

Effect of substitution of $\text{Fe}^{3+}/\text{Cr}^{3+}$ on the alkylation of phenol with methanol over magnesium–aluminium calcined hydrotalcite

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Abstract

Hydrotalcite (HT)-like compounds with the general formula, $\text{Mg}_{0.8}\text{M(III)}_{0.2}(\text{OH})_2(\text{CO}_3)_{0.1}\cdot y\text{H}_2\text{O}$ with $\text{M(III)}=\text{Al}$, Fe and Cr (Mg/Al atomic ratio 4) were synthesized by coprecipitation method using a mixture of $\text{NaOH}/\text{Na}_2\text{CO}_3$ as precipitant. The Powder X-ray diffraction (PXRD) of aluminium and iron containing samples ($\text{M(III)}=\text{Al}$, Fe) showed single phase corresponding to HT when a mixture of HT and $\text{MgCrO}_4\cdot 7\text{H}_2\text{O}$ phase was detected for chromium containing sample ($\text{M(III)}=\text{Cr}$). These samples after calcination at $450^\circ\text{C}/8\text{ h/air}$, were used as catalyst for vapour phase alkylation of phenol with methanol. MgAl 4.0-CHT showed nearly 100% phenol conversion around 400°C and the reaction was found to proceed predominantly through the formation of anisole (O-alkylation). Isomorphous substitution of Al^{3+} by Fe^{3+} or Cr^{3+} in the HT framework resulted in a decrease in phenol conversion in the order MgAl 4.0-CHT > MgCr 0-CHT > MgFe 4.0-CHT and the alkylation reaction was found to proceed exclusively at C-centres (C-alkylation) to give *o*-cresol as a major product. The catalytic performance for the methylation of phenol has been correlated with acid–base properties of the catalysts as determined by test reactions such as decomposition of 2-methyl-3-butyne-2-ol (MBOH) and cyclohexanol. © 1997 Elsevier Science B.V.

Keywords: Hydrotalcite; Layered double hydroxide; Alkylation of phenol; Acid–base catalysis

1. Introduction

Hydrotalcite (HT), which is also referred to as layered double hydroxide (LDH) consists of positively charged brucite $[\text{Mg}(\text{OH})_2]$ -like layers with trivalent cations substituting divalent cations in octahedral sites, separated by interlayer anions and water molecules. They are represented by the general molecular formula, $[\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^{x+}[\text{A}_{x/n}^{n-}]^{x-}\cdot y\text{H}_2\text{O}$ wherein, $\text{M(II)}=\text{Mg}$, Cu , Ni , Co , Mn , Zn ; $\text{M(III)}=\text{Al}$,

Fe , Cr , V ; A^{n-} is any interlayer anion such as CO_3^{2-} , Cl^- , NO_3^- , SO_4^{2-} or any other macrocyclic multivalent anions and $x=0.1\text{--}0.33$ [1,2]. These compounds are receiving considerable interests in recent years owing to their potential technological importance as catalysts, ion exchangers, optical hosts and ceramic precursors [3,4]. They are stable up to around 400°C and transforms into a highly active mixed metallic oxide with high surface area and porosity and used them potentially in acid–base catalyses [5–8].

Alkylation of phenol with methanol is an industrially important reaction: Products such as *o*-cresol

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and 2,6-xyleneol are used as chemical intermediates for synthesis of a variety of fine chemicals, pharmaceuticals, pesticides and plastics [9,10]. The stringent specifications and demand for high purity to use them in drugs and pharmaceuticals necessitate the synthesis of these compounds selectively. In recent times, the vapour phase alkylation of phenol with methanol over various solid catalysts, without causing any environmental impact, is considered to be a promising route for the synthesis of these compounds selectively. A wide variety of solid catalysts including γ -alumina, silica-alumina, metallic oxides, sulphates, phosphates and various types of zeolites, have been employed for this reaction [11–16]. However, use of these catalysts poses drawbacks, such as the lower selectivity for desired product due to the formation of a mixture of O- and C-alkylated products, the lower catalyst life-time, the higher reaction temperature or pressure [11,14,15]. Our earlier investigations on the alkylation of phenol with methanol over a series of magnesium–aluminium calcined hydrotalcites have shown that these catalysts are more promising for the selective synthesis of *o*-cresol and 2,6-xyleneol [17]. Among the catalysts studied in this series, MgAl 4.0-CHT was found to be the most active. Isomorphous substitution of Mg^{2+} by other divalent cations such as Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} and Zn^{2+} in the HT framework resulted in decrease in phenol conversion but the selectivity to *o*-cresol increased [18,19].

The objective of the present investigation is to study the effect of isomorphous substitution of Al^{3+} by other trivalent cations such as Fe^{3+} or Cr^{3+} in the framework of magnesium–aluminium hydrotalcite (Mg/Al atomic ratio=4) on phenol conversion and product selectivity and to correlate the catalytic performance with acid–base properties as determined by the decomposition of 2-methyl-3-butyn-2-ol (MBOH) and cyclohexanol as test reactions.

2. Experimental

$\text{Mg}_{0.8}\text{M(III)}_{0.2}(\text{OH})_2(\text{CO}_3)_{0.1}\cdot y\text{H}_2\text{O}$ with $\text{M(III)}=\text{Fe}$ and Cr were synthesized by coprecipitation method [17,18]. For phase identification, Powder X-ray diffraction (PXRD, Rigaku miniflux) was carried out using Fe filtered Co K_α radiation ($\lambda=1.7902 \text{ \AA}$) with a scan rate of $2\theta=2^\circ/\text{min.}$, while a speed of $0.5^\circ/\text{min}$

was used for the calculation of lattice parameters. For Cr containing samples, a V filtered Cr K_α radiation ($\lambda=2.291 \text{ \AA}$) was used in order to avoid an asymmetric XRD pattern due to the fluorescence of the sample [20]. Elemental Si was used as an external standard. BET surface area, pore size distribution and pore volume study of calcined samples ($450^\circ\text{C}/8 \text{ h/air}$) were performed by N_2 adsorption–desorption experiments at 77 K using a Carlo Erba (Model 1800) sorptometer. The decomposition of MBOH and cyclohexanol over calcined samples were carried out in a fixed-bed flow reactor at 250°C (WHSV, weight hourly space velocity= $19.3 \text{ mol h}^{-1} \text{ kg}^{-1}$) and 300°C (WHSV= $18.0 \text{ mol h}^{-1} \text{ kg}^{-1}$), respectively [21,22]. The alkylation reactions were carried out with 1.5 g of calcined hydrotalcite (CHT) packed in a fixed-bed flow reactor and a 1 : 7 phenol : methanol mixture was used as reactant feed with a space velocity, WSHV= $9.0 \text{ mol h}^{-1} \text{ kg}^{-1}$. The phenolic products were condensed and collected in cold traps. The liquid products collected between 60 and 90 min time-on-stream were analysed using gas chromatography (GC). The catalytic activity and product selectivity were compared with that of the magnesium–aluminium calcined hydrotalcites with Mg/Al atomic ratio 4 (MgAl 4.0-CHT), the most active catalyst for the methylation of phenol from our earlier report [17].

3. Results and discussion

3.1. Synthesis and characterization

The chemical composition, lattice parameters and textural properties of as-synthesized and calcined samples ($450^\circ\text{C}/8 \text{ h/air}$) of MgM(III)-HT are presented in Table 1. A pure HT phase is formed in the case of MgAl 4.0-HT and MgFe 4.0-HT while a mixture of HT and $\text{MgCrO}_4\cdot 7\text{H}_2\text{O}$ (JCPDS File No. 1–243) is noticed for MgCr 4.0-HT. Literature reports on the synthesis and characterization of MgCr 4.0-HT are scarce. Earlier studies in our laboratory on the effect of trivalent cations on physicochemical properties of $\text{M(II)M(III)CO}_3\text{-HT}$ with $\text{M(II)}=\text{Co}$, Ni and $\text{M(III)}=\text{Al}$, Fe , Cr with $\text{M(II)/M(III)}=3$ [23] revealed that the crystallinity of the compound decreased in the order: $\text{M(II)AlCO}_3\text{-HT} > \text{M(II)FeCO}_3\text{-HT} > \text{M(II)CrCO}_3\text{-HT}$.

Table 1

Composition, lattice parameters and textural properties of as-synthesised and calcined MgM(III)–HT

Compound	As-synthesised sample					Calcined sample ^c		
	Mg/M(III) atomic ratio ^a	PXRD phase	Lattice parameters ^b			PXRD phase	Sp.SA ^d (m ² g ⁻¹)	Sp.PV ^e (cm ³ g ⁻¹)
			<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)			
MgAl 4.0-HT	3.7	HT	3.069	23.579	192	MgO	176	0.48
MgFe 4.0-HT	3.8	HT	3.110	23.892	200	MgO	150	0.21
MgCr 4.0-HT	3.7	HT+MgCr	3.118	25.440	214	MgO	143	0.29

MgCr=MgCrO₄·7H₂O (JCPDS File No. 1-243).^aICPES results.^bCalculated employing least square fitting method for hexagonal crystal system.^cCalcination temperature 450°C/8 h/air.^dSpecific surface area of calcined sample.^eSpecific pore volume of calcined sample.

Furthermore, a highly amorphous phase was obtained in the case of NiCrCO₃–HT and CoCrCO₃–HT. Hence it was concluded that the presence of Al plays an important role in the precipitation of pure and well crystalline HT-like structure. The lattice parameter “*a*” of MgM(III)–HT increases when Al³⁺ (ionic radius 0.53 Å) is replaced by Fe³⁺ (ionic radius 0.64 Å) or Cr³⁺ (ionic radius 0.69 Å) in the brucite-like layer (Table 1). A dramatic increase in the value of “*c*” with concomitant increase in “*V*” is seen in the case of MgCr 4.0-HT. This can be attributed to the presence of a different degree of hydration in this sample. The PXRD of calcined samples showed a poorly crystalline MgO phase. No separate Fe or Cr oxide phases are detected. The difference in specific surface area and specific pore volume indicates that the textural properties of these compounds are affected when Al³⁺ is replaced by Fe³⁺ or Cr³⁺ in the HT framework.

3.2. Catalytic studies

3.2.1. Effect of temperature

The effects of temperature on phenol conversion over these catalysts are depicted in Fig. 1. It can be seen that MgAl 4.0-CHT is the most active catalyst, showing nearly 100% phenol conversion around 400°C. Substitution of Al³⁺ by Fe³⁺ or Cr³⁺ in the HT framework results in decrease in phenol conversion. The activity increases abruptly above 300°C, showing, an “S” type behaviour similar to that

obtained for a series of MgAl–CHT [17] and M(II)Al–CHT [18]. MgCr 4.0-CHT is more active compared to MgFe 4.0-CHT at all the reaction temperatures. Furthermore, substitution of Al³⁺ by Fe³⁺ or Cr³⁺ results in direct C-alkylation to give *o*-cresol as the major product without passing anisole as an intermediate. This is in contrast to our earlier results obtained over MgAl–CHT [17]. As temperature increases the selectivity for *o*-cresol decreases at the cost of 2,6-xyleneol and other higher alkylphenols.

3.2.2. Effect of contact time

The effects of contact time on phenol conversion and product selectivity at constant temperature (350°C) performed over MgFe 4.0-CHT and MgCr 4.0-CHT are presented as OPE (optimum performance envelope) curves in Fig. 2(a) and (b), respectively. In the case of MgFe 4.0-CHT, *o*-cresol is the sole product formed at the onset of the reaction (Fig. 2(a)). As the conversion of phenol increases, there is a small drop in *o*-cresol selectivity (from 100% to 90%) with concomitant increase in selectivity to 2,6-xyleneol. The selectivity of these products remains constant with further increase in phenol conversion. On the other hand, a mixture of anisole (≈5%) and *o*-cresol (≈95%) is noticed up to 20% phenol conversion over MgCr 4.0-CHT (Fig. 2(b)). Increase in phenol conversion beyond 20% leads to a drop in *o*-cresol selectivity while the selectivity to 2,6-xyleneol increases. However, the selectivity to anisole is not affected by increased phenol conversion. From these

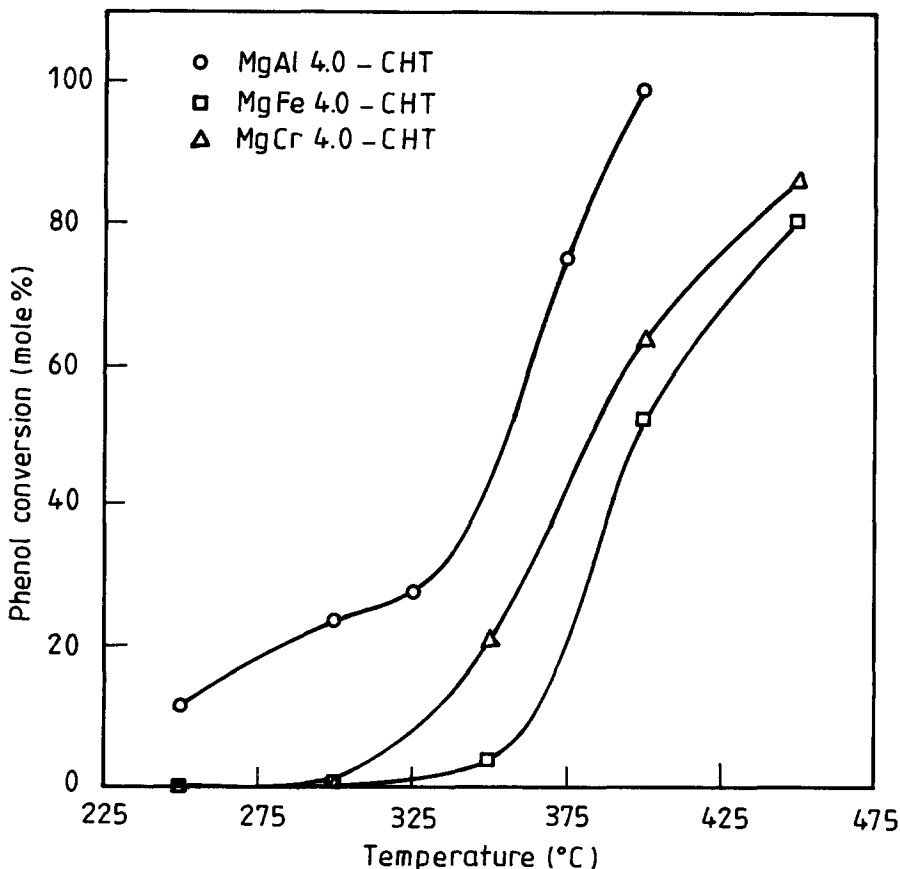


Fig. 1. Effect of temperature on phenol conversion over MgM(III)-CHT, WHSV=9.0 mol h⁻¹ kg⁻¹.

observations, it can be inferred that *o*-cresol formed as a primary alkylation product undergoes secondary reactions to give 2,6-xylene and small amount of higher alkylphenols. In order to get evidence for the above inference, the reaction of a 1 : 7 mixture of *o*-cresol : methanol has been carried out over these catalysts.

The results of alkylation of *o*-cresol with methanol over MgAl 4.0-CHT, MgFe 4.0-CHT and, MgCr 4.0-CHT are presented in Table 2. It is seen that these catalysts are more efficient for the alkylation of *o*-cresol with methanol (30–60% conversion at 350°C) to give 2,6-xylene as the major product (80–90%). MgCr 4.0-CHT is more active for *o*-cresol conversion (nearly 40% at 350°C) compared to MgFe 4.0-CHT (nearly 30% conversion). The catalytic activity for *o*-cresol conversion decreases in the order:

MgAl 4.0-CHT > MgCr 4.0-CHT > MgFe 4.0-CHT. An interesting observation noticed is that in the case of MgAl 4.0-CHT, the selectivity for 2,6-xylene decreases at the cost of higher alkylphenols as the temperature or contact time is increased while, the 2,6-xylene selectivity remains almost the same in the case of MgFe 4.0-CHT and MgCr 4.0-CHT. This could be due to the fact that MgAl 4.0-CHT would favour secondary alkylation of 2,6-xylene into higher alkylphenol, while substitution of Al³⁺ by either Fe³⁺ or Cr³⁺ in the HT framework would not favour such secondary alkylation.

The activity and product selectivity in the alkylation of phenol with methanol over MgM(III)-CHT at 350°C and at constant space velocity (9.0 mol h⁻¹ kg⁻¹) is compared in Fig. 3. An examination of this figure reveals that MgAl 4.0-CHT is the

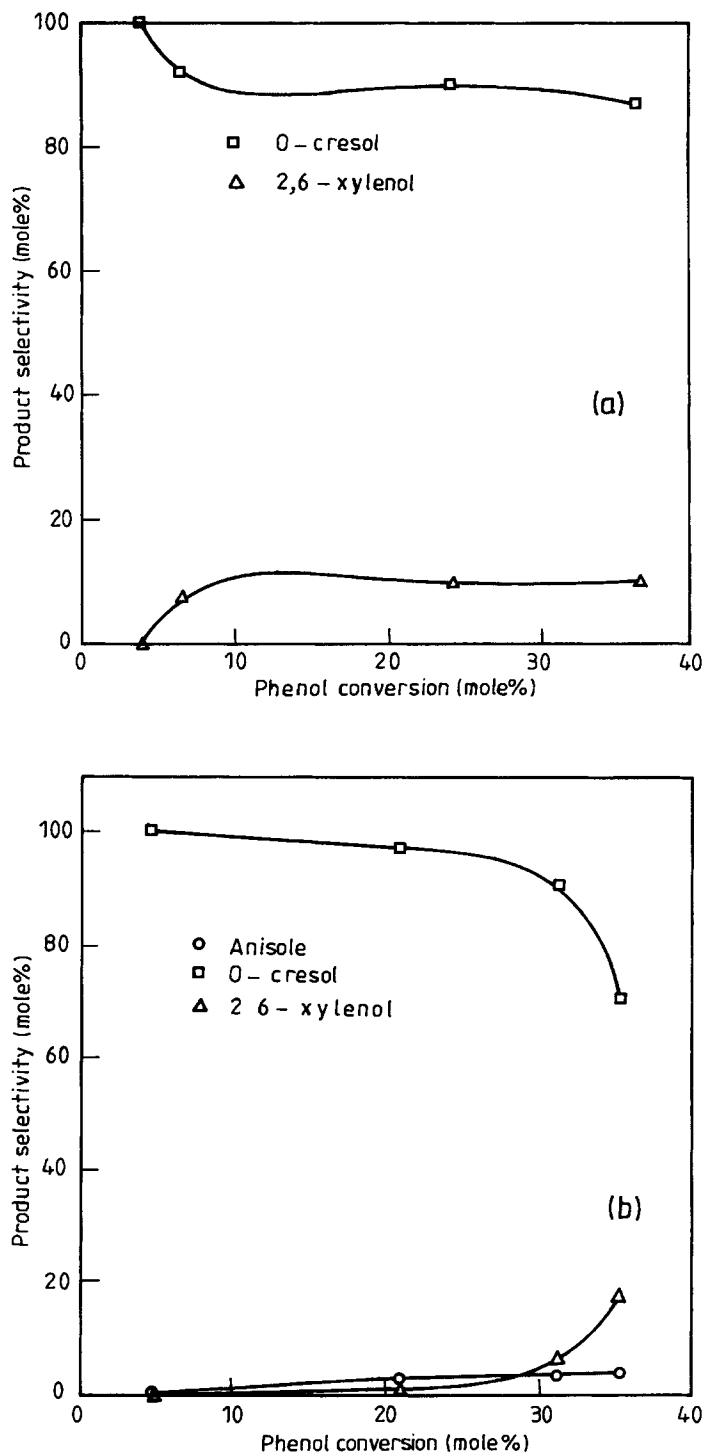


Fig. 2. OPE curves for the alkylation of phenol with methanol over (a) MgFe 4.0-CHT; (b) MgCr 4.0-CHT; temperature=350°C.

Table 2

Activity and product selectivity over MgM(III)-CHT employing *o*-cresol : methanol (1 : 7) mixture, WHSV=8.7 mol h⁻¹ kg⁻¹

Catalyst	Temperature (°C)	<i>o</i> -Cresol conversion (mol%)	Product selectivity (mol%)	
			2,6-Xylenol	Higher alkyl phenol ^a
MgAl 4.0-CHT	300	4.4	100.0	—
	350	55.5	45.5	54.5
	350 ^b	64.0	15.0	85.0
MgFe 4.0-CHT	300	3.1	100.0	—
	350	31.9	95.9	4.1
	400	76.3	83.7	16.3
	350 ^b	45.1	83.4	16.6
MgCr 4.0-CHT	300	4.2	100.0	—
	350	43.9	84.3	15.7
	40	79.6	85.6	14.4
	350 ^b	49.1	81.3	18.7

^aHigher alkyl phenols include a mixture of 2,6-dimethyl anisole, 2,4,6-trimethylphenol and 2,4,6-trimethyl anisole.^bWHSV=4.3 mol h⁻¹ kg⁻¹.

most active catalyst (nearly 60% conversion). Substitution of Al³⁺ by Fe³⁺ or Cr³⁺ in the HT network results in decrease in phenol conversion but the selectivity to *o*-cresol increases substantially (90–100%) with very low selectivity to 2,6-xylenol. In order to get more insight into the selectivity pattern over these catalysts, the product selectivity has been compared at constant phenol conversion at constant temperature by varying the flow rate of the feed mixture. Fig. 4 shows the comparison of product selectivity at constant phenol conversion (35–40%) at 350°C. It can be seen clearly from this figure that the selectivity to *o*-cresol formation decreases in the order MgFe 4.0-CHT>MgCr 4.0-CHT>MgAl 4.0-CHT, whereas the selectivity to 2,6-xylenol follows the reverse trend.

3.2.3. Acid–base properties and catalytic activity

Since the alkylation of phenol is essentially an acid–base reaction, the catalytic activity and product selectivity depends strongly on the acid–base properties of catalysts. Several scientists have attempted to correlate the catalytic performance for phenol alkylation with the strength of the acidic or basic sites present on the catalyst surface. It has been found that catalysts with strong acidic sites favour the O-alkylation of phenol to give anisole as a major product [13,14],

while catalysts with weak acidic or strong basic sites promote the ring alkylation (C-alkylation) to give cresols and xylenols [15]. On the other hand, Marczewski and coworkers [24] claimed that weak acidic sites favour O-alkylation of phenol and by increasing the strength of the acidic sites of catalyst, the formation of *o*-cresol is favoured.

The acid–base properties of MgM(III)-CHT in the present investigation have been evaluated by test reactions such as decomposition of MBOH and cyclohexanol. MBOH undergoes dehydration to yield 3-methyl-3-butene-1-yne (Mbyne) over acidic catalysts while, it undergoes disproportionation to give an equimolar amount of acetone and acetylene in the presence of basic sites [25,26]. Decomposition of cyclohexanol into cyclohexanone in the presence of basic sites and in to cyclohexene in the presence of acidic sites has been used as a simple test reaction to evaluate the acid–base properties of the catalysts [27]. Rao et al. [28] have considered the selectivity to cyclohexene as a measure of the “acidity index” of the catalysts. Our earlier studies [21,22] on the decomposition of MBOH and cyclohexanol over a series of magnesium–aluminium calcined hydrotalcites indicated that these test reactions are more sensitive for the simultaneous characterization of acid–base properties of the catalysts.

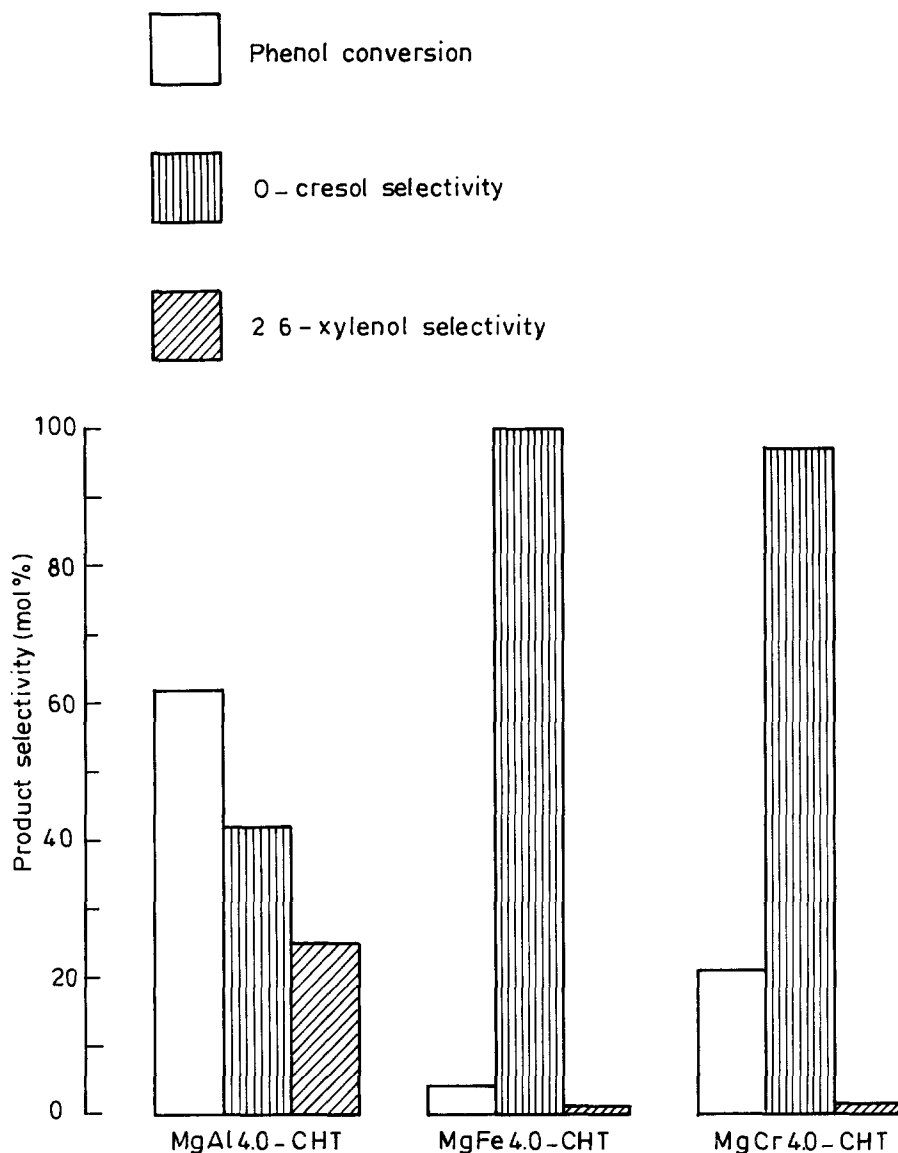


Fig. 3. Activity and product selectivity in the alkylation of phenol with methanol over MgM(III)-CHT; temperature 350°C; WHSV=9.0 mol h⁻¹ kg⁻¹.

Table 3 summarizes the correlation between acid–base properties and catalytic activity in the alkylation of phenol with methanol over these catalysts. The results show that both selectivity for acetone in the decomposition of MBOH and selectivity for cyclohexanone in the decomposition of cyclohexanol decreases in the order MgAl 4.0-CHT>MgCr 4.0-CHT>MgFe 4.0-CHT indicating that MgAl 4.0-

CHT is more basic and the basicity decreases when Al³⁺ in the HT framework is substituted by Cr³⁺ or Fe³⁺. The specific activity (mmol h⁻¹ m⁻² or mmol h⁻¹ g⁻¹) for phenol conversion also decreases in the same order which reveals that the catalytic activity for phenol conversion decreases with decrease in basicity of the catalyst while, the selectivity for *o*-cresol follows the reverse trend. The

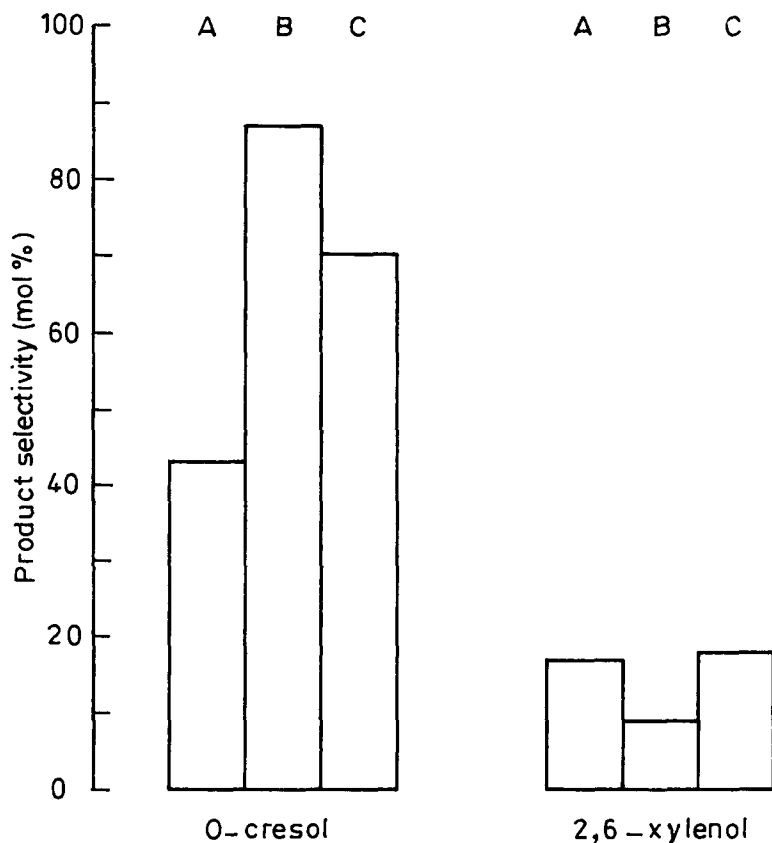


Fig. 4. Product selectivity in the alkylation of phenol with methanol over MgM(III)-CHT at constant phenol conversion (35–40%); temperature: 350°C; (A) MgAl 4.0-CHT; (B) MgFe 4.0-CHT; (C) MgCr 4.0-CHT.

Table 3

Correlation between acid–base properties and catalytic activity in the alkylation of phenol with methanol over MgM(III)-CHT

Catalyst	Specific activity for phenol conversion ^a		$S_{o\text{-cresol}}$	S_{acetone}	$S_{\text{c-none}}$
	$\text{mmol h}^{-1} \text{g}^{-1}$	$\text{mmol h}^{-1} \text{m}^{-2} (\times 10^3)$			
MgAl 4.0-CHT	3.88	22.0	41.7	100.0	99.6
MgFe 4.0-CHT	0.24	1.6	100.0	82.8	46.2
MgCr 4.0-CHT	1.30	9.1	94.7	92.7	83.9

$S_{o\text{-cresol}}$ =Selectivity to *o*-cresol.

S_{acetone} =Selectivity to acetone with 80–90% MBOH conversion at 250°C.

$S_{\text{c-none}}$ =Selectivity to cyclohexanone with 25–35% cyclohexanol conversion at 300°C.

^aTemperature=350°C.

observed trend in activity and selectivity can be attributed to the fact that alkylation reaction over MgAl-CHT proceeds through the formation of anisole (O-alkylation) which is favoured by increased basicity of the catalysts [17]. On the other hand, the decrease in

basicity upon substitution of Al^{3+} by Fe^{3+} or Cr^{3+} in the HT framework resulted in direct C-alkylation to give *o*-cresol as a major product. The preferential formation of *o*-cresol to *p*-cresol over these catalysts can be attributed to the nature of adsorption of phenol

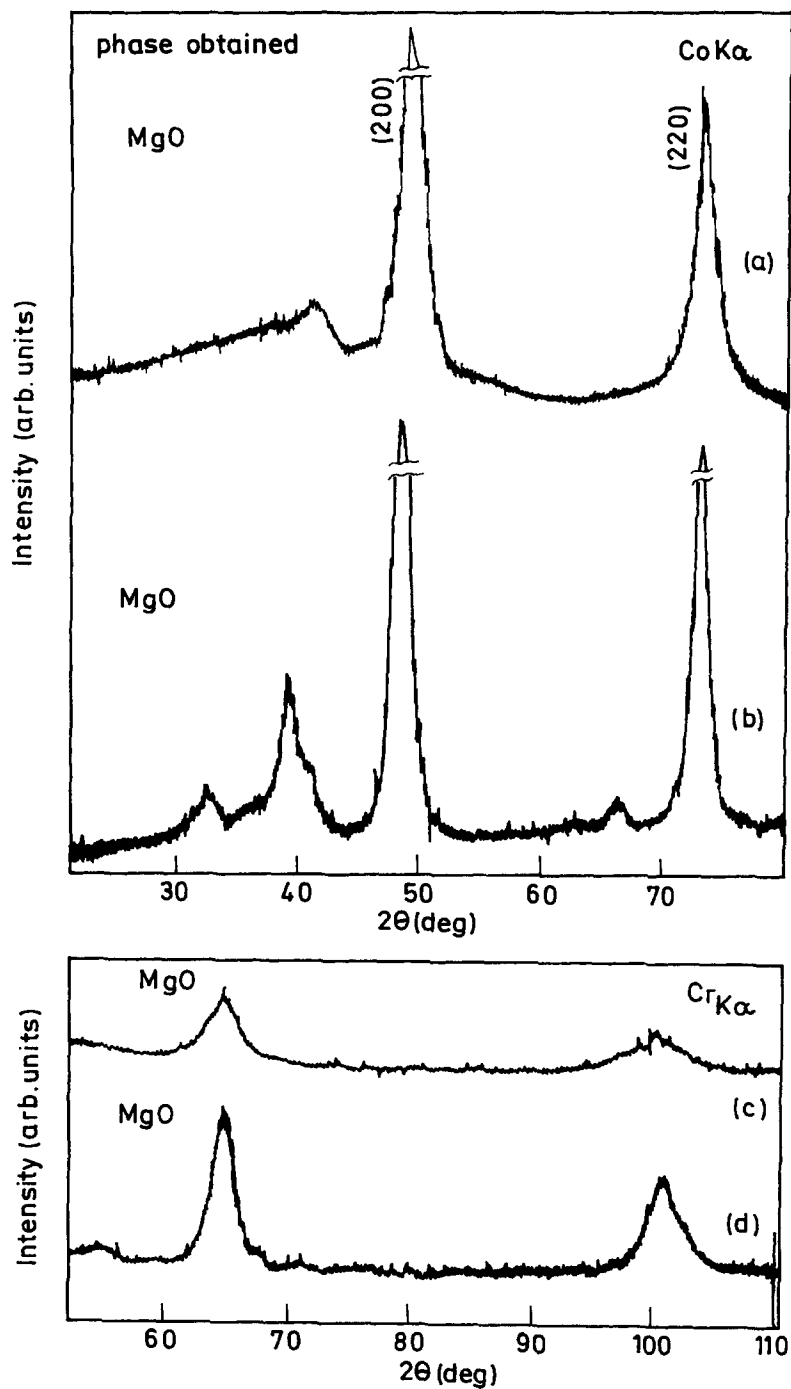


Fig. 5. XRD patterns of (a) MgFe 4.0-CHT; (b) Spent MgFe 4.0-CHT; (c) MgCr 4.0-CHT; (d) Spent MgCr 4.0-CHT.

Table 4
Structural and textural properties of spent MgM(III)–CHT catalysts

Catalyst	PXRD results		Surface area (m ² g ⁻¹)		
	Phase obtained	<i>d</i> ₍₂₀₀₎ (Å)		Spent	Fresh
		Spent	Fresh		
MgAl 4.0-CHT	MgO	2.081	2.086	170	176
MgFe 4.0-CHT	MgO	2.099	2.091	90	150
MgCr 4.0-CHT	MgO	2.105	2.102	110	143

on the catalyst surface. As described by Tanabe [29], the phenolate ion is adsorbed on the catalyst such that the *ortho* position is very near to the catalyst surface, hence only the *ortho* position is selectively methylated.

3.2.4. Analysis of the spent catalysts

Spent catalyst analysis was carried out in order to get an insight into the stability of the catalyst during the reaction. The PXRD patterns of spent MgFe 4.0-CHT and MgCr 4.0-CHT are shown in Fig. 5. For comparison, the PXRD patterns of the fresh catalysts are also shown. It is very interesting to note from this figure that both MgFe 4.0-CHT and MgCr 4.0-CHT shows single phase corresponding to MgO alone which is similar to that observed in the case of MgAl–CHT [17]. No separate Fe or Cr containing phases are detected by PXRD (spent catalyst) even after several catalytic runs (8–10 times) repeated over the same catalyst. The *d*₍₂₀₀₎ of MgO of spent catalyst is comparable with that of the fresh catalyst (Table 4). These results indicate that the structural properties of the catalysts are not affected during the alkylation reaction. The specific surface area of the spent MgAl 4.0-CHT is similar to the corresponding fresh catalyst while it is less in the case of spent MgFe 4.0-CHT and MgCr 4.0-CHT. This can be attributed to the sintering of the particles as evidenced from increase in PXRD peak intensities of spent catalysts as compared to their fresh catalysts (Fig. 5). The drop in surface area is higher in the case of MgFe 4.0-CHT (150–90 m² g⁻¹ as compared to MgCr 4.0-CHT (143–110 m² g⁻¹). Hence it can be concluded that although the structural properties are not affected the textural properties are affected to small extent when Al³⁺ is isomorphously substituted by Fe³⁺ and Cr³⁺ in the HT framework.

4. Conclusions

(1) Isomorphous substitution of Al³⁺ by Fe³⁺ or Cr³⁺ in the MgM(III)–HT framework resulted in decrease in catalytic activity for phenol conversion in the order MgAl 4.0-CHT>MgCr 4.0-CHT>MgFe 4.0-CHT while the selectivity to *o*-cresol follows the reverse trend. This has been attributed to the decrease in basicity of the catalysts in the order MgAl 4.0-CHT>MgCr 4.0-CHT>MgFe 4.0-CHT, as determined by the decomposition of MBOH and cyclohexanol.

(2) The alkylation reaction was found to proceed predominantly through the formation of anisole (O-alkylation) over MgAl 4.0-CHT [17]. On the other hand, selective C-alkylation to give *o*-cresol as a major product was noticed over MgFe 4.0-CHT and MgCr 4.0-CHT.

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