Ship-in-a-Bottle Synthesis of Methylphenols in HSAPO-34 Cages from Methanol and Air

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The conversion of methanol to olefins on the silico-aluminophosphate solid acid catalyst HSAPO-34 usually requires methylbenzenes that function as scaffolds (reaction centers) for carbon−carbon bond making and breaking steps. Here, we report the first high-yield synthesis of heteroatom-substituted methylbenzenes in HSAPO-34 cages. When we metered 20% air into the He carrier gas during methanol conversion at 350 °C the methylbenzenes initially formed were partially oxidized in the HSAPO-34 cages to methylphenols with very high selectivity. 100% N_2O was less effective than 20% air. Methylphenols proved to be substantially less active than methylbenzenes as reaction centers for methanol to olefin (MTO) catalysis on HSAPO-34. Even pentamethylphenol resisted the loss of methyl groups as olefin products, and phenols showed little carbon label scrambling into the ring during methanol conversion. Whereas 1:10 (mol:mol) toluene in methanol was very reactive on zeolite HZSM-5, 1:10 (mol:mol) *p*-cresol in methanol was no more reactive than pure methanol. We speculate that the MTO deactivating effect of oxygen substitution on methylbenzene rings is a consequence of the high gas-phase proton affinities of phenolic groups.

Introduction

The conversion of methanol to olefins or other hydrocarbons on microporous solid acids is an important problem that has generated much research.[1−3] The catalysts most likely to be commercialized are based on silico-aluminophosphates of the CHA topology, SAPO-34 or derivatives thereof.[4] Cages of ca. 1.0 by 0.7 nm interconnected by 8-ring windows ca. 0.38 nm in diameter are the essential features of the CHA topology. The eight-ring windows permit the diffusion of methanol, dimethyl ether, ethylene, propene, and linear C_4 hydrocarbons, but aromatic compounds, even benzene, are unable to pass from one cage to the next.

Drawing on earlier work by Mole and co-workers[5,6] and Kolboe et al.[7,8] we demonstrated that methylbenzene molecules formed in the cages of HSAPO-34 function as reaction centers on which carbon−carbon bonds are made and broken during methanol-to-olefin (MTO) chemistry.[9,10] Without suitable organic molecules in the cages, HSAPO-34 is not active in methanol conversion. Most olefin molecules exit the catalyst, but some remain behind forming additional aromatic species. As the catalyst ages, methylnaphthalenes also form in the cages of HSAPO-34, and these also show some activity as MTO reaction centers.[11] Further aging results in the accumulation of phenanthrene and pyrene in many of the cages, and the catalyst is thus deactivated.[12]

The mechanism by which methybenzenes decompose on HSAPO-34 to form olefinic products, primarily ethylene and propene, is presently unknown, but it may be related to the "paring reaction" described 40 years ago for the decomposition of hexamethylbenzene to form isobutane on a bifunctional catalyst in the presence of hydrogen.[13] The mechanism proposed for the paring reaction involves ring contraction (6 → 5) followed by expansion (5 → 6) that permits extension of an alkyl group that is eliminated as an olefin from a cationic intermediate. Ring expansion and contraction are likely to scramble ^{13}C labels between ring and methyl positions, and Kolboe has observed scrambling in MTO reactions on various catalysts.[14] Alternatively, side-chain methylation may also operate in this chemistry.[15]

We want to substitute various heteroatoms onto the methylbenzenes in HSAPO-34 cages and investigate their activity in MTO catalysis. As the first example, we report the selective synthesis of methylphenols in HSAPO-34 cages which we achieved using 20% air as an oxidant during an otherwise normal procedure in which methanol was flowed onto the catalyst at 350 °C in a He stream. Although the literature provides a number of examples of the conversion of benzene to phenol on aluminosilicate zeolites using N_2O as an oxidant,[16−20] we found that even 100% N_2O was less effective than 20% air (i.e., 4% O_2). We preferentially formed penta-, tetra-, tri-, and dimethylphenols in the HSAPO-34 cages. No hydroquinones, catechols, or other products with multiple oxygens were formed.

Methylphenols, unlike methybenzenes, prove to have very low activity for the formation of olefins in HSAPO-34. Even pentamethylphenol is stable to olefin elimination at 350 °C. Carbon isotope studies suggest that the limited conversion of methanol over an HSAPO-34 catalyst containing methylphenols occurs on the small amounts of methylbenzenes also present on such materials. Although methylphenols on HSAPO-34 exchanged carbon labels only in the methyl positions, tri-, tetra-, and pentamethylbenzene also scrambled carbon into the ring positions. We also found that co-feeding *p*-cresol with methanol into a catalyst bed of HZSM-5 resulted in no MTO rate enhancement whereas a significant enhancement was seen with toluene as a co-feed.[5,6] We interpret the low catalytic activity of phenols in terms of their high gas-phase proton affinities.

Experimental Section

Materials and Reagents. HSAPO-34 was prepared according to a patent procedure.[21] XRD showed a pure crystalline phase with the CHA structure. The product was calcined at 600 °C for 10 h to remove the template agent and pressed into 10−20

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mesh pellets. The Brønsted site concentration was determined to be 1.1 mmol/g. Methanol-^{13}C was obtained from Isotech, Inc. N_2O (99%) was from Aldrich. We also used zeolite HZSM-5 (Si/Al = 15) from Zeolyst International.

Catalysis. Experiments were performed using the pulse quench reactor described elsewhere.[22−24] Aliquots of methanol larger than 20 μL were delivered using a motor-driven syringe pump (Harvard Apparatus model PHD 2000), whereas smaller aliquots were delivered using in pulses using a switchable valve. For each experiment a bed consisting of 350 mg of catalyst was activated at 400 °C in the reactor under 600 sccm He flow for 2 h immediately prior to equilibration at 350 °C for use. To provide for the analysis of the organic compounds in HSAPO-34 samples following either synthesis or subsequent use in catalysis, the catalyst bed was thermally quenched then transferred to a nitrogen glovebox.

Gas Chromatography of Olefin Products. A Hewlett-Packard Model 6890 gas chromatograph with either a flame-ionization detector or a model 5973 mass-selective detector was used to analyze gases sampled from the reactor product streams using a Valco valve. The column was 150 m dh150 (Supelco) operated isothermally at 323 K.

NMR Spectroscopy. ^{13}C solid-state NMR experiments were performed with magic angle spinning (MAS) on a Varian Infinity plus 300 MHz spectrometer operating at 75.4 MHz for ^{13}C. Hexamethylbenzene (17.4 ppm) was used as an external ^{13}C chemical shift standard. Chemagnetics-style pencil probes were used. We measured spectra using cross polarization (CP, contact time = 2 ms, pulse delay = 1 s, 4000 transients) and cross polarization with interrupted decoupling (contact time = 2 ms, pulse delay = 1 s, 4000 transients, dipolar dephasing time of 50 μs).

Ex Situ Analysis of Organic Reaction Centers. Thermally quenched catalyst beds were subjected to acid digestion,[25] extraction, and GC-MS analysis to determine the distributions of entrained organic species and in some cases to identify carbon label scrambling. The entire catalyst bed was ground and then a 60 mg representative sample was treated with 2.0 mL of 1.0 M HCl to destroy the inorganic framework. Entrained organic matter was then extracted into 0.2 mL CCl_4 (Aldrich, 99.99%). 2 μL of this was then injected into a Hewlett-Packard Model 6890 gas chromatograph with a model 5973 mass-selective detector. The split ratio was 0.1:1. The column was a 50 m HP-1, the He gas flow was 0.3 mL per min, and the temperature program was 60 °C to 250 °C at a 4 °C/min ramp.

Results

Synthesis of Methylphenols in HSAPO-34. Figure 1 reports GC-MS total ion chromatograms that profile the organic compounds retrieved from various catalyst samples through acid digestion[25] followed by extraction. This procedure has previously been validated for aromatic hydrocarbons in HSAPO-34 using the alternative method of cryogenic grinding, which does not involve exposure to aqueous acid. The three results in Figure 1 were obtained using otherwise identical procedures except for the composition of the carrier gas. In each case, 100 μL of methanol was flowed onto 350 mg of catalyst at a rate of 50 μLmin^{-1} at a temperature of 350 °C. This temperature was maintained for an additional 5 min, then the catalyst temperature was quenched to ambient.

Figure 1a shows that methylbenzenes are formed selectively in HSAPO-34 when the carrier gas is 100% He. Using instead 100% N_2O (Figure 1b) we observed a modest conversion of the entrained aromatics to phenols, especially tri- and tetramethylphenols, and the yield of naphthalenes was also elevated. Figure 1c reports the result obtained using 20% air. Here, the overall yield of organics is reduced by a factor of ca. two, suggesting some total oxidation, and we do indeed detect (by GC) a small amount of CO_2 in the product stream. However, the predominant species in the HSAPO-34 cages are methylphenols with two to five methyl groups. We used this procedure for much of the work reported below. We also determined that methylphenols could not be extracted from HSAPO-34 without prior acid digestion to destroy the framework.

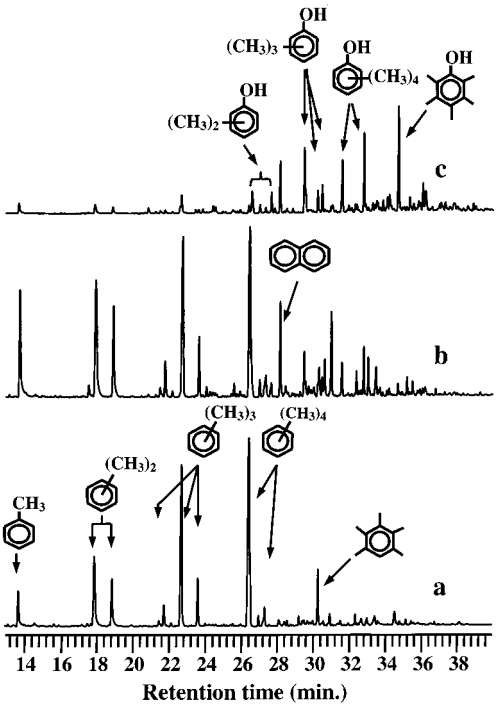

Figure 1. GC-MS total ion chromatograms from the ex situ analyses of aromatics formed from methanol in HSAPO-34 catalyst beds at 350 °C with various carrier gases. **(**a**)** Control experiment using 100% He (200 sccm) as the carrier gas. Methylbenzenes were formed preferentially in the HSAPO-34 cages. **(**b**)** Using 100% N_2O (50 sccm) as the carrier gas, there was a modest yield of methylphenols as well as some conversion to naphthalenes. **(**c**)** Using 20% air in He (250 sccm total) there was some reduction in total aromatics due to total oxidation, but the products remaining in the HSAPO-34 ages were primarily methylphenols.

We also used ^{13}C solid-state NMR to characterize the formation of methylphenols in HSAPO-34. Samples very similar to those in Figure 1a and 1c were prepared using methanol-^{13}C. Following thermal quench, the catalyst beds were transferred to magic-angle spinning rotors without exposure to air, and NMR spectra were measured at room temperature. Inspecting those spectra (Figure 2), one first notes that the degree of spectral overlap is such that ex situ analysis is clearly more informative than an in situ measurement in this case. Yet, even here, NMR provides complimentary information not found in the ex situ analysis. The prominent signals at 56 ppm in all spectra in Figure 2 are due to framework-bound methoxy (methoxonium) groups formed by O-methylation of conjugate base sites on the framework of HSAPO-34.[9] These species, plausible intermediates in ring methylation, are necessarily hydrolyzed by acid digestion, and the liberated methanol is partitioned into the aqueous acid rather than CCl_4. The cross polarization spectrum in Figure 2a reveals intensity near 150 ppm, and this signal is slightly clearer in the spectrum obtained with interrupted decoupling (Figure 2b). This signal is not

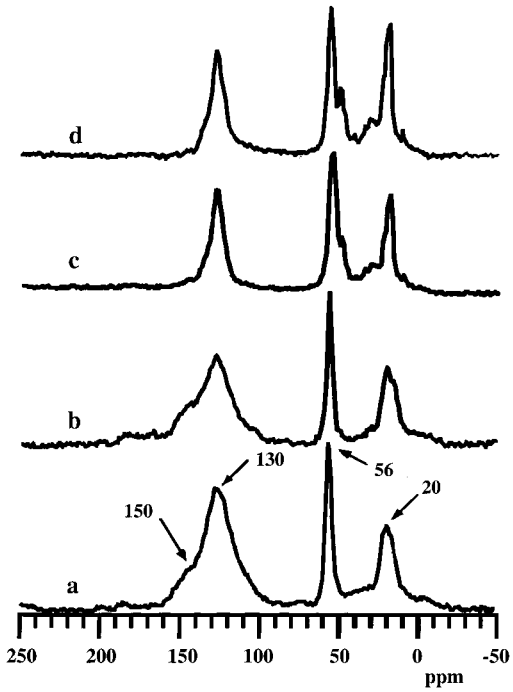

Figure 2. 75 MHz ^{13}C CP/MAS NMR spectra of aromatic products formed in HSAPO-34 from methanol-^{13}C at 350 °C. The signal at 56 ppm in all spectra is due to framework-bound methoxy species. **(**a**)** Cross polarization spectrum of a material prepared using 20% air in He as the carrier gas. The broad signal near 150 ppm is characteristic of phenols. **(**b**)** Interrupted decoupling spectrum of the sample prepared with 20% air confirms that the 150 ppm signal is from a substituted carbon rather than a C−H group. Most signals from this sample survived interrupted decoupling because they were either substituted aromatic carbons or methyl groups. **(**c**)** Cross polarization spectrum from a control experiment in which 100% He was used as a carrier gas. This spectrum is consistent with methylbenzenes and does not show the 150 ppm signal assigned to phenols. **(**d**)** The interrupted decoupling spectrum from the control experiment supports the assignments to methylbenzenes and framework methoxy species.

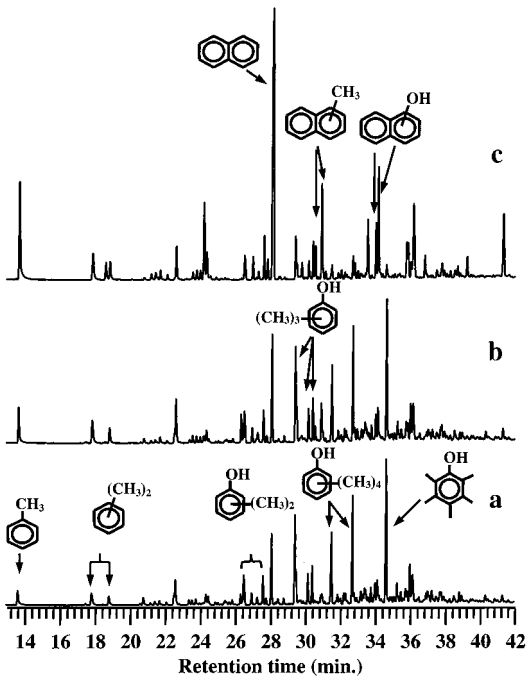

Figure 3. Study of the aging of methylphenols in HSAPO-34 at various times and temperatures. Shown are GC-MS total ion chromatograms from ex situ analyses (acid digestions). All samples were formed by first feeding methanol into HSAPO-34 catalyst beds at 350 °C using 20% air in He as the carrier gas to form phenols and then holding at the indicated temperature and time while flowing 100% He (200 sccm) to age the sample prior to quench. **(**a**)** Control experiment (identical to Figure 1c) without aging. **(**b**)** After aging for 30 min at 350 °C the loss of methyl groups from pentamethylphenol was negligible. **(**c**)** Aging for 30 min at 450 °C resulted in a significant reduction in phenols, large increases in fused polycyclic species, especially naphthalene, indene, and naphthols, and the formation of other oxidation products such as phenalen-1-one.

present in the corresponding spectra of a catalyst containing only methylbenzenes (Figure 2c and 2d). The 150 ppm signal is characteristic of phenols; for example 152 ppm for C1 of *p*-cresol.

In a recent paper, we described experiments in which we synthesized methylbenzenes in HSAPO-34 then abruptly terminated methanol flow and monitored the decrease in the number of methyl groups per ring as these compounds eliminated olefins.[10] Here, we used the acid digestion method to make an analogous study of the stability of methylphenols in HSAPO-34, and these results are reported in Figure 3. Figure 3a is the sample from Figure 1c as a control with no aging. Figure 3b shows that after 30 min of aging at 350 °C, there was little decrease in the amounts of methylphenols. In particular, pentamethylphenol was essentially unchanged, whereas we would expect a substantial decline in pentamethylbenzene as a result of elimination of propene and ethylene. Using more severe conditions, aging at 450 °C for 30 min (Figure 3c) does show a decline in methylphenols, but with a corresponding increase in naphthalenes, indene, and toluene. Some of the more prominent oxygenates remaining in the catalyst after aging at 450 °C included naphthols and phenalen-1-one.

Catalyst Testing. We prepared HSAPO-34 materials with methylbenzenes (very similar to that analyzed in Figure 1a) and methylphenols (cf. Figure 1c) and immediately tested their MTO activity using a 5 μL pulse of methanol-^{13}C. This pulse was small enough so as to not form a significant amount of additional methylbenzenes. The volatile products leaving the catalyst bed 4.0 s after injection were analyzed by GC-MS, and the catalyst bed temperature was quenched to ambient for acid digestion and ex-situ analysis of aromatic compounds by GC-MS. Figure 4 reports the GC-MS total ion chromatograms from the analyses of volatile products as well as bar graphs depicting ion mass distributions in the vicinities of molecular ions from the centers of selected chromatographic peaks.

Figure 4a shows that the HSAPO-34 bed with methylbenzenes in the cages realized ca. 86% conversion of methanol and DME to hydrocarbons. Examination of the ion mass distributions for the ethylene and propene formed in this experiment reveals the presence of both ^{12}C and ^{13}C, a result consistent with olefin synthesis on a hydrocarbon pool. Unreacted DME and methanol however were fully ^{13}C labeled. Aromatic ring methylation by these reagents is very exothermic; thus, the reaction is essentially irreversible, and ^{12}C does not accumulate in the unreacted oxygenates. Figure 4b shows that the sample of HSAPO-34 with methylphenols in the cages was far less active as an MTO catalyst −conversion was only 9%. Ethylene and propene were here also scrambled.

Figure 5 reports GC-MS results from ex situ analyses of the aromatics in the two catalysts used to obtain the results in Figure 4. The methylbenzenes underwent a considerable amount of ring scrambling; a fraction of the *p*-xylene was scrambled in all eight positions and much of the hexamethylbenzene scrambled into 10 to twelve positions. A very different result was obtained for ^{13}C scrambling into the methylphenols. The ion mass distribution patterns in Figure 5 suggest that only methyl group positions

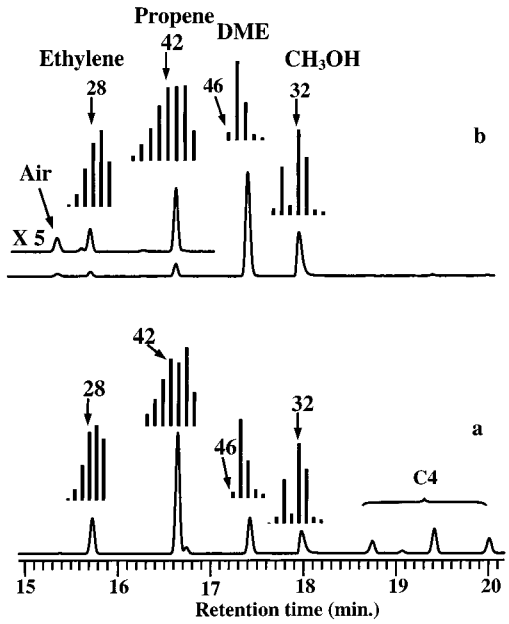

Figure 4. GC-MS total ion chromatograms from the analyses of volatile olefinic products sampled 4.0 s after pulsing 15 μL of methanol-^{13}C onto HSAPO-34 catalyst beds containing either methylbenzenes or methylphenols prepared from natural abundance methanol. Ion mass distributions in the vicinity of the molecular ion are shown for ethylene, propene, dimethyl ether (DME) and methanol. On both catalysts, the olefins showed extensive label scrambling, but methanol and DME maintained their ^{13}C enrichment. Methanol-^{13}C is also slightly enriched in ^{2}H, and this accounts for the presence of small signals at *m*/*e* 34 and 35. **(**a**)** On the methylbenzene material conversion to volatile hydrocarbons was ca. 86%. **(**b**)** On the methylphenol material conversion to volatile hydrocarbons was much lower, only ca. 9%.

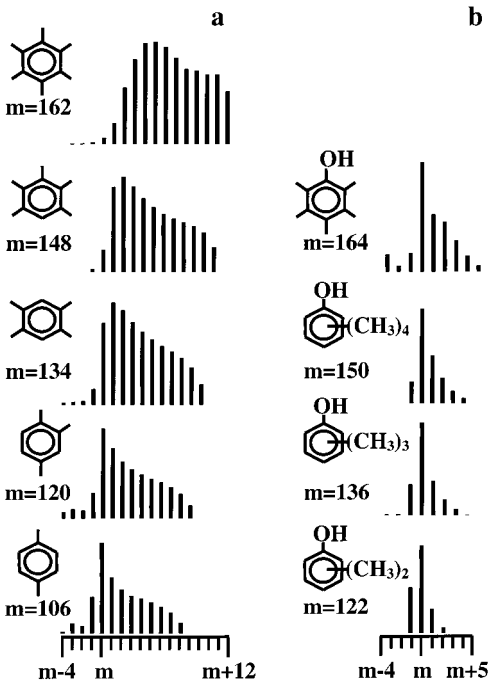

Figure 5. Bar graphs showing ion mass distributions in the vicinities of molecular ions for methylbenzenes and methylphenols from ex situ analyses of the catalyst beds from the same experiments giving rise to Figure 4. **(**a**)** The methylbenzenes originally formed in HSAPO-34 from natural abundance methanol incorporated a substantial amount of ^{13}C into ring positions following a small pulse of methanol-^{13}C. **(**b**)** In contrast, methylphenols exchanged carbon in methyl positions but not ring positions.

exchanged for the methylphenols; for example, pentamethylphenol had an m+5 peak but not an m+6 peak. This conclusion was supported by a detailed interpretation of fragment peaks in the mass spectra (not shown). We also carried out these experiments on a sample of HSAPO-34 with similar amounts of both methylbenzenes and methylphenols. Results analogous to Figure 5 confirmed that ^{13}C label exchange occurred preferentially into the rings of methylbenzenes and not methylphenols in the identical catalyst. As a final test of the potential of methylphenols as reaction centers (hydrocarbon pool species) in MTO chemistry we co-injected a solution of *p*-cresol in methanol (1:10 mol:mol) into the aluminosilicate zeolite HZSM-5 at 375 °C in a flow reactor using conditions very similar to those for the experiments in Figure 4. HZSM-5 has pore openings large enough to admit methylbenzene derivatives, thus they may be introduced in the feed stream and need not be synthesized in situ as with HSAPO-34. The control experiment in Figure 6a shows that the first pulse of pure methanol is almost unreactive on an HZSM-5 catalyst bed. Consistent with the earlier reports of Mole and co-workers, we found that toluene in methanol (1:10 mol:mol) was very reactive on the HZSM-5 catalyst bed (Figure 6b). Substituting *p*-cresol for toluene (Figure 6c) yielded a conversion much closer to that of methanol alone, confirming that methylphenols are inactive or at best very weakly active for MTO chemistry.

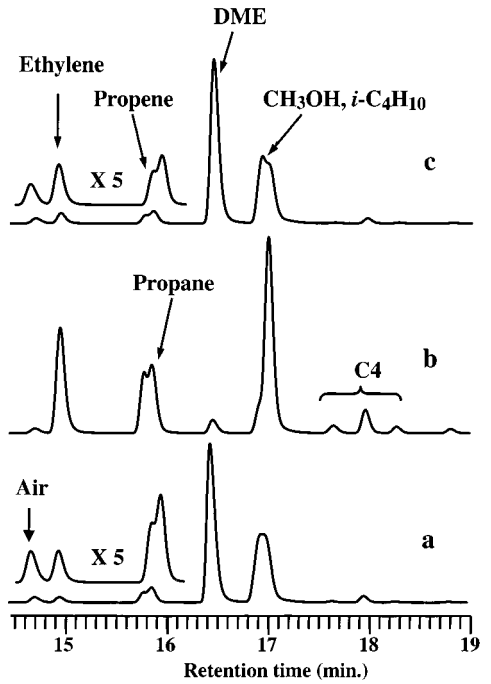

Figure 6. GC (FID) analyses of the volatile products sampled 2.4 s after injecting 12.5 μL of solutions of methanol onto 300 mg catalyst beds of zeolite HZSM-5 at 375 °C. **(**a**)** Control experiment using methanol alone. Conversion was only ca. 9%. **(**b**)** Using toluene in methanol (1:10 mol:mol) conversion was high, ca. 95%. **(**c**)** Using *p*-cresol in methanol (1:10 mol:mol) conversion was also ca. 9%.

Discussion

Feeding 20% air into an otherwise inert carrier gas stream during methanol conversion afforded a high yield of methylphenols trapped in the cages of HSAPO-34. A number of literature reports[16−18] and patents[19,20] describe the use of N_2O for the oxidation of benzene to phenol on various zeolites, either underivatized or treated to introduce transition metals. Given that prior art, we were surprised that N_2O was less active for the oxidation of methylbenznenes in HSAPO-34 cages. Never-

the-less dilute air was effective, and we were able to prepare HSAPO-34 materials with a single phenolic function on the majority of entrained benzene rings. Given the high yields of pentamethylphenol we speculate that the more highly substituted methylbenzenes are more easily oxidized under these conditions, reflecting the decrease in ionization energies for phenols as methyl substitutents are added. A recent study from another laboratory used acid digestion to characterize the methylbenzenes formed in HSAPO-34 during MTO chemistry.[25] That study also reported the formation of low levels of phenols. We reproduced this finding only when traces of air were introduced into the reactor.

By every measurement we made, methylphenols are not active as reaction centers for MTO chemistry in HSAPO-34. Materials with high fractions of methylphenols show much lower conversions than materials with comparable methylbenzene contents and the activity of the phenolic catalysts is traceable to residual methylbenzenes which undergo far more extensive carbon label scrambling including ring scrambling. Methylphenols in HSAPO-34 undergo methyl label exchange with methanol but not ring exchange. Furthermore, when we co-fed *p*-cresol and methanol into zeolite HZSM-5 there was no MTO rate acceleration compared to pure methanol, whereas toluene co-feed showed a considerable rate enhancement, as was originally reported by Mole and co-workers.[6,7]

Methylphenols are not reaction centers on either HSAPO-34 or HZSM-5. The most active methylbenzenes are those with the most methyl groups. Given that we easily made pentamethylphenol in HSAPO-34, methylation is not the limiting factor, yet even this molecule was stable to olefin elimination. The detailed mechanism by which methylbenzenes form olefins on MTO catalysts is unknown, although ring carbon scrambling is consistent with the mechanism proposed for the paring reaction.[13] This mechanism involves ring contraction (6 → 5) followed by expansion (5 → 6) that extends of an alkyl group which is eliminated as an olefin from a positively charged intermediate. This complex sequence of mechanistic steps is ripe with opportunities for perturbation by a heteroatom substituent. Yet, the explanation here may be simple. Phenol is a very basic molecule in the gas phase. Its proton affinity (195.3 kcal/mol) is 16 kcal/mol greater than that of benzene. Furthermore, phenols may be able to form cooperative (donor and acceptor) hydrogen bonds with the acid site of HSAPO-34. Thus, a methylphenol in an HSAPO-34 cage may tie up the acid site in a hydrogen bonding interaction that is too strong to permit entry into a sequence of intermediates with positive charge on carbon rather than oxygen.

If the above interpretation is correct then it is still possible that other heteroatom-substituted methylbenznenes may be active as reaction centers for MTO chemistry. The synthesis of materials with such derivatives is under active investigation.

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