Stamicarbon B.V.

[8] G. Fornasari, A.D. Huysser, L. Mintchev, F. Trifirò, A. Vaccari, J. Catal. 135 (1992) 386.

[9] K. Zhu, C. Liu, X. Ye, Y. Wu, Appl. Catal. A 168 (1998) 365.

[10] A. Alejandre, F. Medina, X. Rodriguez, P. Salagre, J.E. Sueiras, J. Catal. 188 (1999) 311.

[11] V. Rives, S. Kannan, J. Mater. Chem. 10 (2000) 489.

[12] M. Howe-Grant (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Wiley, New York, 1995, p. 996.

[13] I.W.C.E. Arends, R.A. Sheldon, M. Wallau, U. Schuchardt, Angew. Chem. Int. Edit. Engl. 36 (1997) 1144.

[14] JCPDS: Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Swarthmore, PA, 1977.

[15] V. Rives, Adsorpt. Sci. Technol. 8 (1991) 95.

[16] M. Allian, A. Germain, T. Cseri, F. Figueras, Stud. Surf. Sci. Catal. 78 (1993) 455.

[17] A. Alejandre, F. Medina, P. Salagre, A. Fabregat, J.E. Sueiras, Appl. Catal. B 18 (1998) 307.

[18] A. Germain, M. Allian, F. Figueras, Catal. Today 32 (1996) 145.

[19] A.A. Belhekar, T.K. Das, K. Chaudhari, S.G. Hegde, A.J. Chandwadkar, Stud. Surf. Sci. Catal. 113 (1998) 195.

[20] J. Okamoto, S. Nishiyama, S. Tsuruya, M. Masai, J. Mol. Catal. 135 (1998) 133.