ELSEVIER

Applied Catalysis A: General 238 (2003) 319–326

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Note

Catalytic hydroxylation of phenol over CuM(II)M(III) ternary hydrotalcites, where M(II) = Ni or Co and M(III) = Al, Cr or Fe

A. Dubey[a], S. Kannan[a,*], S. Velu[b], K. Suzuki[b]

[a] Silicates and Catalysis Discipline, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India
[b] Ceramic Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya 463 8560, Japan

Received 29 October 2001; received in revised form 18 June 2002; accepted 18 June 2002

Hydroxylation of phenol is one of the industrially important reactions wherein the products of this reaction, namely catechol and hydroquinone finds diverse applications [1]. Recently, copper-containing materials of different classes are receiving an increasing attention for this reaction [2–4]. One of them is hydrotalcites, structurally considered as layered materials with a varied possibility of physicochemical property tuning, thus being explored for various applications [5,6]. Our recent work on copper-containing hydrotalcites has shown interesting results on both physicochemical properties as well as for selective hydroxylation of phenol [7–9]. It is well-known that redox properties of the metal ions can be significantly modified by varying the concentration of active metal ion, matrix and co-presence of other cations in the system. This paper with the focus on the influence of co-cations in hydrotalcites, is evidenced by a classic example wherein addition of Zn to Cu–Al system has been claimed to provide a phenomenal advantage in low-temperature methanol synthesis [10]. Tichit et al. [11] have earlier claimed an optimum concentration of Mg in NiMgAl hydrotalcites for catalytic hydrogenation of acetonitrile to ethylamine, in achieving higher activity and selectivity. Our own studies have demonstrated the influence of trivalent cations in cobalt-containing hydrotalcites on the physicochemical behavior [12] and for catalytic decomposition of nitrous oxide wherein we observed a maximum activity for Al followed by Fe and Cr [13]. Knowing the varied influence of co-cation on the catalytic properties of transition metal ion containing hydrotalcites, in the present paper we had attempted to study the effect of trivalent metal ions in CuNi(Co)M(III) hydrotalcites, where M(III) = Al, Cr or Fe for catalytic hydroxylation of phenol. The selection of nickel and cobalt as bivalent cations were based on our earlier studies [8,9,14], which showed high activity for phenol hydroxylation among the various bivalent metal ions screened.

The samples were prepared by low supersaturation technique using metal nitrates as precursor and $NaOH/Na_2CO_3$ mixture as precipitant, as described earlier [7]. In all cases, the atomic ratio between divalent and trivalent cations was maintained around 3.0, while the Cu/M(II) atomic ratio was maintained around 5.0. 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 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 analyzing samples, taken periodically ($0.2\,cm^3$) using a syringe, by gas chromatography (GC) fitted with OV-17 packed column (2 m × 4 mm i.d.) using flame-ionization detector. The

---

[*] Corresponding author. Tel.: +91-278-567760; fax: +91-278-566970.
E-mail address: salt@csir.res.in (S. Kannan).

PII: S0926-860X(02)00373-3

mass balance of this reaction, done by external standard (*o*-cresol) addition method and quantified the phenol unreacted, was around 95 ± 5%. Details of the experimental procedure are reported elsewhere [9].

Elemental analysis of these solids showed a reasonable agreement with those of the starting solutions, suggesting completion of precipitation. Powder X-ray diffraction (PXRD) of these samples showed a pattern characteristic of hydrotalcite-like phase except for Fe-containing hydrotalcites, which showed additional peaks in the 2θ region 12–18° along with a diffuse diffraction pattern at higher angles, probably due to co-presence of ferric oxide (JCPDS 39-1346) and/or oxyhydroxide (JCPDS 22-353) phases. Among the trivalent metal ions studied, Al offered maximum crystallinity as inferred from intense diffraction lines followed by Cr and Fe, respectively. BET measurements of these samples indicated a trend wherein the specific surface areas of Fe-containing samples were highest (CuNiFe-HT, 171 m^2/g; CuCoFe-HT, 185 m^2/g) followed by chromium (CuNiCr-HT, 138 m^2/g; CuCoCr-HT, 120 m^2/g) and aluminum (CuNiAl-HT, 51 m^2/g; CuCoAl-HT, 74 m^2/g), respectively, for both nickel and cobalt systems.

Table 1 summarizes the activity of fresh hydrotalcite catalysts studied for phenol hydroxylation carried

Table 1
Effect of the reaction temperature for phenol hydroxylation over CuM(II)M(III)-HTs

Catalyst	Temperature (°C)	Conversion (%)[a]	Product distribution (%)			H_2O_2 selectivity (%)[b]
			CAT	HQ	CAT/HQ	
CuNiAl-HT	30	4.3	63	37	1.7	8.6
	50	16.0	61	39	1.5	32.0
	65	23.7	59	41	1.5	47.4
	80	21.2	59	41	1.5	42.4
	90	17.4	60	40	1.5	34.8
CuNiFe-HT	30	11.9	71	29	2.4	23.7
	50	14.2	75	25	2.9	28.3
	65	16.5	78	22	3.5	32.8
	80	11.1	77	23	3.3	22.1
	90	4.1	100	0	∞	8.2
CuNiCr-HT	30	11.3	78	22	3.5	22.5
	50	13.9	72	28	3.0	27.7
	65	16.5	77	23	3.5	33.0
	80	11.0	77	23	3.4	22.0
	90	7.3	70	30	2.3	14.6
CuCoAl-HT	30	16.2	66	34	1.9	32.4
	50	22.6	57	43	1.3	45.2
	65	21.5	59	41	1.4	43.0
	80	15.2	64	36	1.8	30.4
	90	9.3	63	37	1.7	18.6
CuCoFe-HT	30	11.0	73	27	2.7	22.0
	50	11.1	73	27	2.7	22.2
	65	12.7	71	29	2.4	25.4
	80	15.4	70	30	2.5	30.8
	90	6.7	60	40	1.5	13.4
CuCoCr-HT	30	3.4	82	18	4.6	6.8
	50	12.4	77	23	3.3	24.8
	65	15.1	79	21	3.7	30.2
	80	15.2	70	30	2.3	30.4
	90	10.3	67	33	2.0	20.6

[a] Phenol, 1.0 g; phenol/H_2O_2 (mole), 2.0; catalyst, 10 mg; solvent, water (10 ml); time, 2 h; pH, 5.0.

[b] Selectivity of H_2O_2 calculated on the basis of dihydroxybenzenes formed.

out at different temperatures. On all the catalysts, catechol and hydroquinone were formed as major products, The conversion increased with an increase in the reaction temperature up to 65 °C, except for CuCoFe-HT, and decreased with a further increase in temperature, may be due to competitive thermal decomposition of H_2O_2 at higher temperatures without being involved in the reaction. Maximum conversion was obtained for aluminum-containing systems (CuNiAl-HT, 23.7%; CuCoAl-HT, 21.5% at 65 °C) with a CAT/HQ ratio around 1.4, while no significant difference in the activity was noted between the corresponding Fe and Cr systems, despite the fact that the latter systems possessed higher specific surface areas. The conversion observed over these series of catalysts were less than some of the Ti-substituted zeolites [15] and we presume that this could possibly be due to a parallel decomposition of H_2O_2 catalyzed by the transition metal ions in hydrotalcite network (Fenton reaction), thereby limiting the conversion. It should be remembered here that all catalysts contain nearly equivalent concentration of copper, which is the active species involved in this reaction (no measurable conversion was observed for pure NiAl-HT, while low conversion (<5%) was noted for CoAl-HT, MgFe-HT and MgCr-HT at 65 °C), indicating the influence of trivalent cation in affecting the activity. Further, a closer look at the CAT/HQ ratio shows a higher value for iron- and chromium-containing systems. In other words, formation of catechol is more facilitated for these systems compared to aluminum-containing systems, probably due to differed adsorption sites provided by them. Between nickel and cobalt systems, considering for corresponding trivalent metal ion, former were slightly more active. An interesting observation was noted for CuNiM(III) system, wherein at

Table 2
Influence of the substrate:catalyst ratio for phenol hydroxylation over CuM(II)M(III)-HTs

Catalyst	Substrate:catalyst ratio	Conversion (%)[a]	Product distribution (wt.%)			H_2O_2 selectivity (%)[b]
			CAT	HQ	CAT/HQ	
CuNiAl-HT	100	23.7	59	41	1.5	47.1
	40	20.7	58	42	3.3	41.2
	20	12.2	43	57	0.7	24.3
	10	7.8	100	0	∞	15.6
CuNiFe-HT	100	16.5	78	22	3.5	33.0
	40	8.6	76	24	2.8	17.1
	20	6.0	53	47	1.1	11.9
	10	0.0	–	–	–	–
CuNiCr-HT	100	16.5	78	22	3.5	32.8
	40	13.4	72	28	2.6	26.7
	20	13.3	75	25	3.1	26.7
	10	7.7	61	39	1.6	15.3
CuCoAl-HT	100	21.5	59	31	1.4	42.8
	40	18.5	64	36	1.8	37.0
	20	22.5	53	47	1.1	44.8
	10	18.4	58	42	1.4	36.6
CuCoFe-HT	100	12.7	71	29	2.4	25.4
	40	7.4	68	32	2.1	14.7
	20	3.5	60	40	1.5	7.0
	10	0.0	–	–	–	–
CuCoCr-HT	100	15.1	79	21	3.7	30.1
	40	14.1	73	27	2.7	28.1
	20	11.1	69	31	2.3	22.1
	10	4.2	100	0	∞	8.4

[a] Phenol, 1.0 g; phenol/H_2O_2 (mole), 2.0; 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.

room temperature CuNiAl-HT showed poor conversion, while the corresponding Fe- and Cr-containing systems showed better conversion, which was reproducible, for which the reasons are not clear. However, reverse was observed for CuCoM(III) system at room temperature indicating the influence of co-bivalent metal ion. The difference in the activity for different trivalent metal ions could possibly be due to differing electron density of copper due to orbital–orbital interaction, more likely d–d interaction of copper with Fe or Cr orbitals (not there for Al system), which may in turn influence on the redox property of these systems.

Table 2 shows the variation of activity with different substrate:catalyst ratios over these catalysts. An interesting observation was noted wherein the conversion of phenol increased with an increase in substrate:catalyst ratio, for both CuNiM(III)-HT and CuCoM(III)-HT. We presume this result is due to the spontaneous formation of the coke (as the reaction mixture turned dark), at higher catalyst concentration, obtained through consecutive reactions of the primary products (which also involves consumption of hydrogen peroxide). To verify this, 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 the catalyst (calculated after taking due consideration of weight loss due to catalyst upon calcination in air). This is similar to the observation by Figueras and coworkers [16] for faujasites,

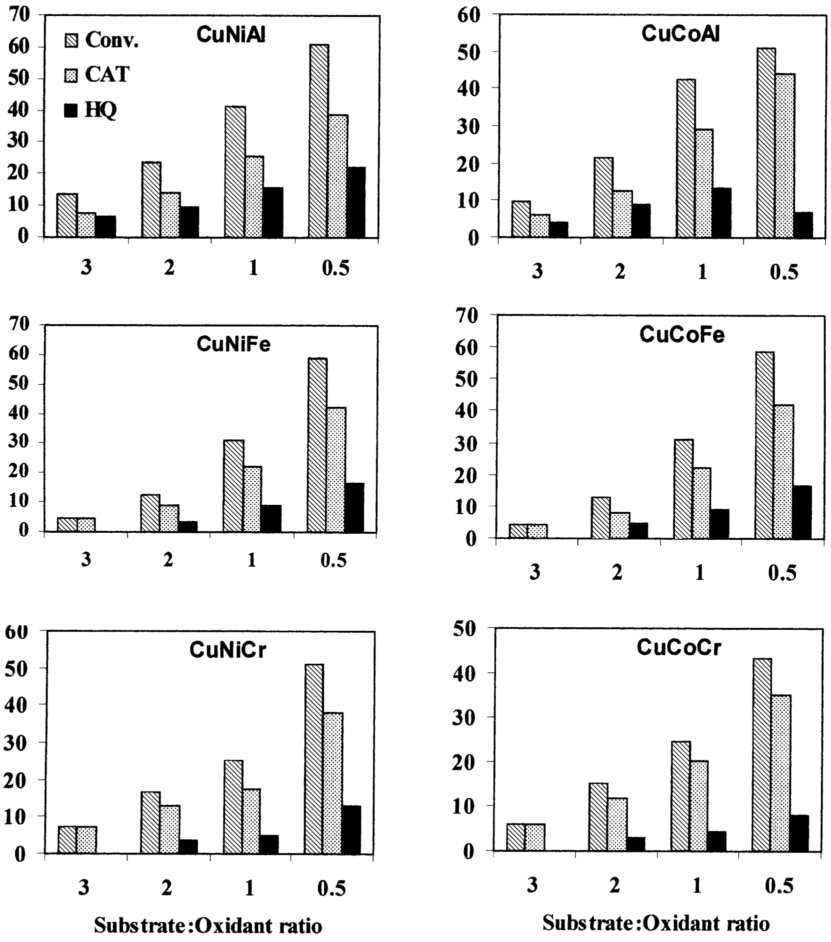

Fig. 1. Influence of substrate:oxidant ratio on the conversion and selectivity of dihydroxylated phenols over CuM(II)M(III)-HTs.

who reported that the yield of the dihydroxybenzenes was unaffected by mass of the catalyst for FAU 15 (Si/Al = 15), while it continuously decreased with an increase in the mass for FAU (Si/Al = 2.5). However, in our case, such an increase in the activity was noted to a certain extent and decreased with a further increase in the substrate:catalyst ratio. This could probably be due to the decrease in the number of available active centers for the reaction. Among the catalysts studied, CuCoAl-HT showed a better resistance with such variation in substrate:catalyst ratio. Further, no measurable conversion was noted for CuNiFe-HT and CuCoFe-HT at a substrate:catalyst ratio of 10. Catalysts with a substrate:catalyst ratio of 100 was selected for further study.

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 all catalysts, none of the solvents other than water showed measurable conversion. We believe that the proximity of the hydroxylating agent and of the substrate molecule on 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, proposed 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 hydroxylated nature for the other organic solvents

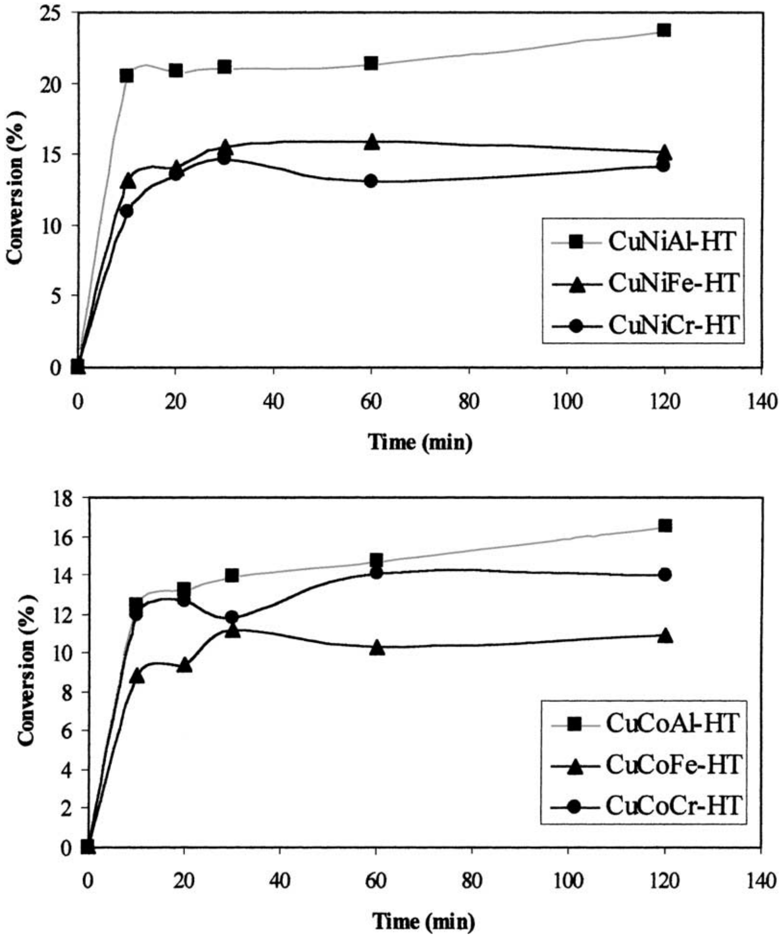

Fig. 2. Effect of reaction time on phenol hydroxylation over CuM(II)M(III)-HTs.

may be responsible for the non-occurrence of this reaction. Furthermore, when the reaction was carried out using different oxidants other than H_2O_2, namely oxygen, air and *t*-butylhydroperoxide, none of them hydroxylated phenol to a significant extent under similar reaction conditions, possibly due to the lack of generation of the active oxidant species and solubility problems associated with the reactant and the oxidant.

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. [17] 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. However, in our case also, for CuNiCr-HT, conversion increased with an increase in pH. The higher activity at pH 5.0 could possibly be due to a better stabilization of 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 higher homologue organic acids as coke, which might have been formed through consecutive oxidation of dihydroxybenzene. However, a ^{1}H NMR study of the reaction mixture did not reveal proton corresponding to organic acids and we at present do not know the reason for such a decrease in the pH after the reaction. Further, for all samples 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.

An increase in the conversion with a decrease in the substrate:oxidant ratio was observed for both series of catalysts, are compiled in Fig. 1. Further, the increase in the conversion was nearly proportional to the increase in H_2O_2 concentration for both series of 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. Among the catalysts studied, CuNiAl-HT exhibited a maximum conversion of phenol, 61%, with CAT/HQ ratio of 1.8 at 65 °C employing 1:2 substrate:oxidant ratio.

Variation in the conversion of phenol over these catalysts at different time intervals, given in Fig. 2, indicated that around 80% of the conversion was achieved in the first 10 min, while a further increase in the reaction time did not significantly enhance the conversion. Further, when we carried out time on stream studies up to 24 h, the conversion of phenol as well as CAT/HQ ratio was not significantly affected with time suggesting no consecutive and inter-conversion reactions. 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]. Further, if one were to look at the conversion of phenol at initial reaction time, a similar trend wherein a better conversion was noted for Al-containing systems than for Fe and Cr systems, corroborating our earlier observation. No significant variation in the CAT/HQ ratio was observed with the reaction time, suggesting the lack of inter-conversion and/or consecutive reactions. An interesting observation was noticed for CuCoAl-HT wherein the conversion decreased with a continuous removal of products from the reaction mixture during

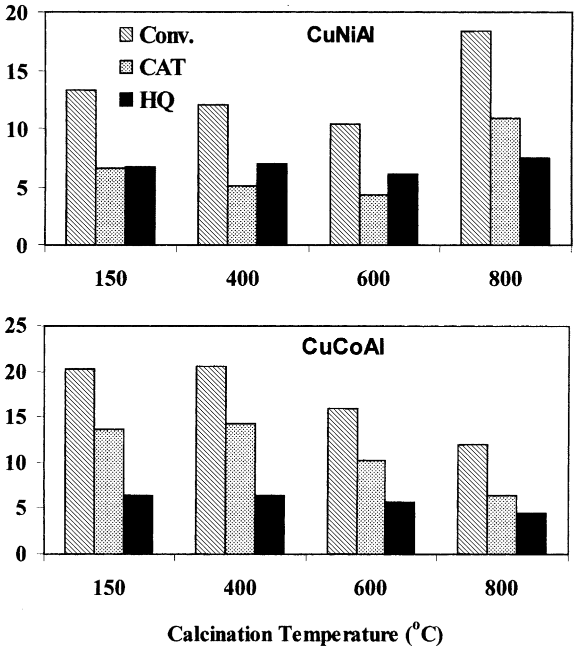

Fig. 3. Influence of calcination temperature on the conversion and selectivity of dihydroxylated phenols over CuNiAl-HT and CuCoAl-HT.

this study. A conversion of around 22% was observed if the product was not removed in between for 2 h, while 16% was observed with intermittent removal of products. The other systems did not exhibit such behavior. We, at this moment, do not know the reason for the same and a closer look at this system is currently underway.

Fig. 3 shows the activity of CuNiAl-HT and CuCoAl-HT calcined at different temperatures (150, 400, 600 and 800 °C). The temperatures were chosen after understanding the thermal decomposition patterns of these materials. The catalyst, CuNiAl-HT, 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 contrast, for CuCoAl-HT, with an increase in calcination temperature the conversion decreased. However, the decrease was not significant up to 400 °C, while decreased significantly with a further increase in temperature. To understand this behavior, PXRD for these samples were done and are given in Fig. 4. At 150 °C, both nickel- and cobalt-containing hydrotalcites possessed a diffuse hydrotalcite pattern with a shift in the basal spacing to higher diffraction angles, which is usually observed, attributed for a decrease in interlayer spacing due to removal of water molecules. The decrease in the conversion for these samples compared to fresh samples ascertains the necessity of ordered arrangement of metal hydroxide in the layered network. However, with a further increase in calcination temperature, both systems followed a varied phase evolution process. In the case of Ni system, up to 600 °C, a nearly amorphous phase was observed with a very weak pattern for copper oxide. However, at 800 °C, sharp evolution of well-crystalline copper oxide along with spinel possibly containing nickel

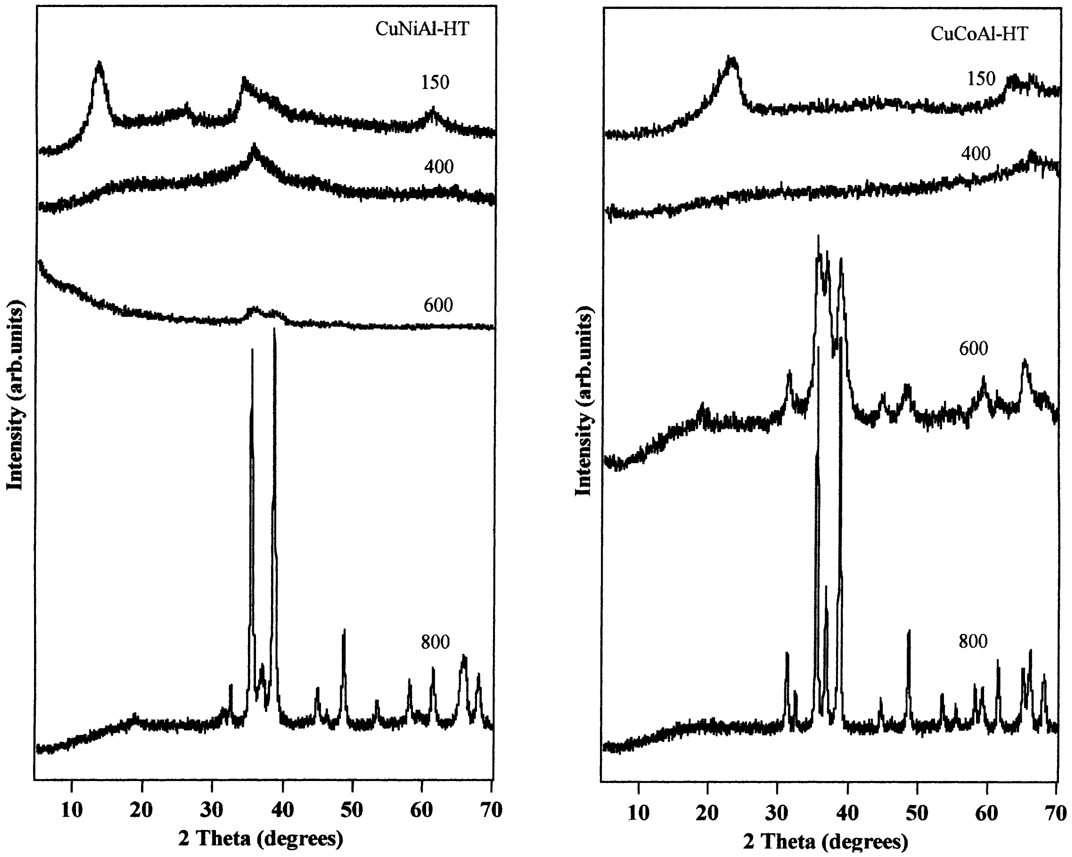

Fig. 4. Powder X-ray diffraction pattern of CuNiAl-HT and CuCoAl-HT calcined at different temperatures in air for 5 h.

and aluminum were noticed. In the case of cobalt system, crystalline copper oxide with well-crystalline spinel phase was observed at 600 °C itself, whose crystallinity improved with a further increase in calcination temperature. It has to be noted here that for both systems, fresh samples were more active, irrespective of co-bivalent metal ions, than their corresponding catalysts calcined at different temperatures. The increase in conversion for CuNiAl-800 may be due to the inherent activity of well-crystalline discrete CuO, as shown by PXRD around this temperature, in mediating the reaction. A closer look at the PXRD of this sample would indicate a larger concentration of crystalline CuO than the spinel phase. However, in the case of cobalt system, although well-crystalline CuO grows, a continuous decrease in the conversion was noted, possibly due to masking of this phase by spinel phase, whose concentration was stronger than that of the corresponding nickel system, thereby preventing the access of the reactant molecules. Furthermore, calculation of crystallite size of CuO (from the strong $d_{(-1\,1\,1)}$ and $d_{(2\,0\,0)}$ reflections) for samples calcined at 800 °C supported the activity correlation wherein the size was smaller for CuNiAl-800 (146 Å) than for CuCoAl-800 (234 Å), thereby providing a larger surface for the reaction to occur. The other members of these series showed no significant difference in the activity with the variation in calcination temperature. However, activity of the calcined samples was lower than the fresh samples, indicating the promise of fresh hydrotalcites as catalysts for this reaction.

Acknowledgements

SK thanks Indian National Science Academy, New Delhi (BS/YSP-22) and Council of Scientific and Industrial Research, New Delhi (CSIR-YSA) for financial support under Young Scientist Schemes.

References

[1] M. Taramasso, G. Perego, B. Notari, US Patent no. 4,410,501 (1983).

[2] F.-S. Xiao, J. Sun, X. Meng, R. Yu, H. Yuan, J. Xu, T. Song, D. Jian, R. Xu, J. Catal. 188 (2001) 273.

[3] Z. Fu, J. Chen, D. Yin, L. Zhang, Y. Zhang, Catal. Lett. 66 (2000) 105.

[4] J. Sun, X. Meng, Y. Shi, R. Wang, S. Feng, D. Jiang, R. Xu, F.-S. Xiao, J. Catal. 193 (2000) 199.

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

[6] F. Basile, M. Campanati, E. Serwicka, A. Vaccari (Eds.), Special Issue on Hydrotalcites, Appl. Catal. Sci. 18 (2001) 1 (and articles therein).

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

[8] A. Dubey, V. Rives, S. Kannan, J. Mol. Catal. A 181 (2002) 151.

[9] A. Dubey, V. Rives, S. Kannan, Phys. Chem. Chem. Phys. 3 (2001) 4826.

[10] O. Ruggeri, F. Trifirò, A. Vaccari, J. Solid State Chem. 42 (1982) 120.

[11] D. Tichit, F. Medina, B. Coq, R. Dutartre, Appl. Catal. A 159 (1997) 241.

[12] S. Kannan, C.S. Swamy, J. Mater. Sci. 32 (1997) 1623.

[13] S. Kannan, Appl. Clay Sci. 13 (1998) 347.

[14] A. Dubey, S. Kannan, unpublished results.

[15] U. Wilkenhöner, G. Langhendries, F. van Laar, G.V. Baron, D.W. Gamon, P.A. Jacobs, E. van Steen, J. Catal. 203 (2001) 201.

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

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

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