Reactions of adsorbed CH_3 species with CO_2 on Rh/SiO_2 catalyst

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Methyl radicals, produced by the high temperature pyrolysis of azomethane, were adsorbed on Rh/SiO_2. The reaction between adsorbed CH_3 and gaseous CO_2 has been followed by determining the intensity changes of the asymmetric stretch of CH_3 and the composition of the gas phase. It was found that adsorbed CH_3 reacts with CO_2 at and above 373 K. It is assumed that similar processes may also take place in the dry reforming of methane, and that they are responsible for the lack of carbon deposition on supported Rh catalysts.

Keywords: adsorption of CH_3 on silica to give methoxy, adsorption of CH_3 radicals on Rh/SiO_2 catalyst, reaction of adsorbed CH_3 with gaseous CO_2, reaction steps in the dry reforming of methane, use of FTIR combined with mass spectrometry

1. Introduction

Synthesis gas, a highly versatile feedstock, can be produced by three main processes: (i) reaction of CH_4 with CO_2, (ii) reaction of CH_4 with H_2O and (iii) partial oxidation of CH_4 [1–5]. In all three processes we may count with the decomposition of CH_4, i.e. with the transient formation of CH_x fragments. In our laboratory we are mainly concerned with the $CH_4 + CO_2$ reaction. Several recent studies showed that supported platinum group metals are efficient catalysts for this process, particularly Rh [6–14]. Its advantage, compared to the Ni catalyst [5], is its less sensitivity to coking, which is probably primarily responsible for the deactivation of the catalyst. In the explanation of this feature we proposed that CH_x fragments formed in the decomposition of CH_4 react with CO_2, without their complete decomposition to surface carbon [9–12]. In the present work, a first attempt is made to examine the reactivity of adsorbed CH_3 on Rh/SiO_2 catalyst towards CO_2. The method used is Fourier transform infrared (FTIR) spectroscopy combined with mass spectrometry.

2. Experimental

The catalyst was prepared by incipient wetting of silica (Cab-O-Sil, 300 m^2/g) with an aqueous solution of rhodium chloride (Johnson-Matthey). In order to obtain a larger metal area, 10 wt% of Rh was applied. After impregnation, the samples were dried in air at 373 K and 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 was oxidized in 100 Torr of O_2 for 30 min at 673 K and reduced in 100 Torr of H_2 at 673 K for 60 min in the vacuum IR cell. This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment.

The generation of CH_3 radicals was performed by high temperature pyrolysis of azomethane following the method of Stair et al. [15,16]. Mass spectrometric analysis of the gas phase showed the signal ($m/e = 15$) corresponding to CH_3: signals due to azomethane were not found indicating that its decomposition was complete.

Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wavenumber 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.

3. Results and discussion

The adsorption of CH_3 on Rh/SiO_2 at 300 K resulted in the appearance of bands at 2960, 2922 and 2854 cm^{-1} (figure 1A). The positions of these bands are basically different from those observed following the adsorption of molecular azomethane. On the basis of previous vibration studies (table 1), the band at 2922 cm^{-1} is assigned to the C–H stretching vibration of adsorbed $CH_{3(a)}$ [17–26], while the doublet at 2960 and 2858 cm^{-1} to the C–H stretchings in $CH_3O_{(a)}$ [29–32]. In the low frequency region we detected weaker bands at 1350 and

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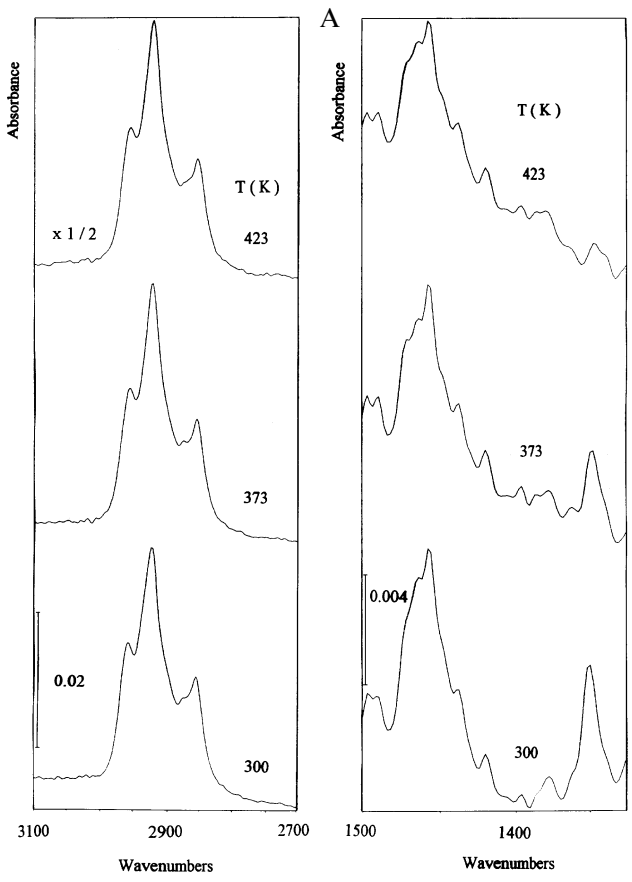

Figure 1. (A) IR spectra taken at 300 K showing the spectral changes of Rh/SiO_2 following CH_3 adsorption at 300 K and after the annealing at different temperatures for 1 min in vacuum. (B) Changes in the ratio of integrated absorbances ($R = I_T/I_0$) of the band at 2922 cm^{-1} due to CH_3(a) as a function of annealing temperature in vacuum and in the presence of 1 Torr of CO_2.

1457 cm^{-1} (figure 1A). The first can be attributed to $\delta_a(CH_3)$ of adsorbed CH_3 and the second one to $\delta_a(CH_3)$ of adsorbed CH_3O. Annealing the adsorbed layer under constant evacuation led to a gradual attenuation of the above bands, but the relatively more intense CH stretching frequencies were detectable even after heating up of the sample to 573 K.

Similar measurements were performed with pure, Rh-free silica under exactly the same experimental conditions. Following the adsorption of CH_3 radicals we obtained practically the same absorption bands (2960, 2927 and 2858 cm^{-1}) in the CH stretching region as observed for the Rh/SiO_2 sample. The intensities of these bands also declined with the increase of the temperature above 400 K, and vanished above 573 K.

The results obtained on pure silica show that CH_3 has a high tendency to adsorb on silica surface. Note that the formation of methoxy following the adsorption of CH_3 on oxides (MoO_3, CeO_2, ZnO) was also assumed to occur by Lunsford et al. [32,33], but IR spectroscopic measurements were not carried out. The reaction was described by the equation

$$M^{(n+1)+}O^{2-} + CH_{3(g)} \rightarrow M^{n+}(OCH_3)^- \qquad (1)$$

In the present case we may count with the surface process

$$Si{-}OH + 2CH_{3(g)} \rightarrow Si{-}OCH_3 + CH_{4(g)} \qquad (2)$$

The occurrence of reaction (2) is supported by the fact that a negative feature at 3743 cm^{-1} (on SiO_2) appeared on the difference spectrum, which shows that the surface concentration of Si–OH groups slightly decreases during the adsorption of CH_3. The existence of adsorbed CH_3 suggests the presence of OH-free silicium ions which can bind CH_3 radicals.

It is an open question which adsorbed species can be formed on Rh during the exposition of CH_3 on Rh/SiO_2. We may certainly count with the adsorbed CH_3, as following the thermal and photo-induced dissociation of CH_3I on Rh(111) and on Rh/SiO_2, we detected the asymmetric stretch (2920 cm^{-1}) of CH_3 up to 400 and 423 K, respectively [21,22,24]. The formation of adsorbed CH_3 following the exposure of Rh(111) to a CH_3 flux was confirmed by two independent studies [23,26]. There is no doubt, however, that CH_3 cannot produce methoxy species on reduced rhodium.

In the next experimental series we studied the effect of CO_2 on the IR spectra of adsorbed CH_3 over Rh/SiO_2. We observed that CO_2 exerts a more significant alteration on the IR spectra compared to the effect of thermal annealing in vacuum. For better comparison, the integrated absorbances of the 2922 cm^{-1} band were calculated and the values of R (ratio of I_T/I_0) were plotted against temperature in figure 1B. (I_T = integrated absorbance defined at time of annealing t and I_0 = integrated absorbance measured after adsorption of CH_3). It appears clearly that in the pres-

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

Surface	Ref.	$\nu_a(CH_3)$	$\nu_s(CH_3)$	$\delta_a(CH_3)$	$\delta_s(CH_3)$	$\rho(CH_3)$	ν(M–C)
				CH_3 species			
Pt(111)	[17]	2925	2775	1425	1165	790	520
Cu(111)	[18]	2950	2820	1370	1180	–	–
Cu(111)*	[19]	2945	2790	1380	1190	890	355
Cu(111)	[20]	2910	2781	1386	1185	854	–
Rh(111)	[21]	2920	–	1350	1185	760	–
Rh(111)*	[23]	2945	2620	1340	1195	695	400
Pd/SiO_2	[24]	2920	–	–	–	–	–
Cu/SiO_2	[25]	2920	–	–	–	–	–
				CH_3O species			
Rh(111)	[30]	2935	–	1450	1130, 1015	–	–
Pd(111)	[31]	3015	2865	1430	1140,1005	–	–
SiO_2	[27]	2956	2860	–	–	–	–

[a] For single-crystal studies HREELS was applied, whereas in the case of supported metals IR spectroscopy was used. CH_3 species was produced by dissociation of CH_3I or CH_3Cl except for the case marked by * where CH_3 was generated by the pyrolysis of azomethane.

ence of CO_2 the 2922 cm^{-1} band disappears at significantly lower temperature (523 K) than on the effect of evacuation. In the next experiments the reactivity of CH_3 species was studied isothermally. After conditioning the adsorbed layer at 300 K for 60 min, the temperature was raised to 373 and 423 K, respectively. Results are plotted in figure 2. While the CH_3 band remained practically unchanged at 373 K in vacuum, it markedly declined in the presence of CO_2. This effect of CO_2 was also exhibited at 423 K, when the 2922 cm^{-1} band completely vanished in 30 min. It is important to point out that in contrast to Rh/SiO_2, the admission of CO_2 on CH_3-covered silica exerted very little influence on the stability of these absorption bands.

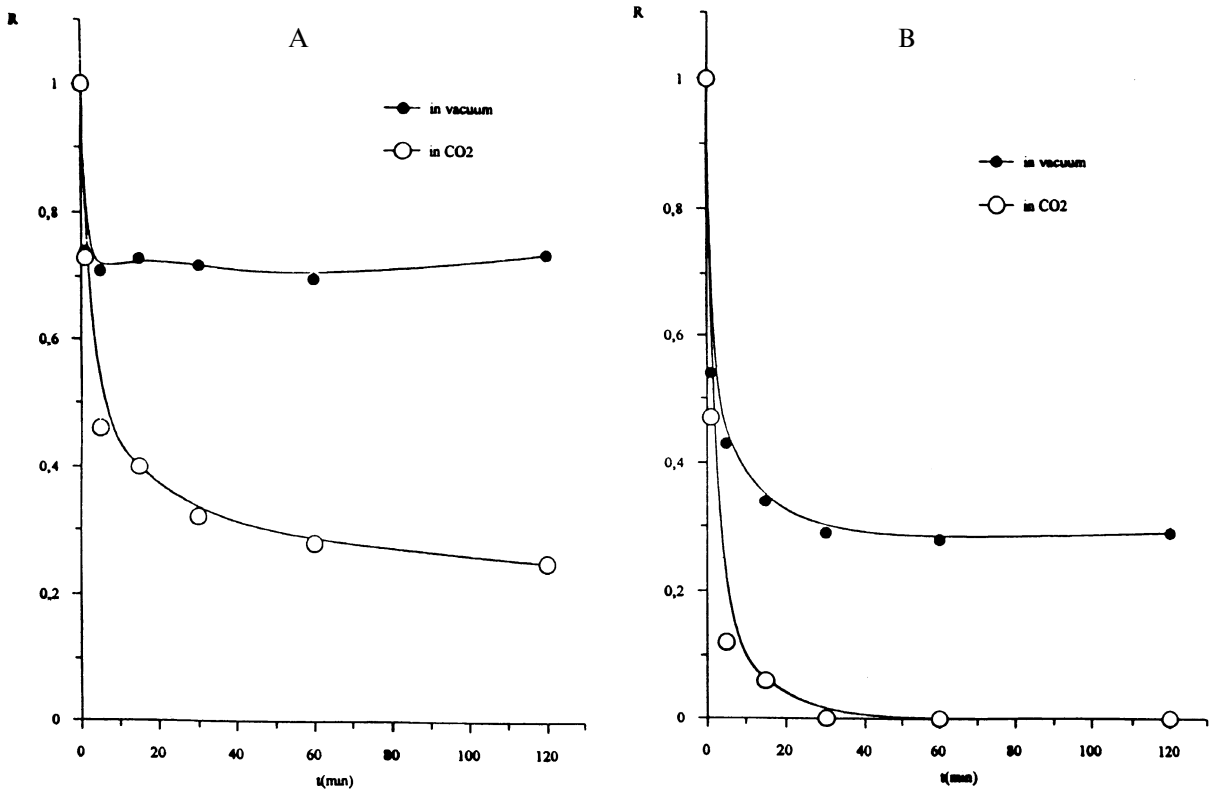

Figure 2. Changes in the ratio of the integrated absorbances (R) of the band at 2922 cm^{-1} due to CH_3(a) in vacuum and in the presence of 1 Torr of CO_2 at 373 K (A) and 423 K (B).

In the analysis of the IR spectra of Rh/SiO_2 in an other region we found the development of an absorption band at 2024 cm^{-1} which we attribute to adsorbed CO. This band was detected first at 373 K slightly growing with the increase of the reaction time. At 423 K, an almost four times more intense CO band was registered following the CO_2 adsorption on the CH_3-covered catalyst. Parallel with the IR measurements, mass spectrometric analysis of the gas phase was also performed. The most striking feature of MS data is the appearance of mass numbers $m/e = 16$ (CH_4) and 28 (CO), when the annealing was made in the presence of CO_2.

Before the interpretation of the above results we note that CO_2 adsorbs weakly on both Rh single crystal and supported Rh: its dissociation is very limited in this temperature range [34–39]. This was also confirmed in the present study: keeping the Rh/SiO_2 sample in CO_2, we obtained extremely weak CO absorption bands. However, the presence of adsorbed hydrogen on the Rh markedly promoted the activation and dissociation of adsorbing CO_2 [34–39]. We may expect a similar interaction and reaction between adsorbed CH_3 and CO_2.

The appearance of CO in gas phase and the concomitant decrease in the integral absorbance of the $CH_{3(a)}$ band strongly suggest the occurrence of a reaction between $CH_{3(a)}$ and $CO_{2(g)}$ leading to the formation of CO:

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

which would be a key step in the dry reforming of CH_4. It seems very likely that CH_2 may also react with CO_2, which needs experimental confirmation. Alternatively, CH_2 may undergo self-hydrogenation to give methane, and/or to a much less extent, dimerizes to ethylene, as was observed for Rh(111) under UHV conditions [21].

Although the large majority of surface species formed during the adsorption of CH_3 are located on the silica of high surface area, the different behavior of Rh-free and Rh-containing silica in the presence of CO_2 suggests the involvement of Rh in the reaction. It appears that the reaction between gaseous CO_2 and adsorbed CH_3 occurs on or at the periphery of Rh crystallites. The area of this interface should not be great, however, we may count with the migration of CH_3 species from the silica to the neighbourhood of Rh, where the reaction may take place. Further investigations are in progress to disclose more details on this process.

Conclusions. (i) Adsorption of CH_3 radicals on SiO_2 and Rh/SiO_2 gives absorption bands in the FTIR spectra which were attributed to the formation of adsorbed CH_3O and CH_3 species. (ii) Adsorbed CH_3 reacted with gaseous CO_2 over Rh/SiO_2 at and above 373 K to give CO and CH_4. (iii) These results strongly support the idea that during the dry reforming of methane over supported Rh, the CH_x fragments formed in the decomposition of methane do not decompose to carbon, but rather react with CO_2.

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