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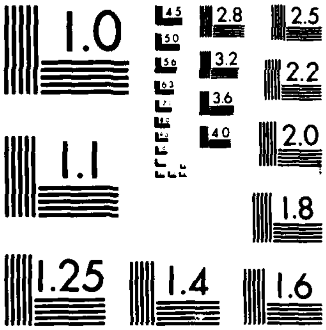

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# A THEORETICAL ANALYSIS OF THE DEACTIVATION OF METAL SURFACES UPON CARBURIZATION

by

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The catalytic activity of transition metal surfaces can be altered significantly by the deposition of carbon adlayers. In the case of nickel surfaces, several catalytic processes are enhanced. For the case of tungsten, a reconstruction occurs and the resultant surface activity is associated with both structural and electronic changes induced by the deposition of carbon. Recent experimental studies on transition metal carbides and carburized transition metals have suggested that the carbon, either present in the bulk or exposed at the surface, affects the adsorption properties of simple gaseous adsorbates. The studies on the transitio

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# A THEORETICAL ANALYSIS OF THE DEACTIVATION OF METAL SURFACES UPON CARBURIZATION

S. A. Jansen and R. Hoffmann

The catalytic activity of transition metal surfaces can be altered significantly by the deposition of carbon adlayers.[1,2] In the case of nickel surfaces, several catalytic processes are enhanced.[3,4] For the case of tungsten, a reconstruction occurs and the resultant surface activity is associated with both structural and electronic changes induced by the deposition of carbon.[5,6] Recent experimental studies on transition metal carbides and carburized transition metals have suggested that the carbon, either present in the bulk or exposed at the surface, affects the adsorption properties of simple gaseous adsorbates. The studies on the transition metal carbides are of interest not only because of their intrinsic surface chemistry, but also because of their relevance to certain carbided surfaces. The following discussion focuses on two systems; TiC and WC. TiC has been the subject of scrutiny for years, as it exhibits remarkable physical properties.[7] Recently, several experiments have been performed on the (100) and (111) faces of TiC, as this material shows several similarities to titanium metal without the same disposition toward corrosion. Similar experiments have been performed on NbC, showing parallel chemical tendencies.[8] The calculations were performed on TiC; however, the general trends and conclusions obtained through the theoretical analysis are valid for either system. The analysis performed focuses on the (100) and (111) faces, as these faces represent the extremes in reactivity. WC(0001) was selected for study, since this material serves as a tenable model for the W(100)-(5x1)-C surface. The properties of these surfaces have been evaluated in terms of simple gaseous adsorption and decomposition by the extended Hückel/tight binding method.

## Surfaces of Study:

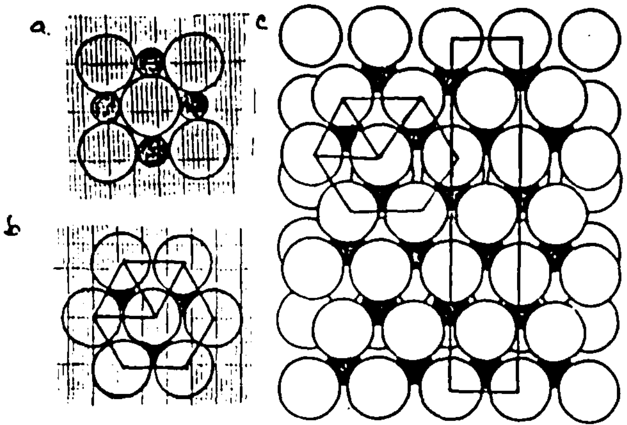
### a. TiC

TiC crystallizes in the rock salt structure with Ti-C distance of 2.164Å and Ti-Ti and C-C distances of 3.06Å. Two faces have been successfully prepared, the (100) and (111), while attempts at preparation of the (110) face have provided only faceted surfaces. The (100) face is a square face in which both Ti and C atoms are exposed. The primary adsorption chemistry is affected by the presence of the surface carbon. The (111) face considered is a Ti terminated face. For the (100) face special consideration was given to the question of the effect of carbon vacancies at the surface. Figure 1a shows the TiC surfaces of interest to this study. (The bond distances and lattice constant for NbC are nearly identical to those of TiC.)

### b. WC

Studies on WC(0001) are proposed to model those of the W(100)-(5x1)-C in which surface reconstruction provides for nearly hexagonal layers of tungsten at the surface. The carbon atoms form the second layer of the substrate, and are also nearly hexagonal. UPS studies have shown that the valence orbitals of the WC and the carbided tungsten surface are nearly identical.[9] For these reasons, WC(0001) is selected as a suitable model for the carbided surface. The W-W distance is 2.900Å and the W-C distance is [illegible]Å. Figures 1b and 1c show the structural similarities between the W(100)-(5x1)-C and WC(0001) surfaces.

Figure 1.



a) Top layer of the (100) face of TiC/NbC.
b) Top layer of the (111) face of TiC/NbC, showing the second layer of substrate carbon in alternating hollow sites. The same structure is observed for the top two layers of WC(0001).
c) The W(100)-(5x1)-C surface, showing the (5x1) unit cell and the nearly hexagonal packing of W and C layers.

## CO on TiC Surfaces

The adsorption of CO on TiC provides for an interesting study of the surface reactivity of related carbides and carburized surfaces. CO is known to dissociate on Ti(0001) surfaces.[10] The C-O overlap population and $2\pi^*$ occupation reflect significant reduction of CO bond strength. At the same time, a large M-C overlap population is observed. Recent experimental studies have shown that CO dissociates on NbC(111), but is observed in both molecular and dissociative states on NbC(100). The dissociative states on NbC(100) are suspected to be due to carbon vacancies at the surface. Calculations on the (111) face have shown a sizeable reduction in C-O overlap population, and a correspondingly large increase in the occupation of the $2\pi^*$ orbital. Table 1 shows the overlap population and FMO populations for TiC(100), TiC(100) with carbon vacancies at the surface, and the (111) face.

Table 1: Overlap population and FMO analysis for CO on selected surfaces of TiC.

| FMO Occupations: | TiC(100) | $TiC_5$(100) | $TiC_0$(100) | TiC(111) | Ti(0001)[11] |
|---|---|---|---|---|---|
| $5\sigma$ | 1.731 | 1.725 | 1.725 | 1.725 | 1.730 |
| $2\pi^*$/orbital | 0.132 | 1.380 | 1.530 | 1.430 | 1.610 |
| Overlap Population | | | | | |
| C-O | 1.173 | 0.437 | 0.473 | 0.469 | 0.430 |
| M-C | 0.616 | [illegible] | 1.060 | 1.053 | 1.110 |

The calculations on the (111) face show many similarities to that of Ti(0001). The explanation for the increased reactivity of this face, relative to that of the (100) face, is twofold. First, the preparation of the (111) face provides for more dangling bonds or orbitals per surface atom than the (100) surface. Second, the M-C surface bonding is quite strong and occurs with significant charge transfer from the M d-block. This reduces the electron density at the metal, hence it donor properties with respect to the $2\pi^*$ orbitals of CO. This is consistent with experimental observations. For the (100) surface, the reactivity is greatly inhibited. The dissociative states of CO are associated with carbon vacancies at the surface.

## Oxygen Containing Adsorbates on TiC:

Methanol is known to adsorb molecularly on NbC(100) while a methoxy species is observed on the (111) face. A theoretical consideration of oxygen adsorption on these two surfaces has suggested adsorption sites for the study of methanol on these two surfaces.

ISS experiments have shown a marked decrease in intensity in the peaks arising from the surface carbon, suggesting that the oxygen sits directly atop the carbon.[12] On TiC(111), the oxygen atom is believed to sit in a threefold hollow site. One other site has also been observed; however, this site is not well characterized, but is suspected to be a twofold bridging site. Calculations on the (111) face have shown that of the possible adsorption sites, a threefold hollow and twofold bridging site are energetically favorable. There is one other threefold site, in which a bulk carbon atom lies directly below the adsorbate. This site is not suggested for oxygen/methanol adsorption as the C-O interaction is antibonding, and hence increases the overall energy of adsorption. The M-O interaction is approximately the same as in the case of the other threefold hollow sites. The twofold bridging site is "stabilized" by a bonding interaction between the bulk carbon and bridging oxygen. The energies of the two preferred sites are approximately the same.

The sites considered for the discussion of methanol on these two surfaces will be those in which the O of the methonol adsorbate is "atop" the surface carbon on the (100) surface. For the (111), the site to be discussed is one suggested by Yates et al.[13] for methanol on Ni(111). The methanolic oxygen occupies a twofold bridging site, while the proton is tilted toward a threefold hollow site. This site is consistent with the studies of oxygen on the (111) face of TiC and also consistent with the observation of bridging atomic adsorbates when surface distances are relatively long. In the case of TiC(111), the shortest metal-metal distance is 3.06Å. The coverage assumed for each surface is 1/4, insuring no adsorbate-adsorbate interaction.

For methanol on the (100) face, there is some weakening of the O-H bond. However, there is a compensating C(surface)-H interaction which may stabilize the methanol on the surface. A comparison of both the bonding and energetics of methanol and methoxy moieties on this surface shows increased C-O interaction for the methoxy species, though no energetic preference is observed for methoxy over that of methanol. This suggests a trade-off in bonding. In the case of methanol on the (100) face, the C-H interaction contributes to the overall stability of the adsorbate, though reducing the $C_{surface}$-O and O-H interactions. The $C_{surface}$-O overlap population has a value of 0.318 for methanol in this site. The value for methoxy similarly oriented with respect to the surface is 0.472. The C-O bond strength of methoxy or methanol is not affected upon adsorption. In the case of methanol, the overlap population between the surface carbon atom and the hydroxyl proton is 0.180, while the O-H bond has an overlap population of 0.480, relative to 0.600 observed for "free" methanol.

The decomposition of methanol into methoxy species on the (111) face of TiC/NbC is not easily or readily understood. A comparison of the interaction of both methoxy and methanol with the surface may provide some insight to the driving force for the deprotonation of methanol. In many cases, the methanol is deprotonated upon adsorption, but is able to recombine such that the only desorption product is methanol, suggesting a delicate equilibrium between methanol and methoxy species. Calculations of methoxy and methanol on the (111) face have shown a large energetic preference for methoxy. This can be traced to stronger M-O and C-O bonding. In the case of methanol, only a small antibonding interaction is observed between the "exchangeable proton" and the substrate atoms. For methanol on this face, the Ti-O overlap population is 0.212, while that for methoxy adsorption is 0.369. The oxygen is multiply coordinated to Ti surface atoms so the increase in overlap population is quite substantial. [illegible], the carbon in the substrate interacts in a bonding way with the oxygen in the case of methoxy adsorption, but in an antibonding way for methanol. The overlap populations for these interactions are 0.020 and -0.013, respectively. This value is critically dependent on the Ti-O distance selected, as this designates the C-O distance. The distance selected for the Ti-O distance is 1.9Å, which is a typical Ti-O bridging distance. The hydroxyl proton does not interact with any substrate atoms in a significant way. The overlap population of the O-H bond is not red[illegible] upon [illegible], however, the presence of the hydroxyl proton seems to reduce the Ti-O bonding. The binding energies of both adsorbates are favorable for adsorption, but that of methoxy is significantly lower as to suggest that deprotonated products are more stable at the surface.

## CO and HCN on WC(0001).

Experimental studies on carbided tungsten have shown only one type of CO at the surface. CO on the pristine surface is known to adopt a variety of sites, of which at least one is dissociative. On the carbided surface, a single state of CO is observed in which the CO is believed to be molecular and in an "atop" site. The vibrational frequencies obtained from HREELS for αCO on W(100) and CO on the carbided surface is slightly less reactive than the pristine surface. The population of the 5σ orbital of CO on either surface is the same, 1.695 electrons. The population of the 2π* orbital is slightly lower for the W(100) surface. Each 2π* level of CO receives 0.650 electrons upon adsorption, giving a total population of 1.300 electrons for the orbital pair. For the WC surface, a total of 1.184 electrons are transferred, providing 0.592 electrons for each orbital. The occupation of the 2π* level and the calculated overlap populations reflect the reduced donor ability of the WC surface. For CO on W(100), the overlap population for the C-O bond is 0.985, while for the WC surface, this value is 1.028, which can be compared with that of "free" CO which shows an overlap population of 1.32. The W-C overlap populations are 0.999 and 0.928 for the pristine and carbided surfaces, respectively. For the atop sites, the WC surface seems slightly less active, though the values of the overlap populations and 2π* occupations suggest similarities between the selected sites consistent with the HREELS studies.

HCN on W(100) and the related carburized surface desorbs molecularly and dissociates into $H_2$ and $N_2$, leaving carbon at the surface. On the carbided surface, a protonation occurs at the nitrogen of the HCN. The decomposition occurs more readily on the pristine surface.[12] The adsorption sites considered for these two surfaces are representative sites selected from studies based on diatomic systems and organometallic models. In both cases, the HCN is assumed to be bent such that the <HCN is 120°. The fragment orbital occupations and overlap populations for HCN on these two surfaces are shown in Table 2.

Table 2: Overlap populations and FMO analysis for dissociative modes of HCN on W(100) and WC(0001).

| FMO Occupations: | W(100) | WC(0001) | Overlap pop. | W(100) | WC(0001) | Reference |
|---|---|---|---|---|---|---|
| 7a' | 0.695 | 0.713 | C-N | 1.278 | 1.422 | 1.681 |
| 2a'' | 0.689 | 0.337 | C-H | 0.593 | 0.622 | 0.770 |
| | | | W-N | 0.100 | 0.135 | 0.555 atop HCN |
| | | | W-C | 0.348 | 0.010 | 0.417 W-$C_{sub}$ |

The chemistry of the carburized surface is similar to that of the pristine surface; however, the surface structure is significantly different to allow for differential adsorption chemistry. The activity of the carbided surface is the result of both bulk carbide interaction and the structural changes induced upon carburization.

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