

Characterization of surface carbon formed during the conversion of methane to benzene over Mo/H-ZSM-5 catalysts

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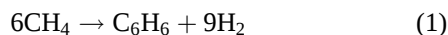
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During the conversion of methane to benzene in the absence of oxygen over a 2 wt% Mo/H-ZSM-5 catalyst at 700 °C, three different types of surface carbon have been observed by X-ray photoelectron spectroscopy: adventitious or graphitic-like C (284.6 eV), carbidic-like C (282.7 eV), and hydrogen-poor sp-type C (283.2 eV), where the C 1s binding energies for the respective forms of carbon are given in parentheses. Pretreatment of the catalyst at 700 °C in CO also resulted in a strong signal at 283.2 eV; thus, the species responsible for this signal appears to be different from the usual aromatic-type coke. The coke with dominantly sp hybridization is concentrated on the external surface of the zeolite and is responsible for the gradual deactivation of the catalyst.

Keywords: carbon, coke, methane conversion, benzene from methane, Mo/H-ZSM-5 catalyst, XPS

1. Introduction

Molybdenum-loaded H-ZSM-5 zeolites are promising catalysts for the conversion of methane to benzene in the absence of oxygen via the reaction [1–10]



Recent investigations in our laboratory have shown that, following an initial induction period, a methane conversion of 8% could be achieved at a benzene selectivity of 70% at 700 °C [9,10]. During this induction period, Mo(VI) is almost completely reduced to the carbide, Mo₂C, which was identified by X-ray photoelectron spectroscopy (XPS). This phase is believed to be responsible for methane activation [9]. Ethylene is first formed, and this is converted to benzene over the acid sites in the zeolite. The role of the metal carbide was further supported by the effect of treating the catalyst in a CH₄/H₂ gas mixture at 700 °C [10], which resulted in the rapid formation of Mo₂C and an almost complete elimination of the initial induction period for methane activation.

Although similar catalytic performances have been reported by several other research groups, different active phases were proposed [1–7]. Recently, Solymosi et al. [8] also reported that Mo₂C was the active phase for methane activation. Discrepancies among various research groups in identifying the active phase for methane activation may result from: (1) different sample preparation and pretreatment; (2) the apparent inactivity of commercial Mo₂C for methane activation; (3) the rapid reoxidation of Mo₂C in air; and (4) the overlap of the carbidic C 1s XPS signal with

other forms of carbon that are formed on the surface during methane activation. In previous studies, considerable attention has been given to the state of the molybdenum, but not to the forms of carbon on the surface.

The present investigation was undertaken to elucidate the nature of the surface carbon species that are formed during methane activation. It will be shown that coke deposition is responsible for the gradual deactivation of Mo/H-ZSM-5 catalysts during methane activation. The coke, however, is not of the aromatic type, which is surprising in view of the aromatic products.

2. Experimental

2.1. Catalyst preparation

The 2 wt% Mo/H-ZSM-5 catalyst was prepared starting from commercial H-ZSM-5 (PQ Corp., CBU 5020E) having a Si/Al ratio of 25. Fully exchanged H-ZSM-5 was obtained by ion exchange with 500 ml of a 1 M aqueous solution of ammonium nitrate (NH₄NO₃, EM Science) at 80 °C for 12 h, followed by drying at 90 °C overnight and calcination at 500 °C for 5 h. An aqueous solution of ammonium paramolybdate ((NH₄)₆Mo₇O₂₄, Spectrum) was used for impregnation of Mo by the incipient wetness method, followed by drying at 90 °C overnight and calcination at 500 °C for 5 h. The freshly prepared 2 wt% Mo/H-ZSM-5 sample was then crushed and sieved to 20/45 mesh granules.

2.2. Catalyst pretreatment and characterization

Reactions were carried out in a flow system, using reactors constructed from alumina tubes (Coors, AD-998, 99.8% Al₂O₃) having an internal diameter of 6.4 mm and

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containing 1.0 g of the catalyst used. To minimize the contribution from any gas-phase reactions, quartz chips filled the space above and below the catalyst beds in the flow reactors. A thermocouple in a smaller alumina tube was attached to the outside wall of each of the reactors.

Reactant gases, which included 10% N_2/CH_4 (UHP), O_2 (UHP), He (UHP) and CO (UHP), were obtained from Matheson. Traces of iron carbonyls were removed from the CO stream by flowing it through an alumina tube filled with quartz chips at 300 °C. Other gases were used without further purification. Gas flows were regulated by mass-flow controllers (MKS model 1159A). In the flow system, the catalyst was heated in an O_2 flow at 500 °C for 1 h, and flushed in He for 30 min (flow rate of 50 ml/min). Some catalysts were then reduced in a stream of CO for several hours at 700 °C (flow rate of 50 ml/min). After calcination and treatment in CO, the catalyst was subjected to a CH_4 stream at 700 °C. The GHSV was 800 h^{-1} . N_2 in CH_4 was used as an internal standard so that the CH_4 conversion could be determined accurately and coke formation during the reaction could be evaluated from a carbon mass balance. The resulting reaction mixtures were analyzed using a HP5890A chromatograph, equipped with a 5% Bentone 34 on Chromosorb W-AW column and a HayeSep D column. All studies were carried out at atmospheric pressure.

XPS spectra were acquired using a Perkin-Elmer (PHI) model 5500 spectrometer. All spectra were obtained using samples prepared in the form of pressed wafers and pretreated in a special quartz reactor system to duplicate the conditions employed in the catalytic reaction experiments. Comparisons between activity/selectivity data obtained with a flow-through catalyst bed and XPS results obtained with pressed wafers have been useful in understanding the transients that result from changes in the chemical state of Mo, as well as the effects of poisons such as CO_2 [9,10]. The quartz reactor system contained an O-ring-sealed port that allowed transfer of the ceramic holder containing the treated sample into a stainless steel vacuum transport vessel (PHI model 609217). The removable vessel was then transferred to a similar port on the inlet system on the XPS spectrometer, which was subsequently evacuated, allowing the sample to be introduced into the UHV analysis chamber of the instrument using magnetically coupled transfer rods without exposure to the air. A typical XPS data acquisition employed a pass energy of 29.35 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. All binding energies were referenced to the zeolitic Al 2p and Si 2p peaks at 74.5 and 102.8 eV, respectively. Near-surface compositions were calculated from peak areas using the appropriate sensitivity factors [11].

3. Results

3.1. Catalytic results

In the first series of experiments, we studied the effect of CO prereduction at 700 °C on the catalytic per-

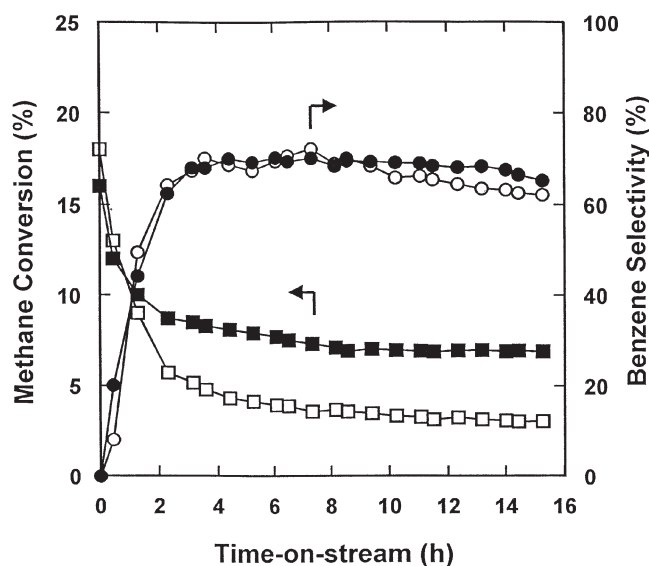


Figure 1. Methane conversion and benzene selectivity results, represented by squares and circles, respectively, for CH_4 reaction over 2 wt% Mo/H-ZSM-5 prereduced at 700 °C with CO for 0 h (solid symbols) and 6 h (open symbols). The catalytic reaction was conducted at 700 °C, 1 atm, and GHSV = 800 h^{-1} .

formances of a 2 wt% Mo/H-ZSM-5 catalyst. Figure 1 shows the methane conversion and benzene selectivity for the reaction of methane with and without CO pretreatment at 700 °C. Following an initial activation period during the first 2 h of reaction, a benzene selectivity of about 70% could be reached at a methane conversion of 8% for a non-prereduced Mo/H-ZSM-5 catalyst. The thermodynamic equilibrium conversion under these conditions is 12% [9]. The catalytic activity then slowly decreased with increasing time-on-stream. A similar catalytic behavior was observed for a 2 wt% Mo/H-ZSM-5 catalyst prereduced at 700 °C with CO for 6 h; however, the methane conversion was only about 5%, and the material deactivated somewhat faster than the non-prereduced catalyst. Other prereduction times at 700 °C resulted in different methane conversions, as illustrated in figure 2. The methane conversion at maximum benzene selectivity (ca. 4 h time-on-stream) gradually decreased with increasing reduction time and was only about 2% after CO prereduction for 12 h at 700 °C.

3.2. X-ray photoelectron spectroscopy

The chemical state of Mo and C in the 2 wt% Mo/H-ZSM-5 catalysts, together with the near-surface composition, were examined by conventional and by angle-resolved XPS. Angle-resolved XPS provides information about changes in the sample composition with depth. Electrons emerging from the solid at low take-off angles characterize properties of the uppermost surface layers of the sample, whereas the electrons measured at high take-off angles more nearly reflect the bulk contribution [12–14].

The XPS spectra obtained in the Mo 3d and C 1s regions of a non-prereduced 2 wt% Mo/H-ZSM-5 catalyst for increasing time-on-stream have been discussed in detail in

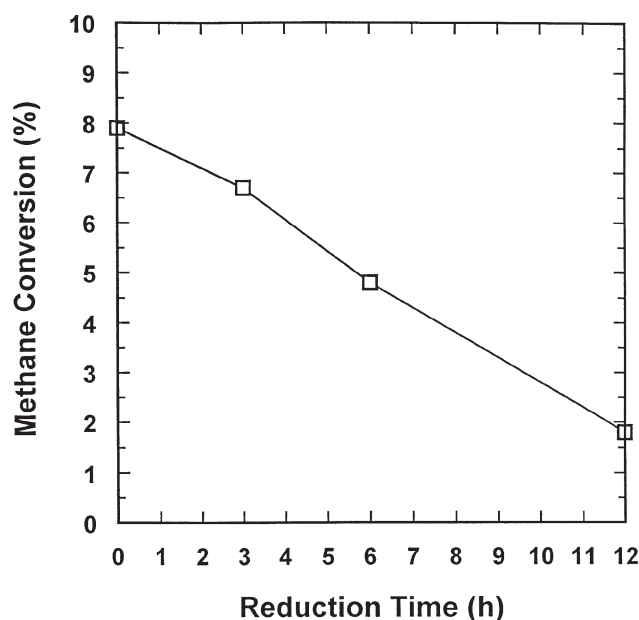


Figure 2. Methane conversion at maximum C_6H_6 selectivity for CH_4 reaction over 2 wt% Mo/H-ZSM-5, prerduced at 700 °C with CO, as a function of the reduction time. The catalytic reaction was conducted at 700 °C, 1 atm and GHSV = 800 h⁻¹.

previous publications [9,10] and will not be repeated. It is sufficient to illustrate the near-surface composition of the catalyst for increasing time-on-stream in CH_4 at 700 °C, which is given in figure 3. The XPS signals due to Mo and (Al + Si + O) gradually decreased with increasing time-on-stream. By contrast, the C signal steadily increased, which indicates that the catalyst was covered by an increasing amount of coke. The effect was more pronounced during the first 6 h on stream. In addition to a C 1s peak at 283.2 eV, an additional one was observed at 282.7 eV for a sample that was treated in a CH_4/H_2 mixture [10]. The latter peak was attributed to carbidic carbon in Mo_2C . In the present work, however, we have used pure CH_4 , and the carbidic C 1s signal was always overshadowed by the C 1s band centered around 283.2 eV.

The XPS spectra in the C 1s region of the Mo/H-ZSM-5 catalyst, treated for 13 h in methane at 700 °C, are given in figure 4. At an electron take-off angle of 60°, two peaks at around 284.6 and 283.2 eV were observed (spectrum (a)). The former peak can be assigned to “adventitious C” or graphitic-like C [12–14], whereas the latter is different from that observed for pure Mo_2C at 282.7 [10]. It is important to note that the C/Mo atomic ratio was around 10, and therefore much larger than the expected value of 0.5 for a pure supported Mo_2C species. This value of 0.5 was previously approached by treating the Mo/H-ZSM-5 catalyst in a CH_4/H_2 mixture, which is known to suppress coke formation [10]. Thus, the 283.2 eV band, which is at an unusually small BE for catalytic coke, most probably encompasses two different types of carbon, a small amount of carbidic C and a new carbon type, which is subsequently referred to as pregraphitic-like C. The band at 283.2 eV gradually increased in intensity with decreasing electron take-off angle

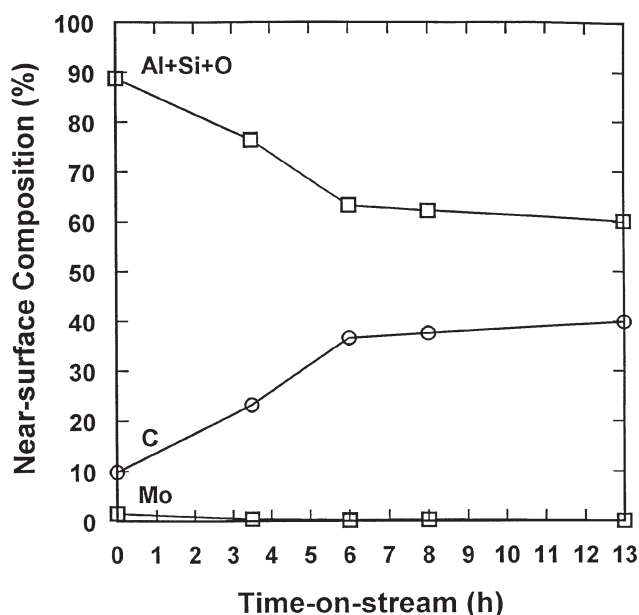


Figure 3. Near-surface composition of a non-prerduced 2 wt% Mo/H-ZSM-5 catalyst, exposed at 700 °C to methane, as a function of time-on-stream.

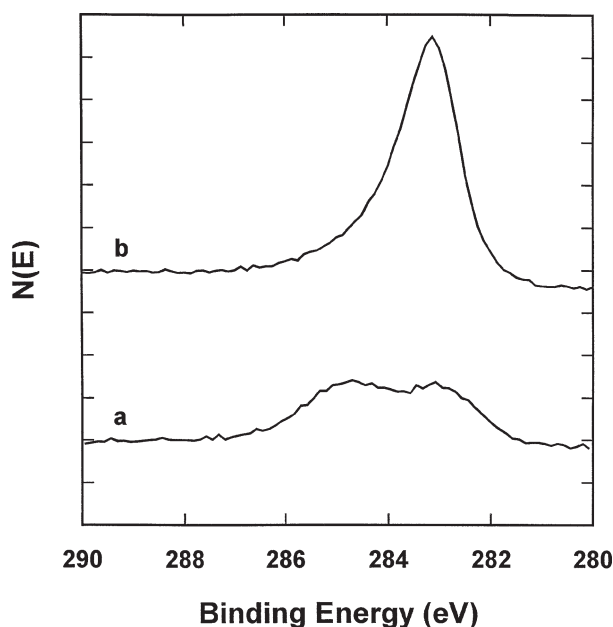


Figure 4. Angle-resolved XPS spectra in the C 1s region of a non-prerduced 2 wt% Mo/H-ZSM-5 catalyst exposed for 13 h to methane at 700 °C: (a) $\theta = 60^\circ$, and (b) $\theta = 20^\circ$.

and was a maximum at $\theta = 20^\circ$ (spectrum (b)). At this low electron take-off angle, the 284.6 eV peak of graphitic-like C was only visible as a weak shoulder. The dominance of the 283.2 eV peak at the low take-off angle indicates that the species responsible for this signal is concentrated on the external surface of the zeolite.

Spectra obtained in the Mo 3d region and C 1s region of a 2 wt% Mo/H-ZSM-5 catalyst, reduced with CO at 700 °C for several hours, are presented in figure 5. The XPS spectrum in the Mo 3d region of the Mo/H-ZSM-5 catalyst,

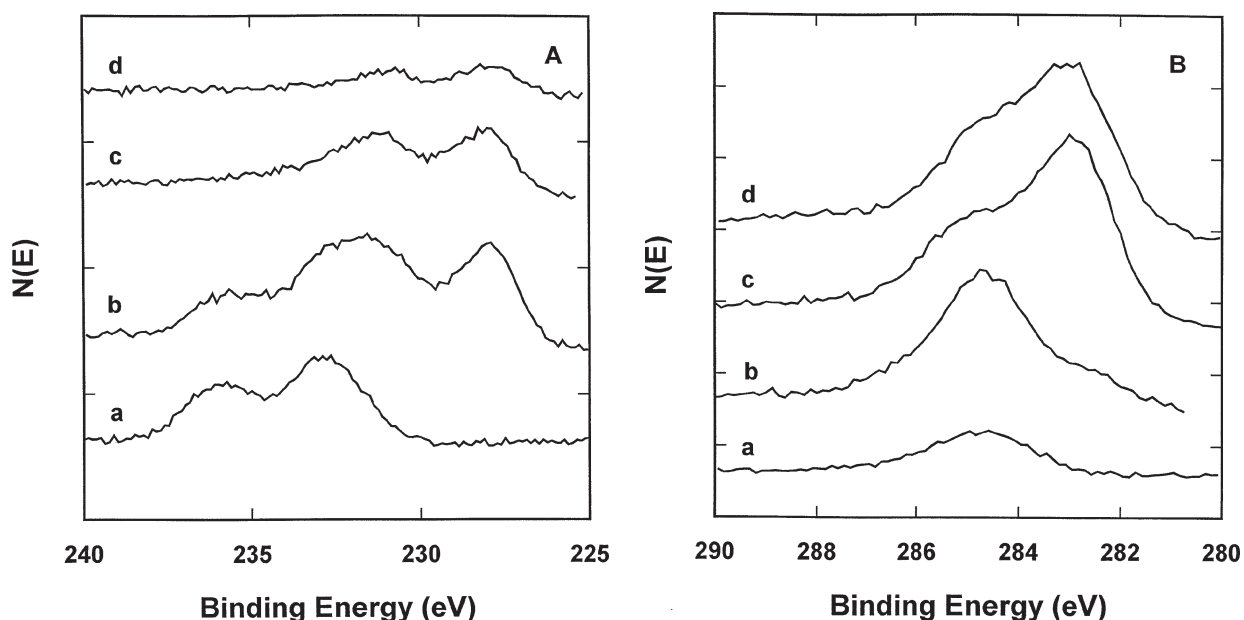


Figure 5. XPS spectra (A) in the Mo 3d region, and (B) in the C 1s region of a 2 wt% Mo/H-ZSM-5 catalyst, exposed to CO at 700 °C, as a function of the reduction time: (a) 0 h, (b) 3 h, (c) 6 h, and (d) 12 h. The electron take-off angle θ was 45°.

treated in O₂ at 500 °C, was characterized by two bands due to Mo(VI)/Mo(V) centered around 233.1 and 236.3 eV (figure 5(A), spectrum (a)). The corresponding C 1s region was typical of graphitic-like carbon. Reduction of the catalyst at 700 °C with CO for 3 h resulted in a large decrease in the Mo(V)/Mo(VI) bands and the formation of new bands located at 227.9 and 231.1 eV (figure 5(A), spectrum (b)). The latter bands indicate the formation of Mo₂C [9,10]. The intensity of these bands decreased upon increasing prereduction time, and after 12 h reduction with CO, a less intense XPS spectrum was obtained (figure 5(A), spectrum (d)). The C 1s region shows that pre-reduction at 700 °C resulted in the formation of the same pregraphitic-like carbon with a band at around 283.2 eV (figure 5(B), spectra (b)–(d)) as that observed following exposure of the catalyst to CH₄. This band became dominant after reduction with CO for 6 h. Thus, Mo₂C can be formed by CO reduction at 700 °C, but is covered to a large extent by C, which is characterized by the band at 283.2 eV.

The near-surface composition of the catalyst, following different prereduction treatments, is summarized in figure 6. The results show that the signals originating from the zeolite and the Mo decrease with increasing reduction time, whereas the intensity of the signal belonging to C steadily increased. In particular, the dominant pregraphitic-like carbon is deposited onto both the Mo and the zeolite surface.

In a final set of experiments, angle-resolved XPS spectra of pure H-ZSM-5 were obtained after treating the sample in methane at 700 °C. Although this material exhibited only limited methane conversion (0.6%) and no benzene selectivity, its color became black after exposure to methane for several hours. For H-ZSM-5 treated for 48 h in methane at 700 °C, the C 1s region was characterized by a single band at 283.6 eV, which broadened towards higher binding

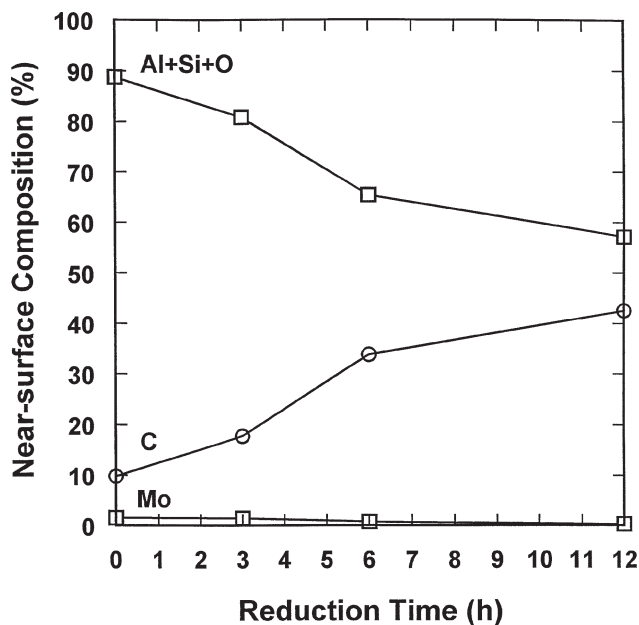


Figure 6. Near-surface composition of a 2 wt% Mo/H-ZSM-5 catalyst, exposed at 700 °C to CO, as a function of the reduction time. The electron take-off angle θ was 45°.

energies, suggesting the presence of some adventitious or graphitic C. The BE of 283.6 eV is somewhat larger than the value given above for the pregraphitic-like carbon on the Mo/H-ZSM-5 catalyst.

4. Discussion

The primary aim of this work was to elucidate the nature of the different surface carbon species that are formed during the conversion of methane to benzene over Mo/H-

ZSM-5 catalysts in the absence of oxygen. Angle-resolved XPS, in combination with reduction treatments, shows that three different types of surface carbon species are present in an active catalyst. The following discussion will include: (1) the nature of surface carbon species, and (2) the deactivation process of Mo/H-ZSM-5 catalysts.

4.1. Nature of surface carbon species

In contrast with the C 1s binding energies of functional groups, such as C–O, C=O, and C–OH, the assignments of the C 1s band positions to C–C, C=C, C≡C, and C–H bonds are less straightforward [13]. Despite this lack of uniqueness in the literature for the binding energies of C 1s bands, it is possible to distinguish between general forms of carbon, and table 1 gives a summary of C 1s binding energies reported in the literature for different hybridizations of carbon. Although octaethylporphyrin (OEP) contains C with sp^2 hybridization, the C 1s binding energy is distinctly less than that in polystyrene. This smaller binding energy may result from the presence of N in the ring structure of OEP [20].

In the present work, the binding energies were corrected for charging by referencing the zeolitic Al 2p and Si 2p bands at 74.5 and 102.8 eV, respectively, in ZSM-5. The corresponding value of graphitic-like or adventitious carbon in pure H-ZSM-5 was 284.6 eV, which is the same value as that reported by Barr [13]. Sexton et al. [21] reported BE's of 284.5–284.7 eV for internal coke, and 284.3 eV for external coke, formed during the conversion of methanol to aromatics over H-ZSM-5. These values are referenced to a Si 2p band at 103.4 eV. If one uses our value of 102.8 eV for the Si 2p reference, the respective BE's for the C 1s bands reported by Sexton et al. become 283.9–284.1 eV and 283.7 eV. The latter is very close to the value of 283.6 eV that we observed following the reaction of CH_4 with H-ZSM-5. By comparison with results

obtained from solid-state ^{13}C NMR studies, Bibby and co-workers [21] conclude that the larger C 1s BE's result from internal coke which is composed of methyl-substituted aromatic coke and the smaller BE results from external coke which is graphitic or composed of highly condensed polycyclic aromatic rings.

Although the band at 283.2 eV has a BE that is near the value of 283.7 eV (corrected) for surface coke, it is distinctly less than the value of 284.2 eV for well defined graphite (table 1). Moreover, this band on Mo/H-ZSM-5 can be formed from CO as well as from CH_4 , thus the surface species need not contain hydrogen. The relatively low BE of 283.2 eV suggests sp hybridization on the carbon, and chains of the type $-(C\equiv C)_n-$ may be precursors in the formation of graphite. This interpretation suggests that there may be an alternative pathway to the formation of graphite that does not involve polycyclic aromatic intermediates. Blackmond et al. [22] have reported a lack of aromatic character in the coke formed over an HY zeolite. Lagow et al. [23] have recently prepared a carbon allotrope, based on sp hybridization, that contains alternating triple and single bonds. The dehydrogenation function of Mo_2C and the temperature of 700 °C may favor this nonaromatic pathway.

4.2. Deactivation process of Mo/H-ZSM-5 catalysts

In this work, we have shown that prereduction with CO at 700 °C did not result in more active materials. Instead, our results clearly demonstrated that CO reduction at 700 °C for increasing periods resulted in the gradual formation of coke which covered the catalytically active phase, Mo_2C . These observations are in contrast with recent characterization results, in which we have shown that prereduction in CH_4/H_2 at 700 °C [9,10] or in CO at 500 °C [24,25] resulted in a large decrease in the initial induction period. However, neither of these pretreatment procedures resulted in significant coke formation. This suggests that (pre)reduction, although necessary for the transformation of Mo(VI) to the catalytically active phase, Mo_2C , may also lead to coke deposition which blocks the active sites. Thus, pretreatment in CH_4/H_2 at 700 °C or in CO at 500 °C is required to obtain the most active Mo/H-ZSM-5 catalyst for methane activation.

Similar results were previously obtained for unsupported Mo_2C [24,25]. Leary et al. [26] concluded from detailed temperature-programmed desorption (TPD) and reduction (TPR) experiments that the decrease in ethylene dehydrogenation activity over Mo_2C is due to accumulation of carbon on the surface, which blocks the active sites. This carbon was produced by the cracking of ethylene over Mo_2C . In addition, Wang et al. [27] observed by angle-resolved XPS that at low electron take-off angles the surfaces of annealed Mo_2C samples were enriched in carbon.

Table 1
Literature survey of C 1s assignments for different types of carbon.

Carbon type	Compound	Binding energy (eV)	Reference
sp^3 C	polyethylene	284.8	[16]
	polypropylene	284.9	
	hydrocarbon oil	284.8	
	OEP ^a	284.6	
sp^2 C	polystyrene	284.2	
	graphite	284.2	
	OEP ^a	283.7	
sp C	CH/Pt(111) (methine)	283.8–284.0	[17]
	$C_2H_2/Fe(110)^b$	283.5	
carbide C	Mo_2C	282.8	[19]

^a OEP, octaethylporphyrin, which contains both aliphatic and aromatic carbon atoms.

^b The reported value of 283.9 eV was corrected by 0.4 eV to compensate for the unusually high binding energy of graphite-like carbon (285.0 eV). Charging effects are usually corrected by referencing to adventitious or graphite-like carbon, which is the major C–C/C–H C 1s peak located at 284.6 eV.

5. Conclusions

Three different types of surface carbon species are present on an active Mo/H-ZSM-5 catalyst: (a) species A, characterized by a C 1s BE of 284.6 eV, is due to adventitious or graphitic-like C and is mainly present in the zeolite channel system as shown by angle-resolved XPS studies; (b) species B, with a C 1s BE of 282.7 eV, is due to carbide-like C in Mo₂C and is predominantly located at the outer surface of the zeolite; and (c) species C, with a C 1s BE of 283.2 eV, is a hydrogen-poor sp-type or pregraphitic-type of carbon. This carbon, which is formed by the decomposition of CH₄ during the catalytic reaction or by pretreatment of the catalyst in CO at 700 °C, is mainly present on the outer surface of the zeolite, and its amount increases with increasing time-on-stream. The sp-type carbon gradually covers both the zeolite surface and the Mo₂C phase during methane activation and is responsible for the deactivation of Mo/H-ZSM-5 materials during the dehydroaromatization of methane.

Since surface carbon is often used as an internal standard for the determination of binding energies, it is worth pointing out that a significant error in binding energies would result if the large carbon signal at 283.2 eV was used as a standard and assigned the value of 284.6 eV for adventitious carbon.

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References

- [1] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, *Catal. Lett.* 21 (1993) 35.
- [2] Y. Xu, S. Liu, L. Wang, M. Xie and X. Guo, *Catal. Lett.* 30 (1995) 135.
- [3] Y. Xu, W. Liu, S. Wong, L. Wang and X. Guo, *Catal. Lett.* 40 (1996) 207.
- [4] L. Chen, L. Lin, Z. Xu, Z. Li and T. Zhang, *J. Catal.* 157 (1995) 190.
- [5] L. Chen, L. Li, Z. Xu, T. Zhang and X. Li, *Catal. Lett.* 39 (1996) 169.
- [6] F. Solymosi, A. Erdöhelyi and A. Szöke, *Catal. Lett.* 32 (1995) 43.
- [7] F. Solymosi, A. Szöke and J. Cserényi, *Catal. Lett.* 39 (1996) 157.
- [8] F. Solymosi, J. Cserényi, A. Szöke, T. Bansagi and A. Oszkó, *J. Catal.* 165 (1997) 150.
- [9] D. Wang, M.P. Rosynek and J.H. Lunsford, *Top. Catal.* 3 (1996) 289.
- [10] D. Wang, M.P. Rosynek and J.H. Lunsford, *J. Catal.* 169 (1997) 347.
- [11] C.D. Wagner, *J. Electron Spectr. Rel. Phen.* 32 (1983) 99.
- [12] J.W. Niemandsverdriet, *Spectroscopy in Catalysis, an Introduction* (VCH, Weinheim, 1993).
- [13] T.L. Barr, *Modern ESCA: The Principles and Practice of X-Ray Photoelectron Spectroscopy* (CRC Press, Boca Raton, FL, 1994).
- [14] *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Eden Prairie, 1992).
- [15] B.M. Weckhuysen, M.P. Rosynek and J.H. Lunsford, unpublished results.
- [16] G. Barth, R. Linder and C. Bryson, *Surf. Interface Anal.* 11 (1988) 307.
- [17] S. Steffenato, G. Comelli, R. Rosei, A. Baraldi, G. Paolucci and M. Kiskinova, *Surf. Interface Anal.* 24 (1996) 321.
- [18] H.P. Bonzel and H.J. Krebs, *Surf. Sci.* 91 (1980) 499.
- [19] M. Textor, I.D. Gay and R. Mason, *Proc. Roy. Soc. London A* 356 (1977) 37.
- [20] D. Briggs, in: *Practical Surface Analysis*, eds. D. Briggs and M.D. Seah (Wiley, New York, 1983) p. 359.
- [21] B.A. Sexton, A.E. Hughes and D.M. Bibby, *J. Catal.* 109 (1988) 126; R.H. Meinhold and D.M. Bibby, *Zeolites* 10 (1990) 121.
- [22] D.G. Blackmond, J.G. Goodwin and J.E. Lester, *J. Catal.* 78 (1982) 34; D.G. Blackmond, J.G. Goodwin and J.E. Lester, *J. Catal.* 78 (1982) 247.
- [23] R.J. Lagow, J.J. Kampa, H.-C. Wei, S.L. Battle, J.W. Genge, D.A. Laude, C.J. Harper, R. Bau, R.C. Stevens, J.F. Haw and E. Munson, *Science* 267 (1995) 362.
- [24] B.M. Weckhuysen, D. Wang, M.P. Rosynek and J.H. Lunsford, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2374.
- [25] B.M. Weckhuysen, D. Wang, M.P. Rosynek and J.H. Lunsford, *J. Catal.*, in press.
- [26] K.J. Leary, J.N. Michaels and A.M. Stacy, *J. Catal.* 101 (1986) 301.
- [27] J. Wang, M. Castonguay, P.H. McBreen, S. Ramanathan and S.T. Oyama, in: *The Chemistry of Transition Metal Carbides and Nitrides*, ed. S.T. Oyama (Blackie Academic & Professional, London, 1996) p. 426.