Alkylation of phenol with 1-propanol and 2-propanol over catalysts derived from hydrotalcite-like anionic clays

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Received 10 January 1996; accepted 14 May 1996

Vapour phase alkylation of phenol with 1-propanol and 2-propanol was carried out in a fixed-bed flow reactor over calcined magnesium aluminium hydrotalcites (MgAl-CHT) with Mg/Al atomic ratios 2, 3 and 4. MgAl 3.0-CHT showed higher phenol conversion (~80% at 350°C) in the alkylation of phenol with 1-propanol. Both O- and C-alkylations were found to be taking place without any skeletal isomerization of the propyl moiety, suggesting an S_N2 type mechanism. Isomorphous substitution of Mg^{2+} by Cu^{2+} or Ni^{2+} in the hydrotalcite framework resulted in the predominant C-alkylation to give 2-*n*-propylphenol (60–70%) with nearly 40–50% phenol conversion at 350°C. When 2-propanol was used as an alkylating agent, the phenol conversion decreased over all these catalysts and the alkylation was noticed exclusively at C-centers. Comparison of the product selectivity at constant phenol conversion revealed that CuAl 3.0-CHT is more selective for 2-*n*-propylphenol and 2-isopropylphenol in the reaction of phenol with 1-propanol and 2-propanol respectively. The participation of a pair of acid–base sites in the calcined hydrotalcites for the alkylation reaction has been proposed. The acid–base properties of these catalysts have been examined by the decomposition of cyclohexanol as a test reaction. Analysis of the spent catalysts revealed that Cu^{2+} in CuO gets reduced into Cu^{1+} and metallic copper during the reaction in the case of CuAl-CHT, while MgO and NiO phases of MgAl-CHT and NiAl-CHT are retained.

Keywords: alkylation; hydrotalcite; anionic clay; acid–base catalysis

1. Introduction

Alkylation of phenol with alcohols is an industrially important reaction since many of the alkylphenols are used as raw materials for the synthesis of several pharmaceuticals, agrochemicals, and other commercially important products [1]. Numerous studies have been devoted to the alkylation of phenol with methanol for the synthesis of cresols and xylenols [2]. Alkylation of phenol with propene/butene over various solid acid catalysts, such as amberlyst-15, gives rise to their corresponding branched alkylphenol due to the formation of a more stable secondary or tertiary carbocation intermediate [3,4]. Kannan et al. [5] observed that, in the alkylation of phenol with 1-propanol over γ-Al_2O_3, O-alkylation takes place without any isomerization of the propyl moiety while a mixture of *n*-propyl and isopropylphenols were noticed in the C-alkylation. On the other hand, no such isomerization was observed by Karuppannasamy et al. [6] over thoria. Klemm et al. [7,8], in their detailed investigation on the reaction of phenol with 1-propanol/2-propanol over γ-Al_2O_3, noticed 16 to 20 products. Moreover, the reaction with 1-propanol gave penta-alkylphenol and in the reaction with 2-propanol the corresponding tri-alkylphenols were obtained.

Hydrotalcite (HT) belongs to a large class of anionic clays. The interest in these materials has increased in recent years owing to their wide application as ion exchangers, industrial adsorbents, ceramics and, most importantly, as catalysts and catalyst supports [9–11]. They consist of brucite $[Mg(OH)_2]$-like layers interspersed with hydrated anions in the interlayer. These compounds are represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$, where M(II) and M(III) are divalent and trivalent cations, A^{n-} is the interlayer anion and $x = 0.1$–0.33. Thermal decomposition of these materials at about 450°C results in the formation of highly active homogeneous mixed metal oxides which are potentially used as base catalysts for a variety of organic transformations [12–17]. Our recent investigations on the alkylation of phenol with methanol over catalysts derived from a series of magnesium–aluminium hydrotalcites (MgAl-HT) revealed that these catalysts are more efficient compared to MgO, γ-Al_2O_3 or zeolites for the synthesis of *o*-cresol and 2,6-xylenol [18]. The reaction was found to proceed predominantly through the formation of anisole as an intermediate. Substitution of Mg^{2+} by other divalent cations such as Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} or Mn^{2+} in the HT framework resulted in the direct C-alkylation to give *o*-cresol as the major product [19,20].

In the present communication, we report our studies on the alkylation of phenol with 1-propanol and 2-pro-

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

Sample	M(II)/Al atomic ratio [a]	Lattice parameters [b]		
		a(Å)	c(Å)	V(Å^3)
MgAl 2.0-HT	1.9	2.980	23.101	177.7
MgAl 3.0-HT	2.7	3.050	23.311	187.8
MgAl 4.0-HT	3.7	3.069	23.580	192.3
CuAl 3.0-HT [c]	3.1	3.111	22.529	218.0
NiAl 3.0-HT	2.8	3.044	23.334	187.2

[a] ICPES results.

[b] Calculated employing the least-squares method for the hexagonal crystal system.

[c] A mixture of HT and malachite [$Cu(OH)_2CuCO_3$] phases is obtained.

panol over catalysts derived from a series of hydrotalcite-like compounds in an effort to examine the nature of catalyst and the effect of structure of alcohol on the catalytic activity and product selectivity in the alkylation process.

2. Experimental

$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(CO_3^{2-})_{x/2}\cdot yH_2O$ with M(II) = Mg, Cu, Ni and M(III) = Al, where $x = 0.2$–0.33, were prepared by coprecipitation method [10]. The vapour phase alkylation of phenol with 1-propanol/2-propanol was carried out at atmospheric pressure using a fixed-bed vertical flow reactor. A premixed phenol–propanol feed (1 : 3 molar ratio; WHSV = 14.8 mol h^{-1} kg^{-1}) was introduced at the top of the reactor by means of an infusion pump. The liquid products were collected in cold traps and analyzed by GC-MS and NMR for qualitative analysis and GC for quantitative estimation. The detailed procedure for the preparation of the catalyst, characterization and catalytic studies can be obtained from our earlier reports [18–21].

3. Results and discussion

3.1. Physicochemical properties

The chemical composition and lattice parameters of all the samples synthesised are presented in table 1. It can be seen that the lattice parameters of MgAl-HT increases with increasing Mg/Al atomic ratio and also with increasing ionic radius of the M(II) cations in the brucite-like layer. Table 2 summarizes the powder X-ray diffraction (PXRD) phase obtained, BET surface area, specific pore volume and acid–base properties of hydrotalcite-like compounds calcined at 450°C/8 h. It can be noted that PXRD of the calcined samples offered corresponding oxide phase. The decomposition of cyclohexanol into cyclohexene and cyclohexanone was used to probe the acid–base properties of the calcined hydrotalcites [22,23]. The selectivity of cyclohexene was taken as the measure of the acidic strength of the catalyst [24,25]. The results indicated that CuAl 3.0-CHT is the most acidic catalyst, giving nearly 80% selectivity for cyclohexene, while the MgAl-CHTs are more basic. The basicity increases slightly with increase in Mg/Al atomic ratio from 2 to 4. NiAl 3.0-CHT shows nearly 50% selectivity to cyclohexene indicating the presence of moderate acidity in this catalyst. The selectivity to cyclohexene decreases in the order CuAl 3.0-CHT > NiAl 3.0-CHT > MgAl 2.0-CHT ≈ MgAl 3.0-CHT ≈ MgAl 4.0-CHT.

3.2. Selection of phenol to 1-propanol ratio

Table 3 shows the results of alkylation of phenol with 1-propanol over MgAl 3.0-CHT at 350°C with various phenol : 1-propanol ratios (1 : 1–1 : 7). It can be seen that there is no marked difference in the phenol conversion with respect to the molar ratio of the feed mixture. However, a slightly higher selectivity for 2-*n*-propylphenol was noticed at 1 : 3 feed ratio. Hence, this feed ratio was maintained throughout the study.

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

Catalyst	PXRD phase obtained	BET surface area [a] (m^2 g^{-1})	Specific pore volume [a] (cm^3 g^{-1})	Decomposition of cylclohexanol [b] (mol%)		
				conversion	$S_{\text{C-hexene}}$	$S_{\text{C-none}}$
MgAl 2.0-CHT [c]	MgO	167	0.60	38.6	43.8	56.2
MgAl 3.0-CHT	MgO	169	0.56	34.2	39.6	60.4
MgAl 4.0-CHT	MgO	136	0.48	32.5	33.5	66.5
CuAl 3.0-CHT	CuO	54	0.28	84.2	83.0	17.0
NiAl 3.0-CHT	NiO	137	0.49	39.2	52.0	48.0

[a] Surface area and specific pore volume determined by the N_2 adsorption–desorption method.

[b] Reaction temperature = 300°C at 1 atm; WHSV = 4.8 mol h^{-1} kg^{-1}. $S_{\text{C-hexene}}$ = selectivity to cyclohexene; $S_{\text{C-none}}$ = selectivity to cyclohexanone.

[c] CHT = calcined hydrotalcite.

Table 3

Selection of phenol : 1-propanol molar ratio. Catalyst: MgAl 3.0-CHT, temperature: 350°C

Phenol : 1-propanol	Phenol conv. (mol%)	Product [a] selectivity (mol%) (1)	(2)	(3)	(4)	(5)
1 : 1	60.2	9.1	32.2	30.0	7.6	21.1
1 : 2	70.7	7.1	30.8	16.3	16.4	29.4
1 : 3	72.1	9.2	35.8	10.0	22.6	22.4
1 : 4	70.4	15.3	32.1	11.4	25.4	15.0
1 : 5	68.8	19.6	26.6	10.9	30.1	12.8
1 : 7	70.1	29.5	20.6	11.0	29.2	9.7

[a] (1) *n*-propylphenyl ether, (2) 2-*n*-propylphenol, (3) *n*-propyl 2-*n*-propylphenyl ether, (4) 2,6-di-*n*-propylphenol, (5) higher alkylphenol.

3.3. *Effect of temperature*

The effect of temperature on phenol conversion in the alkylation of phenol with 1-propanol over various catalysts (fig. 1) shows that phenol conversion increases with increase in reaction temperature and leveled off around 350°C over all these catalysts. MgAl-CHT with Mg/Al atomic ratio 2 and 3 are more active (nearly 80% phenol conversion at 350°C) compared to MgAl 4.0-CHT (nearly 60% conversion) which can be attributed to the lower surface area of the latter catalyst. The higher activity of MgAl 3.0-CHT as compared to CuAl 3.0-CHT or NiAl 3.0-CHT could be due to the higher basicity of MgAl 3.0-CHT, as evidenced by the higher selectivity for cyclohexanone.

3.4. *Effect of contact time*

The effect of contact time on phenol conversion and product selectivity has been carried out in order to examine the reaction sequence in the alkylation reaction. The optimum performance envelope (OPE) curves (fig. 2), which are plots of conversion versus the product yield [19] for the alkylation of phenol with 1-propanol over MgAl 3.0-CHT at 350°C, reveal that *n*-propyl phenyl ether and 2-*n*-propylphenol are primary alkylation products since these products are formed at the onset of the reaction. The yield of *n*-propyl phenyl ether levelled off at around 20% phenol conversion where *n*-propyl 2-*n*-propylphenyl ether and 2,6-di-*n*-propylphenol also appeared. The yield of 2-*n*-propylphenol increases almost linearly with phenol conversion whereas the yield of *n*-propyl 2-*n*-propylphenyl ether showed a maximum at around 40% phenol conversion with consequent increase in the yield of 2,6-di-*n*-propylphenol. From these observations it can be inferred that *n*-propyl phenyl ether, which is formed as primary alkylation product, would undergo secondary reactions to give *n*-propyl 2-*n*-propylphenyl ether and 2,6-di-*n*-propylphenol.

The *n*-propyl phenyl ether can undergo secondary reactions in two different pathways: (i) it can undergo monomolecular rearrangement to give 2-*n*-propylphenol, which can be further alkylated to give *n*-propyl 2-*n*-propylphenyl ether and 2,6-di-*n*-propylphenol, or (ii) a

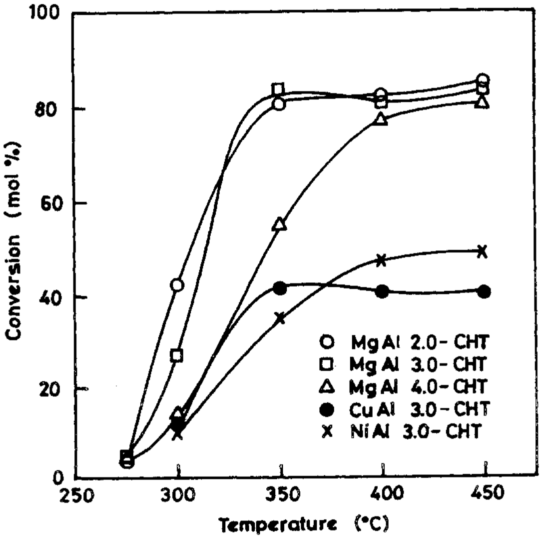


Fig. 1. Effect of temperature on phenol conversion in the alkylation of phenol with 1-propanol over M(II)Al-CHT; WHSV = 14.8 mol h^{-1} kg^{-1}.

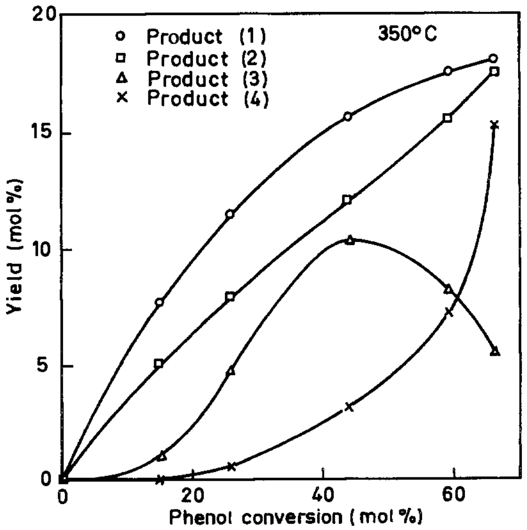
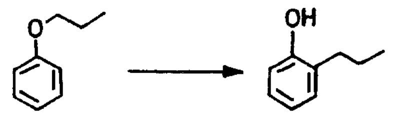
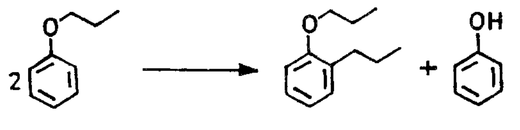


Fig. 2. OPE curves for the alkylation of phenol with 1-propanol over MgAl 3.0-CHT; product (1) *n*-propyl phenyl ether; (2) 2-*n*-propylphenol; (3) *n*-propyl 2-*n*-propylphenyl ether; (4) 2,6-di-*n*-propylphenol.

bimolecular reaction to give a mixture of *n*-propyl 2-*n*-propylphenyl ether and phenol as shown in eqs. (i) and (ii) respectively,



(i)



(ii)

In order to verify these possibilities, the reaction of *n*-propyl phenyl ether as a sole reactant was carried out over MgAl 3.0-CHT. The results are summarized in table 4. The *n*-propyl phenyl ether used in this reaction was synthesised in the laboratory as described in the literature [26]. The formation of considerable amounts of phenol at all the reaction temperatures and contact times clearly demonstrates that the bimolecular reaction in which *n*-propyl phenyl ether served as its own alkylating agent (eq. (ii)) is more predominant as opposed to the monomolecular rearrangement to give 2-*n*-propylphenol (eq. (i)). These results are similar to our earlier investigations on the alkylation of phenol with methanol over MgAl-CHT, wherein anisole was found to undergo bimolecular reactions to give a mixture of phenol and 2-methylanisole [18]. Furthermore, the fact that the selectivity for 2-*n*-propylphenol does not increase with contact time serves as an another evidence for the absence of monomolecular rearrangement of *n*-propyl phenyl ether. Hence, it can be concluded that *n*-propyl phenyl ether is transformed into *n*-propyl 2-*n*-propylphenyl ether through a bimolecular reaction (eq. (ii)) which is subsequently converted into 2,6-di-*n*-propylphenol over MgAl-CHT.

Another interesting feature observed over all these catalysts is the absence of skeletal isomerization of the propyl moiety to give isopropylphenol. This rules out the intermediate formation of free carbonium ion on the catalyst surface. This is in contrast to the previous reports by Kannan et al. [5] who have observed a mixture of 2-*n*-propylphenol and 2-isopropylphenol in the approximate ratio of 4 : 1 in the C-alkylation over γ-Al_2O_3. The lack of isomerization of the propyl moiety in the present study suggests a concerted nucleophilic displacement (an S_N2 type mechanism) for both O- and C-alkylation over these catalysts as shown in scheme 1.

The catalyst can be viewed as possessing a pair of strong Lewis basic sites (O^{2-} ions) and Lewis acidic sites (coordinatively unsaturated Al^{3+} ions) in the calcined hydrotalcites [27,28]. Both phenol and 1-propanol are dissociatively adsorbed as protons, phenoxide ion and propoxide ion. The protons bind to the surface basic sites while the phenoxide ion and propoxide group are attached to the neighbouring Lewis acidic sites. The O-alkylation can be considered as a concerted nucleophilic displacement by the phenoxide at the positively polarized α-carbon atom of the alcohol. On the other hand, in the C-alkylation, nucleophilic attack by C-2 of the adsorbed phenoxide group onto C-1 of the propoxide group takes place. A similar mechanism has been proposed by Karuppannasamy et al. [6] for the alkylation of phenol with methanol over thoria and Klemm et al. [7] for the alkylation of phenol with 1-propanol/2-propanol over γ-Al_2O_3. The O-/C-alkylation ratio is controlled by the surface acid–base properties of the catalysts. The preferential ortho alkylation over these catalysts may be due to the proximity of the adsorbed alcohol fragment to the ortho position of the surface phenoxide group.

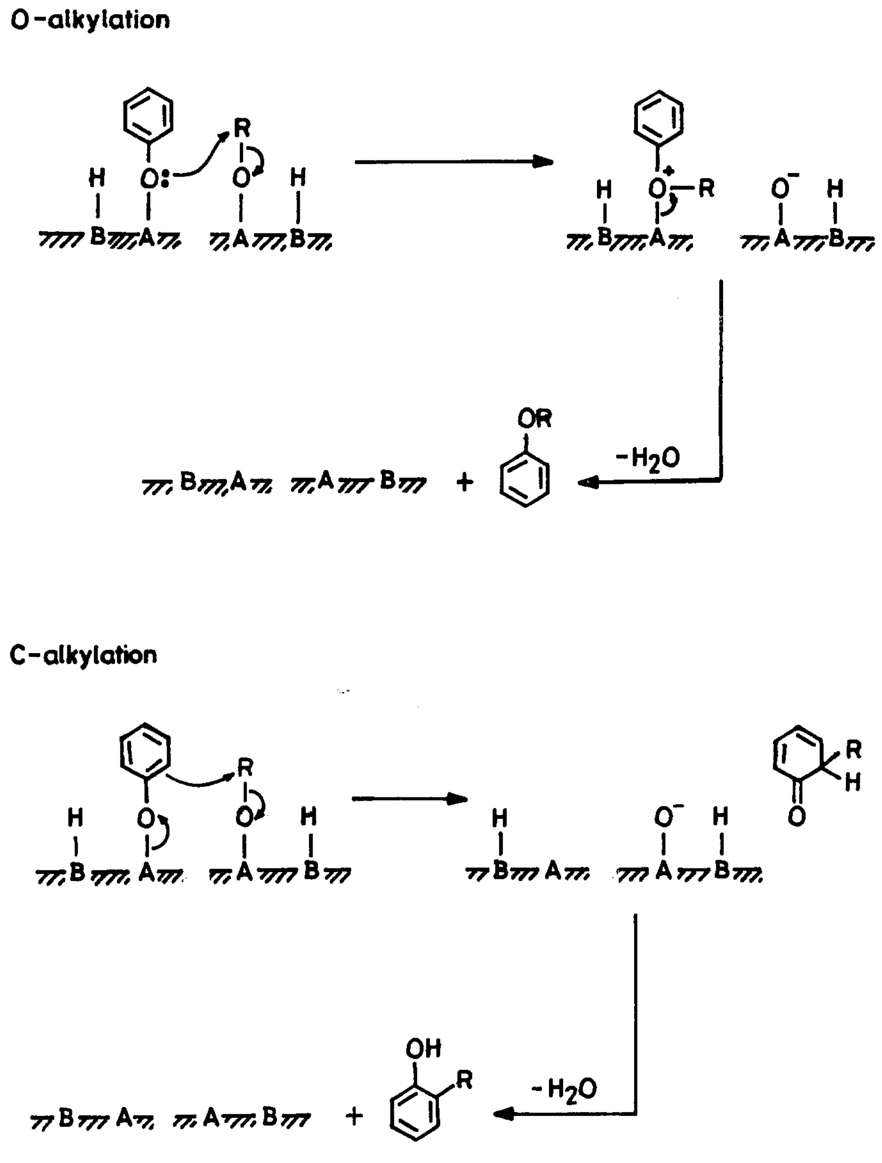
3.5. *Effect of divalent cations*

Isomorphous substitution of Mg^{2+} in MgAl 3.0-CHT by Cu^{2+} or Ni^{2+} results in decrease in phenol conversion (fig. 1) which has been attributed to the difference in the acid–base properties of the catalysts (section 3.1). Comparison of product selectivity at a constant phenol conversion (40–45%) level over MgAl 3.0-CHT, CuAl 3.0-CHT and NiAl 3.0-CHT (fig. 3) reveals that MgAl 3.0-CHT is more selective to O-alkylation giving *n*-propyl phenyl ether as the primary product. On the other hand, substitution of Mg^{2+} by Cu^{2+} or Ni^{2+} in the HT framework results in the predominant C-alkylation to give 2-*n*-propylphenol as the major product. The higher selectivity for O-alkylation in the case of MgAl 3.0-CHT is due to the higher basicity of the catalyst. The O-alkylated *n*-propyl phenyl ether undergoes secondary reactions to give 2,6-di-*n*-propylphenol. In contrast, the higher surface acidity of CuAl 3.0-CHT and NiAl 3.0-CHT favours predominantly C-alkylation to give 2-*n*-propylphenol. The formation of a trace amount of 2,6-di-*n*-propylphenol over the latter catalysts indicates the absence of secondary reactions of 2-*n*-propylphenol.

Table 4
Activity and product selectivity in the reaction of *n*-propyl phenyl ether as a sole reactant over MgAl 3.0-CHT. WHSV = 23.3 mol h^{-1} kg^{-1}

Temp. (°C)	Conv. (mol%)	Product [a] selectivity (mol%)			
		phenol	(2)	(3)	(4)
300	20.2	40.8	–	52.2	7.0
350	48.4	36.4	3.5	43.8	16.3
400	32.8	32.3	5.8	35.6	26.3
350 [b]	54.3	42.2	4.2	28.2	25.4

[a] Products (2), (3) and (4) are as in table 3.
[b] WHSV = 14.0 mol h^{-1} kg^{-1}.



Scheme 1. Mechanism of alkylation of phenol with alcohols over calcined hydrotalcites; (A) acidic sites, (B) basic sites.

3.6. *Effect of structure of alcohol*

In order to study the effect of the structure of alcohol on the catalytic activity and product selectivity, the reaction of phenol with 2-propanol has been carried out over MgAl 3.0-CHT, CuAl 3.0-CHT and NiAl 3.0-CHT. Comparing the results in fig. 4, it can be seen that the activity of the catalysts (phenol conversion) decreases when 2-propanol is used as an alkylating agent. The very striking feature observed in the alkylation of phenol with 2-propanol is that the alkylation takes place exclusively at C-centers (only C-alkylation) to give 2-isopropylphenol as the major product even over MgAl 3.0-CHT (table 5). This is because of the bulkiness of the alkylating agent which hinders the alkylation at the sterically less accessible position. Comparison of the product selectivity at constant phenol conversion (25–30%) at constant temperature (350°C) reveals that CuAl 3.0-CHT is the most selective catalyst for 2-isopropylphenol (as in the alkylation of phenol with 1-propanol) giving 2-propylphenol as a major product (fig. 5). The very low selectivity for 2,6-di-isopropylphenol over CuAl 3.0-CHT and NiAl 3.0-CHT indicates the absence of secondary alkylation of 2-isopropylphenol. Trace amount of 4-isopropylphenol was also noticed over all these catalysts. Based on these results, it can be concluded that the catalytic activity and product selectivity are influenced by the nature of the alcohol (alkylating agent) also.

3.7. *Analysis of the spent catalyst*

Spent catalyst analysis was carried out in order to get an insight into the stability of the catalyst during the reaction. The PXRD of the spent MgAl 3.0-CHT, CuAl 3.0-CHT and NiAl 3.0-CHT are shown in fig. 6. For comparison, the PXRD patterns of the fresh catalysts are also given. An inspection of fig. 6 clearly indicates

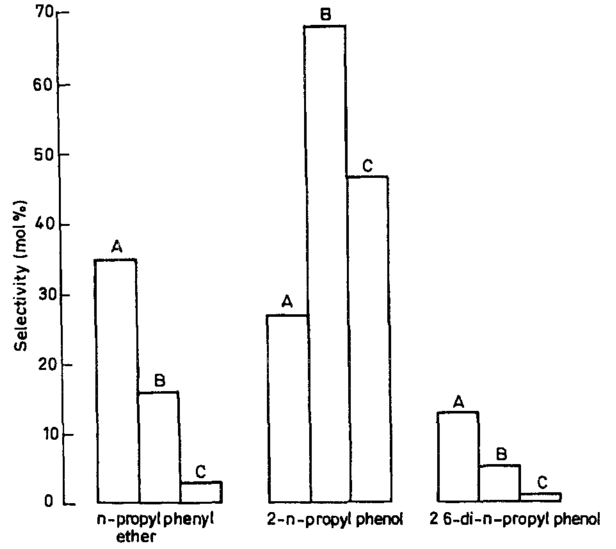


Fig. 3. Product selectivity in the alkylation of phenol with 1-propanol over M(II)Al-CHT at constant phenol conversion (40–45%): (A) MgAl 3.0-CHT; (B) CuAl 3.0-CHT; (C) NiAl 3.0-CHT; temperature = 350°C.

Table 5
Alkylation of phenol with 2-propanol over MgAl 3.0-CHT. WHSV = 14.8 $\mathrm{mol\,h^{-1}\,kg^{-1}}$

Temp. (°C)	Phenol conv. (mol%)	Product[a] selectivity (mol%)				
		(6)	(7)	(8)	(9)	(10)
300	6.1	88.5	8.2	3.3	–	–
350	26.8	75.0	6.3	10.5	6.3	1.9
400	44.2	53.9	20.1	8.8	11.5	5.7
450	36.5	47.1	26.0	4.7	4.4	17.8
350[b]	38.2	63.6	8.2	18.8	7.2	2.2
350[c]	18.5	94.8	2.0	3.2	–	–

[a] (6) 2-isopropylphenol, (7) 4-isopropylphenol, (8) 2,6-di-isopropylphenol, (9) 2,4-di-isopropylphenol, (10) unaccounted.

[b] WHSV = 7.4 $\mathrm{mol\,h^{-1}\,kg^{-1}}$.

[c] WHSV = 5.3 $\mathrm{mol\,h^{-1}\,kg^{-1}}$.

that, except CuAl 3.0-CHT, the phase obtained in all other catalysts is the same as that of the fresh catalyst. In the case of CuAl 3.0-CHT, the PXRD shows that, during the reaction, the Cu^{2+} in CuO gets reduced into Cu^{1+} (Cu_2O) and metallic Cu (compare figs. 6c and 6d). This observation is in contrast to our earlier investigations on the catalytic decomposition of N_2O over these catalysts, wherein the PXRD of the spent CuAl-CHT showed a highly crystalline CuO phase [29]. This may be due to the involvement of redox mechanism proposed for the decomposition of N_2O over these catalysts. On the other hand, studies on the dehydrogenation of 2-propanol over Cu/Al_2O_3 catalyst prepared by methods such as electroless plating [30] or impregnation [31] have shown that, during the reaction, a mixture of Cu^{2+}, Cu^{1+} and Cu is present on the surface of the catalyst. Volta et al. [32] have claimed that 2-propanol with N_2 as carrier definitively reduces CuO obtained by the in situ calcined $Cu(OH)_2$ at 120°C into Cu^{1+} and Cu. Recently, Auer et al. [17] have also noticed the formation of a small amount of Cu^{1+} compound in the reaction of coupling of phenylethylene over catalyst derived from Cu–Mg–Al hydrotalcite. Hence, it can be concluded that, in the present investigations, the alcohol present in the feed mix (phenol: alcohol) is the source for hydrogen which reduces Cu^{2+} in CuO into Cu^{1+} and metallic copper.

The surface area of the spent catalysts is almost similar (±10 $m^2\,g^{-1}$) to that of the fresh catalyst (table 2) indicating that, the textural properties of the catalysts are not affected during the reaction. Further work is in progress on the alkylation of phenol with a series of linear and branched alcohols in order to understand the reaction mechanisms thoroughly.

4. Conclusions

(1) Among the catalysts studied, MgAl 3.0-CHT is the most active catalyst for the alkylation of phenol with 1-propanol/2-propanol.

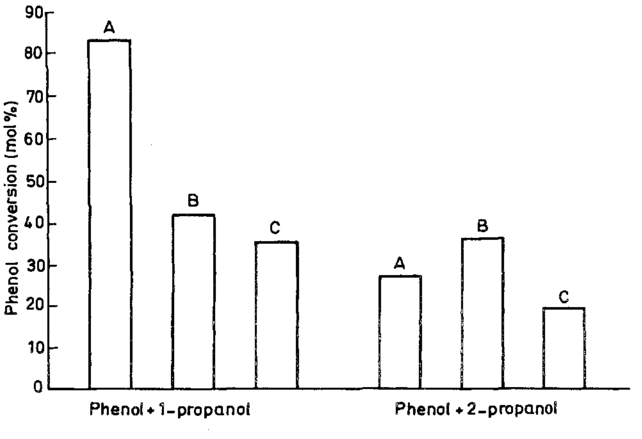


Fig. 4. Catalytic activity in the alkylation of phenol with 1-propanol and 2-propanol over (A) MgAl 3.0-CHT; (B) CuAl 3.0-CHT; (C) NiAl 3.0-CHT: temperature 350°C; WHSV = 14.8 $\mathrm{mol\,h^{-1}\,kg^{-1}}$.

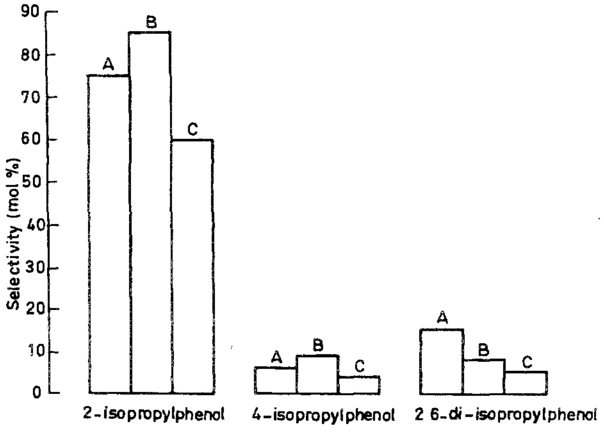


Fig. 5. Product selectivity in the alkylation of phenol with 2-propanol over (A) MgAl 3.0-CHT; (B) CuAl 3.0-CHT; (C) NiAl 3.0-CHT at constant phenol conversion (25–30%); temperature = 350°C.

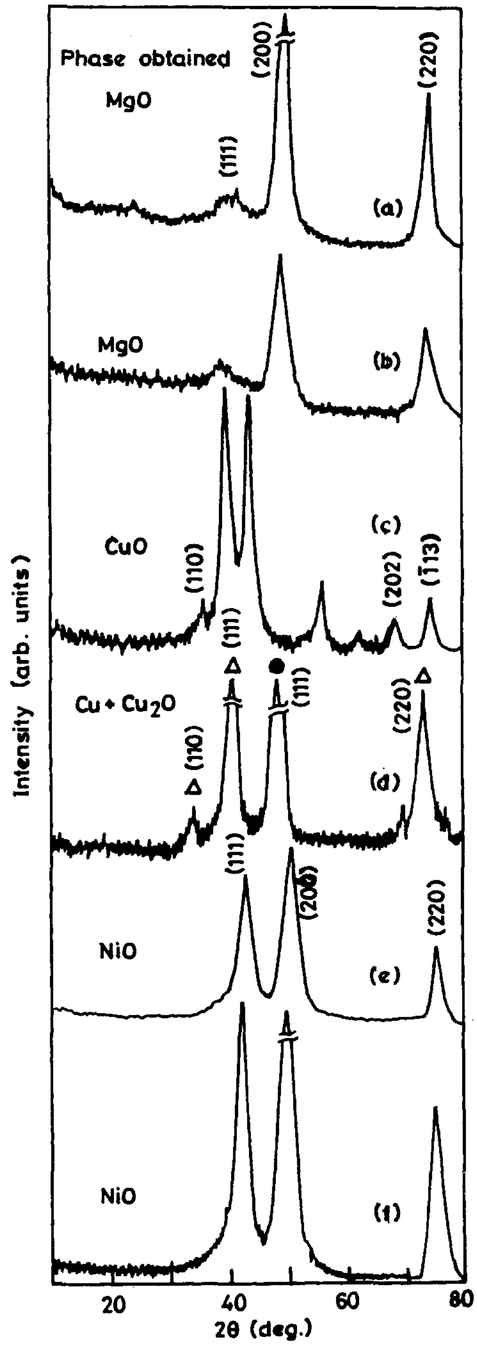


Fig. 6. PXRD patterns of (a) MgAl 3.0-CHT; (b) spent MgAl 3.0-CHT; (c) CuAl 3.0-CHT; (d) spent CuAl 3.0-CHT; (e) NiAl 3.0-CHT; (f) spent NiAl 3.0-CHT; (Δ) Cu_2O (JCPDS file No. 5.0667); (●) Cu (JCPDS file No. 4.0836).

(2) Substitution of Mg^{2+} in MgAl-CHT by Cu^{2+} or Ni^{2+} resulted in decrease in phenol conversion due to the lower basicity of the catalyst.

(3) The reaction of phenol with 1-propanol proceeded without skeletal isomerization of the propyl moiety, suggesting an S_N2 type mechanism.

(4) The activity of the catalysts decreased as the bulkiness of the alkylating group increased and the alkylation takes place exclusively at C-centers.

(5) CuAl 3.0-CHT was found to be the most selective catalyst for 2-*n*-propylphenol (> 70%) or 2-isopropylphenol (nearly 90%) at 350°C.

(6) The PXRD of the spent catalyst showed that during the reaction, CuO of CuAl 3.0-CHT is reduced to Cu^{1+} and metallic copper.

Acknowledgement

The authors are grateful to Professor C.N. Pillai of Department of Chemistry, IIT, Madras and Mr. V. Ramkumar, Mr. A. Narayanan and Miss Dorothy Samuel for their expert technical help. One of the authors (SV) thanks IIT, Madras for the award of a research fellowship.

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