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Coke formation during the methanol conversion to olefins in zeolites studied by UV Raman spectroscopy

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Abstract

Coke formation on/in ZSM-5, USY and SAPO-34 zeolites was investigated during the methanol conversion to olefins at temperatures from 298 to 773 K using ultraviolet (UV) Raman spectroscopy. The fluorescence interference that usually obscures the Raman spectra of zeolites in the conventional Raman spectroscopy, particularly for coked catalysts, can be successfully avoided in the UV Raman spectroscopy. Raman spectra are almost the same for adsorbed methanol on the three zeolites at room temperature. However, the Raman spectra of the surface species formed at elevated temperatures are quite different for the three zeolites. Coke species formed in/on SAPO-34 are mainly polyolefinic species, and in/on ZSM-5 are some aromatic species, but polyaromatic or substituted aromatic species are predominant in USY at high temperatures. Most of the coke species can be removed after a treatment with O_2 at 773 K, while some small amount of coke species always remains in these zeolites, particularly for USY. The main reason for the different behavior of coke formation in the three zeolites could be attributed to the different pore structures of the zeolites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Coke formation; UV Raman spectroscopy; Methanol conversion; SAPO-34; Zeolites

1. Introduction

In recent years, the conversion of methanol to lower alkenes has received great attention [1]. A number of zeolites have been used as catalysts for the reaction, such as ZSM-5 [2], modified USY [3] and SAPO-34 [4] zeolites, etc. SAPO-34 has been found to be the most effective catalyst for the reaction, but the deactivation due to the build-up of surface carbonaceous residues is still a problem. The carbonaceous or coke species block the access of reactant molecules to the catalytic sites, and they have to be removed by combustion with oxygen to regenerate the catalyst [5]. The deposition of coke on/in zeolite catalysts in hydrocarbon conversions has been extensively investigated [6–21]. Various techniques have been employed to characterize the coke species on the catalysts, e.g., IR [8,9], MS [10,11], conventional Raman spectroscopy [12], NMR [13], EPR [14–16] and so on [17,18]. Guisnet and coworkers [19–21] proposed modes of coking and of deactivation of zeolites during *n*-heptane cracking. They considered that

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the pore structure of the zeolite has a great influence on the coking rate and coking selectivity.

Despite many attempts to elucidate the formation and the structure of the coke deposited on catalysts, this matter is still not well understood. Recently developed ultraviolet (UV) Raman spectroscopy shows great advantages over the conventional techniques for the characterization of coke deposits. Not only does it increase the intensity of the Raman signal but also avoids the fluorescence interference, so that it is possible to identify the type of coke species and the deactivation mechanism by using UV Raman spectroscopy.

In this paper, we present the UV Raman spectra of coke species formed during the methanol conversion to alkenes on ZSM-5, USY and SAPO-34 zeolites at various temperatures. The UV Raman spectra can definitely characterize the different coke species formed in these zeolites under reaction conditions. It turns out that the formation of different kinds of coke species mainly depends on the pore structure of the zeolites.

2. Experimental

Raman spectra were obtained using the UV laser source of 257.25 nm as the excitation source generated by frequency doubling of the 514.5 nm line of an argon ion laser. The scattered Raman light was collected and focused on the entrance slit through an ellipsoidal reflector, and detected with a liquid nitrogen-cooled charge-couple detector (CCD). The laser power reaching the sample was kept below 5 mW in order to avoid thermal damage of the sample. All spectra represent accumulations for up to 5 min. The spectral resolution is estimated to be 2.0 cm^{-1}.

ZSM-5 (Si:Al = 25) and USY (Si:Al = 4.2) zeolites were obtained from Nankai University and Amoco Co., respectively. The SAPO-34 molecular sieve was synthesized using pseudoboehmite, phosphoric acid and silica sol as sources of aluminum, phosphorus and silicon, respectively. Trimethylammonium was used as templating agent. The synthesis procedure was described elsewhere [22]. The sample was pressed into a wafer and put into a sample holder in Raman cell. The wafer was heated in O_2 at 773 K for 2 h in order to remove the surface contaminants and then cooled down to room temperature before Raman measurement. Methanol contained in a saturator was kept at a constant temperature of 273 K and introduced into the Raman cell with a carrier flow of N_2 (99.99%). The gas flow was 60 ml/min and $N_2/CH_3OH = 27$ (volume ratio). After the reaction, the catalyst was purged by N_2 flow at high temperatures, followed by recording the Raman spectra. The coked samples were regenerated in an O_2 flow (50 ml/min) at 773 K.

3. Results and discussion

UV Raman spectra of methanol adsorbed on ZSM-5 zeolite at different temperatures are shown in Fig. 1. All these spectra are free from fluorescence interference in the UV region. It can be seen

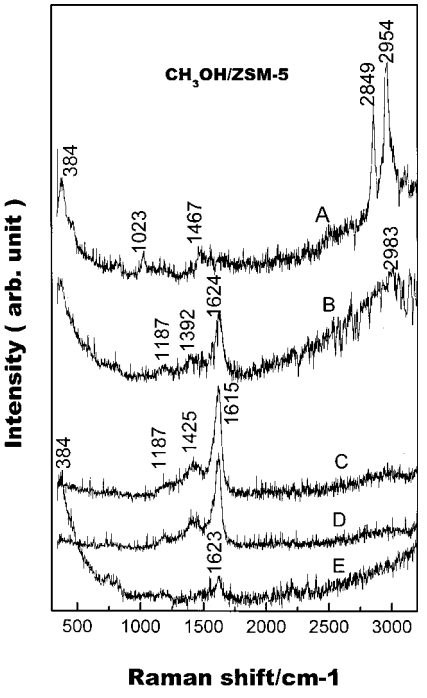

Fig. 1. UV Raman spectra recorded during CH_3OH conversion on ZSM-5: (A) adsorption of CH_3OH on ZSM-5 for 30 min at room temperature; (B) at 523 K for 30 min; (C) at 773 K for 1 h; (D) for 2 h and (E) pure O_2 flow at 773 K for 1 h.

from Fig. 1A that several Raman bands appear at 384, 1023, 1467, 2849, and 2954 cm^{-1} after introducing methanol at room temperature. The band at 384 cm^{-1} is characteristic for ZSM-5. The band at 1023 cm^{-1} is assigned to the C–O stretching vibration, and the band at 1467 cm^{-1} is a deformation mode of the CH_3 group. The two bands at 2849 and 2954 cm^{-1} can be attributed to symmetric and asymmetric stretching vibrations of CH_3 group [23]. All these bands except for the one at 1023 cm^{-1} are shifted to higher wave numbers as compared to those of pure liquid methanol, indicating that methoxyl groups are formed on the zeolite surface [24,25].

The bands of adsorbed methanol disappear upon raising the temperature to 523 K (Fig. 1B), meanwhile four new bands are produced at 1187, 1392, 1624 and 2983 cm^{-1}. The occurrence of these bands indicate that some new surface hydrocarbon species are produced, possibly from the surface reaction of methanol and methoxy species even at 523 K. The band at 1392 cm^{-1} is broad and actually composed of several components, indicating that there are several kinds of adsorbed species formed on the surface. This band is readily assigned to the deformation mode of the CH_3 group [26]. The band at 1624 cm^{-1} is attributed to the C=C stretching vibration of olefinic species [27]. In addition, there is a shoulder band at 1610 cm^{-1} possibly belonging to some conjugated olefinic species.

Fig. 1C and D is the spectra recorded after a reaction at 773 K for 1 h and 2 h, respectively. Compared to Fig. 1B, the band at 1624 cm^{-1} shifts to lower wave numbers, and the C–H vibrational bands at ~3000 cm^{-1} vanish. This suggests that dehydrogenation and oligomerization of the adsorbed species take place at high temperatures, i.e., some aromatic or alkyl-aromatic species are formed. This is in agreement with what has been proposed by Langner [28], i.e., the coke species formed on ZSM-5 are mainly olefinic and aromatic species. Fig. 1E shows that most of the coke species deposited in ZSM-5 can be removed by an oxidation treatment with O_2 at 773 K for 1 h. But a tiny band at 1623 cm^{-1} due to coke species is still detected even after the treatment indicating that some residual coke species still exists.

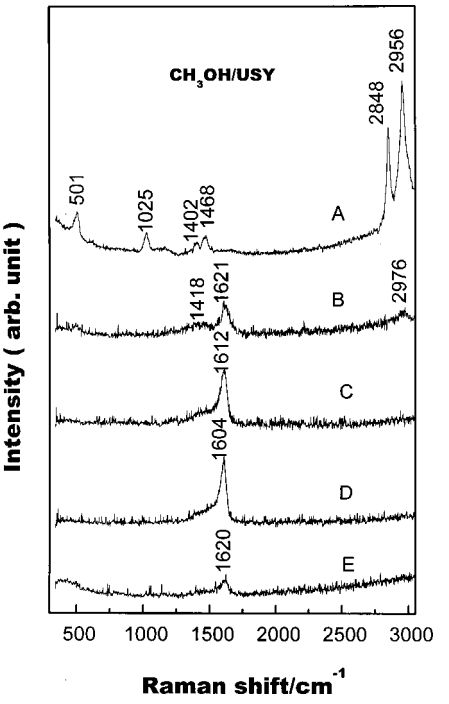

Fig. 2. UV Raman spectra recorded during CH_3OH conversion on USY: (A) adsorption of CH_3OH on USY for 30 min at room temperature; (B) at 523 K for 30 min; (C) at 773 K for 1 h; (D) for 3 h and (E) pure O_2 flow at 773 K for 1 h.

Fig. 2 exhibits the UV Raman spectra recorded for USY under the same reaction conditions as for ZSM-5. Fig. 2A is the spectrum taken after USY was exposed to methanol at room temperature for 30 min. There are six Raman bands observed at 501, 1025, 1402, 1468, 2848 and 2956 cm^{-1}. Except for the band at 501 cm^{-1} which is characteristic of USY zeolite, these Raman bands are very much similar to those for methanol adsorbed on ZSM-5 (Fig. 1A), namely, the methoxy species are also formed in USY zeolite at room temperature. When the temperature is increased, the bands at 1600–1620 cm^{-1} become dominant in the UV Raman spectra (Fig. 2B–D). Fig. 2B is almost identical to Fig. 1B. However, the spectrum of coke species in USY changes more dramatically when the reaction temperature is further increased. The frequency of the band at 1604 cm^{-1} appearing in Fig. 2D is lower than that for Fig. 1D. The band close to 1600 cm^{-1} typically represents polyolefinic,

polyaromatic or substituted aromatic species [29,30] as demonstrated in a previous paper [31]. This result indicates that aromatic species are more easily produced in USY than in ZSM-5.

Fig. 2E is the Raman spectrum recorded after the coked USY was treated with O_2 at 773 K for 1 h. There is still a considerable amount of coke in the zeolite even after an oxidation treatment at 873 K for 1 h. This indicates that part of the coke is chemically stable and difficult to remove. A kinetic limitation of oxygen diffusion to the coke species could also be considered [32].

Figs. 3 and 4 give the UV Raman spectra of the SAPO-34 sample treated with methanol at different temperatures for different times. At room temperature, the spectrum is similar to those of ZSM-5 and USY zeolites, suggesting that the methoxy species is also produced on SAPO-34. The bands at 475 and 1121 cm^{-1} (Fig. 3A) are characteristic of SAPO-34. The coke band at 1632 cm^{-1} appears when methanol is introduced at 523 K (Fig. 3B). This band is due to C=C stretching vibration of olefinic species indicating that some surface olefinic species have been produced. When the temperature is increased to 773 K, the bands at 1395 and 1630 cm^{-1} become more pronounced. At this temperature, SAPO-34 is particularly selective for the formation of light C_2–C_4 alkenes [33]. The new bands at 1392, 2822 and 2987 cm^{-1} (Fig. 3C) are attributed to the symmetric deformation mode of CH_x ($x = 2, 3$), and the symmetric and asymmetric stretching vibrations of CH_x, respectively.

The band near 1630 cm^{-1} is broad, which might indicate the presence of several kinds of olefinic species adsorbed on the zeolite. However, there is no significant change in the Raman spectra when the catalyst is treated with methanol for different times (Figs. 3C and 4C). The band in the 1620 cm^{-1} region is broad, and the bands in 2800–3000 cm^{-1} are still visible even at 773 K for 3 h. These

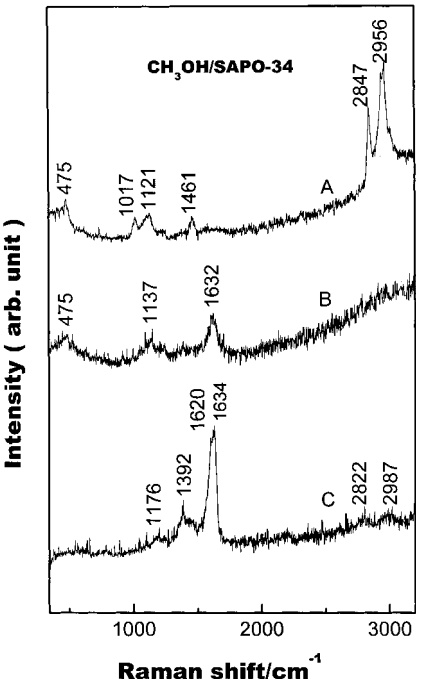

Fig. 3. UV Raman spectra recorded during CH_3OH conversion on SAPO-34: (A) adsorption of CH_3OH on SAPO-34 for 30 min at room temperature; (B) at 523 K for 30 min and (C) at 773 K for 10 min.

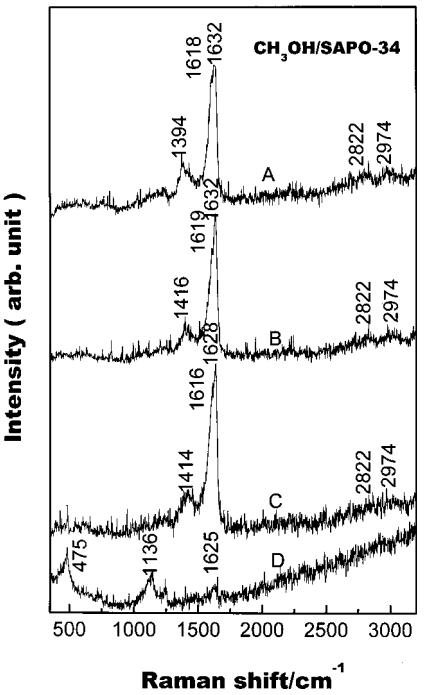

Fig. 4. UV Raman spectra recorded during CH_3OH conversion on SAPO-34: (A) at 773 K for 1 h; (B) for 2 h; (C) for 3 h and (D) pure O_2 flow at 773 K for 1 h.

results indicate that the coke species are mainly composed of polyolefins and oligomers which are rich in hydrogen as presented by the bands near 1400 and 3000 cm^{-1} (Fig. 4C).

The treatment of the coked sample at 773 K with O_2 was also performed in order to remove the surface coke species. The characteristic bands of SAPO-34 at 475 and 1136 cm^{-1} are restored after the oxidation treatment. However, a small Raman band at 1625 cm^{-1} is still present indicating that traces of carbonaceous residues remain in the zeolite.

From the above observations, we can conclude that there are several kinds of coke species formed in the three zeolites during methanol conversion to hydrocarbons. The adsorption and reaction behavior of methanol on the three zeolites is similar at room temperature (Figs. 1A, 2A and 3A) and lower temperatures (Figs. 1B, 2B and 3B), and the main surface species are methoxy groups at room temperature. However, the coke species formed in/on the three zeolites are quite different at high temperatures. This may be explained in terms of the different pore structure of the three zeolites. The pore sizes of ZSM-5, USY and SAPO-34 are 5.5 Å, 7.4 Å and 4.3 Å, respectively. ZSM-5 cannot accommodate big coke species, while USY has supercage cavities in which small coke species can gradually aggregate into big molecules containing several aromatic rings.

For SAPO-34, the pore size is even smaller than that of ZSM-5, and it is smaller than the kinetic diameter of aromatics and multiply branched oligomers of hydrocarbons [33]. Because of this steric inhibition, it is impossible to form heavier oligomers and other coke precursors from light oligomers and light alkenes inside the pores of SAPO-34. The coke formation from methanol conversion might be similar to the mechanism of propene reaction in ZSM-5 and USY zeolites [31]. Because the primary products are mainly light C_2–C_4 alkenes, the coke species may be formed through successive steps including dehydrogenation, oligomerization and cyclization as well as hydrogen transfer and alkylation at elevated temperatures.

On the other hand, the acidity of the zeolite is also an important factor influencing the coke formation and the composition of coke, which in turn will affect the regeneration of the catalysts [5]. A further study is under progress to understand the relationship between the acidic properties and the coke formation in zeolites.

4. Conclusions

UV Raman spectroscopy has been demonstrated to be a potential technique in the characterization of coke species formed in zeolites during methanol conversion processes. The fluorescence interference has been successfully avoided in the UV Raman spectra, and this allows one to investigate the mechanism of coke formation on/in zeolites under working conditions.

UV Raman spectra show that the surface methoxy species are produced when methanol is introduced into USY, ZSM-5 and SAPO-34 zeolites even at room temperature, but different coke species are formed in these zeolites at high temperatures. Aromatic and polyaromatic species are easily formed in USY, polyolefinic and monoaromatic species are dominant in ZSM-5, while only olefin and polyolefin species are formed in SAPO-34. The differences of coke formation in ZSM-5, USY and SAPO-34 are attributed to the different pore structures of the three zeolites.

Most coke species formed in ZSM-5, USY and SAPO-34 can be removed after a treatment with O_2 at 773 K, but some small amounts of coke deposits are difficult to remove. In particular, the coke residues in USY are hard to remove even after a treatment with O_2 at 873 K. This suggests that the ease of coke removal depends on the nature of the coke species and is also affected by oxygen diffusion in the zeolites.

Acknowledgements

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