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XPS evidence for molybdenum nitride formation in ZSM-5

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This communication presents XPS evidence for the formation of molybdenum nitride or oxynitride species in ZSM-5 when HZSM-5 loaded with MoO_3 is subjected to temperature programmed reaction with ammonia. We suggest that this chemistry provides a potential route to zeolite dispersed transition metal nitride catalysts.

KEY WORDS: ZSM-5; molybdenum nitride; XPS.

1. Introduction

Ever since the first suggestion by Levy and Boudart [1] that transition metal carbides should show catalytic properties similar to those of the platinum group metals, there has been an expanding research effort investigating the catalytic potential of metal carbides [2] and more recently metal nitrides [3]. With a few notable exceptions, almost all of the published work on these materials has referred to the unsupported bulk compounds, and increasing the surface area (and hence the catalytic reactivity) has been a major objective. Some studies have used alumina [4], carbon [5] or mesoporous silica [6] supports to enhance the dispersion of the carbide or nitride phase.

The use of zeolite supports to enhance and stabilise the dispersion of platinum group metals is well known. Acid zeolite supports containing a noble metal also allow the possibility of bifunctional catalysis, and the zeolite pore system may impose desirable shape selectivity. The use of zeolite HZSM-5 as a support for transition metal carbides first came to attention when molybdenum ZSM-5 catalysts were reported for the non-oxidative dehydrogenation of methane to form benzene [7]. The chemistry of this system has been extensively investigated. It has been shown by XPS [8] and Mo K-edge EXAFS [9, 10] that the molybdenum oxide precursor in ZSM-5 is converted to molybdenum carbide under reaction conditions, and it is the zeolite dispersed molybdenum carbide species that is responsible for the catalytic activation of methane. Similar chemistry has subsequently been utilised to prepare zeolite dispersed tungsten and vanadium carbide catalysts [11, 12].

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Zeolite dispersed molybdenum nitrides were first prepared by Becue et al. [13]. These workers used a chemical vapour deposition method to introduce $Mo(CO)_6$ into the pores of zeolite EMT (a hexagonal polytype of zeolite Y), followed by reaction with ammonia. XPS and temperature programmed reaction (TPR) methods were used to show that some nitride species were formed at temperatures as low as 523 K. The group of Okamoto subsequently used a similar method to prepare molybdenum nitride species in zeolite NaY at 673 K, although their Mo K-edge EXAFS measurements were unable to distinguish between O and N in the first coordination shell of molybdenum [14].

The $Mo(CO)_6$ precursor route cannot be used to introduce molybdenum into smaller pore zeolites such as ZSM-5. Shi et al. [15] have reported on the activity of ZSM-5 supported molybdenum nitrides prepared from MoO_3 for NO reduction with hydrogen. These workers described the use of XPS and TPR techniques to show evidence for nitride formation, but no information was provided about the location of the molybdenum species.

We have been intrigued by the possibility of applying chemistry similar to that involved in the molybdenum ZSM-5 catalysts used for methane conversion to benzene to obtain zeolite dispersed molybdenum nitride species where the transition metal component is located within the zeolite pores rather than as an external phase. The key to this is achieving migration of oxomolybdenum species into the zeolite during high-temperature calcinations prior to conversion to the carbide or nitride [10].

We report here some initial XPS measurements which indicate that the strategy does work, and suggest a route to a new generation of bifunctional zeolite catalysts containing transition metal nitrides.

2. Experimental

Zeolite NH_4ZSM-5 (Si:Al = 15) kindly provided by Zeolyst Ltd. (batch TZP-302) was calcined in air at 673 K for 12 h to convert it to the hydrogen form. Five grams (5 g) of the zeolite was stirred for 20 h with a solution of 10 mL of ammonium heptamolybdate in water to give a loading of 4 wt% Mo. The impregnated zeolite was oven dried, then calcined in air at 973 K for 10 h. Nitridation was performed in flowing ammonia (94 mL min^{-1}) according to the following temperature program: 298–630 K at 5.6 K min^{-1}, 630–720 K at 0.5 K min^{-1}, 720–1040 K at 2.1 K min^{-1}, then 5 h at 1040 K followed by cooling in either flowing nitrogen or in flowing ammonia to room temperature. The nitrided zeolite was then passivated by flushing with nitrogen at room temperature overnight, then in a 0.1% oxygen in argon mixture at room temperature for 8 h. A sample of bulk Mo_2N was prepared from MoO_3 following a similar protocol. X-ray powder diffraction measurements confirmed that the zeolite structure remained intact in the calcined and nitrided zeolites. No additional diffraction lines were observed for MoO_3 or Mo_2N, indicating that a high level of dispersion had been achieved. The bulk nitride, on the other hand, gave the expected pattern of γ-Mo_2N.

For XPS analysis, samples were pressed into self-supporting disks and mounted on nickel sample stubs with double sided tape. All samples were evacuated at 10^{-7} mbar for 12 h before insertion into the analysis chamber of a VG ESCALAB II spectrometer (base vacuum 10^{-9} mbar). Spectra were obtained using Al Kα X-rays (10 kV, 20 mA, un-monochromatised). Correction for sample charging was made by setting the C 1s binding energy to 285.0 eV (this gives a Si 2p binding energy for ZSM-5 of 103.0 eV). Sample sputtering used an argon ion gun operating at 4 kV accelerating voltage and ion current of around 20 μA cm^{-2}. Curve fitting of the observed spectra was performed using Gaussian line shape functions , constrained by the intensity ratios and peak splittings required for Mo 3d or 3p spin-orbit doublets (intensity ratio 3:2 and splitting of ca. 3.5 eV for Mo 3d, intensity ratio 2:1 and splitting of ca.17.2 eV for Mo 3p). Binding energies were reproducible to within 0.2 eV. Atomic ratios were estimated by dividing peak areas by the appropriate atomic sensitivity factors.

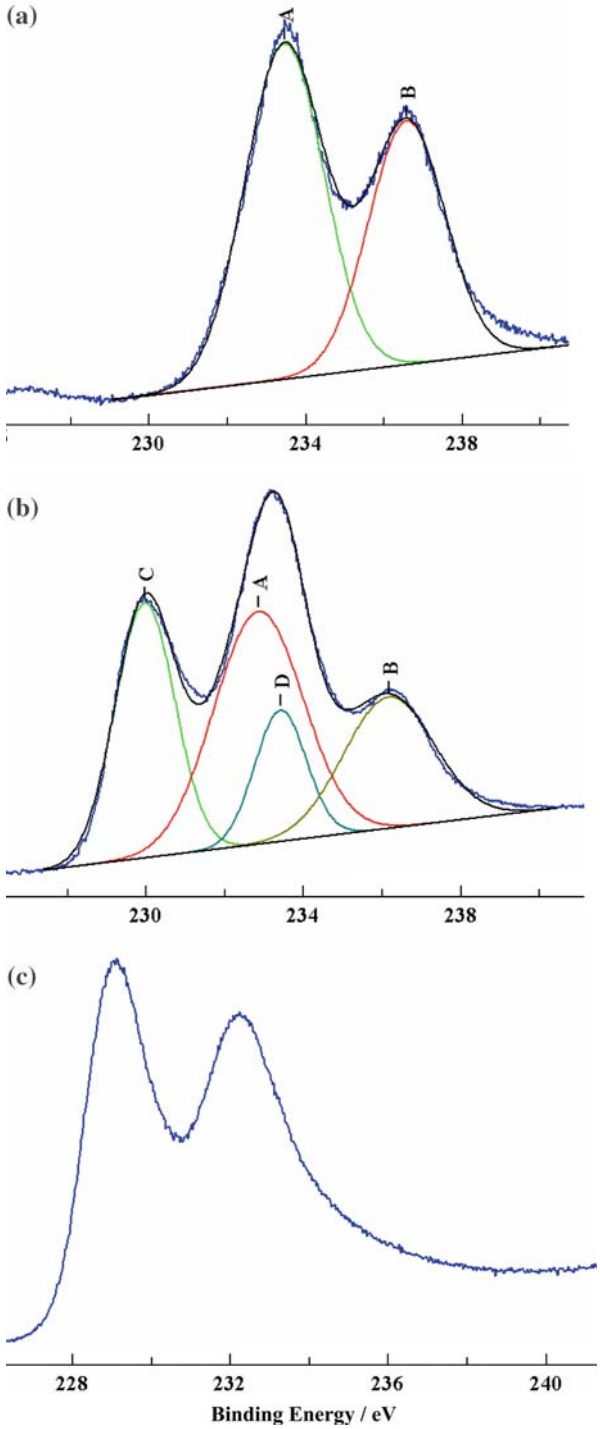

Figure 1. XPS spectra in the Mo 3d region of (a) MoO_3, (b) nitrided and passivated MoO_3, (c) after argon ion etching.

3. Results and discussion

Figure 1 shows spectra in the Mo 3d region of MoO_3 and of the bulk sample of Mo_2N before and after ion beam sputtering. The parent oxide shows a single spin-orbit doublet (Mo $3d_{5/2}$ and Mo $3d_{3/2}$ with an intensity ratio of 3:2) with a Mo $3d_{5/2}$ binding energy of 233.0 eV. The corresponding spectrum of the as-prepared Mo_2N (figure 1(b) shows a superposition of this doublet and a second doublet at lower binding energy (Mo $3d_{5/2}$~229.8 eV). The exact absolute binding energy values depend on the binding energy reference chosen to correct for sample charging, but the difference of 3.2 ± 0.4 eV between Mo^{+VI} in MoO_3 and the lower binding energy component in the nitrided sample is closely similar to that reported by others [13, 15, 16]. The residual Mo^{+VI} doublet in figure 1(b) is attributed to the passivating oxide layer, as shown by the fact that this component is readily

removed by brief argon ion etching (figure 1(c)). The single doublet remaining after etching shows a slightly lower binding energy (Mo $3d_{5/2}$~229.3 eV) which may be due to further reduction by the ion bombardment.

Corresponding spectra in the Mo 3p region are presented in figure 2. In this case, the parent oxide shows a single spin-orbit doublet (Mo $3p_{3/2}$ and Mo $3p_{1/2}$, with an intensity ratio of 2:1) characteristic of Mo^{+VI}. (Mo $3p_{3/2}$ = 399.0 ± 0.2 eV referenced to C 1s = 285.0 eV). The as-prepared bulk nitride shows, as expected from the Mo 3d spectra, two overlapping doublets in the Mo 3p region (figure 2(b)). These Mo 3p components are assigned to the passivating oxide layer and the underlying nitride. The observed peak shape could be correctly simulated however only by including a third component as a single peak (marked E in the figure) at 398.0 ± 0.2 eV. This peak is due to N 1s electrons from Mo_2N (Becue et al. report a value of 397.8 eV for bulk γ-Mo_2N [13]).

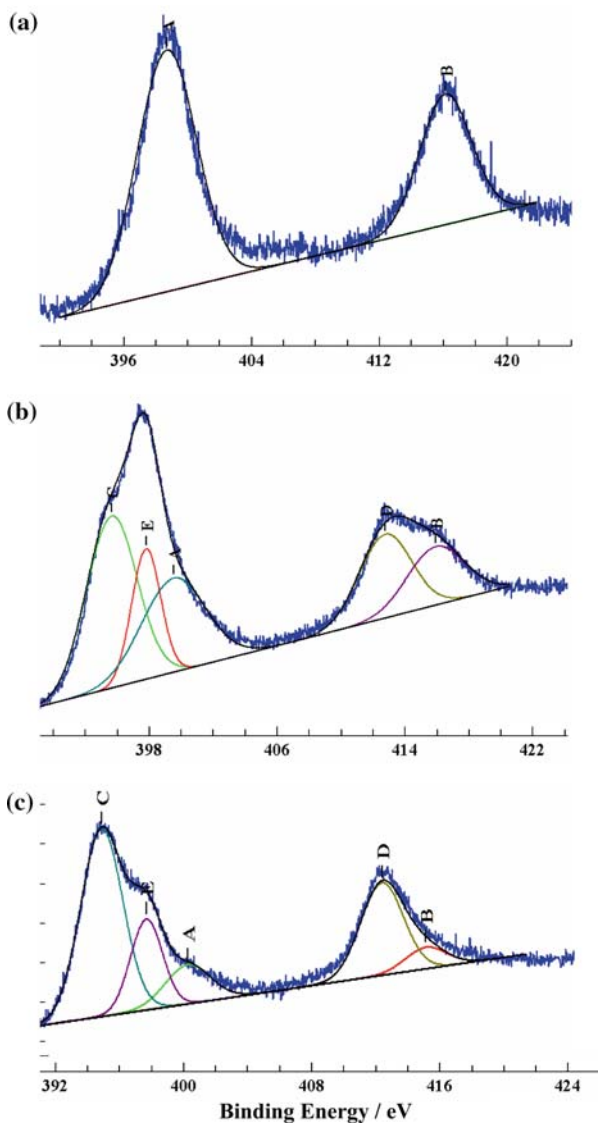

Figure 2. XPS spectra in the Mo 3p region of (a) MoO_3, (b) nitrided and passivated MoO_3, (c) after argon ion etching. E marks the N 1s peak.

After argon ion etching, the Mo 3p region shows largely a single doublet with the N 1s peak present as a shoulder on the $3p_{3/2}$ component (figure 2(c)), although curve fitting indicates the continued presence of a small amount of the oxidised species. Determination of the N:Mo ratio from the relative intensities of the Mo $3p_{3/2}$ and N 1s peaks cannot be done accurately , but an upper limit of around 1.0 is estimated, suggesting that the surface layers probed by XPS are nitrogen-rich compared with the expected bulk stoichiometry of Mo_2N.

Figure 3(a) shows the Mo 3d spectrum of MoZSM-5 (4 wt% Mo) after calcination at 973 K. The Mo $3d_{5/2}$ binding energy of 233.0 eV is that expected for Mo^{+VI}. The surface Mo:Si ratio measured from integrated intensities of Mo 3d and Si 2p binding energy peaks was 0.054, almost twice the value expected from bulk analysis (0.029). This suggests that the calcination process does not succeed completely in dispersing the oxide phase within the zeolite pores. A similar conclusion was reached in our earlier study of methane aromatisation catalysts [9]. The enrichment of molybdenum on the external surface of the zeolite was confirmed by observing a decrease in the Mo 3d signal intensity (to a Mo:Si ratio of 0.027) when the calcined catalyst was briefly argon ion etched.

Figure 3(b) shows the Mo 3d spectrum recorded from a nitrided MoZSM-5 sample. Nitrided samples showed a considerable reduction in Mo 3d (and 3p) signal intensities compared with the calcined catalyst (e.g. the Mo:Si ratio estimated for the sample shown in figure 3(b) is 0.020). The broad Mo 3d envelope could be simulated by including two overlapping Mo 3d doublets with the same splitting and intensity ratios. The lower binding energy doublet (Mo $3d_{5/2} \cong 228.2$ eV) appears to be shifted to lower binding energy from that seen with the bulk Mo_2N in figure 1, although the lower signal to noise in the zeolite dispersed samples means that the curve-fitting process is subject to larger uncertainty. The higher binding energy component (Mo $3d_{5/2}$ = 231.0 eV) is 2.0 eV shifted to lower binding energy relative to the calcined catalyst, suggesting that this species has an oxidation state lower than +6, and is not the same as the passivating oxide layer on the bulk nitride.

This difference between the zeolite dispersed and bulk samples was also seen in different behaviour on argon ion etching (figure 3(c)). Although the contribution of the higher binding energy doublet was reduced on etching, it could not be removed to the extent that was possible with the bulk sample (Figure 1(c)). The Mo:Si ratios estimated for etched samples were comparable (~0.02) with those of freshly nitrided samples. Spectra measured in the Mo 3p region showed similar effects (figure 4). The freshly calcined catalyst gave a single Mo 3p doublet with binding energies similar (within 0.5 eV)

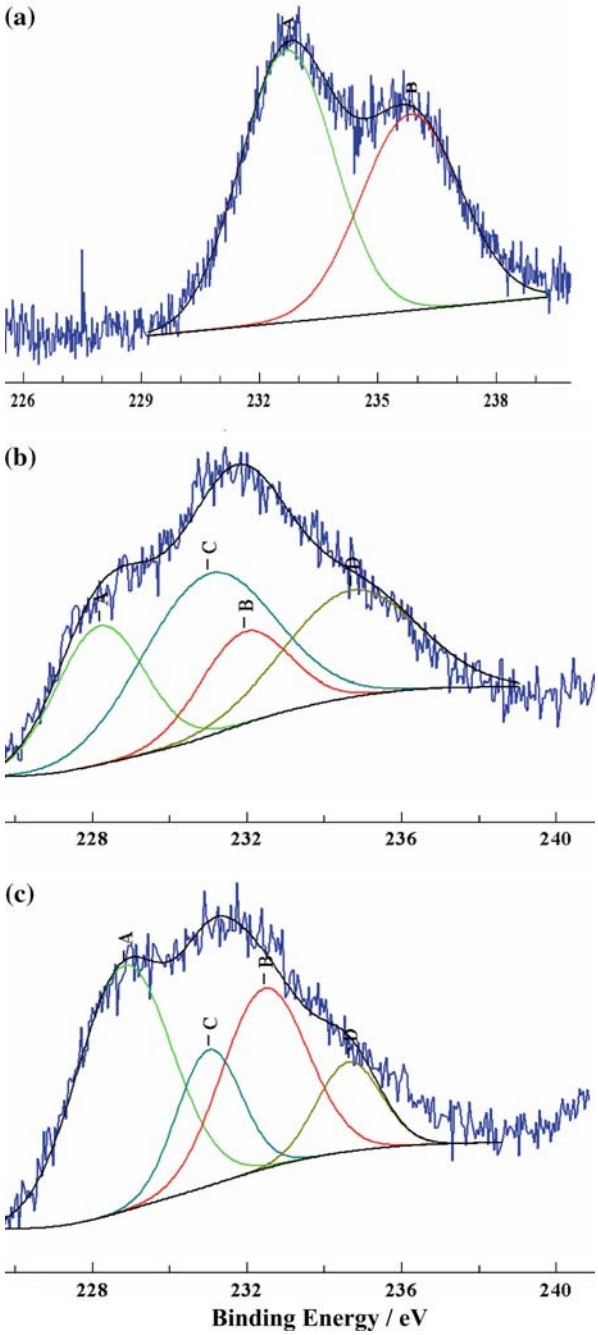

Figure 3. XPS spectra in the Mo 3d region of (a) MoZSM-5 after calcination at 973 K, (b) after nitridation and passivation, (c) after argon ion etching.

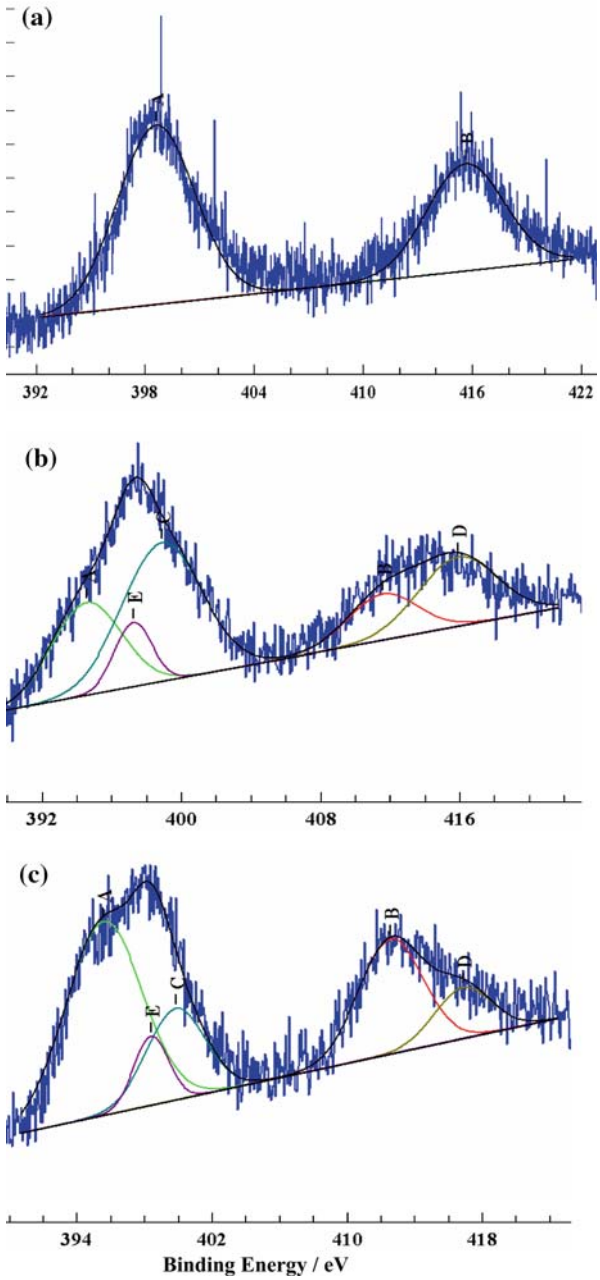

Figure 4. XPS spectra in the Mo 3p region of (a) MoZSM-5 after calcination at 973 K, (b) after nitridation and passivation, (c) after argon ion etching. E marks the N 1s peak.

to the bulk oxide. The spectrum of the freshly nitrided sample could be fitted with two doublets plus a fifth peak (marked E) due to N 1s, at ~398.0 eV. The lower binding energy doublet (Mo $3p_{3/2}$~395.0 eV) is close to that seen with the bulk nitride, but argon ion etching could not remove the higher binding energy doublet (compare with figure 2(c)). The N:Mo ratios estimated from relative areas of the N1 s and lower binding energy Mo $3p_{3/2}$ component were ~1.0 for the freshly nitrided catalyst, and ~0.5 for the etched sample.

Similar measurements were undertaken on MoZSM-5 zeolite samples nitrided with the same protocol used for preparing the bulk nitride, i.e. cooling the sample in flowing ammonia rather than in flowing nitrogen following the high-temperature treatment. Such samples gave similar spectra in the Mo 3d region to those reported here. The Mo 3p region for these samples was however dominated by a much more intense N 1s peak which we attribute to NH_3 adsorbed in the zeolite during the cooling step. Argon ion etching reduced the intensity of this peak and allowed the lower binding-energy Mo 3p

doublet to be observed, but N:Mo ratios of 20 or higher were estimated for these samples.

4. Conclusions

The XPS data presented here suggest in our view that the catalyst preparation protocol employed for preparing zeolite dispersed molybdenum carbide catalysts for methane aromatisation can be modified (replacing methane with ammonia) to prepare zeolite dispersed molybdenum nitride or oxy-nitride catalysts which may have novel properties. The zeolite dispersed species show some differences from the corresponding bulk materials. In particular, it was impossible to fully remove the partially oxidised molybdenum component from the zeolite catalysts by argon ion etching, which suggests that these systems are best described as oxynitrides, possibly interacting strongly with the zeolite lattice. Further evidence for dispersal within the zeolite comes from the fact that Mo:Si ratios measured by XPS were not depleted on etching. The Mo 3d spectra presented here differ significantly from those reported by Shi et al. [15], who considered they were observing a mixture of Mo_2N and MoO_3 on the surface of the zeolite. Any species dispersed inside the zeolite pores will in any event consist of very small clusters with properties very different from those of the bulk nitride.

Further work is in progress to investigate more fully the chemistry involved in nitride or oxynitride formation in ZSM-5, and to better characterise the species generated. We point out here however that the catalytic properties of these novel materials deserve further study.

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