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Effect of photon irradiation on the adsorption of CO₂ on polycrystalline Cu

WANG Shuai^a, XU Guoqin^{b,*}^a College of Chemistry & Chemical Engineering, Xinjiang Normal University, Urumqi 830054, Xinjiang, China^b Department of Chemistry, National University of Singapore, Singapore 117543, Singapore

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ABSTRACT

The adsorption and photochemistry of CO₂ on ordered/disordered Cu surfaces were investigated using X-ray photoelectron and high resolution electron loss technique. Physisorbed CO₂ and chemisorbed CO₂^{δ-} species were isolated on different faces. Studies on the photochemical behavior of physisorbed and chemisorbed species were conducted with 193 nm laser irradiation. No photoinduced reaction occurred with the physisorbed species. Photoinduced dissociation was seen with chemisorbed species.

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Interest in the conversion of CO₂ into useful and nontoxic hydrocarbons has steadily increased over the last decade due to the urgent demand for both the development of alternative fuel sources and prevention of global warming [1]. Unfortunately, the thermal reduction of CO₂ requires high temperature because of the high thermodynamic stability of the CO₂ molecule [2]. The photocatalyzed reduction of CO₂ has received much attention because solar energy is clean and inexhaustible. Cu is known to play a significant role in both thermally induced hydrogenation [3,4] and photo-catalytic reduction [5,6]. It is one of the most widely used materials in CO₂ catalysis.

The adsorption of CO₂ on Cu surfaces has been extensively studied under ultrahigh vacuum (UHV) conditions using various surface sensitive techniques, such as high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), surface enhanced Raman spectroscopy (SERS), and temperature-programmed thermal desorption (TPD). Under UHV conditions, no adsorption of CO₂ occurs on

Cu unless the sample temperature is below 90 K due to an extremely low sticking probability [7,8]. The adsorbate-surface interaction is quite weak both in the physisorbed state with an adsorption energy of 13–25 kJ/mol (coverage dependent) [9,10] and in the chemisorbed state (< 60 kJ/mol) [11,12]. Only physisorbed linear CO₂ molecules were detected on low Miller indices surfaces such as Cu(111) [13], Cu(110) [14] and Cu(100) [15], whereas a bent chemisorbed CO₂^{δ-} species is favored on stepped and polycrystalline Cu surfaces [16,17].

The influence of surface roughness was studied by Akemann and Otto on polycrystalline Cu surfaces at 40 K [18,19]. In their work, both chemisorbed CO₂^{δ-} species and physisorbed CO₂ were observed on disordered Cu surfaces, but on relatively smooth, annealed Cu surfaces, only linear physisorbed CO₂ molecules were detected. The bent CO₂^{δ-} species was first identified on Ni(110) where it was found to react with co-adsorbed hydrogen to give the formate species [20,21]. It is believed that the CO₂^{δ-} species plays a major role in CO₂ conversion. While

* Corresponding author. Tel.: +65-6516-3595; Fax: +65-6779-1691; E-mail: chmxugq@nus.edu.sg

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previous studies have contributed considerably to the thermal chemistry of CO₂ on Cu surfaces, the detailed understanding of the photochemistry of physisorbed and chemisorbed CO₂ species is still not yet obtained.

The present report describes the selective isolation of physisorbed linear CO₂ molecules and chemisorbed bent CO₂^{δ-} species on different Cu faces, and elucidates the effect of photon irradiation on the different surface species. The growth of Cu films on Ta foils by thermal evaporation deposition was investigated. Cu typically grows in a layer-by-layer mode on the Ta substrate at room temperature [22], and on this surface the physisorption of CO₂ is dominant. However, disordered Cu surfaces prepared by depositing Cu on a cooled substrate provide a large variety of atomic scale surface defects and many chemisorption sites [23]. Our XPS and HREELS studies suggest that photon activation only occurs with the chemisorbed bent CO₂^{δ-} species on Cu surfaces.

The ordered/disordered Cu surfaces were obtained by evaporating Cu onto a clean Ta substrate at room temperature or 80 K. Before Cu deposition, the Ta foil was routinely cleaned by argon ion bombardment and annealing. CO₂ adsorption on a clean Ta surface was studied first. However, there was no notable CO₂ related signal detected due to the poor adsorption. The normalized XPS peak intensities for both the Cu 3*p* doublet and the Ta 4*f* doublet are shown in Fig. 1 as a function of Cu evaporation time. As shown in Fig. 1(a) for Cu deposition at room temperature, the amplitudes of the observed Cu 3*p* and Ta 4*f* XPS peaks changed in a characteristic manner. Two coincident break points were clearly observed in the two plots: one at 320 s and another at 650 s. Three linear segments can be distin-

Fig. 1. Normalized XPS intensities for the Cu 3*p* doublet and Ta 4*f* doublet as a function of Cu evaporation time at room temperature (a) and at 80 K (b). The light gray dash lines are drawn as a guide.

guished in the Cu deposition. The first linear section in the two plots indicated a two dimensional growth of the first Cu monolayer on the Ta substrate during 320 s. The second linear section, with a more gradual slope, implied the completion of the second monolayer at 650 s. The shapes of the curves clearly showed that Cu grows on the Ta substrate at room temperature in a layer-by-layer growth mode. Generally, deposition on a cold substrate (< 100 K) provides a large amount of atomic scale surface defects and different chemisorption sites [24,25]. These disordered surfaces are formed because surface diffusion is too slow to enable the adsorbate to form large scale ordered structures. The thermally evaporated metal atoms stick at where they land, which is known as the simultaneous multilayer growth [26]. Our disordered Cu surfaces were prepared by evaporating Cu onto the Ta substrate at 80 K. Figure 1(b) shows the normalized XPS peak intensities for both the Cu 3*p* doublet and the Ta 4*f* doublet as a function of Cu evaporation time at 80 K. With the increase in Cu deposition time, the Cu 3*p* doublet intensity increased and Ta 4*f* doublet intensity decreased. Both curves can be divided into two sections by the point at 650 s into a linear increase section and a smooth curve section. The XPS intensities of Cu 3*p* for the maximum deposited at 1290 s were the same for the simultaneous multilayer growth and the layer-by-layer growth. The Cu evaporation was performed by applying a fixed heating current to the W wire of the Cu evaporator, so that the Cu deposition rate was constant regardless of the temperature of the substrate. After Cu deposition, the Cu surfaces were cooled by liquid nitrogen to 80 K for CO₂ adsorption.

Figure 2 displays the vibrational spectra of CO₂ on the ordered Cu surfaces at 80 K versus CO₂ exposure. The loss regions of the spectra were enlarged by a factor of 20 with respect to the elastic peak. There were five losses due to CO₂ adsorption at 320, 654, 1290, 1395, and 2160 cm⁻¹. Based on known IR and SERS data of gaseous and adsorbed CO₂ from the literature [19], four of the bands were assigned as follows: bending mode δ at 654 cm⁻¹, asymmetric stretching mode ν_{as} at 2160 cm⁻¹, first overtone of the bending mode 2δ and the symmetric stretching mode ν_s coupled Fermi resonance dou-

Fig. 2. HREELS spectra for CO₂ on ordered Cu surfaces under different conditions: (1) 0 L, (2) 10 L, (3) 100 L of CO₂ at 80 K, (4) in 10°-off-specular mode, and after annealing to 110 K (5).

blet at 1290/1395 cm^{-1} . A red shift was observed for the ν_{as} mode. The probable reason is that the stretching is frustrated by the image dipole or the spatial restriction due to the Cu surface. The fact that all the vibration modes were comparable with those of gaseous CO_2 revealed that the CO_2 electron configuration has undergone negligible perturbation on physisorption on the ordered Cu surface. This result strongly supports the linear adsorption geometry of CO_2 in the physisorbed state. Moreover, no losses appeared at ~ 730 and ~ 1100 cm^{-1} for the various CO_2 exposures, thus precluding the presence of the bent chemisorbed $\text{CO}_2^{\delta-}$ species. In addition, in the adsorption study of CO_2 , the molecule-metal vibration in the energy range below 500 cm^{-1} provides important information on the CO_2 coordination mode [27,28,29]. In earlier experiments, due to the technical limitation of this vibrational spectroscopy, the peaks below 500 cm^{-1} were all merged into the broad elastic peak. However, in our experiments, the resolution (FWHM) was 48 cm^{-1} (or < 6 meV), thus a peak at 320 cm^{-1} was clearly observed. Generally, the Cu–O stretching vibration (390 cm^{-1}) [9] is more robust than the Cu–C stretching vibration (355 cm^{-1}). The loss at 320 cm^{-1} is certainly due to a molecule-metal vibration, and it is most likely the Cu–C stretch ($\nu_{\text{Cu-C}}$). Furthermore, it can be concluded that CO_2 physisorbed on Cu surfaces by carbon coordination. As shown in the off-specular mode (Fig. 2(4)), the relative intensities of the ν_{s} and ν_{as} modes increased compared to those of the $\nu_{\text{Cu-C}}$ and δ modes. This is a strong indication that these resonances were dominated by impact scattering and the CO_2 molecules were parallel to the surface. Annealing of the sample to temperatures above 110 K caused all CO_2 induced losses to vanish. This is in good agreement with TPD data reported in the literature [9], and it is also a clear indication that no CO_2 dissociation occurred on the ordered Cu surface during the annealing.

CO_2 physisorption on the ordered Cu surface was further confirmed by the XPS study. The C 1s and O 1s spectra after CO_2 exposure at 80 K are shown in Fig. 3. Due to the low sticking probability of CO_2 on the Cu surface, no detectable peaks were present until the exposure of 50 L. The slopes in the high BE region in the O 1s spectra are the tails of the strong Cu

Fig. 4. HREELS spectra for CO_2 on the ordered Cu surfaces under different conditions: (1) 100 L of CO_2 exposure, (2) 30 min of irradiation with 193 nm laser, (3) 60 min of irradiation with 193 nm laser, and (4) after annealing to 110 K. A 193 nm ArF excimer laser was used with an intensity of 0.5 W/cm^2 to minimize the thermal effect. No temperature change was detected during the laser irradiation.

$\text{L}_{3\text{M}_{45}\text{M}_{45}}$ and $\text{L}_{2\text{M}_{45}\text{M}_{45}}$ Auger lines. Only the physisorbed CO_2 species was identified on the Cu surface by the carbon species at 291.3 eV and oxygen species at 533.4 eV. These values are close to those of physisorbed CO_2 species in the literature (C 1s at 291 eV and O 1s at 534 eV) [12,30]. As shown in Figs. 3(4) and (5), upon CO_2 desorption, a clean Cu surface was obtained at 110 K.

Photons ($\lambda = 193$ nm) were introduced to activate the physisorbed CO_2 molecules on the Cu surfaces at 80 K. The HREELS spectra from these are shown in Fig. 4. A 193 nm ArF excimer laser was used as the photon source, and a low intensity of 0.5 W/cm^2 was used to minimize the thermal effect. No temperature change was detected during the laser irradiation. In the HREELS spectra, no new feature was observed and all the features from physisorbed CO_2 were intact during photon irradiation. The decrease in the vibrational intensity of CO_2 was probably due to photo-induced desorption. Upon increasing the sample temperature to 110 K, CO_2 molecules were desorbed and a clean surface was obtained. It is known that when the

Fig. 3. C 1s (a) and O 1s (b) regions of the XPS spectra from CO_2 on the ordered Cu surface: exposed to 10 L (1), 50 L (2), 100 L (3) of CO_2 at 80 K, and subsequently warmed to 95 K (4) and 110 K (5). Only physisorbed CO_2 species was identified on the Cu surface by the carbon species at 291.3 eV and oxygen species at 533.4 eV. The slopes in the high BE of O 1s region are the tails of the strong Cu $\text{L}_{3\text{M}_{45}\text{M}_{45}}$ and $\text{L}_{2\text{M}_{45}\text{M}_{45}}$ Auger lines.

photon wavelength is above 167.2 nm, the photon adsorption cross section of gaseous CO₂ is quite small [31]. Thus it is reasonable to suggest that the 193 nm photon did not activate the physisorbed CO₂ and no photon-induced reaction occurred during the irradiation. The XPS spectra are not shown because there was no observable change in the spectrum. Based on the HREELS and XPS data, it is clear that CO₂ molecules were exclusively physisorbed on the ordered Cu surface at 80 K and they were completely desorbed at 110 K. No photoinduced reaction occurred with the physisorbed CO₂ species during the 193 nm photon irradiation.

Figure 5 shows the HREELS spectra of CO₂ on the disordered Cu surface at 80 K. After 100 L CO₂ exposure, the observed frequencies in Fig. 5(2) indicated obviously that the spectrum originated from two different CO₂ surface species. Due to the different geometric configurations for physisorbed CO₂ and chemisorbed CO₂^{δ-} species, their vibrational modes are different. The physisorbed CO₂ species shows loss features at 654 (δ), 1290 (2δ), 1395 (ν_s), and 2160 cm⁻¹ (ν_{as}). The new loss features at 760, 1160, and 1620 cm⁻¹ can be assigned to the bending δ' , symmetric stretching ν_s' and asymmetric stretching ν_{as}' modes of chemisorbed CO₂^{δ-} species, which are in good agreement with the literature [19]. Although two surface species coexisted on the disordered Cu surface, there was only one Cu–C stretching ν_{Cu-C} identified at 320 cm⁻¹, which indicated that the two species both adsorb by carbon coordination. Although the chemisorbed species cannot be formed on the ordered Cu surface upon CO₂ exposure, it was formed on the disordered Cu surface. This difference would be due to the unsaturated surface structure, which include steps, terraces and kinks on the disordered Cu surface. It is well known that chemisorption is stronger than physisorption, and the behavior of the spectra during annealing is shown in Figs. 5(3) and (4). Due to their weak adsorption, physisorbed CO₂ molecules desorbed completely at 110 K, while the losses for the chemisorbed species CO₂^{δ-} at 320 (ν_{Cu-C}), 760 (δ'), 1160 (ν_s'), and 1620 cm⁻¹ (ν_{as}') remained. Upon annealing the sample to 140 K, complete desorption of the chemisorbed CO₂^{δ-} species was seen. This result implied that no CO₂ dissociation occurred on the disordered Cu surface during the adsorption and heating.

Fig. 5. HREELS spectra for CO₂ on the disordered Cu surfaces under different conditions: (1) clean surface, (2) 100 L of CO₂ at 80 K, after annealing to (3) 110 K, and (4) 140 K.

Fig. 6. HREELS spectra for chemisorbed CO₂^{δ-} species on the disordered Cu surfaces: (1) 30 min of laser irradiation, (2) 60 min of laser irradiation, and after annealing to (3) 150 K, and (4) 300 K.

Photo-activation of the chemisorbed CO₂^{δ-} species was investigated by introducing photo-irradiation ($\lambda = 193$ nm) onto the chemisorbed species at 80 K. After 30 min laser irradiation, two new features at 390 and 2050 cm⁻¹ were observed in the HREELS spectrum of Fig. 6(1), that coexisted with the chemisorbed CO₂^{δ-} species induced losses at 320, 760, 1160 and 1620 cm⁻¹. These two new losses correspond to the Cu–O stretching mode (ν_{Cu-O} at 390 cm⁻¹) and C–O stretching mode (ν_{C-O} at 2050 cm⁻¹), which indicated that a photoinduced dissociation of chemisorbed CO₂^{δ-} species to CO_(a) and O_(a) species had occurred during the photo-irradiation. After further photo-irradiation for 60 min, the spectrum in Fig. 6(2) clearly displayed an intensity increase in the CO stretching and intensity decreases in the CO₂^{δ-} vibrations. Some residual CO₂^{δ-} species were still found on the Cu surface even after prolonged photo-irradiation. This can be explained by that the rough Cu surface sheltered some CO₂^{δ-} species from the irradiation. As shown in Fig. 6(3), these unreacted chemisorbed CO₂^{δ-} species thermally desorbed on annealing the sample to 150 K, and then only CO species were present on the surface. Due to a stronger chemisorption bond of CO on the Cu surface, the CO surface species desorbed at a higher temperature of 300 K. This was in good agreement with previous TPD results showing CO desorption from Cu surfaces at 240 K [32]. Upon annealing to 300 K, only oxygen species at 390 cm⁻¹ remained on the surface, as shown in Fig. 6(4). Due to the low coverage of chemisorbed CO₂^{δ-} species, the C 1s and O 1s XPS spectra for CO₂^{δ-} species were indistinct and are not shown here. However, a weak chemisorbed oxygen species was still observed at 530.6 eV after the photon irradiation and 300 K annealing, which is consistent with the HREELS results and confirmed the occurrence of photo-induced dissociation reaction for the chemisorbed CO₂^{δ-} species on the disordered Cu surface [12,33]. Compared to physisorbed CO₂, the chemisorbed CO₂^{δ-} species has a higher energy ground state and a longer C–O bond. The change in the electronic structure and molecular symmetry would give a higher photo-absorption cross section and a lower dissociation energy barrier.

In summary, the adsorption and photochemistry of CO₂ on

Graphical Abstract

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WANG Shuai, XU Guoqin*

Xinjiang Normal University, China;

National University of Singapore, Singapore

The physisorbed CO₂ species and chemisorbed CO₂^{δ-} species are routinely isolated on the ordered and disordered Cu surfaces. It was found that the photo-induced dissociation occurs only on the chemisorbed species by the 193 nm laser irradiation; while there is no photo-induced dissociation occurred on the physisorbed species.

ordered and disordered Cu surfaces were studied by XPS and HREELS. The ordered and disordered Cu surfaces were, respectively, obtained by depositing Cu onto a Ta substrate at room temperature and at 80 K. Physisorbed CO₂ species and chemisorbed CO₂^{δ-} species were present on the two different faces, facilitated a study of their photochemical behavior. Only the chemisorbed CO₂^{δ-} species dissociated into CO_(a) and O_(a) surface species upon 193 nm photo-irradiation. We suggest that the CO₂^{δ-} species is the transition state in CO₂ conversion, and its role must be considered in the mechanism of photocatalyzed CO₂ reduction.

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二氧化碳在铜表面的吸附研究及其光致分解

王 帅^a, 许国勤^{b,*}^a新疆师范大学化学化工学院, 新疆乌鲁木齐830054^b新加坡国立大学化学系, 新加坡117543

摘要: 使用X光电子能谱(XPS)及高分辨电子能量损失谱(HREELS)研究了二氧化碳在铜表面的吸附及其光化学反应。通过实验

条件控制将物理吸附及化学吸附的二氧化碳吸附物种分别分离在规整铜表面及无序铜表面上, 并使用193 nm激光对其照射研究其相应的光化学反应. 结果表明只有化学吸附的二氧化碳物种在光诱导下发生了解理反应, 而物理吸附的二氧化碳未发生反应.

关键词: 二氧化碳; 铜表面; 化学吸附; 物理吸附; 光致解理

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*通讯联系人. 电话: +65-6516-3595; 传真: +65-6779-1691; 电子信箱: chmxugq@nus.edu.sg

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