Adsorption and Reactivity of Sulfur Dioxide on Cu(110). Influence of Oxidation and Hydroxylation of the Surface

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The interaction of sulfur dioxide with a Cu(110) surface, oxidized to different levels or hydroxylated, was investigated at room temperature by in situ infrared reflection−absorption spectroscopy. The initial surface chemical state was checked by Auger electron spectroscopy and photoelectron spectroscopy. Oxidation of sulfur dioxide into sulfites or sulfates was observed upon exposure to SO_2, depending on the reactivity of oxygen and hydroxyls in the surface layer. The more oxidized the surface, the less reactive it becomes toward sulfur dioxide. Hydroxylation also reduces the surface reactivity as deduced from band intensities. Adsorption of SO_2 on Cu(110), only partially covered with oxygen, generates sulfates whereas only sulfites are formed by interaction of SO_2 with a surface copper oxide. Coadsorption of sulfur dioxide with oxygen favors the formation of sulfates whether the surface is only partially covered with oxygen or oxidized. When the surface is oxidized and hydroxylated before being exposed to sulfur dioxide, hydrogenosulfates are detected in the adsorbed phase. A mechanism is proposed where hydrogenosulfates are formed by a reaction of SO_2 with surface hydroxyl groups. The adsorption sites as well as the symmetry of the identified species are discussed in view of the number and position of vibration frequencies. These in situ IR analyses make clear that the interaction of sulfur dioxide with copper oxide substrate is highly sensitive to the chemical state and to the structure of the oxide surface layer.

1. Introduction

The oxidation of sufur(IV) oxides, catalyzed by transition metal oxides, has been extensively documented due to its major role in environmental chemistry as well as in industrial processes. Metal oxides play an important role in the industrial catalytic oxidation of SO_2, e.g., for the production of sulfuric acid. A recent paper reviews oxidation phenomena involving sulfur(IV) oxides in atmospheric processes.[1] In this article, the role of the transition metal oxide surface and the nature of the active oxygen have been addressed. The authors note that on CuO and CoO no oxidation of SO_2 occurs in the absence of O_2 in the gas phase. Upon adsorption of sulfur dioxide, several types of complexes have been observed on copper, depending on the oxidation and hydroxylation level of the metal. It has been demonstrated that the relative humidity is an important factor in controlling the oxidation of SO_2, and one can infer the role of the surface OH groups in the surface reactions. This has been particularly investigated by Persson and Leygraf, who submitted a polycrystalline copper sample to humid air containing a few ppm of SO_2. By in situ infrared spectroscopy, they identified sulfite species and proposed the mechanism of their formation.[2]

The influence of surface chemistry on the interaction of SO_2 with metallic substrates has also been investigated by XPS, and intermediates have been clearly identified. Depending on the metal and on the experimental conditions, SO_2 may decompose as it does on platinum[3] or disproportionate into S_{ads} and $SO_{4,ads}$ as on nickel. On copper, despite numerous studies, the situation

is less clear. On Cu(100) and Cu(111), Polcik et al.[4] showed that, at room temperature, SO_2 decomposes into SO, O, and S. Different SO_2 bindings to surface sites were evidenced depending on the surface structure; in particular, SO_2 dissociation was shown to be easier on Cu(100), on which SO_2 is adsorbed through both S and one of its O atoms, than on Cu(111). The molecular and dissociative chemisorption of SO_2 has been investigated by Wassmuth on a Cu(111) surface using TPD and Auger spectroscopy. These authors showed in particular a desorption peak for SO_2 at 280 K and pointed out the role of defects upon SO_2 dissociation.[5,6] The interaction of SO_2 with copper surfaces and the effect of surface oxidation have been well characterized by Baxter et al.,[7] using X-ray photoelectron spectroscopy. At room temperature, SO_2 does not adsorb on clean Cu(111), while it reacts to form SO_3 when oxygen is preadsorbed. Moreover, on a preoxidized surface, it was proposed that, depending upon the temperature, copper sulfate, $CuSO_4$, or copper sulfide was formed, both via a Cu_2SO_3 intermediate, preceding a dissociation reaction. Pradier et al. recently studied the adsorption of SO_2 on a well-defined copper surface using high-resolution core-level photoelectron spectroscopy. On clean Cu(100) and Cu(100)-c(2×2)−O surfaces, S and SO_3 species were observed; preadsorbed oxygen was shown to inhibit SO_2 decomposition and favor oxidation of SO_2 into SO_3.[8] A similar study on the more opened Cu(110) surface is in progress.

Adsorption of water on metal oxide surfaces has also given rise to a wide range of studies on transition metals and metal oxides, in particular on copper oxide. The dissociation of water was shown to be greatly enhanced by the presence of defects such as oxygen vacancies.[9] On a well-defined surface, Cu_2O-(100), Cox and Schulx showed, using UPS and XPS, that at

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RT adsorption of water is dissociative,[10] leading to hydroxyl groups and protons. Those adsorbed entities give specific acid–base properties depending on the nature of the oxide. Davydov reminded that the IEPS (isoelectric point of the surface) of M_2O type oxides is close to 10, which implies Brønsted basic properties of the surface.[11] Concerning the electronic and reactive properties of Cu_2O surfaces, several theoretical studies can be found in the literature,[12–14] showing an ionic character for this solid (Cu, +0.86, O, −1.72). This high ionicity confirms the basic character of the surface which is likely to facilitate nucleophilic attack of the sulfur atom of SO_2 by adsorbed hydroxyl groups.[15]

Among the numerous studies dealing with surface reactivity, Madix et al. provide clear examples of the influence of the solid electronic structure on the surface reactivity by using surface science spectroscopies for studying interaction of SO_2 with well-controlled surfaces.[16–19] As an example, this group demonstrated the role of the local electron density of the substrate upon the adsorption mechanism of SO_2 on Pd (100) and Ag(110). The authors explained the decomposition of SO_2 on Pd(100) by the ability of the sulfur and oxygen atoms to react with the "d" orbitals of the substrate. In the case of silver surface, SO_2 decomposition is impossible because the metal d levels are too deep in energy to be involved in a strong bond with S or O. The authors made clear a charge transfer from the surface to the molecule similar to the one in the $(CH_3)_3NSO_2$ complex.[19] These electronic criteria explain why SO_2 decomposes on most metallic surfaces, leading to mixed oxide–sulfide compounds. On ionic surfaces, and especially on oxides, SO_2 is generally molecularly adsorbed and possibly converted to more oxidized molecular entities. On one hand, the empty electronic states of the metal cations make them likely to be attacked by the oxygen atom of SO_2. On the other hand, the substrate valence band, comprised of the 2p orbitals of the oxygen anions, will be responsible for the nucleophilic attack on the sulfur atom of SO_2. Bulk oxide surfaces or adsorbed oxygen on metallic crystal surfaces are thus expected to lead to oxidation of SO_2. Madix et al. studied the role of oxygen preadsorption upon the interaction of SO_2 on Pd(100) and Ag(110) surfaces. They, in particular, showed the nucleophilic character of the adsorbed oxygen atom, leading to sulfate species on Pd(100) and a mixture of sufites and sulfates on Ag(110) (ref 17 and references therein, ref 20). Formation of sulfite species was accompanied by an increase of the surface work function consistent with a charge transfer from the substrate to the molecule.

These few examples, from the recent literature, are conclusive, showing that in all adsorption processes involving SO_2, the chemistry, the geometry, and the electronic structure of the surface are important parameters that govern the adsorption process and the nature of the final molecular adsorbed entities. They also show how important it is to work on well-defined surfaces.

SO_2 is an interesting, though complicated, probe molecule. It can be considered as a Lewis base due to the oxygen negative local charge or as a Lewis acid due to the positively charged sulfur atom. It also acts as a Brønsted base when oxygen binds to an hydrogen atom from an acidic entity. All these possible types of interactions of SO_2 with metals or other ligands lead to a great diversity of sulfur containing organometallic compounds.[21]

Though numerous studies have already dealt with SO_2 adsorption on copper and copper oxide surfaces, its reactivity on well-defined surfaces in relation to the surface composition and structure as well as the influence of the coadsorbed oxidizing species has been rarely described. This paper relates a new study of the interaction of SO_2 a Cu(110) surface covered with different oxygen amounts and structures. This surface orientation is interesting for its high reactivity. It exhibits several well-characterized oxygen surstructures, p(2×1), c(6×2), and finally a Cu_2O surface oxide when the oxygen coverage increases.[22–25] As on the other 3d transition metals, oxygen-induced reconstruction occurs leading to metal–oxygen chains parallel to the [001] direction in the case of the p(2×1) arrangement. For the c(6×2)-O structure, the reconstruction geometry is similar, resulting in high-density copper–oxygen buckled chains. On both structures, oxygen is strongly adsorbed on low coordinated metallic atoms leading to highly ionic copper–oxygen bonds.[24] The charge transfer from copper to oxygen was evaluated to about 1 electron.[26] The reactivity of these typically $O(n×1)$ structures has attracted special attention for their interesting properties in the oxidation of small molecules, CO, H_2, H_2S, and NH_3.[24] In these reactions, the active centers seem to be the oxygens at the end of the chains.[27–29]

In this work, adsorption of SO_2 was investigated by surface infrared spectroscopy on a copper (110) single-crystal surface under UHV conditions, following different oxidation treatments. The surface was submitted to oxygen and possibly to water before SO_2 adsorption. The influence of oxygen and water, coadsorbed with SO_2, upon the nature of the adsorbed species has been addressed.

2. Experimental Section

All experiments were performed in a vacuum chamber (Meca 2000) especially designed for cleaning the surface by ion sputtering, heating the substrates up to 1200 K, and analyzing it with Auger electron and IR spectroscopies.

IR measurements were carried out at grazing incidence (6°) using a Fourier transformed infrared spectrometer (NICOLET, Magna 550) with a MCT wide band detector and two ZnSe windows transmitting infrared light between air and vacuum. A typical spectrum was obtained by averaging the signal over 800 scans in 10 min. at a resolution of 4 cm^{-1}. All spectra were ratioed against a background spectrum recorded on a clean sample before admitting the gases.

The single crystal was oriented to within 0.5° by X-ray back-reflection. After being mechanically polished down to 0.1 μm, the sample has been electrochemically polished. In the UHV chamber, the Cu(110) surface was cleaned by cycles of argon sputtering (500 V)–annealing to 800 K in a vacuum. It was then treated in oxygen ($P_{O_2} = 10^{-4}$ Torr at 400 °C for 10 min, then cooled to room temperature) in order to oxidize the topmost copper layers. Sulfur contamination was eliminated by annealing in 10^{-5} Torr of oxygen. A residual oxygen contamination was always detected after our cleaning procedure ($Cu_{LVV}/O_{KLL} = 20$). A slightly oxidized sate of the surface was obtained by exposure of 200 langmuirs of oxygen at 500 K. These conditions correspond to the obtention of a c(6×2) structure.[25] A higher oxidation state of the surface was obtained by heating the sample to 800 K in 10^{-2} Torr of oxygen. Cu_2O was formed in the overlayers as shown by further XPS analyses. In both cases, no carbon or sulfur contamination was detected. Hydroxylation of the preoxidized surfaces was obtained by exposure of 30.000 langmuirs of the surface to water vapor at 300 K. Auger electron spectroscopy was systematically utilized before and after adsorption procedures.

The nature of the copper oxide obtained by this way has been checked by repeating the same preparation procedure in another vacuum chamber equipped with a photon source and a hemi-

spherical VG analyzer for XPS measurements. An Al Kα source was used (1486.6 eV), and the pass energy was 20 eV for analyzing the Cu 2p, Cu$_{LMM}$, O 1s, and C 1s regions.

Water and sulfur dioxide adsorption experiments were achieved by means of leak valves at pressures around 10^{-5} Torr under dynamic conditions by maintaining a constant pumping with a turbopump. IR measurements were made in situ under adsorption conditions, while Auger analyses were done after gas evacuation.

3. Results

3.1. Auger Electron Spectroscopy Surface Characterization. The chemical state of the surface was systematically checked by Auger electron spectroscopy (AES) before admission of sulfur dioxide to the chamber. The surface was considered as clean when no carbon and no sulfur *KLL* Auger peaks could be detected. The initial oxidation level was checked by measuring the ratio of the oxygen (*KLL*) peak at 503 eV and copper (*LVV*) at 62 eV after oxidation pretreatment. A ratio of approximately 0.25, obtained by exposure of the clean surface to oxygen under conditions well established in the literature, characterized a slightly oxidized surface called the O$_{ads}$—Cu(110) surface in the following text. A ratio of the same Auger peak intensities equal to 0.5 corresponded to the formation of Cu$_2$O in the topmost layers as confirmed by XPS measurements.

An AES analysis was carried out after exposure and pumping of the SO$_2$-containing gas phase. It always revealed a noticeable decrease of the oxygen peak to the benefit of the sulfur one. The surprising decrease in the AES oxygen signal to the benefit of the sulfur one is a general phenomenon that we observed after all our experiments. It is probably due to a higher sensitivity of the AES to sulfur compared to oxygen and to a partial lose of slightly bound surface oxygen-containing species when evacuating the chamber. It may also result from a molecular dissociation due to the impinging primary electrons of 2500 eV used in Auger electron spectroscopy.

3.2. X-ray Photoemission Spectroscopy Surface Characterization. To correlate the IR data to the chemical state of the surface, in particular to the nature of the oxide formed under the most oxidizing conditions and after hydroxylation, the oxidation and hydroxylation procedures were repeated on the same copper sample in another UHV chamber equipped for X-ray photoemission spectroscopy (XPS), and analyses were carried out without transferring the sample. The surface state was checked at two different stages: (i) after oxidation pretreatment and (ii) after oxidation and water adsorption performed under conditions identical to the ones used before our IR measurements.

Three regions are of interest: (1) the region of O$_{1s}$, which enables to evaluate the level of oxidation and hydroxylation of the surface, (2) the regions of Cu$_{2p}$ and of the Auger lines Cu$_{LMM}$ which, both together, characterize the oxidation state of copper, and (3) the C$_{1s}$ region, also screened for checking the cleanness of the surface.

a. XPS Analysis of Cu(110) after in Situ Oxidation Treatment. The absence of a satellite to the Cu$_{2p}$ peak and the broad *LMM* Auger line at a kinetic energy of ca. 917 eV makes it easy to identify Cu$_2$O. A single narrow peak is observed for O 1s at 530.6 eV, also characteristic of lattice oxygen in cuprous oxide. It also shows the absence of OH groups, in the limit of XPS sensitivity, on the surface after this preparation procedure (see Figure 1). No carbon peak and a negligible sulfur peak were observed in that case.
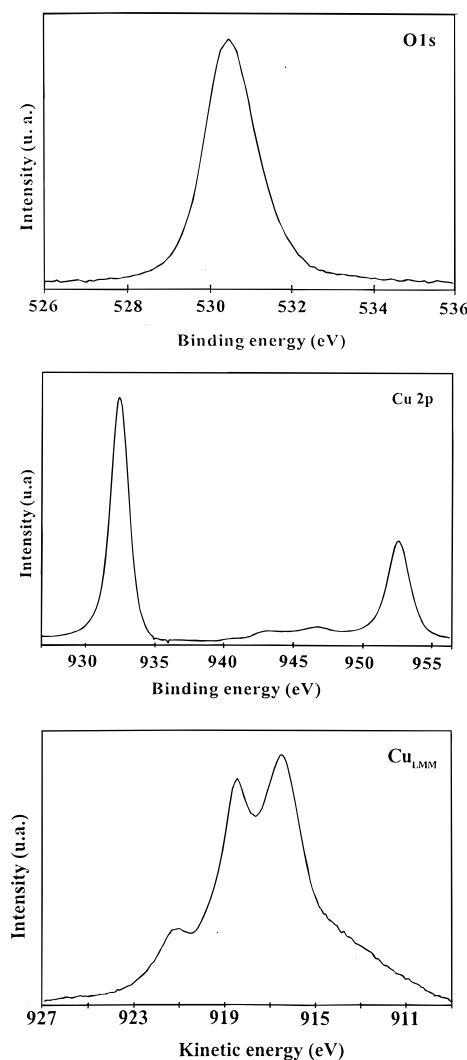

Figure 1. XPS Cu 2p, Cu *LMM* and O 1s signals of the Cu(110) surface after treatment under oxygen (see text).

b. XPS Analysis of Cu(110) after in Situ Oxidation Treatment, Followed by Water Adsorption. The major difference, compared to the sample only oxidized, appears on the O 1s peak which is now made of two components: one main contribution at 531.4 eV, characteristic of adsorbed hydroxyl groups, and a second one at 530.6 eV, showing that adsorption of OH occurred on an oxidized copper surface (see Figure 2).

The Cu$_{2p}$ and Auger lines confirm the Cu$^+$ oxidation level after these treatments under oxygen and water.[30]

3.3. IRRAS in Situ Investigation of SO$_2$, SO$_2$ + O$_2$, and SO$_2$ + H$_2$O Adsorptions. *a. Adsorption of SO$_2$.* Adsorption of SO$_2$ was held at room temperature with a pressure of 10^{-6} Torr. Interaction with different oxidized surfaces was followed by in situ IRRAS

On the slightly oxidized or "O$_{ads}$—Cu(110)" surface, spectral changes were observed between 1400 and 900 cm^{-1} where oxidized sulfur species show stretching S—O vibrations.[17] Three main absorption bands appear at 1250, 1150, and 1120 cm^{-1} as shown in Figure 3a. Low-intensity bands were also present near 1060, 1033, 993, 853, and 820 cm^{-1}. All these bands appear after 600 s of exposure to $P_{SO_2} = 10^{-6}$ Torr (600 langmuirs) and are stable in position and intensity after 5400 s (5400 langmuirs).

When adsorption of SO$_2$ was held on a surface Cu$_2$O oxide, only two intense and large absorption bands were detected at
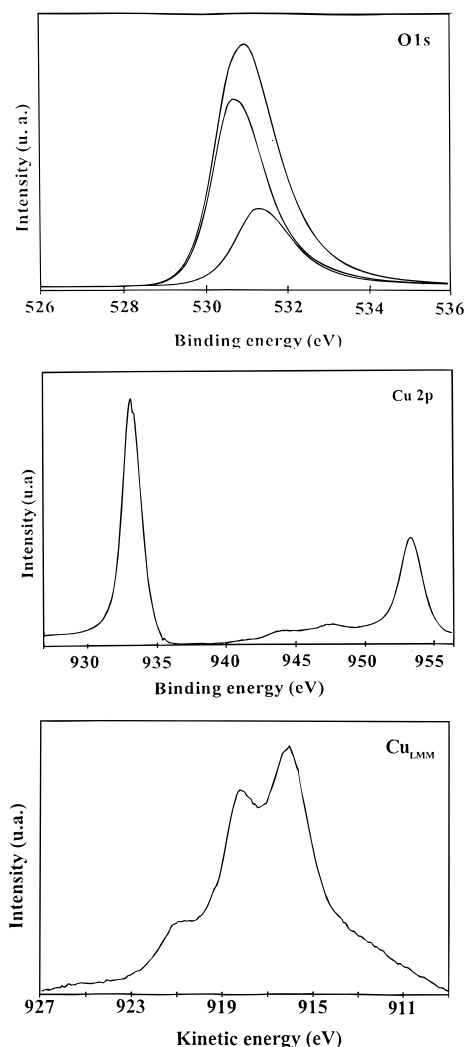
Figure 2. XPS Cu 2p, Cu *LMM*, and O 1s signals of the Cu(110) surface after treatment under oxygen and water (see text).

respectively 940 and 840 cm^{-1}; a weak band was also detected at 1080 cm^{-1} (Figure 3b). The spectrum was unchanged after 600 s of SO$_2$ exposure.

When the Cu$_2$O surface was prehydroxylated as described previously, SO$_2$ adsorption led to the spectrum shown in Figure 3c, with significant bands at 1287, 1130, 1050, 965, 895, and 843 cm^{-1}.

Note that the IR intensities are almost 1 order of magnitude higher on the O$_{ads}$–Cu(110) surface than on the two other, more oxidized, surfaces.

(b) Adsorption of SO$_2$ + O$_2$. The three types of substrates described above, O$_{ads}$–Cu(110), oxidized Cu(110), and oxidized + hydroxylated Cu(110) surfaces, have been exposed to an equimolecular mixture of SO$_2$ + O$_2$ with a total pressure of 2 × 10^{-6} Torr at room temperature.

On the O$_{ads}$–Cu(110) surface, the IR spectrum shows three well-resolved bands at 1250, 1150, and 1120 cm^{-1} (Figure 4a). These bands are similar in shape and intensity to the ones observed when SO$_2$ was adsorbed alone (see Figure 3a). However, the vibration bands appearing at low frequency in Figure 3a are missing when SO$_2$ and O$_2$ are coadsorbed on the same surface.

When a SO$_2$ + O$_2$ gas mixture interacts with a Cu$_2$O surface, the IRAS spectrum shows five main bands at ca. 1250, 1130, 1030, 1000, 965, 940, and, 870 cm^{-1} (see Figure 4b). Compar-
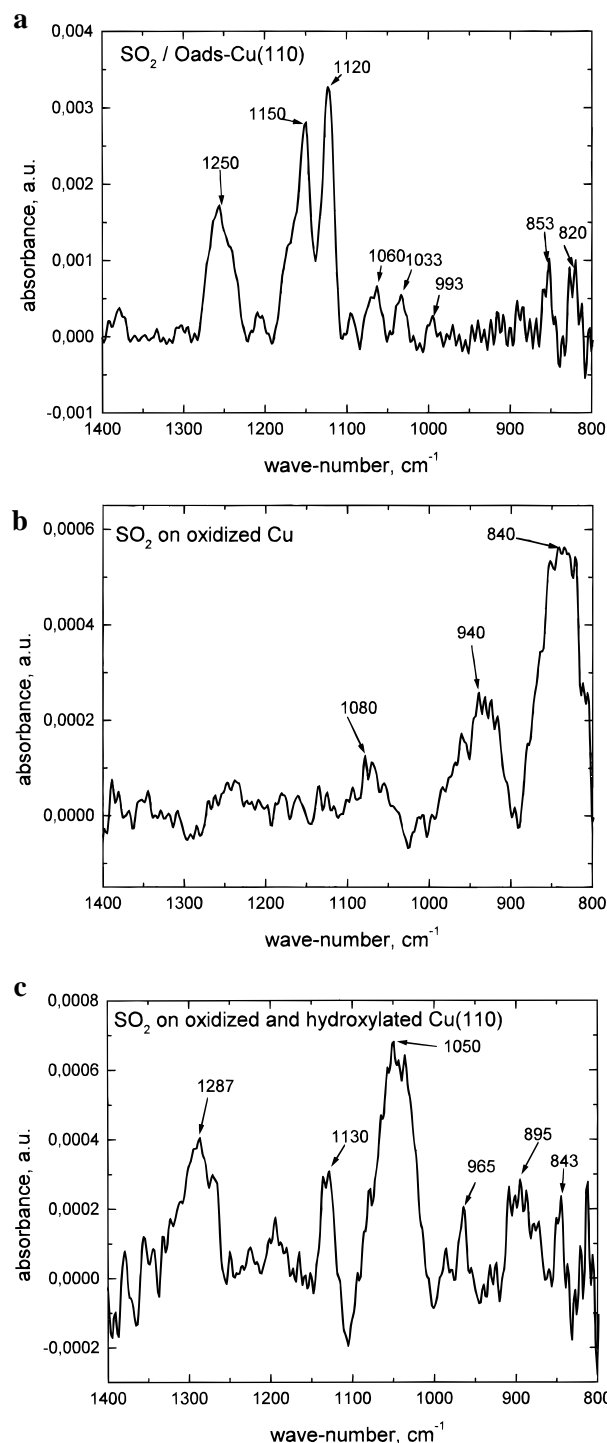

Figure 3. IRRAS spectra during SO$_2$ interaction, P_{SO_2} = 10^{-6} Torr: (a) of the O$_{ads}$–Cu(110) surface, (b) of the Cu$_2$O surface, and (c) of the hydroxylated Cu$_2$O surface.

ing with the case where SO$_2$ was adsorbed alone on the same surface, coadsorption with O$_2$ involves several additional features at higher wavenumbers.

On the prehydroxylated Cu$_2$O surface, the IRAS spectrum obtained upon SO$_2$ + O$_2$ adsorption and shown in Figure 4c shows very weak signals. Vibration bands, though hardly detectable, were reproducible at 1300–1280, 1150–1070, and 950 cm^{-1}. Conversely to the preceding experiments, a sharp negative adsorption band, located at 880 cm^{-1}, revealed the disappearance of a surface vibration during adsorption. To interpret that band, an IR spectrum was recorded during
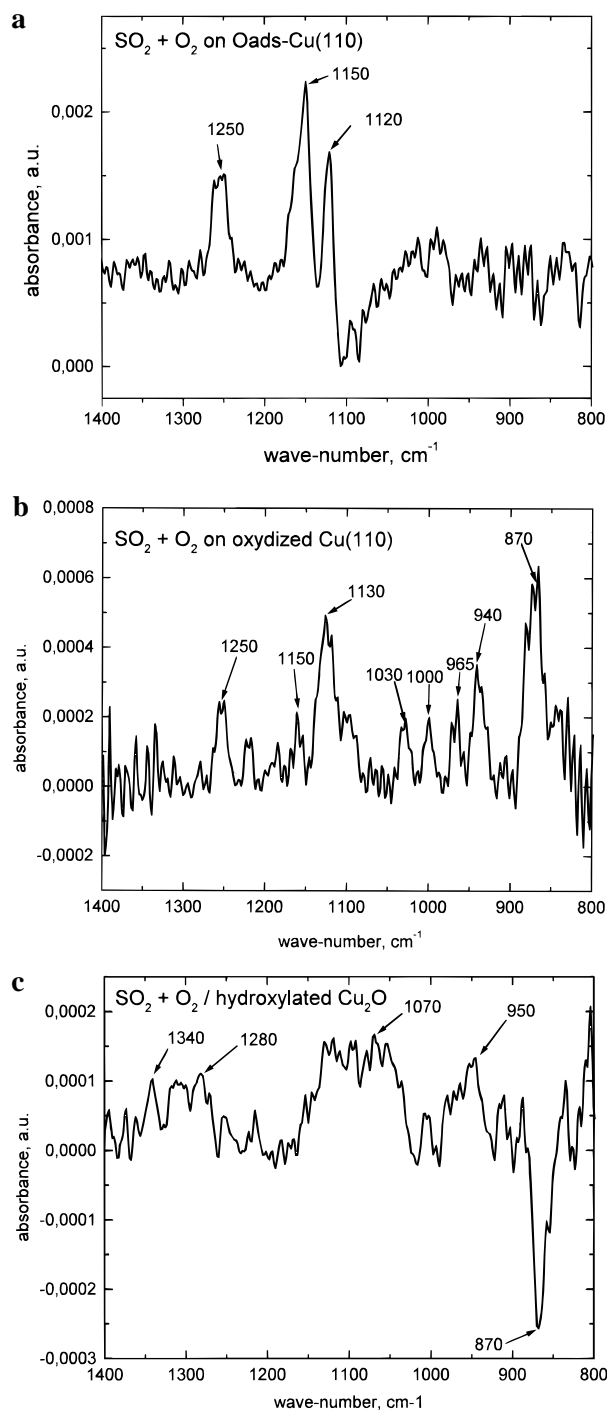
a SO₂ + O₂ on Oads-Cu(110)

b SO₂ + O₂ on oxydized Cu(110)

c SO₂ + O₂ / hydroxylated Cu₂O

Figure 4. IRRAS spectra, during SO₂ + O₂ interaction, $P_{SO_2} = P_{O_2} = 10^{-6}$ Torr: (a) of the $O_{ads}-Cu(110)$ surface, (b) of the Cu₂O surface, and (c) of the hydroxylated Cu₂O surface.

H₂O on oxydized Cu(110)

Figure 5. IRRAS spectra of the Cu₂O surface during H₂O adsorption, $P_{H_2O} = 10^{-5}$ Torr.

a SO₂ + H₂O /oxidized Cu(110)

b SO₂ + H₂0 on oxidized and hydroxylated Cu(110)
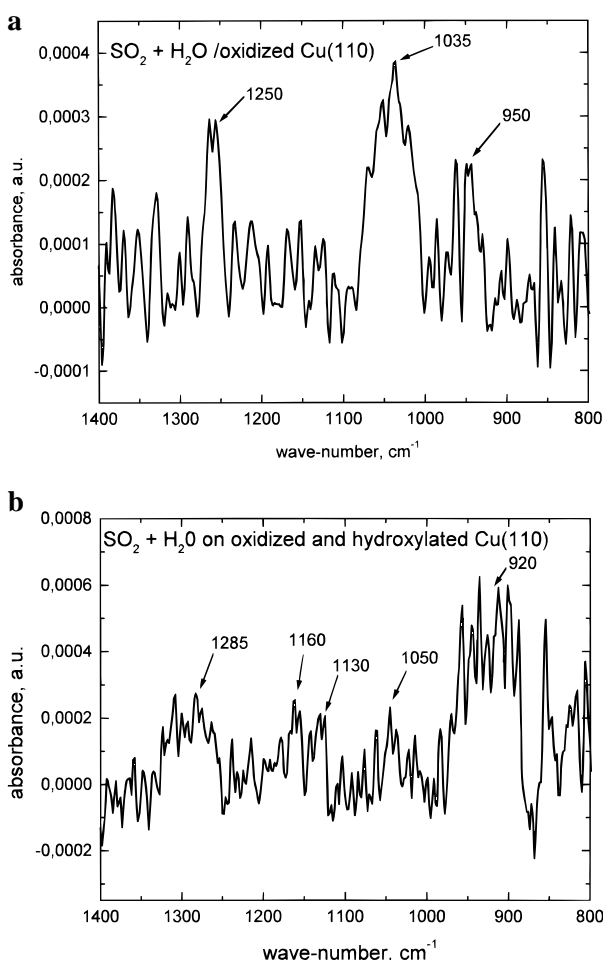
Figure 6. IRRAS spectra during SO₂ + H₂O interaction, $P_{SO_2} = P_{H_2O} = 10^{-6}$ Torr: (a) of the Cu₂O surface and (b) of the hydroxylated Cu₂O surface.

hydroxylation of the surface. It indeed shows a positive band located at 880 cm⁻¹ (Figure 5) appearing upon interaction of water on the oxidized copper surface.

(c) Adsorption of SO₂ + H₂O. Only two substrates were submitted to an equimolecular gas mixture of SO₂ + H₂O (total pressure = 2 × 10⁻⁶ Torr for 100 s i.e., 2000 langmuirs): the dry and the hydroxylated oxidized Cu₂O surfaces. On both substrates, the IR features are weak, we will only mention the peaks that were reproducible among the noise of the background.

On the Cu₂O surface, the IR spectrum is dominated by a broad band centered at 1035 m⁻¹ (see Figure 6a). This band structure is accompanied by two less intense bands at 1250 and 950 cm⁻¹.

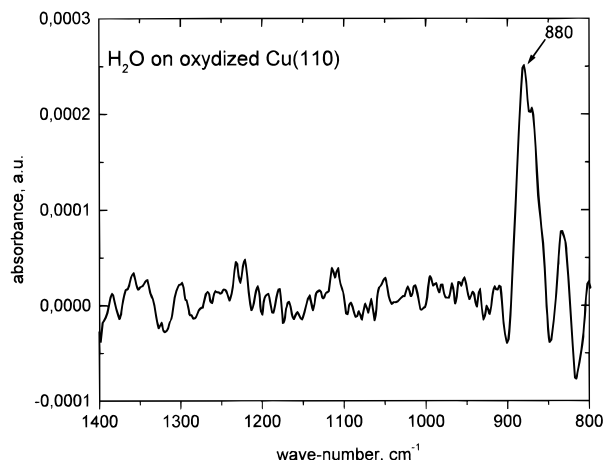On the hydroxylated Cu₂O surface, the IRRAS spectrum was even more difficult to obtain. It exhibits weak, broad vibration bands at 1300−1285, 1150−1130, and 1050 cm⁻¹ plus a broad signal at ca. 920 cm⁻¹ (Figure 6b).

IV. Discussion

Some general comments can be given before discussing the band attributions and the mechanism of SO₂ interaction with the surface:

TABLE 1: Some Molecular Characteristics of Free Oxidized Sulfur Entities Computed with MOPAC in the MINDO3 Approximation

entity	ν_{as} (cm^{-1})	charge		
		O	S	H
SO$_2$	1295	−0.71	+1.43	
SO$_3^-$	1126	−0.99	+1.96	
SO$_4^-$	1293	−1.24	+1.84	
		−0.64		
HSO$_3$	1173	−1.01	+1.75	+0.15
		−0.87		
HSO$_4^-$	1308	−0.97	+1.68	+0.11
		−0.52		
		−0.32		
H$_2$SO$_4$	1375	−0.24	+1.57	+0.23
		−0.75		

(i) Preadsorbed oxygen being necessary to bind nondissociated sulfur-containing species, it is probable that SO$_2$ is present in the form of complexed species.

(ii) Differences in the vibrational modes appearing in the IRRAS spectra indicate formation of various oxidized sulfur species and/or changes of the molecular orientation of the adsorbed molecules on the surface depending on the substrate preoxidation state.

On identical surfaces, differences appear in the spectra whether SO$_2$ was adsorbed alone or in the presence of oxygen or water in the gas phase.

Keeping these remarks in mind, our discussion will emphasize the results on the slightly oxidized surface and then compare with the other spectra obtained after strong oxidation or hydroxylation of the surface.

When SO$_2$ is adsorbed on the O$_{ads}$−Cu(110) surface, multiple absorption bands have been identified in the IR spectrum (Figure 3a). The main peaks are located at 1250, 1150, and 1120 cm^{-1}. Smaller peaks appear at lower frequencies 1060, 1033, 993, 853, and 820 cm^{-1}. The three main absorption bands, plus possibly the one at 993 cm^{-1}, are close to the ones observed by Lavalley et al. on CuO powders and ascribed to bidentate SO$_4$ species.[31] Similar bands were identified by Ferraro et al. for anhydrous CuSO$_4$, shifted by some tenths of cm^{-1} with respect to ours.[32] Compared to the free sulfate ion, belonging to the T_d point group and characterized by two stretching vibration modes, additional bands are expected when the symmetry is lowered due to adsorption process and site geometry. This is the case when SO$_4$ entities are formed by adsorption of SO$_2$ on an oxygen-enriched oxide surfaces. Several structures of SO$_4$ complexes have been characterized and their point groups identified by the number of associated vibrations.[16−18] This vibrational mode representation, which takes into account the selection rule induced by reflection of the infrared beam at the surface, will help us to determine the configuration of the sulfate groups observed in this work. Monodentate or polydentate, chelating, or bridging configurations can be considered. First, it has been established and explained by a simple Lewis argument that, conversely to monodentate, bidentate complexes do have a S−O stretch at frequency higher than 1200 cm^{-1}.[18] Second, the highest wavenumber, band located at 1250 cm^{-1}, has been ascribed to the asymmetric stretching vibrational mode of adsorbed SO$_4$ molecules chelated to a surface cation.[33,34] The observed value for the asymmetric vibration band, ν_3 (1250 cm^{-1}), is also in agreement with Table 1 which presents semiempirical calculations of vibration frequencies and atomic charges for oxidized sulfur-containing entities in the gas phase. Additional information about the symmetry of the adsorbed sulfate is given by the number of stretching vibrations. Here,

three or four stretches are observed depending on the attribution of the 993 cm^{-1} weak band. This number of stretching modes implies a C_s or a C_1 symmetry,[16,18] consistent with a bonding via two oxygen atoms with no mirror-symmetry plane between the two pending oxygens. Kent et al. also identified sulfate groups on CuO, assessing that chelating groups have a ν_3 asymmetric stretching band at 1210−1240 cm^{-1} whereas the ν_3 band of bridging species is below 1200 cm^{-1}.[35] We thus conclude that, on a O$_{ads}$−Cu(110) surface, the main species formed upon adsorption of SO$_2$ are chelating bidentate sulfates having a C_s symmetry or less and being identified by absorption bands at 1250, 1150, 1120, and possibly 993 cm^{-1}. The absorption band located at 1033 cm^{-1} can be attributed, following Berger et al.[36] and Bellamy,[37] to the symmetric stretching vibration (ν_1) of sulfite molecules. If we stick to this attribution, we expect the asymmetric stretching mode, ν_3, near 980 cm^{-1}. In that case, there are two possible assignments for the 993 cm^{-1} peak observed in this work: the ν_3 vibration of SO$_3^{2-}$ entities or the ν_1 vibration of SO$_4^{2-}$ as suggested by Babaeva and Tsyganenko.[38] The authors adsorbed SO$_2$ on highly ionic oxides such as CaO and attributed the 990 cm^{-1} band to the symmetric vibration mode, ν_1, of sulfate adsorbed molecules, which becomes IR-active because of a symmetry reduction. Considering the low intensity of the band at 993 cm^{-1} in our work, we rather attribute it to sulfites. Note that adsorption of this type of species suggests some geometric considerations. Free SO$_3^{2-}$ molecules possess a C_{3v} symmetry and are characterized by a nondegenerate vibration mode, ν_1, at 960 cm^{-1} and a doubly degenerate vibration mode, ν_3, near 1010 cm^{-1}. Upon adsorption on a less symmetric site, the latter mode is split into a doublet. In organometallic chemistry,[39] this splitting has been evidenced for bidentate sulfite groups having a C_s symmetry. The ν_1 vibration remains close to 980 cm^{-1} while the ν_3 doublet lies in the 1093−1070 and 1033−1042 cm^{-1} ranges. When the sulfite molecule is linked to the surface by the sulfur atom, the C_{3v} symmetry is preserved, and the stretching frequencies are shifted to higher numbers. On the contrary, when the molecule is bonded to the substrate through one of its oxygen atoms, the symmetry is lowered and the vibration stretching frequencies are shifted to lower values.[40] Note that absorption bands at 960, 1010, and 1070 cm^{-1} have already been attributed to SO$_3^{2-}$ adsorbed ions on metallic surfaces by Lavalley[41] and Mohammed Saad.[42] Frequencies observed in this work are also in agreement with the values observed by Schoonheydt et al. for sulfites on MgO(100) ($\nu_1 = 975$ cm^{-1} and $\nu_3 = 1040$ cm^{-1}).[31] The relatively high frequencies of the stretching vibration frequencies observed in our work ($\nu > 950$ cm^{-1}) suggest adsorbed monodentate sulfites, coordinated to the substrate by the sulfur atom or by both sulfur and oxygen atoms as described by Nyberg et al.[43] Note that our calculation gives a value around 1100 cm^{-1} for the ν_3 stretching mode of free SO^{3-} entities (see Table 1).

To summarize our data and discussion concerning SO$_2$ interaction on a O$_{ads}$−Cu(110) surface, we suggest that the three most important peaks located at 1250, 1150, and 1120 cm^{-1} correspond to the stretching vibrations of an adsorbed bidentate chelated sulfate molecule. This species belongs to a C_s or a C_1 symmetry point group whether the 993 cm^{-1} band is ascribed to this species or not. We attribute the low intense absorption bands at 1060, 1033, and 993 cm^{-1} to monodentate sulfite species adsorbed in lower quantity and with a site symmetry characterized by a point group C_s or C_1 (see Scheme 1). The two weak bands at 853 and 820 cm^{-1} can be ascribed to S−O stretching modes of a second type of sulfites, characterized by

SCHEME 1: Adsorption of Sulfite and Sulfate Species Resulting from the Adsorption of SO$_2$ on the Slightly Oxidized Copper (110) Surface[a]
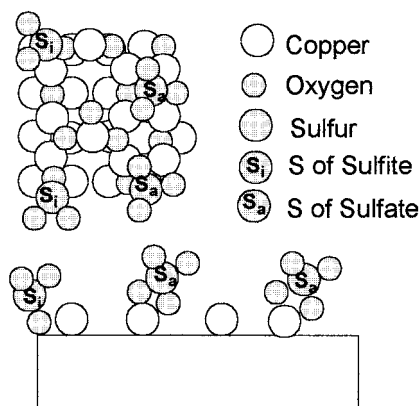
[a] Substrate C(6×2) structure corresponding to our experimental conditions of oxidation is presented.

SCHEME 2: Adsorbed Sulfite Molecules (Si) Resulting from the Adsorption of Sulfur Dioxide on the Cu$_2$O Surface[a]

[a] When molecular oxygen is coadsorbed with SO$_2$, sulfate entities are obtained by oxygen dissociation on cationic sites. The substrate (111) surface is presented.

a weaker electron transfer, formed on another site of the O$_{ads}$—Cu(110) surface.

Two mechanisms can explain the coexistence of sulfate and sulfite species on this surface. The first one is in favor of adsorption of SO$_2$ molecules on a surface site where two oxygen atoms are in a convenient geometry to form the chemisorbed sulfate molecule (static chemisorption process). The formation of sulfite species would conversely result form the adsorption on defect edge points where only one oxygen atom is sterically available for the oxidation reaction. The nucleophilic attack of SO$_2$ by surface oxygens can be understood considering the high local charge borne by the S atom of SO$_2$ species (see Table 1). Following this static mode of interaction, SO$_3^{2-}$ would appear from the beginning of the adsorption kinetics together with SO$_4^{2-}$. The reactivity of the oxygen-covered Cu(110) surface has already been demonstrated in the conversion of CO to CO$_2$.[44] We suggest a second hypothesis that lies on an oxidation process in two steps. First a sulfite molecule is produced in any site of the Cu—O chain and then diffuses to a next oxygen site to be converted into SO$_4^{2-}$- species (dynamic chemisorption process). Considering this process, sulfite species would appear as a final reaction product when Cu—O sites are lacking or are no longer accessible to the intermediate SO$_3^{2-}$. Two arguments lead us to prefer the first mechanism of sulfate formation: (i) SO$_3^{2-}$ and SO$_4^{2-}$- vibration bands grow simultaneously during the experiment, and (ii) diffusion of sulfite species is unlikely to be significant on the surface at room temperature.

Coadsorption of O$_2$ and SO$_2$ on the slightly oxidized surface leads to the IR spectrum presented in Figure 4a, where only absorption bands attributed to the sulfate groups are present. The formation of sulfates, exclusive in that case, is in agreement with the above-suggested criteria, i.e., SO$_2$ encountering two oxygen anions when its interacts with the surface. As a matter of fact, we assume that oxygen molecule from the gas phase will coadsorb with sulfur dioxide, enriching the surface in reactive oxygen in its vicinity.

When SO$_2$ is adsorbed on an oxidized Cu(110) surface (Cu$_2$O from our XPS analysis) (Figure 3b), only three adsorption bands were observed at 1080, 940, and 860—840 cm^{-1} which can be ascribed to sulfite groups. The frequencies are very close to the ones observed by Outka et al.[16] for adsorbed SO$_3$ on the Ag(110) surface. The absorption band located at 940 cm^{-1} can be attributed to the ν_1 vibration mode of sulfites adsorbed in a
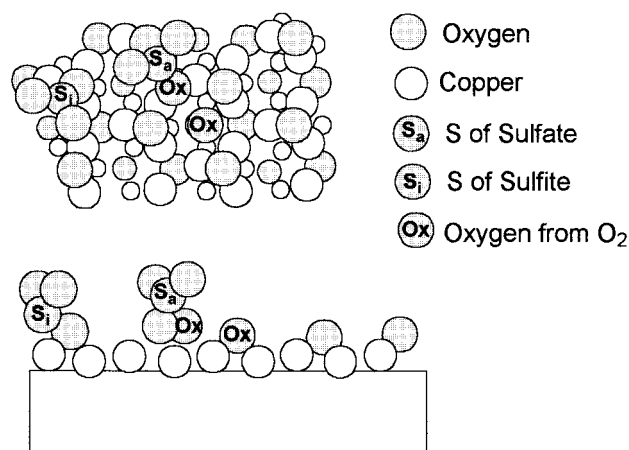
local C_{2v}, C_s, or C_1 geometry with a monodentate coordination (see Scheme 2). The wavenumbers values observed in this work, higher than those measured for monodentate sulfites on Ag(110), reveal a more ionic interfacial bond, in agreement with the ionicity difference of the two substrates. This result is confirmed by the work of Schoonheydt,[33] who also found a pair of absorption bands in the spectral range 925—895 cm^{-1} for sulfite species formed on an ionic substrate, MgO, and coordinated to the surface through its oxygen atom. The formation of monodentate sulfites on Cu$_2$O surface can be considered as a surface acid—base reaction where the oxygen anions of the topmost atomic layer behave as nucleophilic species. Conversely to the case of the O$_{ads}$—Cu(110) surface, no sulfate molecules are formed. We think that this is due to the fact that the surface oxygens are strongly coordinated to the copper atoms in the oxide structure and submitted to a more stabilizing Madelung potential compared to the case of the O$_{ads}$—Cu(110) structure. Consequently, oxygen anions are less reactive and mobile than adsorbed oxygen toward SO$_2$ molecules for an oxidation reaction. The same argument was used by Pacchioni to explain the low reactivity of highly coordinated surface oxygens toward SO$_2$ on MgO(100).[45]

When SO$_2$ is coadsorbed with O$_2$ on the oxidized Cu$_2$O surface (Figure 4b), new features appear in the IR spectrum in addition to two bands very similar to the previous case. Vibration bands at 870—940 cm^{-1} are accordingly ascribed to sulfites. The IR structures at 1250, 1150, and 1130 cm^{-1} are at similar frequencies to the one identified when SO$_2$ is adsorbed on O$_{ads}$—Cu(110) (Figure 3a). These are easily ascribed to sulfates, showing that, though the reactivity of the oxidized surface is reduced in terms of amount of adsorbed complex species, part of these are fully oxidized (S^{6+}) when SO$_2$ is coadsorbed with O$_2$. Let us recall that only sulfites were detected when SO$_2$ was adsorbed alone on the same surface. Promotion of sulfate formation by oxygen in the gas phase has already been noticed on the slightly oxidized surface (Figure 4a). The two main bands at 1250 and 1130 cm^{-1} are close to the ones identified by Kent and Ferraro[30,35] for sulfates on CuO. More difficult is the attribution of the bands at 1030, 1000, and 940 cm^{-1}. Conversely to the case of Figure 3a, their intensities are of the same order of magnitude as the ones of the high-

SCHEME 3:   Model Mechanism Proposed for the Formation of Bridged Bidentate Hydrogenosulfates and the Disappearance of Surface Hydroxyl Groups when SO$_2$ Is Adsorbed on the Hydroxylated Cu$_2$O Surface
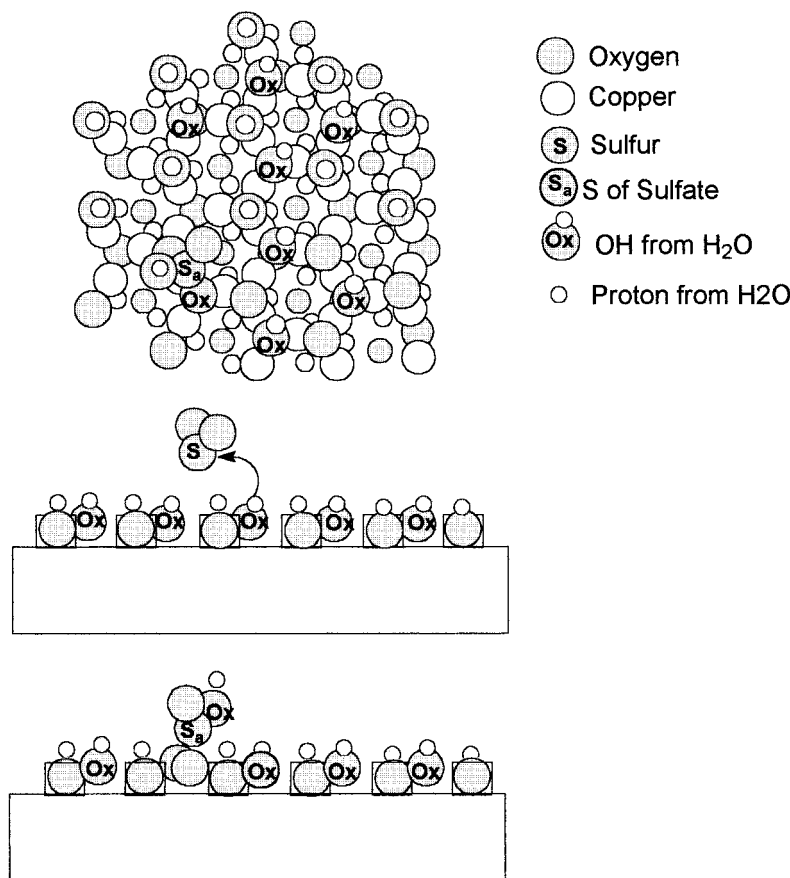
frequency bands. They may belong to chelating sulfates with less than C_{2v} symmetry.[30] Following this hypothesis, the two remaining relatively intense bands at 940 and 870 cm^{-1} can be ascribed to monodentate sulfites.[34] They may also, together with the bands at 940 and 870 cm^{-1}, characterize low symmetry sulfites.[18]

To explain the role of gaseous oxygen in the sulfate formation, we recall that when a monodentate sulfite is adsorbed on Cu$_2$O surface, it is expected that the new chemical bond between SO$_2$ and the surface anion weakens the bond between lattice oxygen and the neighboring cations. As a consequence, the copper cations in the vicinity of adsorbed SO$_3$ will become more reactive toward a nucleophilic species, like the oxygen molecules present in the gas phase. Adsorption of oxygen on those sites gives rise to activated Cu−O or Cu−O$_2$ which can then react with the monodentate SO$_3$ entities adsorbed in the vicinity. This reaction takes place on adsorption sites where oxygen anions and their neighboring cations are accessible by SO$_2$ and O$_2$ molecules. Surface structural heterogeneities thus explain the coexistence of both sulfite and sulfate molecules upon SO$_2$ interaction. Bonnelle et al. also concluded from their results that the nature of the products resulting from SO$_2$ interaction on a Cu$_2$O polycrystalline surface depends on the number of surface defects, oxygen vacancies favoring SO$_2$ dissociation whereas sulfites and sulfates are formed on a stoichiometric oxide.[46]

When SO$_2$ is coadsorbed with H$_2$O on the Cu$_2$O surface (Figure 6a), three vibration bands were identified at 1250, 1035, and 950 cm^{-1}. Their intensity is low, indicating a poor reactivity of the surface. It seems difficult to attribute these weak signals. We only remark that the band at 1250 cm^{-1}

suggests the existence of species having a high order S=O bond, like sulfates as already identified. The absence of stretching vibration near 1300 cm^{-1} shows that neither H$_2$SO$_4$ nor HSO$_3^-$ entities are formed on this basic surface or, if so, are rapidly converted to adsorbed sulfate molecules with elimination of water.[36]

*When SO$_2$ interacts with the highly oxidized surface following hydroxylation (*Figure 3c), the IRRAS spectrum shows multiple bands, in a noisy background, located at 1287, 1130, 1050 cm^{-1} (broad and intense), 965 cm^{-1}, a broad weak band structure at 900−890 cm^{-1}, and 843 cm^{-1}. The appearance of absorption bands in the high-frequency range, >1100 cm^{-1}, again reveals a strong oxidation of SO$_2$. The shift of the S=O vibration band from 1250 to 1287 cm^{-1} can be correlated to an increase of the bond order as explained by Jin et al.[47] This originates from a nucleophilic attack of the sulfur atoms of the SO$_2$ entities by the surface OH groups (see Scheme 3). We then ascribe the band located at 1287 cm^{-1} to the ν_{as} stretching vibration mode of a monohydrogenosulfate HSO$_4^-$. Patel et al.[48] already attributed an absorption band at 1300 cm^{-1} to the adsorption of HSO$_4^-$ on a mixed oxide. Note that the same vibration in the dihydrogenosulfate entity is expected at even higher wavenumber, near 1330 cm^{-1} or above. The other bands observed at 1130, 1050, and 965 cm^{-1} correspond well to an adsorbed ionic sulfate. In light of the preceding experiments, we attribute the three high wavenumbers at 1130, 1050, and 965 cm^{-1} to sulfate species of low symmetry, while the massif at 890−900 cm^{-1}, close to the bands at 940 and 850 cm^{-1} observed on the dry oxidized surface, to sulfites.[18] It is probable that, on a

prehydroxylated surface, there exist an equilibrium between sulfites, sulfates, and hydrogenosulfates as already noticed by Vedrine.[49]

When SO_2 is coadsorbed with O_2 on the hydroxylated Cu_2O surface (Figure 4c), low signals are observed, hardly resolved in a noisy background. Three weak and broad structures are observed at $1300-1280$, $1130-1070$, and 950 cm^{-1} in addition to the negative band at 870 cm^{-1}. A vibration band located at 880 cm^{-1} has been identified by Sueyoshi et al.[50] and by Carley et al.[51] and ascribed to the $\delta(OH)$ vibrational mode of surface hydroxyls. As we also identified the growth of a positive band at $870-880$ cm^{-1} upon water exposure, we expect that hydroxyl groups are either replaced upon $SO_2 + O_2$ interaction or participate in a surface mechanism. Cu_2O, being an ionic oxide like MgO or CaO, exhibits a surface strong basic character; this induces surface hydroxyls relatively weakly adsorbed compared to the same species on a covalent oxide like SiO_2 or P_2O_5. OH$^-$ groups are likely to attack the sulfur atom of the SO_2 molecules while the latest is adsorbed or in close interaction with the surface oxygen anions. Following this hypothesis, we suggest the formation of a bidentate bridging hydrogenosulfate as depicted in Scheme 3. This interpretation is in agreement with the presence of a broad band at $1280-1330$ cm^{-1}. The inhomogeneous broadening of all IR bands can be due to the diversity in the surface sites after hydroxylation. This phenomenon was observed on all spectra taken on hydroxylated surfaces. Note that, compared to the "dry" surface (Figure 4b), hydroxylation considerably reduces the surface reactivity as indicated by the low intensity of the vibration bands.

Note finally that, when SO_2 was adsorbed alone on the hydroxylated surface, the consumption of surface hydroxyls could not detected on the IR spectrum because sulfites were formed, having vibration bands in the $840-890$ cm^{-1} range.

When H_2O is coadsorbed with SO_2 on the hydroxylated Cu_2O surface (Figure 6b), and though signals are also weak, one can infer the formation of complex species, hydrogenosulfates, identified by the structure at 1285 cm^{-1}. Let us note that the spectrum is very similar to the one obtained upon coadsorption of $SO_2 + O_2$ on the same surface, including a negative band at ca. 870 cm^{-1} (Figure 4c). Compared to SO_2 adsorbed alone on the hydroxylated surface (Figure 3c), the main difference lies in the band at 1050 cm^{-1}, dominating when no water is in the gas phase, but almost nonexistent when water is coadsorbed with SO_2 while it is the opposite for the band at $950-920$ cm^{-1}. Both wavenumbers and 1050 cm^{-1} are characteristic of $\nu(S-O)$ stretching bands whose relative intensities are probably a function of the ionic sulfate orientation in the adsorbed state.

4. Conclusion

This paper presents a characterization and a discussion of the species resulting from interaction of SO_2 with a Cu(110) surface oxidized under different conditions. Depending on the surface chemical state, interaction of SO_2 with the surface leads to different types and geometries of sulfur-containing species.

On the Cu(110) surface covered with an adlayer of oxygen or on the oxidized Cu(110) surface, SO_2 binds to the surface by interaction of its S atom with the nucleophilic surface oxygens, forming SO_x compounds, $x > 2$. Sulfates are obtained on a slightly oxygen-covered surface whereas only sulfites are observed on a Cu_2O surface, showing a restricted reactivity of oxygen anions when embedded in an oxide lattice. These adsorbed species are influenced by coadsorption of SO_2 with another oxidant O_2 or H_2O, resulting in a promotion of sulfates

to the detriment of sulfites. Attention was paid to a prehydroxylated surface on which hydrogenosulfate species are formed by reaction with surface OH groups. This reaction process is linked to the basic properties of the Cu_2O oxide.

The IRRAS technique allows to in situ study the reactivity of sulfur dioxide with a low area well-defined surface. A better knowledge of the species resulting from interaction of SO_2 with a metallic or oxidic surface is essential for the understanding of its role upon the mechanism of catalytic reactions.

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