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Liquid phase hydroxylation of benzene over Cu-containing ternary hydrotalcites

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Abstract

One step liquid phase hydroxylation of benzene to phenol over ternary hydrotalcites of general formula CuM(II)M(III)–HT, where M(II) = Mg, Co, Ni and Zn and M(III) = Al, Fe and Cr was carried out in the temperature range 30–80 °C using pyridine as solvent and H_2O_2 as oxidant. Influence of various reaction parameters, such as reaction temperature, substrate:catalyst ratio, substrate weight, volume of the solvent, calcination temperature and reaction time were studied. Among the catalysts screened, CuCoAl–HT and CuNiAl–HT with (Cu + Co(or Ni))/Al = 3.0 and Cu/Co(or Ni) = 3.0 showed maximum activity with nearly 100% selectivity of phenol. The hydroxyl radical generated upon interaction of catalyst with oxidant is believed to be the active species involved in this reaction.

1. Introduction

One step hydroxylation of benzene to phenol is a challenging reaction of current interest both synthetically and commercially due to difficulties of the direct oxygenation of energetically stable benzene and formation of acetone as a byproduct in the widely used cumene process, respectively. The importance of the reaction stems from the wide-spread industrial use of phenol in the production of antioxidants, agrochemicals and polymers. Numerous attempts have been made on this challenging reaction over Cu supported zeolites [1], Cu–MCM-41 [2], Cu catalysts supported on various oxides and zeolites [3], Fe/MFI, Fe/ZSM-5 [4–6] and pioneering work of Panov and Iwamoto [7–9] using various oxidants, such as N_2O, oxygen and H_2O_2. Xiao et al. [10] have reported a remarkable activity for a novel copper hydroxyphosphate catalyst for benzene hydroxylation under aqueous conditions using H_2O_2 as oxidant while a sharp drop in the activity was noted when acetone was used as solvent and attributed the activity to the unique structure of the catalyst. Stockmann et al. [11] have explored various transition metal containing amorphous microporous mixed oxides for benzene hydroxylation using H_2O_2 as oxidant. Among the metal ions studied, Fe showed the maximum activity wherein nearly 10% yield of phenol was noted while Cu-containing oxides showed less than 2% yield of phenol under similar conditions using a benzene:H_2O_2 mole ratio of 1:4 where significant contributions of homogeneous reaction was also noted. Very recently, Bahidsky et al. [12] have studied gas phase oxidation of benzene using oxygen as oxidant over copper modified phosphate catalyst at 450 °C in the presence of ammonia and noted a conversion of phenol in the range 0–2% with more than 95% selectivity wherein activity varied with copper loading and the state of copper in the phosphate matrix.

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Although various copper containing materials have been explored for this reaction, however, to the best of our knowledge, no report is available concerning the use of hydrotalcites for this interesting reaction. Hydrotalcites, otherwise referred as layered double hydroxides (LDHs) are having an increasing attention due to their interesting properties like in the synthesis of multicomponent redox catalysts and solid base catalysts and their applications for various chemical transformations [13–17]. 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 in the interlayer [13]. 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 [18,19]. In our earlier work, we have disclosed the use of Cu-containing hydrotalcites for liquid phase hydroxylation of phenol to dihydroxybenzenes [20–22]. In this communication, we report for the first time the potential use of Cu-containing ternary hydrotalcites of general formula CuM(II)M(III)*xy*–HT (where '*xy*' stands for Cu:M(II) atomic ratio) for direct hydroxylation of benzene to phenol in liquid phase using pyridine as solvent and H_2O_2 as an oxidant.

2. Experimental

CuM(II)M(III)–HTs with different atomic compositions of M(II)/M(III) and (Cu + M(II))/M(III), where M(II) = Ni, Co, Mg or Zn and M(III) = Al, Fe or Cr, were synthesized by coprecipitation method at a constant pH (9–10). The details of the synthesis of these materials have been compiled elsewhere [20,22]. The hydroxylation of benzene was carried out in a custom designed temperature controlled stainless steel closed reactor (70 ml) under stirring. Typically, 5 g of benzene and desired amount of catalyst (10–100 mg) were added in pyridine acting as a solvent (usually 15 ml). The hydrogen peroxide (molar ratio of benzene:H_2O_2 = 3:1) was added slowly to the reaction mixture, however, all at once and the reactor was subjected to desired temperatures (30–80 °C) in a controlled pre-temperature set oil bath. The products of the reaction mixture were quantified using the authentic samples by considering the response factors of reactant, solvent and products. The weight of the benzene remained after the reaction was quantified using an external standard namely, *o*-cresol, which indicated a 8–12% weight loss of benzene (i.e., mass balance of ~90%), probably due to work-up procedure and high exothermic nature of this reaction.

3. Results and discussion

Powder X-ray diffraction of all catalysts studied in this work have showed a single phase whose pattern resembles that of hydrotalcite (HT) except for CuAl binary hydrotalcite which showed gerhardite phase in addition to HT phase, well known due to Jahn–Teller distortion [23]. Details of physicochemical characterization of these samples are disclosed in our earlier work [21,22,24]. All catalysts yielded phenol as the reaction product with nearly 100% selectivity without formation of any dihydroxybenzenes. This is probably uniqueness of these catalysts, which, however, differed from the other Cu-based catalysts. On screening of various bivalent metal ions in a binary hydrotalcite of general formula M(II)Al–HT (M(II)/Al atomic ratio of 3.0), where M(II) = Mg, Co, Ni or Zn, it was concluded that none of them were active for hydroxylation under our reaction conditions, while CuAl–HT, showed around 1.6% conversion of benzene. Hydroxylation over ternary hydrotalcites indicated that the activity (most of them showed a nearly 100% selectivity towards phenol) was better than the binary systems, however, was significantly influenced by both the nature of bivalent metal ions as well as trivalent metal ions of HT-like lattice (Table 1). Comparison of activity of non-copper containing binary hydrotalcites with that of Cu-containing systems substantiated the necessity of copper in mediating the hydroxylation reaction.

Considering an individual series of ternary hydrotalcites (CuM(II)Al*xy*–HT, where M(II) = Ni or Co), the

Table 1
Catalytic hydroxylation of benzene over various catalysts

Catalyst[a]	Conversion (%)[b]	Selec. H_2O_2 (%)
MgAl3–HT	0	0
CoAl3–HT	0	0
NiAl3–HT	0	0
ZnAl3–HT	0	0
CuAl3–HT	1.6	4.8
CuNiAl15–HT	2.8	8.4
CuNiAl13–HT	3.5	10.5
CuNiAl11–HT	3.8	11.4
CuNiAl31–HT	4.8	14.4
CuCoAl15–HT	3.7	11.1
CuCoAl13–HT	4.3	12.9
CuCoAl11–HT	4.5	13.5
CuCoAl31–HT	4.7	14.1
CuMgAl31–HT	4.0	12.0
CuZnAl31–HT	3.6	10.8
CuNiFe31–HT	2.5	7.5
CuNiCr31–HT	3.6	10.8
CuCoFe31–HT	2.0	6.0
CuCoCr31–HT	3.7	11.1

[a] Benzene: 5 g; catalyst: 10 mg; oxidant–H_2O_2; benzene:H_2O_2 mole ratio: 3.0; solvent-pyridine: 15 ml; temperature: 65 °C; time: 24 h; M(II)/M(III) atomic ratio = 3.0.

[b] Conversion of benzene based on phenol calculated using external standard (*o*-cresol).

activity of the reaction decreased with a decrease in the concentration of copper metal ion suggesting its direct dependence. It is to be mentioned here that the binary catalyst namely CuAl–HT showed only 1.6% conversion of benzene while a nearly threefold increase in the conversion was noted upon incorporation of co-bivalent metal ions suggesting that although copper ions are the active centers involved in the reaction, but the overall activity is varied by the nature and concentration of co-bivalent metal ions present in the hydrotalcite lattice. The results observed here have advantages over some of the copper supported systems such as Al–MCM-41 where the maximum yield of phenol was around 0.5–1.2% with 97% selectivity, however, varied depending on the type of support [1,2]. Influence of reaction time studies showed an initial induction time of around 30 min over these catalysts and the conversion of benzene increased up to 6 h (Fig. 1) of the reaction time while no significant change was observed with a further increase in the time up to 48 h. This suggests the stability of these catalysts under our conditions because the product of the reaction namely, phenol, is more susceptible for further oxidation. Variation of reaction temperature showed (Fig. 2) that the conversion of benzene increased up to 65 °C while a further increase decreased the conversion. This may be due to the thermal decomposition of H_2O_2 at higher temperatures. This behavior is similar to other Cu-based microporous and mesoporous materials like Cu–NaY and Cu–MCM-41 catalysts, however, the reduction in the conversion of benzene was attributed to reduced solubility of oxygen at higher temperatures [3]. Among the catalysts screened, those containing Ni and Co as co-bivalent metal ions with Al as trivalent cation with an atomic composition of (Cu + Ni)/Al = 3 and (Cu + Co)/Al = 3 yielded maximum conversion and hence were selected for further studies.

The effect of substrate:catalyst mass ratio indicated a decreasing trend in the activity with a decrease in this ratio (Fig. 3(A)). This may be due to the spontaneous formation of coke (as the reaction mixture turned dark black) which probably blocks the active sites of the catalysts and utilization of H_2O_2 for undesired reactions, thereby decreases the activity. The influence of the weight of the benzene as plotted in Fig. 3(B) indicated that the conversion of benzene increased continuously with an increase in its weight. This is due to the higher heat capacity of benzene which avoids an uncontrolled heating of the system thereby decreases the occurrence of undesired consecutive reactions [6]. The weight of the substrate was optimized at 5 g for further studies.

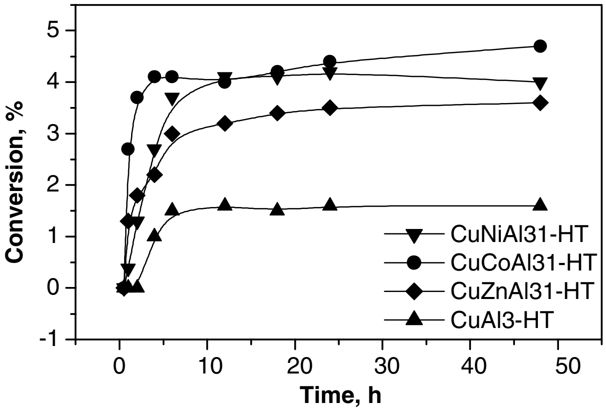

Fig. 1. Influence of reaction time on the benzene conversion over CuM(II)Al*xy*–HTs (conditions as given in Table 1 except for time).

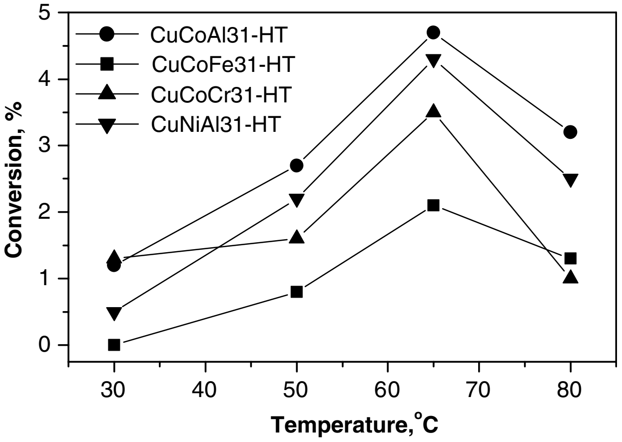

Fig. 2. Influence of the reaction temperature on the benzene conversion over CuM(II)M(III)*xy*–HTs (conditions as given in Table 1 except for temperature).

In order to see the influence of various solvents, solvents such as acetonitrile, acetone, THF, DMF, chloroform and pyridine were tried for this reaction. None of the solvents except pyridine showed any conversion of benzene at 3:1 molar ratio of benzene:H_2O_2. We presume that this may be due to ionic nature coupled with basic character of this solvent which can hold phenol more strongly than non-ionic solvents. Further, it is also known on the promotional influences of such bases in oxidation of organic substrates [25]. However, it should be mentioned here that no catalytic activity was found when catalyst was not added in the reaction mixture, despite when pyridine was used as solvent. The influence of the volume of the solvent (Fig. 3(C)) indicated that the conversion of benzene increased up to 15 ml and decreased with a further increase in the volume of the solvent. This may be due to variations in the local heat balance and decrease in the active sites per unit volume of the reaction mixture. An optimized solvent volume of 15 ml was selected for further studies.

In order to test the catalytic contributions of homogeneous metal ions, that probably might have leached during the reaction, the screened catalysts were suspended (with stirring) in H_2O_2 and pyridine for 24 h at

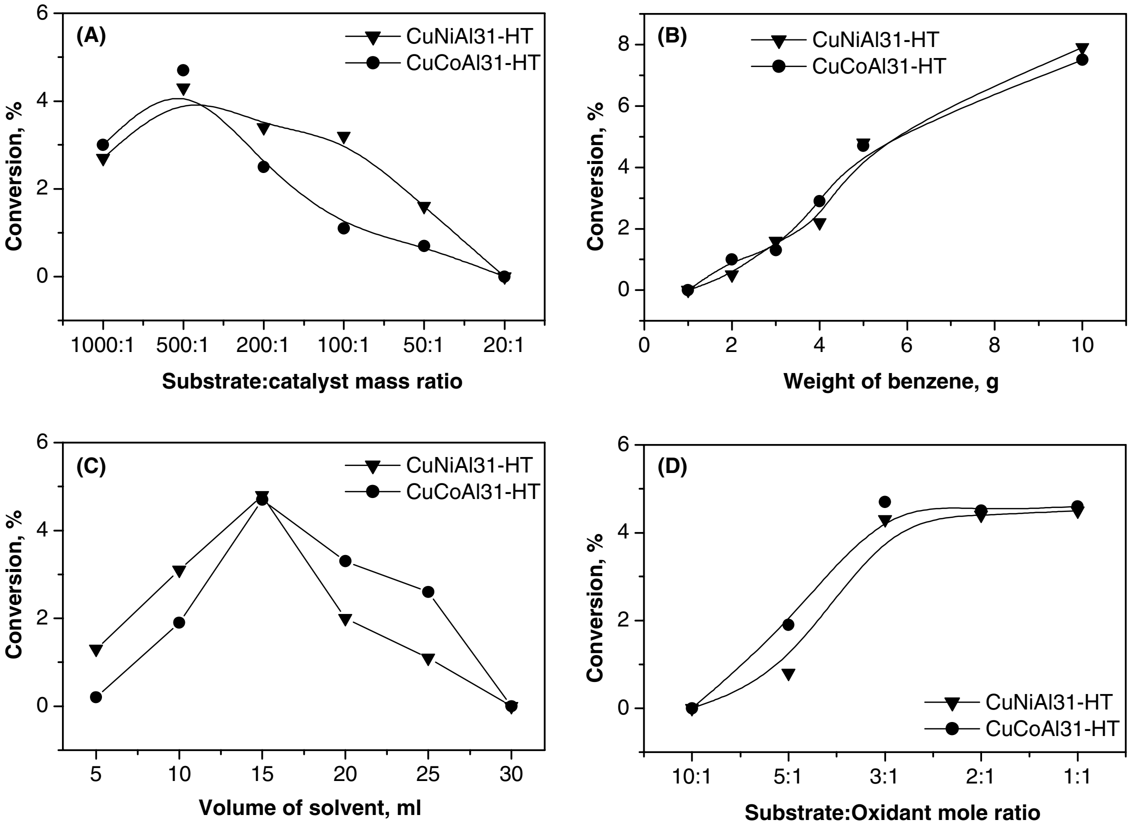

Fig. 3. Influence of: (A) substrate:catalyst mass ratio, (B) weight of benzene, (C) volume of solvent and (D) substrate:oxidant mole ratio on the catalytic hydroxylation of benzene over CuNiAl31–HT and CuCoAl31–HT (time: 24 h; temperature: 65 °C).

65 °C. After 24 h, the catalysts were centrifuged and the filtrate and residue were tested for a fresh reaction under similar experimental conditions. No conversion of the benzene was noted in both (residue and filtrate) cases indicating that the reaction is a concerted one. Further, in one of our experiments the catalyst CuNiAl31–HT was centrifuged after 2 h of reaction time and the reaction was continued. No variation in the conversion was noted during the course of reaction (till 24 h) suggesting the heterogeneous nature of these catalysts. The influence of the substrate:oxidant ratio, given in Fig. 3(D), indicated an increasing trend with an increase in H_2O_2 concentration up to 3:1 benzene:H_2O_2 mole ratio but becomes nearly constant with a further increase in the H_2O_2 concentration. This may be due to the high exothermic nature of the reaction wherein at higher concentration of H_2O_2, the reaction temperature shoots up in leading to decomposition and undesired consumption of H_2O_2. To assess the reusability of these catalysts, they (CuNiAl31–HT and CuCoAl31–HT) were centrifuged after the reaction, washed with water and acetone and tested for the reaction. However, the conversion decreased to 3% after three cycles for both catalysts, probably due to changes in the crystallinity of the samples (as evidenced from PXRD patterns; not given).

In order to study the activity of mixed metal oxides obtained after calcination, CuNiAl31–HT and CuCoAl31–HT were calcined at different temperatures (150, 400, 600 and 800 °C) in air for 6 h. These temperatures were chosen based on their thermal decomposition profiles revealed by thermogravimetric analysis. However, the activity of all catalysts (for CuNiAl31–HT, the values were in between 1.8% and 2.8% while for CuCoAl31–HT it was between 2.6% and 3.6%) irrespective of calcination temperature was lower than the fresh (uncalcined) catalysts. This may be due to the structural loss of the hydrotalcite phase at higher temperature in addition to the loss in the specific surface area of the calcined catalysts. These results are similar to our earlier studies over these catalysts for phenol hydroxylation [20].

We believe, the reaction occurs similar to Fenton chemistry, through the participation of hydroxyl radicals in activating benzene toward the formation of phenol. In order to explain this fact, two different experiments were performed by taking into the consideration of induction time (30 min) observed in this reaction. In one of the experiments, benzene and catalyst were mixed under stirring for 30 min and in another experiment the catalyst was suspended with H_2O_2 for

30 min. Subsequently, H_2O_2 was added to the former while benzene was added to the later experiment and monitored the reaction. The results indicted that no induction time was observed for the later experiment while similar induction time was noted for the first case. This suggests that the hydroxyl radicals are produced with the interaction of H_2O_2 with the catalyst. Addition of radical quenchers, like ethanol, during the reaction also lowered the conversion, augment their participation.

In conclusion, we have reported for the first time the potential use of Cu-containing hydrotalcites for the one step liquid phase hydroxylation of benzene to phenol under mild reaction conditions. The results obtained indicated that these materials are promising alternative to some of the copper or iron supported zeolites cited in the literature. Obtaining nearly 100% selectivity of phenol (thereby avoiding separation problems) despite low conversion at such high substrate:catalyst (500:1) and substrate:oxidant (3:1) ratios suggests the scope of tailoring reaction engineering design for better utilization of this system. The detailed investigation of the role of solvent and the nature of metal ions for this reaction is currently underway.

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References

[1] T. Ohtani, S. Nishiyama, S. Tsuruya, M. Masai, J. Catal. 155 (1995) 158.
[2] T. Ohtani, S. Nishiyama, S. Tsuruya, M. Masai, in: L. Guczi, F. Solymosi, P. Tetenyi (Eds.), Proceedings of the 10th International Congress on Catalysis, Budapest, Elsevier, Amsterdam, 1992, p. 1999.
[3] J. Okamura, S. Nishiyama, S. Tsuruya, M. Masai, J. Mol. Catal. A 135 (1998) 133.
[4] K.S. Pillai, J. Jia, W.M.H. Sachtler, Appl. Catal. A 264 (2004) 133.
[5] Q. Zhu, R.M. van Teeffelen, R.A. van Santen, E.J.M. Hensen, J. Catal. 221 (2004) 575.
[6] A. Waclaw, K. Nowinska, W. Schwieger, Appl. Catal. A 270 (2004) 151.
[7] G.I. Panov, A.S. Kharitonov, G.A. Sheveleva, US Patent 5 756 861, 1998.
[8] G.I. Panov, Appl. Catal. A 82 (1992) 31.
[9] M. Iwamoto, J. Hirata, K. Matsukami, S. Kagawa, J. Phys. Chem. 87 (1983) 903.
[10] F.-S. Xiao, J. Sun, X. Meng, R. Yu, H. Yuan, D. Jiang, S. Qui, R. Xu, Appl. Catal. A 207 (2001) 267.
[11] M. Stockmann, F. Konietzni, J.U. Notheis, J. Voss, W. Keune, W.F. Maier, Appl. Catal. A 208 (2001) 343.
[12] M. Bahidsky, M. Hronec, Catal. Today 91–92 (2004) 13.
[13] F. Trifirò, A. Vaccari, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle, 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.
[14] D. Tichit, B. Coq, CATTECH 7 (2003) 206.
[15] B.F. Sels, D.E. De Vos, P.A. Jacobs, Catal. Rev. Sci. Eng. 43 (2001) 443.
[16] K. Zhu, C. Liu, X. Ye, Y. Wu, Appl. Catal. A 168 (1998) 365.
[17] D. Kishore, S. Kannan, Appl. Catal. A 270 (2004) 227.
[18] F. Marquez, A.E. Palomares, F. Rey, A. Corma, J. Mater. Chem. 11 (2001) 1675.
[19] K. Iwai, T. Yamauchi, K. Hashimoto, T. Mizugaki, K. Ebitani, K. Kaneda, Chem. Lett. 32 (2003) 58.
[20] A. Dubey, V. Rives, S. Kannan, J. Mol. Catal. A 181 (2002) 151.
[21] A. Dubey, S. Velu, S. Suzuki, S. Kannan, Appl. Catal. A 238 (2003) 319.
[22] V. Rives, A. Dubey, S. Kannan, Phys. Chem. Chem. Phys. 3 (2001) 4826.
[23] S. Kannan, V. Rives, H. Knozinger, J. Solid State Chem. 177 (2004) 319.
[24] S. Kannan, V. Rives, J. Mater. Chem. 10 (2000) 489.
[25] D.T. Sawyer, A. Sobkowiak, T. Matsushita, Acc. Chem. Res. 29 (1996) 409.