A trend in the C–O bond strength of $CH_3O_{(ad)}$ on NiAl(100), FeAl(100) and TiAl(010). Effect of the alloy Fermi level

Sanjay Chaturvedi [b,‡] and Daniel R. Strongin [a,*]

[a] *Department of Chemistry, Temple University, Philadelphia, PA 19122, USA*
[b] *Department of Chemistry, State University of New York, Stony Brook, NY 11794, USA*

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Research is presented that investigates the C–O bond stability of surface methoxy bound on Al-terminated NiAl(100), FeAl(100), and TiAl(010). Temperature-programmed desorption suggests that a fraction of methoxy individually bound on the Al component of all three surfaces undergoes C–O bond cleavage to evolve gaseous methyl radicals. The trend in the temperature of maximum methyl ejection rate, T_m, is as follows: T_m(NiAl)> T_m(FeAl)> T_m(TiAl), suggesting that the nature of the transition metal in the underlying layer affects of the C–O bond energy. Results are shown that suggest that the position of the Fermi level in these materials plays a role in determining the C–O bond strength, consistent with the prediction of recent theory by Shiller and Anderson.

Keywords: methoxy, methanol, alloy, aluminide, methyl ejection, Fermi level

1. Introduction

The chemical bonding between dissimilar metals in an alloy often leads to a unique surface reactivity, not easily describable in terms of the reactivities of the individual components. These unique chemical properties of an alloy surface often benefit many technologically important areas such as catalysis, electrochemistry and microelectronics fabrication [1–4]. It is of fundamental interest to determine and understand the geometric and electronic properties of the alloy that determine its reactivity.

In this contribution we investigate the stability of the C–O bond of methoxy, $CH_3O_{(ad)}$, on three bimetallic surfaces: NiAl(100), FeAl(100), and TiAl(010). NiAl and FeAl have a body-centered cubic CsCl structure and the (100) surface of each of these alloys have Al as the top layer with the transition metal lying in the layer below [5,6]. TiAl has a face-centered tetragonal structure and an ideal termination of (010) face would have alternate layers of Ti and Al on the outermost layer. A recent low energy electron diffraction (LEED) analysis of the (010) surface, however, has shown that the clean surface reconstructs such that the Ti atoms in the first layer are exchanged with the Al atoms in the second layer [7]. The important point for this study is that the stable TiAl(010) structure, similar to NiAl(100) and FeAl(100), has an outermost layer composed solely of Al and a second layer composed of Ti. In contrast to cubic NiAl and FeAl, however, the TiAl(010) surface is a rectangular mesh (one side is 4.0707 Å and the other is 4.005 Å) [8]. Methoxy groups can be prepared on all three surfaces by adsorbing methanol at low temperature and then heating to 200–300 K to induce O–H bond cleavage. A fraction of the methoxy prepared in this manner is stable up to relatively high temperatures. We present data in this contribution that shows that the activation energy, E_a, for a methyl ejection process resulting from the thermally induced cleavage of the C–O bond of this methoxy on Al-terminated NiAl, FeAl, and TiAl follows the trend: $E_a(\mathrm{NiAl}) > E_a(\mathrm{FeAl}) > E_a(\mathrm{TiAl})$. Prior theoretical calculations by Shiller and Anderson [9] suggest that the stability of the C–O bond of methoxy should be a function of the substrate Fermi level, E_F. Based on this theory, we contend that the trend in activation energies for methyl radical desorption from the aluminides can be correlated with the relative positions of E_F, which is controlled by the transition metal component. In effect, the transition metal is tuning the C–O bond strength of methoxy residing on the outermost Al.

2. Experimental

All experiments were performed in a bakeable stainless-steel ultra-high vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. The details of this apparatus are described elsewhere [10]. We only mention that all samples were cleaned by 1 keV Ar^+ bombardment, followed by annealing to 1173–1273 K. Oxygen and carbon were the main impurities as determined by Auger electron spectroscopy (AES). Carbon was removed by heating in 1×10^{-6} Torr oxygen. After cleaning, each crystal gave a sharp 1 × 1 LEED pattern.

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[*] To whom correspondence should be addressed.
[‡] Present address: Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA.

The samples were mounted on a liquid-nitrogen cryostat by spot-welding three Ta wires to each side of the sample. The sample mounted in this way had cooling capabilities down to 120 K. A chromel–alumel thermocouple, spot-welded to the back of the sample, allowed accurate temperature measurements. TPD experiments were carried out by heating the sample at a rate of 7 K/s. Mg K_α (1253.6 eV) and He I (21.2 eV) radiation were used in X-ray photoelectron spectroscopy (XPS) and work function measurements, respectively. The pass energy of the double pass cylindrical mirror analyzer used in these experiments was set at 50 eV for XPS experiments. The binding energy scale was calibrated by aligning the $2p_{3/2}$ level of a pure Fe sample to 706.8 eV below the Fermi level (E_F). Work functions of the aluminides were measured by irradiating the individual samples with He I radiation and acquiring photoelectron energy distribution curves with an analyzer pass energy of 25 eV. The work function, Φ, was then calculated from the difference of 21.2 eV and the energy width of the electron energy distribution curve.

Methanol (CH_3OH, HPLC grade, Fischer Chemical) was purified by several freeze–pump–thaw cycles and its purity was confirmed by the mass spectrometer. Dosing was accomplished by backfilling the chamber up to the desired pressure for a known period of time. All exposures quoted in this letter have not been corrected for the cracking efficiencies of molecules in the ion gauge used for pressure measurements.

3. Results and discussion

Figure 1 shows TPD results for the different aluminide surfaces after exposure to 6.0 L of CH_3OH at ~120 K. The only gaseous reaction products that are evolved from these Al-terminated surfaces during the thermal decomposition of CH_3OH are methyl radicals and hydrogen. Approximately 15, 50, and 45% of a saturated monolayer of methoxy decomposes to form methyl radical on NiAl(100) [11], and FeAl(100) [12], and TiAl(010), respectively. The remaining methoxy forms surface bound oxygen and carbonaceous species. It is suspected that decomposition product serves to block sites so that a fraction of methoxy cannot dehydrogenate, and instead remains intact until temperatures are achieved where thermal homolysis of the C–O bond can occur. Only the $m/e = 15$ (i.e., CH_3^+) trace is shown, and we assign the peaks above 400 K for all three surfaces to the desorption of CH_3. The rationale for this assignment is presented in earlier publications from our laboratory [11–13]. All three desorption traces show an additional sharp feature near 145 K that is due to the sublimation of CH_3OH from the condensed layer formed during adsorption at 120 K.

For the purposes of this letter, the most important aspect of these TPD data is that the temperature (T_m) of maximum CH_3 desorption rate, is higher for NiAl(100) ($T_m = 575$ K) than on FeAl(100) ($T_m = 540$ K), and lowest for TiAl(010) ($T_m = 450$ K). For all three surfaces T_m is invariant with the initial methoxide coverage, suggesting first-order desorption kinetics. We also suspect that the CH_3 desorption occurs in a concerted fashion with the thermal homolysis of the C–O bond of methoxide. Prior studies [11–13] in our laboratory using electron energy loss spectroscopy (EELS), XPS, ultraviolet photoelectron spectroscopy, and TPD suggest that C–O bond cleavage and CH_3 desorption occur at similar temperatures supporting such a mechanism. Furthermore, decomposition of a mixed adlayer of $CD_3O_{(ad)}$ and $CH_3O_{(ad)}$ produces only CD_3 and CH_3 consistent with a mechanism that has methyl desorbing concurrently with C–O bond cleavage.

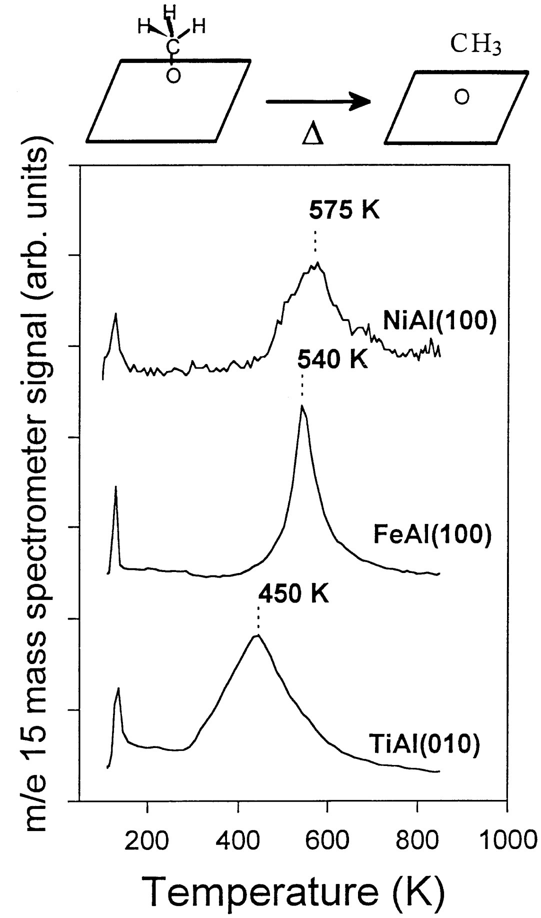

Figure 1. TPD of CH_3OH/NiAl(100), CH_3OH/FeAl(100), and CH_3OH/TiAl(010). The features in the desorption traces between 400 and 600 K are associated with the desorption of methyl radicals. The features near 150 K are due to desorption of CH_3OH from a multilayer.

Using the experimentally determined T_m for each aluminide in conjunction with a Redhead analysis [14] (preexponential factor of 10^{13} is assumed) the activation energy for C–O bond cleavage on NiAl(100), FeAl(100), and TiAl(010) are estimated to be 32, 30, and 28 kcal/mol, respectively. A presumption of ours is that the C–O bond strength of the surface methoxy that undergoes methyl radical ejection will show the same trend as the activation energies. In other words, we infer from the TPD data that the C–O bond strength of that fraction of methoxy, which thermally decomposes to surface oxygen and gaseous methyl radical, is stronger on NiAl(100) than on FeAl(100), and weakest on TiAl(010).

Before possible reasons for this difference in C–O bond stability are presented, complementary XPS data and some prior results obtained in our laboratory are presented that address the surface species involved in this process. Figure 2 shows O 1s core level data obtained after NiAl(100), FeAl(100), and TiAl(010) are individually exposed to 6 L of CH_3OH at 120 K, which produces a multilayer, heated to 300 K to form methoxy, and to 600 K to decompose the adsorbed intermediate. Examination of the 600 K spectra indicates that the surface oxygen remaining on the surface after methoxy decomposes exhibits almost identical O 1s binding energies. EELS data of a methoxy overlayer on NiAl(100) [11] and FeAl(100) [12] that has been heated to 600 K, shows that aluminum oxide is the end product, and thus, the 531.6 eV features are taken to be representative of O, presumably bound as an Al_xO_y product. This result is not unexpected considering the high affinity of Al for oxygen. Furthermore, surface oxygen on Fe [15] or Ti [16] surfaces would be expected to exhibit an O 1s binding energy closer to 530 eV.

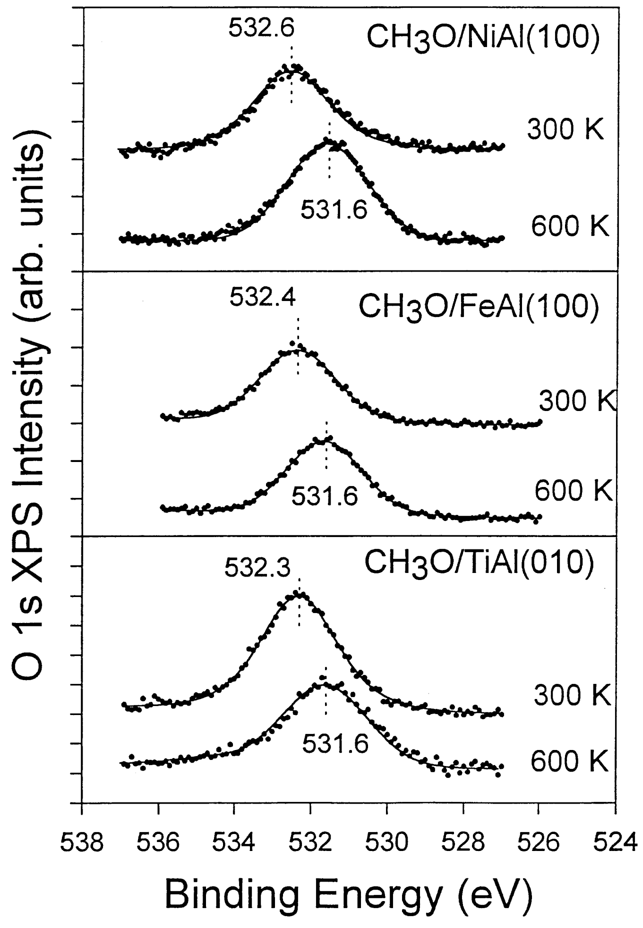

Figure 2. Individual O 1s XPS of methoxy on NiAl(100), FeAl(100), and TiAl(010) at 300 K. Also presented are O 1s XPS of methoxy overlayers that have been heated to 600 K to completely decompose the adlayer. The similarity of the O 1s binding energies in this circumstance suggest that O of methoxy is binding to Al.

Examination of the 300 K spectra of figure 2, which are associated with adsorbed methoxide, suggests that there may be an O 1s binding energy trend, but it is proposed that the relative constancy of the O 1s binding energy of methoxide on the three aluminides, suggests that this intermediate is interacting preferentially with the Al component in the outermost layer. It is implicit in any discussion of an alloy that its components have a different electronic structure than the respective individual monometallic metals (how different, depends on the specific alloy). Nevertheless, it is mentioned that prior research shows that the O 1s binding energy of methoxide on monometallic Al is ~ 532.7 [17], close to the O 1s binding energies measured for methoxy on the Al-terminated planes used in the current study. Further experimental evidence to support a surface picture that has methoxy binding preferentially (or exclusively) with Al comes from EELS data of CH_3O/NiAl(100) and CH_3O/FeAl(100). Methoxy on NiAl(100) [11] exhibits a metal–oxygen stretch of 640 cm^{-1}, close to the same mode of methoxy on Al(111) that resides at 655 cm^{-1} [18]. Recent research in our laboratory also shows that the metal–oxygen stretch for methoxy on FeAl(100) [12] resides at a position (i.e., 640 cm^{-1}) that is indistinguishable within our experimental error from the analogous mode on NiAl(100). The position of this mode is in stark contrast to the ν(M–O) mode of methoxy bound on NiAl(110) or FeAl(110). These crystallographic planes have both transition metal and Al in the outermost layer and the ν(M–O) modes resides near 540 cm^{-1}, suggesting that transition metal in this circumstance participates more directly in the binding of methoxy.

Within the resolution of our experimental techniques, the picture of the methoxy includes its binding almost exclusively to the outermost Al layer. The small shift of the O 1s binding energy of methoxy to lower binding energy from CH_3O/NiAl(100) to CH_3O/TiAl(010) may be consistent with the trend in methyl radical ejection. One might expect the O 1s binding energy of methoxy to shift toward the 531.6 eV limiting value as the C–O bond weakens due to the increased interaction of the O with Al. It is postulated that methyl to be ejected into the gas phase from any of the aluminides, a significant perturbation of the C–O bond of methoxy must occur. TPD results suggest that the activation energy of desorption of methyl ranges between 25 and 32 kcal/mol, depending on the aluminde surface. These values are considerably less than the 85 kcal/mol bond strength of the C–O bond of CH_3OH. These values suggest that the C–O bond of methoxy is considerably weaker than the analogous bond in CH_3OH. We point out that on all three surfaces oxidation of the Al component has occurred to some extent by the temperature of methyl ejection. Thus, methyl ejection may be aided by the weakening of the C–O bond due to oxide formation or by the presence of coadsorbed oxide.

In prior theoretical research Shiller and Anderson [9] have calculated the C–O bond strength of a methoxy anion (CH_3O^-) created by binding $CH_3^{\bullet}$ with adsorbed O^{2-} on Mo(110). Their calculations suggest that the resultant C–O bond of the methoxy anion is approximately 32 kcal/mol, significantly weaker than the 85 kcal/mol C–O bond of methanol. The calculated value agrees well with the experimental observation that methyl ejection resulting from the decomposition of methoxide on O/Mo(110) occurs near 590 K [19]. Figure 3a exhibits the essence of the interaction diagram (specific energies for the CH_3O/Mo(110) system are omitted) used by Shiller and Anderson to illustrate the relevant interactions. The C–O σ bond forms between the HOMO of the methyl radical and the p_z orbital of the surface O^{2-} and a charge transfer energy due to putting an electron into the conduction band (c.b.) contributes. The bond forming reaction between $CH_3^{\bullet}$ and the surface O is then

$$CH_3^{\bullet}(g) + O^{2-}_{(ad)} \rightarrow CH_3O_{(ad)} + e^-(c.b.)$$

It is argued that the strength of the C–O bond should be a function of the position of E_F; as E_F moves in the direction of decreasing stability (i.e., increases in energy) the C–O bond becomes weaker, because of destabilization of the conduction band electron.

We are not aware of calculated values for the energy positions of E_F for the three aluminides used in this study. Relative positions, however, may be estimated from comparing the experimentally determined work functions for each surface. It is emphasized that the work function is a strong function of surface structure [20]. The similarity of the surface structures of NiAl(100) and FeAl(100) minimizes this concern to some extent, but due to the different crystal structure of TiAl(010) more error may be involved in any quantitative comparison. We have experimentally determined (see experimental for method) the work function of clean NiAl(100), FeAl(100), and TiAl(010) to be 4.6, 4.2, and 4.0 eV, respectively[1]. It is inferred from this result that E_F exhibits *decreasing* stability in going from NiAl to TiAl. This trend is schematically shown in figure 3b and it is contended here that the C–O bond of methoxy becomes weaker as E_F decreases in stability in going from NiAl to TiAl due to the increased potential of the electron that is transferred to the surface.

The trend in E_F is then consistent with the TPD results from which it is inferred that the strength of the C–O bond of the fraction of methoxy that decomposes to form methyl radical is strongest on NiAl(100) and weakest on TiAl(010). We believe then that the transition metal in these materials is controlling the relative position of E_F and is in effect tuning the C–O bond strength of the methoxy binding to the outermost Al atoms.

While we believe that the E_F trend for the aluminides contains the essential features for the explanation of our desorption results, it is worth mentioning that it is presumed that a strong substrate oxygen bond is a facilitator of the methyl ejection process. We suspect that the high affinity of Al for O facilitates methyl ejection on the aluminides due to some compensation of C–O bond loss by formation of the final "Al–oxide" product. Formation of this latter product may also require the rupture of transition metal–Al bonds. Hence, it might be argued that aluminide surfaces with weaker transition metal–Al bonds may facilitate C–O bond cleavage. With

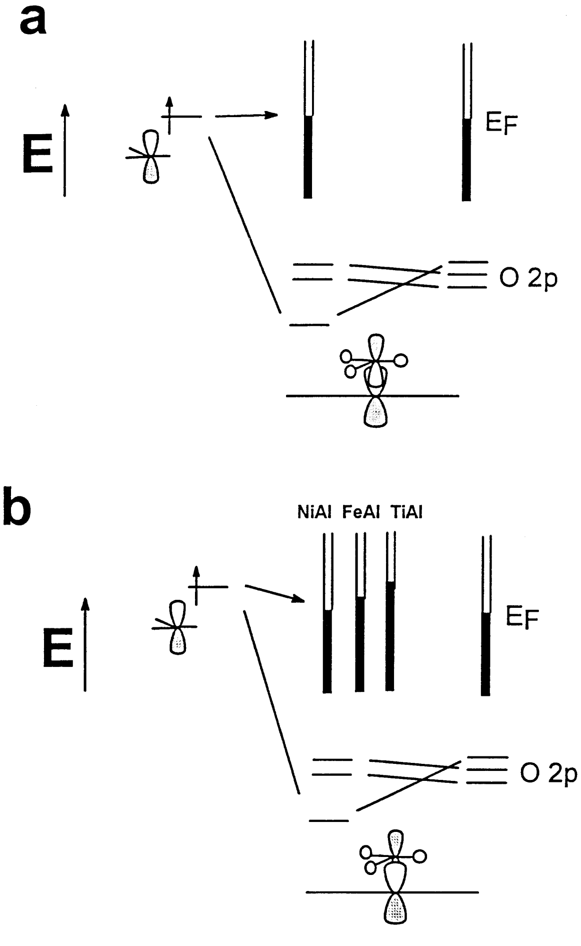

Figure 3. (a) Interaction diagram between $CH_3^{\bullet}$ and O^{2-}, after Shiller and Anderson [9]. The C–O bond of the CH_3O^- anion is weakened due to the loss of electron transfer stabilization. (b) The C–O bond of methoxy is progressively weakened with decreased Fermi level stability in the order NiAl(100)>FeAl(100)>TiAl(010) due to the increasing potential of the electron that is transferred to the surface. Note that levels below E_F are filled.

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[1] We do not have experimental work function measurements for these surfaces with adsorbed oxygen that may offer more relevant data for the model. It is expected, however, that the same trend as the clean surface would be present, except that absolute values would be different.

regard to this point it is mentioned that heat of formation [21,22] (cohesive energy [23]) of NiAl and FeAl are −14 (98 kcal/mol) and −6 (93 kcal/mol), respectively. The heat of formation of TiAl is −9 kcal/mol, but we are unaware of published values for its cohesive strength. These data suggest that the Ni–Al bond is stronger than either the Fe–Al or Ti–Al bond, consistent with methyl ejection occurring at the highest temperature on this material. This line of reasoning based on the transition metal–Al bond strengths, however, would suggest that the C–O bond should be thermally more stable on TiAl than on FeAl, which is contrary to our experimental results. Therefore, we believe the location of E_F in these materials is more consistent with our experimental observations.

4. Summary

TPD results have been presented in this letter that suggest that the decomposition of methoxy on NiAl(100), FeAl(100), and TiAl(010) leads in part to the desorption of methyl radical. T_m for this process follows the trend; T_m[NiAl(100)]> T_m[FeAl(100)]> T_m[TiAl(010)]. This trend is consistent with prior theoretical studies that suggest that the C–O bond of methoxy should increase as a function of increased E_F stability. This theoretical model for methyl ejection is consistent with our experimental results, since it is inferred from work function measurements that in order of decreasing stability of E_F: NiAl(100)>FeAl(100)>TiAl(010). It is argued that even though methoxy binds preferentially to Al, the nature of the transition metal controls the relative position of E_F for the different alloys, and in turn the relative strength of the C–O bond of that methoxy that decomposes to yield methyl radical.

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