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Alkylation of phenol with methanol over magnesium–aluminium calcined hydrotalcites

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Abstract

Vapour phase alkylation of phenol with methanol was carried out in a fixed-bed flow reactor over thermally calcined magnesium aluminium hydrotalcites, with Mg/Al atomic ratios from 3 to 10. The main products were anisole, *o*-cresol, and 2,6-xylenol. The influence of phenol-to-methanol molar ratio, reaction temperature and contact time on the product yields were examined. The activity of these catalysts was compared with MgO, Al_2O_3 and physically mixed MgO–Al_2O_3. Of the catalysts studied, Mg–Al 4.0:1 calcined hydrotalcite (CHT) was the most active. These catalysts are more active than magnesia and γ-alumina. On the basis of the results obtained, a suitable reaction pathway was proposed. The participation of combined acidic and basic sites in the calcined hydrotalcites for the alkylation of phenol with methanol over magnesium–aluminium calcined hydrotalcites has been suggested. Prior to the reaction, the catalyst precursors were characterised by X-ray powder diffraction and surface area measurements.

Keywords: Acid–base properties; Alkylation of phenol; Hydrotalcite ; Mg/Al atomic ratio

1. Introduction

Hydrotalcite (HT), $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$ is one of the naturally occurring anionic clay minerals containing positively charged brucite-like [$Mg(OH)_2$] layers with interlayer space filled with carbonate ion and water molecules [1]. Hydrotalcite-like compounds [HTlc], structurally similar to HT but with cations and anions other than Mg, Al and CO_3^{2-} can be synthesised by coprecipitation from aqueous solutions of corresponding metal salts and/or by anion exchange methods [2,3]. The general formula of HTlc is

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

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where M^{II} and M^{III} are divalent and trivalent metal ions respectively. 'A' is the inter layer exchangeable anion and $x = 0.1–0.33$.

Thermal decomposition of these compounds above 400°C results in the formation of a highly dispersed metallic oxide and a well discernible channel system [4] with a high-surface area resulting from the evolution of structural water and carbon dioxide. The metallic oxide so obtained is found to be an efficient solid base catalyst for aldol condensation, polymerisation of β-propiolactone, alkene isomerisation and condensation of aldehydes or ketones with active methylene groups [5–10]. Recently, we have reported [11] that calcined hydrotalcite (CHT) effectively decomposes N_2O, a green house gas. Application of hydrotalcites for other catalytic reactions such as aromatic alkylation have not been reported.

Alkylation of phenols with methanol is an industrially important reaction as of the products, anisole is an additive in gasoline to boost octane, *o*-cresol is an important organic intermediate for herbicides and insecticides, and 2,6-xylenol is used in the manufacture of polyphenylene oxide (PPO) and in special grade paints [12,13]. The catalysts employed for this reaction include various types of zeolites, γ-alumina, silica–alumina, Nafion-H, phosphoric acid, ALPO, SAPO, metal phosphates, acidic and basic oxides; and produced a mixture of C- and O- alkylated products [14–25]. The selectivity of the reaction depends on the acid–base properties of the catalysts. Oxide catalysts are more selective for the synthesis of 2,6-xylenol than zeolites owing to the pore constraints in the latter [13,22]. Acidic catalysts generally produces a mixture of cresols and xylenols and also get deactivated with time due to coking. Tanabe [23] have reported that, basic catalysts such as MgO selectively alkylate at the *ortho*-position. Others have reported that acidic catalysts also gave predominantly *ortho*-alkylation [13]. The aim of the present investigation is to check the activity and selectivity of calcined hydrotalcites with various Mg/Al atomic ratios for the vapour phase alkylation of phenol with methanol.

2. Experimental

2.1. Preparation of catalyst

$[Mg_{1-x}Al_x(OH)_2]^{x+}\ CO_3^{2-}\cdot mH_2O$ with Mg/Al atomic ratios of 3, 4, 4.5, 5, 7 and 10 were prepared by coprecipitation under low supersaturation conditions [26] by adding simultaneously a mixture of aqueous solutions of metal nitrates (80 ml/h) and a mixture of aqueous solutions of NaOH (2–3 *M*) and Na_2CO_3 (0.2–0.35 *M*) at room temperature, with vigorous stirring maintaining the pH 9–10. The resulting heavy slurry was aged at 65°C for 30 min with vigorous stirring. The precipitate was filtered, washed several times with distilled water and dried in an air oven at 110°C overnight. For calcination, about 3 g of the sample was placed in a 20 ml Pyrex tube calcined in air at 450°C and kept at this temperature for 8 h and then cooled to room temperature.

2.2. Characterisation

The bulk elemental analysis for magnesium and aluminium were carried out by inductively coupled plasma emission (ICPE) spectroscopy (Model 3410, ARL) by dissolving about 50 mg of the sample in a minimal amount of dilute hydrochloric acid. The X-ray diffraction (XRD) patterns of the samples were recorded using a Philips X-ray generator (Model PW1050/81 controlled by a PW1710 unit) using Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å) at a scan speed of 3°/min. The surface area of the samples were determined employing the BET method in a Carlo-Erba (Model 1800) sorptometer at 77 K.

2.3. Catalytic study

2.3.1. Apparatus and procedure

The vapour phase alkylation of phenol with methanol was carried out at atmospheric pressure using a vertical flow-type reactor consisting of 2.2 cm I.D. and 30 cm length, kept in a cylindrical furnace mounted vertically. The catalyst (1.5 g of powdered CHT, 450°C/8 h) was loaded in the middle of the reactor and packed with glass beads. The temperature of the reactor was measured by a thermocouple placed in the middle of the catalyst bed. Before the start of the experiment, the catalyst was activated at 450°C/3 h in nitrogen flow (23 cm^3/min) and then brought to the reaction temperature. A premixed phenol–methanol (1:7 molar ratio) was introduced at the top of the reactor by means of an infusion pump (Electronic Corporation, India) in the absence of carrier gas. The activity test of the catalyst lasted for at least 5 h while other experiments were carried out for 1 h. After each run, the same catalyst was reactivated at 450°C/8 h in nitrogen for subsequent runs.

2.3.2. Product analysis

The liquid products were collected in cold traps and were analysed by gas chromatograph (GC; Nucon instrument with an Oracle-1 computing integrator) with a 3.2 m SE30 column using a flame ionisation detector. The percentage composition reported is based on the GC analysis of the phenolic compounds. The products were mainly anisole, *o*-cresol, 2,6-xylenol and 2-methylanisole. In some cases, a small amount of solid product was deposited on the wall of the reactor which was scraped out, washed with benzene then crystallised in methanol and weighed after drying. It was identified as hexamethylbenzene (HMB) by ^{1}H-NMR (60 MHz, Hitachi 1700) and by melting point determination (164°C; authentic sample, 167–168°C Aldrich Chemical Co. Inc., Catalog No: 32, 237.7) The gaseous products were analysed using an Orsat apparatus [27].

3. Results and discussion

The physico-chemical characterisation of the synthetic hydrotalcites are presented in Table 1. The results show that with the exception of Mg/Al = 10, the measured Mg/Al atomic ratios of all the catalysts are very similar to the original calculated ratio indicating that the precipitation is complete. The XRD of the synthesised samples show sharp and symmetric peaks for (003), (006), (110), and (113) planes and broad and asymmetric peaks for (102), (105), and (108) planes (Fig. 1) which are characteristic of clay minerals possessing layered structure [28]. We achieved the formation of single phase corresponding to HT for all the samples including Mg/Al = 10 ($x = 0.1$). This is in contrast to the previous report by Schaper et al. [7] who observed the formation of a mixture of HT and hydromagnesite for the sample with Mg/Al = 10. However, we cannot rule out the formation of any X-ray amorphous phases in that sample. The lattice parameters '*a*' and '*c*' calculated for hydrotalcites with a hexagonal crystal system (Table 1) increased with an increase of the Mg/Al ratio (except for Mg/Al = 10). The increase of '*a*' with an increase of the Mg/Al ratio can be attributed to the difference in the ionic radius of Mg^{2+} (0.65 Å) and Al^{3+} (0.50 Å). The increase in the '*c*' value is due to the decrease in the electrostatic attraction between the layers.

3.1. Selection of phenol-to-methanol molar ratio

In order to choose an optimum feed mix, the alkylation reaction on Mg–Al 4.0:1–CHT was carried out at 350°C using several phenol-to-methanol molar ratios.

Table 1
Composition, lattice parameters and specific surface area of the samples

Sample	Mg/Al atomic ratio [a]	Lattice parameters (Å)		Surface area (m^2/g) [b]
		a	*c*	
Mg–Al 3.0:1	2.73	3.05 4	23.31 1	125
Mg–Al 4.0:1	3.72	3.06 9	23.57 9	176
Mg–Al 4.5:1	4.39	3.07 2	23.87 7	139
Mg–Al 5.0:1	4.89	3.09 4	23.94 7	150
Mg–Al 7.0:1	6.30	3.09 7	23.87 5	149
Mg–Al 10.0:1	8.47	3.08 4	23.85 1	124
Hydrotalcite [c]	–	3.10 2	23.40 4	–
MgO [d]	–	–	–	111
Al_2O_3 [e]	–	–	–	246
$MgO + Al_2O3$ (mix) [f]	–	–	–	122

[a] ICPES results.
[b] Specific surface area of samples calcined at 450°C/8 h.
[c] JCPDS No. 22-700.
[d] Obtained by calcining $Mg(OH)_2$ at 450°C/8 h.
[e] Obtained by calcining $Al(OH)_3$ at 450°C/8 h.
[f] Obtained by mixing d and e in the atomic ratio of 3.72:1.

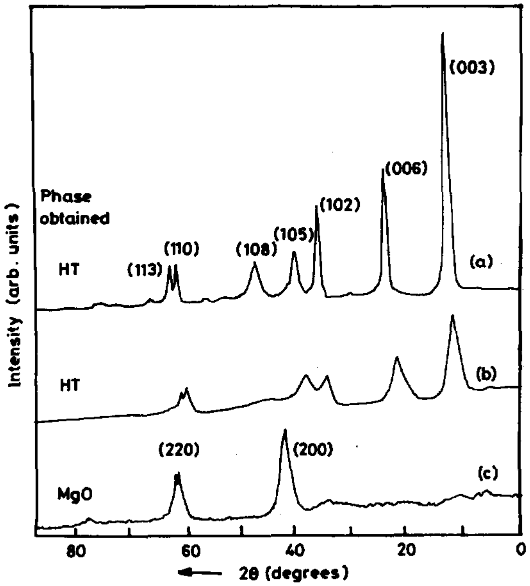


Fig. 1. X-ray powder diffraction patterns of (a) Mg–Al 4.0:1–HT, (b) Mg–Al 10.0:1–HT, (c) Mg–Al 4.0:1–CHT.

Phenol conversion and selectivities were plotted against phenol-to-methanol molar ratio (Fig. 2). As, phenol conversion and selectivities towards *o*-cresol and 2,6-xylenols were maximal at a phenol-to-methanol molar ratio of 1:7, this feed ratio was maintained throughout the study.

3.2. Phenol conversion with time-on-stream

The activity of all the catalysts studied at 350°C over a period of 5 h (WHSV: moles of phenol/h kg = 9.30 mol h^{-1} kg^{-1}) is shown in Fig. 3. The phenol conversion on samples with Mg/Al = 3, 4 and 4.5 remained constant throughout

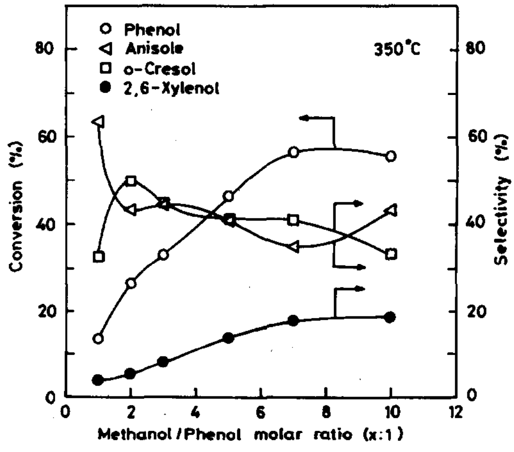


Fig. 2. Effect of molar ratio of reactants on phenol conversion for Mg–Al 4.0:1–CHT.

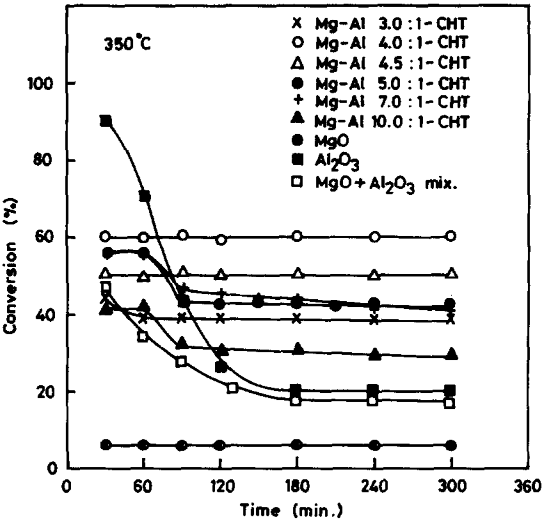


Fig. 3. Time-on-stream. WHSV = 9.3 mol h^{-1} kg^{-1}.

the study, while an initial deactivation was observed before the reaction reaches a steady state in the case of samples with Mg/Al = 5, 7 and 10. A similar deactivation was reported on metallic oxides [24] and basic $Ca_3(PO_4)_2$ [20] for the alkylation of phenol with methanol. Of the catalysts studied Mg–Al 4.0:1–CHT was the most active. This may be attributed to the large surface area of the sample (Table 1) which is in agreement with the results of Schaper et al. for the isomerisation of 1-pentene [7]. For comparison we have also carried out reactions on Al_2O_3 and MgO which have been obtained by calcination of $Al(OH)_3$ and $Mg(OH)_2$ at 450°C/8 h, respectively. To make proper comparisons, the preparation conditions employed for $Al(OH)_3$ and $Mg(OH)_2$ were similar to those used to form hydrotalcites. The results showed that, MgO had very low activity (phenol conversion = 5%) whereas Al_2O_3 showed very high initial activity, deactivated rapidly with time which may

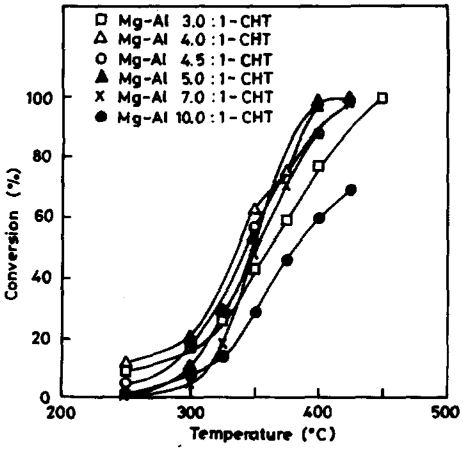


Fig. 4. Effect of temperature on phenol conversion. WHSV = 9.0 mol h^{-1} kg^{-1}.

Table 2
Effect of temperature on phenol conversion and product selectivity on Mg–Al 4.0:1–CHT
WHSV = 9.0 mol h^{-1} kg^{-1}

Temp. (°C)	Phenol conversion (%)	Product distribution (%)		
		Anisole	*o*-Cresol	2,6-Xylenol
250	11.7	100	–	–
300	20.4	94.6	5.4	–
325	27.8	59.7	25.2	11.5
350	62.6	15.8	41.7	40.3
375	75.2	12.0	31.6	50.5
400 [a]	99.0	7.8	20.3	52.7

[a] 2-Methylanisole (9.1%) and HMB (10.1%) also obtained.

be due to coking and then remained constant after 2 h (phenol conversion = 20%). The activity of the catalyst (Mg–Al 4.0:1–CHT) was also compared with that of physically mixed MgO–Al_2O_3 (Mg/Al = 3.72). The results showed that, the former was more active than the latter. The high activity of CHT can be accounted for by the dissolution of some of the aluminium ions in the MgO lattice creating Lewis acidic sites [29] as evidenced from XRD. The d_{200} values of Mg–Al 4.0:1–CHT decreased from 2.106 Å (for MgO, JCPDS No. 4-829) to 2.094 Å owing to the difference in ionic radius of Mg^{2+} and Al^{3+}. In the case of MgO and physically mixed MgO–Al_2O_3, the d_{200} values were similar to that of the JCPDS (2.105 and 2.103 Å, respectively). Furthermore, a synergetic interaction exists between the metal oxides obtained by thermal calcination of precursor [30] with high surface area and porosity leading to the formation of active sites controlling the reaction which is absent in the case of physically mixed oxides.

3.3. *Effect of temperature*

The alkylation reactions were carried out in the temperature range 250–450°C. The effect of temperature on phenol conversion is shown in Fig. 4 which shows

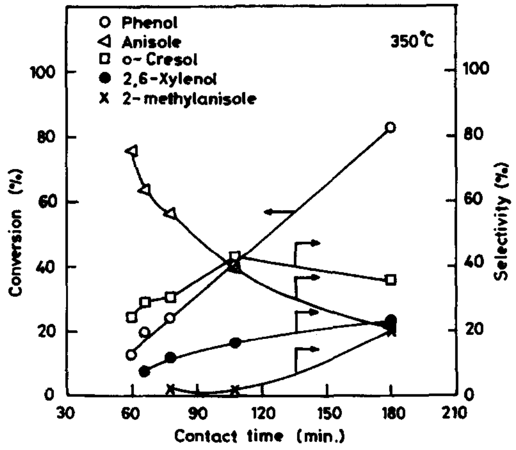


Fig. 5. Effect of contact time on conversion/selectivity for Mg–Al 4.5:1–CHT.

Table 3
Activity and product distribution on Mg-Al 4.0:1–CHT employing anisole as unique reagent
WHSV = 31.9 mol h^{-1} kg^{-1}

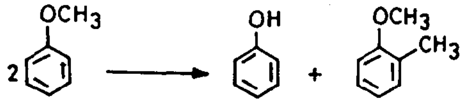
Temp. (°C)	Anisole conversion (%)	Product distribution (%)			
		Phenol	2-Methyl anisole	*o*-Cresol	2,6-Xylenol
250	6.8	30.9	57.3	11.8	–
350	60.3	43.1	18.2	26.4	13.0
400	22.7	43.6	30.4	19.8	6.2
350[a]	71.5	47.7	11.2	27.1	14.0

[a] WHSV = 13.5 mol h^{-1} kg^{-1}

that, Mg–Al 4.0:1–CHT attained 100% phenol conversion at 400°C, while others attained 100% conversion at 450°C. Only about 70% conversion was achieved on Mg–Al 10.0:1–CHT at 425°C. A trace amount of HMB was obtained on Mg/Al = 4, 4.5 and 5 above 400°C. The effect of temperature on product selectivity is shown in Table 2. At low temperatures (250°C) only anisole was formed by the primary alkylation reaction (O-alkylation). At high temperatures *o*-cresol and 2,6-xylenol were also formed by both primary and secondary reaction (C-alkylation). This is because the activation energy of O-alkylation is lower than that of C-alkylation [16].

3.4. Effect of contact time

The effect of contact time on product selectivity (Fig. 5) showed that, at low contact times, anisole was the main product. As the contact time increased, the anisole selectivity decreased and 2-methylanisole and 2,6-xylenol increased. This meant that, anisole is to a large extent responsible for the formation of *o*-cresol, 2-methylanisole and 2,6-xylenol. In order to confirm this hypothesis, the reaction of anisole and an 1:7 mixture of anisole and methanol were carried out. When anisole alone was used as reagent a large amount of phenol was obtained at all temperatures (Table 3 and Table 4). This showed that the bimolecular reaction, in which anisole served as its own alkylating agent (Eq. 1)



... (1)

was predominant as opposed to the monomolecular rearrangement (Eq. 2)

... (2)

The increase in the phenol/2-methylanisole ratio at higher temperatures could be due to the rapid further reaction of 2-methylanisole to give *o*-cresol and 2,6-xylenol [18].

Table 4
Activity and product distribution on Mg–Al 7.0:1–CHT employing anisole as unique reagent
WHSV = 31.9 mol h^{-1} kg^{-1}

Temp. (°C)	Anisole conversion (%)	Product distribution (%) [a]			
		Phenol	2-Methyl anisole	*o*-Cresol	2,6-Xylenol
300	11.5	32.2	47.8	–	5.2
350	35.1	43.3	23.1	22.2	10.5
400	31.5	50.8	19.0	19.7	10.5
350 [b]	40.1	42.1	24.2	22.7	10.5

[a] Some unidentified product also obtained.
[b] WHSV = 13.5 mol h^{-1} kg^{-1}.

When an 1:7 anisole-to-methanol mixture was passed through the catalyst at 300°C, 2-methylanisole was the main product. (Table 5) When the temperature or contact time was increased, the selectivity of 2-methylanisole decreased and gave 2,6-xylenol as the main product. This supported the above statement that, 2-methylanisole rapidly reacts to give 2,6-xylenol.

3.5. Acid–base property and catalytic activity

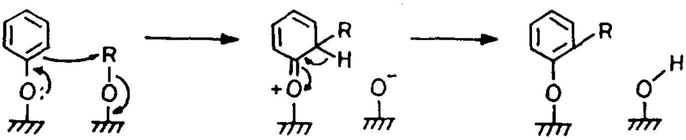
In our alkylation experiments, we observed that the reaction proceeded predominantly through anisole as the intermediate. It has been reported in the literature that acidic catalysts such as SiO_2–Al_2O_3 or condensed phosphoric acid promote the reactions giving phenyl ethers while basic catalysts such as MgO or ZnO–Fe_2O_3 promote the direct alkylation giving *o*-cresol without passing through the phenyl ethers as an intermediate [20]. On the other hand Balsama et al. [14] and Rao et al. [13] have reported that strongly acidic catalysts promote ring alkylation. We do not have strong evidence as to whether the alkylation reaction over CHT is due to base catalysis or acid catalysis. In order to check this, we tried to determine the basicity of the calcined samples by a titration technique as described previously

Table 5
Activity and product distribution obtained on Mg–Al 4.0:1–CHT employing anisole:methanol (1:7) mixture
WHSV = 8.5 mol h^{-1} kg^{-1}

Temp. °C	Anisole conversion (%)	Product distribution (%)			
		2-Methyl anisole	4-Methyl anisole	*o*-Cresol	2,6-Xylenol
300	3.8	100	–	–	–
350	34.6	18.8	–	24.8	56.4
400 [a]	45.6	7.9	12.9	14.5	64.7
350 [b]	53.7	11.0	2.0	16.2	70.8

[a] Trace amount of HMB was obtained.
[b] WHSV = 3.9 mol h^{-1} kg^{-1}.

[7]. The basicity range (pK_a) of Al_2O_3 is 7.1–15 while it is 15–26.5 for MgO. The basicity of CHT is also in the range 15–26.5. From ^{27}Al-NMR and XPS results, McKenzie et al. [31] have reported that in CHT, the surface aluminium is in a local oxide environment that does not favour acid catalysed reactions that typically occur over pure alumina. Moreover, most of the catalytic reactions reported over CHT including aldol condensation, H–D exchange reactions, and isomerisation of alkenes, are base catalysed reactions [5,7,8]. On the other hand Cheng and Lin [29] have reported that, Lewis acidic sites are introduced in with the incorporation of aluminium. Therefore, the determination of acidic and basic site density and correlation with activity and selectivity of the catalyst will be the subject of further investigation. From the results obtained, the reaction pathway of methylation over CHT which may be due to the combined acid–base property of the catalyst can be depicted as in the following scheme:



The *ortho*-selectivity of the catalysts (formation of *o*-cresol, 2,6-xylenol and 2-methylanisole but not *meta*- or *para*-cresols or 4-methylanisole) can be attributed to the nature of adsorption of phenol on these catalysts. As described by Tanabe [23] the phenolate ion is adsorbed on these catalysts such that the *ortho*-position is very near to the catalyst surface, hence only the *ortho*-position can be methylated.

A closer look at the variation of product selectivity with x (Al/Al+Mg) indicated that sample with $x=0.1$ (Mg/Al=10) was more selective for O-alkylation while $x=0.2$ (Mg/Al=4) for C-alkylation (Fig. 6) The reason for this observation is unanswered. One possible reason could be the difference in the acidity and basicity of the samples.

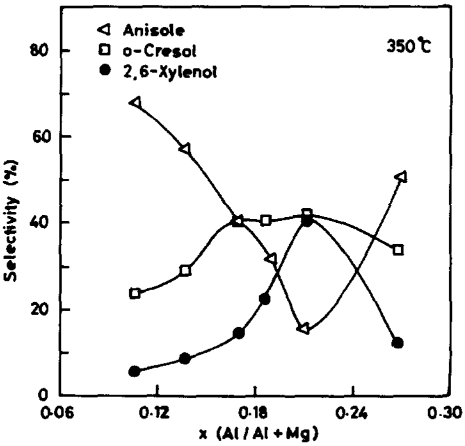


Fig. 6. Variation of product selecivity with x. WHSV $=9.0$ mol h^{-1} kg^{-1}.

Based on the experimental results, the following are the important characteristics of the calcined hydrotalcites:

(1) CHT does not undergo deactivation significantly with time-on-stream while alumina and zeolite does [16,18].

(2) When methanol alone is passed on these catalysts, no evolution of gas is observed, so the gasification of methanol which is a side reaction on many of the zeolites and some oxide catalysts [15,24] is absent on CHT.

(3) Calcined hydrotalcite is more active compared to MgO and/or Al_2O_3 for the alkylation of phenol with methanol.

4. Conclusions

In the alkylation of phenol with methanol, MgO/Al_2O_3 mixed oxides obtained by thermal calcination of HT precursors at 450°C/8 h are more active compared to magnesia or γ-alumina. The alkylation reaction over CHT proceeded through anisole formation. Mg–Al 10.0:1–CHT was found to be more selective for anisole formation while Mg–Al 4.0:1–CHT was found to be more selective for 2,6-xylenol formation. A participation of combined acidic and basic sites in calcined hydrotalcite for the alkylation reaction has been suggested.

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