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The chemical and electronic properties of oxygen-modified C/Mo(110): a model system for molybdenum oxycarbides

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Abstract

We have utilized oxygen-modified C/Mo(110) surfaces as model systems to determine the modification effect of oxygen in "oxycarbides." Using cyclohexene, ethylene, and methanol as probe molecules, we observed that the reactivity of the O/C/Mo(110) surfaces depended strongly on the temperature at which oxygen was introduced onto the C/Mo(110) surface. The reaction pathways were determined using both temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). For example, the O/C/Mo(110) surface obtained by exposing the carbide surface to oxygen at 600 K became chemically inert toward all three molecules. On the other hand, the 900 K O/C/Mo(110) surface was active toward all three molecules, and for the most part retained the Pt-like reaction pathways observed on unmodified C/Mo(110). Furthermore, we have also compared the electronic properties of the O/C/Mo(110) surfaces using two synchrotron spectroscopies, soft X-ray photoelectron spectroscopy (SXPS) and near-edge X-ray absorption fine structure (NEXAFS); the results revealed similar electronic properties between the 900 K O/C/Mo(110) and unmodified C/Mo(110) surfaces.
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1. Introduction

It has been well documented that early transition metal (Groups IV–VIB) carbides, when compared to their parent metals, often exhibit catalytic properties that are similar to those of Pt-group metals [1,2]. For example, in our previous surface science studies we have demonstrated that the surface reactivities of carbide-modified V(110) [3,4], Mo(110) [5–7], W(111) [8,9], W(110) [10,11], and Ti(0001) [12] are often very similar to those of the Pt(111) surface.

For catalytic reactions, the surfaces of carbide materials are often oxidized by air or by oxygen-containing reactants or products. Several research groups have reported that the reactivity of carbides can be significantly modified by the presence of oxygen [13–15]. For example, Iglesia and

co-workers have reported that unmodified tungsten carbide catalysts were active toward the dehydrogenation of alkanes and the hydrogenation of alkenes [13]. The presence of chemisorbed oxygen on these surfaces, however, directed the catalytic selectivity toward isomerization and dehydration pathways, which were not observed on the unmodified surface [13,14]. These oxygen-modified carbides, or "oxycarbides," were characterized as bifunctional in their ability to catalyze both dehydrogenation and carbenium-ion reactions [13].

We have recently investigated the effect of oxygen modification on the surface reactivity of carbide-modified W(111) [9,16]. We found that the reactivity of the oxygen-modified C/W(111) surfaces depended strongly on the surface temperature at which oxygen was introduced. The C/W(111) surface, after exposure to oxygen at 900 K, or 900 K O/C/W(111), retained the Pt-like reactivity toward cyclohexene. On the other hand, the C/W(111) surfaces that were exposed to oxygen at 600 or 100 K were nearly inert [9]. Ad-

ditional vibrational spectroscopic studies revealed that when introduced at 600 or 100 K, the atomic and/or molecular oxygen occupied the on-top sites of the C/W(111) surface. In contrast, the vibrational results on the 900 K O/C/W(111) surface suggested that the oxygen atoms did not occupy the on-top sites, which would enable the cyclohexene to interact more strongly with the surface [9]. Using methanol as a probe molecule, the 900 K O/C/W(111) surface appeared to be less active toward C–O bond scission than C/W(111), as evidenced by its increased selectivity toward the production of gas-phase CO [17].

In this paper we report the effect of oxygen modification on C/Mo(110). We have used several types of probe molecules, including linear olefin (ethylene), cyclic olefin (cyclohexene), and oxygenate (methanol) to investigate the activity of oxygen-modified C/Mo(110), or O/C/Mo(110). In addition, we have utilized several electron spectroscopies, including soft X-ray photoelectron spectroscopy (SXPS) and near-edge X-ray absorption fine structure (NEXAFS) to compare the electronic properties of the C/Mo(110) and O/C/Mo(110) surfaces.

For the purpose of comparison, we will briefly summarize our previous studies of the reactions of cyclohexene [6,7], ethylene [5], and methanol [17] on unmodified C/Mo(110). Cyclohexene adsorbed via a di-σ configuration on C/Mo(110), and subsequently dehydrogenated to produce gas-phase benzene. Quantitative analysis revealed that approximately 70% of the adsorbed cyclohexene underwent selective dehydrogenation to produce benzene [6,7]. In the reaction of ethylene, HREEL studies following the low-temperature adsorption of ethylene showed vibrational spectra features consistent with those of the ethylidyne intermediate (CCH_3) when the overlayer was heated to 260 K [5]. Both the selective hydrogenation of cyclohexene to benzene and the conversion of ethylene to ethylidyne were strong indications that the surface reactivity of Mo(110) became "Pt-like" upon carbide modification [2]. Finally, studies probing the interaction of methanol on C/Mo(110) revealed the formation of a stable methoxy intermediate at temperatures between 120 and 330 K [17].

2. Experimental

2.1. Techniques

One of the ultrahigh vacuum (UHV) chambers used in the current study was located at the University of Delaware, and has been described in detail previously [5]. Briefly, it was a three-level stainless-steel chamber equipped with Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) in the top two levels, and high-resolution electron energy loss spectroscopy (HREELS) in the bottom level. The HREEL spectra reported here were acquired with a primary beam energy of 6 eV. Angles of incidence and reflection were 60° with respect to the surface normal

in the on-specular direction. Intensities of the elastic peak were typically in the range of 3×10^4 to 3×10^5 counts per second, and the spectral resolution was between 40 and 55 cm^{-1} FWHM (full width at half-maximum). For TPD and HREELS experiments the Mo(110) sample was heated with a linear heating rate of 3 K/s.

The NEXAFS and SXPS experiments were conducted at the U1A and U12A beamlines, respectively, at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. These beamlines and their respective UHV end stations have been previously described in detail [18,19]. SXPS data were recorded on U12A with an incident energy of 150 eV for the Mo valence states [18]; each spectrum represented the average of 10 consecutive scans. The binding energy of each spectrum was then calibrated based on the Fermi energy. The end station contained a VSW EA125 electrostatic analyzer, which was set to operate in constant pass energy mode (10 eV) for photoemission measurements. The instrument resolution was better than 0.5 eV for all spectra. The carbon K-edge NEXAFS spectra were recorded on U1A by measuring partial electron yield using a channeltron multiplier located near the sample surface [19]. Both UHV chambers were equipped with an Auger electron spectrometer and a UTi quadrupole mass spectrometer to ensure identical experimental conditions with the UHV chamber at the University of Delaware.

The single crystal sample was a (110) oriented, 1.5-mm-thick molybdenum disk (99.999%), 10 mm in diameter, and was purchased from Metal Crystals and Oxides, Ltd., Cambridge, England. The crystal was spot welded directly to two tantalum posts that served as electrical connections for resistive heating, as well as thermal contacts for cooling with liquid nitrogen. With this mounting scheme, the temperature of the crystal could be varied between 90 and 1200 K. Cyclohexene (Aldrich, 99% purity) and methanol (Aldrich, 99+% purity) were purified by successive freeze–pump–thaw cycles prior to their use. Ethylene (99.99% purity) and oxygen (99.99% pure) were obtained from Matheson and were used without further purification. The purity of the above gases was verified in situ by mass spectrometry. In all experiments, the gas exposures were made at a crystal temperature of 120 K with the crystal located in front of the leak valve. The gas exposures were made by backfilling the vacuum chamber. Doses are reported in Langmuirs (1.0 Langmuir (L) $= 1 \times 10^{-6}$ Torr s) and are uncorrected for ion gauge sensitivity.

2.2. Preparation of C/Mo(110) and O/C/Mo(110)

A clean Mo(110) crystal surface was prepared by cycles of Ne$^+$ bombardment at 500 K (sample current $\sim$ 5 µA) and flashing to 1150 K. These 5-min cycles were generally repeated 3 times before annealing at 1150 K. To remove carbon contamination, excess O_2 was used to react with carbide layers at 900 K. This oxygen treatment process was repeated several times to remove both surface and bulk carbon. Auger