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Electron spectroscopic study of adsorption of methane on titanium dioxide surfaces *

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The chemisorption of methane has been investigated on titanium surface, the polycrystalline TiO_2 film surface and the $TiO_2(100)$ surface with and without defects (oxygen vacancies).

It has been found that the activation of C-H bonds depends on surface oxygen species. The different adsorption behavior between methane adsorption and methane-oxygen coadsorption, together with the different adsorption results on the $TiO_2(100)$ surface with and without defects, shows that the electrophilic oxygen species on the surface are active species for the activation of C-H bonds of methane. The temperature dependence of adlayer provides possible evidence for electrophilic oxygen species reacting with CH_x on the surface.

Keywords: Chemisorption of methane; titanium dioxide; oxygen vacancy; photoelectron spectroscopy; adcarbon species; adoxygen species

1. Introduction

Following the pioneering work of Keller and Bhasin [1], much interest has focused on the use of oxides as catalysts for the oxidative coupling of methane. However, very few studies have been made of the interaction of methane with oxides. Recently, several studies of interaction of methane with clean nickel surfaces have been reported [2–4]. It was found [2] that the chemisorption of methane on the nickel surface was very strong, and that oxygen adatoms can promote the dissociative chemisorption of methane on Ni(100) and Ni(111) surfaces. The results of Ullmann et al. [3,4] showed no enhancement of oxygen adatoms to the activation of methane. Pure TiO_2 and Na-doped TiO_2 showed high activity of oxidative coupling methane [5,6]. The difference in activity between anatase TiO_2 and rutile TiO_2 [6] gave evidence for the dependence of the reaction on the structure of catalysts. The decomposition of methanol and

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ethanol on the $TiO_2(100)$ surface via CH_3O species has been proved by XPS and UPS [7], and the conversion of CH_3O into CH_x was also observed by Au and coworkers using XPS [7]. These results showed that CH_x may exist on the TiO_2 surface under the UHV. We expected that the adsorption of methane would give CH_x or CH_xO etc. species on TiO_2 surfaces. In the present work, the interaction of methane with titanium and titanium dioxide has been studied at room temperature using XPS to analyze the carbon and oxygen species present on these surfaces.

2. Experimental

1. All data were recorded using a VG ESCA LAB MK II (U.K.) using a Mg Kα X-ray source.

2. Clean Ti metal film and TiO_2 surface: The pure titanium foil was first treated with diluted HNO_3, and cleaned by cycles of argon-ion bombardment (4 kV, 50UA) and annealing at 700 K. Sometimes the sample was exposed to dioxygen at 700 K in order to facilitate the removal of carbon contamination from the bulk of the foil. Generally, the sample was cleaned until the oxygen and carbon could not be detected by XPS. The polycrystalline TiO_2 film was obtained by exposing the clean titanium foil at 700 K to the dioxygen gas, which was treated through a liquid nitrogen cooled trap. The single crystal $TiO_2(100)$ was cleaned by cycles of argon-ion sputtering and annealing at 700 K in situ. After such repeated treatments, more oxygen vacancies were found to exist on the $TiO_2(100)$ surface.

3. Adsorption on the surface: The adsorption process was carried out by exposing the surface to gas through a gas-introduction needle valve to leak gas for adsorption into the preparation chamber at the desired temperature and pressure. The gas to be adsorbed was purified by passing through a liquid-nitrogen cold trap. The exposure of surface to the gas was controlled by time of exposure and gas pressure and registered in unit of Langmuir.

4. Calculation of the concentration of surface species: Determination of the concentration of surface species is based on the Roberts-Carley equation [8]:

$$\frac{n_1}{n_2} = \frac{y_1}{y_2} \cdot \frac{\mu_2}{\mu_1} \cdot \frac{(E_1)^{0.25}}{(E_2)^{0.25}},$$

where
n_i: the concentration of surface species,
y_i: the amount of photoelectron count,
μ_i: photoelectron cross section,
E_i: electron kinetic energy.

3. Results and discussion

ADSORPTION OF METHANE AND COADSORPTION OF METHANE AND OXYGEN ON THE POLYCRYSTALLINE TITANIUM SURFACE

On titanium surfaces, the adsorption of methane results in the formation of a small amount of adcarbon with C1s binding energy (B.E.) of 282.0 eV, which was assigned to TiC, indicating strong interaction between methane and titanium. Two kinds of adcarbon species on the titanium surfaces were formed under the condition of coadsorption of methane and oxygen, as shown in fig. 1. One with C1s B.E. of 284.6 eV is assigned to CH_x, and the other with C1s B.E. of 282.0 eV to TiC. The corresponding adoxygen species have binding energy of 530.5 eV and 531.7 eV, and were assigned to O^{2-} and O^-, respectively.

There is not much change for both C1s and O1s spectra by heating the adlayer to 500 K, suggesting that the adsorbed species are stable at 500 K, as shown in fig. 2. However, after heating the adlayer at 700 K for 10 minutes the concentration of CH_x decreased sharply and that of the TiC decreased a little, and the concentration of both O^{2-} and O^- species decreased. The results suggested that surface reaction between CH_x and adoxygen or desorption and dissolution of hydrogen and oxygen might take place.

ADSORPTION OF METHANE AND METHANE-DIOXYGEN MIXTURE ON THE POLYCRYSTALLINE TITANIUM DIOXIDE FILM SURFACE

The polycrystalline titanium foil was oxidized by exposing it to dioxygen at 700 K. The $Ti3p_{3/2}$ spectrum from the clean metal surface has a binding energy

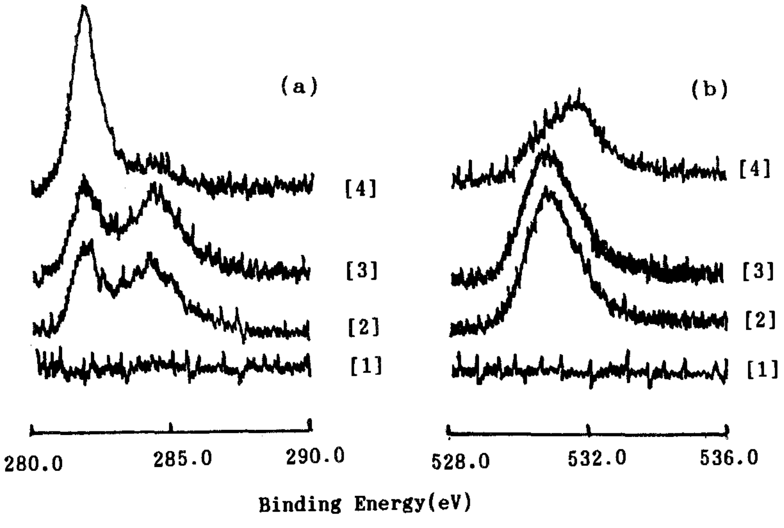

Fig. 1. (a) C1s and (b) O1s spectra for adsorption of methane and dioxygen mixture at 300 K and heated to 500 K and 700 K on titanium surface. [1] Clean, [2] 600 L, [3] 500 K, [4] 700 K.

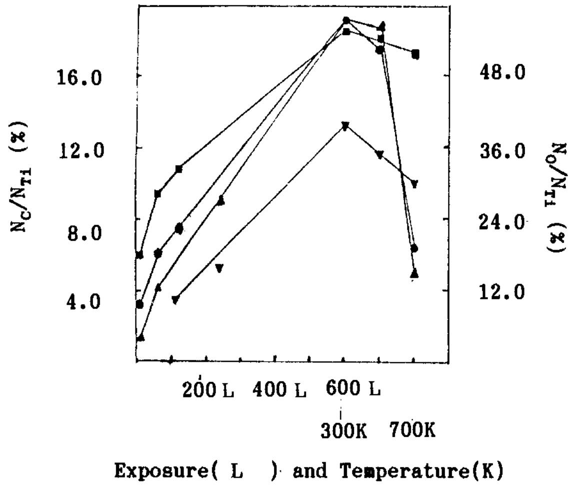

Fig. 2. Concentration of the various surface species as a function of exposure and temperature in the titanium-methane-dioxygen system. ● CH_x, ■ C(a), ▲ O^{2-}, ▼ O^-.

of 453.9 eV [7], the peak shifts to 458.9 eV with no evidence for any Ti^0, Ti^{2+}, or Ti^{3+} species after oxidation. O1s peak has a binding energy of 530.3 eV.

The results of adsorption of methane and methane-dioxygen mixture on the polycrystalline TiO_2 film surfaces are shown in fig. 3. Two adcarbon species were observed. One with C1s B.E. of 284.6 eV was assigned to CH_x, and the other with C1s B.E. of 286.3 eV to CH_xO on the surface [7]. Larger amount of adcarbon species was obtained under the condition of coadsorption of methane and dioxygen under the same exposure as that of adsorption of methane,

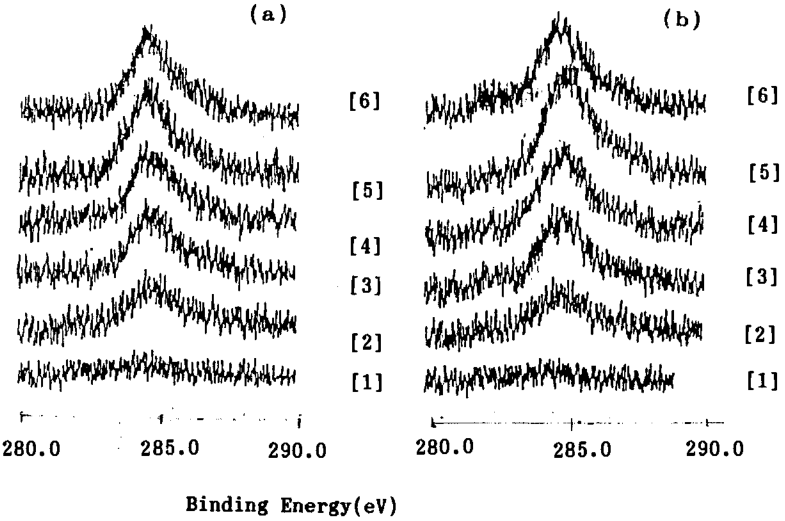

Fig. 3. C1s spectra for adsorption of methane (a) and methane-dioxygen mixture (b) at 300 K and heated to 500 K and 700 K on polycrystalline TiO_2 film. [1] Clean, [2] 10 L, [3] 60 L, [4] 600 L, [5] 500 K, [6] 700 K.

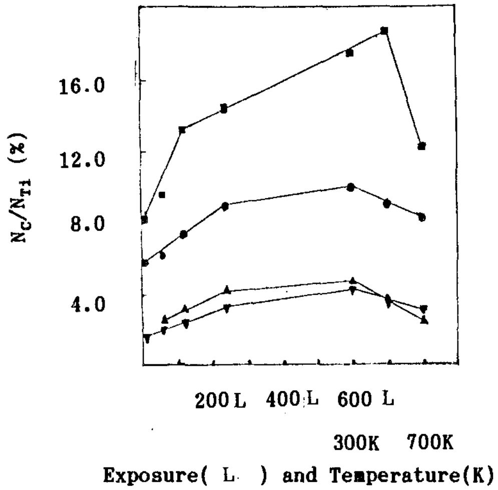

Fig. 4. Concentration of the various surface species as a function of exposure and temperature in the TiO_2-CH_4-O_2 system. ■ CH_x on polycrystalline TiO_2 film, ● CH_x on $TiO_2(100)$, ▲ CH_xO on polycrystalline TiO_2 film, ▼ CH_xO on $TiO_2(100)$.

indicating that oxygen or adoxygen species formed from adsorption of dioxygen on the surface play an important role in methane adsorption.

After heating the adlayer to 500 K for 10 minutes the concentration of CH_xO species decreased and that of CH_xO increased, as shown in fig. 4, showing that CH_xO converted into CH_xO, which were in good agreement with the result of Au et al. [7]. When temperature was raised to 700 K, both carbon species decreased. This gave possible evidence for the surface reaction between adcarbon species and adoxygen species or coupling of CH_x.

ADSORPTION OF METHANE ON THE $TiO_2(100)$ SURFACE

On the single crystal $TiO_2(100)$ surface only a little amount of methane was adsorbed, as shown in fig. 5. There was no obvious difference between methane

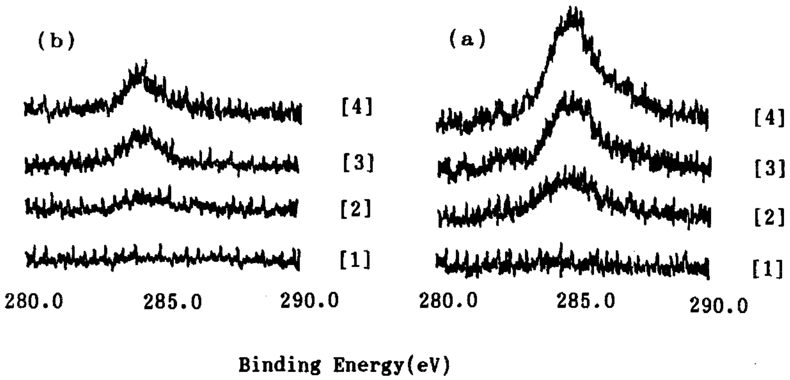

Fig. 5. Cls spectra for adsorption of methane on $TiO_2(100)$ with (a) and without (b) Ar^+ bombardment. [1] Clean, [2] 10 L, [3] 60 L, [4] 600 L.

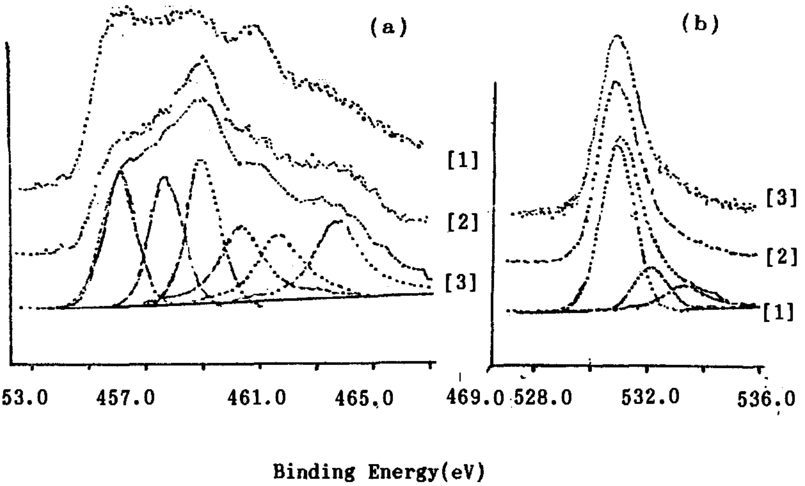

Fig. 6. Ti2p (a) and O1s (b) spectra of $TiO_2(100)$ with Ar^+ bombardment. [1] Clean, [2] exposing 600 L CH_4-O_2, [3], [2] heated to 700 K.

adsorption and methane-dioxygen coadsorption, indicating scarcity of active sites on the surface. However, large amount of adsorbed methane was observed on the $TiO_2(100)$ with Ar^+ bombardment pretreatment. On the $TiO_2(100)$ surface with Ar^+ bombardment pretreatment there were two kinds of oxygen species with O1s B.E. of 530.8 eV and 532.0 eV and three kinds of titanium species with $Ti2p_{3/2}$ B.E. of 455.4 eV, 457.2 eV and 458.9 eV, as shown in fig. 6, corresponding to Ti^{2+}, Ti^{3+}, and Ti^{4+}, respectively.

The heating behavior of the adlayer on the $TiO_2(100)$ with Ar^+ bombardment was different from that on the polycrystalline TiO_2 film and titanium surface. The concentration of CH_x species remained unchanged after heating at 700 K for 10 minutes, showing strong bonds were formed between CH_x and the surface.

THE ACTIVE OXYGEN SPECIES RESPONSIBLE FOR ACTIVATION OF METHANE

On titanium(Ti^0) surfaces, the C-H bonds of CH_4 may be activated via interaction with the electropositive titanium on certain surface sites, but such active sites appear to be very limited in number because only a small amount of adcarbon was formed as mentioned above. Little amount of methane was adsorbed on the $TiO_2(100)$, on which there existed practically only O^{2-} species, indicating that the interaction between O^{2-} and methane was very weak. However, on the $TiO_2(100)$ after Ar^+ bombardment, oxygen species such as O^- were formed due to Ar^+-bombardment-induced Ti-O bond breakage, in which Ar^+ bombardment actuated the electrons transfer from O^{2-} to Ti^{4+} with consequence of reduction of TiO_2 [8], while increment of oxygen vacancies observed by us on the $TiO_2(100)$ after Ar^+ bombardment may be favorable for the activation of gas phase oxygen and the formation of oxygen adspecies such as O^- on these vacancies. This is in agreement with experimental result of Anshits et al. [10], although the possibility that disordered surface created by Ar^+ sputtering may provide sites of different coordination for methane adsorption can not be excluded. A large amount of methane was shown to adsorb on this kind of surfaces, indicating O^- might take part in the activation of methane. In conjunction with the above results the formation of a large amount of adcarbon species on titanium surfaces under the condition of coadsorption of methane and dioxygen showed that oxygen species such as O^- might play an important role in the process of methane activation. On polycrystalline TiO_2 film surface layers, it is possible that formation of considerable amount of O^- species may be thermally induced due to the interaction between titanium in the bulk and titanium dioxide on the surface [9]. Because of the formation and promotion of the O^- species, large amount of methane was found to adsorb on this kind of surface, indicating again that O^- could activate C-H bonds of methane molecule. Thermal effects of the adlayers on the titanium and titanium dioxide also showed the possible role of O^- in the surface reaction. In conclusion, adoxygen species such as O^- etc. on titanium or TiO_2 surfaces could promote the activation of methane, but O^{2-} has little effect on the activation of methane.

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