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論文内容の要旨

Photo- and thermal reactions of atomic oxygen on Ag(110)

Silver is known as the only metal to catalyze the reaction for producing ethylene oxide from ethylene economically. It is widely accepted that chemisorbed atomic oxygen on silver surfaces is responsible for the partial oxidation of the hydrocarbon. Therefore, numerous studies have been conducted for clarifying the adsorption states of atomic oxygen and the oxidation reactions of hydrocarbons on Ag surfaces, particularly on a Ag(110) surface. Several unique characteristics of atomic oxygen adsorption on Ag(110) have been reported. For example, oxygen restructures the Ag(110) surface in such a way that one-dimensional Ag-O chains grow along the [001] direction. As the coverage of oxygen increases, the structure of the chains changes from $p(7\times 1)$ to eventually $p(2\times 1)$.

We studied on the photo and thermal reactions on atomic oxygen on Ag(110). Although there are many reports on the reactions of atomic oxygen on Ag(110), there are only a few reports describing the effects of surface additives. Therefore, this thesis concentrates on the following two themes: 1) The photoelimination reaction of oxygen at a Ag(110) surface influenced by surface carbon species, and 2) Methyl chemistry on halogen-free Ag(110)- $p(n\times 1)$ -O surfaces. The both reactions are strongly affected by surface additive atoms.

The photoelimination of atomic oxygen occurs only if carbon species exist at the Ag(110) surface, and the atomic oxygen desorbs as CO_2 . It is quite unusual that strongly chemisorbed oxygen is removed photochemically from a metal surface. We clarified the mechanisms of the photoreaction.

The reactions of methyl group with atomic oxygen are also affected by surface additives. So far, most of the chemistry of alkyl groups is examined on halogen-contaminated Ag surfaces, because alkyl groups used in the experiments are produced by photo- and thermal dissociation of alkylhalides. On such surfaces, the reactions of alkyl group might be affected by the co-adsorbed halogen atoms. To clarify the influences of halogens, we produced the methyl group by the electron bombardment of methane adsorbed on halogen-free Ag(110) surfaces. It has been reported that atomic oxygen on a Ag(110) surface acts as a nucleophile for the alkyl groups. Alcohols and ethers are produced from the alkyl group and the atomic oxygen adsorbed on Ag(110). However, we found that ethylene is selectively from methyl group and atomic oxygen on the halogen-free Ag(110) surfaces. Atomic oxygen can act as a Brønsted base for methyl group on the halogen-free Ag(110) surfaces.

I describe in this thesis the reaction mechanisms of the photo and thermal reactions of atomic oxygen on Ag(110) and the roles of surface additives in these reactions.

1) Photoinduced elimination of oxygen at Ag(110)- $p(2\times 1)$ -O: The role of surface carbon species.

It has been reported that atomic oxygen adsorbed on Ag(110) is eliminated by UV irradiation. We found that the reaction takes place only if carbon exists at the surface. Furthermore, the

reaction yield strongly depends on the bonding scheme of the surface carbon. We studied the photo-elimination reaction focusing on the following questions: What is the role of the carbon species on the reaction? What type of electronic excitation associated with UV irradiation is responsible for the photoreaction? Where do oxygen atoms in the Ag-O chains go?

To clarify how the photoelimination reaction depends on the carbon species, we examined photochemical activities at Ag(110)-p(2×1)-O in three different conditions: a clean surface, a surface covered with carbidic carbon and a surface with graphitic carbon. The coverage and the bonding scheme of the surface carbon species were characterized by Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) of CO₂ after oxygen adsorption.

Each Ag(110) surface was saturated by atomic oxygen of 0.5 ML (1 ML = 8.4×10^{14} cm⁻²). The coverage of atomic oxygen on Ag(110) was determined by x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Then, the surface was irradiated by a Xe arc lamp through the band-pass filter at 320 nm. Even after the UV irradiation for 60 min, the oxygen on clean and graphitic carbon covered surfaces does not decrease considerably by the UV irradiation. In contrast, the oxygen coverage on the surface covered with carbidic carbon definitely decreases. The surface temperature was raised by 10 K at most and such a small temperature rise is not enough to eliminate oxygen atoms thermally. Thus, the depletion of the oxygen coverage originates in nonthermal excitation induced by the UV photoirradiation. Note that the photochemical activity strongly depends on the surface condition. Only the carbidic carbon is effective for the photoelimination reaction.

Two photoexcitation mechanisms are considered for the photoreaction as follows: (1) direct absorption of light by adsorbates, (2) indirect excitation via absorption of light by substrates (substrate-mediated excitation). To obtain information on the excitation mechanism, the wavelength dependence of the effective photochemical cross section was measured for the surface covered with carbidic carbon. The wavelength of the incident light ranges from 410 nm to 193 nm. The cross section increases with decreasing the wavelength of the incident light and steeply rises at around 350 nm. Compared with the wavelength dependence predicted from that of absorbance of the substrate, the photoexcitation mechanism of the photoelimination reaction was confirmed to be the substrate-mediated excitation.

The next important question is where the oxygen atoms go out of the surface region. To clarify this point, photodesorbed species were measured by using a pulsed laser at $\lambda = 193$ nm. The laser was fired at $t = 0$ and desorbed species were detected by a mass spectrometer. Only CO₂ desorption was observed during the UV irradiation. Surprisingly, O₂, O, or CO was not detected within the detection limit.

In summary, the reaction and excitation mechanisms of the photoelimination reaction of atomic oxygen at Ag(110)-(2×1)-O are examined. Ag-O bonds in Ag-O chains are activated by hot electrons produced by the absorption of UV light by the substrate. Only if carbidic carbon exists near the activated oxygen atom, the oxygen atom reacts with the carbidic carbon and then desorbs as CO₂. In contrast, the reaction does not occur on the clean Ag(110) surface and the surface covered with graphitic carbon.

2) Methyl chemistry on halogen-free Ag(110): influence of co-adsorbed atomic oxygen

The influence of atomic oxygen on the adsorption state and the electron induced reactions of methane on Ag(110) surfaces were studied with TPD and infrared reflection absorption spectroscopy (IRAS). To clarify the effect of co-adsorbed oxygen, the reactions of methane on a clean Ag(110) surface were examined at first. Methane adsorbs on the Ag(110) surface keeping T_d symmetry and simply desorbs at around 60 K without dissociation. After electron bombardment (50 eV), methane is dissociated to a methyl group. When the methyl coverage is low, the CH stretching modes of the methyl group were observed at 2850 cm^{-1} and 2760 cm^{-1} by IRAS measurements. In contrast, only one peak was observed at 2880 cm^{-1} when the coverage is high. This indicates that the adsorption states of the methyl group change depending on its coverage. The methyl group adsorbs on the Ag(110) surface with C_s symmetry at low coverage and adsorbs with C_{3v} symmetry with the three fold axis normal to the surface.

The reactions of the methyl group were examined varying its coverage. When the methyl coverage is low, hydrogen, methane and ethane are desorbed. When the surface temperature increases, the methyl group partly desorbs as methane at 240 K. Since the desorption of hydrogen is also observed at the same temperature, the desorption of methane at this temperature is assigned to the recombinative desorption of methyl group and atomic hydrogen. By further heating of the surface, remained methyl groups desorb as ethane and methane at around 330 K and 340 K, respectively. The desorption of ethane at the temperature is due to C-C coupling of methyl groups. Note that methane desorbs at 340 K although hydrogen created by the electron bombardment does not remain on the surface at this temperature. This indicates that a methyl group partly dissociates to a methylene group and a hydrogen atom. Then the hydrogen reacts with a methyl group to desorb as methane.

At high coverage, the reaction of methyl groups is more complicated. Except for methane and ethane, various hydrocarbon species are also formed. A new ethane peak at around 100 K was observed. Ethylene and propane desorption peaks were also observed 130 K and 125 K, respectively. This indicates that molecular ethane, ethylene and propane are produced by the electron bombardment. At around 170 K, methyl groups with C_{3v} symmetry partly desorb as ethane via the C-C coupling. The methyl groups remained on the surface change their adsorption symmetry from C_{3v} to C_s due to the reduction of methyl coverage. Over 200 K, the reactions of methyl group are same as those occur at the low coverage of methyl group.

The influences of atomic oxygen on the methyl chemistry on Ag(110)-p($n\times 1$)-O ($n = 2-4$) surfaces are examined. In contrast the clean surface, only the desorption of ethylene was observed at around 300 K at the coverage less than 0.33 ML ((4×1), (3×1)-O); ethane production is negligible. The desorption temperature of ethylene on the (3×1)-O surface is slightly higher than that of (4×1)-O. On the (2×1)-O surface, both ethane and ethylene were not observed.

To clarify the reaction mechanism, IRAS measurements were performed. On the (4×1)-O surface, the peak at 2880 cm^{-1} was observed after the electron bombardment. The peak is assigned to the CH symmetric stretching mode of methyl adsorbed with C_{3v} symmetry as in the case of the clean surface. When the surface was heated to 200 K, the 2880 cm^{-1} peak disappears and new

peaks at 2850 cm^{-1} and 2760 cm^{-1} grow. After the surface is heated to 300 K, these two peaks disappear simultaneously. On the (3×1) -O surface, the results are similar to that of (4×1) -O surface at the lower temperature region. However, when the surface was heated to 250K, the 2880 cm^{-1} peak disappears and 2890 and 2820 cm^{-1} peaks become apparent. These frequencies are higher than those observed on the (4×1) -O surface. On the (2×1) -O surface, no hydrocarbon species were detected by TPD and IRAS after the electron bombardment except for unreacted methane.

In summary, methyl groups are produced by the electron bombardment on both clean and oxygen-covered surfaces. On the clean Ag(110) surface, the methyl groups react with each other and desorb as ethane. In contrast, on the oxygen-covered surfaces, ethylene is produced exclusively owing to dehydrogenation by co-adsorbed oxygen atoms.

論文の審査結果の要旨

出願された博士論文は表面化学に関するもので、Ag(1 1 0)表面における炭素や酸素といった表面修飾物に注目し、これらが光反応および熱反応に及ぼす影響を実験的に調べた結果をまとめたものである。次の2つの中心的な主題について詳しく述べられている。

(1) 酸化された Ag(1 1 0)表面上に形成された銀酸素列における光誘起酸素消失反応。

従来の表面光化学では金属上に吸着した簡単な原子・分子に対象が限られていたが、ここでは銀と酸素原子が交互に並んだいわば擬一次元化合物とでも言うべき物質が紫外光照射によって消失するというきわめて珍しい光反応について研究がなされた。特筆すべきことは、表面近傍に不純物としてある炭素原子がこの反応に重要な役割を果たしていることを見出した点である。すなわち、清浄な銀表面によく制御された条件でカーバイド的な炭素原子、あるいは、グラファイト的な炭素原子を少量形成し、これらがこの光反応効率にどのように影響するかを低速電子線回折、X線光電子分光、オージェ電子分光、昇温脱離などの様々な手段を駆使して定量的に調べた。その結果、カーバイド的な炭素原子が表面に存在するときのみ実効的に光反応が誘起されることを明らかにした。また、励起のメカニズムとしては基盤による光吸収が支配的であり、これによって励起された酸素原子はカーバイド的な炭素と反応することにより二酸化炭素として真空中に脱離することなどを実証し、これらの実験事実を矛盾無く説明できる光反応機構モデルを提出した。通常、ここで議論された炭素原子は金属表面における不純物として取り扱われ、これが反応に及ぼす影響はよく研究されていない。しかし、実用触媒にはこのような炭素原子をはじめとする種々の不純物、あるいは、表面修飾物が存在するため、これらの反応への影響を明らかにすることはきわめて重要である。本論文ではこの問題を真っ向から捉え、炭素原子の表面での存在様式を制御することによりこれを規定し、光反応における役割を明確にした点が今までの表面光反応研究には無かった独創的な点であると考えられる。

(2) Ag(1 1 0)表面におけるメチル基の反応とこれに及ぼす酸素原子の影響。

メチル基は炭化水素の触媒反応においてきわめて重要な反応中間体であるが、銀表面におけるその吸着状態や反応性についてはあまり研究されてこなかった。本論文では、メタンを電子衝撃することにより Ag(1 1 0)表面上にメチル基を生成し、その吸着状態および反応を反射赤外吸収分光や昇温脱離によって調べた。振動分光の結果から、メチル基は低被覆率の場合にその分子軸を表面法線方向から傾けて吸着していると推定し、この構造が熱反応におけるエタンやメタン生成にどのように関与しているかについて詳しく議論をした。この研究における最も注目すべき点は、酸素原子を表面修飾物として用いることによりメチル基の反応がどのように変化するかを研究した点である。すなわち、清浄表面で C-C 結合形成の結果生成されるエタンが酸素原子の表面導入によりほとんどまったく生成されなくなる代わりにエチレンのみが生成されるというきわめて高い生成物選択性を見出している。また、酸素飽和吸着表面ではメチル基自体が表面に安定に存在しないことも明らかにした。この選択性に表面酸素がどの

ように関与しているかについて詳しい議論を展開した。

本論文は、上記のように新規性、意外性の高いいくつかの現象を発見しており、その現象の解析についても詳しい議論がなされている。したがって、そのオリジナリティは高く、博士論文として十分な質と量を備えたものと考えられ審査に合格ということで審査員の意見が一致した。