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Ultraviolet Raman spectroscopy characterization of coke formation in zeolites

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Abstract

Ultraviolet (UV) Raman spectroscopy has been used to characterize coke formation in ZSM-5 and USY zeolites under propene at temperatures from 300K to 773K. The strong fluorescence background always present with normal Raman spectra is completely avoided in UV Raman spectra. Three groups of UV Raman bands near ~ 1390, ~ 1600 and ~ 3000 cm^{-1} regions were detected for the two zeolites, and these bands varied significantly at different stages of coke formation. At room temperature, adsorbed propene was formed in the two zeolites and showed similar spectra. At elevated temperatures, the coke formation behavior in the two zeolites is quite different. For example, at 773K the coke species in ZSM-5 are mainly polyolefinic and aromatic species, but polyaromatic and pregraphite species are predominant in USY. The major portion of coke species formed in ZSM-5 can be removed even by He purging at 773K while the coke species in USY are very stable and can only be removed in O_2 flow at temperatures above 773K. The difference in coke formation in ZSM-5 and USY is likely due to the different pore structure and acidity of the two zeolites.

Keywords: UV Raman spectroscopy; Resonance Raman; Coke formation; Carbonaceous; USY; ZSM-5; Zeolites; Deactivation

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1. Introduction

A common problem with zeolite catalysts used in hydrocarbon conversion is deactivation by coke deposits which are formed from undesirable side reactions [1–3]. Coke formation and its impact on catalytic performance are important issues in catalysis and petroleum chemistry, however, coke structures and mechanism of coke formation are still not well understood. A technique capable of identifying chemically different coke species formed under working conditions would be a very powerful tool for understanding the mechanisms of coke formation and resultant deactivation.

Raman spectroscopy is potentially an ideal technique for studying the chemical structure of coke species in zeolite catalysts. Conventional Raman spectroscopy using visible wavelength excitation has been shown to be a good tool to study coke species in a few special systems [4–6], but for most samples it is difficult to get information on coke formation. The early stage of coke formation seems to be particularly difficult to study because the initial carbonaceous contaminants induce extremely strong fluorescence from the surface. We have attempted to

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measure conventional Raman spectra from a number of working catalysts used in fluid cracking catalysis (FCC) and reforming processes. Unfortunately we failed to detect any Raman signals because of strong fluorescence. In fact fluorescence from the catalyst surface often overwhelms the Raman signal, particularly when catalyst surface is contaminated by carbonaceous species.

Recently we set up a UV Raman spectroscopy instrument for catalysis and surface science studies. UV Raman spectroscopy was developed with an intent of avoiding fluorescence and enhancing the Raman intensity by the resonance effect. Our previous study [7] concerning the sulfated zirconia catalyst showed that UV Raman spectroscopy did avoid the fluorescence interference which always appears in conventional Raman spectra. In this report, we present UV Raman spectra of coke species formed in ZSM-5 and USY zeolites treated under propene at different temperatures to demonstrate the feasibility of UV Raman spectroscopy for coke studies and to identify the chemical nature of coke species in the zeolites. It will be seen that various types of coke species in the two zeolites are observed from the UV Raman spectra, and the surface fluorescence interference is again completely avoided in the UV Raman spectra.

2. Experimental

Raman spectra were recorded on a UV Raman spectrograph which was recently set up in this laboratory. A description of the instrument was given previously [7]. Briefly, a 257.2 nm line generated by frequency doubling the 514.5 nm line of a 12 W Ar^+ laser was used as the laser source for UV Raman scattering. The Raman scattered light from the sample was collected by an $AlMgF_2$ coated ellipsoidal reflector using a backscattering geometry, and focused into a single grating spectrograph through a notch filter. The spectrograph detector is an imaging multichannel photomultiplier tube (IPMT). The laser power delivered to the sample was kept below 5 mW in order to avoid thermal damage of the sample. Each spectrum was signal averaged for 10 min. The slit width was adjusted to 100 μm. The uncertainty in the absolute band positions is estimated to be ±10 cm^{-1}.

A Raman cell was specially designed for interfacing to the UV Raman spectrograph. Fig. 1 schematically shows the structure of this Raman cell. The cell is made of quartz and consists of an outer part and an inner part which are connected and sealed by an o-ring fitting. The outer part has a spherical bubble whose center is exactly located at the focus point of the collecting mirror in order to better collect the Raman scattering. A furnace tube is placed behind the spherical bubble. The inner part has a sample holder which is movable. The sample in the inner part can be moved to the furnace area for pretreatment and then positioned at the center of the spherical ball for UV Raman measurement without exposing the sample to air. The sample in the cell can be treated over a wide temperature range, 293–1200K, in the flow of reactants or carrier gas, He.

ZSM-5 and USY zeolites, were obtained from Amoco Co. Propene (> 99%) was chosen as the reactant for coke formation. Propene was introduced into the cell by either pulse or continuous flow in a carrier flow of He (99.99%). The samples were pressed into wafers for Raman

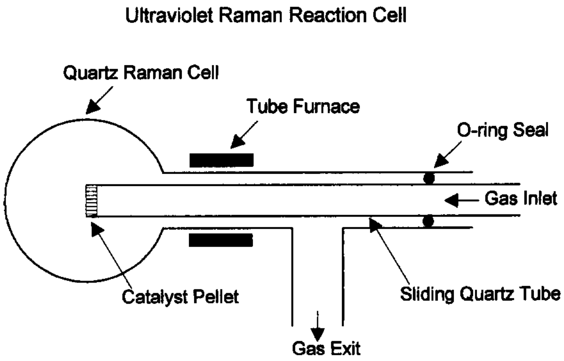

Fig. 1. Schematic description of Raman cell.

measurements. The sample wafer was put into the sample holder of the Raman cell, in which the sample was first treated at 773K in flowing O_2 (99.5%) for 2 h to remove contaminants and then cooled to room temperature for propene adsorption. The coke reaction was carried out by simply heating the sample to high temperatures under the flow of C_3H_6 + He.

3. Results and discussion

Fig. 2 shows the UV Raman spectra in the 200–2300 cm^{-1} region from ZSM-5 after exposure to a C_3H_6 pulse at room temperature and then treated in He and O_2 flows at high temperatures. All these spectra are nearly free of fluorescence background. A pulse of propene at room temperature produced two bands at 1390 and 1635 cm^{-1} (Fig. 2A) which are mainly due to adsorbed propene in ZSM-5. The two bands can be respectively assigned to the deformation mode of CH_x ($x = 2,3$) and the stretching mode of $C=C$ bonds in adsorbed olefinic species [8,9], i.e., adsorbed propene and conjugated propene species. After purging in He flow for 40 min (Fig. 2B) the intensities of both the bands decreased significantly indicating that some of the adsorbed propene was removed. This means that there are at least two types of adsorbed species, weakly and strongly adsorbed species. The remaining bands still possessed the olefinic characteristics of adsorbed propene. The weakly adsorbed species can be assigned to adsorbed propene and the strongly adsorbed species may be attributed to polymerized olefinic species originating from the adsorbed propene.

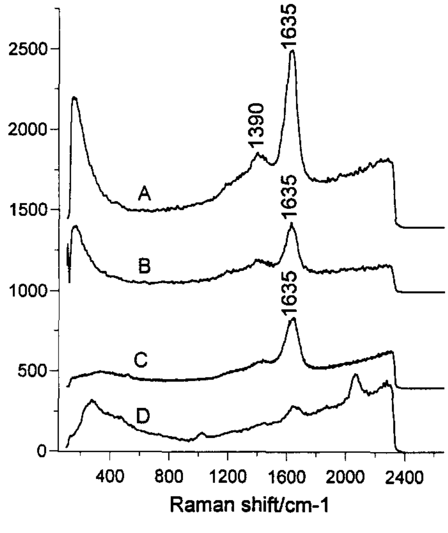

Fig. 2. UV Raman spectra of coke species formed in ZSM-5. (A) Pulse of C_3H_6 in He flow at room temperature; (B) subsequent purging in He flow at room temperature for 40 min; (C) heated at 773K in He flow for 1 h; (D) treated in O_2 flow at 773K for 2.5 h.

The strongly adsorbed species formed at room temperature are quite stable and can be detected even after heating to 773K in He flow as seen in Fig. 2C. It appears that the surface carbonaceous species formed at room temperature are still olefinic in character even after the heating at 773K since the spectrum remains similar from Fig. 2B to 2C. These coke species might be highly isolated so that no further reaction occurs. But these species can be removed easily by an oxidation at 773K (Fig. 2D) indicating that the carbonaceous species are still hydrogen rich and most likely olefinic species. A number of weak bands at ~ 440, ~ 1100, ~ 1610, ~ 2050 cm^{-1} emerge when the sample is calcined in pure O_2 as seen in Fig. 2D. The band at ~ 1610 cm^{-1} may be from trace amounts of residual carbonaceous species which are difficult to remove by oxidation at 773K. The bands at ~ 440 and 1100 cm^{-1} appear to be characteristic bands of ZSM-5. The band at ~ 2050 cm^{-1} could be assigned to combination modes of zeolite lattice vibrations and/or to some impurities.

Fig. 3 exhibits the UV Raman spectra in the 1200–3300 cm^{-1} region recorded from ZSM-5 treated in flowing C_3H_6 + He at room temperature and at 773K. Again, no fluorescence interference is observed in these spectra. Fig. 3A shows three groups of Raman bands at ~ 1390, ~ 1635, and ~ 2980 cm^{-1} (2970 and 2990 cm^{-1}) after exposing ZSM-5 to the flow of C_3H_6 + He at room temperature. The band at 1390 cm^{-1} is broad and actually composed of several bands indicating that there are several

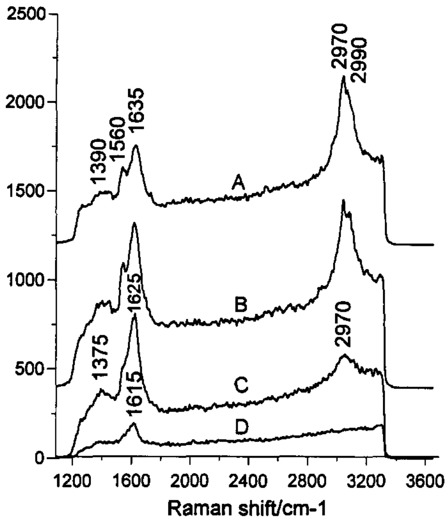

Fig. 3. UV Raman spectra of coke species formed in ZSM-5. (A) C_3H_6 + He flow at r.t. for 30 min.; (B) C_3H_6 + He flow at 773K for 1 h; (C) for 3 h, (D) He flow for 1 h.

types of adsorbed species. The band at 1635 cm^{-1} analogous to that in Fig. 2A is attributed to the C = C stretching vibration of olefinic species [8]. The strong bands in the 3000 cm^{-1} region can be assigned to the stretching vibrations of C–H bonds of adsorbed olefin [8–10]. In comparison with Fig. 2A, there is an additional band at 1560 cm^{-1} which could be due to conjugated olefinic species [8,10] which would be a possible precursor to aromatic species. The positions and the relative intensities of the bands in the 3000 cm^{-1} region can reveal more about the nature of the adsorbed hydrocarbon fragments as well as the quantity of hydrogen retained in the carbonaceous species. It is worthwhile to note that the C–H vibrations near 3000 cm^{-1} are usually difficult to detect by conventional Raman spectroscopy. UV Raman spectroscopy gives intense signals at this frequency. This appears to be an advantage of UV Raman spectroscopy that can make it a powerful tool for characterizing surface hydrocarbon species.

Fig. 3B presents the UV Raman spectrum taken after heating the sample in flowing propene and He at 773 K for 1 h. The spectral contour is similar to Fig. 3A. This result clearly demonstrates that the hydrocarbon species present at 773K remain similar to those formed at room temperature, but some fraction of them may transform into more stable species by, for example, polymerization and dehydrogenation.

After further heating in C_3H_6 + He flow at 773K for 3 h, the spectrum has changed considerably as seen in Fig. 3C. The relative intensities of the bands at 2970 and 2990 cm^{-1} decreased significantly while the band at 1635 cm^{-1} becomes narrower and shifts to 1625 cm^{-1}. The feature at 1560 cm^{-1} diminished and the multiband near 1390 cm^{-1} became sharper and shifted to 1375 cm^{-1} indicative of chemical changes in the coke species. The fact that the bands near 3000 cm^{-1} are weakened dramatically allow us to suggest that the adsorbed hydrocarbon species has been dehydrogenated. From the peak positions and intensities in both 1600 and 3000 cm^{-1} regions, these bands can be attributed to conjugated olefinic species which were dehydrogenated.

Fig. 3D is the spectrum recorded after purging in He flow at 773 K following the treatment corresponding to Fig. 3C. The bands near 3000 cm^{-1} are gone, and the band at 1625 cm^{-1} shifted to 1615 cm^{-1}. The band at 1375 cm^{-1} broadened and diminished. All these facts suggest that the fraction of adsorbed species containing C–H bonds was removed or transformed into some hydrogen – deficient species that produced a band at 1615 cm^{-1}. This band might be due to aromatic species, basically mono- or di-benzene species, since the band at 1615 cm^{-1} is still in the frequency region of benzene derivatives [8,10–12]. Based on the results shown in Fig. 2 and Fig. 3, it is clear that most of the adsorbed hydrocarbon species formed at room temperature or 773K in ZSM-5 can be removed by purging in flowing He at 773K, indicating that these species are mainly olefinic species. The small amount of strongly adsorbed species can be attributed to an aromatic species which does not yet correspond to a heavy coke. The spectra in Fig. 2 and Fig. 3 confirms that the coke species formed in ZSM-5 are mainly olefin and aromatic species, and formation of the aromatic species requires a hydrocarbon atmosphere at elevated temperatures

To explore different coke formation behavior, the reaction of propene in USY zeolite was also performed following a similar procedure as for ZSM-5. Fig. 4 displays the UV Raman spectra of coke species formed in USY zeolite under the flow of $C_3H_6 + He$ at room temperature, 573K, and 773K. Fig. 4A is the spectrum taken after propene was introduced into USY at room temperature. The spectrum is nearly identical to that for ZSM-5 (Fig. 3A). The bands at 1390, 1635, 2980 and 3010 cm^{-1} mainly due to adsorbed propene are detected. However, the spectrum from USY changed significantly when the sample was heated to higher temperatures. Fig. 4B shows that at 573K the band intensities near 3000 cm^{-1} have decreased dramatically while the band at 1635 cm^{-1} shifted to 1610 cm^{-1}. Apparently, some of the adsorbed hydrocarbon species desorb, and some of them convert into highly dehydrogenated species since the C–H band nearly vanishes. The striking shift of the band in the ~ 1600 cm^{-1} region is also indicative of chemical changes in the adsorbed hydrocarbon species. The spectrum is likely characteristic of aromatic species formed in USY [10–12]. This is a very different behavior from ZSM-5 for which the spectra recorded from room temperature to 773K are similar. For example, the bands in the ~ 3000 cm^{-1} region from ZSM-5 persist up to 773K. The results provide convincing evidence that dehydrogenation is more facile in USY than in ZSM-5, and that aromatic species are more easily produced in USY than in ZSM-5.

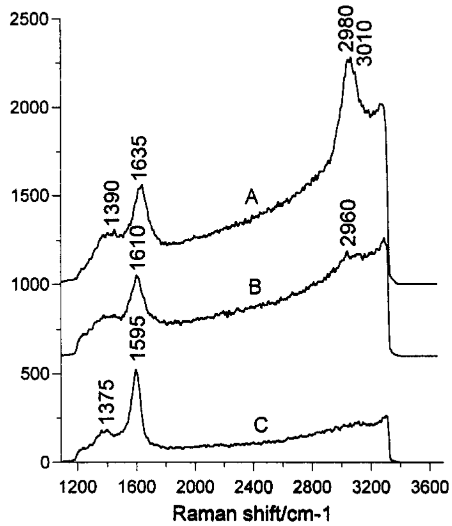

Fig. 4. UV Raman spectra of coke species formed in USY. (A) C_3H_6 + He flow at r.t. for 30 min.; (B) C_3H_6 + He flow at 573K for 1 h; (C) C_3H_6 + He flow at 773K for 1 h.

When the temperature is increased to 773K the spectrum from USY evolved further (Fig. 4C). The band in the ~ 3000 cm^{-1} region became very weak and broad. This suggests that the adsorbed hydrocarbon species experienced further dehydrogenation, and the remaining species contain much less hydrogen. Another important feature is that the band at 1610 cm^{-1} shifts further to 1595 cm^{-1}, and the band at 1390 cm^{-1} also shifts down to 1375 cm^{-1}. The spectrum is very close to the characteristic spectrum of polyaromatic species which usually have ring vibrations near or below 1600 cm^{-1} [10–15].

The spectrum of coke species in USY continued to change during a longer period of heating under flowing $C_3H_6 + He$ at 773K, unlike the case for ZSM-5 whose spectrum no longer changed obviously after 3 h. Fig. 5 shows the UV Raman spectra from USY after additional heating at 773K continued after the treatment for Fig. 4C. Fig. 5A is the spectrum of coke formed in $C_3H_6 + He$ flow at 773K after 5 h. By comparing the spectrum to Fig. 4C, the band at 1595 cm^{-1} shifts to 1585 cm^{-1} and becomes sharper which is characteristic of large particles of graphite-like species. The intensity of the band also increased enormously, indicating that a considerable amount of the pregraphite species formed after prolonged heating. The band at 1375 cm^{-1} shifted to 1365 cm^{-1} and also developed somewhat along with the increase of the band at 1585 cm^{-1}. The weak bands in the 3000 cm^{-1} region are barely detectable. The spectrum hardly changed when the reactant flow was switched to He flow at 773K, indicating that the coke species are inert and strongly

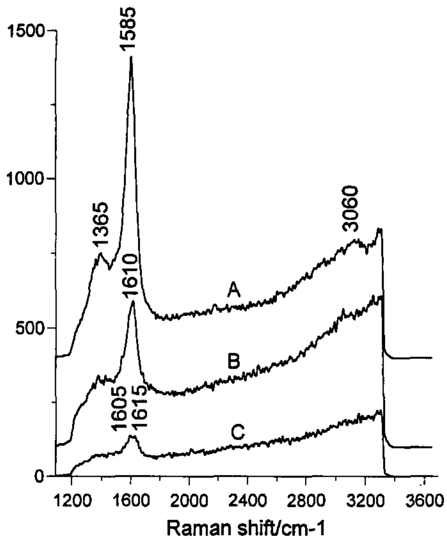

Fig. 5. (Continued from Fig. 4C). (A) C_3H_6 +He flow at 773K for 3 h; (B) O_2 flow at 773K for 1 h; (C) O_2 flow at 873K for 1 h.

adsorbed. This is quite different from the case of ZSM-5 where some of the adsorbed hydrocarbon species can be removed by He purging at 773K.

The spectrum changed when the sample was exposed to oxygen flow at 773K (Fig. 5B). The band intensity at 1585 cm^{-1} decreased significantly, and the band at 1365 cm^{-1} is also diminished. This surely suggests that most of the polyaromatic and pregraphite species can be removed by oxidation at 773K. However, there is still a considerable amount of coke remaining in the zeolite even after oxidation treatment for one hour as indicated by the band near 1610 cm^{-1}. This may signify that either the persistent coke species were more inert and stable chemically and/or the diffusion of oxygen to the coke species is kinetically limited. The remaining bands further diminished when the sample was heated to 873K in flowing O_2 (Fig. 5C), and at the same time the broad bands in the 3000–3100 cm^{-1} region disappeared completely. The bands at 1610 cm^{-1} split into two separate bands at 1605 and 1615 cm^{-1} and are still visible even after the sample was treated at 873K in O_2 for one hour. This means that the USY sample retains some coke contaminant that cannot be removed.

To compare the coke spectrum with that graphite, a UV Raman spectrum of a graphite sample was also measured. As shown in Fig. 6, the UV Raman spectrum of graphite gives a sharp and strong band at 1575 cm^{-1} which has been assigned to the E_{2g} carbon–carbon in-plane stretching vibration [16]. In the literature the band near 1575 cm^{-1} is referred as a G-band or E-band. Another band near 1360 cm^{-1} which often appears together with the 1575 cm^{-1} band has been attributed to defects present in the structural units of graphite, and has been designated the D-band [17]. The fact that no D-band at 1360 cm^{-1} was observed in Fig. 6 indicates that the graphite sample is composed of large crystals with a small concentration of defect edges [18]. The narrow band at 1575 cm^{-1} is also evidence of crystalline graphite since the Raman band becomes narrow as the graphite domain size increases. It is clear that the coke species formed in USY (Fig. 5A) is very similar to crystalline graphite (Fig. 6). The band at 1365 cm^{-1} in Fig. 4 and Fig. 5 may be due to the defects or edges of pregraphite species be-

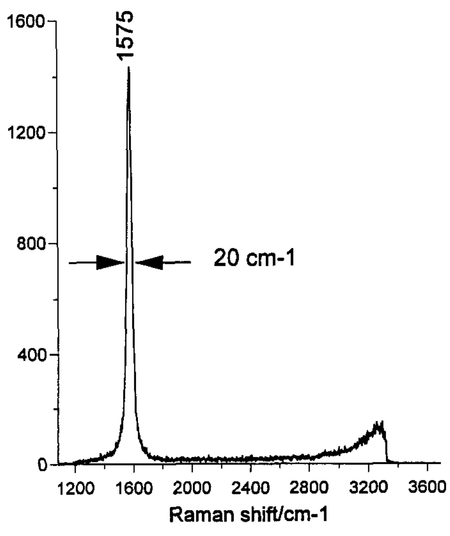

Fig. 6. UV Raman spectrum of graphite.

cause the size of the graphite-like species formed in USY would be limited by the pore structure. In contrast, the coke species formed in ZSM-5 (Fig. 3) is very different from graphite (Fig. 6).

From the above observations, there are a number of coke species formed in both the zeolites via the adsorption and reaction of propene. According to the UV Raman spectra the coke species can be categorized into the following groups, adsorbed olefinic and polyolefinic species (1390, ~ 1635, ~ 2980 cm^{-1}), aromatic species (~ 1385, 1610 cm^{-1}), polyaromatic species (1365–1385, 1595 cm^{-1}), and pregraphite species (1365, 1585 cm^{-1}). The adsorbed species at room temperature for the two zeolites are almost the same, i.e., mainly adsorbed propene and polyolefinic species (Fig. 3A and Fig. 4A), however the coke evolution in these two zeolites is different at elevated temperatures. The coke formation in ZSM-5 seems to start from adsorbed olefinic species and terminates at aromatic species, i.e.,

$$C_3H_6(a) \to C_3H_x(a) \to C_6H_y(a) \to nC_6H_z(a),$$

where $x \le 6$; $y \le 12$, $z \le 6$; n, $1 \sim 2$, and (a) denotes the adsorbed species. The coke formation in USY involves more steps and pregraphite species are derived eventually,

$$C_3H_6(a) \to C_3H_x(a) \to C_6H_y(a) \to mC_6H_z(a) \to \text{pregraphite},$$

where m can be greater than n because polyaromatic species were detected in USY. The n and m should depend on the size of channels and super cages in zeolites.

The different coke formation behaviors in ZSM-5 and USY can be explained in terms of the different pore structure and acidity of the two zeolites. The acidity of ZSM-5 is different from that of USY [19], so the extent of polymerization of olefinic species in the two zeolites should be different since the acidity affects the olefin polymerization which is one of the crucial steps in the growth of coke particulates. On the other hand, the pore size of USY is bigger than ZSM-5, and USY has super cage cavities which can accommodate a number of benzene rings. The reason why the coke formation stopped at small aromatic species in ZSM-5 may be mainly due to the small channel size which is not capable of housing big coke species [20]. The coke can gradually aggregate from polyaromatic species to pregraphite in USY (Fig. 4 and Fig. 5) because the super cage of USY can contain relatively large coke species.

Adsorbed aromatic species can be removed by He purging since they are still mobile and hydrogen rich. Once the coke species grow into polyaromatic and graphite-like species, it is too large to move, and is highly unsaturated in nature and strongly adsorbed. It is also reasonable that the pregraphite species are more difficult to oxidize than olefinic and aromatic species. The pregraphite species are likely to be the insoluble coke observed previously [19] and this kind of coke is irreversibly adsorbed and could be the main cause of zeolite deactivation.

UV Raman spectroscopy appears to be particularly sensitive to coke species containing olefin, conjugated olefin, aromatic, polyaromatic and graphite mainly owing to the resonance Raman effect [21,22]. The resonance phenomenon occurs because all these species have electronic absorption bands in the 200–300 nm region [23,24] near 250 nm the excitation wavelength of the laser we used in this study. On one hand resonance effects enhance the Raman sensitivity greatly, but on the other hand the resonance effect will change the relative intensities of different bands. It should be pointed out that the decrease in band intensity of the bands near ~ 3000 cm^{-1} (Fig. 3 and Fig. 4) may partly arise from a decrease in resonance enhancement.

4. Conclusion

UV Raman spectroscopy is a sensitive technique for characterizing different coke species formed in zeolites under hydrocarbon conversion processes. The fluorescence interference which obscures conventional Raman spectra using visible wavelength excitation has been totally avoided in the UV Raman spectra. The high sensitivity of UV Raman spectroscopy to coke species is partly due to the resonance effect. UV Raman spectra show that the coke species and coke formation mechanism in ZSM-5 and USY are different. There are adsorbed olefinic and aromatic species detected for ZSM-5 and these species can be removed by He purging at 773K, while polyaromatic and graphite-like species are dominant in USY. The pregraphite species in USY are very stable and can not be entirely removed even by oxidation at 773K. The difference in coke formation in ZSM-5 and USY can be attributed to the different pore structure and acidity of the two zeolites, especially, the pore structure of ZSM-5 plays a major role in prohibiting the formation of polyaromatic and pregraphite species.

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