ALKYLATION OF PHENOL AND *m*-CRESOL OVER ZEOLITES

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The alkylation of phenols and phenol derivatives such as *m*-cresol are important reactions in a sequence of syntheses for the production of many important fine chemicals. Specifically it is of great importance to develop catalysts and processes, which are able to selectively produce one or other particular isomer or derivative. This paper presents results of an investigation into the alkylation of phenol and *m*-cresol, respectively, using methanol in the former case and propene in the latter. The catalysts of choice were H-ZSM-5 and H-MCM-22. In the case of phenol methylation it was found that controlling diffusivity by increasing crystal size was most conducive to the formation of *p*-cresol. H-MCM-22 showed a high selectivity to *p*-cresol. In the case of *m*-cresol propylation the selectivity over H-ZSM-5 to thymol was greater than 90% at conversions of around 50%, and 80% at conversions of around 85%. This high selectivity to thymol was considerably greater than reported in previous papers. In both systems mild reaction temperature and pressure conditions were desirable so as to minimize the formation of oligomeric products of methanol (*via* dimethyl ether) and propene, which could cause deactivation of the zeolite.

Keywords: Electrophilic aromatic substitutions; Alkylation; H-ZSM-5; H-MCM-22; Thymol; Cresol; Phenols; Zeolites; Heterogeneous catalysis.

Phenol and its various derivatives are important industrial base and fine chemicals with a wide range of industrial applications ranging from use as antiseptics, disinfectants, perfume additives, preserving agents, herbicides, *etc.*, as well as being used more widely in the manufacture of engineering plastics. Some of the main compounds of interest are phenol itself, its derivative cresols (methylphenols) obtained by the methylation of phenol, and thymol (2-isopropyl-5-methylphenol) obtained by the propylation of *m*-cresol. In the methylation of phenol it is highly desirable to promote the selective formation of individual cresol isomers and usually to minimize the formation of anisole. In a mixture of anisole, *p*-cresol and *o*-cresol it is possible to separate the individual products by distillation because their

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boiling points, *viz*. 155, 201.9 and 191 °C are sufficiently dissimilar. However, *m*-cresol with a boiling point of 202.2 °C is difficult to separate from *p*-cresol. Hence a process in which only *p*-, *o*-cresol and anisole are formed is desirable.

An important second derivative of phenol alkylation is thymol. Natural thymol is extracted from the oil of thyme and mint. It has antiseptic properties and antimicrobial activity on bacteria involved in upper respiratory tract infections[1]. It is also an important intermediate used in the synthesis of perfumes and hydrogenation of thymol leads to menthol, a component of fragrances with a peppermint odour. Thymol is currently prepared industrially using the Bayer process by the liquid phase propylation of *m*-cresol at 350–365 °C and 5 MPa over activated alumina[2].

It is clear from the molecular structure of both *p*-cresol and thymol that it is possible that shape-selective zeolites may be ideal acid catalysts for the synthesis of both these products since they are both the slimmest of the various possible isomers of each family and therefore may be favoured through product-shape selectivity.

Phenol Alkylation with Methanol

Cresols can be formed *via* the alkylation of phenol with methanol. Typical catalysts used for the alkylation of phenols are H_2SO_4, BF_3, MgO, Al_2O_3 and SiO_2-supported Fe/V (refs[3,4]). The methyl group can alkylate in two ways on the phenol; first, on the side chain OH group (*O*-alkylation) and second, on the benzene ring (*C*-alkylation). *C*-Alkylation leads to the formation of cresol isomers and *O*-alkylation to the formation of anisole. Anisole in turn can react with itself or with methanol to form methylanisoles. Cresols can also be formed *via* a secondary reaction of anisole with phenol or *via* internal rearrangement of anisole. Cresols can react further with methanol to form xylenols or methylanisoles. Phenol itself can undergo self-condensation to produce diphenyl ether which, it is worth noting, if subsequently methylated in the 4 position can lead *via* subsequent cleavage of the *O*-phenyl bond to the formation of *p*-cresol and phenol. Preliminary studies of this route by the authors will be briefly referred to in the results section of this paper. Methanol of course is well known to convert readily to dimethyl ether particularly over acidic zeolite catalysts such as H-ZSM-5 and dimethyl ether can as well be considered to be a reactant in the case of H-ZSM-5. Similar propositions have been made in the case of the alkylation of, for example, toluene with methanol[5] or of olefins with methanol[6].

With respect to cresols, thermodynamically *m*-cresol is the dominant of the three cresol isomers. Stull *et al.*[7] have reported the equilibrium ratios of *p*- to *o*-cresol in the temperature range 200 to 350 °C to be in the range of 0.25–0.3 (ref.[7]). However, recently Imbert *et al.*[8] have reported that the equilibrium *p*-:*o*-cresol ratio is higher and for example have reported a value of 0.43 at 350 °C. The authors are in agreement with these latter values.

Zeolites are well known to have shape-selective properties, which enable the thermodynamic limitations to be superseded. In the present context the voluminous literature on toluene alkylation with methanol is relevant[5]. Thus it would be reasonable to expect that in the methylation of phenol the use of shape-selective zeolites may promote the formation of *p*-cresol, the slimmest of the cresol isomers and therefore the most easily capable of diffusing from the porous structure of the shape-selective zeolite. Anisole, however, will also probably diffuse relatively easily out of these zeolites.

The *O*-:*C*-alkylation ratios obtained in the methylation of phenol over various catalysts is of interest. Landau *et al.*[9] have shown in studies using H-Y, H-ZSM-5, H-Beta and H-Mordenite, carried out at 180 °C, that these ratios were 2.3, 2.7, 2.1 and 1.3, respectively. For H-Y, Garcia *et al.*[10] and Marczewski *et al.*[11] observed ratios of 3 and 3.2 at 200 °C. Marczewski *et al.*[11] also found higher ratios than Landau *et al.*[9] for H-Mordenite (2.3) and H-ZSM-5 (9.0). Santacesaria *et al.*[12] observed *O*-:*C*-alkylation ratios at 200 °C over amorphous silica-alumina, γ-alumina, Nafion-H and phosphoric acid of 2, 5, 9 and 9, respectively. It is clear that if the results of the zeolites are compared with those of the amorphous acid catalysts, the zeolites generally appear to favour ring as opposed to side chain alkylation (although the ratio of *O*-:*C*-alkylation is still greater than 1). The reports on the activity of H-ZSM-5, however, give contradictory results.

The formation of *p*-cresol and the ratio of *p*-:*o*-cresol are of particular interest in the present study. There are many reports on the methylation of phenol over a range of zeolite catalysts such as H-USY, H-ZSM-5, H-Beta and H-Mordenite[9–15]. In an analysis by one of the authors[16] of 47 different reports on the use of zeolites for phenol methylation, the experimentally observed ratio of *p*- to *o*-cresol in the temperature range 180 to about 300 °C was generally in the region of 0.5 which should be compared with the thermodynamically expected equilibrium ratio of around 0.43 and the statistically expected ratio of 0.5, based on the probability of the electrophilic attack taking place at either of two ortho-sites as opposed to only one para-site. However, *o*-cresol can also form as a secondary product *via* intramolecular rearrangement of anisole or, more likely, as a product of the reaction of anisole with phenol.

In the case of H-USY, in particular, some studies have investigated the use of partially alkali-exchanged samples[15,17]. In all cases of H/alkali-USY, however, notwithstanding the quoted high selectivity to *p*-cresol the lifetimes are very short and yields are very low. The *p*- to *o*-cresol ratios observed are not a strong function of the phenol conversion.

Although *m*-cresol is the most favoured isomer thermodynamically, it is not kinetically favoured in terms of the electrophilic attack of the aromatic ring, the OH-group of the phenol being very strongly ortho- and para-directing in electrophilic aromatic substitution. It is worth noting in the present context that the ortho- and para-directing effect is in the order $CH_3 < OCH_3 < OH$. Kinetically therefore *o*- and *p*-cresol will dominate over *m*-cresol in the methylation of phenol and this is indeed what is observed experimentally.

With respect to the relative formation of cresols and anisole, thermodynamically, cresol formation is almost entirely favoured over anisole. This is because the C–C bond in the case of cresols is more stable than the O–C anisole bond. However, anisole is the kinetically preferred product under mild reaction conditions.

Previous studies have indicated that an increase in reaction temperature increases the phenol conversion and results in a reduction of the anisole:cresol ratio possibly due to the system moving towards the thermodynamic equilibrium concentrations[9,12,14]. Moreover, the activation energy of cresols formation is twice that of anisole formation[11] and, therefore, an increase in temperature will also increase the rate of formation of cresols, much more than that of anisole. An increase in reaction temperature also results in a greater degree of formation of *m*-cresol and a decrease in the *p*-:*o*-cresol ratio.

Increasing the methanol-to-phenol ratio caused a slight increase in the *p*-:*o*-cresol ratio while at the same time results in an increase in the ratio of anisole to cresols, *i.e.*, lower methanol:phenol ratios increased the selectivity to cresols[9]. Increasing the reaction pressure also resulted in an increase in the ratio of anisole to cresols[18].

Since the primary objective of this study was the formation of *p*-cresol, it was proposed that there may be greater benefit in using a ten membered ring zeolite. Jacobs *et al.*[19] studied the use of H-ZSM-22 and H-Ferrierite for the conversion of anisole but did not observe any particular increase in the formation of *p*-cresol compared with H-ZSM-5. They concluded that the reaction occurred dominantly on the external surface of the zeolite crystallites. In the present study, it was nevertheless proposed that the use of

H-MCM-22 may promote the formation of *p*-cresol, this zeolite having its unique dual twelve- and ten-membered ring structure.

m-Cresol Alkylation with Propene

As mentioned above, thymol (2-isopropyl-5-methylphenol) is currently prepared industrially using the Bayer process[2]. In the gas phase, supported metal sulfates[20], wide- and medium-pore zeolites[21], and γ-Al_2O_3 (refs[20,22]) have all been reported as suitable catalysts for propylation of *m*-cresol using propene. Isopropyl alcohol can also be used as an alkylating agent as shown over Mg-Al-hydrotalcites[23] and Zn-aluminate[1].

Of the two alkyl substituents present, the isopropyl group is much more reactive than the methyl group so that isomerisation of the latter is insignificant. This is because intermediates and transition states for the shift of a methyl group involve comparably unfavourable methyl carbenium ions or related structures. The selectivity towards thymol is rather high, as thymol is the kinetically preferred isomer in this reaction. The major by-products are 3-isopropyl-5-methylphenol and 4-isopropyl-5-methylphenol, where the isopropyl group is in different position. In addition, the 2-isopropyl-3-methylphenol isomer is sterically hindered so that it does not form in substantial amounts.

The aim of the present paper is to present selected results from a recent comprehensive study of the methylation of phenol[16] and the propene propylation of *m*-cresol. The paper focuses on the activity and selectivity of zeolite H-ZSM-5 and, in the case of phenol methylation, zeolite H-MCM-22, over a range of reaction conditions. The main purpose of this work was to investigate the extent to which these zeolites are able, *via* product shape selectivity, to promote the production of the most readily diffusible isomers, *viz*. *p*-cresol and thymol.

EXPERIMENTAL

In the case of the alkylation of phenol with methanol, the zeolites used were H-MCM-22 and H-ZSM-5. The Si/Al ratios were between 10–30 for the former and 45–90 for the latter. Amorphous silica-alumina (Si/Al = 6, BET = 508m^2/g) used as a benchmark example of a non-shape-selective acid catalyst. H-MCM-22 has a pore structure that consists of two independent channel systems[24]. The first, a two-dimensional channel system consists of supercages defined by twelve-membered rings having a diameter of 7.1 Å and a length of 18.2 Å. These supercages are interconnected through ten-membered ring openings with dimensions of 4.0 x 5.4 Å forming a two-dimensional channel system. The second channel is a two-dimensional sinusoidal channel defined by ten-membered rings (4.0 × 5.9 Å). Both channel systems extend in the same two dimensions but there is no direct access between these two systems. The external surface of H-MCM-22 has twelve-membered ring pockets, which have a depth of 7.1 Å made up by half supercages. H-ZSM-5 has a three-dimensional pore structure consisting of two interconnecting ten-membered ring channels, one of which is sinusoidal (5.3 × 5.6 Å) and the other straight (5.1 × 5.5 Å).

Four samples of H-MCM-22 were synthesized by the authors in their own laboratories (UCT sample) as well as by one of the authors[16] in the laboratory of Prof. R. Lobo at the University of Delaware (DE samples). The crystal diameters observed from electron micrographs were variously 0.2 μm (UCT), 0.8 μm (DE-1) and 1 μm (DE-2 and DE-3). The morphology was observed to be platelet in nature with the channel systems extending in the direction of the platelet diameter.

Prior to use all catalysts were calcined at 500 °C in a synthetic air mixture (79 vol.% pure nitrogen mixed with 21 vol.% pure oxygen) for 2 h. In the case of the methylation of phenol, experiments were carried out in the gas phase and temperatures between 250 and 400 °C. The feed mixture, of equimolar amounts of methanol and phenol, unless otherwise stated, was pumped *via* an evaporator to a fixed-bed plug flow reactor. Nitrogen was added as the diluent gas. The feed partial pressure was 20 kPa, total pressure 100 kPa and $\text{WHSV}_{\text{total reactants}}$ 14 h^{-1}. The products were cooled after leaving the reactor and liquid samples were analysed on-line using a Chrompack CP Cresols capillary column. For determining mass and ring balances, toluene was used as an internal standard in the reactor system.

In the case of *m*-cresol propylation the zeolites used were H-ZSM-5 and H-Beta. The Si/Al ratios were 45 and 110 for H-ZSM-5 and 75 for H-Beta. H-Beta has a three-dimensional pore structure consisting of three interconnecting twelve-membered ring channels, perpendicular to each other. Two of the channels are linear (6.6 × 6.7 Å). The third channel is non-linear (5.6 × 5.6 Å).

H-ZSM-5 was used in extruded form and H-Beta as crystal powder. Prior to use the catalysts were calcined under nitrogen at 250 °C. Gaseous propene was fed *via* a thermal mass flow controller. The liquid *m*-cresol was fed *via* a HPLC pump to an evaporator where it was mixed with the gaseous propene. The mixture was fed to a fixed-bed plug flow reactor. The products were condensed after leaving the reactor, and liquid samples were taken. The total reaction pressure was usually maintained at atmospheric pressure but in some instances varied up to 400 kPa. The reaction temperature was usually held at 250 °C but also varied between 180 and 350 °C. The WHSV (*m*-cresol) was generally held at 1 h^{-1} but varied in some cases between 0.21–1.44 h^{-1}. The propene:cresol molar ratio was held at 1 but varied in some cases. Product samples were analyzed by capillary gas chromatography using a Stabilwax DA column.

Ammonia TPD experiments were carried out with a view to determining the temperature at which the maximum desorption occurred, this being indicative of the relative strength of the acid sites. In these experiments the ammonia, which was fed as a 4% NH_3 in He mixture, was adsorbed on 0.25 g sample of the catalyst at 150 °C. The sample was then flushed at that same temperature in flowing helium for 8 h before ramping began. The temperature was ramped at 10 °C/min from 150 to 600 °C.

RESULTS AND DISCUSSION

Phenol Alkylation with Methanol

The system was deliberately run at differential conversions throughout in order to ensure that it was possible to compare the performance of catalysts. The catalysts initially deactivated rapidly over the first two hours and then reached essentially a steady state with respect to phenol conversion. Table I shows the quasi-steady state phenol conversion, *O*-:*C*-alkylation ratio and *p*-:*o*-cresol ratio over H-MCM-22, H-ZSM-5 and amorphous silica-alumina, at 300 °C. In terms of phenol conversion, H-ZSM-5 was the most active catalyst studied. Although this zeolite had a relatively low Al content, it is unlikely that this difference in conversion was due to differences in strength of acid sites. The temperature at which the maximum desorption peak occurred in ammonia TPD experiments was used as an estimate of acid site strength. In the case of H-ZSM-5 this occurred at 372 °C and for H-MCM-22 at 282 °C. No correlation was observed between these temperatures and either the *O*-:*C*-alkylation ratio or the *p*-:*o*-cresol ratio. However, it has been suggested that weaker acidity favours *O*-alkylation[10] and there are slight indications here to support this proposal as the amorphous silica-alumina catalyst showed a slightly greater degree of *O*-alkylation. All the catalysts showed very similar product distributions with anisole and cresol isomers dominant. Small amounts (<4% selectivity) of secondary products, *viz*. methylanisoles and xylenols, were present. The zeolites showed slightly enhanced selectivity to *p*-cresol compared to silica-alumina. In the latter case there are Lewis acid sites and the highest incidence of *o*-cresol (Table I) is consistent with this, given the reports in the

TABLE I
Phenol methylation over H-ZSM-5, H-MCM-22 and amorphous silica-alumina (gas phase, 300 °C, 20 kPa feed partial pressure, $W/F = 0.07\ g_{cat}\ h/g_{feed}$)

Catalyst	Phenol conversion %	*O*-:*C*-Alkylation ratio	*p*-:*o*-Cresol	*m*-Cresol
H-ZSM-5	10.2	1.7	0.55	4.2
H-MCM-22	3.8	1.7	0.50	5.8
SiO_2-Al_2O_3	2.5	1.8	0.37	3.1

literature of the relationship between Lewis acidity and preferential *o*-cresol formation[12]. As shown in Table I the *m*-cresol content was always less than 5% of the cresol fraction.

Although thermodynamic equilibrium calculations predict that at 300 °C the products should be almost entirely cresols, at this temperature the *O*-:*C*-alkylation ratio was approximately 1.7 over all the catalysts studied. At this temperature, the *p*-:*o*-cresol ratio was about 0.5, only slightly higher than the expected equilibrium value of about 0.43 and almost identical to the statistically expected value. These product distributions indicate that the reaction appears to be kinetically or diffusion-controlled and not thermodynamically controlled under the reaction conditions used. Calculations were made of apparent activation energies. The values were in the region of 50 kJ/mol, which is indicative of a diffusion-controlled situation.

In order to shed light on the reaction pathways followed in the methylation of phenol, a study was made of the reactions over H-MCM-22 at 300 °C of each of the major products formed during phenol methylation, *viz*. anisole, *o*-cresol, *p*-cresol and *m*-cresol. These results are shown in Tables II and III. Anisole formed mainly methylanisoles, phenol and cresols. These results are similar to those observed by Jacobs *et al.*[19]. This is due to a methyl transfer mechanism, which initially forms phenol and methylanisoles. Further methyl transfer then occurs from anisole to the phenol product to form cresols and more phenol. This is confirmed in the reaction where an equi-

TABLE II

Phenol methylation major products converted over H-MCM-22 (gas phase, 300 °C, 20 kPa feed partial pressure, $W/F = 0.07\ g_{cat}\ h/g_{feed}$)

Reactants	Conversion %	Selectivity of products formed, mole %				
		anisole	cresols	methylanisoles	xylenols	phenol
Phenol + methanol	3.8	60.4	37.4	1.2	1.0	–
Anisole	6.5	–	19.2	37.8	2.1	40.9
Anisole:phenol (1:1 molar ratio)	3.7[a]	–	68.7	12.7	1.6	17.0
o-Cresol	3.9	0.2	68.0	0.0	15.9	15.9
p-Cresol	7.3	0.7	88.2	0.0	5.7	5.4
m-Cresol	3.6	0.0	97.7	0.0	1.2	1.1

[a] Conversion of anisole.

molar amount of phenol was co-fed with the anisole. The conversion of anisole decreased as expected from its reduced partial pressure. Cresols were the major product. The decrease in the amount of *o*-cresol was almost quantitatively equivalent to the increase in *p*-cresol. This implies that, in the absence of phenol, monomolecular methyl rearrangement occurs producing *o*-cresol from anisole. In the presence of phenol as reactant, however, a bimolecular transfer from the anisole to the phenol para-position is now possible. Each cresol isomer was converted over H-MCM-22. In the case of *o*-cresol and *p*-cresol, *m*-cresol was the major product as expected. Since in the methylation of phenol over all the catalysts studied, only a small amount of methylanisoles, xylenols (<4% selectivity) and *m*-cresol (<5% of the cresols fraction) were formed, it can be deduced that secondary reactions of anisole and the cresols occur only to a small extent at 300 °C.

The effect of temperature on the product distribution from phenol methylation over H-MCM-22 was investigated in the range 250–400 °C. Consistent with previous findings[14] increasing the temperature caused the *O*-:*C*-alkylation ratio to decrease from 1.89 (250 °C) to 0.73 (400 °C). The *p*-:*o*-cresol ratio decreased from 0.54 (250 °C) to 0.41 (400 °C). Increasing the reaction temperature also increased the formation of *m*-cresol from 4 to 16% in the cresol fraction. Since the cresols distribution at 300 °C is hardly influenced by conversion and extrapolation to zero conversion still shows some *m*-cresol, these observations indicate that at higher temperatures the primary formation of *m*-cresol is enhanced.

TABLE III
Cresol distribution formed when converting the phenol methylation major products over H-MCM-22 (gas phase, 300 °C, 20 kPa feed partial pressure, $W/F = 0.07\ g_{cat}\ h/g_{feed}$)

Reactants	Cresol distribution, %		
	o-cresol	*p*-cresol	*m*-cresol
Phenol + methanol	61.9	32.3	5.8
Anisole	69	11	20
Anisole:phenol (1:1 molar ratio)	53	28	19
o-Cresol	–	15	85
p-Cresol	9	–	91
m-Cresol	26	74	–
Thermodynamic equilibrium[8]	37	16	47

As mentioned above, the apparent activation energies indicated that diffusion may be the controlling mechanism. This was observed to be the case even when the crystallite size of H-MCM-22 was as small as that of the H-ZSM-5 sample, *viz.* 0.2 μm. It would thus be expected that this effect would be even greater in the case of the other H-MCM-22 samples which had crystallite sizes in the range 0.8–1 μm, thus having a much longer diffusional path length. It was thus decided to investigate in greater depth the effect of the crystallite size of the zeolites studied on the *p*-:*o*-cresol ratio. The H-ZSM-5 sample and four samples of H-MCM-22 were selected as described in Experimental, *viz*. UCT, DE-1, -2, -3. As it is well known, the effect of diffusion on shape selectivity is most appropriately typified by the use of the Thiele modulus, ϕ. For example, for an *n*-th order reaction:

$$\phi = \xi L\sqrt{}[(n + 1)k\, C_{\mathrm{A}}^{n-1}]/[2D_{\mathrm{eff}}] ,$$

where ξ is geometric factor for the particular morphology, *L* is characteristic length of the particle, *k* is rate constant, *n* is overall reaction order of the irreversible reaction, C_{A} is exit concentration and D_{eff} is effective diffusivity.

For a platelet H-MCM-22 crystal with its channels extending in the direction of the platelet diameter, the effective geometry is that of a cylinder and therefore the radius *R* of the platelets is taken as the characteristic length. In the present study the shapes and geometric factors for each catalyst are given in Table IV.

For a differentially operating plug flow reactor and irrespective of the reaction order, the mass balance equation becomes:

$$X = k \cdot \text{constant} ,$$

TABLE IV
Shapes and geometric factors for H-MCM-22 and H-ZSM-5 catalysts

Catalyst	Shape	Geometric factor ξ	Characteristic length
H-MCM-22	cylinder	0.5	radius of platelets
H-ZSM-5	sphere	0.33	radius of sphere

where X is conversion. Thus the Thiele modulus and a modified Thiele modulus can be expressed as follows:

$$\phi/(1/D_{\text{eff}})^{0.5} = (\text{constant}')\ \xi\ L\ X^{0.5}$$

$$\phi_{\text{mod}}/(1/D_{\text{eff}})^{0.5} = \xi\ L\ X^{0.5}\ .$$

Figure 1 shows the relationship between the *p*-:*o*-cresol ratios obtained and a modified Thiele modulus, *viz*. for DE and UCT samples of H-MCM-22 and one sample of H-ZSM-5 which had a crystallite size of 0.2 μm. It is clear that the *p*-:*o*-cresol ratio is a strong function of crystal size. From this figure it becomes clear that arguably the most dominant variable influencing the *p*-:*o*-cresol ratio is the diffusional path length and that it is possible to increase this ratio by using larger crystallite sizes. At crystal sizes of H-MCM-22 up to about 0.8 μm it was not possible to observe this effect. It is worth noting that previous studies have focused generally on the role of the strength

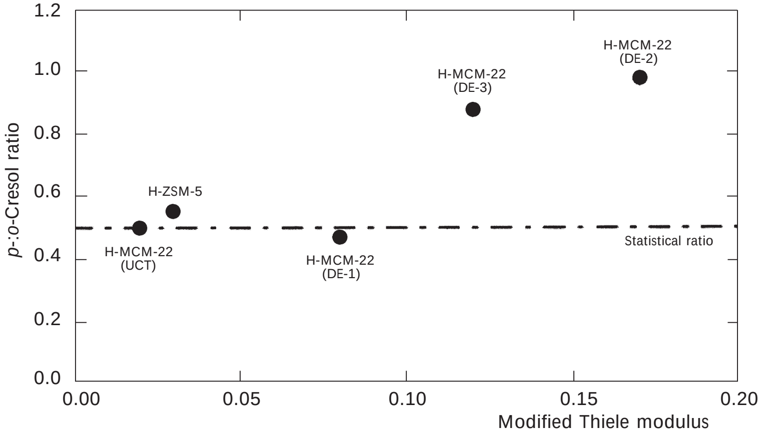

FIG. 1

The relationship between *p*-:*o*-cresol ratio and a modified Thiele modulus $\phi_{\text{mod}}/(1/D_{\text{eff}})^{0.5} = \xi\ RX^{0.5}$ (assumed rate constant k can be approximated by conversion X for differential operation; assumed characteristic length is radius of crystallites, R). Shapes and radii R (in μm) of crystallites were as follows: H-ZSM-5 (spheres) 0.2, H-MCM-22 (UCT) (platelets) 0.2, H-MCM-22 (DE-1) (platelets) 0.8, H-MCM-22 (DE-2) (platelets) 1.0, H-MCM-22 (DE-3) (platelets) 1.0

and nature of acid sites in explaining the *p*-:*o*-cresol ratios but the importance of the crystallite size has been largely ignored.

Finally mention should be made here of preliminary experiments carried out to synthesize selectively the ether 4-phenoxytoluene. These molecules are obtained by methylating diphenyl ether in the 4 position. Recent preliminary investigations carried out in the authors' laboratory have shown that zeolite Mordenite is capable of rather selectively producing 4-phenoxytoluene at high selectivity compared to either of its other isomers, *viz*. 3- or 2-phenoxytoluene. Subsequent cleavage of the phenoxy bond will then lead to highly selective formation of *p*-cresol and phenol. The results of this investigation will be published shortly.

m-Cresol Alkylation with Propene

In the present study of the alkylation of *m*-cresol with propene, the catalysts were zeolites H-ZSM-5 and H-Beta, both having similar, high Si/Al ratios of 110 and 75, respectively. Figure 2 shows how the selectivity to thymol over H-ZSM-5 varies as a function of conversion for various times-on-stream. This figure represents the case for a sample with a low Si/Al ratio. The conversion increased initially for the first three hours and then decreased slowly from 55 to 20% over 50 h. Steady state was attained after about 100 h. At the same time the selectivity to thymol increases steadily to about 90% over the same time-on-stream. Initially there are indications

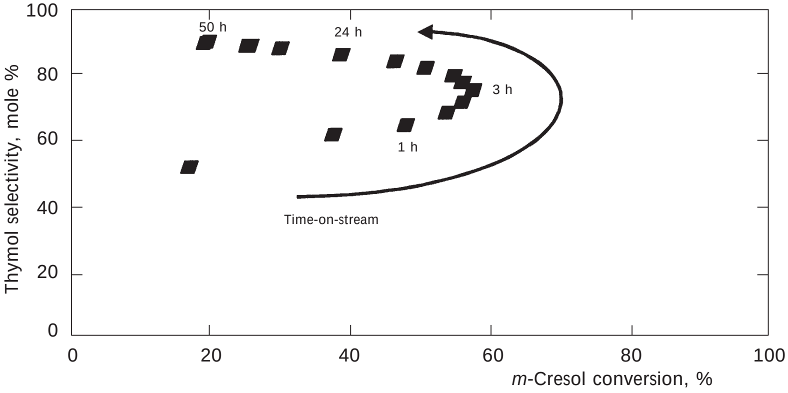

FIG. 2
Typical course of selectivity to thymol as a function of conversion for various times-on-stream (H-ZSM-5, Si/Al = 45, 250 °C, 100 kPa, WHSV$_{m\text{-cresol}}$ = 1 h^{-1}, propene:*m*-cresol molar ratio = 1)

from the product spectrum that considerable propene oligomerization is occurring, which probably results in the formation of soft coke and consequent deactivation. This is indicated by a multiplicity of peaks in the low carbon number range at the beginning of the chromatogram of the products typical of a propene oligomerization spectrum.

Figures 3 and 4 show the results of an extensive set of experiments in which the effects of varying reaction temperature, space velocity and

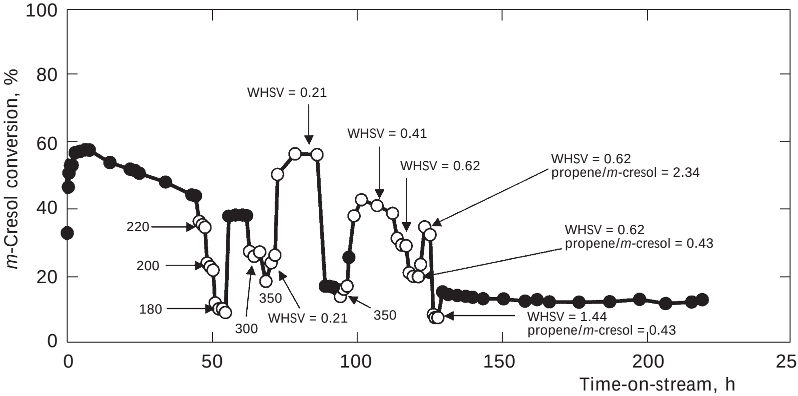

FIG. 3

Conversion of *m*-cresol with propene over H-ZSM-5 (Si/Al = 110) as a function of time-on-stream for different $\text{WHSV}_{m\text{-cresol}}$ (0.21, 0.41, 0.62, 1.44 h^{-1}), reaction temperatures (180, 200, 220, 250, 300 and 350 °C) and propene:*m*-cresol molar ratios (0.43, 1, 2.34). Reaction pressure 100 kPa. Black symbols: standard conditions (250 °C, WHSV = 1, propene:*m*-cresol molar ratio = 1)

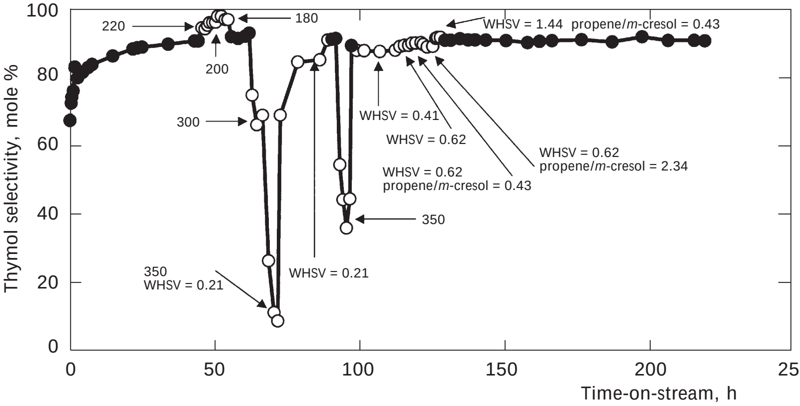

FIG. 4

Selectivity to thymol as a function of time-on-stream over H-ZSM-5 (conditions as for Fig. 3). Black symbols: standard conditions (as for Fig. 3) propene:*m*-cresol ratio on conversion and thymol selectivity over H-ZSM-5 were investigated. Measurements made at non-steady state conditions were found to be comparable and, as shown in Fig. 6, for example, selectivities did not change significantly with conversion. Not surprisingly conversion is seen to decrease with reaction temperature during the first 50 h. Thereafter conversion increased as temperature increased but the deactivation of the first period on stream was not fully overcome. The original conversion was recovered when the temperature increased to 350 °C and the space velocity was reduced fivefold. However it is clear that it was ultimately not possible to recover this original concersion by changing temperature or space velocity or phenol:*m*-cresol feed ratios. A steady-state conversion was reached after 150 h on stream. Figure 4 shows importantly that at this steady state condition the selectivity to thymol also attained a steady state of about 90% which was not significantly different to that observed in the first 50 h on stream. Figure 5 shows that there were two optima with respect to reaction temperature when all the other conditions are equal. One at a reaction temperature in the region of 200 °C which corresponds to maximum selectivity to thymol and the other at a reaction temperature of about 250 °C which indicates maximum conversion. At higher reaction temperature, conversion declines again due to equilibrium limitations. In the temperature range 180–250 °C, however, the selectivity to thymol was again not significantly altered when conversion decreased.

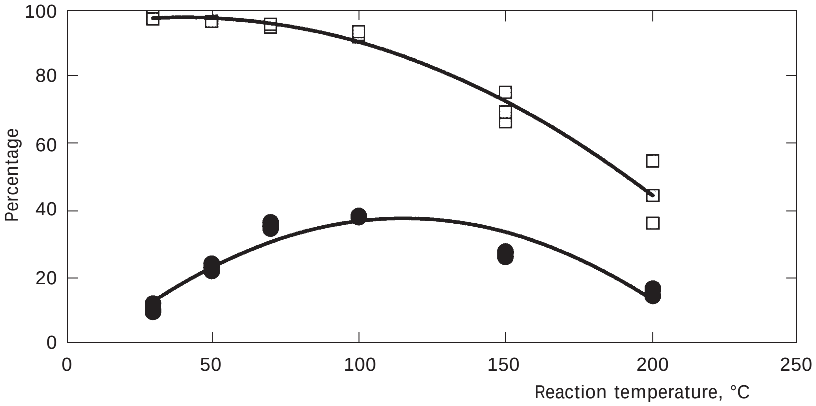

FIG. 5

Variation in *m*-cresol conversion and selectivity to thymol at different reaction temperatures over H-ZSM-5 (Si/Al = 110, $\text{WHSV}_{m\text{-cresol}} = 1\ \text{h}^{-1}$, propene:*m*-cresol molar ratio = 1, reaction pressure 100 kPa). □ Thymol selectivity, ● *m*-cresol conversion

Figure 6 shows the thymol selectivity as a function of *m*-cresol conversion over H-ZSM-5 (Si/Al = 110) at 200, 250 and 250 °C. Conversion was varied by varying space velocity, reaction pressure and propene:*m*-cresol ratio. The following conclusions can be drawn:

– Conversion has a significant influence on selectivity, which declines with increasing conversion.

– Reaction temperature has a strong influence on selectivity, which declines with increasing temperature at a given conversion.

– Reaction temperature is the only parameter having direct influence on selectivity.

– The influence of all other reaction parameters (space velocity, reaction pressure, feed ratio) is essentially of indirect nature, *i.e. via* conversion.

The equilibrium distribution of the three major thymol isomers were obtained by isomerizing binary mixtures of thymol and the thymol isomers over H-ZSM-5. At 250 °C the distribution was found to be 20% thymol, 75% 3-isopropyl-5-methylphenol and 5% 4-isopropyl-5-methylphenol. It should be noted that 6-isopropyl-5-methylphenol hardly forms due to severe steric constraints. With sufficiently increased space time, each and every starting mixture reached the same point of isomer distribution, which only contained *ca* 20% thymol in the total thymol isomers fraction. This is another indication of the kinetic control of the thymol synthesis from propene and *m*-cresol on H-ZSM-5.

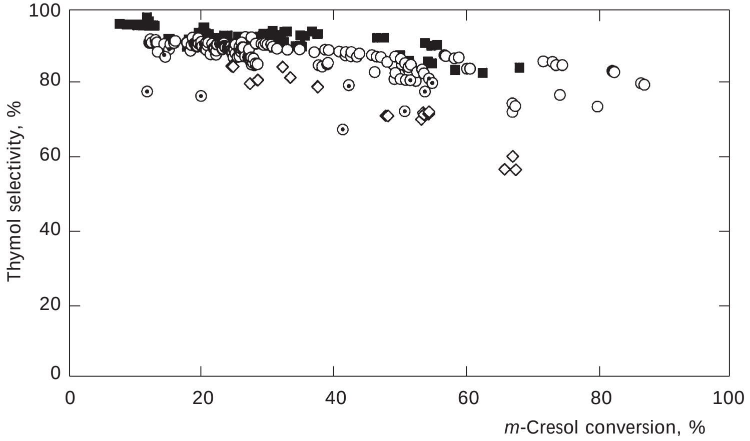

FIG. 6

Thymol selectivity as a function of *m*-cresol conversion over H-ZSM-5 (Si/Al = 110) at 200 (■), 250 (○) and 250 (◇) °C. Conditions additionally varied at the different temperatures were space velocity, reaction pressure and propene:*m*-cresol molar ratio. Initial samples, <4 h on (⊙)

Figure 7 shows the variation in thymol selectivity as a function of *m*-cresol conversion over H-ZSM-5 (Si/Al = 110) and H-Beta (Si/Al = 75) at 250 °C and 100 kPa and, in the case of H-ZSM-5, at different space velocities and propene:*m*-cresol ratios. Compared to Fig. 6, where selectivity *versus* conversion is shown for H-ZSM-5 at the same reaction temperature, two major differences attract attention, *viz*. a lower thymol selectivity at zero conversion (extrapolated) of less than 90% over H-Beta compared to almost 95% over H-ZSM-5 and a steeper decline of selectivity with increasing conversion over H-Beta (full data points). Apparently, the more shape-selective one of the two different zeolites used, H-ZSM-5, promotes the formation of the slimmer isomer beyond chemical kinetics, being in its primary product (higher zero conversion selectivity) or in its secondary product (higher selectivity at high conversion). The latter indicates that shape-selective properties play a role inhibiting secondary isomerization.

Table V shows selected results obtained in the present study. It should be noted that the selectivity to thymol was always in excess of 75%. Small amounts of the 3-isopropyl-5-methylphenol and 4-isopropyl-5-methylphenol isomers form in approximately equal amounts, which account for most of the rest of the total product. It is also useful to compare the above results with those published to date using a variety of catalysts. These are briefly summarized in Table VI.

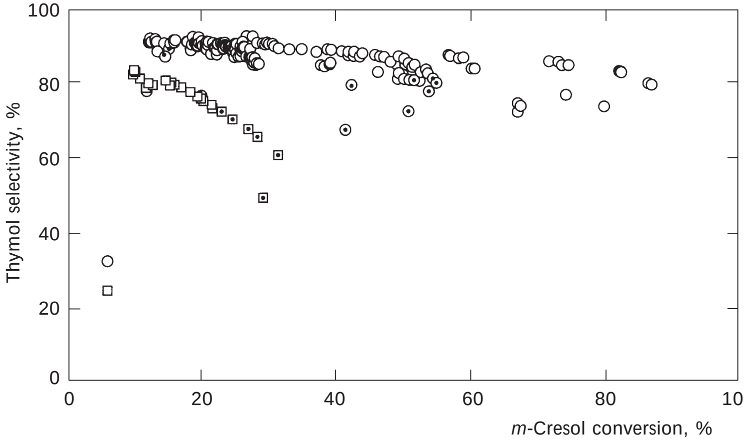

FIG. 7

Thymol selectivity as a function of *m*-cresol conversion over H-ZSM-5 (Si/Al = 110, ○) and H-Beta (Si/Al = 75, □) at 250 °C and 100 kPa (also different space velocities and propene:*m*-cresol molar ratios over H-ZSM-5). Initial samples, <4 h on (⊙ and ⊡)

As can be seen from the results above, the use of H-ZSM-5 is conducive to the formation of high yields of thymol and especially to minimize the formation of oligomeric and polyisopropylated or polyaromatic compounds. This will not only facilitate the separation of the desirable thymol but also result in a less rapid deactivation of the catalyst. As can be seen from Tables V and VI, H-ZSM-5 allows operation at much milder temperature and lower pressure conditions than the present commercially used γ-Al_2O_3 catalyst, which is highly desirable.

TABLE V
Summary of results in the reaction of *m*-cresol with propene using H-ZSM-5

Conversion %	Temperature °C	Pressure kPa	WHSV h^{-1}	Propene:cresol molar ratio	Thymol selectivity mole %	Thymol yield mole %
55	200	400	0.4	1	90	49.5
80	250	100	0.2	1	75	60
85	250	400	1.0	8	80	68

TABLE VI
Summary of some key findings on the formation of thymol from the alkylation of *m*-cresol using propene over various catalysts

Reference	Catalyst	*m*-Cresol conversion %	Temperature °C	WHSV h^{-1}	Propene:*m*-cresol molar ratio	Thymol selectivity %
Fiege[2]	activated alumina	75	350–365[a]	0.25	0.7	80
Biedermann *et al.*[21]	γ-Al_2O_3	75	360[a]	0.25	0.83	75
Nitta *et al.*[19]	γ-Al_2O_3	63	250	*ca* 0.15	1	80
Grabowska *et al.*[1,b]	Zn-aluminate	78	155	0.5	5	70
Wimmer *et al.*[20]	H-ZSM-5	34	250	3.5	1	75

[a] 5 MPa reaction pressure. [b] Isopropanol feed.

CONCLUSIONS

This paper has reported on the use of zeolites for two important alkylation reactions of a similar type, *viz*. the methylation of phenol and the propylation of *m*-cresol. In both of these reactions the role of the OH group is important since it can influence the position of electrophilic attack by virtue of its strong ortho- and para-directing influence. In the case of phenol methylation, two parallel primary reactions take place, *viz*. side chain alkylation to form anisole and ring alkylation to form cresols. The dominant product at low temperature is the anisole. Cresols, however, can also be formed *via* secondary reactions of anisole with phenol or anisole with itself, the latter reaction occurring, however, half as fast as the reaction of anisole with phenol[16]. One of the main objectives was to investigate the extent to which shape-selective zeolites, H-ZSM-5 and H-MCM-22, would be able to promote the formation of *p*-cresol. In that regard the ratio of *p*- to *o*-cresol was closely monitored. It was shown that the crystallite size of the zeolites was most influential in increasing the *p*-:*o*-cresol ratio. A modified Thiele modulus was used to illustrate this effect quantitatively.

In a manner analogous to the case of methylation of phenol, the alkylation of *m*-cresol is essentially influenced by the presence of the phenolic OH group in terms of structure directing properties. However, this reaction differs in two important respects. The presence of the methyl group meta to the OH group will constrain the possibility of alkylation in the ortho-position between the OH group and the CH_3 group. In this case the isomers most likely to form are the 2-isopropyl-5-methylphenol and 4-isopropyl-5-methylphenol. It was observed that the selectivity to the slimmer 2-isomer, *viz*. thymol, was dominant and this is probably due to the fact that it is already strongly favoured from the point of view of chemical kinetics. The shape-selective properties of the catalyst appear to play the role of increasing its primary selectivity as well as inhibiting the possibility of isomerization of thymol in secondary reactions.

Finally, in both reaction systems, side reactions promoted by the acid catalyst play a role. In the case of the methylation of phenol, methanol converts readily to dimethyl ether, which in turn is able to undergo conversion to olefins and high-boiling-point oligomers thus resulting in the formation of "soft" coke in the pore system. This was indicated by the deactivation, which occurred at high reaction temperatures. Similarly, propene in the latter reaction can oligomerize and this was again indicated by the deactivation at higher reaction temperatures. In both cases higher reaction temperatures also resulted in less formation of the slim molecule, *viz*. lower *p*-:*o*-cresol ratios and less thymol in the thymol isomers fraction.

Selectivity to the slim isomer decreased moderately with increasing conversion. Increasing the space time, the reaction pressure or the concentration of the alkylating reactant resulted commonly in an increase in the conversion of the phenol and *m*-cresol, respectively, but with no or very little direct effect on the selectivity. Conversion and reaction temperature appear to be the only parameters influencing selectivity over a given catalyst.

In summary it has been shown that zeolites such as H-ZSM-5 and H-MCM-22 are good catalysts for the alkylation of phenol molecules. A major advantage is that much milder conditions can be applied than in the current technical processes. However, it appears that the structure-directing role of the OH group already plays a greater role in the selectivity to various products but the shape-selectivity property of the zeolites contributes particularly in the case of large zeolite crystals or more bulky product molecules, both of which promote transport control, *i.e.* product shape selectivity. Moreover, the relative sorptive properties of the reactants will also play a role in this regard.

The expected reaction mechanism is an Eley–Rideal mechanism where, in the case of phenol alkylation, methanol is preferentially the adsorbed species. The structure-directing property of the OH group will then favour alkylation in the ortho-position. In the case of the thymol synthesis, propene will be the preferentially adsorbed species and, due to the geometric constraint of the CH_3 group, the preferential attack by propene will not take place at the ortho-position on the ring, which is adjacent to the methyl group but at the opposite position resulting in the very high selectivity to thymol.

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REFERENCES

1. Grabowska H., Mista W., Trawczynski J., Wrzyszcz J., Zawadzki M.: *Appl. Catal., A* **2001**, *220*, 207.
2. Fiege H.: *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., Vol. 25, p. 619. Wiley–VCH, Weinheim 2003.
3. Fiege H.: *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., Vol. 25, p. 631. Wiley–VCH, Weinheim 2003.
4. Beck J. S., Haag W. O. in: *Handbook of Heterogeneous Catalysis* (G. Ertl, H. Knözinger and J. Weitkamp, Eds), Vol. 5, p. 2131. Wiley–VCH, Weinheim 1997.

5. Čejka J., Wichterlová B.: *Catal. Rev.* **2002**, *44*, 375.
6. Möller K. P., Böhringer W., Schnitzler A. E., O'Connor C. T. in: *Proc. 12th Int. Zeolite Conf., Baltimore, 1998* (M. M. J. Treacy, B. K. Marcus, M. E. Bischer and J. B. Higgins, Eds), p. 591. Materials Research Society, Warendale (PA) 1999.
7. Stull D. R., Westrum E. F., Jr., Sinke G. C.: *The Chemical Thermodynamics of Organic Compounds*. Wiley, New York 1969.
8. Imbert F. E., Guisnet M., Gnep S.: *J. Catal.* **2000**, *195*, 279.
9. Landau M. V., Kogan S. B., Tavor D., Herskowitz M., Koresh J. E.: *Catal. Today* **1997**, *36*, 497.
10. García L., Giannetto G., Goldwasser M. R., Guisnet M., Magnoux P.: *Catal. Lett.* **1996**, *37*, 121.
11. Marczewski M., Perot G., Guisnet M.: *Stud. Surf. Sci. Catal.* **1998**, *41*, 273.
12. Santacesaria E., Grasso D., Gelosa D., Carra S.: *Appl. Catal.* **1990**, *64*, 83.
13. Venuto P. B.: *Microporous Mater.* **1994**, *2*, 297.
14. Parton R. F., Jacobs J. M., Huybrechts D. R., Jacobs P. A.: *Stud. Surf. Sci. Catal.* **1989**, *46*, 163.
15. Parton R. F., Jacobs J. M., van Ooteghem H., Jacobs P. A.: *Stud. Surf. Sci. Catal.* **1989**, *46*, 211.
16. Moon G.: *Ph.D. Thesis*. University of Cape Town, Cape Town 2003.
17. Namba S., Yashima T., Itaba Y., Hara N.: *Stud. Surf. Sci. Catal.* **1980**, *5*, 105.
18. Pierantozzi R., Nordquist A. F.: *Appl. Catal.* **1986**, *21*, 263.
19. Jacobs J. M., Parton R. F., Boden A. M., Jacobs P. A.: *Stud. Surf. Sci. Catal.* **1988**, *41*, 221.
20. Nitta M., Aomura K., Yamaguchi K.: *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2360.
21. Wimmer P., Buysch H.-J., Puppe L.: U.S. 5,030,770 (1991).
22. Biedermann W., Köller H., Wedemeyer K.: U.S. 4,086,283 (1978).
23. Nitta M., Yamaguchi K., Aomura K.: *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2897.
24. Lawton S. L., Leonowicz M. E., Partridge R. D., Chu P., Rubin M. K.: *Microporous Mater.* **1998**, *23*, 109.