



The chemistry of iodomethane on MoAl alloy thin films formed on dehydroxylated alumina: Formation and reaction of surface methyl species

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Abstract

The surface chemistry of iodomethane is studied in ultrahigh vacuum using X-ray and Auger spectroscopies and temperature-programmed desorption, on a MoAl alloy film formed by reacting molybdenum hexacarbonyl with dehydroxylated alumina. The alloy is grown by reacting $\text{Mo}(\text{CO})_6$ with a thin alumina film on a molybdenum substrate at 700 K and heating to 1500 K. A portion of the iodomethane dissociates following adsorption at ~ 150 K. Heating to ~ 220 K desorbs molecular iodomethane from the surface leaving adsorbed methyl species and iodine, where the iodine appears to adsorb preferentially on the aluminum. The resulting methyl species can either decompose to deposit carbon and evolve hydrogen, hydrogenate to yield methane or oligomerize yielding predominantly ethylene and propylene, and a small amount of ethane is formed. Both methyl and ethyl radicals are found to desorb from the surface suggesting that the ethylene is formed by methylene insertion into the methyl surface bond to form an ethyl intermediate, which forms ethylene by β -hydride elimination, or hydrogenates to yield ethane. Propylene is likely to form by further methylene insertion into the ethyl-surface bond.

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1. Introduction

$\text{Mo}(\text{CO})_6$ has been extensively used to deposit molybdenum on oxides to generate catalysts and/or catalyst precursors [1–12]. Such a procedure has been applied in ultrahigh vacuum to generate

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model catalysts supported on planer alumina thin films, where surface-sensitive spectroscopic probes can be used to investigate the surfaces and catalytic reactions [13–16]. Our recent studies have shown that reacting $\text{Mo}(\text{CO})_6$ with aluminum [17] and dehydrogenated alumina [18] thin films at 500 K and above forms molybdenum carbide films incorporating a small amount of oxygen. Efforts have been made to perform hydrocarbon conversion reactions on these surfaces and it is found that these surfaces are rather inert. Such inertness has been found recently by Chen et al. [19] by adsorbing O_2 on molybdenum carbide and has been rationalized by site blocking rather than electronic modification effects. Annealing these films to temperatures higher than 1200 K causes CO desorption through alumina reduction by the carbidic carbon, and results in MoAl alloy film formation [17,18].

In the following, the surface chemistry of iodomethane is investigated on the MoAl alloy film. Such a strategy has been extensively used to examine the surface chemistry of hydrocarbons on surfaces since organic iodides tend to decompose by scission of the C–I bonds at relatively low temperatures to deposit hydrocarbon fragments on surfaces, along with chemisorbed iodine [20,21].

It has been shown previously that reaction of low exposures of $\text{Mo}(\text{CO})_6$ with alumina films above 500 K results in the formation of molybdenum carbide nanoparticles on the surface, while higher exposures (of ~ 5000 L of $\text{Mo}(\text{CO})_6$) forms a thin film that completely covers the surface [18]. A MoAl alloy is formed by heating the carbide to ~ 1200 K. The chemistry of hydrogen and CO on MoAl nanoparticles compared with thin films has been investigated to explore particle size effects in these systems [22]. This work explores the chemistry of iodomethane on a MoAl alloy formed by exposing dehydroxylated alumina to 5000 L of $\text{Mo}(\text{CO})_6$ at 700 K and then annealing, to examine the chemistry on the bulk alloy.

Iodomethane is selected for study for a number of reasons. First, the thermal chemistry of methyl species provides insight into understanding many catalytic processes [20,21]. Second, the chemistry on both components of the surface alloy, Mo

and Al, has been investigated previously, where it was found that methyl species start to decompose at ~ 135 K to form methylene species on Mo(100) [23,24]. These persist on the surface to about 200 K and undergo further decomposition at higher temperatures. The only gaseous products are methane and hydrogen, which desorb at ~ 230 and ~ 380 K, respectively. No higher hydrocarbons are detected indicating that C–C bond formation reactions do not occur. The reaction of Al(111) with iodomethane has been investigated by Yates and co-workers [25,26] where $\text{CH}_{3(a)}$, $\text{CH}_{(a)}$ and $\text{I}_{(a)}$, but no $\text{CH}_{2(a)}$ were detected. No gas-phase reaction products were reported. Al–I bond formation was found following CH_3I adsorption on aluminum at 150 K using high-resolution electron energy loss (HREELS), and the depletion of $\text{I}_{(a)}$ from the surface by 650 K was verified by Auger electron spectroscopy (AES).

2. Experimental

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber operating at a base pressure of $\sim 8 \times 10^{-11}$ Torr that has been described in detail elsewhere [13,17,18] where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample. This chamber was also equipped with a double-pass, cylindrical-mirror analyzer for collecting Auger spectra.

X-ray photoelectron spectra (XPS) were collected in another chamber operating at a base pressure of $\sim 2 \times 10^{-10}$ Torr, which was equipped with Specs X-ray source and double-pass cylindrical mirror analyzer [17,18]. Spectra were typically collected with a Mg $K\alpha$ X-ray power of 250 W and a pass energy of 50 eV. The deposited film was sufficiently thin that no charging effects were noted and the binding energies were calibrated using the Mo $3d_{5/2}$ feature (at 227.4 eV binding energy) as a standard.

Temperature-programmed desorption spectra were collected at a heating rate of 10 or 15 K/s as indicated. Temperature-dependent XP and Auger spectra were collected by heating the sample to the indicated temperature for 5 s, allowing the

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