

# Roles of oxygen for methanol adsorption on polycrystalline copper surface revealed by sum frequency generation imaging microscopy



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## ABSTRACT

The adsorption of atmospheric pressure methanol on the polycrystalline copper surface has been studied by a combination of sum frequency generation imaging microscopy (SFGIM) and temperature programmed desorption (TPD). Methoxy species can be generated by exposing the polycrystalline copper surface to methanol vapor at room temperature. SFGIM results demonstrate that oxygen promotes the surface adsorption of methanol and the increase in the amount of methoxy produced on copper surface. SFGIM orientation analysis suggests the methoxy monolayer is oriented closer to the surface normal with introduction of oxygen. Employing the image statistical analysis approach, the heterogeneities and conformation distribution of methoxy monolayers on copper surface with and without oxygen adsorption are compared. These results illustrate SFGIM indeed could provide more insight for understanding the heterogeneous metal/metal oxide surface in the molecular level.

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## 1. Introduction

The adsorption of methanol on metal surfaces has been widely studied as a model system in both fundamental surface science and industry due to a number of relevant heterogeneous catalytic reactions such as hydrogenation of CO to methanol and syntheses of formaldehyde [1–5]. The methoxy fragment is always produced following methanol adsorption as a stable and abundant species at room temperature and it has been proved to be an important intermediate during industrial methanol and formaldehyde production with well-documented use of metal and metal oxide catalysts [2,6]. The generation of methoxy group requires copper atoms to induce metal activated O–H bond scission on the adsorbed methanol atom. In many cases, such process can be promoted with the assistance of the adsorbed oxygen [2,6–9]. However, in some conditions the formate group is identified on copper surface as a less abundant but more stable intermediate following methanol adsorption [4,10].

A variety of surface science techniques have been performed to detect methanol adsorption on the copper surface, such as electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) [6–8,11–13]. While these traditional surface science techniques could only be operated in

ultra-high vacuum (UHV) conditions, with a large enough free mean path for the ion or electron to reach the sample or be collected by detectors, many interesting surface phenomena including the adsorption of methanol were uncovered [14,15]. However, realistic heterogeneous catalytic reactions are mostly carried out in a high pressure environment, which are essential in understanding the mechanism of methanol adsorption under atmospheric pressure. Vibrational spectroscopy is generally a very powerful tool to deduce the chemical identity and structure of adsorbates on the surface. Nevertheless spectroscopic studies are typically based on an assumption that metal surface is homogeneous within the involved field-of-view on the sample. By analyzing an average response over the probe area without any spatial resolution, local heterogeneities (i.e., surface defects, molecular coverage, chemical composition, etc.) would be overlooked. Even though scanning probe microscope (SPM) studies (i.e., atomic force microscope and scanning tunnel microscope) have investigated the copper surface with atomic resolution, these techniques could only provide a limited range of chemical information [16,17]. Thus modeling of methanol adsorption on the heterogeneous metal surface, emphasizes the importance of in-situ molecular level spectroscopic studies of adsorbed species with spatial resolution under practical catalytic conditions.

Sum frequency generation (SFG), as a vibrational spectroscopic technique, provides chemical information through a more specific identification of chemical functionalities and conformational order of molecular layer within a broad temperature and pressure range. Comparing with other linear vibrational spectroscopy techniques such as IRAS, and EELS, SFG is intrinsically surface sensitive based on the fact that this second-order nonlinear optical process is forbidden in isotropic medium. Various catalytic reactions such as CO oxidation [18] and hydrocarbon conversion [19] on transition metals have been successfully

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investigated by SFG, which demonstrates its applicability for studying gas interaction with metal surface. Lin et al. employed the SFG to in-situ probe the polycrystalline copper surface during methanol synthesis and identified the formation of formate intermediate on copper surface [10]. Shultz et al. applied SFG to identify the methanol and methoxy species on anatase TiO<sub>2</sub> nanoparticle film [20]. A very recent study, using SFG vibrational spectroscopy to study the dissociation and photo-oxidation reaction of CH<sub>3</sub>OH on the TiO<sub>2</sub> thin film, demonstrates that O<sub>2</sub> promotes CH<sub>3</sub>OH dissociation and produces more methoxy adsorbed on the TiO<sub>2</sub> thin film [21]. Considering the presence of local features and heterogeneities of metal surfaces, SFGIM, shows unique advantages for investigating chemical processes on metal surface with spatial and chemical resolution [22,23]. In this paper, SFGIM has been employed to study the methanol adsorption on polycrystalline copper at atmospheric condition. The aim of this paper is to present the two-dimensional distribution of conformational information of the methoxy monolayer heterogeneity and clarify the role of oxygen in affecting the heterogeneity of the methoxy monolayer and copper surface. From the TPD and SFGIM results, the major surface product, methoxy, is chemically identified and the conformation order of methoxy monolayer is characterized. The oxygen exposure promotes the formation of the methoxy monolayer and, hence, increases the surface density of monolayer with homogeneous arrangement on the copper surface.

## 2. Experimental section

### 2.1. Sum frequency generation process

In previous works, SFG theory has been described in detail [24–27]. SFG is a second-order nonlinear optical technique involving a frequency tunable mid-infrared beam and a fixed pump beam overlapped, spatially and temporally, on the sample surface. To minimize the background noise, the 1064 nm beam was selected as the pump beam, instead of 532 nm which was the more common choice in previous SFG studies [28–30]. An output beam with a frequency equal to the sum of the two input beams is generated from the surface wherein both total energy and momentum are conserved. In dipole approximation, only certain non-centrosymmetric media (i.e. interfacial monolayers) allow the SFG process to occur. Thus, SFG is a highly surface sensitive technique [31]. In Eq. (1), the SFG intensity is proportional to the square of the second-order polarization on the surface. The second-order susceptibility  $\chi_{\text{eff}}^{(2)}$  correlates the relationship between the second-order polarization with the intensity of the input beams.

$$I_{\text{SFG}} \propto |P_{\text{SF}}^{(2)}|^2 \propto |\chi_{\text{eff}}^{(2)}|^2 I_{1064\text{nm}} I_{\text{IR}} \quad (1)$$

Eq. (2) demonstrates the tensor  $\chi_{\text{eff}}^{(2)}$  consists of two terms, which is the non-resonant term  $\chi_{\text{NR}}^{(2)}$  from the substrate contribution and the resonant term  $\chi_{\text{R}}^{(2)}$  from the contribution of interfacial monolayer. The  $\chi_{\text{eff}}^{(2)}$  is related to molecular hyperpolarizability  $\beta^{(2)}$  through ensemble average over all possible molecular orientations including tilt angle ( $\Theta$ ), azimuth angle ( $\varphi$ ), and rotation angle ( $\psi$ ) as sketched in Fig. 1. Eq. (3) is the basis equation for the nonlinear curve fitting of the experimental SFG spectra.  $N$ ,  $A_q$ ,  $\omega_{\text{IR}}$ ,  $\omega_q$ , and  $\Gamma_q$  denote the surface molecular density, resonant amplitude, IR beam frequency, resonant frequency and the damping factor of the  $q$ th mode, respectively. When the frequency of the infrared beam  $\omega_{\text{IR}}$  approaches the resonant frequency of  $q$ th vibrational mode, the  $\chi_{\text{R}}^{(2)}$  drastically changes in magnitude, as well as the SFG intensity, which is presented as a peak or dip in SFG spectra.

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{R}}^{(2)} + \chi_{\text{NR}}^{(2)} = \sum_q \frac{N \langle \beta^{(2)} \rangle}{\omega_q - \omega_{\text{IR}} - i\Gamma_q} + \chi_{\text{NR}} \quad (2)$$

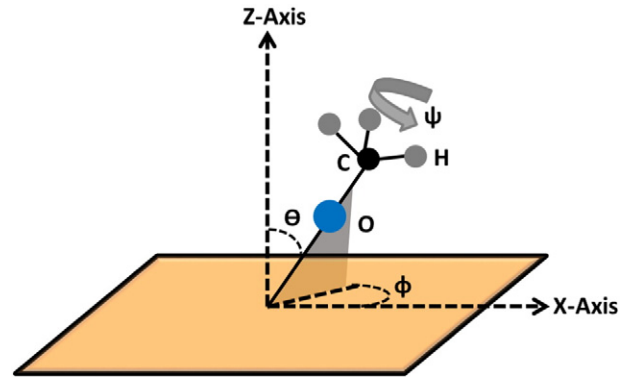


Fig. 1. Definition of the tilt angle ( $\Theta$ ), azimuth angle ( $\varphi$ ), and rotation angle ( $\psi$ ) of the methoxy adsorbed on the copper surface.

$$\chi_{\text{eff}}^{(2)} = \sum_q \frac{A_q}{\omega_q - \omega_{\text{IR}} - i\Gamma_q} + A_{\text{NR}} e^{i\delta} \quad (3)$$

Metal or semiconductor surfaces usually contribute to a strong non-resonant background  $\chi_{\text{NR}}^{(2)}$  due to the nearly free electrons in the surface region. As shown in Eq. (4), SFG spectra are complicated by the convolution of  $\chi_{\text{R}}^{(2)}$  and  $\chi_{\text{NR}}^{(2)}$ , which are both complex number quantities and wavelength dependent ( $\chi_{\text{NR}}^{(2)}$  is relatively constant within a narrow frequency range) [24,32]. The  $\varepsilon$  and  $\delta$  denote phase of  $\chi_{\text{R}}^{(2)}$  and  $\chi_{\text{NR}}^{(2)}$ , respectively. The phase difference between  $\chi_{\text{R}}^{(2)}$  and  $\chi_{\text{NR}}^{(2)}$  is named as relative non-resonant phase  $\phi$  in Eq. (3). Normally each vibration mode has the same relative phase  $\phi$ . The SFG spectral line-shape transformations at different relative non-resonant phases ( $\phi$ ) are simulated in Fig. S1 of Supporting Information. The non-resonant phase and intensity vary widely on different metals, even with their corresponding metal oxides [24,33]. The sensitivity of SFG to substrate characteristic is highly advantageous for studying distinct molecular information as an effect of the metal surface properties [33].

$$I_{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 = \left| \chi_{\text{NR}}^{(2)} e^{i\varepsilon} + \chi_{\text{R}}^{(2)} e^{i\delta(\omega_{\text{IR}})} \right|^2 = |\chi_{\text{NR}}^{(2)}|^2 + |\chi_{\text{R}}^{(2)}|^2 + 2|\chi_{\text{NR}}^{(2)}||\chi_{\text{R}}^{(2)}| \cos[\varepsilon - \delta] \quad (4)$$

### 2.2. Sample preparation in UHV chamber

Polycrystalline copper (Goodfellow, 99.99%) is used as the substrate material. These samples are rectangular with an area of 1 cm<sup>2</sup> and a thickness of 3 mm. The samples are polished down to 0.1  $\mu\text{m}$  using diamond compound. The copper substrates are then mounted on a sample stage supporting an  $x$ - $y$ - $z$  rotational manipulator housed in a stainless steel UHV chamber. The schematic diagram of the UHV system is shown in Fig. S2. This UHV chamber is equipped with a turbomolecular pump with a base pressure  $1 \times 10^{-9}$  Torr. A resistive tungsten filament situated at about 2 mm at rear of copper surface enables the control of surface temperature from 300 K to 800 K. Sample temperature measurement is carried out by a K-type thermocouple spot welded on the edge of the copper surface. The surface of the copper substrates is cleaned with several cycles of heating to 800 K and argon ion sputtering with beam energy of 3000 eV. Cleanliness of the metal surface is evaluated by a combination of TPD analysis of the methanol (CD<sub>3</sub>OD) adsorption and the experimental SFG spectra obtained in CH stretching region (2750–3000 cm<sup>-1</sup>). The efficiency of the cleaning procedure is assessed by the extinction of the methylene ( $-\text{CH}_2-$ ) vibrational peaks at 2850 cm<sup>-1</sup> in the SFG spectra (an example shown in Fig. S3) that arise from hydrocarbon contaminations. The UHV chamber is coupled to a quadrupole mass spectrometer (QMS) (Extorr XT 200) to

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