Characterization of early transition metal carbides and nitrides by NEXAFS

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Powder materials of a series of early transition metal (groups 4–6B) carbides and nitrides, including TiC, VC, NbC, Mo_2C, WC, TiN, VN and Mo_2N, have been characterized by near-edge X-ray absorption fine structure (NEXAFS). A comparison of the carbon and nitrogen K-edge features reveals systematic trends in the electronic properties of these materials. These results are compared to an earlier NEXAFS characterization of thin VC films produced on a single crystal V(110) surface. In addition, the NEXAFS data are also compared to existing band-structure calculations for carbides and nitrides of early transition metals.

Keywords: NEXAFS; metal carbides; metal nitrides

1. Introduction

It has been known for some time that carbides and nitrides of the early transition metals have catalytic properties resembling those of the noble group metals [1–3]. This similarity was suggested to be due to a modification of the electronic structure of the metal by carbon and nitrogen [4–6]. The parent metal alone was found to react too strongly with the reactants, such as hydrogen, oxygen, carbon monoxide, and unsaturated hydrocarbon molecules so that catalytic cycles involving these species would stop with the adsorption step. For carbides and nitrides the presence of the non-metal in the host lattice increased the electron to metal ratio in a way to "tame" this aggressiveness [1].

The modification of the electronic properties in the carbides and nitrides has been the subject of many experimental and theoretical investigations [5–14]. In an

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effort to further understand the systematic trends in the electronic properties of these materials, we have applied the near-edge X-ray absorption fine structure (NEXAFS) technique to characterize and compare a series of carbides and nitrides of groups 4B–6B transition metals. Such a systematic investigation revealed some characteristic similarities, as well as differences, in the electronic properties of these materials. In addition, the NEXAFS experiments were carried out by measuring both the electron yield (surface sensitive) and fluorescence yield (bulk sensitive), which provided a direct comparison of the surface and bulk compositions of these materials [15].

2. Experimental

The carbides and nitrides used in this study were TiC, VC (two samples), NbC, Mo_2C, WC, TiN, VN and Mo_2N. The TiC and one of the VC samples were commercially obtained and used as received. The rest of the carbide and nitride samples were synthesized by a temperature programmed reaction (TPR) method [16–18]. The TPR method involves uniform heating of a solid transition metal oxide (V_2O_5, MoO_3, etc.) in a stream of flowing gas, such as pure ammonia or a methane–hydrogen mixture, until the sample is transformed to a nitride or carbide. The end of the transformation is determined by monitoring real time mass-spectrometer traces of effluent gas species. After the synthesis, a 0.5% O_2/He gas mixture is passed over the product to passivate the sample by depositing a layer of oxygen on the active surface. The samples are then characterized by X-ray powder diffraction to determine the product phases. In our synthesis of these materials, the amount of oxide loaded into the reactor cell was 0.4–5.0 g, the gas flow rates were between 1000 and 3000 $cm^3\ min^{-1}$, and the heating rate was between 0.03 and 0.08 $K\ s^{-1}$.

For the NEXAFS experiments, the powder samples were pressed into a stainless steel sample holder of about 6 mm in diameter and about 1 mm in depth. The powder samples were heated by resistively heating two tungsten wires (0.025 cm in diameter) spot-welded onto the sample holder. The sample temperature was measured by a chromel–alumel thermocouple. As will be discussed in detail later, the carbide and nitride samples were pretreated by heating in a stream of H_2 to 723 K at 8.0 kPa pressure, and maintaining the temperature and pressure in static H_2 for 0.5 h. The NEXAFS measurements were carried out after the reaction chamber was evacuated to below 10^{-5} Pa.

The 1-butene hydrogenation study was done under in situ conditions following hydrogen pretreatment. The process involved heating the sample to 623 K and leaking in a 2 : 1 mixture of H_2 and 1-butene to a total pressure of 5.3 kPa into the chamber. The reaction was allowed to proceed for 0.5 h under the same conditions. The chamber was then evacuated to 10^{-5} Pa before the NEXAFS measurements.

The NEXAFS experiments were carried out at the U1 beamline of the National Synchrotron Light Source, Brookhaven National Laboratory. The NEXAFS spectra were recorded near the K-edges of C, N and O, the L-edges of Ti and V, the M-edges of Nb and Mo and the N-edge of W. As described previously [15], the fluorescence-yield intensity was measured by using a differentially pumped, UHV-compatible proportional counter filled with 200 Torr of P-90 (90% methane, 10% argon) gas as counter-gas. The electron-yield intensity was recorded by a channeltron electron multiplier located near the sample holder. To make the electron-yield method more surface sensitive, the entrance of the channeltron was biased by a negative voltage of 100 eV to repel low-energy, secondary electrons [15]. All NEXAFS spectra were recorded with the incoming photon beam normal to the sample surface. Unless otherwise noted in the figure captions, the NEXAFS spectra in each figure were normalized to have the same step-height to eliminate the possible concentration effect among the different samples.

3. Results and discussion

This section is divided into five parts. The first presents NEXAFS results following the removal of surface oxygen impurities by pretreating VC samples in H_2. The second describes the general near-edge features observed for VC spectra and compares the near-edge features of VC powders with those of VC/V(110) single crystals. The next two parts present the results on characterization of early transition metal carbides and nitrides, respectively. The final portion provides some preliminary results on 1-butene hydrogenation on VC and VN.

3.1. PRETREATMENT OF VC POWDERS IN H_2

Fig. 1 shows the O K-edge and V L-edge electron yield NEXAFS spectra of the commercial (VC-com) and synthesized (VC-TPR) VC samples. For comparison, fig. 1 also shows the NEXAFS spectra of V_2O_5 (bottom spectrum) and a well-characterized VC thin film produced on a V(110) single crystal surface (top spectrum). As discussed in detail in an earlier publication [5], the NEXAFS spectra in this energy range can be divided into two regions: The peaks observed at <530 eV are related to the V L_{III} and L_{II} near-edge features, and the peak positions of these features are related to the oxidation state of vanadium [5]. The near-edge features at >530 eV are associated with the oxygen K-edge features, which are due to the electronic transitions of O 1s electrons to several partially-filled and unfilled molecular orbitals of vanadium oxides [5].

The presence of oxygen near-edge features in a carbide or nitride sample indicates surface contamination by oxygen. Thus, it can be seen from fig. 1 that both untreated VC samples have surface oxygen impurities, with the commercial one having much higher oxygen content. Additionally, the oxidation state of vanadium can be determined by the peak positions of the V L_{III} and L_{II} near-edge features [5]. For example, as shown in fig. 1, the peak positions of these two features appear

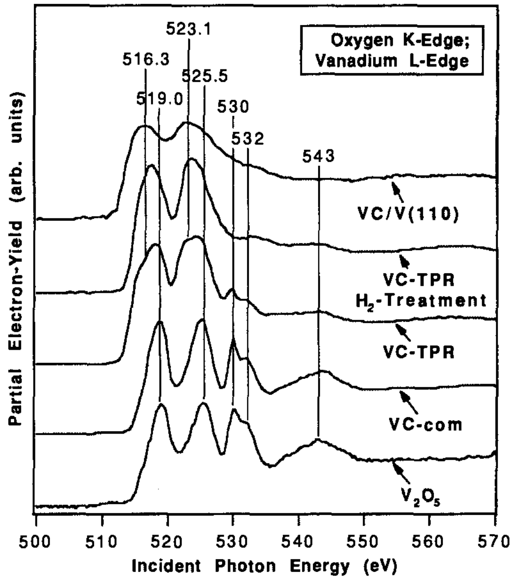

Fig. 1. A comparison of electron-yield NEXAFS spectra, in the O K-edge and V L-edge, of untreated commercial and synthesized VC powders and H_2-treated synthesized VC powder. The NEXAFS spectra of V_2O_5 and VC/V(110) are also included. The differences in the V L-edge positions among various samples are related to the different oxide contents on the surface.

at 519.0 and 525.5 eV for V_2O_5 and 516.3 and 523.1 eV for VC/V(110), respectively. A comparison of the V L_{III} and L_{II} near-edge features therefore suggests that the surface composition of the untreated commercial VC sample is primarily V_2O_5. The surface composition of the untreated synthesized VC sample, on the other hand, consists of both VC and V_2O_5. The oxide impurities of the latter surface can be readily removed by heating the sample in H_2 (100 Torr, 723 K, 0.5 h), as indicated by the disappearance of the O K-edge features. As expected, the removal of oxygen impurities is accompanied by the observation that the peak centers of the V L_{III} and L_{II} features of VC-TPR shift towards those of VC/V(110).

A similar hydrogen treatment was carried out for all carbide and nitride samples used in this study. The impurity levels of residual oxygen on a carbide or nitride sample was estimated by comparing the intensities of the O K-edge features to those of the parent metal oxides (V_2O_5, MoO_3, etc.). Based on the peak intensities of the O K-edge features, the surface oxygen impurities of the H_2-treated samples were estimated to be less than 10% for carbides and less than 30% for nitrides.

3.2. COMPARISON OF VC POWDERS WITH VC/V(110)

The surface compositions of several VC samples are compared in fig. 2 by plotting the electron-yield NEXAFS spectra of carbon K-edge features. As observed previously for VC/V(110) [5], the electron yield spectrum of a well-characterized

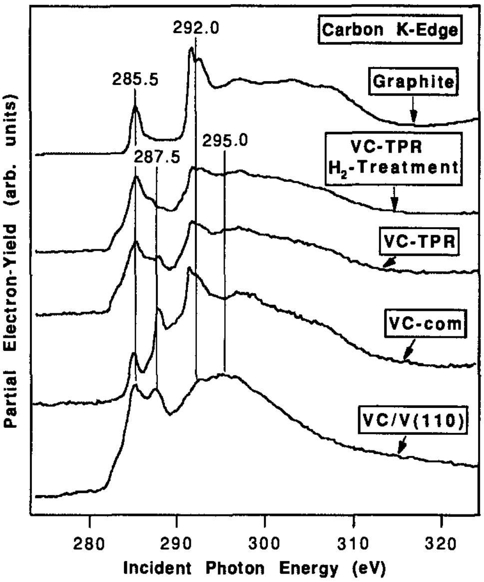

Fig. 2. A comparison of electron-yield NEXAFS of C K-edge features of VC thin films on the V(110) single crystal, VC powders and graphite.

VC film shows two sharp resonances at 285.5 and 287.5 eV, and a broad feature at 295.0 eV. As will be discussed next, similar sets of carbon K-edge features, i.e., two sharp resonances at <290 eV and a broad feature at ≥295 eV, are observed for other early transition metal carbides. Band-structure calculations, using a linearized augmented plane wave (LAPW) method, have been carried out for three early transition metal carbides, namely TiC [11], NbC [12] and WC [19]. In addition, band structures of Mo_2C [20] and VC [21] have also been investigated by other semiempirical calculation methods. These calculations suggest that the carbon 2p and metal d orbitals undergo significant hybridization as a result of carbide formation, giving rise to several partially-occupied and unoccupied orbitals. By applying the band-structure calculations to the current study, the two sharp resonances at <290 eV can be assigned to the transitions of C 1s electrons to the p–d(t_{2g}) and p–d(e_g) hybridized orbitals, respectively. Similarly, the broad feature at ≥295 eV can be assigned to the transition of C 1s electrons to an unoccupied orbital that involves contributions from 2p and 3p orbitals of carbon and the d and s states of metals [11,12,19–21].

As shown in fig. 2, the three VC-related features, at 285.5, 287.5 and 295.0 eV, are present for all three VC powders samples, although the relative intensities among these three peaks are different. In particular, the intensity of the near-edge feature at 287.5 eV is markedly different for the three VC powder samples. Earlier studies on the VC/V(110) suggest that the 287.5 eV feature is only detected on the surface VC layer and its intensity depends strongly on the local environment of carbon atoms on the surface [5]. The varying amounts of surface oxygen impurities present on the three VC samples could therefore give rise to the differences in the relative intensity of 287.5 eV feature. In addition, the presence of graphite on the surfaces of VC samples is also observed, as indicated by the detection of the graphite C K-edge feature at 292.0 eV for all three VC samples.

Fig. 3 shows the bulk-sensitive fluorescence-yield spectra of VC/V(110), commercial VC and synthesized VC samples. For all three samples, the peak centers of the two C K-edge features characterizing the bulk VC appear at 285.5 and 295.0 eV, respectively, and the relative intensities of these two features are also almost identical. The spectra in fig. 3 therefore indicate that the bulk compositions of the VC samples are very similar. However, the peak widths of the 285.5 eV feature for the VC powder materials are broader than that of the VC/V(100) sample. This can be expected since the powders are a mixture of various phases and orientations of VC, which would most likely give rise to a broadening of the near-edge features.

3.3. TRANSITION METAL CARBIDES

The powder materials of early transition metal carbides of Ti, V, Nb, Mo, and W were characterized by scanning the C K-edge features using both electron-yield and fluorescence-yield methods. It was hoped that the sensitivity of the NEXAFS spectroscopy to the chemical environment might reveal information on the similarities and differences in the electronic properties of these materials. The electron-yield NEXAFS spectra of these carbides are compared in fig. 4.

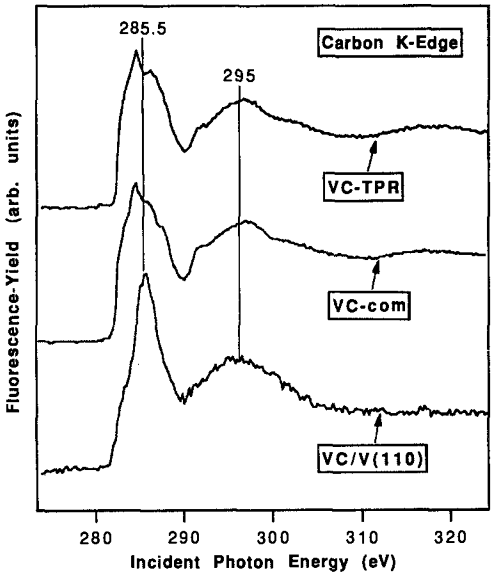

Fig. 3. Fluorescence-yield NEXAFS spectra of VC/V(110) and powder materials of commercial and synthesized VC.

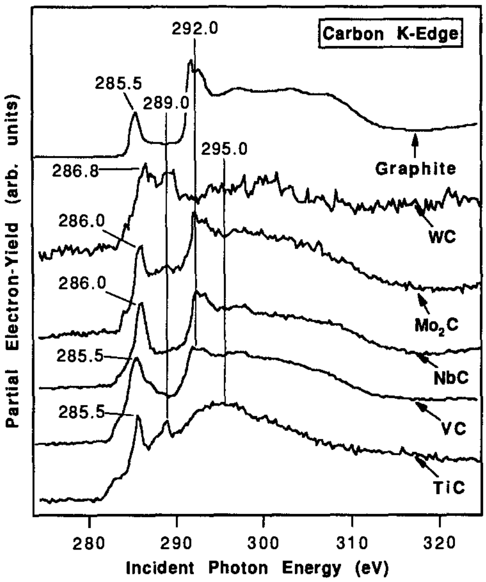

Fig. 4. The electron-yield NEXAFS of C K-edge features of TiC, VC, NbC, Mo_2C and WC. All carbide samples were pretreated by heating in hydrogen at 723 K. For comparison, the leading C K-edge features of metal carbides are normalized to have similar intensities.

As shown in fig. 4, the set of three carbide-related features observed for VC is detected for other carbides as well. However, there are slight differences in each spectrum as the positions of the leading K-edge features shift to higher energies, from 285.5 eV for TiC to 286.6 eV for WC. In addition, the intensity and peak position of the second resonance at 287.5–289.0 eV is also different for different carbides. Further inspection of the spectra reveals that the lineshapes and relative intensities of the five carbides are significantly different from those of graphite. However, the observation of the 292 eV feature on several carbides (VC, NbC and Mo_2C) suggests the presence of some graphite impurities.

The general similarities in the carbon K-edge features, along with the gradual shifts in the peak positions of the leading carbon K-edge features, suggest that the local chemical environment of carbon is similar but not identical for the five carbides. Similar trends were also observed for the fluorescence-yield measurements of the five carbides (spectra not shown). The NEXAFS results support the general agreement in the literature that the early transition metal carbides possess similar electronic properties, although the ionicity of these carbides decreases from group 4B to group 6B. For example, XPS measurements of the chemical shift of the C 1s level indicate that electron charge is polarized in the direction from metal to carbon, with electron density around the carbon decreasing with the increasing period and group number of the metal ($TiC > VC_{0.88} > Cr_3C_2$; $Cr_3C_2 > WC$) [22]. In the current study, the gradual shift in the leading K-edge features may be related to the change in the ionicity of different carbides. For example, one could argue that the energy level of the hybridized p–d(t_{2g}) orbital of a metal carbide should depend strongly on the charge distribution between the metal and carbon. Differences in charge distributions among various carbides should therefore give rise to different peak positions in the NEXAFS measurements.

We should also point out that, for other carbon-containing compounds such as graphite and diamond, the peak positions of the leading C K-edge features are sometimes related to the degree of hybridization of the C–C bonds [23]. For carbon compounds with only sp^2 hybridization, such as graphite, the leading C K-edge feature is observed at 285.5 ± 1 eV. On the other hand, for those with only sp^3 hybridization, such as diamond, the onset of the C K-edge feature is observed at 289 ± 1 eV [23]. If a similar trend can be adopted for the analysis of carbides, the gradual shift in fig. 4 would suggest that the local environment of carbon atoms changes from more sp^2-like for TiC to more sp^3-like for WC.

3.4. TRANSITION METAL NITRIDES

The powder samples of early transition metal nitrides of Ti, V and Mo were characterized by scanning the N K-edge features, as shown in fig. 5. In addition, the NEXAFS spectrum of boron nitride (BN), which is isoelectronic to graphite, is also compared in fig. 5. Similar to their carbide counterparts, the N K-edge features of TiN and VN are characterized by two sharp resonances and one broad feature at higher energy. The fluorescence-yield spectra (not shown) of these two nitrides are

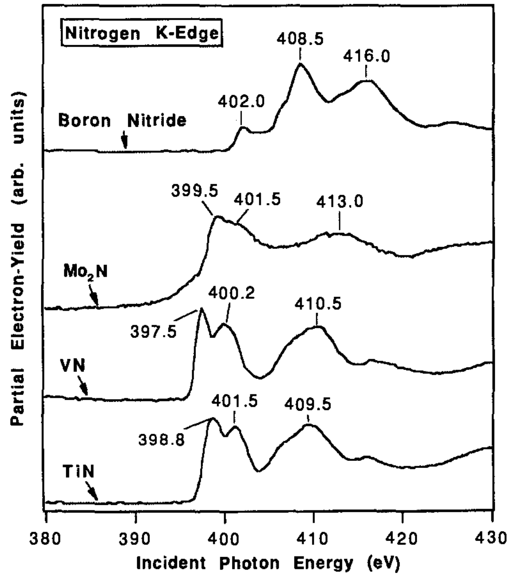

Fig. 5. A comparison of N K-edge features of TiN, VN, Mo_2N and boron nitride. All nitride samples were pretreated by heating in hydrogen at 723 K. For comparison, the leading N K-edge features of metal nitrides are normalized to have similar intensities.

identical to the electron-yield spectra. By adopting the band-structure calculations for TiN [11,24], VN [11,25] and MoN [26], the N K-edge features can be assigned to the transition of N 1s electrons to the hybridized orbitals involving nitrogen and metals. The two sharp resonances can be assigned to the transitions of N 1s electrons to the p–d(t_{2g}) and p–d(e_g) hybridized orbitals, respectively, and the broad feature at 409.5–413.0 eV can be assigned to the transition of N 1s electrons to an orbital that involves contributions from 2p and 3p orbitals of nitrogen and the d and s states of metals [11,12]. Although the NEXAFS spectrum of Mo_2N shows a similar set of three K-edge features at approximately 399.5, 401.5 and 413.0 eV, the first two resonances are no longer well-resolved. This is likely due to the complication that the M_{III} and M_{II} features of molybdenum also appear in this spectroscopic range.

In general, the N K-edge features are not as well understood as the C K-edge features. The lack of NEXAFS characterization on single crystal metal nitrides makes the data analysis even more difficult. At present, we do not intend to interpret the differences observed for the three nitrides. We would only like to point out that the N K-edge features of the three metal nitrides show a similar general spectroscopic characteristics, which are at the same time significantly different from those of boron nitrides.

3.5. HYDROGENATION OF 1-BUTENE ON CARBIDES AND NITRIDES

In this section we will present some of our preliminary results on the use of NEXAFS spectroscopy for catalytic studies on carbides and nitrides. Fig. 6 shows the C K-edge spectra of VC and VN taken before (solid line) and after (dotted line) 1-butene hydrogenation reactions. The reaction studies were carried out in situ in the NEXAFS chamber and have been described in the experimental section.

In hydrogenation studies a good catalyst is expected to maintain its activity and have a clean surface without excessive deposition of carbonaceous species. As shown in fig. 6, the C K-edge features of VC are very similar before and after 1-butene hydrogenation. There is no graphite formation after the reaction, suggesting that there is very little deactivation of the VC catalyst. Similar results were observed for all other carbides reported in the current study (not shown). The C K-edge spectrum of VN shows the build up of a very small amount of carbon on the surface after the hydrogenation reaction. This again shows that the catalysts have long lifetimes. Further reaction studies will be carried out to investigate the catalytic performance of VC and VN.

4. Conclusions

Early transition metal carbides and nitrides have been characterized using NEXAFS, some of them for the first time. The C K-edge features for most of the car-

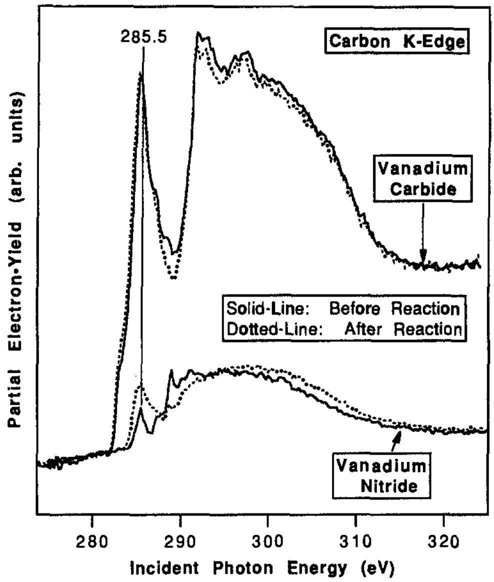

Fig. 6. The electron-yield NEXAFS of C K-edge features of VC and VN recorded before and after 1-butene hydrogenation reactions. The step-heights of the NEXAFS spectra are not normalized.

bides show the same general carbide-related features, but intensities and energy positions differ somewhat for different compounds. The systematic shift in the leading C K-edge features suggests that the local chemical environment is similar but not identical. Similar conclusions can also be made for the local environment of nitrogen for the three metal nitride samples. Furthermore, the NEXAFS spectroscopic method was used to probe the surface of VC and VN for deposit of carbonaceous species after the 1-butene hydrogenation reaction. No appreciable amounts of carbon were detected and it is suggested that the carbide and nitride catalysts do not deactivate and have long lifetimes.

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