Polycyclic aromatics formation in HSAPO-34 during methanol-to-olefin catalysis: *ex situ* characterization after cryogenic grinding

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Cryogenic grinding using a freezer mill is shown to be a useful adjunct to acid digestion for the *ex situ* analysis of aromatic hydrocarbons entrained in microporous catalysts. In the course of converting methanol to olefins, HSAPO-34 contains first methylbenzenes and later methylnaphthalenes. As the catalyst deactivates, significant amounts of phenanthrene and pyrene form as well.

KEY WORDS: methanol conversion; aromatic hydrocarbons; deactivation; *ex situ* analysis; solid state NMR; solid acid catalysts

1. Introduction

In several recent papers [1–5] we have shown that cyclic organic species are part of the active sites for methanol-to-olefin (MTO) catalysis on microporous solid acids [6,7]. On zeolite HZSM-5 these "reaction centers" are either methyl-substituted cyclopentenyl carbenium ions or methylbenzenes [2]. On the silico-aluminophosphate acid catalyst HSAPO-34 [7], the reaction centers are methylbenzene molecules [3,5], and we cannot rule out the possibility that other types of arenes, *e.g.*, methylnaphthalenes, could also be reaction centers. HSAPO-34 has the CHA topology (its 1 nm cages are interconnected through 0.37 nm windows), and aromatic molecules, even benzene, once formed cannot escape.

The reaction centers work in tandem with a Brønsted acid site to make and break carbon–carbon bonds without recourse to the higher energy intermediates and transition states that would be required without an organic "scaffold" to stabilize these reactions. The most specific evidence for the roles of methylbenzenes in MTO catalysis on HSAPO-34 is from *in situ* NMR studies [3,5], but earlier work by Kolboe and co-workers used isotope scrambling to obtain evidence for a phenomenological "hydrocarbon pool" of unspecified structure [8,9]. The first evidence that aromatics could accelerate the rate of methanol conversion on any solid acid catalyst was reported by Mole *et al.* who identified a co-catalytic effect when toluene was co-fed with methanol on HZSM-5 [10,11].

As a step toward a kinetic analysis of MTO chemistry in HSAPO-34, we treated each nanocage containing a methylbenzene as an independent supramolecule capable of unimolecular decomposition to either ethylene, $\{n\} \rightarrow \{n-2, \mathrm{e}\}$, or propene, $\{n\} \rightarrow \{n-3, \mathrm{p}\}$, where n implies a methylbenzene molecule with n methyl groups, and $\{\}$ designates the nanocage and its associated Brønsted acid site [5]. We found that when $n = 5$ or 6, the unimolecular decomposition to olefins proceeds rapidly and favors propene, and when $n = 3$ the supramolecule is more stable but yields ethylene with enhanced selectivity. Any unique molecule that we may assemble in an HSAPO-34 cage provides a unique supramolecule that could be tested for correlations between structure, activity, and selectivity, and we have embarked on a synthetic program to synthesize and test a variety of supramolecules. This program necessarily requires the analytical capability to identify and quantify mixtures of supramolecules (or more specifically their organic constituents). Unfortunately, the ^{13}C solid state NMR method that first identified roles for methylbenzenes in HSAPO-34 catalysts [3] is, for lack of resolution, ill-suited to the study of catalysts containing diverse aromatic species. Thus, when we characterized a deactivated HSAPO-34 catalyst containing 16 wt% C, the ^{13}C CP/MAS NMR spectrum was consistent with an average structure similar to methylnaphthalene [3], but the NMR data said nothing about the distribution of different ring systems, and did not preclude other interpretations such as a mixture of methylbenzenes and graphitic coke on the exterior of the catalyst particles.

A standard method for the analysis of organic species in zeolites and similar catalysts is acid digestion followed by chromatographic analysis. Magnoux *et al.* found that aluminosilicate zeolites could be digested using 40% aqueous HF, liberating organic compounds which could be extracted using methylene chloride [12]. Control experiments were performed in which reactive hydrocarbons were first adsorbed onto inert silica and then recovered intact following HF digestion. As demonstrated by Arstad and Kolboe, SAPO-34 can be digested using 1 M HCl, and the organics thus released are conveniently extracted using CCl_4 [13].

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While we have every reason to believe that acid digestion is generally a reliable method for *ex situ* analysis of organics in microporous catalysts, we are concerned about the possibility that *some* compounds formed in SAPO-34 might prove to be acid sensitive, either alone or in combination. Furthermore, ^{13}C label scrambling within a molecule or between molecules is a sensitive mechanistic probe, and we need a way to control against scrambling as a result of acid digestion. As an adjunct method to confirm the results of acid digestion we considered cryogenic grinding, a mechanical method for liberating organic compounds from inorganic matrices. Cryogenic grinding using a freezer mill is used to pulverize bone and dental material to liberate DNA for forensic analysis [14]. Most famously, this method was used in the conclusive identification of the skeletal remains of Tsar Nicholas II and his family [15].

Here we report the application of cryogenic grinding to the *ex situ* study of aromatic compounds in SAPO-34. ^{31}P NMR showed that the long-range crystalline structure of this catalyst is destroyed after *ca.* 40 min of grinding. Control experiments using physical mixtures of *p*-xylene and HSAPO-34 or *p*-xylene adsorbed onto zeolite HZSM-5 showed that cryogenic grinding does not promote reactions such as xylene isomerization or disproportionation. We carried out a series of MTO reactions in which HSAPO-34 converted varying amounts of methanol in a flow reactor at 400 °C at a fixed space velocity prior to thermal quenches. Activity and selectivity were measured immediately prior to quench and quenched samples were characterized by ^{13}C solid state NMR. NMR showed that the amount of methylated aromatics entrained in the catalyst increased with time on stream and suggested an increase in fused rings as the catalyst deactivated, but, as before, the distribution of aromatics could not be deduced. Following NMR analysis, the samples were divided for both acid digestion (1 M HCl) and cryogenic grinding. GC analysis produced essentially identical traces for CCl_4 extracts of samples prepared by the two methods. We confirmed that methylbenzenes are the dominant aromatics in HSAPO-34 early in the life of the catalyst, but methylnaphthalenes are present at comparable levels well before deactivation occurs. As the catalyst deactivates it accumulates appreciable amounts of phenanthrene and pyrene.

2. Experimental

2.1. Materials and reagents

HSAPO-34 was prepared according to a patent procedure [16]. XRD showed a pure crystalline phase with the CHA structure. The product was calcined at 873 K for 10 h to remove the template agent and pressed into 10–20 mesh pellets. The Brønsted site concentration was determined to be 1.1 mmol/g. We used 10% ^{13}C enriched methanol (Isotech, Inc.) to facilitate NMR characterization.

2.2. Catalysis

Experiments were performed using the pulse quench reactor [17] with a motor-driven syringe pump (Harvard Apparatus model PHD 2000) as described previously [5]. For each experiment a bed consisting of 0.3 g of catalyst was activated at 673 K in the reactor under 200 sccm He flow for 2 h immediately prior to use. This carrier gas feed rate was also used during methanol introduction in all experiments. Methanol flow was abruptly ceased several seconds prior to quench. Previous studies have shown that the temperature of the catalyst pellets decreases 150 K in the first 170 ms of a quench. After quenching each reacted catalyst sample, the reactor was sealed off and transferred into a glove box filled with nitrogen. The catalyst pellets were ground and transferred to a 7.5 mm MAS rotor which was sealed with a Kel-F end-cap.

2.3. Gas chromatography

A Hewlett–Packard model 6890 gas chromatograph with flame-ionization 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 to permit sampling of the gas stream more frequently than the total analysis time for any given sample. Extracted aromatic hydrocarbons were analyzed using the HP 5973 mass selective detector on a second model 6890 gas chromatograph. The column was a HP-1 (cross linked methyl silicone gum, 0.5 μm film), 50 m long, 0.2 mm diameter. The oven temperature was programmed from an initial temperature of 60 °C to a final temperature of 250 °C, and the He carrier gas was maintained at a constant flow rate of 0.3 ml/min.

2.4. 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, and 85% H_3PO_4 was used for ^{31}P. Chemagnetics-style pencil probes spun 7.5 mm zirconia rotors at typically 6.5 kHz with active spin speed control ($\pm$3 Hz).

Typical ^{13}C experiments included: cross polarization (CP, contact time 2 ms, pulse delay 1 s, 2000 transients); cross polarization with interrupted decoupling (contact time 2 ms, pulse delay 1 s, 2000 transients, dipolar dephasing time of 50 μs); single pulse excitation with proton decoupling (Bloch decay, pulse delay 10 s, 400 transients). CP and Bloch decay spectra gave very similar values for the average number of methyl groups per aromatic ring carbon. All spectra reported here were measured using Bloch decay.

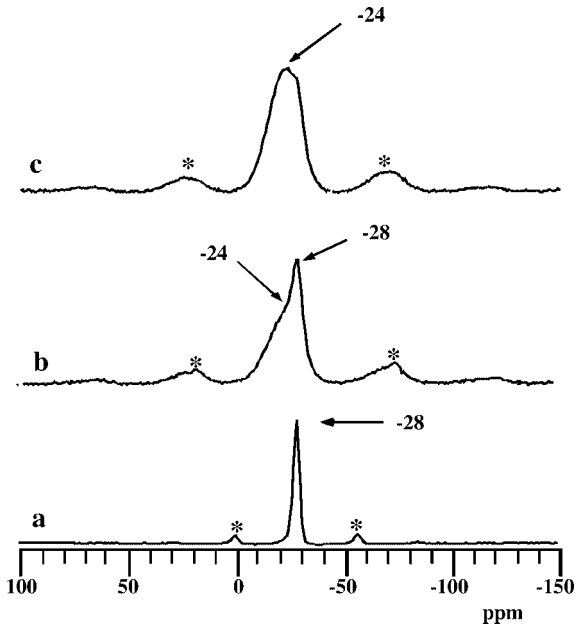

Figure 1. 121.4 MHz ^{31}P MAS NMR spectra showing the effect of cryogenic grinding on HSAPO-34 catalyst. (a) Without grinding HSAPO-34 shows a single, very narrow resonance characteristic of a crystalline material. (b) After 24 min of grinding the catalyst is partially degraded to amorphous material. (c) After 60 min of grinding the NMR spectrum shows little evidence of crystallinity.

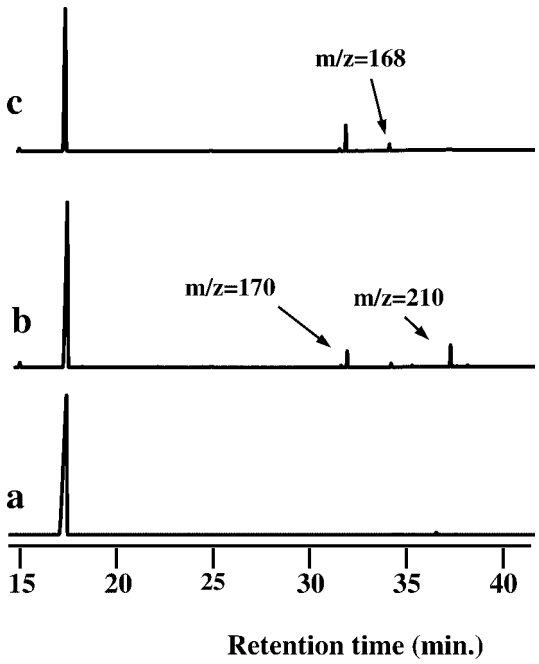

Figure 2. GC/MS total ion chromatograms from control experiments testing whether or not cryogenic grinding promotes the reaction of *p*-xylene. (a) After 40 min of grinding a mixture of HSAPO-34 and *p*-xylene, there is no evidence of reaction. (b) *p*-xylene was adsorbed onto zeolite HZSM-5 and ground for 40 min. No isomerization or disproportionation occurred but several higher mass products were found at low yields. (c) *p*-xylene was adsorbed onto zeolite HZSM-5 and this was then extracted with CCl_4 without grinding. Some of the higher mass products were observed here implying that these reactions were due to adsorption in the zeolite and not grinding.

2.5. Cryogenic grinding

The freezer mill was a SPEX (Metuchen, NJ) CertiPrep 6750 with 6751C polycarbonate tubes. We programmed 12 grinding cycles of 3.5 min with 4 min between cycles. The grinding frequency was 6 Hz for the first cycles and this was progressively increased to 12 Hz for the final cycles. The sample was bathed in liquid nitrogen for the entire procedure.

3. Results

Mechanical grinding must destroy the crystalline structure of a microporous material in order to expose entrained organic compounds for extraction. We used ^{31}P MAS NMR to confirm that HSAPO-34 looses long-range order as a result of freezer milling. Figure 1(a) shows that HSAPO-34 has a sharp ^{31}P resonance at -28 ppm prior to treatment. Following 24 min of cryogenic grinding most of the integrated intensity is in a broad shoulder at -20 ppm, but the sharper feature at -28 ppm is still evident. With longer grinding times (*e.g.*, 60 min, figure 1(c)), the sharp feature is no longer evident. We used 40 min total of grinding for all of the work reported here.

Figure 2 reports GC traces (total ion chromatograms) from control experiments in which we probed whether or not cryogenic grinding was likely to promote the reactions of aromatic hydrocarbons in the presence of debris from microporous solid acids. *p*-xylene could isomerize to *o*- or *m*-xylene, it could disproportionate to toluene and trimethylbenzene, or it could dimerize to substituted diphenylmethanes, all familiar reactions on microporous solid acids. *p*-xylene is too large to be adsorbed into SAPO-34, so we ground a physical mixture. The GC-MS trace in figure 2(a) shows that *p*-xylene was the only organic recovered by extraction. An analogous grinding experiment with *p*-xylene adsorbed onto zeolite HZSM-5 initially seemed more equivocal; figure 2(b) shows several minor products with appreciably higher molecular weights, but these are apparently a consequence of adsorption rather than freeze milling. We adsorbed *p*-xylene onto HZSM-5 and then extracted the zeolite with CCl_4, omitting grinding. As figure 2(c) shows, we were able to recover all but the highest mass species by this simple procedure. We assume that even the m/z 210 product is formed upon adsorption, and conclude that cryogenic grinding alone is not likely to promote the reactions of aromatic hydrocarbons.

We carried out five experiments in which totals of 0.5–8 ml of methanol were delivered onto fresh HSAPO-34 catalyst beds at 400 °C with a space velocity of 8 h^{-1}. The GC traces in figure 3 reflect the product streams from these reactions immediately prior to thermal quench. A decrease in activity was evident after the first 4 ml of methanol, and activity was all but lost after 8 ml. As noted previously, there was an increase in ethylene selectivity as the catalyst began to deactivate.

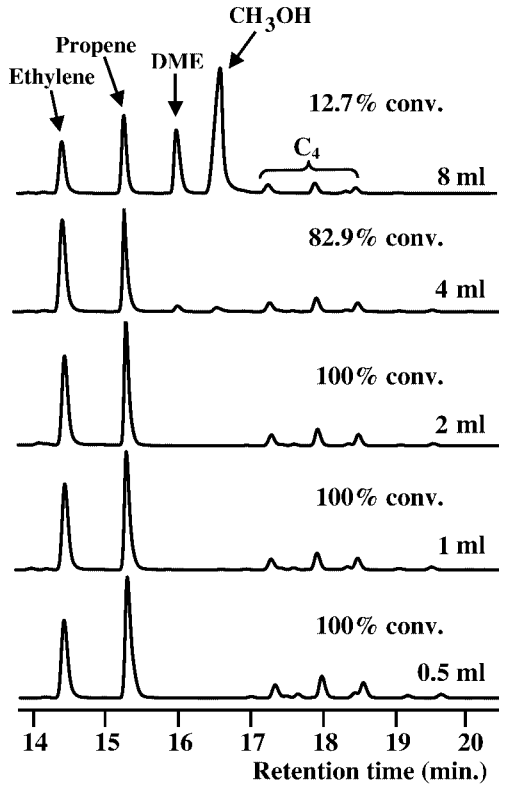

Figure 3. Gas chromatography (flame-ionization detection) analyses of the volatile products captured immediately prior to thermal quench from the experiments used to prepare the HSAPO-34 samples for NMR analysis and cryogenic grinding. Various total volumes of methanol were delivered at a weight-hourly space velocity of 8 h^{-1} to form volatile olefinic products and aromatic compounds entrained in the SAPO-34 cages. The catalyst was almost completely deactivated after 8 ml of reactant. DME denotes dimethylether.

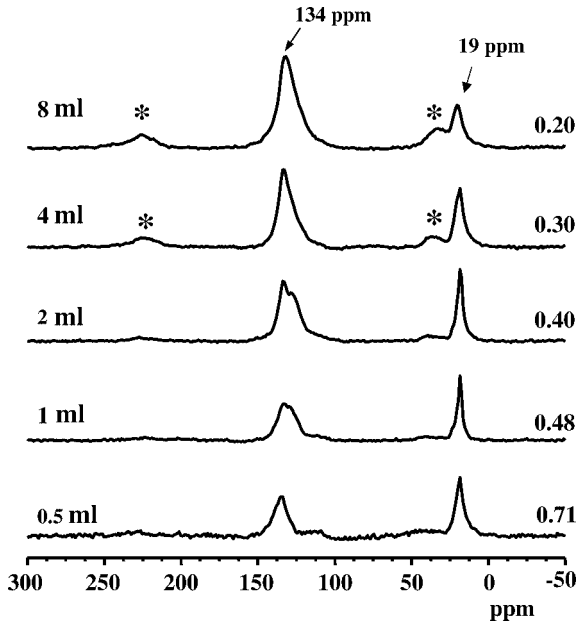

Figure 4. 75 MHz ^{13}C MAS NMR spectra (Bloch decays) of the HSAPO-34 catalysts prepared in the experiments described in figure 3. The aromatic hydrocarbons trapped in the HSAPO-34 cages are reflected in the aromatic carbon signal at *ca.* 134 ppm and the methyl carbon signal at 19 ppm. While it is clear that the total content of aromatics increases with time on stream, the identities and relative compositions of various compounds cannot be deduced from these spectra. $*$ denotes spinning sidebands. Numbers to the right of the spectra report ratios of methyl carbons to aromatic ring carbons from integrated intensities.

Figure 4 reports the ^{13}C CP/MAS spectra of the catalyst beds obtained by thermal quenching the experiments in figure 3 immediately after sampling the product stream for GC analysis. In each case the reactor was opened in a glove box and the contents were transferred to a magic angle spinning rotor for spectral acquisition at room temperature. As in our previous NMR studies of organic species on HSAPO-34 [3,5], the spectra do not show many features. The signal at 19 ppm is, in every case, indicative of methyl substituents on aromatic rings. The aromatic signal near 134 ppm suggests that most of the ring carbons are either substituted by methyl groups or at bridgehead positions in fused rings. In each case the ratio of methyl groups to aromatic carbons, CH_3/C_{Ar}, is reported next to the spectra. This number is only 0.20 for the nearly deactivated (8 ml) catalyst.

The NMR spectra in figure 4 also show the progressive accumulation of carbon on the catalyst during methanol conversion. We submitted the 1 and 4 ml samples for carbon weight percentage analysis and obtained values of 5.3 and 13.3%, respectively. We previously found that fully deactivated HSAPO-34 catalyst contains *ca.* 16% carbon.

We selected the 4 ml sample for a detailed comparison of acid digestion and cryogenic grinding. We used Kolboe's acid digestion procedure [13] in which the spent catalyst is treated with 1 M HCl to liberate the aromatics, which are then extracted into CCl_4. Cryogenic grinding was carried out for 40 min based on the results in figure 1. GC-MS total ion chromatograms from the analyses of these extracts are compared in figure 5. The differences between these two results are so slight as to be considered insignificant. The compounds present at the highest levels include methylbenzenes from toluene to durene, naphthalene and methylnaphthalenes up to trimethyl isomers, phenanthrene, and pyrene.

Figure 6 presents GC-MS total ion chromatograms for all five samples. The catalyst that saw only 0.5 ml of methanol contains methylbenzenes and only small amounts of naphthalenes, while the latter are very significant after 4 ml of methanol. The deactivated (8 ml) catalyst contains significantly reduced amounts of methylbenzenes, methylnaphthalenes, and a great deal of both phenanthrene and pyrene. No methyl-substituted pyrene was observed and only a very small fraction of the phenanthrene was substituted. Yet, a large fraction of the benzene and naphthalene rings were methylated in the deactivated catalyst.

4. Discussion

The results of this first application of cryogenic grinding to catalyst samples are very encouraging. While acid digestion was not detrimental to the samples studied here, our expectation is that grinding at liquid nitrogen temperature is less likely to alter more acid sensitive compounds than those

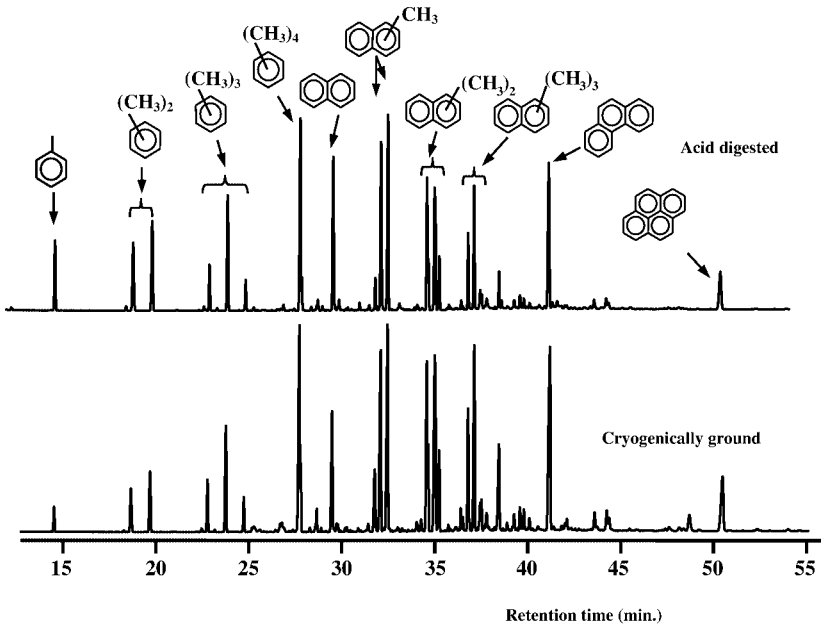

Figure 5. GC-MS total ion chromatograms from analyses of CCl_4 extracts of samples prepared from the catalyst bed that received 4 ml of methanol: (a) a fraction digested using 1 M HCl, and (b) a fraction cryogenically ground for 40 min. The two methods yield essentially identical results for the analysis of aromatic hydrocarbons in the HSAPO-34 catalyst bed. We were able to identify all major species from the mass spectra and/or comparison of retention times with authentic samples. Some of the more prominent peaks are assigned in the figure.

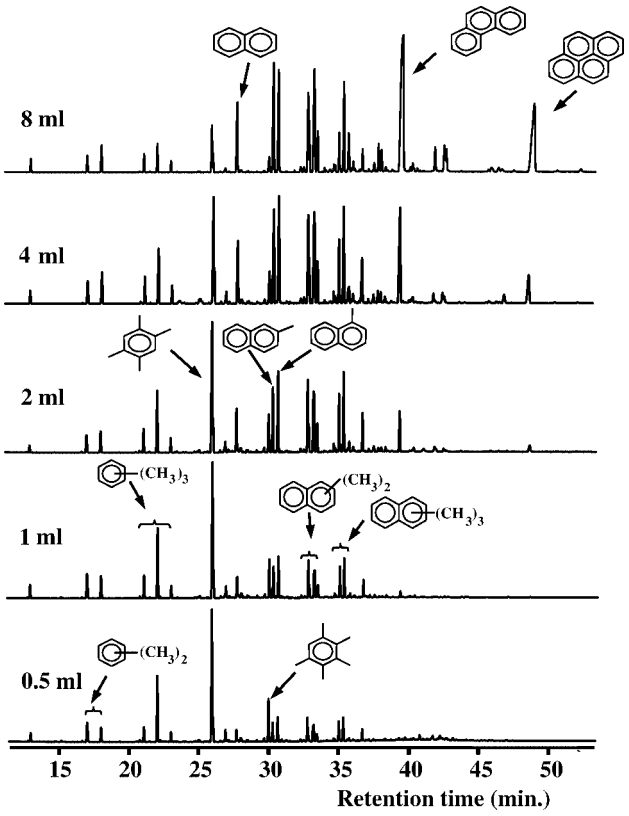

Figure 6. GC-MS total ion chromatograms from analyses of CCl_4 extracts of cryogenically ground samples from all five catalyst beds (*cf.* figures 3 and 4). Several peaks are assigned on the figure to provide benchmarks; others can be identified by reference to figure 5. While methylbenzenes are the major species present early in the lifetime of the catalyst, methylnaphthalenes are also significant after 1 or 2 ml of methanol. Phenanthrene and pyrene are prominent on the deactivated catalyst.

studied here. Agreement between the two approaches, as obtained here, builds confidence in the application of either method.

We used elemental analysis (before and after grinding) to asses the fraction of the organic compounds liberated. For both samples studied (1 and 4 ml) *ca.* 30% of the carbon initially present was removed by milling followed by CCl_4 extraction. We also observe a black, CCl_4 insoluble residue following acid digestion, but we have not sought to quantify the amount of carbon associated with this. It may be that some of the carbon on spent HSAPO-34 is indeed graphite-like material on the outside of the crystallites, and this can not be extracted. It also seems likely that a fraction of the aromatic compounds remains associated with the inorganic debris after grinding. For example, it may be that milling for 40 min produces very small crystallites of SAPO-34 only a few nm in dimension, and some of the organic compounds are still included in intact cages within the debris. For the present we are satisfied with the result that cryogenic grinding and acid digestion liberate organic species that are equally representative of those in the used catalyst.

A recent paper applied acid digestion to determine the aromatic compounds confined in HSAPO-34 after short times on stream [13]. That study identified methylbenzenes and a small amount of naphthalene, but not phenanthrene and pyrene, which presumably would have formed with longer time on stream. The earlier study also found that di- and trimethylphenols formed in the catalyst in moderate amounts. We observed phenols in only one case, but then they were determined to be an artifact. During cryogenic grinding the sample is contained in a polycarbonate capsule. In one case this capsule failed while milling a catalyst sam-

ple, and the interior of the capsule was heavily scored. The CCl_4 extract of this sample contained small amount of phenols, but since we had used methanol-^{13}C for the experiment, the origin of the phenols was readily attributed to debris from the capsule. We also did not observe methylphenols in our acid digested samples of HSAPO-34. We currently have no explanation for the formation of phenols in the earlier study but not in the present.

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