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Adsorption of CH_3 and its reactions with CO_2 over TiO_2

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The adsorption, decomposition of CH_3 and its reactions with CO_2 were followed by means of Fourier transform infrared spectroscopy combined with mass spectrometry. Methyl radicals were produced by the pyrolysis of azomethane. Absorption bands, observed at room temperature adsorption, were attributed to adsorbed CH_3 and CH_3O species. The decomposition of adsorbed CH_3 in vacuum started above 400 K and was accelerated by CO_2. In the study of the interaction of methane with titania, activated in different ways, we found no convincing spectroscopic evidence for the activation of methane at 300 K.

Keywords: adsorption of CH_3 on titania, decomposition of adsorbed CH_3, reaction of adsorbed CH_3 with CO_2, formation of CH_3O, adsorption of methane on activated titania, use of FTIR combined with mass spectrometry

1. Introduction

After the pioneering work of our laboratory on the use of TiO_2 as a support for metal catalysts [1,2], titania support has been extensively applied in the heterogeneous catalysis [3,4]. Taking into account the specific activities of the supported metals, the titania-supported metals exhibited the highest activity in several catalytic reactions. For example, in the case of the hydrogenation of CO and CO_2, the specific activity of Rh/TiO_2 was almost by two orders of magnitude higher than that of Rh/SiO_2 [5,6]. To achieve this high catalytic performance, the catalyst should be reduced at 673 K or below. Reduction at higher temperatures causes the decoration of metals, e.g., the loss of active area, by TiO_x [3,4].

Titania was found to be a very efficient support in the reaction involving CH_4 ($CH_4 + CO_2$ reaction [7–11] and oxidation of CH_4 [12,13]). There was speculation, whether some parts of the reactions proceeded on the titania support, or whether the active sites of titania played a role even in the activation of methane. Titania was found to be a rather poor catalyst for the oxidative coupling of methane [14,15], which was ascribed to the inefficiency in CH_3 formation and/or to the high oxidation rate of CH_3 species formed [16]. Its catalytic performance, however, can be improved by doping it with lower-valence cations which enhanced the number of the active sites on its surface [17]. As regards the interaction of methane with titania, there are few investigations. A noteworthy exception is the work of Fancheng et al. [18], who followed the adsorption of methane on titania by means of XPS. They claimed that adsorption of methane on titania activated by Ar ion bombardment gave CH_x and CH_xO species.

In the previous paper, we reported the reaction of adsorbed CH_3 with gaseous CO_2 on Rh/SiO_2 catalyst [19]. As a continuation of this research, in the present paper we examine the surface chemistry of adsorbed CH_3 on titania and its reaction with CO_2 by means of Fourier transform infrared spectroscopy combined with mass spectrometry. The interaction of methane with titania treated in different ways is also investigated.

2. Experimental

Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wave number accuracy of ± 2 cm^{-1}. Typically 136 scans were collected. All subtractions of the spectra were made without the use of a scaling factor ($f = 1.000$). All the IR spectra have been taken at room temperature. Mass spectrometric analysis was performed with a QMS (Balzers) quadrupole mass spectrometer.

TiO_2 was a product of Degussa denoted by P.25. It was pressed onto a Ta mesh (30×10 mm, 5 mg/cm^2). The mesh was fixed to the bottom of a conventional UHV sample manipulator. It was resistively heated and cooled by liquid nitrogen pumped through the sample holder. Before any measurements, the catalyst disc underwent different pretreatments indicated in the text. The argon ion bombardment (2 kV, 30 μA) was performed at 300 K for 10 min. After any treatments, the cell was evacuated to attain a pressure of 1.0×10^{-6} Torr.

The generation of CH_3 radicals was performed by high-temperature pyrolysis of azomethane following the method of Stair et al. [20]. Mass spectrometric analysis of the gas showed the signal ($m/e = 15$) corresponding to CH_3: signals due to azomethane were not found indicating that its decomposition was complete. The reaction between ad-

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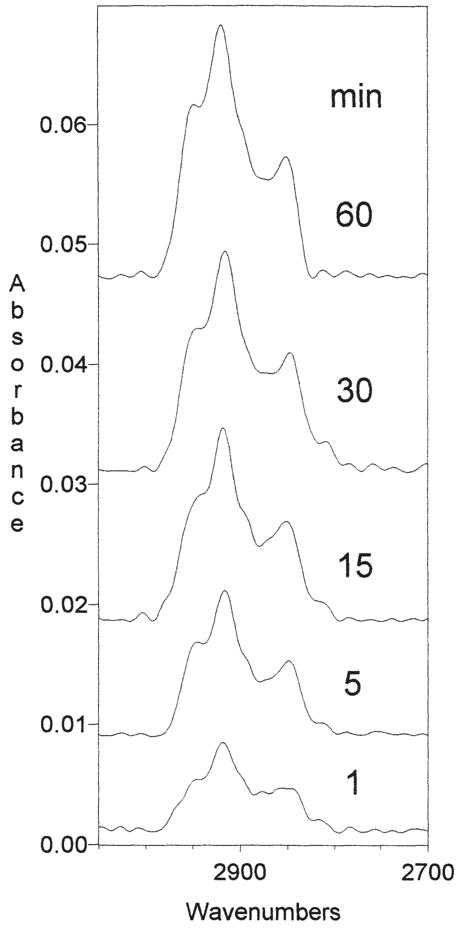

Figure 1. IR spectra of TiO_2 as a function of exposition time of CH_3 flow at 300 K.

sorbed CH_3 and gaseous CO_2 was followed by simultaneous registration of the IR spectra and the composition of the gas phase. CH_4 and CO_2 used were of commercial purity.

3. Results

3.1. Adsorption of CH_3

The adsorption of CH_3 on titania (evacuated at 673 K for 1 h) produced intense absorption bands at <2954, 2920, >2852, (1616, 1550), 1459, (1416), 1356, 1175, (1116) and 1063 cm^{-1} (figure 1). The intensities of all these bands increased with the time of exposure of the sample to CH_3 flow up to 30 min. Afterwards, no or only very slight spectral changes were observed. The bands at 2920 and 1356–1175 cm^{-1} are tentatively assigned to the C–H stretching and deformation vibrations of adsorbed CH_3. The doublet at 2954 and 2852 cm^{-1} is attributed to the C–H stretching, the 1459 cm^{-1} band to the deformation mode of CH_3, and the 1063 cm^{-1} band to ν(C–O) in $CH_3O_{(a)}$, respectively (table 1).

In the next experimental series, the TiO_2 sample saturated with CH_3 has been heated up quickly to different temperatures and kept there for 1 min. Afterwards, it was cooled back to room temperature and the spectra were taken. All these manipulations were performed under continuous evacuation. Some spectra are presented in figure 2(A). Absorbance values are plotted against the temperature in figure 2(B). It appears that the 2920 cm^{-1} band remained stable up to 375–400 K, but underwent a gradual attenuation above this temperature: disappeared at 650–670 K.

Some experiments were also carried out under isotherm conditions. At 423 K, the decline in the intensity of the 2920 cm^{-1} was about 30%, while that at 473 K was about 55%. In both cases the decline occurred in the first minutes; afterwards, only slight changes were experienced. The same features were observed at 523 K. Results obtained are shown in figure 3.

A great effort was made to determine the gaseous products formed during annealing the adsorbed layer. As the surface concentration of adsorbed species is very low, several blank experiments were made to avoid any false conclusions. The formation of hydrogen and water was established, but no convincing mass spectrometric evidence was obtained for the formation of other products.

After annealing the adsorbed layer by extended evacuation at 673 K and cooling the sample back to 300 K, the sample was heated in O_2 up to 673 K with concomitant monitoring of the changes in the gas-phase composition. We observed only the formation of CO_2 ($T_{\max} = 523$ K), no production of CO and H_2O was detected.

3.2. Effects of CO_2

In the next experimental series, the reaction of adsorbed species produced by CH_3 adsorption was examined towards CO_2. We obtained that the attenuation of the 2920 cm^{-1} band set in even at 300 K and was eliminated at 500–525 K. As it can be seen in figure 2(B), these temperature values are considerably lower compared to those observed in the absence of CO_2. An interesting feature is that exposing the adsorbed layer to higher pressure of CO_2 (10 Torr) at 300 K we observed a clear intensification of the band at 1063 cm^{-3} due to the C–O stretch in methoxy species. Analysing the IR spectra in the C–H stretching region no unambiguous changes can be established.

Under isotherm conditions, the effects of CO_2 were exhibited at and above 473 K, where a sudden decrease in the intensity of the 2920 cm^{-1} band occurred in the first minute. In contrast to the annealing in vacuum, the 2920 cm^{-1} band was eliminated even at 473 K in 50–60 min (figure 3(B)).

From the comparison of mass spectra obtained in the absence and in the presence of CO_2 we observed a clear increase in the intensity of amu 18 which is due to H_2O.

3.3. Adsorption of CH_4

Detailed IR spectroscopic measurements were carried out concerning the interaction of CH_4 with TiO_2 treated in different ways. Following the adsorption of 0.1–100 Torr of

Table 1
Vibrational frequencies of adsorbed CH_3 and CH_3O groups (cm^{-1}).

Surface	Ref.	ν_a(C–H) in $CH_3O_{(a)}$	ν_a(C–H) in $CH_{3(a)}$	ν_s(C–H) in $CH_3O_{(a)}$	$\delta_a(CH_3)$ in $CH_3O_{(a)}$	$\delta_a(CH_3)$ in $CH_{3(a)}$	$\delta_s(CH_3)$ in $CH_{3(a)}$	ν(C–O) in $CH_3O_{(a)}$
SiO_2	[19]	2956	–	2860	–	–	–	–
Rh/SiO_2	[19]	2960	2922	2858	1457	1350	–	–
TiO_2	this work	2954	2920	2852	1459	1356	1175	1063

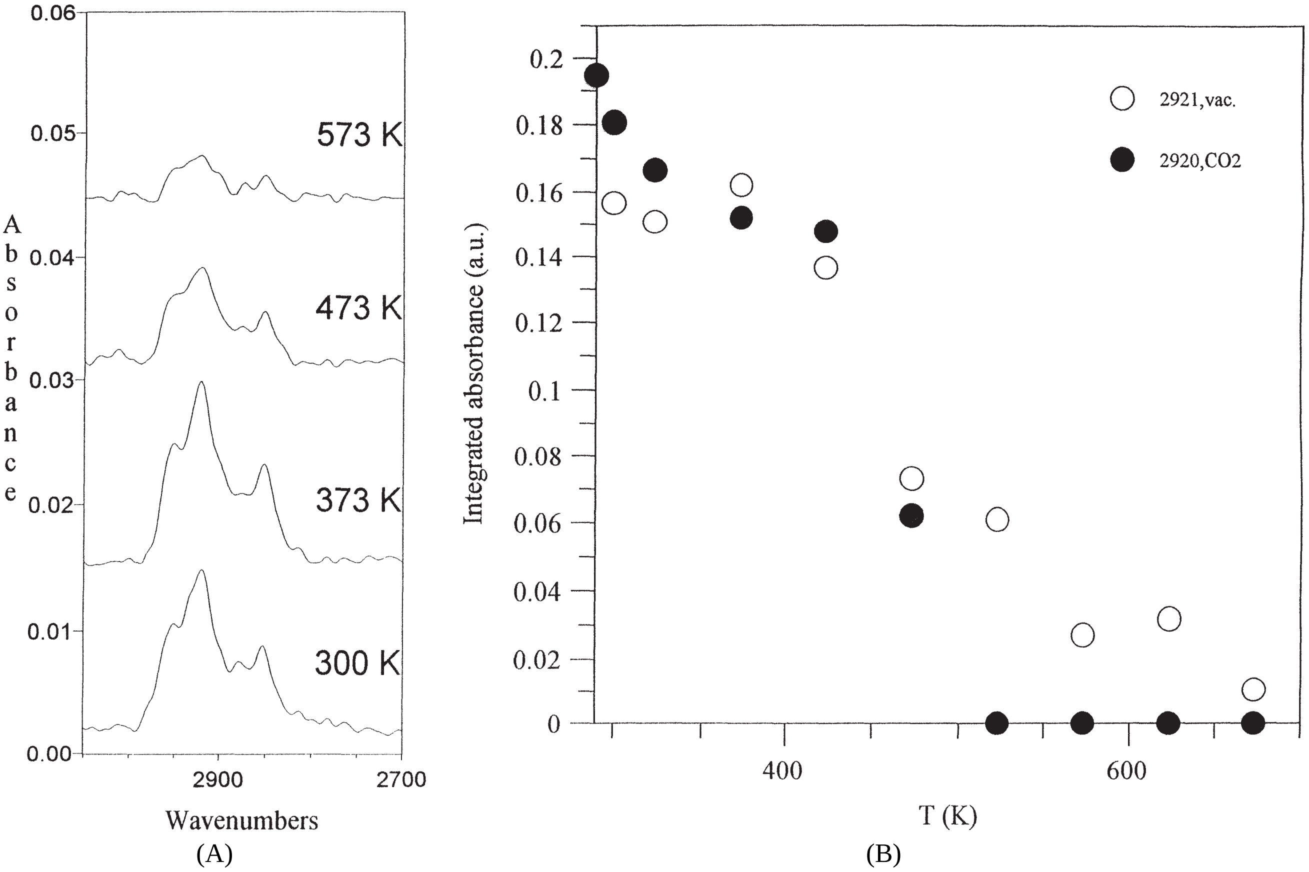

Figure 2. (A) Effects of annealing in vacuum on the IR spectra of TiO_2 exposed to CH_3 radicals at 300 K. (B) Integrated absorbances of the 2920 cm^{-1} band as a function of annealing temperature in vacuum and in the presence of 1 Torr of CO_2.

CH_4 on titania (evacuated at 673 K) for 60 min at 300 K, we could not identify stretching vibrations attributable to adsorbed CH_3 or CH_3O species. The situation was practically the same when titania has been previously reduced at 673 K. When the titania was bombarded with argon ions before CH_4 adsorption, very weak absorption bands at 2920, 2849 and 2958 cm^{-1} were detected in the magnified difference spectra after extended adsorption time. The absorbency of these bands, however, was extremly low and only slightly higher than that registered in the absence of CH_4.

Taking into account the XPS results of Fancheng et al. [18], it seemed worthwhile to perform similar IR spectroscopic measurements with CD_4. Adsorption of 1–100 Torr of CD_4 either on evacuated (673 K) or on reduced (673 K) titania produced no convincing spectral features due to adsorbed CD_3 or CD_3O species. The same was experienced when titania was bombarded with argon ions at 300 K.

Analysis of the spectra, however, revealed the presence of a weak band at 3010 cm^{-1}. This band appeared with higher intensities when titania was bombarded with Ar ions for 60 min. No enhancement of this band occurred when $CH_4 + O_2$ was coadsorbed on titania. Evacuation at 300 K caused the disappearance of this band.

4. Discussion

4.1. Survey of previous studies

As regards the activation of CH_4 on titania, the results of Fancheng et al. [18] are worth mentioning. Following the adsorption of CH_4 and a $CH_4 + O_2$ mixture on polycrystalline TiO_2 film by XPS, they observed two adcarbon species characterized by C(1s) binding energies of 284.6 and 286.3 eV: their concentrations were higher after the coadsorption of the $CH_4 + O_2$ mixture. The first one was

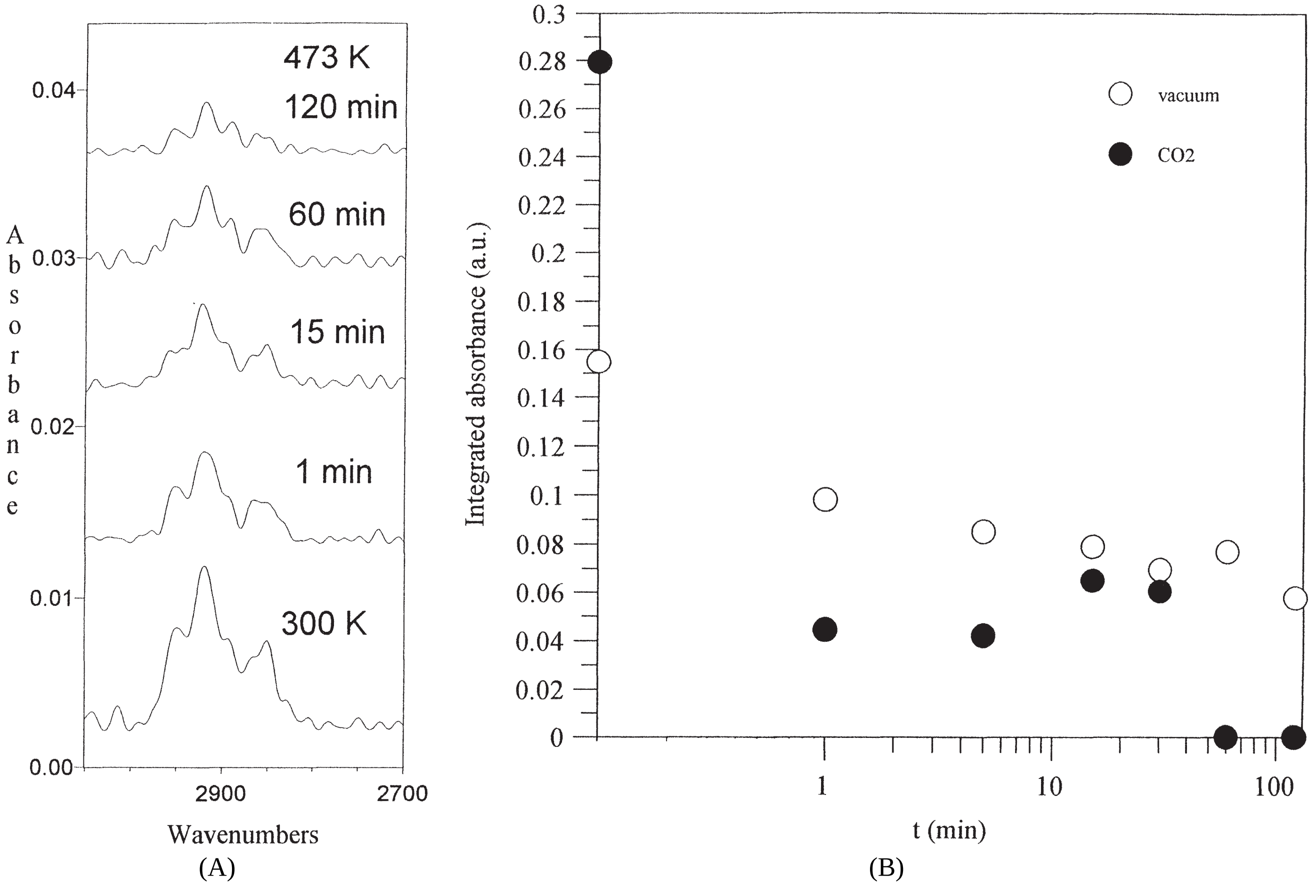

Figure 3. (A) IR spectra of TiO_2 exposed to CH_3 radicals at 300 K and kept at 473 K for different times. (B) Changes of integrated absorbances of the band at 2920 cm^{-1} as a function of annealing temperature in vacuum and in the presence of 1 Torr of CO_2.

attributed to CH_x, and the second one (which appeared only as a shoulder) to a CH_xO surface complex, but no reasoning was presented for this assignment. After heating the adlayer to 500 K for 10 min, the concentration of CH_xO species decreased and that of CH_x increased, showing that CH_xO converted into CH_x [18]. In the case of $TiO_2(100)$ single crystal, they found very little adsorption of methane. However, after Ar^+ ion bombardment, a large amount of CH_4 adsorbed from pure CH_4 and the $CH_4 + O_2$ mixture. This was attributed to the formation of O^- which activated the methane molecule.

As regards the chemistry of adsorbed CH_3, several detailed studies have been performed. Vibrational characteristics for adsorbed CH_3 were collected in our previous paper [19]. Independently of the metals, the most intense peak, due to $\nu_a(CH_3)$, appeared in the range 2910–2945 cm^{-1} [21–29]. The situation is more complex on oxides, as CH_3 easily interacts with oxygen ions to give methoxy species. This was the case for silica surface where the absorption bands identified at 2960 and 2858 cm^{-1} agreed well with those obtained following methanol adsorption on silica [19,30]. The formation of methoxy following the adsorption of CH_3 on several oxides was also assumed by Lunsford et al. [31–33]: its existence was confirmed by IR spectroscopic measurements for CeO_2 and V_2O_5/SiO_2 systems [32,33]. Concerning the existence of Ti–CH_3 species, we note that during the high-temperature decomposition of methanol on TiO_2 the formation of Ti–CH_3 surface species has been postulated [34].

4.2. Adsorption of CH_3 radicals on titania

The adsorption of CH_3 radicals on titania produced several new absorption bands listed in table 1, which also contains our data obtained for silica sample. It appears that the IR spectrum of adsorbed CH_3 on titania is more complex than that for silica, indicating the occurrence of other surface processes, too. The most important is that we obtained intense absorption bands at 2920 and 1350 cm^{-1} which – based on the previous studies performed with silica and metal single crystals [19,21–29] – are assigned to the C–H stretching vibration and δ(CH) of adsorbed CH_3 species. The existence of adsorbed CH_3 suggests the presence of OH-free titanium ions which can bind CH_3 radicals. In addition, we also obtained a doublet at 2954 and 2854 cm^{-1} and weaker absorption bands at 1459 and 1063 cm^{-1}, which are the characteristic vibrations of adsorbed methoxy species (table 1). Accordingly, we can count with the occurrence of the following reactions suggested before [19,33]:

$$CH_3 + M^{n+1}O^{2-} \rightarrow M^{n+}(OCH_3)^-$$

$$\text{Ti–OH} + 2CH_3 \rightarrow \text{Ti–OCH}_3 + CH_4$$

The latter process is supported by the appearance of a negative feature at 3743 cm^{-1} in the difference spectrum which suggests the consumption of surface OH groups during the adsorption of CH_3.

4.3. Reaction of adsorbed CH_3 with CO_2

The fact that the integrated absorbances of adsorbed CH_3 decline at lower temperature and with higher rates in the presence of CO_2 compared to the effect of thermal annealing in vacuum (figures 2 and 3) suggests the occurrence of a reaction between $CH_{3(a)}$ and CO_2.

We may assume that, in the first step, CO_2 reacts with adsorbed CH_3 to produce CH_2 fragments:

$$2CH_{3(a)} + CO_{2(g)} \rightarrow 2CH_{2(a)} + CO_{(g)} + H_2O$$

Alternatively, CO_2 can combine with CH_3 to give methoxy species:

$$CH_{3(a)} + CO_2 \rightleftharpoons CH_3O_{(a)} + CO$$

and/or with CH_2 to yield formaldehyde:

$$CH_{2(a)} + CO_2 \rightleftharpoons CH_2O + CO$$

Both compounds decompose to H_2 and CO. If these reactions are fast enough, then the probability of the complete decomposition of CH_x fragments to surface carbon can be greatly reduced. Similar steps have been proposed to describe the reaction of CH_3, formed in the dissociation of CH_4, with CO_2 over supported Rh catalysts [7,19].

4.4. Activation of CH_4 on titania

Sensitive mass spectrometric measurements showed that methane enters into reaction with titania only above 800 K producing different gaseous compounds, such as H_2, CO, C_2H_4, and C_2H_6. The formation of these compounds was observed even with titania evacuated at 673 K, when we can exclude the presence of adsorbed oxygen, and can count with the presence of oxygen vacancies or Ti ions of lower valence state.

Analysis of the FTIR spectra also showed no convincing evidence for absorption bands characteristic for adsorbed CH_3 and CH_3O species on our sample. This was also the case when the titania surface was bombarded with argon ions. These results do not support the conclusion of Fancheng et al. [18] drawn from the analysis of XPS spectra, namely that CH_x and CH_xO species are formed following the adsorption of CH_4 on polycrystalline titania. Nevertheless, an absorption band at 3010 cm^{-1}, which can be attributed to physisorbed CH_4, was detected following the adsorption of methane on Ar^+ bombarded titania. This suggests that the bonding (and/or activation) of CH_4 may occur on oxygen vacancies or on O^- ions. Further measurements on $TiO_2(110)$ single crystal using high-resolution electron-loss (HREELS) and temperature-programmed desorption (TPD) spectroscopies are in progress.

5. Conclusions

(i) Adsorption of CH_3 on titania produces adsorbed CH_3 and CH_3O species.

(ii) These species are stable on titania up to 375–400 K, and their complete elimination occurs around 523 K.

(iii) In the presence of CO_2, the bands due to these species are eliminated at lower temperatures with the accompaniment of the formation of H_2O.

(iv) No convincing spectroscopic evidence was found for the activation of CH_4 on differently treated titania surface.

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