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# Comparative studies of methanol decomposition on carbide-modified V(1 1 0) and Ti(0 0 0 1)

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## Abstract

The reaction pathways of methanol on V(1 1 0), carbide-modified V(1 1 0), Ti(0 0 0 1), and carbide-modified Ti(0 0 0 1) have been studied using high-resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES), and temperature-programmed desorption (TPD). On V(1 1 0) and C/V(1 1 0), methanol undergoes complete dissociative adsorption producing a methoxy intermediate for exposures less than 2 L at 100 K. On Ti(0 0 0 1) and C/Ti(0 0 0 1), methanol dissociates to produce methoxy at exposures of 3 L at 100 K. The combination of TPD and AES reveals that the number of methoxy per surface metal atom is 0.13 on C/V(1 1 0) and 0.41 on C/Ti(0 0 0 1) at 100 K. All methoxy species undergo further decomposition on C/V(1 1 0) at higher temperatures. However, a significant fraction (~39%) of methoxy species undergo recombinatory reaction to produce gas-phase methanol on C/Ti(0 0 0 1). The reaction pathways on the C/V(1 1 0) and C/Ti(0 0 0 1) surfaces are compared with previous studies of methanol on other carbide-modified surfaces, as well as on single crystal VC and TiC surfaces.

*Keywords:* Ti(0 0 0 1); C/Ti(0 0 0 1); V(1 1 0); C/V(1 1 0); Vanadium carbides; Titanium carbides; Methanol; Methoxy

## 1. Introduction

The fundamental understanding of the surface reaction of methanol on transition metal carbides is important for both tribological [1–3] and catalytic [4–9] applications. For example, adsorption studies of methanol on model surfaces can assist in understanding the interaction between carbide coatings and lubricant additives [3]. In addition, Groups 4–6 early transition metal carbides often show catalytic properties similar to those of the Pt-group metals [10–18]. The "Pt-like" reactivity

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of carbides has in turn motivated many surface science and electrochemical studies of carbides as alternative electrocatalysts in direct methanol fuel cells [19–23].

Our research group has recently performed a series of fundamental surface science and electrochemical studies examining the reactivity of transition metal carbide surfaces toward methanol for potential application as electrocatalysts [4–9,12–15]. Surface science studies indicate that both carbide-modified W(1 1 1) and W(1 1 0) surfaces are very active toward the dissociation of methanol. On C/W(1 1 1), methanol dissociates upon adsorption at 100 K to form the methoxy ($CH_3O$) intermediate. When heated to higher temperatures, the methoxy intermediate further decomposes to yield $H_2$, CO, and $CH_4$. Overall, 55% of the methanol species undergoes complete decomposition, with 31% and 14% going to CO and $CH_4$, respectively [5]. On C/W(1 1 0), the methanol decomposition pathways are qualitatively similar to those on C/W(1 1 1), but with slightly different product distributions [8]. Parallel studies have demonstrated that the C/Mo(1 1 0) surface is also active toward the dissociation of methanol [9]. The thermal decomposition of methanol on C/Mo(1 1 0), however, does not result in the evolution of gas-phase $CH_4$ [9].

The surface science studies summarized above were all conducted on carbide surfaces prepared by cracking unsaturated hydrocarbons on W(1 1 1), W(1 1 0), or Mo(1 1 0) surfaces. Alternatively, Frantz et al. have investigated the surface chemistry of methanol on bulk carbide single crystals such as TiC(1 0 0) and VC(1 0 0) [3]. These authors showed that partial decomposition (77%) of methanol to methoxy on TiC(1 0 0) occurred at liquid nitrogen temperature [3]. As the surface temperature was increased, the predominant reaction pathway was the recombinatory desorption of methanol. On the other hand, methanol on VC(1 0 0) led to the decomposition of ~65% of methanol to methoxy at liquid nitrogen temperature [3]. The methoxy intermediate was found to be stable and the recombinatory methanol desorption was detected at 300 K. Unlike on TiC(1 0 0), approximately half of the methoxy intermediates on VC(1 0 0) underwent further decomposition to yield gas-phase products of formaldehyde, methane, hydrogen and additional recombinatory desorption of methanol at temperatures above 350 K [3].

The objectives of the current study are primarily twofold: (1) to correlate the surface reactivity of 3d metal carbides, C/Ti(0 0 0 1) and C/V(1 1 0), with our previous studies on carbide-modified 4d and 5d metals surfaces and (2) to compare the C/Ti(0 0 0 1) and C/V(1 1 0) surfaces with previous studies on the bulk TiC and VC single crystals. In the current manuscript we will first present the high-resolution electron energy loss spectroscopy (HREELS) and temperature-programmed desorption (TPD) results of methanol on V(1 1 0) and C/V(1 1 0), followed by those on Ti(0 0 0 1) and C/Ti(0 0 0 1). For discussion, we will first compare the reaction pathways of methanol on V(1 1 0), C/V(1 1 0), Ti(0 0 0 1), and C/Ti(0 0 0 1). We will then compare the activity and product selectivity on C/V(1 1 0) and C/Ti(0 0 0 1) surfaces to those on carbide-modified C/W(1 1 0), C/W(1 1 1), and C/Mo(1 1 0) surfaces [5,8,9]. Finally, we will compare the reaction pathways of methanol on C/V(1 1 0) and C/Ti(0 0 0 1) to those on the bulk VC and TiC single crystal surfaces [3].

## 2. Experimental

### 2.1. Techniques

The UHV chamber used in the current study has been described in detail previously [17]. Briefly, it is a three-level stainless steel chamber equipped with AES and TPD in the top two levels, and HREELS in the bottom level. The HREELS 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 specular direction. Count rates in the elastic peak were typically in the range of $3 \times 10^4$ to $3 \times 10^5$ counts/s, and the spectral resolution was between 40 and 60 $cm^{-1}$ FWHM (full-width at half maximum). For TPD and HREELS experiments the V(1 1 0) and Ti(0 0 0 1) samples were heated with a linear heating rate of 3 K/s.

The vanadium single crystal sample was a [1 1 0] oriented, 1.5 mm thick, and 10 mm in diameter