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FTIR study of the photoinduced dissociation of CO_2 on titania-supported noble metals

J. Raskó

*Reaction Kinetics Research Group of the Hungarian Academy of Sciences**, PO Box 168, H-6701 Szeged, Hungary*

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The effect of illumination on the activation and dissociation of CO_2 was investigated at 190 and 300 K on titania-supported noble metals by means of Fourier transform infrared spectroscopy. The photoinduced dissociation of CO_2 (through the formation of $CO^-_{2(a)}$) resulting in $CO_{(a)}$ occurred on Pt/TiO_2, Rh/TiO_2 and Ir/TiO_2; no $CO_{(a)}$ formation, however, was observed on Pd/TiO_2 and Ru/TiO_2. It is assumed that the CO_2 on supported noble metals is bonded to the surface with both C (linked to a noble metal atom) and one of the O atoms (linked to the oxygen vacancy of the supports), and an extended charge transfer induced by illumination leads to the cleavage of a C–O bond.

Keywords: thermal and photoinduced dissociation of CO_2, CO_2 adsorbed on oxide-supported noble metals, the effect of the nature of noble metals and supports, FTIR spectroscopy

1. Introduction

In the conversion of CO_2 into more valuable compounds, the activation of rather inert and stable CO_2 plays a decisive role. This activation very likely involves an electron transfer to CO_2 and, hence, the transformation from linear structure into a bent form in which the C–O bond is much more reactive.

Attempts have been made to activate CO_2 on the single-crystal surfaces of Pt-metals [1,2]; the electron transfer process, however, is greatly limited by the high work function of these catalysts. The deposition of electropositive alkali metals on the above surfaces lowers the work function of Pt-metals, consequently promoting the formation of $CO^-_{2(a)}$ [2]. Illumination of a $CO_2 + K/Rh(111)$ system further increased the surface concentration of $CO^-_{2(a)}$ species [3,4].

The activation of CO_2 on oxide-supported metals would have more practical importance, since these catalysts proved active in CO_2 hydrogenation into methane at relatively high temperatures [5–7]. Graetzel et al. [8] have found that the illumination of a Ru/TiO_2 catalyst leads to the methanation of CO_2 even at room temperature.

Recently we have found by FTIR that the UV illumination of CO_2/TiO_2 and $CO_2/Rh/TiO_2$ systems enhances the intensities of the bands at 1640 and 1219 cm^{-1} due to the formation of bent CO_2 [9]. Bent CO_2 having negative charge ($CO^-_{2(a)}$) is the activated form of the rather inert and stable CO_2 on the catalyst surface. The enhanced reactivity of CO_2 adsorbed in a bent form has been demonstrated [9] during the illumination of the $CO_2/Rh/TiO_2$ system, where as a result of the photodissociation of CO_2, CO bands at 2020–2040 cm^{-1} developed at 190 K, far below the temperature at which the thermal decomposition of CO_2 occurs on this surface.

The present work is a continuation of the above study, in which the research is extended to other noble metals supported on titania. We also studied the effect of the nature of supporting oxides on these processes in the case of Rh.

2. Experimental

The catalysts were prepared by incipient wetting of titania (P25 Degussa) with aqueous solutions of H_2PtCl_6 (Reanal), H_2IrCl_6 (Ventron), $PdCl_2$ (Johnson–Matthey) and $RuCl_3$ (Ventron), respectively. The noble metal content was 5 wt%. $A1_2O_3$ (Degussa), SiO_2 (Cab-O-Sil) and MgO (DAB6) were used similarly for the preparation of supported Rh catalysts. In these cases $RhCl_3$ (Johnson–Matthey) was the parent compound. For preparation, triply distilled water was used. After impregnation, the samples were dried in air at 373 K and pressed into self-supporting wafers (30×10 mm, 10 mg/cm^2). The pretreatment of samples was performed in a vacuum IR cell: the samples were (a) heated (20 K/min) to 673 K under continuous evacuation, (b) oxidized with 100 Torr O_2 for 30 min at 673 K, (c) evacuated for 15 min, and (d) reduced in 100 Torr H_2 for 30 min at 673 K. This was followed by degassing for 30 min at this temperature and by cooling the samples to the temperature of the experiment.

A mobile IR cell housed in a metal chamber was used for illumination. The sample can be heated and cooled *in situ*. The chamber can be evacuated to 10^{-6} Torr. The sample was irradiated in the presence of CO_2 by an LPS 220 Hg arc lamp (PTI). The IR (heat) component of the lamp was filtered out by using of a 15 cm long quartz tube filled

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* This laboratory is part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

with triply distilled water. The light passed through a high-purity CaF_2 window into the cell and was focussed to the sample. The output produced by this setting at a nominal 60 W supply was 300 mW/cm^2 in a focus of 35 cm. After illumination, the IR cell was moved to its regular position in the IR beam.

Infrared transmission spectra were recorded with FTS-7 (Bio-Rad) and Genesis (Mattson) Fourier transform IR spectrometers, respectively, with a wave number accuracy of ± 2 cm^{-1} and a spectral resolution of 4. Typically 16 scans were recorded. All the spectra presented in the paper are difference spectra. The spectrum of pretreated catalysts (without CO_2) registered at the adsorption temperature of CO_2 was always the spectrum to be subtracted from the actual spectra. Subtractions of the spectra were taken without the use of a scaling factor ($f = 1.000$).

3. Results

The adsorption of CO_2 (10 Torr) between 190 and 300 K was first investigated on titania-supported noble metal catalysts reduced at 673 K. Figure 1 presents the change of the surface concentration (integrated absorbance) of $CO_{(a)}$ formed on the surfaces, when the catalysts were heated up in CO_2 without illumination. In the production of $CO_{(a)}$ Pt/TiO_2 catalyst proved to be the most active: the infrared band at 2072 cm^{-1} due to adsorbed CO appeared at 210 K in its spectrum. The formation of $CO_{(a)}$ was first detected at 230 K on Rh/TiO_2 and at 260 K on Ir/TiO_2 catalysts. No IR band due to adsorbed CO was observed on Pd/TiO_2 and Ru/TiO_2 under the same experimental conditions.

In the next series of experiments the catalysts ($T_R = 673$ K) were kept in CO_2 (10 Torr) at 190 K for 1 h, and then they were illuminated at 190 K in CO_2. In harmony with the previous findings in dark (figure 1), no IR band due to adsorbed CO appeared during CO_2 adsorption at 190 K on Rh/TiO_2 (figure 2), on Pt/TiO_2 (figure 3) and on Ir/TiO_2 (figure 4) catalysts. A dramatic change during illumination at 190 K has been observed: a band due to adsorbed CO appeared on the spectra at 2038 cm^{-1} for Rh/TiO_2 (figure 2) and at 2072 cm^{-1}, for Pt/TiO_2 (figure 3) even after 15 min illumination. A longer time of illumination (30 min) was necessary for the first appearance of the 2036 cm^{-1} band (assigned to $CO_{(a)}$) on the spectra of Ir/TiO_2 (figure 4). The intensity of the CO band was the highest on Pt/TiO_2, and the extent of the development of this band decreased in the order of $Rh/TiO_2 > Ir/TiO_2$. There was no sign for the $CO_{(a)}$ band in the cases of Pd/TiO_2 and Ru/TiO_2 under the same conditions.

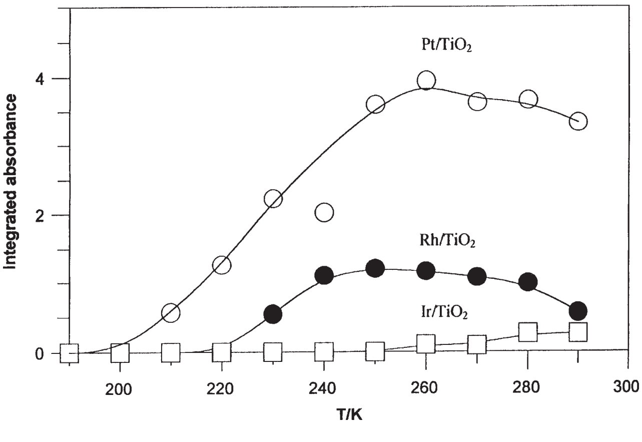


Figure 1. The integrated absorbances of the bands due to $CO_{(a)}$ on TiO_2-supported noble metals in CO_2 (10 Torr) as a function of the temperature.

The effect of illumination was also investigated at 300 K. The catalysts ($T_R = 673$ K) were first kept in CO_2 (10 Torr) at 300 K for 1 h and then they were illuminated in CO_2 at the same temperature. In the dark period of these experiments the extent of CO_2 dissociation resulting in $CO_{(a)}$ was the highest on Pt/TiO_2 (figure 5). The integrated absorbances of the $CO_{(a)}$ band on Pt/TiO_2 were 5–10 times higher in dark than on Rh/TiO_2 and Ir/TiO_2, respectively. The CO band dramatically changed on the effect of subsequent illumination at 300 K: its integrated absorbance observed in the 60th min in dark increased to a three times higher value even after 5 min illumination on Pt/TiO_2. This value went through a maximum (30 min illumination) and then – probably due to desorption – it decreased. In the

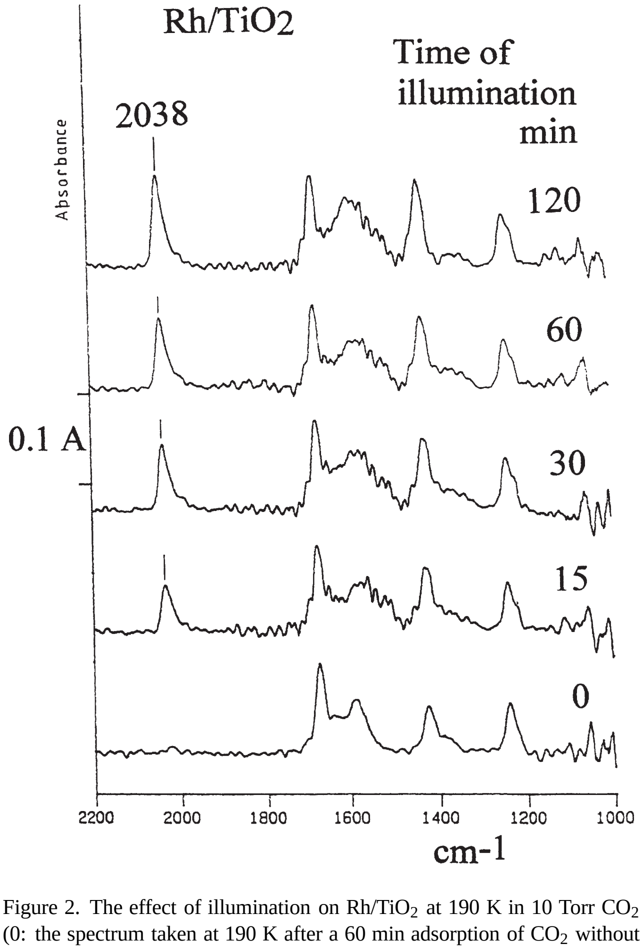


Figure 2. The effect of illumination on Rh/TiO_2 at 190 K in 10 Torr CO_2 (0: the spectrum taken at 190 K after a 60 min adsorption of CO_2 without illumination).

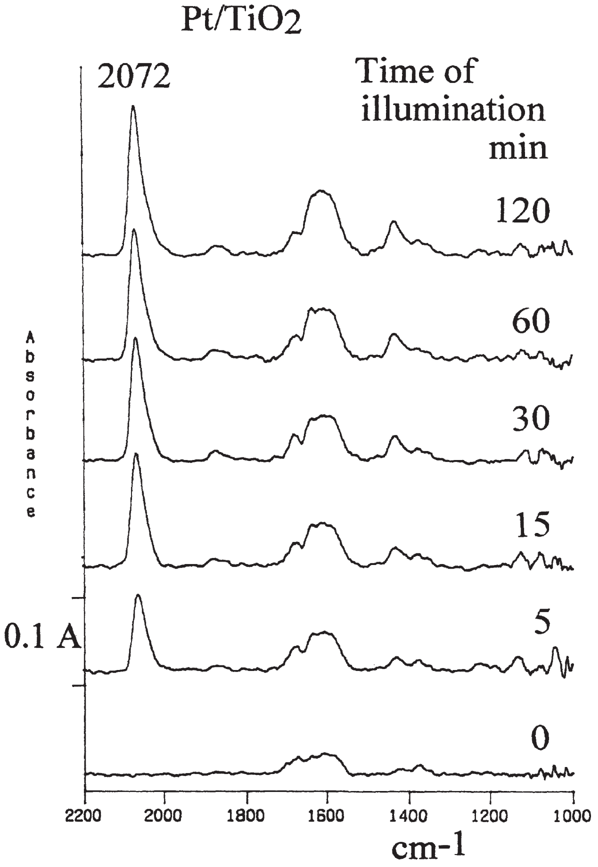


Figure 3. The effect of illumination on Pt/TiO_2 at 190 K in 10 Torr CO_2 (0: the spectrum taken at 190 K after a 60 min adsorption of CO_2 without illumination).

case of Ir/TiO_2, the development of the band due to $CO_{(a)}$ on the effect of illumination was slower than on Pt/TiO_2; in the 180th min of illumination, however, the integrated absorbance of this band was 20 times higher than its value in dark. The illumination has only a slight effect on the further development of the $CO_{(a)}$ band on Rh/TiO_2 at 300 K. Interestingly, the development of the band due to $CO_{(a)}$ was not observed neither in dark, nor during illumination on Pd/TiO_2 and Ru/TiO_2 at 300 K.

The effect of illumination on CO_2 dissociation was also investigated at 190 K on Rh/$A1_2O_3$, Rh/SiO_2 and Rh/MgO catalysts. The spectra registered in these experiments are shown in figure 6. The adsorption of CO_2 (10 Torr) at 190 K for 1 h did not cause the appearance of the band due to $CO_{(a)}$ on any catalysts investigated. This band, however, appeared in the 5th min of illumination on Rh/$A1_2O_3$ (2038 cm^{-1}) and Rh/SiO_2 (2036 cm^{-1}) in CO_2 at 190 K. The intensity of $CO_{(a)}$ increased slightly with the increase of illumination time. There was no band due to $CO_{(a)}$ neither in CO_2 adsorption nor during illumination at 190 K on the spectra of Rh/MgO catalyst. From the comparison between figures 2 and 6 it can be stated that the effectiveness of the catalysts in producing $CO_{(a)}$ during illumination at 190 K decreased in the order of Rh/TiO_2 $>$ Rh/$A1_2O_3$ $>$ Rh/SiO_2.

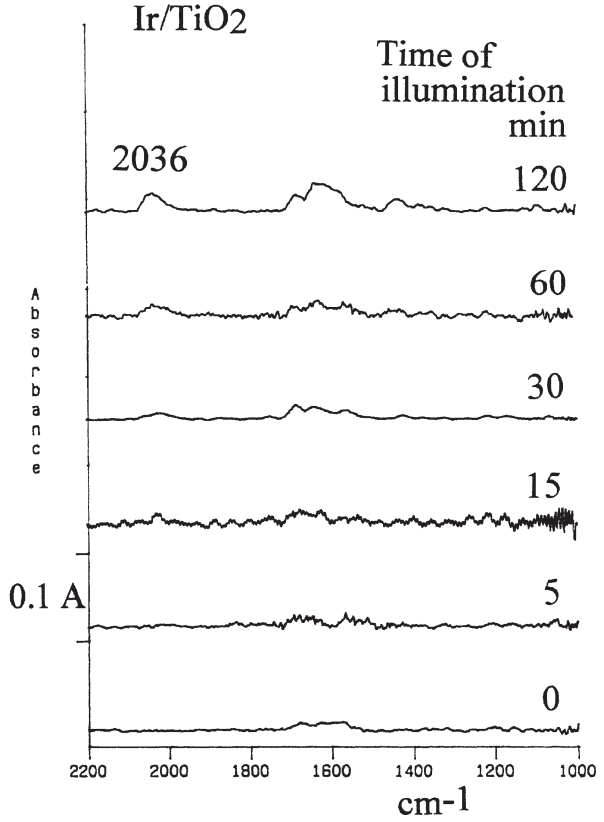


Figure 4. The effect of illumination on Ir/TiO_2 at 190 K in 10 Torr CO_2 (0: the spectrum taken at 190 K after a 60 min adsorption of CO_2 without illumination).

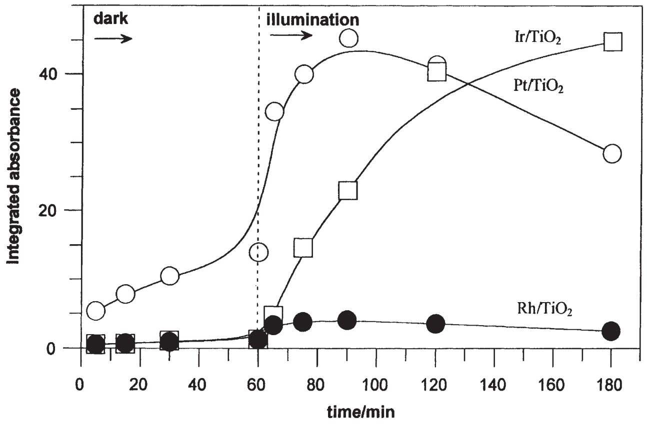


Figure 5. The changes in the integrated absorbances of the bands due to $CO_{(a)}$ on TiO_2-supported noble metals in the presence of 10 Torr CO_2 at 300 K in dark and during illumination.

4. Discussion

The adsorption of CO_2 on clean noble metal surfaces is weak and nondissociative [10–12]. Under UHV conditions the CO_2 adsorbed on single-crystal noble metal at 100 K completely desorbs below 300 K without detectable dissociation [10,11]. Deposition of potassium on Rh(111) and Pd(100) surfaces, respectively, activated the CO_2 molecule and caused its dissociation even at 150–200 K [11,13].

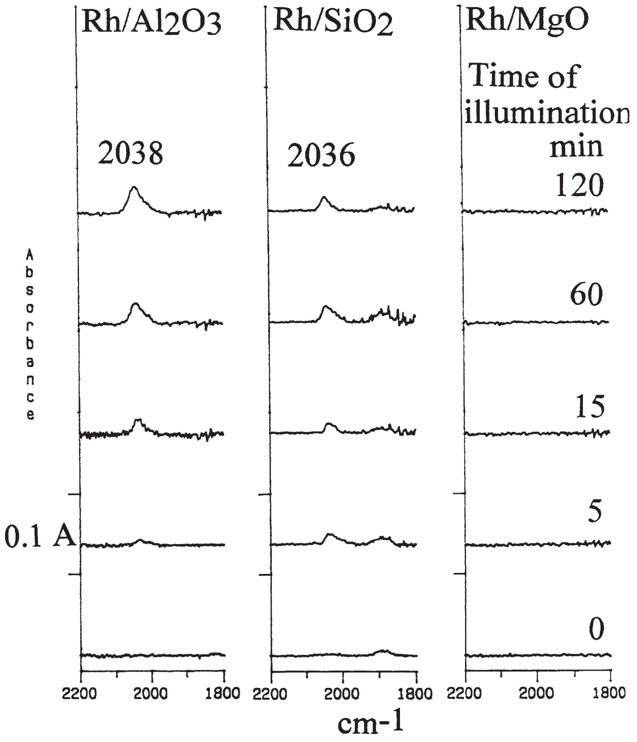


Figure 6. The effect of illumination on oxide-supported Rh at 190 K in 10 Torr CO_2 (0: the spectrum taken at 190 K after a 60 min adsorption of CO_2 without illumination).

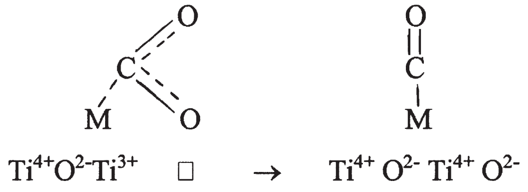
The adsorption of CO_2 on titania leads to the formation of numerous stable surface species. Among these, the most important one is the partially negatively charged bent CO_2 form. This form of activated CO_2 can be produced on titania even without illumination [9,16]. The illumination increased the concentration of this form of CO_2 [9].

The easy formation of this kind of CO_2 on titania may be attributed to its electronic and defect structure. TiO_2 is an n-type semiconductor which contains oxygen vacancies, the number of which can be increased by reduction. It seems likely that CO_2 can be activated on these sites through an electron transfer from Ti^{3+} to adsorbed CO_2, yielding a partially negatively charged species. Illumination of the TiO_2 surface leads to an enhancement of this charge transfer process.

An important observation is that this activation of CO_2 did not lead to the dissociation of CO_2 on TiO_2 [9].

On supported noble metals, the dissociation of CO_2 depends on the nature of the support. Among the oxidic supports, titania proved the most effective, but even on noble metal/TiO_2 catalysts the dissociation was detected only above 373 K [14,15].

In the high activity of titania-supported noble metals, two factors may play an important role. The first is the activation of CO_2 at the noble metal/TiO_2 interfaces. In this respect we may speculate that CO_2 is bonded to the surface with both C and O ends. The carbon atom of the CO_2 is linked to a noble metal atom, while one of the oxygens is bonded to the oxygen vacancy of titania produced by the reduction:



$$Ti^{4+}O^{2-}Ti^{3+} \ \square \ \rightarrow \ Ti^{4+}\,O^{2-}\,Ti^{4+}\,O^{2-}$$

where M denotes the noble metal atom.

Even in this form of adsorbed CO_2, however, the cleavage of a C–O bond requires energy, as the dissociation of CO_2 in dark was observed previously only at higher temperature [14,15]. In the present case, through the use of very sensitive FTIR spectroscopy and a larger amount (5 wt%) of noble metal loadings, a weak CO band was observed for Pt/TiO_2 at 210 K, for Rh/TiO_2 at 230 K and for Ir/TiO_2 at 260 K (figure 1). The importance of the oxygen vacancy on the surface of oxidic supports is demonstrated in the case of oxide-supported Rh, where the possibility of $CO_{(a)}$ formation is in harmony with the decreasing number of oxygen vacancies on different oxides (figures 2 and 6).

Another important factor of the effect of titania is the occurrence of an electronic interaction between noble metal and reduced titania [17]. The work function of reduced titania is 4.8 eV [18]. The work functions of polycrystalline noble metals are summarized in table 1. We think that the noble metals on oxidic supports are mainly in polycrystalline form. From the comparison between the work function of reduced TiO_2 and that of polycrystalline noble metals it can be stated that electrons may flow to the noble metals (Pt, Ir and Rh) at the interface, as a result of the back donation of electrons from noble metals into the π^* orbital of CO_2, and the formation of partially negatively charged CO_2 will be increased. As a consequence, the probability of the formation of adsorbed CO (dissociation of CO_2) is also increased.

The work function of polycrystalline Ru is smaller than that of reduced titania; consequently there is no driving force for electron flow from the titania to Ru. The work function of polycrystalline Pd may allow the charge transfer from TiO_2 to Pd, the work function of Pd, however, is dramatically lowered by the absorption of H_2 in Pd crystallites [23] during the reduction of Pd/TiO_2.

In harmony with the above statements, we detected CO band in the cases of Pt/TiO_2, Rh/TiO_2 and Ir/TiO_2, respec-

Table 1
The work functions of polycrystalline noble metals [19].

Metal	$\Delta\phi$ (eV)
Pt	5.65
Ir	5.27
Pd	5.12
Rh	4.98
Ru	4.71

tively, even in dark experiments, and there was no CO formation on Pd/TiO_2 and Ru/TiO_2.

The fact that illumination greatly promoted the dissociation of CO_2, even at 190 K, is very likely due to an extended electron transfer from the solid to the π^* orbital of adsorbed CO_2. The extended electron transfer originates from the photoexcitation of the TiO_2 semiconductor with UV light having energy equal to or larger than the band gap of TiO_2 (3.2 eV) [20–22]. This makes the adsorbed CO_2 more anionic, and, hence, the cleavage of the C–O bond is induced. The formation of the strongly bonded CO to noble metals (M_x–CO) may be considered as an additional driving force for the easier dissociation of adsorbed CO_2.

5. Conclusions

(i) The photoinduced dissociation of CO_2 resulting in $CO_{(a)}$ occurred on Pt/TiO_2, Rh/TiO_2 and Ir/TiO_2 catalysts at 190 K far below the temperature, at which the thermal CO_2 dissociation was observed.

(ii) The extent of this process depends on the nature of the noble metals and the supports.

(iii) The oxygen vacancy of the support, the electronic interaction between noble metals and titania, and the extended electron transfer originating from the photoexcitation of titania play decisive role in the dissociation of adsorbed CO_2.

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