



Selective C-alkylation of phenol with methanol over catalysts derived from copper–aluminium hydrotalcite-like compounds

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Abstract

Copper aluminium hydrotalcites (CuAl-HT) with a Cu/Al atomic ratio of 2, 3 and 4 (CuAl 2.0-HT, CuAl 3.0-HT, CuAl 4.0-HT) were synthesised by the coprecipitation method using a mixture of NaOH/Na₂CO₃ as precipitant. The pure crystalline hydrotalcite (HT) phase was detected by X-ray diffraction when the copper–aluminium hydrotalcite was prepared without ageing (CuAl 3.0-WAHT). Vapour phase alkylation of phenol with methanol was carried out over CuAl-HT calcined at 450°C/8 h in air (CuAl-CHT). The activity and selectivity of these catalysts were compared with those of magnesium–aluminium calcined hydrotalcites (MgAl 4.0-CHT) from our earlier report. MgAl 4.0-CHT showed higher selectivity for 2,6-xylenol whereas CuAl-CHT was selective for *o*-cresol. Among the CuAl-CHT studied, CuAl 3.0-CHT showed higher phenol conversion at low temperatures (250–350°C). The catalyst derived from pure copper–aluminium hydrotalcite (CuAl 3.0-WAHT) showed lowest phenol conversion compared to other copper based catalysts obtained from a mixture of HT and malachite phases. The selectivity for *o*-cresol decreased in the order CuAl 3.0-CHT > CuAl 2.0-CHT > CuAl 3.0-WAHT ≈ CuAl 4.0-CHT > MgAl 4.0-CHT at low phenol conversion levels (15–20%). A suitable reaction pathway for the alkylation of phenol with methanol over these catalysts has been proposed after a careful examination of the reaction sequence. The selective C-alkylation to give *o*-cresol and 2,6-xylenol over CuAl-CHT could be attributed to the higher acidity of these catalysts as evidenced by the higher cyclohexanol dehydration activity.

Keywords: Hydrotalcite; Alkylation of phenol; Acid–base properties

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1. Introduction

In recent years, there is an increasing interest for the synthesis of alkyl phenols especially *o*-cresol and 2,6-xyleneol because of their importance as intermediates for the synthesis of a variety of resins, herbicides, insecticides and other important chemicals [1,2]. For example, epoxy cresol novolac (ECN) and polyphenylene oxide (PPO) used in the electronic industries and automobile industries are derived from *o*-cresol and 2,6-xyleneol, respectively [3]. A wide variety of catalysts such as γ -alumina, silica–alumina, metallic sulphates, phosphates, ALPOs, SAPOs, zeolites, acidic and basic oxides have been employed for this reaction [4–11]. However, they produce a mixture of O- and C-alkylated products. Moreover, most of these catalysts exhibit unsatisfactory stability with time on stream due to coking from phenol or methanol [4,5,8]. Since, the alkylation of phenol with methanol is essentially an acid–base reaction, the product selectivity depends on the catalyst acidity and basicity. It has been found that catalysts with strong acidic sites favour O-alkylation while weak acidic sites or strong basic sites favour C-alkylation [10]. On the other hand, Tliemat-Manzalji et al. [12] and Marczewski et al. [7] have claimed that weak acidic sites favour C-alkylation. Recently, we have found [13] that thermally activated magnesium–aluminium hydrotalcites are more active and selective catalysts for the synthesis of 2,6-xyleneol compared to either γ -Al₂O₃ or MgO.

Hydrotalcites (HT) are a class of layered materials of current interest. They consist of positively charged brucite (Mg(OH)₂)-like layers interspersed with hydrated anions in the interlayer. They are represented by the general formula, (M(II)_{1-x}M(III)_x(OH)₂)ⁿ⁺ Aⁿ⁻_{x/n} · yH₂O, where, M(II) and M(III) are divalent and trivalent cations such as Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Al³⁺, Fe³⁺, Cr³⁺ respectively, Aⁿ⁻ is the interlayer anion such as Cl⁻, NO₃⁻, CO₃²⁻ etc. and $x = 0.1$ – 0.33 [13–15]. Thermal calcination of these materials around 450°C results in the formation of highly active mixed metallic oxides which are found to be promising base catalysts [16–19].

We have been interested in studying the effect of isomorphous substitution of Mg²⁺ by other divalent transition metal ions in the HT framework on the phenol conversion and product selectivity and to correlate their catalytic performance with acid–base properties as determined by the decomposition of 2-methyl-3-butyne-2-ol (MBOH) and cyclohexanol [20]. In this paper, we report our results on the alkylation of phenol with methanol over copper–aluminium calcined hydrotalcites with Cu/Al atomic ratio 2, 3, 4 for the first time. Since the copper containing hydrotalcites are always mixed with other phases such as malachite, attempts have been made to synthesis a pure copper–aluminium hydrotalcite precursor and the catalytic performance for the title reaction has been compared with that of other copper–aluminium and magnesium–aluminium samples. The results on the other catalyst systems will be reported elsewhere [21]. In the

following sections, the copper–aluminium hydrotalcites are represented as CuAl *N*.0-HT and their calcined samples (450°C /8 h in air) are represented as CuAl *N*.0-CHT where, '*N*' is the Cu/Al atomic ratio. For example, copper–aluminium hydrotalcite with Cu/Al atomic ratio 3 will be represented as CuAl 3.0-HT and the corresponding calcined sample as CuAl 3.0-CHT.

2. Experimental

Copper–aluminium hydrotalcite-like compounds with Cu/Al atomic ratios of 2, 3 and 4 were synthesised by coprecipitation from a mixture of aqueous solutions with $\text{Cu}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ as precursors and a mixture of aqueous solutions of $\text{NaOH}/\text{Na}_2\text{CO}_3$ ($\text{CO}_3^{2-}/\text{Cu} + \text{Al} = 20$) as precipitant at room temperature and pH around 9. The resulting slurry was aged at 65°C/30 min. For comparison, copper–aluminium hydrotalcite-like compound with a Cu/Al atomic ratio of 3 was prepared without giving any ageing treatment (abbreviated as CuAl 3.0-WAHT). For phase identification, the powder X-ray diffraction (PXRD; Rigaku miniflex) was carried out using Fe-filtered CoK_α radiation ($\lambda = 1.7902 \text{ \AA}$) with a scan speed of $2\theta = 2^\circ/\text{min}$ while a speed of $0.5^\circ/\text{min}$ was used for the calculation of lattice parameters [22]. Elemental Si was used as an external standard. BET surface area, pore size distribution and pore volume study of calcined samples (450°C/8 h in air) was performed by N_2 adsorption–desorption at 77 K using a Carlo Erba (Model 1800) sorptometer. The alkylation reactions were carried out with 1.5 g of calcined hydrotalcites (CHT) packed in a fixed bed flow reactor and a 1:7 phenol:methanol mixture was used as reactant feed with a space velocity, $\text{WHSV} = 9.0 \text{ mol h}^{-1} \text{ kg}^{-1}$ ($\text{WHSV} = \text{weight hourly space velocity} = \text{flow rate of phenol (mol h}^{-1})/\text{weight of the catalyst (kg)}$). The phenolic products were condensed and collected in cold traps and analyzed using GC. The catalytic activity and product selectivity of these catalysts were compared with those of magnesium–aluminium calcined hydrotalcite with an Mg/Al atomic ratio = 4 (MgAl 4.0-CHT), the most active catalyst for the phenol alkylation from our earlier report [13].

3. Results and discussion

3.1. Synthesis and characterization

It is generally known that copper–aluminium hydrotalcites (CuAl-HT) are always mixed with other phases such as malachite or gerhardtite [23–25] due to the Jahn–Teller effect in the Cu^{2+} ion. An acceptable CuAl-HT has been prepared by decomposing a copper ammoniacal complex on $\gamma\text{-Al}_2\text{O}_3$ in vacuum [26]. According to Reichle [27], CuAl-HT could only be made by using aqueous

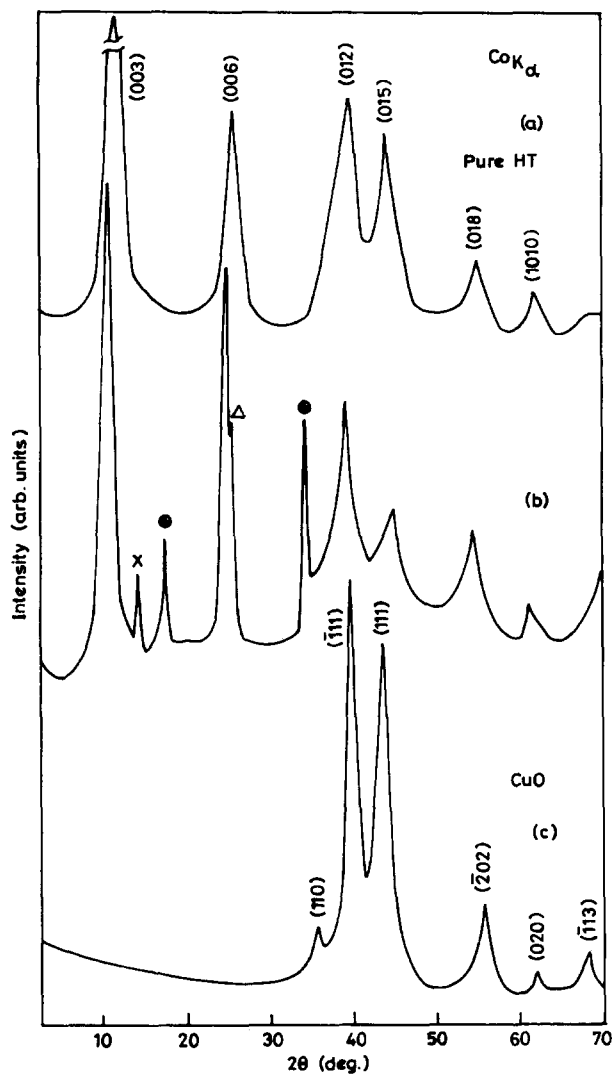


Fig. 1. Powder X-ray diffraction patterns of (a) CuAl 3.0-WAHT; (b) CuAl 3.0-HT, (x) $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (JCPDS: 21-296), (\oplus) $\text{CuCO}_3\text{Cu}(\text{OH})_2$ (Malachite; JCPDS: 10-399), (Δ) $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ (JCPDS: 10-442); (c) CuAl 3.0-CHT.

solutions of bicarbonate as precipitant, because, at high pH, copper precipitates as copper hydroxycarbonate (malachite). In a detailed investigation on the synthesis of a wide range of CuAl-HT using Na_2CO_3 as precipitant Yamaoka et al. [23] employed the sequential precipitation method. However, they noticed that $\text{Na}_2\text{Al}_2(\text{CO}_3)_2 \cdot 2.9\text{H}_2\text{O}$ mixed with HT in the whole range studied. In our experiments, we obtained a pure and crystalline HT phase (CuAl3.0-WAHT) when the sample was not digested (Fig. 1a). When the samples were aged at 65°C for 30 min, in addition to the HT phase, malachite and other phases were

Table 1
Chemical composition and lattice parameters of hydrotalcite-like compounds

Sample	M ²⁺ /Al ³⁺ ratio ^a	Lattice parameters ^b		
		a (Å)	c (Å)	V (Å) ³
CuAl 2.0-HT	2.0	2.977	22.087	195.7
CuAl 3.0-WAHT ^c	3.0	3.041	21.992	176.1
CuAl 3.0-HT	3.1	3.111	22.529	218.0
CuAl 4.0-HT	4.1	3.116	22.847	192.1
MgAl 4.0-HT	3.7	3.070	23.580	192.5

^a Determined by inductively coupled plasma emission spectroscopy.

^b Calculated employing the least square method for hexagonal crystal systems (Ref. [22]).

^c Sample obtained without giving ageing treatment.

also detected by XRD (Fig. 1b). These results indicate that it is possible to precipitate pure crystalline CuAl-HT using a mixture of NaOH/Na₂CO₃ as precipitant without digesting the slurry.

The chemical composition and lattice parameters of synthetic samples are presented in Table 1. Comparing the lattice parameters of CuAl 3.0-WAHT and CuAl 3.0-HT the ageing procedure seems to increase the lattice parameters 'a', 'c' and cell volume 'V'. The values of 'a' and 'c' also increase with increase in Cu/Al atomic ratio owing to the difference in effective ionic radius of Cu²⁺ and Al³⁺ (0.69 and 0.5 Å, respectively). However, the cell volume varies randomly because of the contamination of malachite and other phases along with HT in the aged samples. Upon calcination at 450°C/8 h in air, these samples offered a well crystalline CuO phase (Fig. 1c) whose d($\bar{1}11$) is similar to that of pure CuO (2.523 Å; JCPDS file No. 5-0661). The physicochemical properties of

Table 2
Physicochemical properties of hydrotalcite-like compounds calcined at 450°C/8 h in air

Sample code	Sample	PXRD phase obtained	Average crystal size (Å) ^a	BET Surface Area ^b (m ² g ⁻¹)	Specific pore volume ^b (cm ³ g ⁻¹)	Decomposition of cyclohexanol ^c (mol-%)		
						Conversion	S _{c-hexene}	S _{c-none}
A	CuAl 2.0-CHT	CuO	90	47	0.10	73.4	80.4	19.6
B	CuAl 3.0-WAHT	CuO	203	54	0.16	78.6	75.2	24.8
C	CuAl 3.0-CHT	CuO	199	54	0.28	84.2	83.0	17.0
D	CuAl 4.0-CHT	CuO	110	52	0.10	80.5	76.2	23.8
E	MgAl 4.0-CHT	MgO	44	176	0.48	32.5	33.5	66.5

^a Calculated by the X-ray line broadening method taking the reflections of ($\bar{1}11$) and (111) planes in CuO and (200) and (220) planes in MgO.

^b Surface area and specific pore volume determined by N₂ adsorption-desorption method.

^c Reaction temperature = 300°C at 1 atm and WHSV = 4.8 mol h⁻¹ kg⁻¹.

S_{c-hexene} = selectivity to cyclohexene; S_{c-none} = selectivity to cyclohexanone.

calcined hydrotalcites (450°C/8 h in air) are summarized in Table 2. The average particle size calculated by the X-ray line broadening technique employing the Debye–Scherrer equation [22] is maximal (203 Å) for CuAl 3.0-WACHT and CuAl 3.0-CHT (199 Å) while it is almost similar in the case of CuAl 2.0-CHT (90 Å) and CuAl 4.0-CHT (110 Å). The decomposition of cyclohexanol over copper–aluminium calcined hydrotalcite (CuAl-CHT) showed predominantly the dehydration activity indicating the presence of mainly acidic sites [28,29]. Furthermore, comparison of the selectivity of cyclohexene/cyclohexanone for samples A–D reveals that the variation of Cu/Al atomic ratio or the ageing treatment does not influence the acid–base properties of these catalysts. These results are similar to those obtained over a series of MgAl-CHT (Mg/Al atomic ratio 3–12) by the microcalorimetric determination of heat of adsorption of NH₃ and CO₂ [30]. In the present study, MgAl 4.0-CHT showed low dehydration activity indicating lower acidity or strong basicity of the sample. The acidity (Lewis type) in these catalysts is attributed to the dissolution of Al³⁺ in the oxide lattice during calcination around 450°C and coordinatively unsaturated O²⁻ ion acting as a strong Lewis basic site [31,32].

3.2. Catalytic studies

3.2.1. Effect of temperature

The alkylation reactions were carried out in the temperature range 250–450°C. The effect of temperature on phenol conversion (Fig. 2) shows that MgAl 4.0-CHT (the most active catalyst reported in [13]) attained 100% phenol conversion at 400°C itself, whereas CuAl-CHT attained only around 80% phenol conversion at 450°C. Among the CuAl-CHT series, CuAl 3.0-CHT showed

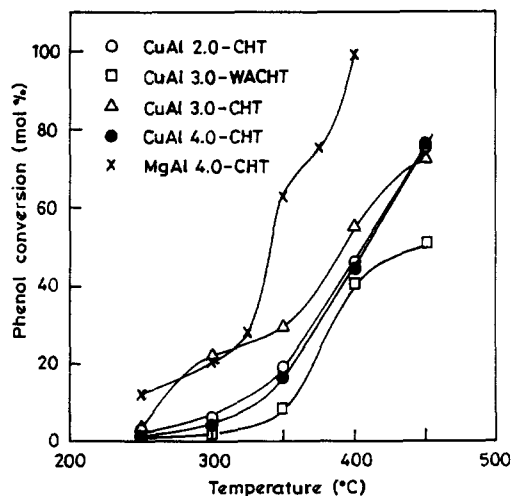


Fig. 2. Effect of temperature on phenol conversion over M(II)Al-CHT.

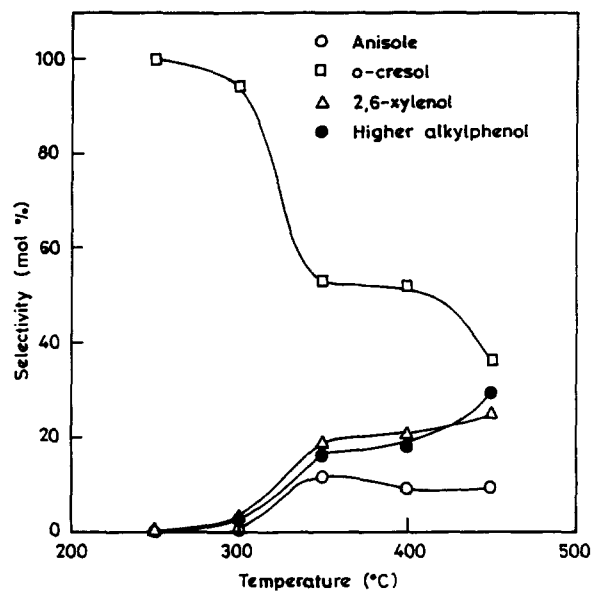


Fig. 3. Effect of temperature on products selectivity over CuAl 3.0-CHT.

higher phenol conversion in the temperature range 250–400°C which reveals that the Cu/Al atomic ratio of 3 is the optimum composition for higher phenol conversion over CuAl-CHT. On the other hand, copper–aluminium hydrotalcite with a Cu/Al atomic ratio of 3 obtained without ageing and calcined at 450°C/8 h in air (CuAl 3.0-WACHT) exhibited lowest activity indicating that the initial ageing of the slurry (65°C/30 min) is necessary for higher activity of these catalysts. Since the ageing treatment does not influence either the acid–base property or particle size or the surface area of the calcined sample, we presume that the malachite phase formed along with the HT phase in the aged sample enhances the catalytic activity. This is in accordance with the observation by Gusi et al. [33] in the low pressure methanol synthesis over the Cu–Zn–Al catalyst. The effect of temperature on product selectivity over CuAl 3.0-CHT is shown in Fig. 3 which indicates that the selectivity of *o*-cresol declined while that of 2,6-xyleneol and higher alkyl phenols increased with the increase in temperature. This could be due to the consecutive reactions of *o*-cresol to give 2,6-xyleneol and higher alkyl phenols. The selectivity to anisole increased slightly (around 10%) in the temperature range 300–350°C and then remained constant with further increase in temperature indicating that the secondary reactions of anisole are less favourable over these catalysts.

3.2.2. Effect of contact time

The effect of contact time on phenol conversion and product selectivity was studied in order to understand the reaction sequence in the alkylation reaction.

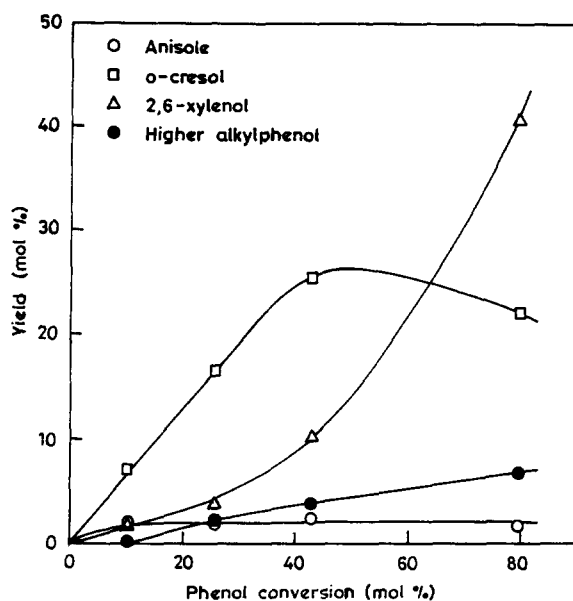


Fig. 4. OPE curves for phenol methylation over CuAl 3.0-CHT. Temperature = 350°C.

The optimum performance envelope (OPE) curves for the methylation of phenol over CuAl 3.0-CHT (Fig. 4) shows that anisole and *o*-cresol are primary alkylation products since both these products are formed at the onset of the reaction. The yield of anisole practically remained constant with the increase in phenol conversion while the yield of *o*-cresol passed a maximum around 40% conversion with consequent increase in the yield of 2,6-xyleneol and higher alkyl phenols. These results indicate that *o*-cresol did undergo secondary reactions to give 2,6-xyleneol and other higher alkyl phenols to a great extent. In order to verify these assumptions, reactions of anisole alone, an 1:7 mixture of anisole and methanol and 1:7 mixture of *o*-cresol and methanol were carried out over CuAl 3.0-CHT.

Table 3

Activity and product selectivity over CuAl 3.0-CHT employing anisole as unique reagent WHSV = 31.9 mol h⁻¹ kg⁻¹

Temp. (°C)	Anisole conversion (mol%)	Product selectivity (mol%)			
		Phenol	2-methyl anisole	<i>o</i> -cresol	2,6-xyleneol
300	1.7	88.2	–	11.8	–
350	2.4	70.8	–	29.2	–
400	5.0	46.0	30.0	22.0	2.0
350 ^a	5.5	67.3	–	27.3	5.4

^a WHSV = 13.5 mol h⁻¹ kg⁻¹.

Table 4

Activity and product distribution over CuAl 3.0-CHT employing anisole:methanol (1:7) mixture WHSV = 8.5 mol h⁻¹ kg⁻¹

Temperature (°C)	Anisole conversion (mol-%)	Product selectivity (mol-%)					
		2-Methyl- anisole	4-Methyl- anisole	Phenol	<i>o</i> -Cresol	2,6-Xylenol	Higher alkyl phenol
300	4.3	14.0	–	–	9.3	76.7	–
350	23.4	10.7	3.4	–	10.3	49.1	26.5
400 ^a	63.6	0.6	1.7	8.8	8.5	27.0	53.3
350 ^b	55.9	3.2	6.5	3.8	5.9	51.3	29.3

^a A trace amount of hexamethylbenzene was obtained.

^b WHSV = 3.9 mol h⁻¹ kg⁻¹.

When anisole alone was passed over CuAl 3.0-CHT, a large amount of phenol was noticed with a small quantity of *o*-cresol (Table 3). However, 2-methyl anisole was not observed in the temperature range 250–350°C indicating that anisole does not undergo a bimolecular reaction as observed previously over MgAl 4.0-CHT [13]. The formation of a large quantity of phenol is due to the dealkylation of anisole which can be attributed to the higher acidity [7] of CuAl 3.0-CHT compared to MgAl 4.0-CHT as evidenced from the higher cyclohexanol dehydration activity of the former (Table 2) [9,10]. The *o*-cresol may be formed through the monomolecular rearrangement of anisole. The formation of 2-methyl anisole at 400°C could be due to the alkylation of *o*-cresol with anisole, since the activation of OH group in *o*-cresol is much easier compared to the activation of anisole [34]. Increase in contact time (WHSV = 13.5 mol h⁻¹ kg⁻¹) results in an increase in anisole conversion and the selectivity for 2,6-xylenol while the selectivity for phenol and *o*-cresol were not affected. However, the very low anisole conversion ($\approx 5\%$ at 400°C) substantiates that the reactions of anisole (inter/intra molecular) over these catalysts is less probable.

The reaction of anisole with methanol (1:7) over CuAl 3.0-CHT (Table 4) demonstrates that anisole readily undergoes methylation to give 2-methyl anisole, *o*-cresol and 2,6-xylenol. When either the contact time (WHSV = 3.9 mol h⁻¹ kg⁻¹) or temperature is increased, the selectivity for *o*-cresol decreased with a consequent increase in the selectivity to 2,6-xylenol and higher alkyl phenols indicating that *o*-cresol is subsequently transformed into 2,6-xylenol and higher alkyl phenols.

The reaction of a 1:7 mixture of *o*-cresol and methanol over the same catalyst (Table 5) shows that *o*-cresol effectively undergoes methylation to give 2,6-xylenol and higher alkyl phenols over these catalysts. The very low selectivity for 2-methyl anisole (<5%) at all reaction temperatures and contact times reveal that *o*-cresol is selectively C-alkylated to 2,6-xylenol rather than O-alkylated.

Table 5

Activity and product distribution over CuAl 3.0-CHT employing *o*-cresol:methanol (1:7) mixture WHSV = 8.7 mol h⁻¹ kg⁻¹

Temp.(°C)	<i>o</i> -cresol conversion (mol%)	Product selectivity (mol%)		
		2-Methylanisole	2,6-Xylenol	Higher alkylphenol
300	31.2	2.9	92.9	4.2
350	43.2	4.4	83.1	12.5
400	75.8	4.9	44.0	51.1
350 ^a	66.9	4.9	70.1	25.0

^a WHSV = 4.3 mol h⁻¹ kg⁻¹.

kylated to give 2-methyl anisole. Increase in *o*-cresol contact time (WHSV = 4.3 mol h⁻¹ kg⁻¹) increases the conversion. However, the selectivity for 2,6-xylenol decreases with concomitant increase in the selectivity for higher alkyl phenol indicating that higher alkyl phenols are obtained by the consecutive reactions of 2,6-xylenol. These results confirm our hypothesis that *o*-cresol formed as the primary alkylation product undergoes secondary reaction to give 2,6-xylenol and higher alkyl phenols over CuAl-CHT.

Based on the above results, the reaction pathway for the alkylation of phenol with methanol over CuAl-CHT can be depicted as shown in the following scheme wherein the reaction proceeds predominantly through C-alkylation (path

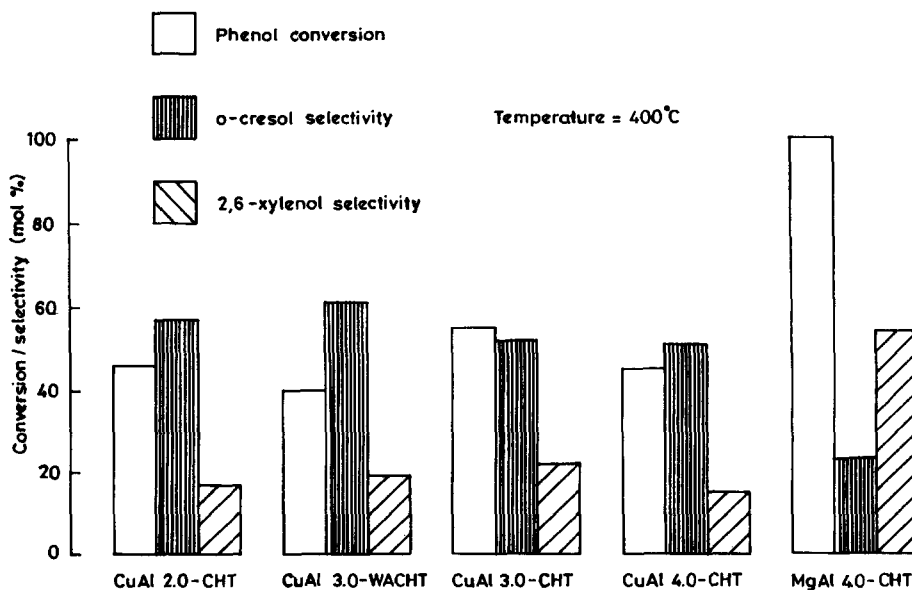


Fig. 5. Phenol conversion and product selectivity over M(II)Al-CHT at constant temperature (400°C).

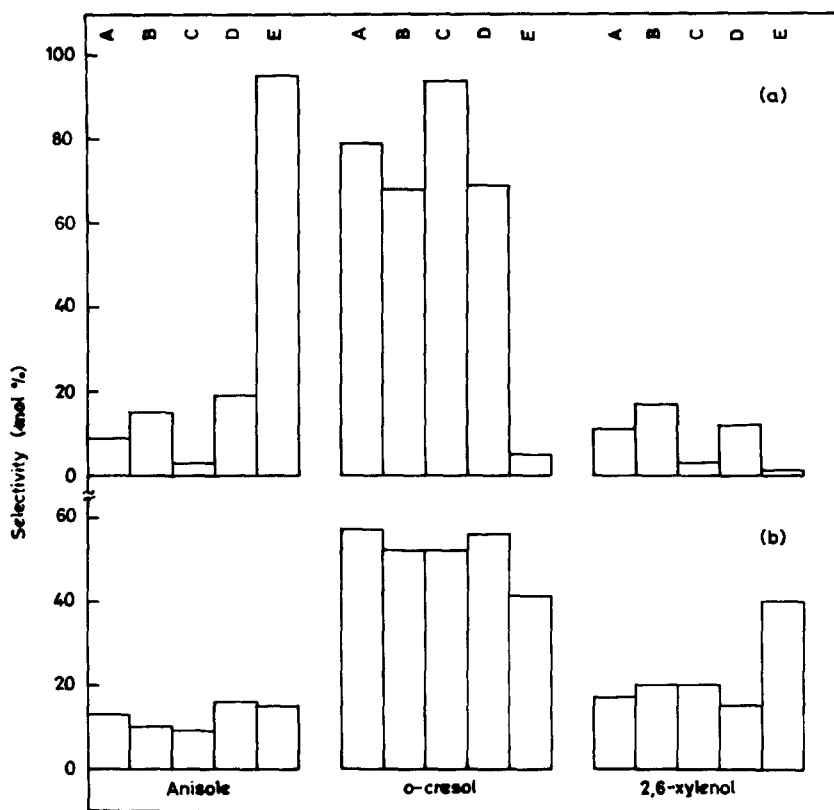
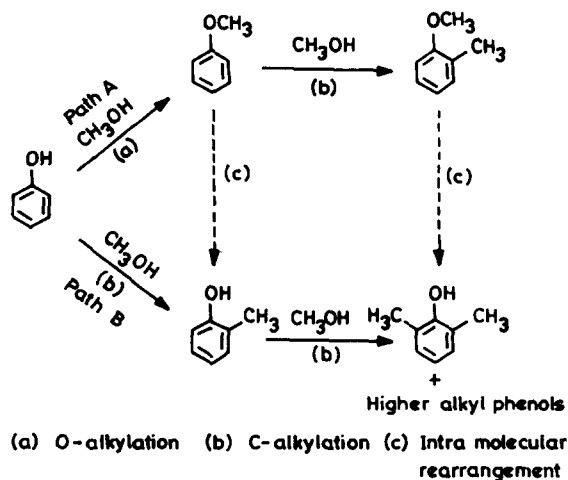


Fig. 6. Product selectivity over M(II)Al-CHT in the alkylation of phenol at constant phenol conversion (a) 15–20% (b) 45–55%. A, B, C, D and E are as in Table 2.

B) to give *o*-cresol and 2,6-xylene rather than O-alkylation (path A) to give anisole followed by *o*-cresol and 2,6-xylene.



In Fig. 5, the activity and selectivity for *o*-cresol and 2,6-xylenol at 400°C over all the catalysts derived from CuAl-HT (Cu/Al = 2, 3, 4) are compared with those of MgAl 4.0-CHT from our earlier report [13]. It can be seen that MgAl 4.0-CHT is the most active (nearly 100% phenol conversion) and more selective for 2,6-xylenol (around 60%). Substitution of Mg²⁺ by Cu²⁺ in the HT framework resulted in decrease in phenol conversion and increase in selectivity to *o*-cresol which follows the order CuAl 3.0-WACHT ≈ CuAl 2.0-CHT > CuAl 3.0-CHT ≈ CuAl 4.0-CHT > MgAl 4.0-CHT. In order to get more insight into the selectivity pattern over these catalysts, the product selectivity was compared at constant phenol conversion levels (Fig. 6). At low phenol conversion (15–20%), MgAl 4.0-CHT gave maximum selectivity (nearly 100%) for anisole while it is very low (10–20%) over CuAl-CHT. The selectivity for *o*-cresol is in the order CuAl 3.0-CHT > CuAl 2.0-CHT > CuAl 3.0-WACHT ≈ CuAl 4.0-CHT >> MgAl 4.0-CHT. At higher phenol conversions (45–55%) the selectivity for anisole decreases with consequent increase in selectivity for *o*-cresol and 2,6-xylenol over MgAl 4.0-CHT, whereas the selectivity for *o*-cresol decreases at the cost of 2,6-xylenol over CuAl-CHT. Furthermore, among the CuAl-CHT, there is no remarkable change in selectivity for *o*-cresol at higher phenol conversion indicating the presence of similar active sites in these catalysts. From these observations, it can be inferred that the alkylation reaction proceeds through the formation of anisole over MgAl-CHT which is due to the higher basicity of the catalysts, and on the other hand, by direct C-alkylation over CuAl-CHT which can be attributed to the higher acidic properties of these catalysts.

4. Conclusions

(1) Pure and well crystalline copper aluminium hydrotalcite-like compounds without other phases such as malachite can be prepared by using a mixture of aqueous solutions of NaOH/Na₂CO₃ as precipitant.

(2) MgAl-CHT was found to be a selective catalyst for the synthesis of 2,6-xylenol [13] and CuAl-CHT for *o*-cresol.

(3) Owing to the higher basicity of MgAl-CHT, the *o*-cresol and 2,6-xylenol were formed mainly through anisole formation, and on the other hand, by direct C-alkylation over CuAl-CHT which is due to the higher acidity of catalysts.

(4) The initial ageing treatment (65°C/30 min) for CuAl-HT precursors was found to be important for higher phenol conversion and selectivity for *o*-cresol.

(5) At low phenol conversion (15–20%) the selectivity for *o*-cresol decreases in the order CuAl 3.0-CHT > CuAl 2.0-CHT > CuAl 3.0-WACHT ≈ CuAl 4.0-CHT >> MgAl 4.0-CHT while at higher phenol conversion it is similar for all the CuAl-CHT.

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