The effect of oxygen on the aromatization of methane over the Mo/HZSM-5 catalyst

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The aromatization of methane over a Mo/HZSM-5 catalyst was carried out in the presence of oxygen. It is shown that the addition of a small amount of oxygen is beneficial to improve the durability of the catalyst. UV-Raman spectra disclose that the carbonaceous deposits formed on the HZSM-5 are mainly polyolefinic and aromatic, while that on the Mo/HZSM-5 is mainly polyaromatic. The small amount of O_2 added may partly remove the coke deposits on the active sites and keep the catalyst as MoO_xC_y/HZSM-5, thus resulting in an improvement of the catalytic performance of the Mo/HZSM-5 catalyst.

Keywords: methane, oxygen, aromatization, Mo/HZSM-5, coke formation, UV-Raman spectroscopy

1. Introduction

Extensive studies have been done on the reaction of methane over Mo/HZSM-5, which was found to be a good catalyst for the aromatization of methane in the absence of oxygen in 1993 [1]. But this catalyst generally shows low conversion of methane and short lifetime. To improve the catalytic properties, several promoters were added into the Mo/HZSM-5 [2,3], or a small amount of higher hydrocarbons was introduced into the gas feed [4]. Recently, it was reported that the mixing of CO or CO_2 with CH_4 could greatly retard the deactivation of the catalyst [5].

Most work on aromatization of methane on the Mo/HZSM-5 catalyst was performed in the absence of an oxidant, because it is commonly believed that the addition of an oxidant is harmful to the formation of benzene. Nevertheless, several groups observed that the performance of Mo_2C/HZSM-5 was partly improved after a pretreatment with O_2 [6]. Moreover, under oxygen-free conditions, the production of benzene was accompanied by the formation of CO at the early stage of the aromatization, and CO had been detected even when benzene reached its maximum production rate. So, it is reasonable to assume that oxygen may be involved in the aromatization, or the active phase of the catalyst contains oxygen. It has been reported [7] that the following reactions between MoO_3 and hydrocarbons proceed at higher temperatures:

$$MoO_3 \underset{O_2}{\overset{R–H}{\rightleftharpoons}} MoO_xC_y \underset{O_2}{\overset{R–H}{\rightleftharpoons}} Mo_2C \tag{1}$$

(R–H represented as C_3 or C_4 hydrocarbons.)

Hydrogenolysis of hydrocarbons takes place easily on Mo_2C, while introduction of oxygen into Mo_2C changes its catalytic performance [7,8]. So, Mo_2C modified by oxygen (MoO_xC_y) and supported on HZSM-5 might give rise to an active phase for the aromatization reaction of CH_4. If this is true, then the addition of a suitable amount of oxygen into the reactants may not only depress coke formation, but also be favorable for formation of the active phase, MoO_xC_y, and as a result, the durability of the catalyst should be improved. In this paper, the effect of oxygen on the aromatization of methane was investigated. Coke formation is one of the main reasons for the deactivation of the catalyst. Because UV-Raman spectroscopy is highly sensitive to carbonaceous deposit resulting from its effective avoiding of fluorescence and the resonance Raman effect from the coke deposition [9,10], the coke species formed on the Mo/HZSM-5 and HZSM-5 at different reaction stages were studied by UV-Raman spectroscopy.

2. Experimental

The Mo/HZSM-5 catalyst was prepared by incipient wetness impregnation of HZSM-5 (Si/Al = 25, Nankai University) with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, followed by drying at 393 K for 12 h, and calcination at 773 K in air for 5 h.

The aromatization of methane was carried out under ambient pressure in a fixed-bed, continuous-flow quartz microreactor (8 mm i.d.), in which 0.3 g of catalyst granules (20–40 mesh) was placed. The catalyst sample was heated at a rate of 5 K/min to the reaction temperature in Ar flow and kept at the reaction temperature for 0.5 h. Then the gas feed, a mixture of CH_4, O_2 and Ar, was introduced into the reactor with a flow rate of 15 ml/min. Ar and CH_4 were further purified by deoxidizers before use.

The products were analyzed by an on-line gas chromatograph (102G, Shanghai) equipped with TCD, using one column packed with 601-carbon molecular sieve for

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separating CO, CO_2, Ar/O_2, CH_4 and H_2, and another column with SE-30 for separating C_6H_6, C_7H_8 and $C_{10}H_8$. At the same time another chromatograph (102G, Shanghai) equipped with FID was used with a SiO_2 column for separating CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. The conversion of CH_4 and the selectivity for products were calculated on the carbon basis (coke was not taken into account).

UV-Raman spectra were recorded on a home-made spectrograph, which consisted of an intracavity frequency-doubled Ar^+ ion laser (Coherent, Innova 300 FRED), using a line at 257 nm as the excitation source, a three-grating spectrometer (Spex Triplemate 1877D) and a CCD detector (EG&G Co., Ltd.). The resolution of the Raman system was about 1.5 cm^{-1} (at 257 nm excitation) and the power of the 257 nm laser line at the sample was kept at $\sim$2 mW to avoid overheating of the sample.

The sample was pressed into a wafer for recording the UV-Raman spectra. The sample wafer of the used Mo/HZSM-5 catalyst was rotated to decrease the reaction or the decomposition of the sample irradiated by the UV laser. To study the coke formation on the catalysts under reaction conditions, a quartz reaction cell was designed specially for the *in situ* study.

3. Results and discussion

Figure 1 shows the effect of O_2 on the aromatization of methane over a 3 wt% Mo/HZSM-5 catalyst at 973 K. For O_2/CH_4 molar ratios below 6.5×10^{-3} (figure 1(a), curves (A)–(D)), the main products were aromatics, C_2H_4, C_2H_6, CO and small amounts of C_3H_6 and C_3H_8. CO was the only detectable oxygen-containing product. The conversion of methane decreased with the time on stream, and the addition of O_2 (figure 1(a), curves (B)–(D)) caused the deactivation of the catalyst to become relatively slower as compared to that without O_2 (figure 1(a), curve (A)). Furthermore, the higher the amount of O_2 in the feed gas, the slower the decrease in the conversion of methane with the time on stream. It is interesting to note that with an increase of the O_2/CH_4 molar ratio, the yield of aromatics remained almost unchanged, though the selectivity towards aromatics decreased due to the increase of the selectivity to CO (figure 1(b)). At the same time, this result implies that aromatization of CH_4 and the partial oxidation of CH_4 by the oxidant into syngas can coexist under certain conditions. This can be related to the result reported by York et al. [11], who showed that Mo_2C is a good catalyst for the partial oxidation of CH_4 by an oxidant into syngas. When the O_2/CH_4 molar ratio was increased to 6.5×10^{-3} (figure 1(a), curves (E) and (F)), the conversion of CH_4 decreased dramatically and the product distribution changed correspondingly (figure 1(b)). CO_x was the predominant product besides 3–5% of C_2H_4 and C_2H_6. This shows that the reaction behaves more like combustion or oxidative coupling of methane.

As shown in figure 2, the effect of O_2 on the reaction at 1023 and 1073 K was basically similar to that at 973 K. When no oxygen was added, the yield of aromatics de-

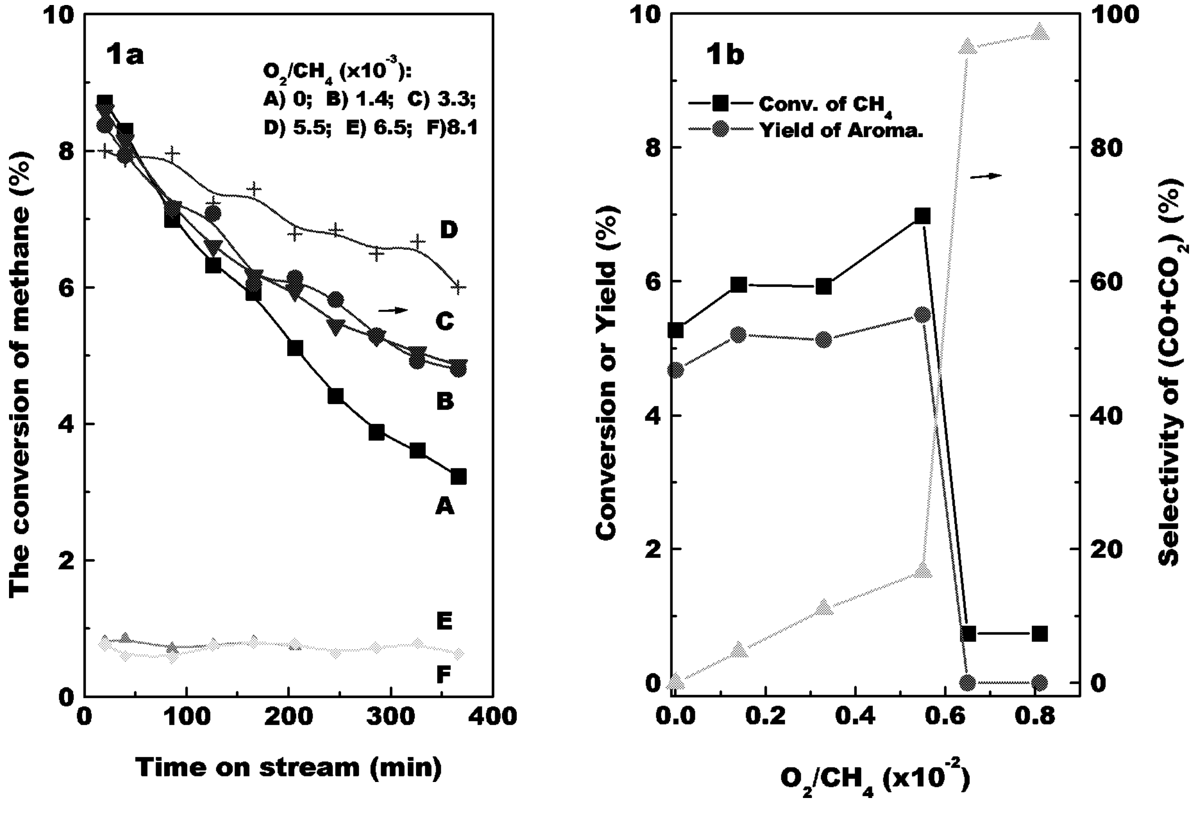

Figure 1. Effect of O_2 on the aromatization of CH_4 over a 3 wt% Mo/HZSM-5 catalyst at 973 K.

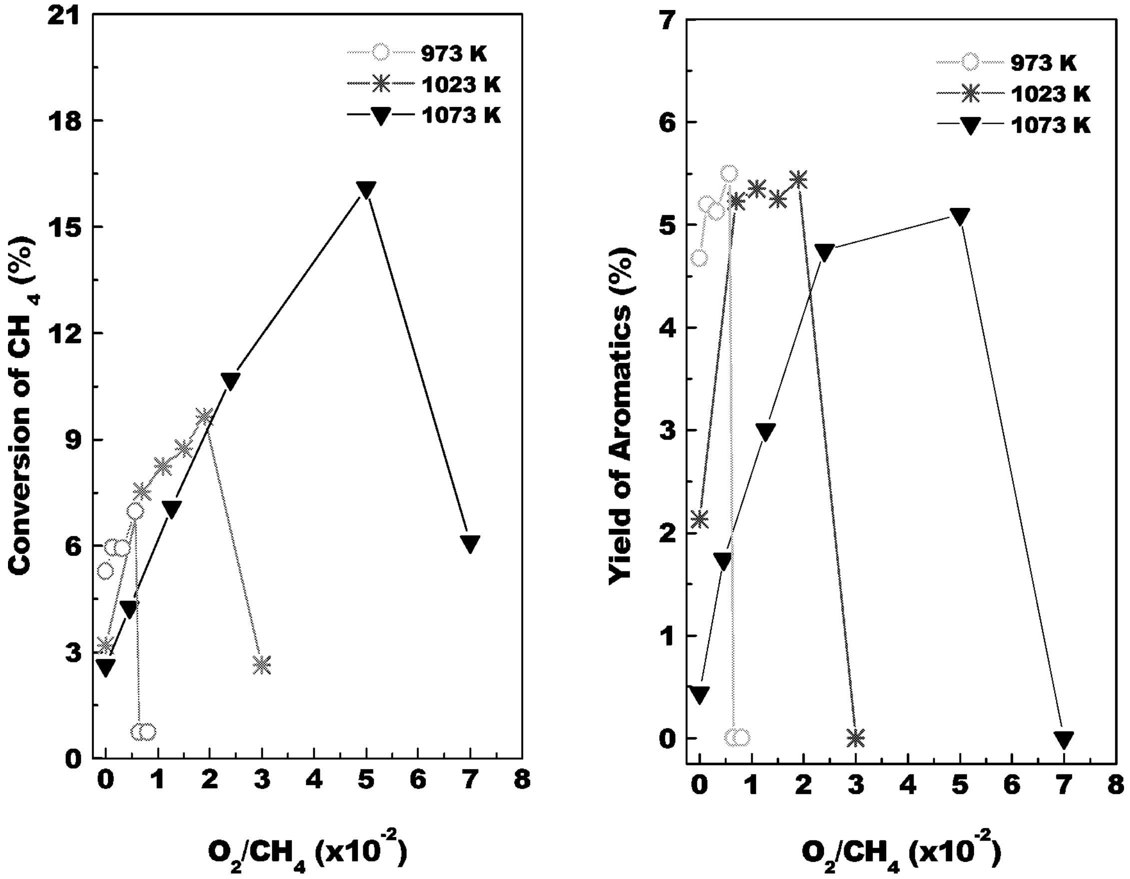

Figure 2. Effect of O_2 on the aromatization of CH_4 over a 3 wt% Mo/HZSM-5 catalyst at different temperatures. Data are taken at 200 min on stream.

creased with the rising of the reaction temperature. This seems to be conflicting with the expectation, since the yield of aromatics should be increased with the reaction temperature according to the calculation from thermodynamics. However, with the addition of a small amount of O_2, at the beginning of the aromatization reaction, the yield of aromatics increased with the increase of the reaction temperature. So, the observed lower yield of aromatics at higher temperatures under conditions without oxygen obviously resulted from the faster deactivation of the catalyst. It was also noted that the yield of aromatics was improved with the addition of O_2. This positive effect was more significant at higher reaction temperatures, but the effect of O_2 was only effective within certain limits. When the amount of O_2 was increased up to certain values (the O_2/CH_4 molar ratio was about 7×10^{-3} at 1023 K and 2.4×10^{-2} for 1073 K), the yield of aromatics almost kept stable with further increase of the concentration of O_2. The range of O_2/CH_4 for the "stable" yield of aromatics was wider for the higher reaction temperatures.

The above results demonstrate clearly that the addition of a suitable amount of oxygen is beneficial to improving the stability of the activity for the aromatization of CH_4 over Mo/HZSM-5. However, there is a critical value for the concentration of oxygen, which is found to be increased with the rising reaction temperature. If the concentration of oxygen is below the critical value, then the aromatization reaction proceeds, and when the concentration of O_2 is higher than the critical value, total oxidation and oxidative coupling of methane become predominant. Furthermore, below this threshold, the concentration of O_2 could change in a certain range with the improvement of the durability of the catalyst, without remarkable change in the aromatization of CH_4.

According to the literature [12,13], 10–30% of the converted methane is usually transformed into coke deposits on the Mo/HZSM-5 catalyst at 973 K. The present results show that the addition of even ~0.5% of oxygen at 973 K could improve the stability of the reaction effectively. The used catalysts with an O_2/CH_4 molar ratio below the critical value were all black in color, which indicates that there is still a certain amount of coke deposited on the catalyst, although the lifetime of the catalyst was remarkably improved. In addition, in a certain O_2/CH_4 molar ratio range, the yield of aromatics did not change with the O_2/CH_4 molar ratio. So the depletion of the coke formed during the reaction can only explain part of these results. We consider that another important factor is related to the active phase of the catalyst.

As shown in formula (1), higher temperatures and longer reaction time will increase the degree of the carburization of MoO_3 under a hydrocarbon atmosphere, while the resulting Mo_2C can be gradually oxidized by O_2 above 623 K [7]. During the aromatization of CH_4 over MoO_3/HZSM-5, the

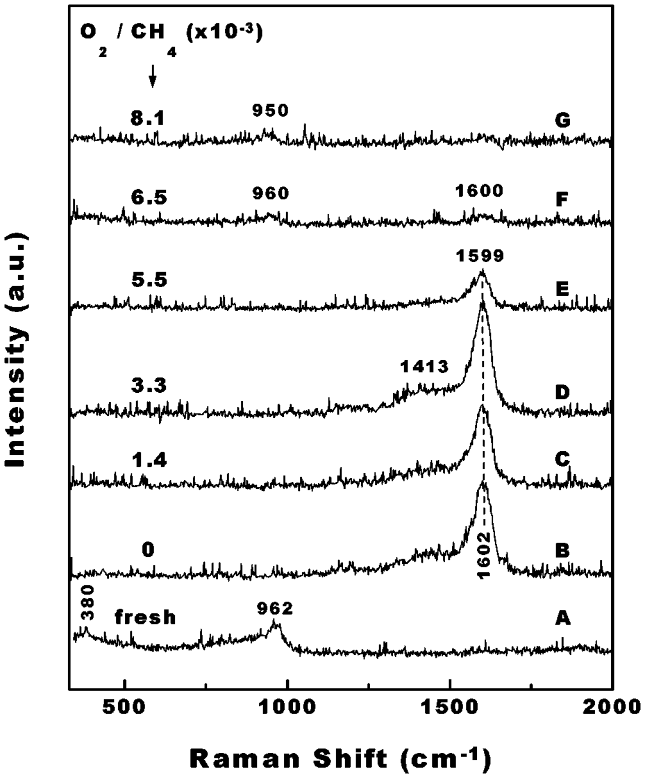

Figure 3. UV-Raman spectra of the fresh Mo/HZSM-5 and of the coke species formed on the catalysts after the reaction with different O_2/CH_4 molar ratios.

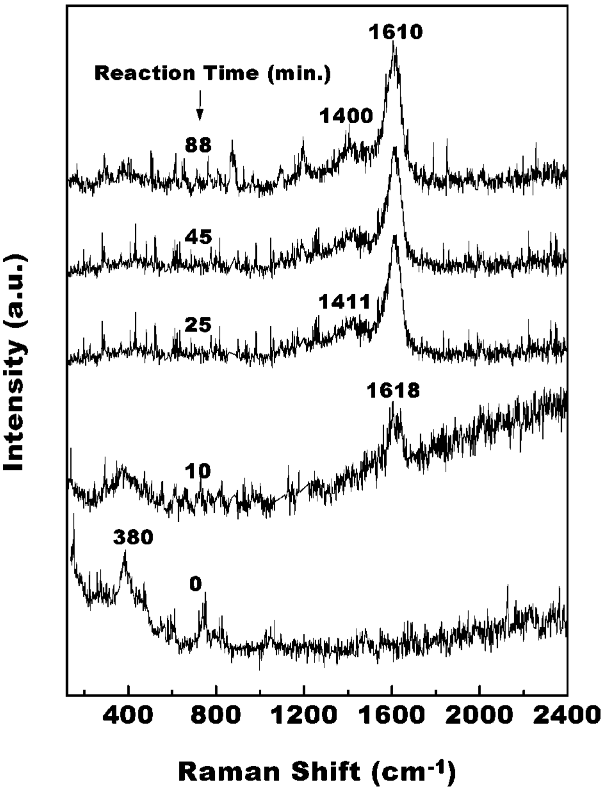

Figure 4. UV-Raman spectra of coke species formed on HZSM-5 during the aromatization of CH_4 in the absence of O_2.

existence of $Mo^{\delta+}$ ($0 < \delta < 4$) disclosed by XPS [13,14] led us to assume that the same relationship (1) existed during the reaction of CH_4 with MoO_3. So for the aromatization reaction of CH_4, it can be assumed that at the very beginning of aromatization, MoO_3 is partially carburized, the formed intermediate phase can be represented as MoO_xC_y. At the latter stage, with the proceeding of the reaction, MoO_xC_y becomes deeply carburized and transformed into more carbon-enriched MoO_xC_y, and finally Mo_2C. Correlating these with the performance of the catalyst, it is evident that deeply carburized MoO_3/HZSM-5 is not a very efficient active phase for the production of aromatics. However, the deeply carburized MoO_3/HZSM-5 or the carbon-enriched MoO_xC_y/HZSM-5 can be partially oxidized by the added O_2, and accordingly, the catalyst can be kept in the state of MoO_xC_y/HZSM-5 for a longer time than without O_2, and the durability of the catalyst is improved. At the same time, because a rather low amount of MoO_3 is loaded on HZSM-5, the small amount of O_2 would be enough to keep the Mo species in the MoO_xC_y/HZSM-5 state.

Figure 3 exhibits the UV-Raman spectra of fresh and used MoO_3/HZSM-5 catalysts (the samples are the same as those in figure 1) which were recorded in air at room temperature. For the fresh MoO_3/HZSM-5, two bands at 960 and ~380 cm^{-1} are observed (figure 3(A)), and these bands are usually assigned to the stretching vibration of Mo=O of dispersed MoO_3 [15] and the characteristic band of ZSM-5, respectively. For the used catalysts operated with O_2/CH_4 molar ratio lower than 6.5×10^{-3} (figure 3 (B)–(G)), there are bands at ~1600 cm^{-1} which are readily attributed to the coke species, and accompanied by a shoulder at ~1410 cm^{-1}, which is assigned to the C–H bending vibration of the coke species. The bands at ~960 cm^{-1} are undetectable in figure 3 (B)–(E), which is probably due to the reduction of MoO_3 under the reaction conditions. In the cases with O_2/CH_4 higher than 6.5×10^{-3} (figure 3 (F) and (G)), when total oxidation was predominant, the bands at ~950 cm^{-1} appear again. These results reveal clearly that with the increase of the O_2/CH_4 molar ratio, the amount of the coke deposited on the catalyst was reduced, and meanwhile the catalyst was gradually reoxidized.

Figure 4 shows the UV-Raman spectra of HZSM-5 after the aromatization of CH_4, where the weak and sharp bands in the spectrum are plasma lines of the laser. The characteristic band at 380 cm^{-1} was observed for the fresh HZSM-5. This band was weakened when methane was introduced. Meanwhile, the bands due to coke species at ~1410 and ~1610 cm^{-1} appear with the reaction time. The appearance of these two bands indicates that the coke species are still rich in hydrogen, although the reaction temperature was as high as 973 K. The band of the coke species formed at the early stage is at 1618 cm^{-1}, and the frequency shifts gradually down to 1610 cm^{-1} with the coke formation time on stream. But the frequency of this band for HZSM-5 is always higher than that for Mo/HZSM-5 (figure 3), and this indicates that the coke species deposited on the HZSM-5 catalyst are more hydrogen-rich species than that on Mo/HZSM-5.

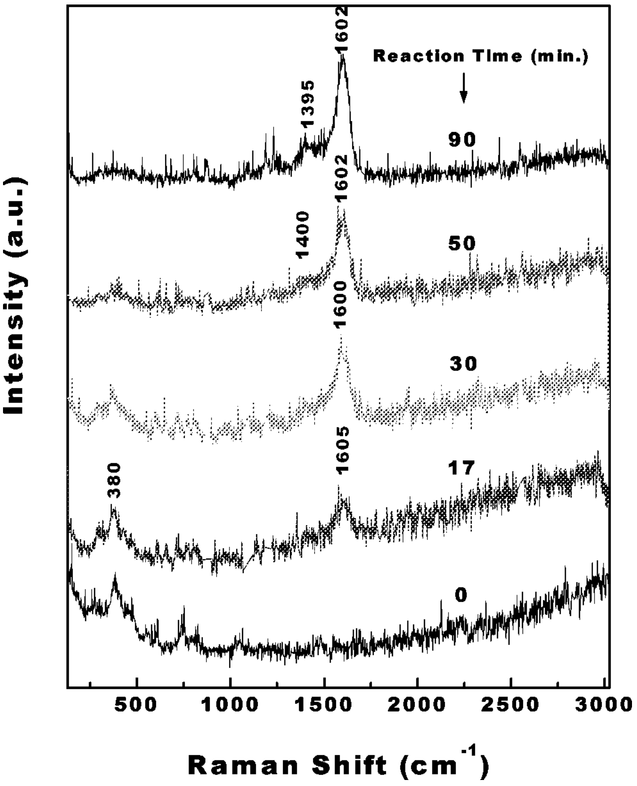

Figure 5. UV-Raman spectra of coke species formed on HZSM-5 during the aromatization of CH_4 in the presence of O_2.

Figure 5 gives the UV-Raman spectra of the coke species formed on HZSM-5 at 973 K in the presence of O_2. The typical band of HZSM-5 at 380 cm^{-1} is observed in all the spectra, while the frequency of the band due to coke species is $\sim$1600 cm^{-1}, which was nearly the same as that of the coke species deposited on the Mo/HZSM-5.

The band due to coke species at 1610–1620 cm^{-1} can be assigned to either aromatic species or polyolefinic species, and the band at 1600 cm^{-1} to polyaromatic species [9,10]. Comparing the coke deposits on HZSM-5 with that on Mo/HZSM-5, it can be found that the degree of the polymerization and cyclization of the coke species on the Mo/HZSM-5 was higher. The effect of the length of the reaction time on the coke species can be excluded, because a separate experiment showed that the frequencies of the bands of coke species deposited on Mo/HZSM-5 hardly changed after 60 min on stream. Thus, the detected polyaromatic coke deposit is probably caused by the Mo species, so the Mo species not only plays an important role in the activation of methane, which lead to the increase of the conversion as suggested by many research groups, but also causes the intermediates to cyclize and aromatize more easily. The similarity of the coke species on the HZSM-5 in the presence of O_2 to that on the Mo/HZSM-5 leads us to the conclusion that the most polyolefinic species either on HZSM-5 or on Mo/HZSM-5 are relatively easy to be oxidized into CO_x as compared to the aromatic species, so the bands of aromatic species left behind are more pronounced after the oxidation.

4. Conclusions

For the Mo/HZSM-5 catalyst, under certain conditions, the aromatization of methane and the partial oxidation of CH_4 into syngas can coexist in the presence of a small amount of O_2. The O_2 added could maintain the active phase possibly (MoO_xC_y/HZSM-5) and remove part of the coke species, which results in the improvement of the lifetime of the catalyst. The coke species on the HZSM-5 are of polyolefinic and aromatic in nature, while those on the Mo/HZSM-5, are moderately polymerized aromatic species.

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