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Calcined Mg–Al, Mg–Cr and Zn–Al hydrotalcite catalysts for *tert*-butylation of phenol with *iso*-butanol—a comparative study

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Abstract

Calcined hydrotalcites (CHTs) are studied for the *tert*-butylation of phenol using *iso*-butanol in the temperatures ranging from 350 to 500 °C. The major products of this reaction on calcined magnesium–aluminium hydrotalcites (CMA-HTs) are *O*-*tert*-butyl phenol (*tert*-butyl phenyl ether, OTBP) and 2-*tert*-butyl phenol (*o*-*tert*-butyl phenol, 2TBP) with *O*-butenyl phenol (butenyl phenyl ether, OBP) and 2-butenyl phenol (*o*-butenyl phenol, 2BP) as useful by-products. With a view to understand the reaction mechanism and the reaction path, *tert*-butylation of phenol is studied by changing both Mg[M(II)] and Al[M(III)] ions with Zn^{2+} and Cr^{3+}, respectively. Thus, Mg–Al (MA), Mg–Cr (MC) and Zn–Al (ZA) hydrotalcites (with M^{2+}:M^{3+} ratio = 2) are prepared and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic absorption spectroscopy (AAS), differential thermal analysis/thermo gravimetric analysis (DTA/TG), BET-surface area (BET-SA) and acidity–basicity measurements (temperature-programmed desorption (TPD) of NH_3 and CO_2). Mixed oxides obtained from CHTs are found to be more active over their individual oxides for the *tert*-butylation of phenol. The butylation activities of the three different CHTs are in the order CMA-HT > CZA-HT > CMC-HT. A different product distribution is obtained over calcined Mg–Cr and Zn–Al hydrotalcites for the *tert*-butylation of phenol showing the influence of acid–base properties on the activity of the catalysts. A probable mechanism based on the experimental observations has been proposed in order to explain the formation of butenyl phenols.
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Keywords: Calcined hydrotalcite; Acid–base properties; *tert*-Butylation; Butyl phenols; Butenyl phenols

1. Introduction

Hydrotalcite (HT) or hydrotalcite-like compounds (HTlc) are layered double hydroxides belonging to the class of anionic clays. The structure of these compounds are very similar to that of brucite, $Mg(OH)_2$, where some of Mg^{2+} represented as [M(II)] are isomorphously replaced by Al^{3+} represented as [M(III)] and the net positive charge is compensated by the inter-layered exchangeable anion (A^{n-}). The general formula of these compounds can be represented as:

$$[M(II)_{1-x}M(III)_x(OH)_2] \cdot A^{n-}_{x/n} \cdot mH_2O$$

The structure can accommodate wide variations in different M(II) ions, M(III) ions and mixture of M(III) and M(II) ions, M(II):M(III) atomic ratios (represented by $x = M(III)/M(II) + M(III)$ ranging from 0.1 to 0.33), different types of inter-layered anions with charge from −1 to −3, crystal morphology and size [1]. A possibility of incorporation of M^+ and M^{4+} ions has also been reported in the synthesis of these compounds [2,3]. Thermal decomposition of

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these materials by calcination above 450 °C results in the formation of a high surface area basic mixed oxides which are reported to be potential candidates in catalyzing various reactions involved in the synthesis of a variety of fine chemicals [4–7]. In an earlier publication, we found that calcined magnesium–aluminium hydrotalcites (CMA-HTs) are active for the *tert*-butylation of phenol with *iso*-butanol [8].

The *tert*-butylation of phenol is an industrially important reaction to produce *tert*-butyl phenols, which are important starting materials in the synthesis of antioxidants, agrochemicals, pharmaceutical intermediates, thermo-resistant polymers, protecting agents for plastics and fragrance compounds. The other products, like *O*-butyl and butenyl phenols also find application in the synthesis of flavoring, fragrance compounds and pharmaceutical intermediates, chromans [9]. The by-product, 2-ethyl hexanal obtained over the CMC- and CZA-HTs is also reported to be useful in the synthesis of 2-ethyl hexenol which is used as an intermediate in the synthesis of plasticizers and cetane improvers, lubricant additives, surfactants, etc. [9]. In liquid phase, this reaction is generally carried out over acid catalysts, like $AlCl_3$, ion-exchange resins and super acid catalysts, like Nafion-H, sulfated zirconia [10–13] using *iso*-butene or *iso*-/*tert*-butanols and in vapor phase on zeolite catalysts with *iso*-/*tert*-butanols [14–16]. The conventional acidic catalysts employed are environmentally hazardous and although cation-exchange resins do not pollute the environment, they involve a tedious work-up and are unstable at higher temperatures. These catalysts produce a mixture of *o*-, *p*- and *m*-butylated products or predominantly *para* products. Although catalysts like γ-Al_2O_3 are more *ortho* selective [9], they undergo significant deactivation with time-on-stream. In our recent study [8], over solid base catalysts, CMA-HTs, we found them to be more active for *tert*-butylation of phenol than that over MgO and γ-Al_2O_3 and the formation of unusual products, like butenyl phenols is also observed over these catalysts. The present investigation is aimed at the study of the effect of substitution of Mg^{2+} by Zn^{2+} and Al^{3+} by Cr^{3+} in the MA-HT structure on the butylation activity of the catalysts. The catalysts are characterized by X-ray diffraction (XRD), BET-surface area (BET-SA), X-ray photoelectron spectroscopy (XPS), atomic absorption spectroscopy (AAS), differential thermal analysis/thermo gravimetric analysis (DTA/TG) and temperature-programmed desorption (TPD) of NH_3 and CO_2. The acid–base properties of these catalysts are correlated with the product distribution and a probable mechanism for the formation of butenyl phenols is proposed based on these studies.

2. Experimental

2.1. Preparation of catalysts

All the HT catalysts used in this study are prepared using Reichle's method [5] with M(II):M(III) atomic ratio of 2 by co-precipitation at room temperature (at 65 ± 5 °C in case of MC-HT) from the aqueous solutions of their corresponding nitrates with a mixture of aqueous solutions of NaOH and Na_2CO_3 at a pH =∼ 11. The precipitate is then subjected to hydrothermal treatment at 65 ± 5 °C for 18 h and the resultant gel obtained after thorough washing (until Na content is <0.1 wt.%) and filtration is dried in an oven at 110 °C overnight. The dried samples are calcined in air for 18 h at 500 °C and termed as calcined Mg–Al (CMA), calcined Mg–Cr (CMC) and calcined Zn–Al (CZA) HTs. To compare the activities of these catalysts with their corresponding pure oxides, MgO, Cr_2O_3 and ZnO are also prepared by precipitation using aqueous NaOH in the case of MgO and aqueous NH_3 in the case of Cr_2O_3 and ZnO from their corresponding aqueous nitrate salt solutions followed by calcination in air (N_2 for Cr_2O_3) at 500, 500 and 450 °C, respectively, for 5 h. γ-Al_2O_3 used is a commercial (Harshaw) catalyst. The catalysts are pelletized, crushed and sieved to 18/20 BSS mesh before use.

To study the effect of preparation conditions on the *t*-butylation of phenol, another MA-HT was prepared by hydrothermal treatment at 65 ± 5 °C for 1 h and calcining the oven dried gel at 500 °C for 8 h in air to get CMA-1.

2.2. Characterization and activity study

The XRD patterns are obtained from a Siemens D-5000 powder X-ray diffractometer using nickel filtered Cu Kα radiation (λ = 1.5405 Å). The XPS spectra of the hydrotalcites are recorded on a Kratos axis 165 spectrometer equipped with a Mg Kα source.

The binding energy (B.E.) correction is performed by using the C with 1s peak at 284.6 eV as a reference. The B.E.s were determined and the relative intensities of the surface composition of different elements are measured by correcting them with their corresponding atomic sensitivity factors using Vision 2 software in Unix system. The bulk composition of the M(II) and M(III) ions are determined by AAS (Perkin-Elmer A Analyst 300). The DTA/TG profiles are recorded on a Metler Toledo 851E (Switzerland) instrument at a heating rate of 10 °C min^{-1} both in air and N_2. BET-SAs of the catalysts are measured on an all glass high vacuum system (10^{-6} Torr) by N_2 adsorption at liquid nitrogen temperature. Acidity and basicity measurements are carried out by TPD of NH_3 and CO_2, respectively, using a micro-reactor assembly. Typically about 200 mg of the catalyst is secured between quartz wool plugs in the micro-reactor, pre-treated in nitrogen at 450 °C for 3 h and then cooled to 80 °C prior to the adsorption of NH_3 or CO_2 at this temperature. After the adsorption of NH_3 or CO_2 (40 ml min^{-1}) for 60 min, the catalyst is flushed with nitrogen (40 ml min^{-1}) for 60 min at 100 °C to remove the physisorbed gas from the surface of the catalyst. The desorption pattern has been recorded at a heating ramp of 12 °C min^{-1} from 80 to 500 °C using a recorder connected to a GC equipped with a TCD detector.

The vapour phase *tert*-butylation of phenol using *iso*-butanol is carried out in a vertical fixed bed glass reactor using ~1 g of catalyst at the reaction temperatures ranging from 350 to 500 °C. A feed mixture of phenol:*iso*-butanol (1:7) is fed to the catalyst at a rate of 4 ml h^{-1} using a microprocessor controlled syringe pump (B. Braun, Germany) [8]. The products are cooled, collected and analyzed by a GC equipped with a flame ionization detector using a 10% SE-30 column (2.5 m × 3 mm, SS). The products are confirmed by GC–MS (Varian 7070).

3. Results and discussion

3.1. XRD, BET-SA, acidity and basicity measurements

Fig. 1(A–C) show the XRD patterns of MA-, ZA- and MC-HTs both uncalcined and calcined varieties.

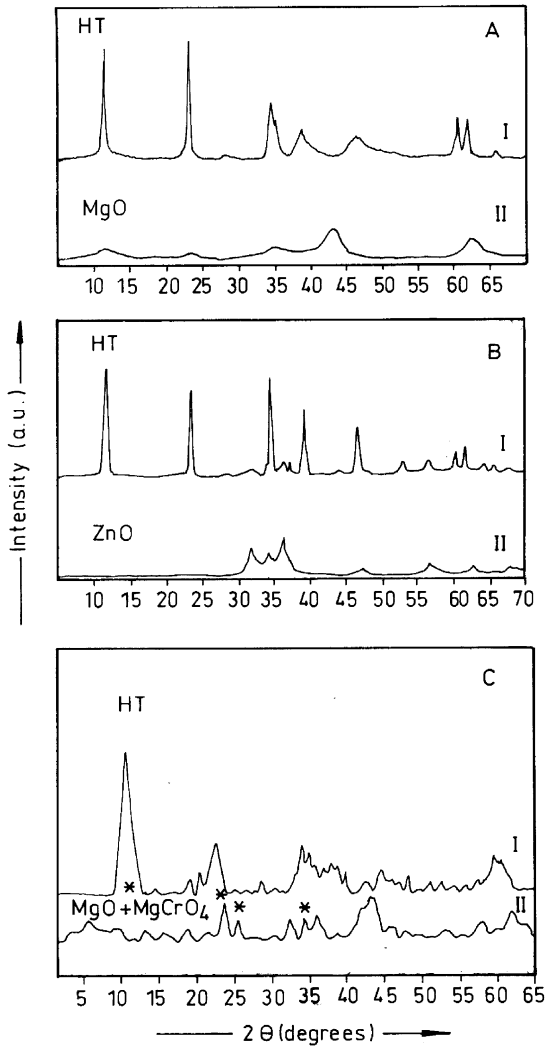

Fig. 1. The X-ray powder diffractograms of: (A) MA-HT (I) and CMA-HT (II); (B) ZA-HT (I) and CZA-HT (II); (C) MC-HT (I) and CMC-HT (II); (*) indicates $MgCrO_4$ phase.

All the uncalcined samples show hydrotalcite structure. The lattice parameters calculated for the MA-HT are $a = 3.050$ Å and $c = 22.953$ Å for the sample treated hydrothermally for 1 h and for the sample that is treated for 18 h, the values are $a = 3.048$ Å and $c = 22.980$ Å. These values changed with the substitution of Mg^{2+} by Zn^{2+} in HT structure to $a = 3.070$ Å and $c = 22.596$ Å and on the substitution of Al^{3+} by Cr^{3+} to $a = 3.096$ Å and $c = 23.697$ Å. Upon calcinations the MA-HT catalysts show only poorly

Table 1
Characteristics of calcined hydrotalcites, alumina and magnesia

Catalyst	BET-SA ($m^2 g^{-1}$)	NH_3 uptake ($mmol\,m^{-2}$) × 10^3				CO_2 uptake ($mmol\,m^{-2}$) × 10^3				CO_2/NH_3
		I	II	III	Total	I	II	III	Total	
CMA-1	120	0.42	1.00	0.50	1.92	6.25	9.30	20.83	36.42	19.00
CMA	229	0.04	1.14	1.35	2.53	1.66	4.98	12.75	19.39	7.65
Al_2O_3	220	0.09	0.64	0.86	1.59	0.59	2.64	5.77	9.00	5.66
MgO	110	0.09	0.27	1.09	1.46	2.00	13.82	27.54	43.36	29.80
CMC	135	–	0.07	0.37	0.44	0.89	0.59	3.41	4.89	11.01
CZA	230	0.70	2.83	2.17	5.70	–	3.39	11.74	15.13	2.66

I, From TPD in the temperature ranges of 200–300 °C; II, from TPD in the temperature ranges of 300–400 °C; III, from TPD in the temperature ranges of 400–500 °C.

crystalline MgO phase (d = 2.11, 1.49, 1.22 Å; ASTM no. 4-0829). The CMC-HT, shows in addition to MgO, $MgCrO_4$ phase (d = 5.0, 3.77, 6.0, 10.8 Å; ASTM no. 1-0243) also. Only ZnO phase (d = 2.48, 2.82, 2.60 Å; ASTM no. 5-664) is observed in CZA-HT catalyst. Table 1 shows the BET-SA and NH_3 and CO_2 uptakes of various catalysts. NH_3 uptake of the catalysts shows the presence of acidity of different strengths and is found to be very high in ZA-HT indicating that the substitution by Zn^{2+} enhances the acidity of the catalyst. On MC-HT, both the NH_3 and CO_2 uptakes are found to be very low in comparison to other HTs indicating that substitution of Al^{3+} by Cr^{3+} resulted in a drastic reduction of the acid–base properties of the catalyst. This behavior may be attributed to the formation of $MgCrO_4$ spinel in this catalyst which also may be the reason for the lower activity of the catalyst towards butylation of phenol. According to Di Cosimo et al. [17] while pure MgO possesses strong basic sites consisting predominantly of O^{2-}, calcined hydrotalcites contain surface sites of low (OH^- groups), medium (Mg-O pairs), and strong (O^{2-}) basicities. Our experimental results on TPD of CO_2 conform to this viewpoint. The basic sites in the temperature range of 200–300 °C are designated as of low strength, the sites in the range of 300–400 °C as of medium strength and those in the range of 400–500 °C as high strength ones. It is observed that while the density of high temperature basic sites (>400 °C) is greater in MgO catalyst, the CMA-HTs showed relatively more density of low strength basic sites in comparison to the basic sites of other strengths. This behavior may be attributed to the formation of weakly basic –OH groups on CHT with the incorporation of Al^{3+} in the brucite layer resulting in the lowering of the average surface strength of basicity [17]. These differences in site densities may be the reason for the low temperature activity seen on CHT catalysts and high temperature activity that is (above 450 °C) seen on MgO catalyst [18].

The total basicity per unit surface area of the catalysts showed the following order: MgO > CMA-1 ≫ CMA > CZA > Al_2O_3 > CMC, and the acidity in the following order: CZA > CMA > CMA-1 > Al_2O_3 ≈ MgO > CMC. The CMA-HTs showed higher acidity as compared to MgO. This may be the probable reason for the CMA-HT to have shown higher activity towards butylation of phenol than by MgO as the reaction is reported [7] to take place by the participation of acid–base pairs. The CZA catalyst although showed the highest acidity among all the catalysts studied, this acidity seems to correspond to high strength sites which probably do not contribute to this particular reaction. This is further confirmed by the formation of other products of condensation and dehyrogenation observed in good measure over this catalyst. The basicity:acidity ratio is the highest on MgO followed by CMA-1, which appears to be the most basic among all the hydrotalcites studied here, even more basic than CMA. The acidity of CMA is higher than that of CMA-1 probably due to the contribution of more surface enriched Al^{3+} towards acidity as a result of longer hours of hydrothermal treatment given to CMA during the preparation step.

3.2. XPS and AAS results

Table 2 shows the surface and bulk compositions of hydrotalcites determined by XPS and AAS techniques, respectively. Fig. 2 shows X-ray photoelectron

Table 2
Surface and bulk compositions of hydrotalcites determined by XPS and AAS

Catalyst	Surface composition (XPS) M(II):M(III) atomic ratio	Bulk composition (AAS) M(II):M(III) atomic ratio
MA-HT	1.15	1.98
MA-HT-1	1.3	1.98
MC-HT	2.13	2.25
ZA-HT	1.97	1.93

spectra of different hydrotalcites. The binding energies of M(II) and M(III) ions (Fig. 2) suggest their existence in hydroxide form. The Mg 2p B.E. value is found to be around 50.0 eV in all the Mg containing HTs and the Al 2p B.E. is observed to be 74.0 eV in MA- and ZA-HT samples. The Cr 2p B.E. value is 578.0 eV in MC-HT sample. The B.E. value of 1s of O (532.0 eV) also indicates it to be present in hydroxide form. No significant change in the B.E. of 1s of O is observed corresponding to the substitution of Zn^{2+} or Cr^{3+} in the original HT structure, i.e. w.r.t. ZA- and MC-HTs.

The bulk atomic ratios of M(II):M(III) determined by AAS are close to '2'. But a surface enrichment of Al^{3+} is observed in case of MA-HT with lower Mg:Al atomic ratio (1.15) as evident from XPS analysis. Di Cosimo et al. [17] showed that increasing Al content in CHT samples, segregation of Al^{3+} to the surface takes place as observed from the increase in Al_s:Al_b ratios. The surface M(II):M(III) atomic ratios in the other hydrotalcites, viz. MC- and ZA-HTs determined by XPS are close to their bulk compositions as obtained from AAS. The main peak of 1s of C observed at a B.E. value of 285.0 eV and another one around 289.0 eV in all the samples clearly suggest the presence of carbonate anion in the structure of HT.

Sachez et al. [19] observed a small difference of about 0.5 eV between MgFe- and MA-HTs in the O 1s B.E. These compounds are reported to have shown a difference of 0.9 eV shift to lower energy and an increase in their basicity upon decarbonation. Upon rehydration these materials have also shown higher basicity than that of MgO. From calorimetric measurements, the heat of adsorption of CO_2 (110 kJ mol^{-1}) is found to be the same for CHTs and MgO [19]. Figueras et al. [20,21] have reported high activities for the aldolisation and

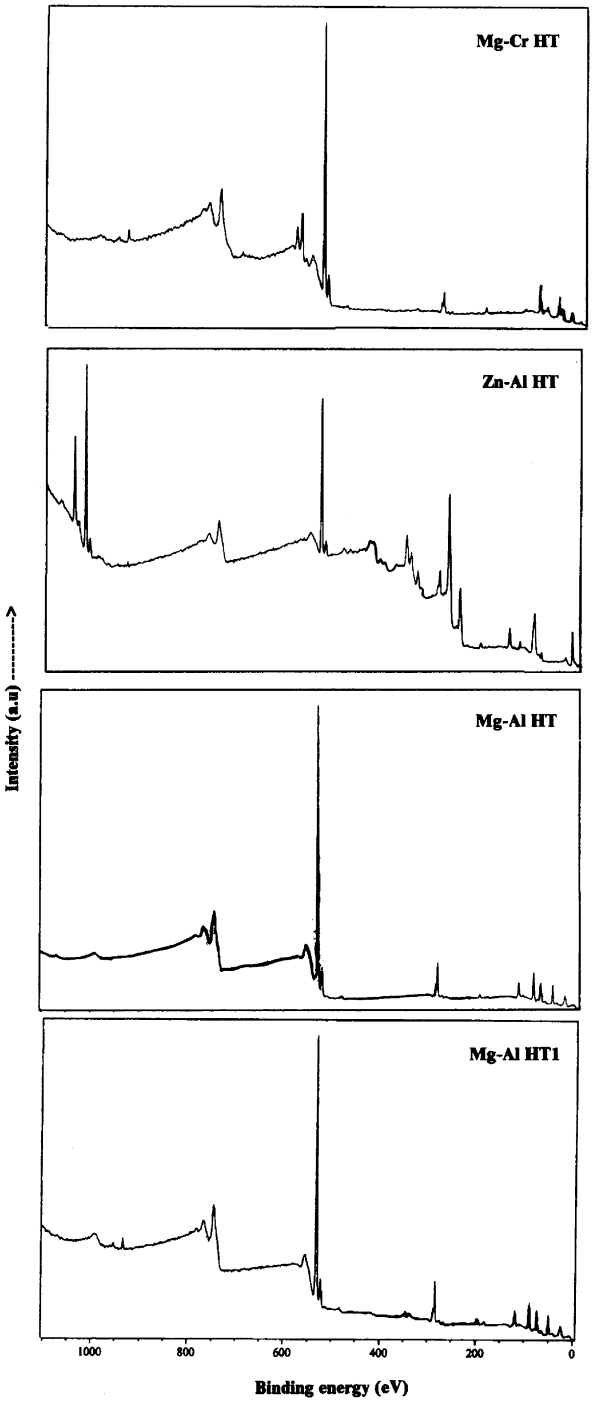

Fig. 2. The XPS spectra of MA-HT, MA-HT-1, MC-HT and ZA-HT.

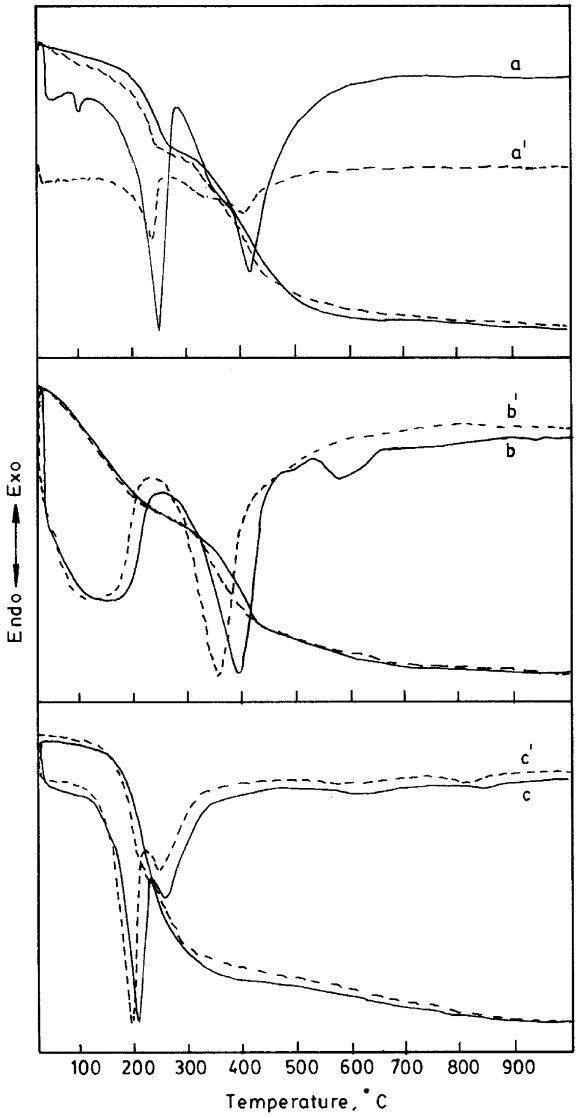

Fig. 3. The DTA/TG patterns of: (a) MA-HT (air) and (a′) MA-HT (N_2); (b) MC-HT (air) and (b′) MC-HT (N_2); (c) ZA-HT (air) and (c′) ZA-HT (N_2).

Michael reactions over the rehydrated or modified MA-HTs.

3.3. DTA/TG

Fig. 3 illustrates the DTA/TG curves of the three different HTs synthesized with M(II):M(III) atomic ratio = 2, recorded in air and N_2. Two major endothermic peaks are observed in all the HTs recorded both in air and N_2 corresponding to the two stages of weight decrease. Except for MC-HT, all the samples exhibited similar DTA patterns in both the atmospheres (N_2 and air). However, a slight shift in the t_{max} towards lower temperatures is observed in all the samples recorded in N_2, which is more pronounced in MC-HT. The first endotherm corresponds to the loss of inter-layer water and, the second one is attributed to the loss of hydroxyl groups from the brucite-like layer as well as of the anion (CO_3^{2-}) in MA-HT [22]. A very broad, small endothermic peak around 350 °C (before the second main transition) is also observed in MA-HT sample. This may be assigned to the loss of part of the OH^- in the brucite-like layer [23].

Two low temperature peaks at 205 and 260 °C and a high temperature peak at 820 °C are observed in ZA-HT samples. The peaks at 205 and 260 °C are attributed to the loss of interlayer water and de-hydroxylation due to the loss of OH^- in the brucite-like layer and loss of inter-layered anion (CO_3^{2-}), respectively [24,25]. The high temperature peak at 820 °C may be attributed to the heat absorbed during the formation of spinel ($ZnAl_2O_4$) phase at this temperature. The XRD analysis of ZA-HT calcined at 900 °C in air for 5 h confirmed the formation of $ZnAl_2O_4$ (ASTM no. 5-669).

In MC-HT samples, first weight loss due to removal of molecular water is seen to extend from room temperature up to 200 °C. We observed only a single and a very broad endotherm in the DTA profiles unlike Kooli et al. [26] who reported to have observed two peaks at 118 and 240 °C probably due to the differences in the preparation conditions adopted. Kooli et al. [26] have hydrothermally treated the precipitated sample at 120 °C for 48 h, whereas, we have prepared the MC-HT by hydrothermal treatment at 65 ± 5 °C for 18 h. A second weight loss is observed from the broad endothermic peak with a t_{max} = 360 °C in the sample recorded in N_2 and at 400 °C for the sample recorded in air. This weight loss may be ascribed to removal of hydroxyl groups from the layers and CO_2 from carbonate species in the interlayer space. An additional endotherm around 580 °C is also observed in the sample recorded in air, which may be attributed to the redox process of the chromium ions [26]. Confirmation of this is evidenced from the absence of this transition in the profile recorded in nitrogen.

3.4. *tert*-Butylation of phenol over CMA-, CMC- and CZA-HTs

The *tert*-butylation of phenol has been carried out on two different CMA-HTs prepared by varying the preparation conditions. It is found that the catalyst, CMA prepared by hydrothermal treatment for 18 h and calcined in air for 18 h showed higher butylation activity as compared to that of the CMA-1, which is hydrothermally treated for 1 h and calcined for 8 h in air. The difference in the activity probably corresponds to the difference in their acidities and basicities as seen from Table 1. Thus, the other two HT catalysts, viz. CMC- and CZA-HTs, are prepared identical to that of CMA-HT.

Fig. 4 shows the effect of temperature on the *t*-butylation activity and the product selectivities over the three different CHTs, viz. CMA, CMC and CZA. It is observed that the substitution of Mg^{2+} and Al^{3+} by Zn^{2+} and Cr^{3+} influences the conversion of phenol as well as the selectivity to various products. Although, CZA showed good activity corresponding to the high basicity and enhanced acidity of the catalyst, CMC showed a lower activity probably due to a drastic decrease in the acidity and basicity of the catalyst by Cr^{3+} substitution. There is an increase in the activity with temperature in all the catalysts, except that there is a slight decrease in the activity above 450 °C in CMC and CZA catalysts, which may be the result of increased dehydration of alcohol, and

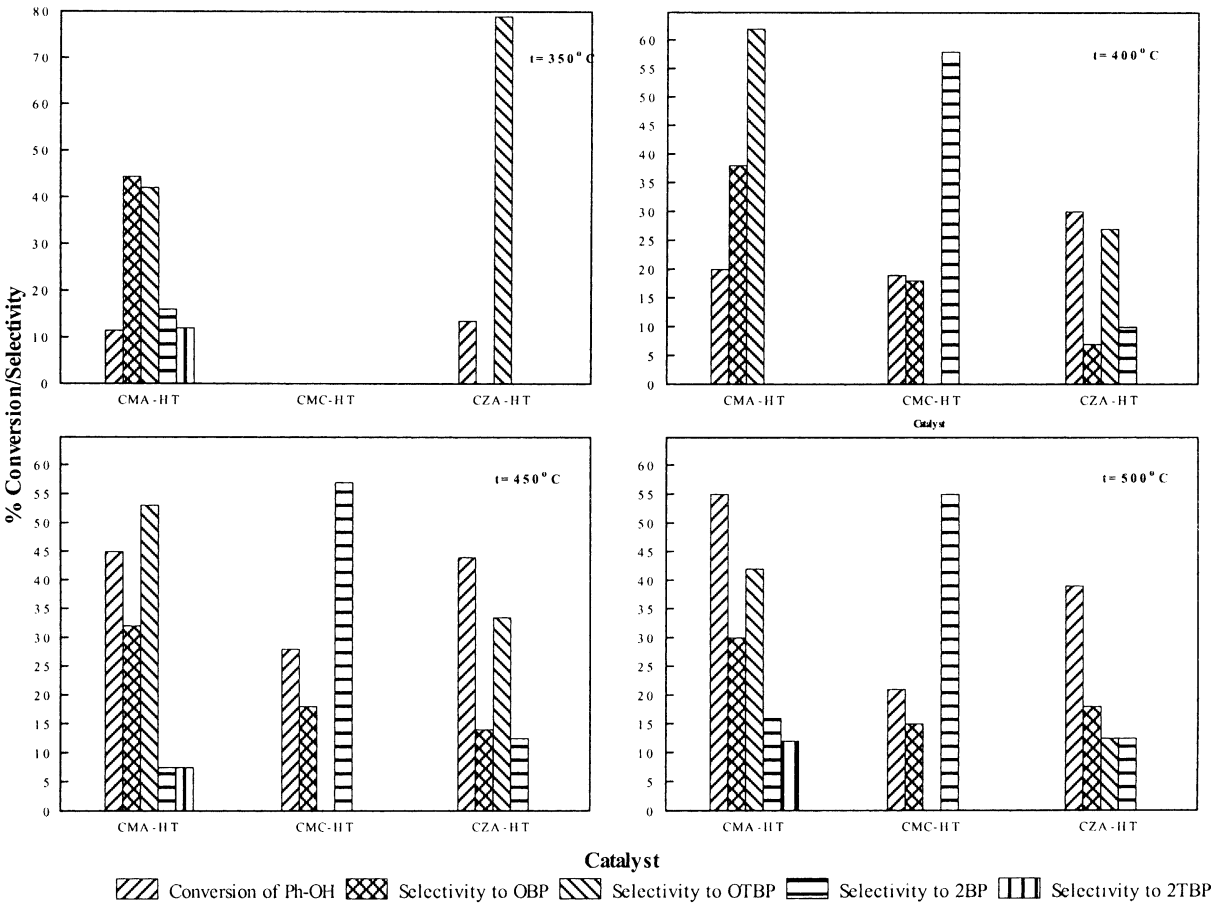

Fig. 4. Effect of temperature on the *t*-butylation of phenol over the calcined hydrotalcites: OBP, *O*-butenyl phenol; OTBP, *O*-*tert*-butyl phenol; 2BP, 2-butenyl phenol; 2TBP, 2-*tert*-butyl phenol.

consequent coking over these catalysts. From these results, a reaction temperature of 450 °C appears to be optimum for the *t*-butylation of phenol. The reaction has been found to attain steady state in ∼1 h. When the reaction is continued for a further period of 5 h, the conversion and selectivity levels were found to be nearly steady on all the catalysts.

The absence of formation of OTBP and 2TBP over CMC catalyst may be attributed to the absence of good amount of strong basic and acidic sites required for the formation of these products [27,28]. In CZA, although the basicity is observed to be high, this basicity seems to be involved more in other reactions, viz. dehydrogenation and condensation. The other products that are obtained in good amounts and identified to be the dehydrogenation and condensation products, viz. phenyl butyrate, 2-ethyl hexanal and 2-methyl propyl ester from GC–MS analysis over this catalyst suggest that the strong basic sites available on this catalyst are somewhat different from those available on MgO or mixed oxides of CMA and CMC. The formation of 2TBP over CMA at higher temperatures may be attributed to the availability of strong basic sites of MgO at higher temperatures [18]. The formation of OBP and 2BP over all the three catalysts also confirms the formation of these compounds by the combined action of acid–base pairs present on these catalysts as evidenced from the NH_3 and CO_2 uptakes.

Table 3 shows the comparative activities of different catalysts towards *tert*-butylation of phenol studied at the optimum reaction temperature of 450 °C. It is evident from this table that the mixed oxides obtained by the calcination of the HTs are more active than their corresponding individual oxides for the *t*-butylation of phenol. In fact, the conversion of phenol over Cr_2O_3 and ZnO is nil.

Table 3
t-Butylation activity of different catalysts at 450 °C and at a feed (Ph-OH:*i*-BuOH = 1:7) rate of 4 ml h^{-1}

Catalyst	Conversion of Ph-OH (%)	Selectivities (%)				
		OBP	OTBP	2BP	2TBP	Others
MgO	17.8	28.0	–	54.0	18.0	–
Al_2O_3	7.0	–	29.5	–	70.5	–
Cr_2O_3	–					
ZnO	–					
CMA-1	34.7	16.8	71.4	–	11.8	–
CMA	44.9	32.0	53.0	7.5	7.5	–
CZA	43.7	14.0	33.5	12.5	–	40.0[a]
CMC	27.9	18.0	–	57.0	–	25.0[b]

[a] Phenyl butyrate = 25%, 2-ethyl hexanal = 10% and 2-methyl propyl ester = 5%.
[b] 2-Ethyl hexanal = 25%.

Table 4 shows the selectivities of various products at an *iso*-conversion of phenol at ∼30% on the three different hydrotalcites studied in the temperature ranges of 400–450 °C. Formation of OBP is seen on all the catalysts and 2BP did not form over CMA at the studied reaction temperature (400 °C). The formation of 2TBP is seen to be absent on all the catalysts at this level of conversion of phenol.

In general, alkylation of phenol is a reaction sensitive to the acid–base properties of the catalysts employed. It has been reported that while *O*-alkylation of phenol is favored by the strong acid sites of the catalyst [27,28], *C*-alkylation is promoted by weak acidic or strong basic sites [29–31]. According to another report *O*-alkylation of phenol is favored by weak acidic sites [32]. It is also reported that methylation of phenol over CHTs takes place by the combined action of acid–base sites of the catalysts [7]. In our earlier [8] and the present study, alkylation of phenol using *iso*-butanol

Table 4
Product distribution at iso-conversion of phenol over the calcined hydrotalcites using a feed (Ph-OH:*i*-BuOH) molar ratio of 1:7 in the temperature range of 400–450 °C

Catalyst	Conversion of Ph-OH (%)	Selectivities (%)				
		OBP	OTBP	2BP	2TBP	Others
CMA at t = 400 °C and FR = 2 ml h^{-1}	31	35.3	64.7	–	–	–
CMC at t = 450 °C and FR = 2 ml h^{-1}	29	16.3	–	55.8	–	27.9[a]
CZA at t = 400 °C aand FR = 4 ml h^{-1}	30	7.3	26.4	10.3	–	55.9[b]

FR: feed rate.
[a] 2-Ethyl hexanal.
[b] Phenyl butyrate, 2-ethyl hexanal and 2-methyl propyl ester.

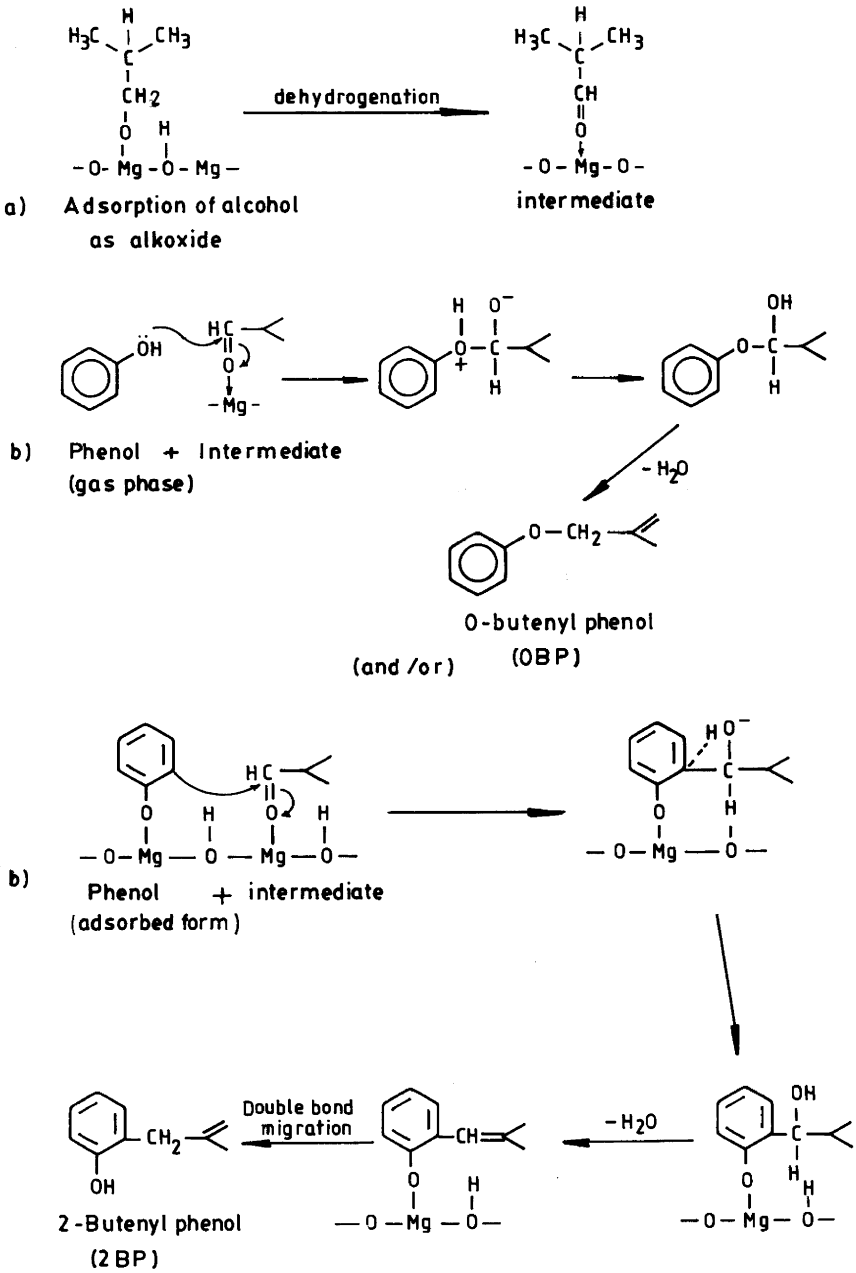

Fig. 5. A plausible mechanism for the formation of butenyl phenols.

is found to yield other products, namely butenyl phenols in good amounts besides *O-tert*-butyl phenol and 2-*tert*-butyl phenol over CHTs. Acid–base properties of CHTs appear to be important for the *tert*-butylation of phenol and the obtained product distribution may be explained in terms of mode of adsorption of phenol over the different acid–base sites available. Marczewski et al. [32] reported that methanol which is

more basic than phenol, is adsorbed on protonic centers of acid catalysts as $CH_3O^+H_2$, resulting in the formation of anisole by the reaction between adsorbed methanol and either phenol in the gas phase or phenol adsorbed on weak acidic sites. Tanabe and Nishizaki [30] proposed two different modes of adsorption on acidic and basic sites. On MgO which is very weakly acidic, the phenol is shown to adsorb in the form of phenolate ion in a vertical mode of adsorption with the benzene ring held perpendicular to the catalyst surface and on SiO_2–Al_2O_3 catalyst with high acid strength, the acid sites are shown to interact with the π-electrons of the benzene ring showing a horizontal mode of adsorption with the benzene ring parallel to the catalyst surface. This is reported to be the reason for the high selectivity towards *ortho* product over MgO catalysts and the formation of various other isomers over SiO_2–Al_2O_3 catalyst. Thus, the mode of adsorption which is governed by the acid–base strengths of the catalysts in turn seem to influence or control the selectivities of the products. The possible formation of various products may, thus be explained in terms of the two modes of adsorption of phenol over the acid–base sites. The formation of normal products, OTBP and 2TBP may occur due to the action of both acidic and basic sites of HT. A plausible mechanism (Fig. 5) has been proposed for the formation of OBP and 2BP, based on the present observations and earlier studies on the *tert*-butylation of phenol.

Solid base catalysts, such as MgO are highly selective for the hydrogen transfer from alcohols to carbonyl compounds through a mechanism similar to that of the Meerwin–Ponndorf–Verley reaction [33,34]. It has also been reported that if alkoxide intermediates are formed on the surface, they dehydrate into olefins on acidic sites [35,36] and dehydrogenate on basic sites [37,38]. Figueras et al. [39] have shown that in the dehyrogenation of methanol and *t*-butanol over alumina and silica–alumina catalysts, alumina which has a basic character, is more active than silica–alumina. They found the inhibition of dehydration activity upon poisoning the basic sites by pyridine, Na^+ or tetracyano ethylene and suggested that the reaction requires both acidic and basic sites. Therefore, one would expect from the dehydrogenation of *tert*-butyl phenols, (the normal products of *tert*-butylation) to yield the butenyl phenols. It may be mentioned here that the reaction of 2-*tert*-butyl phenol on CMA-HTs at 450 °C, did not produce any 2-butenyl phenol ruling out the possibility of formation of butenyl phenols through this route. So, it is proposed that *iso*-butanol adsorbs as an alkoxide over MgO or CHT and dehydrogenate forming an intermediate similar to that of *iso*-butyraldehyde (in adsorbed form). This intermediate reacts with phenol, either in gas phase or in horizontal mode of adsorption (over the acidic sites of the catalysts) forming *O*-butenyl phenol. The formation of 2BP is possible in the same way wherein the intermediate in this case reacts with the phenol, in vertical mode of adsorption over the basic sites of the catalyst.

4. Conclusions

Mixed oxides obtained from CHTs are found to be more active than their individual oxides for the *tert*-butylation of phenol. The butylation activities of the three different HTs are in the order: CMA > CZA > CMC. The substitution of Al^{3+} by Cr^{3+} has resulted in the drastic reduction of acid–base properties of CMC accounting for the lower activity in the *tert*-butylation of phenol. The substitution of Mg^{2+} by Zn^{2+} resulted in the enhanced acidity of the hydrotalcite formed and has also shown a good basicity and activity. But, this basicity and acidity of the catalyst seemed to contribute to the side reactions giving rise to dehydrogenation and condensation products lowering the selectivities towards butylation products. A probable mechanism has been proposed for the formation of butenyl phenols based on the correlation obtained between the acid–base properties of the catalysts and product distribution. This study has also shown that it is possible to design a suitable catalyst at chosen reaction conditions to get a desired product of *tert*-butyl or -butenyl phenol and/or condensation products.

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