

氏 名 渡 邊 一 雄

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学 位 論 文 題 目 Laser-induced reactions of methane adsorbed on
transition metal surfaces

論 文 審 査 委 員 主 査 教 授 西 信之
教 授 宇理須 恆雄
教 授 松本 吉泰
助 教 授 鎌田 雅夫
助 教 授 鈴木 俊法
教 授 堂免 一成（東京工業大学）

The C-H bond activation of methane has been one of the most important processes in the conversion of methane into useful chemical reagents. Although thermal activation with various kinds of catalysts has been extensively studied, there still remain formidable problems in efficiency and selectivity. In addition to thermal methods, the other way to tackle these problems is to activate methane photochemically. We have found for the first time that methane weakly adsorbed on Pt(111) and Pd(111) is efficiently dissociated into hydrogen and methyl, or desorbed as methane or methyl radical by the irradiation with 6.4-eV photons, in spite of the fact that the excitation energy for the photodissociation of gaseous methane is ~ 10 eV. This surprising result leads us to the following questions:

- (1) Excitation mechanisms of the photochemistry of methane on these metal surfaces
- (2) Interactions between methane and the metal surfaces
- (3) Photoreaction dynamics of methane

To elucidate them, the detailed study has been performed using an excimer laser as a light source and various surface analytical methods: temperature programmed desorption (TPD), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), angle-resolved time-of-flight (TOF) measurements, and work function change measurements.

Furthermore, the photodissociation of methane with 6.4-eV photons allows us to investigate the dynamics of the associative desorption of methane between hydrogen and methyl adsorbates as well as its molecular desorption from a clean Pt(111) surface by using laser induced thermal desorption (LITD). This study provides us with information about the mechanism of the dissociative adsorption, which is one of the most important steps in the thermal activation of methane with catalysts.

The present thesis mainly consists of three parts: (1) the photochemistry of methane on Pt(111), (2) the photochemistry of methane on Pd(111), and (3) the mechanism of the associative desorption and the molecular desorption of methane from Pt(111).

(1) Photochemistry on Pt(111) (Chapter 3)

Since methane is isoelectronic to neon, its interaction with solid surfaces is known to be weak. Actually, the interaction between methane and Pt(111) is found to be weak. The desorption peak temperature of methane in the first monolayer is 72 K, and the activation energy for thermal desorption is estimated to be 0.23 eV, which falls in the range of physisorption. No LEED pattern induced by methane adsorption is observed. The change

of work function from the clean Pt(111) surface by methane adsorption is relatively large (~ 0.5 eV). A simple perturbation theory suggests that there is small ($\sim 3\%$) contribution of the excited charge transfer state.

The photodissociation of methane with a 6.4-eV photon is unambiguously evidenced by appearance of associative desorption peak between hydrogen and methyl adsorbates at 260 K in the TPD results of the methane from Pt(111) after irradiation with 6.4-eV photons. Photodesorption of methane and methyl is studied by the TOF measurements. There are three velocity components in the TOF distribution of methane with mean translational energies ($\langle E_t \rangle$) of 0.53 eV, 0.26 eV, and 0.06 eV. In contrast, there is only a single velocity component in the TOF of methyl with $\langle E_t \rangle = 0.27$ eV. The first two velocity components of methane are sharply peaked at the surface normal. The desorption mechanism of the fastest component is identified as photoinduced associative desorption between H^* and $CH_3(a)$ using the isotope labeling method¹. It is found that the photochemistry of methane is quenched by the accumulation of methyl adsorbates on the surface.

No methane photochemistry is induced by 5.0-eV photon irradiation in contrast to 6.4-eV photon. The power dependence of the photoreaction cross section at 6.4 eV clearly shows that the electronic transition of methane occurs via a one-photon process. No photochemistry occurs on a xenon precovered Pt(111) surface, i.e., the direct contact between methane and Pt(111) surface is essential for the photoexcitation. The measurement of polarization dependence of the photoreaction cross section clearly shows that a direct electronic transition within the adsorbate-substrate complex is involved in the photoexcitation.

Based on the above experimental results and recent ab initio calculations, the photoexcitation mechanism is discussed in detail. It is proposed that the excitation from the adsorbate-localized orbital to the excited state of methane which is significantly mixed with substrate electronic states plays a major role in the photochemistry of methane on Pt(111). In addition, the mechanism of the quenching of photochemistry by coadsorbates is also discussed.

The dynamics of (1) the direct desorption of methane molecule, and (2) the desorption of methyl radical are discussed in terms of the MGR and Antoniewicz models, and the “vibrational activation” model proposed in this thesis. The latter model assumes that desorption is induced by the conversion from vibrational energy to translational

¹ H^* and $CH_3(a)$ denote an energetic hydrogen atom produced by photodissociation of CH_4 , and CH_3 adsorbate on the surface, respectively.

energy (V - T conversion) in the electronic ground state potential, based on the analogy from the gas phase result - rapid internal conversion of the electronic excited state to high vibrational levels of the ground state takes place. The desorption dynamics for CH_3 is also discussed in terms of the strong quenching model and the vibrational activation model. Although the detailed information of the potential energy surfaces relevant to these reactions is necessary for the quantitative discussion, the applicability of the above models are examined qualitatively by the comparison between the predictions of the models and the experimentally observed translational energy distributions.

Lastly, the photochemistry of CH_4 on D-covered Pt(111) surfaces is studied. The effects of the hydrogen coadsorption on the adsorption state and the photochemistry of methane are described. The D atom coadsorption reduces the photoreaction cross section but does not quench the photoexcitation completely. This indicates that the quenching of methane photochemistry after prolonged irradiation with 6.4-eV photons is mainly due to the poisoning effect by methyl adsorbates. In addition, the photoinduced associative reaction between CH_3^* and D(a) to form $\text{CH}_3\text{D(a)}$ is observed.

(2) Photochemistry on Pd(111) (Chapter 4)

The photochemistry of methane adsorbed on Pd(111) is studied in order to clarify how the electronic structure of metal surface affects the adsorption state, photoexcitation mechanism, and photochemistry of methane. Although Pd(111) and Pt(111) surfaces share the same surface geometry with very similar lattice constants, the level of sp-derived surface state is significantly different between the two surfaces. It is 0.2 eV below the Fermi level at Pt(111), whereas 1.3 eV above at Pd(111); the surface state is occupied at Pt(111) while unoccupied at Pd(111). Thus, methane is expected to interact more strongly with Pd(111) than Pt(111) because repulsion by electrons in the surface state is lacking on the former surface.

As is expected, TPD results shows that methane adsorbs more strongly on Pd(111) than Pt(111). The LEED super-structures of methane observed on Pd(111) but absent on Pt(111) also suggest the stronger interaction of methane with the former than latter. Furthermore, the larger (~50%) photoreaction cross section on Pd(111) than Pt(111) is consistent with the model of the hybridization between methane excited states and empty states of the metal substrate, by which the larger photoreaction cross section is interpreted as the larger extent of hybridization due to the stronger interaction. The relative yield ratio of the photoproducts is also different between the two surfaces. On Pt(111), the dissociative adsorption channel is dominant (~80%), while on Pd(111) the desorption

channel is major (~60%) of the total reacted methane. These effects can be attributable to the difference in their surface electronic structures.

In the last section, the photodesorption dynamics is further studied by the extensive measurements of angle-resolved TOF distributions. The difference in the surface electronic structure also influences the translational energy distributions of the photodesorbed species. The mean translational energy $\langle E_t \rangle = \sim 0.64$ eV for the direct molecular desorption. $\langle E_t \rangle = 0.26$ eV for the photoinduced associative desorption between H* and CH₃(a), whereas $\langle E_t \rangle = 0.53$ eV for Pt(111). $\langle E_t \rangle = 0.034$ eV for desorption induced by collision of photoexcited species with neighboring adsorbates. The activation barrier height of the thermal associative desorption between H(a) and CH₃(a) is also low (~0.26 eV) on Pd(111) than Pt(111) (~0.56 eV). This suggests that the $\langle E_t \rangle$ of the photoinduced associatively desorbed methane correlates with the activation barrier height for the thermal associative desorption. The lowering of the barrier height for the associative desorption results in the lowering of the barrier height for the reverse process, i.e., the dissociative adsorption according to the principle of detailed balance.

The coverage dependence of desorption rate and the angular distribution shows that methane desorption is influenced by the collision with surrounding adsorbates. The direct molecular desorption is depressed and is very sharply peaked to the surface normal when methane coverage is high. The slowest component is peaked ~6° from the surface normal which is attributable to the collision with energetic species. These results are discussed in terms of adsorbate-adsorbate interactions. The effects of the hydrogen coadsorption are also studied.

(3) Mechanism for Associative Desorption and Molecular Desorption of Methane on Pt(111) (Chapter 5)

Since dissociative adsorption of methane onto metal catalysts is the primary step of various reactions such as conversion into larger hydrocarbons, the understanding of its mechanism is important both practically and basically. One of the approaches to this goal is to study the reverse process, i.e., the associative desorption of methane from hydrogen and methyl adsorbates. The photodissociation of methane on Pt(111) described in the previous chapter have enabled the facile preparation of the surface covered with only hydrogen and methyl. Using this method, we study the mechanism of molecular and associative thermal desorption of methane from Pt(111) by LITD. The 532-nm laser pulses (≤ 130 mJ/cm²) from a frequency-doubled Nd:YAG laser are used as a light source for

thermal heating of the surface. The translational energy distribution of methane is measured by the TOF method.

The LITD of physisorbed methane is close to the ordinary thermal desorption: its angular distribution is broad ($\cos^{2.5}\theta_{des}$, θ_{des} : desorption angle) and a translational energy distribution is fitted by a Maxwell-Boltzmann function with $\langle E_t \rangle$ equal to the maximum surface temperature (~ 120 K) transiently attained under the laser irradiation. In contrast, the associative desorption of methane has a very sharp angular distribution ($\cos^{31}\theta_{des}$) and a translational energy distribution fitted by a shifted M.-B. function with $\langle E_t \rangle/2k=2500$ K, which is much higher than the maximum surface temperature (~ 400 K).

The above data are used to examine the statistical (RRKM) model developed by Ukraintsev and Harrison (UH) that is able to explain qualitatively the sticking coefficient data of the dissociative adsorption on Pt(111) obtained by methane molecular beam experiments of Luntz and coworkers. By using the fitting parameters obtained by UH from the sticking coefficient data, we perform an RRKM calculations for the molecular and associative desorption based on the UH model. It is found that the model is able to qualitatively account for our experimental results of the molecular desorption, however, it fails completely to predict those of the associative desorption. This discrepancy is attributed to the essential limitation of the statistical theory in predicting the partitioning of the available energy beyond the transition state with a large exit barrier.

論文の審査結果の要旨

本論文は遷移金属である白金およびパラジウム表面に物理吸着したメタン分子が、6.4 eV の光励起によってメチル基と水素原子に解離吸着し、これが昇温あるいはレーザー照射によって再結合して脱離することを発見した画期的な内容を含んでおり、導入から結論に至る6章226頁のすべてがほぼ完璧な英語で書かれている。内容の主要部分は、本人が第一著者の論文として、Physical Review Letters 及び、Surface Science 誌に公表されている。関連の結果も共同研究として Journal of Chemical Physics 誌をはじめとする主要国際誌3誌に発表されており、論文博士の申請者として十分な研究歴を持っていると審査員全員が判断した。

化学的には不活性な分子であるメタンは、白金の(111)面においてでさえ弱い物理吸着しか示さず、70K以上では脱離してしまう。しかし申請者は、70 K以下の温度で吸着したメタン分子に193nm光を照射するとC-H結合が切断され、メチル基と水素原子に解離した状態で吸着すること、及び、260Kまで昇温するとこれらが再結合してメタンとして脱離することを見出した。また、飛行時間スペクトルの測定を行い、この解離吸着種の再結合によって生成脱離するメタンのエネルギー分布が、物理吸着状態にあるメタンのそれとは大きく異なっていることを見出した。このような解離吸着が起こる理由を、白金の6s、6p原子軌道とメタンの3sリユドベリ軌道との混成によるためと説明し、更に、再結合光脱離の過程が、MGRモデルやAntoniewiczモデルでは説明できず、なんらかの振動励起過程を取り込んだ新しい脱離過程であることを示唆した。

パラジウムの(111)表面の状態は白金とは異なり、非占有sp由来表面準位を含んでいるため、メタン分子がより強くパラジウムの表面原子と相互作用を行うと予想される。実際、光反応収量は1.5倍に増加し、メタンの励起電子配置が金属表面の空軌道を大きく取り込んだ混成状態になっていることが示唆された。この電子状態の違いのために、パラジウム系においては反応過程の60%がメタン分子の脱離過程であり、白金表面では約80%が解離吸着に留まっていたのとは大きな違いであった。解離吸着した水素原子とメチル基の再結合活性化エネルギーは0.26eVで、白金表面での値の半分以下に低下していることが示された。また、このような表面反応は、表面へのメタン分子の被覆率にも依存し、被覆率が高くなると高エネルギー成分が表面での衝突によって減速し、表面と垂直な軸から6°の方向に鋭い分布をもった低エネルギー成分が出現することを明らかにした。

解離吸着について更に詳しい情報を得るために、可視レーザー光による熱脱離実験を行い、解離吸着種の再結合脱離機構を調べた。

本研究は、精密さを要する高度の実験手法を用いて、メタン分子の解離吸着、再結合、脱離の過程を詳細に、しかも可能な限り多くの手段によって追求・証明しており、金属表面における化学反応研究の分野に大きな足跡を残すものである。全審査委員が、本論文は論文博士の学位論文として十分なレベルにあるとの認識で一致した。

さらに、口述試験では学位論文の内容に関して本人が約1時間発表し、続いて各審査委員からの質問とそれに基づいた議論を2時間行った。質問に対する応答は大変的確であり、十分な学問的背景があることを感じさせた。解離吸着が起こる理由、物理吸着種と再結合脱離種の運動エネルギー分布の違いの理由、解離機構が従来理論で説明できない理由、解離吸着種の再結合脱離における振動励起機構の詳しい説明などについて突っ込んだ質問がなされたが、納得のゆく説明が返ってきた。論文の英語の質の高さから、英語力も相当に高いと判断した。

また公開発表会においても質疑応答は満足なものであったので審査委員会は全員一致で合格と判断した。