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An investigation into factors which influence the formation of *p*-cresol in the methanol alkylation of phenol over MCM-22 and ZSM-5

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Abstract

In the methanol alkylation of phenol, the primary products are anisole and cresol. Secondary reactions mainly result from further reactions of anisole. In the present study, it was observed that *p*-cresol formed preferentially, i.e. greater than the thermodynamically expected amount, over H-MCM-22, especially in the case of catalysts where the crystallite sizes were greater than approximately 1 μm. It is thus proposed that in the case of MCM-22 the 10MR pores in the layers allow easy diffusion of *p*-cresol and that the effect of this phenomenon is enhanced when the crystallite sizes are relatively large. Many similar observations have been made in the case of the methylation of toluene. Steaming of H-MCM-22 also produces the enhanced diffusional resistance due to the presence of the extra-framework Al species. Further investigations in which the internal acid sites were inertized supported the above observations.

Keywords: Phenol alkylation; *p*-Cresol; MCM-22; ZSM-5

1. Introduction

para-Cresol is an important intermediate in the formation of antioxidants and preservatives for plastics, motor oil and foods [1]. *p*-Cresol can be formed in 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 [1–3]. In this reaction, the methyl group can alkylate in two ways on the phenol; first, on the oxygen, which is know as O-alkylation, which produces anisole, and second, on the benzene ring, known as C-alkylation, which produces cresol isomers, as shown in Fig. 1. Under mild conditions, the primary products of this reaction are anisole, *o*-cresol and *p*-cresol. *m*-Cresol is the thermodynamically favoured cresol isomer but is not kinetically favoured by electrophilic substitution as the hydroxyl group on the phenol is strongly *ortho*- and *para*-directing [4]. Possible secondary products are xylenols (dimethylphenols) and methylanisoles.

It is possible to produce a high selectivity to *o*-cresol by phenol methylation over basic catalysts such as MgO or amphoteric catalysts such as alumina [2,5,6]. It is also possible to produce *p*-cresol with high selectivity from toluene hydroxylation [1]. However, this is environmentally unfriendly due to the huge co-product yield of inorganic salts (sodium sulphites). Highly selective synthesis of *m*-cresol and *p*-cresol, respectively, is desirable due to the high cost of separating these isomers but no successful process, other than toluene hydroxylation, has yet been developed [7]. On the other hand, a mixture of *o*- and *p*-cresol without *m*-cresol can easily be separated by distillation. Various zeolites have been studied for this reaction. These include H-Y [7–10], H-ZSM-5 [7,11–13], H-mordenite [6] and H-beta [14]. However, these zeolites have shown poor *para*-selectivity with *p*:*o*-cresol ratios not exceeding 0.7. Partially alkali exchanged (H/K-Y and H/Na-Y) zeolites were found to produce a *p*:*o*-cresol ratio >1 [7] but their lifetime was

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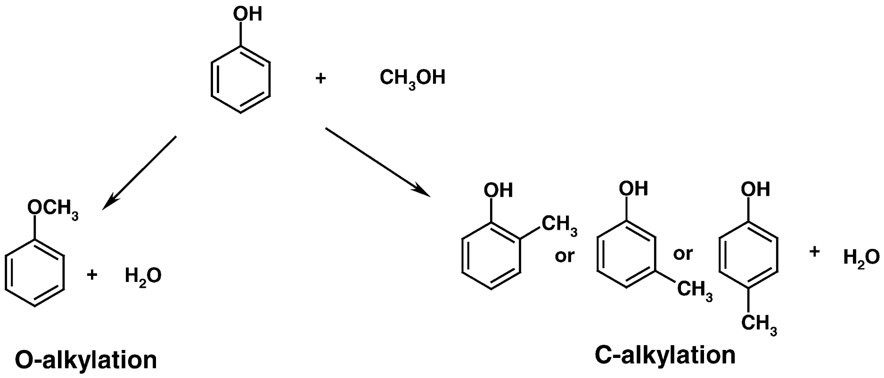

Fig. 1. Alkylation of phenol with methanol.

irrelevantly short with respect to an economically viable process.

It is well known that shape-selective zeolites tend to promote the *para*-isomer as a result of their pore geometry. Therefore, zeolites MCM-22 and ZSM-5 were used in this study. Zeolite MCM-22 has a pore structure that consists of two independent channel systems [15]. The first, a two-dimensional channel system, consists of supercages defined by 12-membered rings having a diameter of 7.1 Å and a length of 18.2 Å. These supercages are interconnected through 10-membered ring openings with dimensions of 4.0 × 5.5 Å. The second channel is a two-dimensional system of interconnected sinusoidal channels defined by 10-membered rings (4.1 Å × 5.1 Å). Both channel systems extend in the same direction, but there is no direct access between these two channel systems. Diffusion in the direction perpendicular to the plane, the channel system extends in, is impossible. Zeolite ZSM-5 has a three-dimensional pore structure consisting of two perpendicular 10-membered ring channels, one of which is sinusoidal (5.3 Å × 5.6 Å) and the other straight (5.1 Å × 5.5 Å) [16]. Channels are interconnected in a way, which allows diffusion in the third dimension through constant change of channels.

This paper presents factors that influence the formation of *p*-cresol over zeolites H-ZSM-5 and H-MCM-22 in the phenol methylation reaction. The factors investigated are zeolite crystal size, steaming and selective sodium exchange of the internal acid sites of the zeolites.

2. Experimental

Catalytic experiments were carried out at 200 and 300 °C. Low-temperature (200 °C) experiments were carried out in a 600 ml batch reactor, in the liquid phase. The reactor was loaded with 200 g reactants (methanol and phenol, molar ratio of 1) and 5 g zeolite crystal powder. Liquid-phase reactions were run under autogeneous pressure of approximately 23 bar. The high-temperature experiments (300 °C) were carried out in the gas phase in an isothermal flow reactor loaded with 0.8 g zeolite crystallite powder diluted 1:9 by mass with sand. Further reaction conditions were: feed methanol and phenol, molar ratio of 1 and $W/F = 0.07\ g_{cat}\ h/g_{feed}$. Gas-phase reactions were run under atmospheric pressure with carrier gas N_2 and a feed partial pressure of 0.2 bar.

Analysis of the products from liquid-phase reactions was done by gas chromatography with a RH-1 capillary column. Analysis of the product from gas-phase reactions was done on-line by gas chromatography using a Chrompack CP Cresols capillary column. In both cases, toluene was added as an internal standard. Carbon balances of between 95 and 100% were obtained.

Four samples of H-MCM-22 were synthesized by the authors in their own laboratories as well as by one of the authors (G.M.) in the laboratory of Prof. R Lobo at the University of Delaware using the syntheses procedures as described in [17] and [18], respectively. The crystal diameters observed from electron micrographs were from 0.2 to 1 μm and Si/Al atomic ratios ranging from 11 to 29. The morphology was observed to be platelet in nature with the channel systems extending in the direction of the platelet diameter [15]. Commercial samples of H-ZSM-5 (crystal powder, Si/Al = 45, spherical morphology, average crystal diameter 0.2–0.3 μm) and amorphous silica–alumina (SiO_2–Al_2O_3, Si/Al = 8, BET = 508 m^2/g, particle size > 106 μm) were obtained from Süd-Chemie and Kali Chemie, respectively.

In order to further study the influence of the pore geometry of the zeolite on the cresol selectivity, the H-zeolites were selectively reverse ion-exchanged with sodium following a method described by Chester et al. [19]. In this way, only the external sites remained active and the internal sites were inertized with sodium.

In order to study the influence of extra-framework aluminium (EFAl), a sample of H-MCM-22 was steamed. The steaming was carried out in situ in the fixed-bed reactor at 500 °C for 8 h using a steam partial pressure of 0.31 bar with nitrogen as the carrier gas.

3. Results and discussion

In all experiments in this study phenol conversions were kept below 11% and hence the system operated differen-

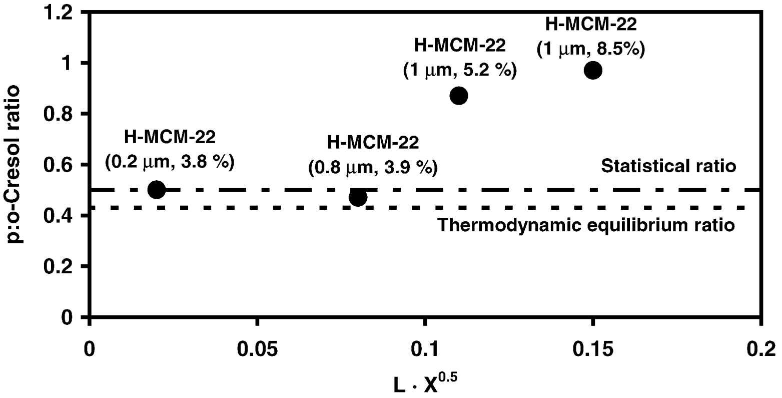

Fig. 2. The relationship between *p*:*o*-cresol ratio and a modified Thiele modulus $\phi_{\text{mod}} = LX^{0.5}$. Brackets indicate crystal platelet diameters (2*L*) and phenol conversion in the phenol methylation reaction (gas phase). Thermodynamic equilibrium ratio derived from data observed at 380 °C [24,25].

tially. This facilitated observing the formation of primary products. It was clearly observed, by using the results of the alkylation reactions and the reactions of the major individual product molecules, that anisole and cresols appear both as primary products, forming in a parallel manner [20,21,22].

It was found useful to analyse the results from phenol methylation in terms of a modified Thiele modulus in which the diffusional path length *L* depends on the directions that the pore system extends as well as the morphology of the zeolite crystals. MCM-22 has a two-dimensional non-interconnecting pore system and platelet morphology. Its pore system extends in the direction of the platelet diameter, which is 2*L*. The diffusivity, *D*, and the shape factor, ξ, were considered equal and constant with zeolite samples of the same type.

For a differentially operating plug flow reactor and irrespective of the reaction order, the mass balance equation for any reaction can be reduced to the following form:

$$k \propto X \tag{1}$$

where *k* is the rate constant and *X* the conversion. Thus a modified Thiele modulus (ϕ_{mod}) can be expressed as follows [23]:

$$\phi_{\text{mod}} = LX^{0.5} \tag{2}$$

with *L* and *X* being the only ‘‘variables’’ remaining and all other parameters being constant and included in the ϕ_{mod}.

Fig. 2 shows the relationship between the *p*:*o*-cresol ratio and the modified Thiele modulus, obtained over four samples of H-MCM-22. The samples had different crystal sizes and different Si/Al ratios and therefore different activities (indicated by conversion). Details are discussed in [23]. From this figure, it becomes clear that arguably the most dominant variable influencing the *p*:*o*-cresol ratio in phenol methylation over zeolite H-MCM-22 is the diffusional path length and activity. Therefore, it is for instance possible to increase the *p*:*o*-cresol ratio by using larger crystals or crystals with higher density of acid sites i.e. lower Si/Al ratio.

In order to confirm the shape-selective constraints, the pore system effects on the product from the internal sites these sites were selectivity poisoned with sodium. Confirmation of this was made via standard probe reactions, namely *n*-hexane cracking (to determine the overall activity) and 1,3,5-triisopropyl benzene (1,3,5-TIPB) cracking (to determine the external acid sites activity) [26]. As can be derived from Table 1, overall activity declined substantially compared to the only moderate decline of the activity of the external surface of the zeolite crystals.

Table 2 shows clearly that, in the case of MCM-22, in the absence of internal sites (H/Na-sample) the *p*:*o*-cresol ratio decreased substantially. This indicates that the internal sites produce *p*-cresol with preference. Poisoning the internal sites results in reduced conversion and correspondingly reduced yields of both *p*- and *o*-cresol (Table 2, middle column). Subtracting the yields obtained from the internally poisoned sample (H/Na-MCM-22) from the yields obtained from the parent sample (H-MCM-22) reveals the contribution of the internal sites to the formation of *p*- and *o*-cresol as given in the last column of Table 3. These *p*- and *o*-cresol

Table 1
Conversions (%) obtained from 1,3,5-TIPB cracking (external acid sites activity) and *n*-hexane cracking (overall activity) test reactions over the H-zeolites and the internally selectively sodium-exchanged H/Na zeolites

Zeolite	1,3,5 TIPB[a] cracking conversion (%)	Hexane[b] cracking conversion (%)
H-ZSM-5	37	79
H/Na-ZSM-5	24	15
H-MCM-22 (0.2 μm)	99	50
H/Na-MCM22 (0.2 μm)	99	29

[a] 1,3,5-TIPB cracking conditions: fixed-bed reactor, 270 °C, 1,3,5-TIPB partial pressure = 0.0016 bar, 0.6 h^{-1}, nitrogen carrier gas [27].

[b] *n*-Hexane cracking reaction conditions: fixed-bed reactor, 500 °C, *n*-hexane partial pressure = 0.04 bar, 1.6 h^{-1}, nitrogen carrier gas [24].

Table 2
Phenol conversion, cresol isomer yields and *p*:*o*-cresol ratio over acid and internally selectively sodium-exchanged MCM-22 (0.2 μm) (liquid phase)

	H-MCM-22	Internally sodium-exchanged H/Na-MCM-22	Calculated internal contribution (by difference: H − H/Na)
Phenol conversion (%)	5.7	2.3	3.4
Yield of cresols (mol%)	0.31	0.13	0.18
Yield of *p*-cresol (mol%)	0.17	0.05	0.12
Yield of *o*-cresol (mol%)	0.14	0.08	0.06
p:*o*-Cresol ratio	1.2	0.6	2.0

Table 3
Phenol conversion, cresol isomer yields and *p*:*o*-cresol ratio over acid and internally selectively sodium-exchanged ZSM-5 (0.2 μm) (liquid phase)

	H-ZSM-5	Internally sodium-exchanged H/Na-ZSM-5	Calculated internal contribution (by difference: H − H/Na)
Phenol conversion (%)	9.7	1.2	8.5
Yield of cresols (mol%)	2.08	0.23	1.85
Yield of *p*-cresol (mol%)	0.57	0.05	0.52
Yield of *o*-cresol (mol%)	1.50	0.18	1.32
p:*o*-Cresol ratio	0.4	0.3	0.4

Table 4
The effect of steaming of H-MCM-22 (0.8 μm) on activity and *p*:*o*-cresol ratios (gas phase)

	H-MCM-22	Steamed H-MCM-22
Phenol conversion (%)	3.9	11.1
p:*o*-Cresol ratio	0.47	0.53

yields from the internal sites were used to calculate the *p*:*o*-ratio of cresols produced internally. The result is a striking high *p*:*o*-cresol ratio (2.0) produced inside the pore system. It is concluded that this effect is due to internal mass transfer control, which favours the ‘‘slimmest’’ molecule, namely *p*-cresol. Table 3 shows that poisoning the internal sites produced only an insignificant effect in the case of ZSM-5, which sample was not shape-selective towards *p*-cresol anyway. Since the decrease in the *p*:*o*-cresol ratio was irrelevant in the case of H/Na-ZSM-5 but was much pronounced in the case of H/Na-MCM-22 this result is indicating that in zeolite MCM-22 it is indeed the internal pore geometry, i.e. the smaller pore size and only two-dimensional pore system, which strongly favours the formation of *p*-cresol. Note that this was observed to be the case even when the crystallite size of MCM-22 was the same as ZSM-5, viz. 0.2 μm. It can be derived from the isomer yields that the pore system of MCM-22 (0.2 μm) itself produces a *p*:*o*-cresol ratio of 2.0, which is not so of ZSM-5 of equal crystal size.

It may be noted that it is of course well known that increasing the basicity of a catalyst enhances the extent of side chain alkylation as opposed to ring alkylation. Although no measurements were made of the relative acidity of the sodium exchanged samples it should be noted that there was a small increase in the selectivity to anisole (O-alkylation product) over H/Na-MCM-22 to 81 mol% as opposed to 77.7 mol% for the H-MCM-22 sample. This could possibly be ascribed to the change in acidity/basicity of the catalyst.

Finally a sample of MCM-22 (0.8 μm) was steamed with a view to examining the effect of the extra-framework Al (EFAl) species so generated. Steaming resulted in a higher activity and a higher *p*:*o*-cresol ratio as shown in Table 4. It is known that mild steaming removes the aluminium from the framework and produces EFAl by a stepwise process with the removal of the aluminium proceeding bond by bond. This aluminium, which is partially bonded to the framework, is regarded as highly active and may explain the higher phenol conversions obtained over the steamed H-MCM-22. This has also been observed in hydrocarbon reactions over zeolites, namely isomerization [24–27], alkylation [28] and cracking [25,29]. The EFAl species formed in the steaming process [30], as is well known, usually migrate to the external surface of the crystallites [31]. These species will obstruct the narrow pores of MCM-22, thus increasing the diffusional resistance in the pores and thereby favouring the formation of the ‘‘slimmest’’ isomer, namely *p*-cresol. Both effects, increased activity and decreased effective diffusivity, contribute to an enhanced selectivity to *p*-cresol. Since the radial distribution of the active sites in the steamed crystals cannot be considered unchanged, comparison with unsteamed samples on the basis of Thiele modulus is not possible.

4. Conclusions

Over amorphous catalysts or wide pore zeolites, the cresol isomer distribution from phenol methylation is still governed by the *p*- and *o*-directing effect of the OH-group [4], i.e. a *p*:*o*-ratio of about 0.5 is obtained, corresponding to the prevalence of the positions (1:2) on the phenol ring [21].

Over zeolite H-MCM-22, the effect of pore geometry and its concomitant shape selectivity strongly influences selectivity to *p*-cresol when the zeolites are sufficiently active and the crystallite sizes are sufficiently large, resulting in modified Thiele moduli, $LX^{0.5} > 0.1$. In this case it is observed that *p*-cresol formation increases significantly. At modified Thiele modulus values <0.1, the *p*:*o*-cresol ratios are close to equilibrium and statistical ratio.

Selectively ion-exchanging the internal sites of H-MCM-22 with sodium proves that it is shape-selective internal mass transfer control, which favours the formation of the *p*-cresol. The observed effects are much more pronounced over

MCM-22 than over ZSM-5. This results in a higher *p*:*o*-cresol ratio over H-MCM-22 than over H-ZSM-5 even though they have the same crystal diameter (0.2 μm) and similar activity.

Steaming effects of the phenol conversion over H-MCM-22 due to the higher activity of the partially hydrolysed aluminium species. Steaming also formed extra-framework aluminium, which obstructs the narrow pores leading to increased diffusional resistances in the pores. Both effects promote the formation of the ‘‘slimmest’’ cresol isomer, namely *p*-cresol.

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