

An ultraviolet Raman spectroscopic study of coke formation in methanol to hydrocarbons conversion over zeolite H-MFI

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Abstract

The formation of retained hydrocarbons or coke in the conversion of methanol and dimethylether to hydrocarbons over zeolite H-MFI was studied using ultraviolet Raman spectroscopy. Polyolefin, cyclopentadienyl species, and polyaromatic hydrocarbons have been identified among the retained hydrocarbons from the Raman spectra. The results strongly support a reaction mechanism, proposed previously, where cyclopentadienyl species are identified as a key intermediate in the formation of aromatic and polyaromatic hydrocarbons by ring expansion. The spectra also suggest that the polyaromatic hydrocarbons have a chain-like topology, similar to polycenes, rather than a two-dimensional, sheet-like topology, similar to pyrene or coronene.

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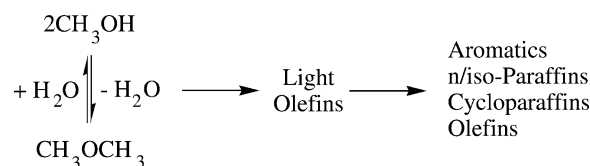
Keywords: Coking; Methanol; H-MFI; Raman; Polyolefin; Cyclopentadiene; Polyaromatic

1. Introduction

The deactivation of heterogeneous catalysts caused by the build-up of carbonaceous deposits or coke is an issue of concern for many industrial chemical processes. As a consequence, a great deal of research has focused on the mechanism of coke formation, the chemical nature of coke, and methods for its removal. Coke formation in zeolites or molecular sieves has received particular attention both because of their importance in industrial chemistry and because the network of nanoscale channels and cavities that impart their desirable shape-selective catalytic properties also make them especially susceptible to blockage by coke build-up. Much of this work has centered on determining the chemical nature of the coke deposit. Typically, in these studies, the zeolite matrix is dissolved in hydrofluoric acid, followed by solvent extraction of the organic coke and traditional chemical separations and analysis to determine the chemical constituents. While this is an effective procedure for gaining access to the chemical species that are otherwise locked in the pores of the zeolite and dealing with a chemically complex material, it is a laborious process, and the mechanism of coke forma-

tion can be deduced only indirectly from the nature of the final coke produced.

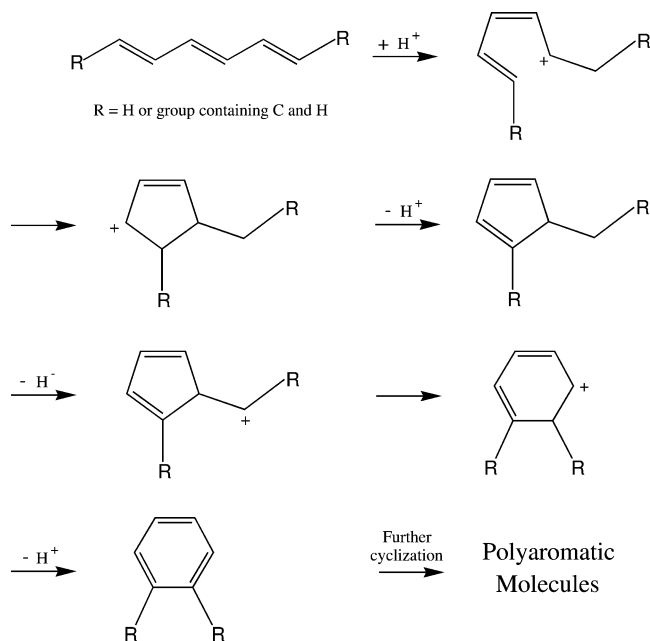
In the present paper we describe an investigation, using in situ ultraviolet Raman spectroscopy, which looks directly into the nature of the chemical species retained in the catalyst under the conditions of the methanol-to-hydrocarbons (MTH) process catalyzed by zeolite H-MFI. MTH chemistry has been studied extensively, and a number of excellent reviews have appeared [1–3]. A simplified representation of the MTH process is shown in Scheme 1. Methanol and dimethylether rapidly equilibrate at a reaction temperature of 360 °C. This equilibrium mixture reacts to form a range of light olefins which subsequently react further to form a mixture of paraffinic, olefinic, and aromatic hydrocarbons. The product distribution can be controlled, within limits, by the reaction conditions. Coke formation during this reaction has also been studied extensively. There is general agreement as to the location and chemical nature of the carbona-



Scheme 1.

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aceous deposits that make up the coke and on its evolution with time [3–8]. However, there is only indirect information on the reaction pathway(s) to form coke [9,10]. In particular, Schulz and Wei [11] proposed a detailed reaction scheme (see Scheme 2) for coke formation under low-temperature reaction conditions. This reaction scheme is based (1) on previous observations of UV absorption bands that are consistent with the presence of highly unsaturated hydrocarbons retained in the zeolite [12], (2) on the recovery of alkyl-substituted benzene from used H-MFI catalysts [11], and (3) on sensible, acid-catalyzed organic chemistry [11]. In this paper, we present UV Raman spectra measured at several reaction times during the formation and transformation of retained hydrocarbons formed under various conditions of MTH catalyzed by zeolite H-MFI. These spectra provide direct evidence for two of the chemical species proposed in Scheme 2 and suggest a topology for the polyaromatic hydrocarbons that are the ultimate products of coke formation chemistry.

2. Experimental

In situ UV Raman spectroscopy measurements were performed using a fluidized bed reactor/Raman cell. Briefly, the catalyst, in the form of a loose powder, was placed on a stainless steel porous disk located near the end of a vertical stainless steel tube, which also served as the gas inlet. The stainless steel tube assembly was surrounded by a concentric quartz tube with the top end sealed by a UV-transparent window for Raman spectroscopic measurements. The space between the inner stainless steel tube and the outer quartz tube served as the gas outlet. An oven surrounded the entire assembly to provide heating for catalyst pretreatment and

elevated reaction temperatures. Gas flow and mechanical vibration were adjusted to produce stirring of the catalyst powder without lifting the powder bed off the porous disk. All spectra were measured using 244-nm radiation at a power of 2 mW. Data collection times varied from ~ 500 s to 2 h depending on signal levels. Details of the UV Raman instrument [13–17] and the fluidized bed reactor [18] have been described previously.

The H-MFI zeolite (Si/Al = 90) used in this study was provided by BP Amoco Chemical Company. Methanol (99.93% HPLC grade; Aldrich) and dimethylether (99+%; Aldrich) were used as starting reagents without further purification. In a typical experiment, ~ 200 mg of catalyst was placed in the fluidized bed reactor and calcined at 500 °C in oxygen (60 ml/min) for 2 h. The temperature was lowered to the appropriate reaction temperature and oxygen was switched to helium. Methanol was introduced to the reactor by admitting helium (30 ml/min) into a bubbler containing the liquid. For dimethylether, the gas was allowed to flow into the reactor at a rate of 15 ml/min in 30 ml/min of helium. After a timed dose of reagent was passed through the catalyst bed, the gas flow was switched to helium. The doses cited in the results are given as molecules per zeolite unit cell based on the known volume of reagent gas passed through a measured quantity of catalyst. UV Raman spectra were measured in flowing helium at reaction temperature. Since recording the Raman spectra required lengthy signal averaging and the fluidizing gas contained no hydrocarbon reagent during the measurements, the spectra characterize only the stable, nonvolatile carbonaceous species in the zeolite after various contact times. Volatile reactants and products would desorb during the initial portion of the signal averaging interval.

3. Results

At all the reaction temperatures studied, a weak band at 2910 to 2940 cm^{-1} was observed in the C–H stretching region. The position of this band is consistent with an alkyl hydrocarbon C–H stretch rather than an aromatic hydrocarbon C–H stretch, which appears near 3050 cm^{-1} .

3.1. Reaction at 360 °C

Figure 1 shows spectra in the CC stretching and CH deformation region after various doses of methanol as the starting reactant. Spectrum a was measured from calcined H-MFI prior to reaction. The bands at 805 cm^{-1} and ~ 1000 to ~ 1250 cm^{-1} correspond to symmetric and asymmetric stretching vibrations, respectively, of T–O–T units in the zeolite framework, where T is either Si or Al [19,20]. The indicated doses correspond to the number of reagent molecules per MFI unit cell, calculated from the measured volume flow rate and the vapor pressure of methanol at 25 °C. Spectrum b corresponds to a methanol

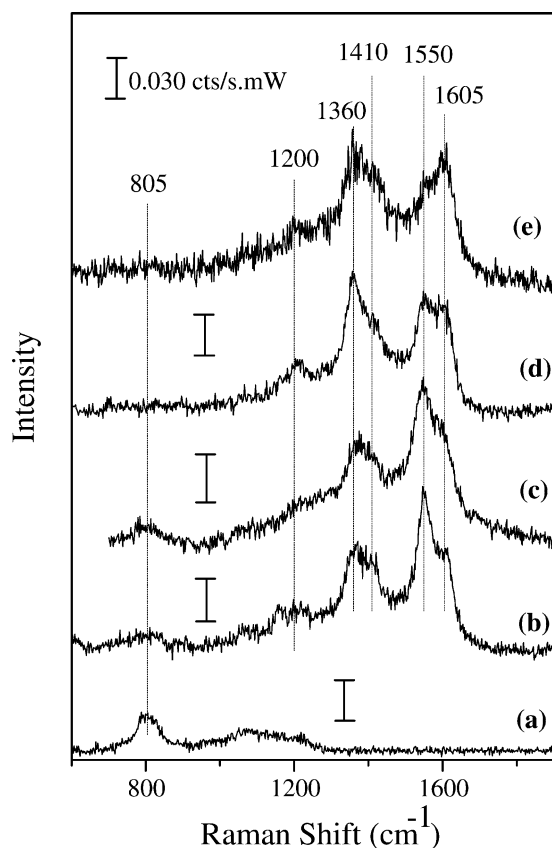


Fig. 1. UV Raman spectra of the reaction of methanol in zeolite H-MFI at 360 °C. (a) Calcined H-MFI before reaction. (b) After dosing 1.5 molecules per unit cell. (c) After dosing 1.5 molecules of CD_3OH per unit cell. (d) After dosing 7.5 molecules per unit cell. (e) After dosing 3600 molecules per unit cell.

dose of 1.5 molecules per unit cell. Following this dose, several strong bands appear between 1000 and 1700 cm^{-1} . There is no detectable signal from molecular methanol. To distinguish which of the overlapping bands from ~ 1300 to ~ 1450 cm^{-1} are due to CH deformations and which are due to CC stretches, experiments with deuterated methanol, CD_3OH , were also conducted. With the exception of the peak at ~ 1200 cm^{-1} , no significant deuterium shifts are observed for these bands (spectrum c), indicating that the bands are associated with CC stretching vibrations. This Raman spectrum (and all others reported here) is stable with time, at a constant temperature, following the methanol dose. When the methanol dose was increased to 7.5 molecules per unit cell, the relative intensity of the band at 1550 cm^{-1} decreased, and the bands near 1360 and 1605 cm^{-1} increased (spectrum d). The bands due to zeolite vibrations are no longer detectable due to strong absorption of the UV light by the retained hydrocarbons. Spectrum e was recorded after a large methanol dose corresponding to an additional 3600 molecules per unit cell. The intensity and band shape in the region 1300 to 1450 cm^{-1} and the intensity of the band near 1605 cm^{-1} remained essentially unchanged. The 1550 cm^{-1} band intensity decreased to the point where it was barely detectable.

Raman spectra measured during coke formation with dimethylether as the starting reagent are very similar to Fig. 1. At this reaction temperature, it has been shown that rapid equilibrium is achieved between methanol and dimethylether [2,3,21]. Therefore, at 360 °C, it does not matter which of the two compounds is the starting reagent, as the equilibrium between the two species is quickly attained before further reactions occur.

3.2. Reaction at 270 °C

Figure 2 shows spectra in the CC stretching and CH deformation region after low and high doses of methanol. Spectrum a was measured from calcined H-MFI prior to reaction. The activity of the catalyst for methanol conversion was significantly lower at 270 °C than 360 °C so that larger methanol doses were required to obtain detectable concentrations of retained hydrocarbons in the zeolite in Fig. 2 compared to Fig. 1. Spectrum b corresponds to a methanol dose of 30 molecules per unit cell. Following this dose, the strong bands between 1000 and 1700 cm^{-1} ,

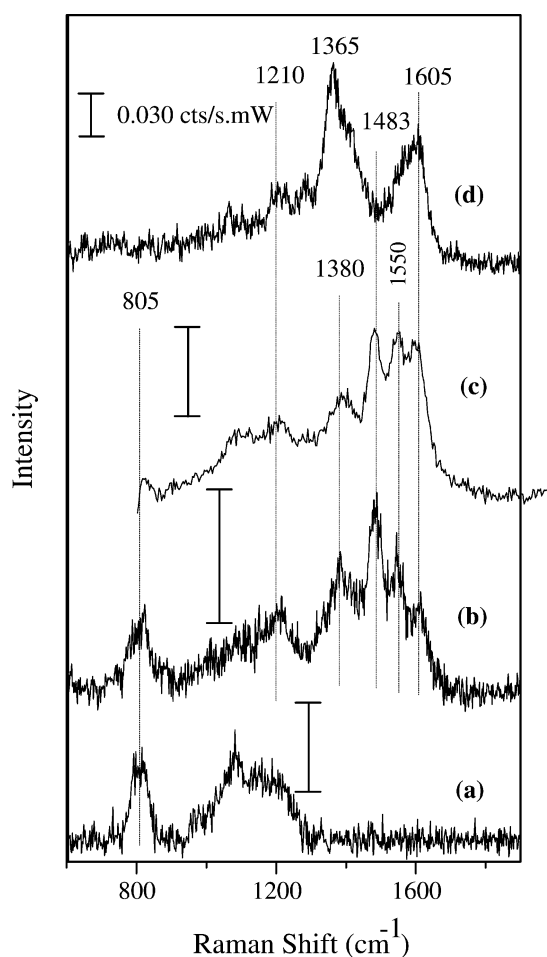


Fig. 2. UV Raman spectra of the reaction of methanol in zeolite H-MFI at 270 °C. (a) Calcined H-MFI before reaction. (b) After dosing 30 molecules per unit cell. (c) After dosing 30 molecules of CD_3OH per unit cell. (d) After dosing 720 molecules per unit cell.

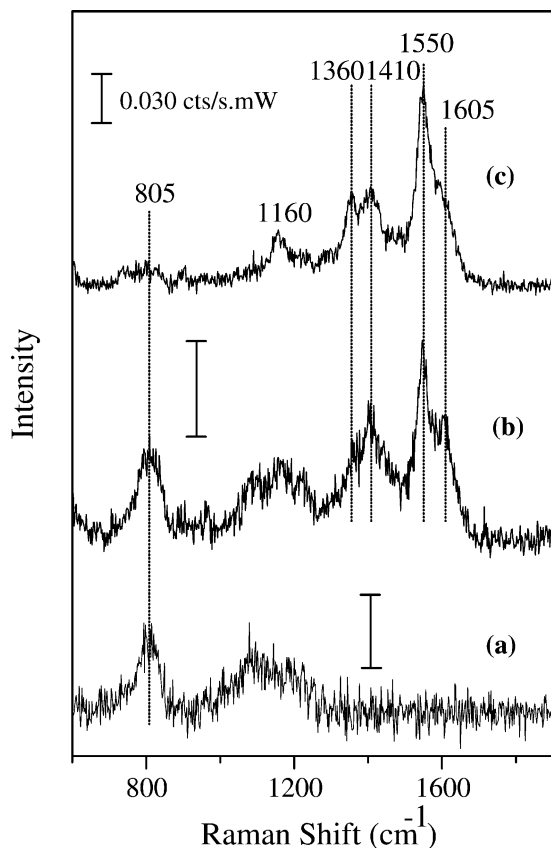


Fig. 3. UV Raman spectra of the reaction of methanol in zeolite H-MFI at 200 °C. (a) Calcined H-MFI before reaction. (b) After dosing 720 molecules per unit cell. (c) After dosing 4320 molecules per unit cell.

observed in Fig. 1 are also present in Fig. 2. However, an additional prominent band is observed at 1483 cm^{-1} . To distinguish which of the overlapping bands from ~ 1300 to ~ 1450 cm^{-1} are due to CH deformations and which are due to CC stretches, experiments with CD_3OH were also conducted. No significant deuterium shifts are observed for these bands (spectrum c), indicating that the bands are due to CC stretches. When the methanol dose was increased to 720 molecules per unit cell, the band at 1483 cm^{-1} disappeared, the intensity of the band at 1550 cm^{-1} decreased, and a band near 1365 cm^{-1} increased (spectrum d). The bands due to zeolite vibrations are no longer detectable.

3.3. Reaction at 200 °C

Figure 3 shows the UV Raman spectra measured after dosing methanol at 200 °C. Spectrum a was measured from calcined zeolite H-MFI before reaction. Spectrum b was measured after dosing 720 molecules per unit cell. The 805 cm^{-1} due to the zeolite is only very slightly attenuated, consistent with a small accumulation of hydrocarbon species and a low reactivity at this temperature. Spectrum c, measured after dosing 4320 molecules per unit cell, is very similar to the spectrum measured from the smallest methanol dose at 360 °C (Fig. 1). There is no detectable band at

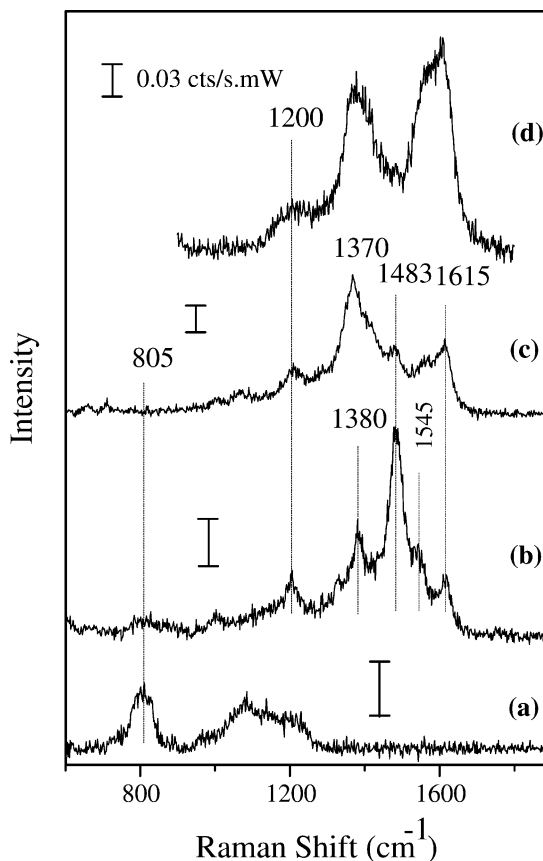


Fig. 4. UV Raman spectra of the reaction of dimethylether in zeolite H-MFI at 200 °C. (a) Calcined H-MFI before reaction. (b) After dosing 6 molecules per unit cell. (c) After dosing 2350 molecules per unit cell. (d) After heating the sample of spectrum (b) to 360 °C.

1483 cm^{-1} from methanol dosing at 200 °C. After dosing 6 molecules of dimethylether per unit cell at 200 °C, the 1483 cm^{-1} band is very pronounced (Fig. 4b). Spectrum b is very similar, but not identical, to the spectrum measured after dosing 30 molecules of methanol at 270 °C (Fig. 2b). The 1483 cm^{-1} peak decreases but remains detectable with additional dimethylether dosing up to 2350 molecules per unit cell (Fig. 4c). However, the species responsible for the band at 1483 cm^{-1} is thermally unstable. After the sample of Fig. 4b is heated to 360 °C the 1483 cm^{-1} band is no longer detectable, and the spectrum is similar to that obtained after high doses of methanol at 360 °C (Fig. 1e).

4. Discussion

4.1. Band assignments

The spectra shown in Figs. 1–4 are clearly from a complex mixture of chemical species. However, it is possible to make band assignments to general classes of molecular vibrations and chemical species. The Raman band assignments for vibrations in the region from 1000 to 1650 cm^{-1} are listed in Table 1. Except for the bands at 1483 cm^{-1} and

Table 1
Raman band assignments of retained hydrocarbons

Raman shift (cm^{-1})	Raman band assignments
1605–1615	Ring stretches of polyaromatic species
1360–1410	Ring stretches of polyaromatic species
1200–1210	C–C stretches of polyaromatic species
1545–1550	C=C stretches of conjugated olefins
1483	In-phase C=C stretch of cyclopentadienyl species

1545–1550 cm^{-1} , the vibrational features are assigned to CC or ring stretches of polyaromatic hydrocarbons. These assignments are based on the small deuterium isotope shifts observed with deuterated reagents and on a comparison to the UV Raman spectra of a series of polyaromatic compounds, naphthalene, phenanthrene, anthracene, fluorene, pyrene, pentacene, and coronene, shown in Fig. 5. UV Raman measurements for some of these compounds have been reported previously by Asher and co-workers [22,23]. The

polyaromatic compounds typically have strong bands in two spectral regions, ~ 1300 to $\sim 1450 \text{ cm}^{-1}$ and ~ 1600 to $\sim 1650 \text{ cm}^{-1}$, as do the spectra from retained hydrocarbons. Interestingly, the intensity in the spectral region 1600 to 1650 cm^{-1} is significantly higher than that in the region 1300 to 1450 cm^{-1} for the polyaromatic compounds with a two-dimensional, sheet-like topology (pyrene and coronene). By contrast, the intensity is more nearly equal in these two spectral regions for the polyaromatic compounds with chainlike topologies (phenanthrene, anthracene, and pentacene). The spectra measured from the retained hydrocarbons in H-MFI exhibit an intensity pattern more similar to that for the chainlike polyaromatic compounds. While this similarity is by no means a proof, a chainlike structure would be expected for retained hydrocarbons located in the zeolite pores, where the pore diameter is too small to accommodate the sheetlike topology. We also note that the spectra from retained hydrocarbons show subtle, but reproducible, changes

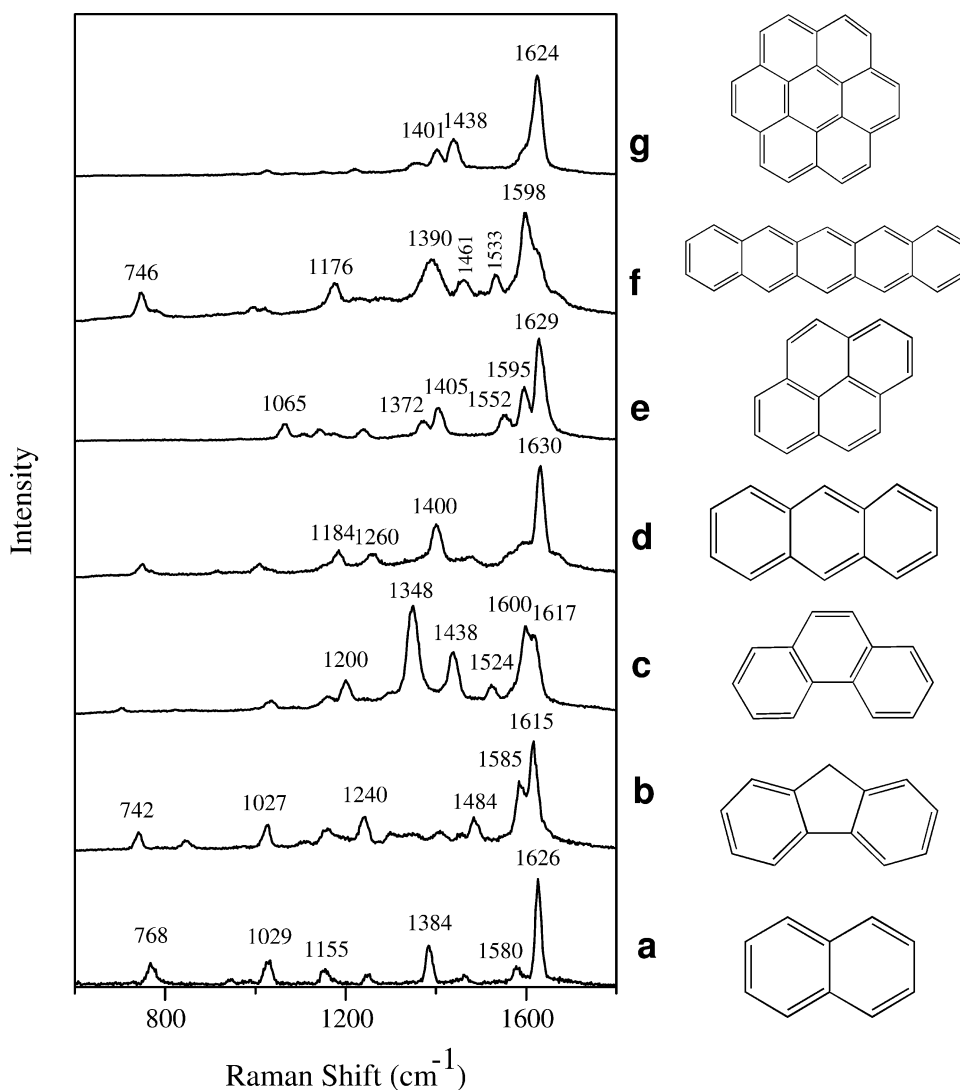


Fig. 5. UV Raman spectra of polyaromatic hydrocarbons. (a) Naphthalene. (b) Fluorene. (c) Phenanthrene. (d) Anthracene. (e) Pyrene. (f) Pentacene. (g) Coronene.

in the band positions and intensities with reaction temperature and the amount of reagent dosed into the zeolite. In the future it may be possible to obtain a more detailed picture of the polyaromatic hydrocarbon mixture from a larger data set by using chemometric procedures [24,25]. Finally, the only detectable C–H stretching band is at a Raman shift characteristic of alkyl C–H. Since the CH₂ scissor band at 1450 cm⁻¹, characteristic of *n*-paraffins, is not observed, it appears that the retained hydrocarbons detected by Raman spectroscopy are alkyl polyaromatic species. This assignment is consistent with the results of Schulz et al. [8,26], where primarily methylated aromatics were recovered by dissolving the coked zeolite catalyst.

None of the Raman spectra from the polyaromatic compounds shown in Fig. 5 show strong bands at 1483 cm⁻¹ or 1545–1550 cm⁻¹, which suggests that these bands arise from a different class of species. The Raman shifts in these two regions are too high for CC single bonds (~1060 cm⁻¹) and too low for isolated CC double bonds (1640–1660 cm⁻¹). Additionally, these bands cannot be associated with CH bending vibrations since they do not exhibit the expected deuterium isotope shift. An examination of collections of Raman spectroscopy data reveals a remarkable absence of strong bands in this region of Raman shifts [27,28]. The only plausible assignment for the band at 1545–1550 cm⁻¹ is the C=C double bond stretching vibration of conjugated olefins or polyenes [28]. The strong intensity of this band suggests that its Raman cross section is resonance-enhanced under 244-nm excitation. Indeed, polyenes with 4 to 10 double bonds exhibit strong optical absorption at 244 nm [29]. In polyenes the frequency of the conjugated C=C stretch varies systematically with chain length [30–32]. For example, the C=C stretching frequencies for C₂H₅OOC(CH=CH)_{*n*}COOC₂H₅ for *n* = 6, 7, 8 are 1562, 1550, and 1540 cm⁻¹, respectively [31]. A general empirical formula established by Baruya [30] indicates that a band at 1545–1550 cm⁻¹ is consistent with a polyene having six to eight double bonds. It is not clear why only this particular chain length of polyene is observed. Since polyenes with chain lengths both shorter and longer than 6–8 double bonds absorb at 244 nm, the observation of only one band does not seem to be caused by selective resonance enhancement of the Raman cross section. Possibly, polyenes with fewer double bonds may not be retained by the zeolite or they may react more quickly to form subsequent products at the temperatures used in our study. Polyenes with 9 to 10 double bonds would produce a Raman shift of 1530–1536 cm⁻¹, outside the range of the measured peak position from retained hydrocarbons; thus it appears that polyenes larger than 6 to 8 double bonds are not formed during the MTH process. The disappearance of the 1545–1550 cm⁻¹ band with increasing methanol or dimethylether dose suggests that polyenes are converted into aromatic and polyaromatic hydrocarbons.

The band at 1483 cm⁻¹ falls within a range which is possible for polyenes with ~25 double bonds. However, the behavior of this band with reaction temperature, the

level of reagent dose where it appears, and the absence of evidence for polyenes between 9 and 25 double bonds are not consistent with an assignment as a polyene. The low reaction temperatures and small reagent doses where the 1483 cm⁻¹ band appears are conditions where shorter polyenes should be more prevalent than longer polyenes. Moreover, we would expect longer polyenes to be formed in a distribution of chain lengths which would include polyenes between 9 and 25 double bonds. Such a distribution would produce a series of vibrational bands or a broad, indistinct vibrational band rather than the sharp, intense band observed in Figs. 2 and 4.

A class of compounds with a strong Raman band in this spectral region has the five-membered aromatic ring structure of cyclopentadiene (1500 cm⁻¹) [33,34], furan (1490 cm⁻¹) [35,36], pyrrole (1472 cm⁻¹) [35,36], and thiophene (1409 cm⁻¹) [36]. The band in this spectral region has been assigned to the in-phase stretch of the conjugated C=C bonds, which are a common structural element in the five-membered-ring aromatic compounds [34–40]. Therefore, we assign the 1483 cm⁻¹ observed in Figs. 2 and 4 to the in-phase stretch of the conjugated C=C bonds in an alkylated cyclopentadienyl species.

4.2. Reaction mechanism

The literature on coke formation in acidic zeolites is extensive, and there is general agreement on the overall mechanism (see, for example, [41]). The current results are most relevant to the previous work of Karge [4,12] and of Schulz and Wei [11]. Karge identified the presence of polyolefin species under methanol conversion conditions using in situ UV absorption. Schulz and Wei identified the aromatic products retained in the zeolite pores by liquid chromatography after dissolving the zeolite in hydrofluoric acid. Based on these results Schulz and Wei proposed a mechanism wherein conjugated olefins undergo cyclization via proton and hydride transfer reactions to form cyclopentadienyl species which subsequently form aromatic and, ultimately, polyaromatic hydrocarbons (Scheme 2). The central role of cyclopentadienyl species in coke formation at metal sites on supported noble metal catalysts for catalytic reforming has been known for some time (see, for example, [42–46]). The mechanism of Schulz and Wei is the first, to our knowledge, to propose the cyclopentadienyl species as a key intermediate for coke formation in a metal-free, zeolite catalyst. Our results strongly support this mechanism by providing specific spectroscopic evidence for polyolefins with chain lengths in the range from six to eight double bonds and for a cyclopentadienyl species in the hydrocarbons retained in the catalyst. To our knowledge this is the first time the adsorbed cyclopentadienyl structure has been detected in a heterogeneous catalyst.

Our results also suggest some additional subtleties in the chemistry that are not captured by the mechanism of Scheme 2. The spectra in Figs. 1–4 show that polyolefins,

in a specific range of chain lengths, and polyaromatic hydrocarbons are formed in the initial stages of reaction at all three temperatures studied. Scheme 2 also seems to require that polyolefins should all convert to polyaromatics over time. However, since the Raman spectra do not change with time in the absence of additional reagent, the retained hydrocarbon species produced at a particular temperature appear to be stable at that temperature. At the highest reagent doses, the intensity of the band 1545–1550 cm^{-1} generally decreases relative to those of the bands assigned to polyaromatic hydrocarbons. Polyolefins may simply be excluded as the zeolite pores are filled by polyaromatic species.

With added reagent the 1483 cm^{-1} band attributed to a cyclopentadienyl species decreases relative to the bands from polyaromatic species, presumably due to pore filling. The cyclopentadienyl species also disappears when the temperature is raised to 360 °C, an indication of its thermal instability. The absence of detectable cyclopentadienyl species during methanol reaction at 200 °C is not understood at this time. This species is readily produced from dimethylether at 200 °C or from methanol at 270 °C, and the spectra in Fig. 3 indicate that the polyolefin precursor is present in the catalyst during methanol reaction at 200 °C. One possible explanation is associated with the higher water content in the catalyst with methanol at 200 °C. If water increased the rate of the hydride transfer step associated with the ring expansion step in Scheme 2, then the cyclopentadienyl species may not build up to a detectable level. Another explanation is associated with the low activity of the catalyst with methanol compared to dimethylether at 200 °C. The amount of retained hydrocarbon produced by a large dose of methanol is much less than the amount produced by a small dose of dimethylether as judged by the attenuation of the zeolite bands (compare spectra 3b and 4b) and by changes in catalyst color. From the fact that the spectra in Figs. 3 and 4 show that different species are formed by the two reagents at 200 °C, it is also apparent that the methanol-to-dimethylether equilibrium was not established at this low reaction temperature. With this explanation the formation of the cyclopentadienyl species would depend on the concentration of hydrocarbon species adsorbed in the zeolite, consistent with the concept of the “carbon pool” mechanism for MTH put forth by Kolboe and Haw [47–49].

The discussion so far has focused on the mechanism of coke formation, the nonvolatile species that remained in the zeolite. The detection of cyclopentadiene species has implications for the MTH reaction mechanism as well. As alluded to in Scheme 1, some of the useful volatile components produced from the MTH reaction are alkylated benzenes that are small enough to diffuse out of the zeolite pores. Haw and co-workers have proposed that these alkylated benzenes are produced from an alkylated cyclopentadienyl cation which subsequently loses a proton to form alkylated cyclopentadiene [47]. The latter species converts to aromatic molecules through a series of isomerization reactions and hy-

dride and proton transfers. The alkylated cyclopentadiene species though not detected in the NMR experiments, is a possible reaction intermediate according to theoretical calculations [50]. The detection of cyclopentadienes in our experiments supports the mechanism proposed by Haw and co-workers.

It is interesting that the cyclopentenyl carbenium ion, which is very prominent in the NMR measurements reported by Haw [47], was not detected in the Raman spectra reported here. The UV Raman spectrum of the cyclopentenyl carbenium ion has been measured in separate experiments reported elsewhere [51], and the signals were found to be very weak. The absence of detectable cyclopentenyl carbenium ion in our measurements is likely due to the small acid site density in our H-MFI catalyst or the temperature at which measurements were performed. The density of carbenium ions is directly related to the acid site density in the zeolite H-MFI. The acid site density in the H-MFI catalyst used in our experiments is only 1/6 the density in the zeolites used by Haw. The relative populations of neutral diene and carbenium ion are related by the corresponding proton transfer equilibrium. At the elevated temperatures used in our experiments compared to Haw's (200 °C vs 25 °C), the equilibrium population of the neutral species may exceed that of the ion.

5. Conclusions

The formation and reaction of conjugated olefins, cyclopentadienyl species, and polyaromatic hydrocarbons retained in zeolite H-MFI during the MTH reaction were observed by UV Raman spectroscopy. Spectroscopic detection of these species strongly supports the reaction mechanism of Schulz and Wei as shown in Scheme 2 [11]. The pattern of peak intensities in the spectra of the polyaromatic hydrocarbons suggest that these species have a chain-like topology rather than a 2-D, sheet-like topology.

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