Infrared study of the adsorption of CO and CH_3 on silica-supported MoO_3 and Mo_2C catalysts

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Abstract

It was demonstrated that polymeric carbon formed during the preparation of Mo_2C/SiO_2 from MoO_3/SiO_2, which is located on the support. The adsorptions of CO and CH_3 on silica-supported MoO_3 and Mo_2C catalysts was investigated by FTIR. While CO did not adsorb strongly on MoO_3/SiO_2, stable bands at 2089 and 2032 cm^{-1} on Mo_2C/SiO_2 were detected in CO adsorption, which can be regarded as an indication for noble metal-like character of supported Mo_2C. $CH_{3(a)}$ on MoO_3/SiO_2 (2920 cm^{-1}) proved to be more stable, than $CH_{3(a)}$ on Mo_2C/SiO_2 (2924 cm^{-1}). In the surface reaction of $CH_{3(a)}$ on Mo_2C supported on silica ethylene formation was detected by mass spectrometric analysis. Ethylene did not form on SiO_2 and on MoO_3/SiO_2.
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1. Introduction

During the last two decades molybdenum carbide has received increasing attention as catalytic material. Excellent catalytic performance has been reported for hydrocarbon synthesis from CO and H_2 [1–5], hydrogenation of benzene [5,6], hydrogenolysis of alkanes [4,7], alcohol synthesis [8], and hydrotreating [9,10].

A new catalytic application of molybdenum carbide has recently been established in the non-oxidative catalytic transformation of methane: as regards the formation of benzene in this reaction, $MoO_3/ZSM-5$ proved to be the best catalyst [10–16], but MoO_3/SiO_2 (even MoO_3/Al_2O_3) exhibited also a reasonable activity for methane-benzene conversion [12]. Further studies, however, revealed that MoO_3 is transformed into Mo_2C in the high-temperature interaction of CH_4 with MoO_3, and the Mo_2C formed is considered to be the active site for the production of CH_3 and CH_2 fragments from methane [13–16].

The present study was undertaken to elucidate the nature of the active surface sites on Mo_2C/SiO_2 and on its precursor, MoO_3/SiO_2, by CO adsorption, and to investigate the further reactions of $CH_{3(a)}$ produced on both surfaces.

2. Experimental

MoO_3/SiO_2 samples (MoO_3 content 2 and 10 wt.%, respectively) were prepared by impregnation of

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SiO_2 (Cab-O-Sil) with an aqueous $(NH_4)_6Mo_7O_{24}$ (Aldrich) solution, the basicity of which was adjusted to pH = 9 by addition of NH_4OH (Reanal). After drying of the slurries at 380 K in air, the dried powders were heated at 863 K for 5 h in air.

For the Mo_2C/SiO_2 preparation the MoO_3/SiO_2 powder was heated up in O_2 flow (40 ml/min) up to 973 K and was kept at this temperature in O_2 for 30 min. After oxidation the sample was cooled in Ar flow (40 ml/min) to 773 K and at 773 K the Ar flow was changed to CH_4:H_2 = 1:4 gas mixture (150 ml/min), in which the sample was heated up (3 K/min) from 773 to 1023 K and was kept at 1023 K for 3 h in this gas mixture flow. The sample was cooled to 300 K in Ar flow (40 ml/min) [7]. After their preparation the Mo_2C-containing catalysts were passivated at 300 K for 1 h in a gas flow of 1% O_2 in He (50 ml/min).

The homogenized powders were pressed onto a Ta-mesh (30 mm × 10 mm, 5 mg/cm^2). The mesh was fixed to the bottom of a conventional UHV sample manipulator and was placed in a stainless steel UHV chamber capable for producing a vacuum of 1×10^{-7} Torr routinely. The mesh was resistively heated and the temperature of the sample was measured by a NiCr–Ni thermocouple directly spot-welded to Ta-mesh. Before measurements the catalyst disc was activated by heating at 773 K for 1 h under constant evacuation. In some cases the activation of the sample in vacuum was followed by a H_2 treatment at 773 K for 1 h and evacuation at 773 K for 30 min.

The generation of CH_3 radicals was performed by high-temperature pyrolysis of azomethane following the method of Stair and co-workers [17]. Mass spectroscopic analysis of the gas phase showed the signal of amu 15 corresponding to CH_3; no signals due to azomethane were found indicating that its decomposition was complete.

Infrared spectra were recorded in transmission mode with a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of ± 2 cm^{-1}. Typically 136 scans were collected. All substractions of the spectra were made without the use of a scaling factor (f = 1.0000). All the IR spectra have been taken at room temperature. Mass spectrometric analysis was performed with a QMS (Balzers) quadrupole mass-spectrometer.

3. Results

3.1. Spectra of the catalysts after different pretreatment

On evacuation at 773 K the broad absorption at around 3500 cm^{-1} due to hydrogen bridge bonded water disappeared and above 3000 cm^{-1} only the band due to OH-groups of silica at 3741 cm^{-1} can be observed in the spectra of 2% MoO_3/SiO_2 (and that of SiO_2—not shown) and 2% Mo_2C/SiO_2. No other bands remained on the spectra of 2% MoO_3/SiO_2 and SiO_2 after this pretreatment (Fig. 1).

The spectrum of 2% MoC_2/SiO_2 shows another band at 2282 cm^{-1}, which proved to be stable against evacuation at 773 K for 60 min (Fig. 1). Even a H_2-treatment at 773 K did not reduced appreciably this band. Mass spectrometric analysis of the gas phase during heating up of 2% Mo_2C/SiO_2 revealed the formation of H_2 (from 523 K), H_2O (from 623 K), small amount of C_2H_4 (from 573 K), CO and CO_2 (from 623 K). Neither the 2282 cm^{-1} band, nor the formation of C_2H_4 was observed during heating up of SiO_2 and MoO_3/SiO_2, respectively.

The appearance of the 2282 cm^{-1} should only be the consequence of the Mo_2C/SiO_2 preparation from MoO_3/SiO_2 sample, as in the spectrum of the in situ prepared Mo_2C/SiO_2 this band was also observed.

3.2. CO adsorption

After the activation of 2% MoO_3/SiO_2 (evacuation at 773 K for 1 h) 1–100 Torr CO was added to the sample at 300 K. The spectra were registered in CO at different time at 300 K and the gas phase spectrum of 1–100 Torr CO was subtracted. The spectra resulted in this process in 10 Torr CO can be seen in Fig. 2A. The bands of low intensity at 2195, 2128 and 2084 cm^{-1} appeared in the spectra. These bands were completely disappeared due to a short (15 min) evacuation at 300 K (Fig. 2C), which shows that slightly bonded CO species exist on the surface on MoO_3/SiO_2 in CO atmosphere.

The same phenomena were observed on 10% MoO_3/SiO_2. A H_2-treatment at 773 K did not affect the above results.

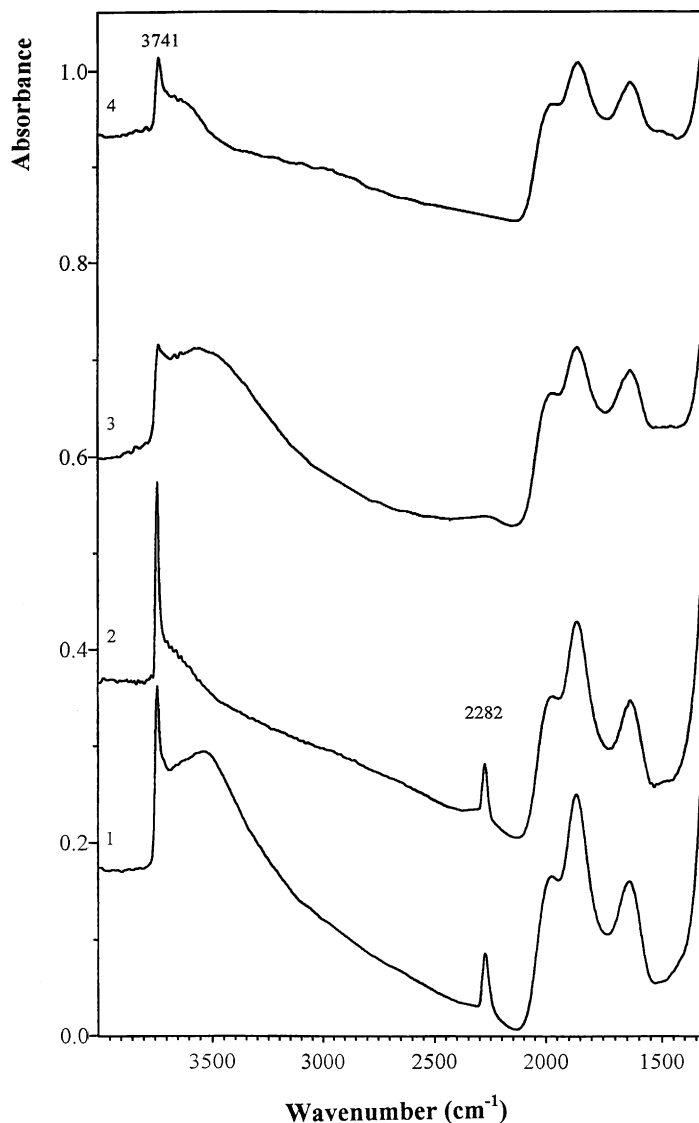In the spectra of 2% Mo_2C/SiO_2 (activated by evacuation at 773 K for 1 h) the bands of higher

Fig. 1. Spectra of the catalysts recorded at 300 K: 1–2% Mo_2C/SiO_2 after evacuation at 300 K for 22 h; 2–2% Mo_2C/SiO_2 after evacuation at 773 K for 1 h; 3–2% MoO_3/SiO_2 after evacuation at 300 K for 22 h and 4–2% MoO_3/SiO_2 after evacuation at 773 K for 1 h.

intensity at 2127, 2079 and 2055 cm^{-1} were detected in CO atmosphere (Fig. 2B). A dramatic difference between MoO_3/SiO_2 and MoC_2/SiO_2 is the fact, that bands at 2089 and 2032 cm^{-1} remained in the spectrum of Mo_2C/SiO_2 after evacuation at 300 K 15 min (Fig. 2C). Similar results were obtained on Mo_2C/SiO_2 treated with H_2 at 773 K.

Unfortunately the low transparency of 10% Mo_2C/SiO_2 did not permit any evaluable experiments.

3.3. Interaction between CH_3 and catalyst surfaces

Before the experiments with SiO_2, the SiO_2 sample was pretreated according to the preparation of MoC_2/SiO_2 from MoO_3/SiO_2. This involved: heating up SiO_2 in O_2 flow (40 ml/min) up to 973 K and kept it at this temperature in O_2 for 30 min; the sample was cooled in Ar flow (40 ml/min) to 773 K and at 773 K
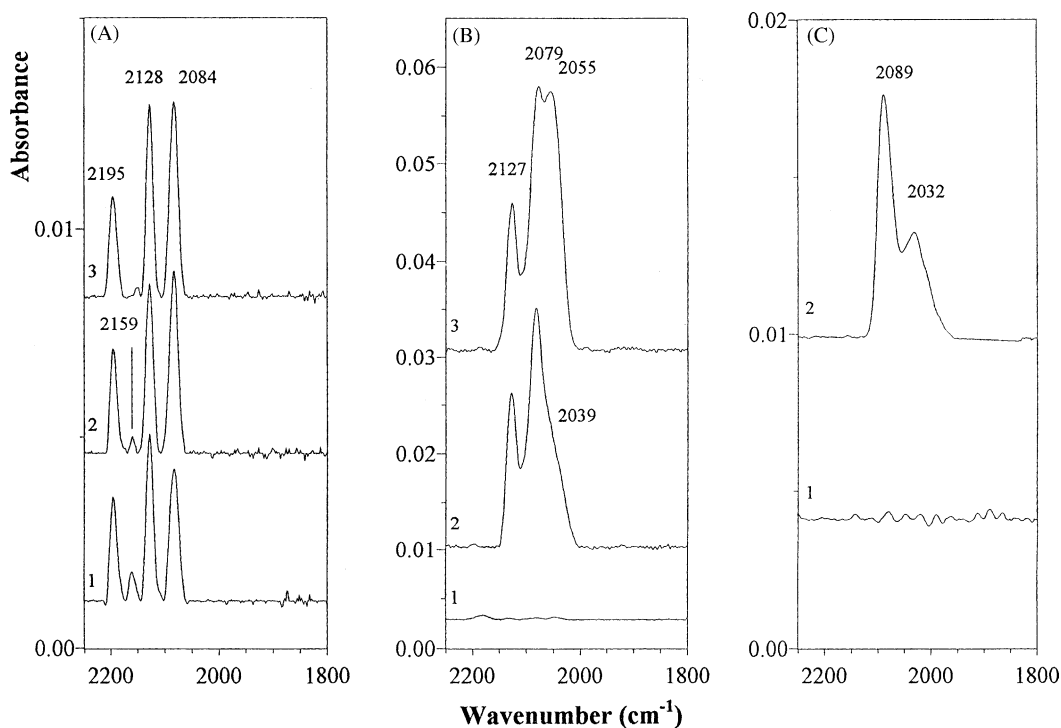
Fig. 2. (A) Spectra of 2% MoO$_3$/SiO$_2$ during the adsorption of 10 Torr CO at 300 K in time: 1–15, 2–30 and 3–60 min. Spectra were taken in CO atmosphere and the gas phase spectrum of 10 Torr CO was subtracted. (B) Spectra of 2% Mo$_2$C/SiO$_2$ in different CO pressure at 300 K for 60 min: 1–1, 2–10 and 3–100 Torr. Spectra were taken in CO atmosphere and the gas phase spectra of CO at adequate pressure were subtracted. (C) Spectra taken after the adsorption of 10 Torr CO at 300 K for 60 min and evacuation at 300 K for 15 min: 1–2% MoO$_3$/SiO$_2$ and 2–2% Mo$_2$C/SiO$_2$.

the Ar flow was changed to H$_2$ flow (150 ml/min), in which the sample was heated up from 773 to 1023 K and was kept at 1023 K for 3 h in H$_2$; then the SiO$_2$ was cooled to 300 K in Ar flow (40 ml/min). SiO$_2$ wafer was further evacuated at 773 K for 1 h in the IR cell.

The interaction of CH$_3$ with SiO$_2$ (pretreated in the above process) at 300 K caused the appearance of the bands at 2954, 2853 and 1449 cm^{-1} (due to CH$_3$O$_{(a)}$) and at 2924 and 1365 cm^{-1} (attributed to CH$_{3(a)}$) (Fig. 3A). The change of the integrated absorbance of the 2918 cm^{-1} band is depicted in Fig. 4.

The adsorption of CH$_3$ at 300 K on 2% MoO$_3$/SiO$_2$ (evacuated at 773 K for 1 h) caused the appearance of the bands at 2955, 2920, 2852, 1452 and 1366 cm^{-1} (Fig. 3B), among theme the 2955 and 2852 cm^{-1} (ν_{as}(CH$_3$) and ν_s(CH$_3$)), and the 1452 cm^{-1} (δ(CH$_3$)) are attributed to CH$_3$O$_{(a)}$, while the bands at 2920 cm^{-1} (ν(CH$_3$)) and 1366 cm^{-1} (δ(CH$_3$)) are

assigned to CH$_{3(a)}$, respectively. The integrated absorbances of the 2920 cm^{-1} band grows with the time of the above interaction (Fig. 4).

When the interaction was studied on 10% MoO$_3$/SiO$_2$ under the same experimental conditions, this band exhibited 2–3 times higher integrated absorbances (Fig. 4).

The bands at 2955, 2924, 2856, 1449 and 1373 cm^{-1} appeared in the spectra of 2% Mo$_2$C/SiO$_2$ (evacuated at 773 K for 1 h) due to the interaction between CH$_3$ and the sample at 300 K (Fig. 3C). The bands at 2955, 2856 and 1449 cm^{-1} are attributed to CH$_3$O$_{(a)}$ surface species, while the bands at 2924 and 1373 cm^{-1} are due to CH$_{3(a)}$. The integrated absorbance of the 2924 cm^{-1} band (CH$_{3(a)}$ on Mo$_2$C/SiO$_2$) slightly enhanced to that of 2920 cm^{-1} band (CH$_{3(a)}$ on MoO$_3$/SiO$_3$) in the first 30 min of the interaction, in the 60th minute, however, their surfaces concentrations were nearly the same (Fig. 4A).
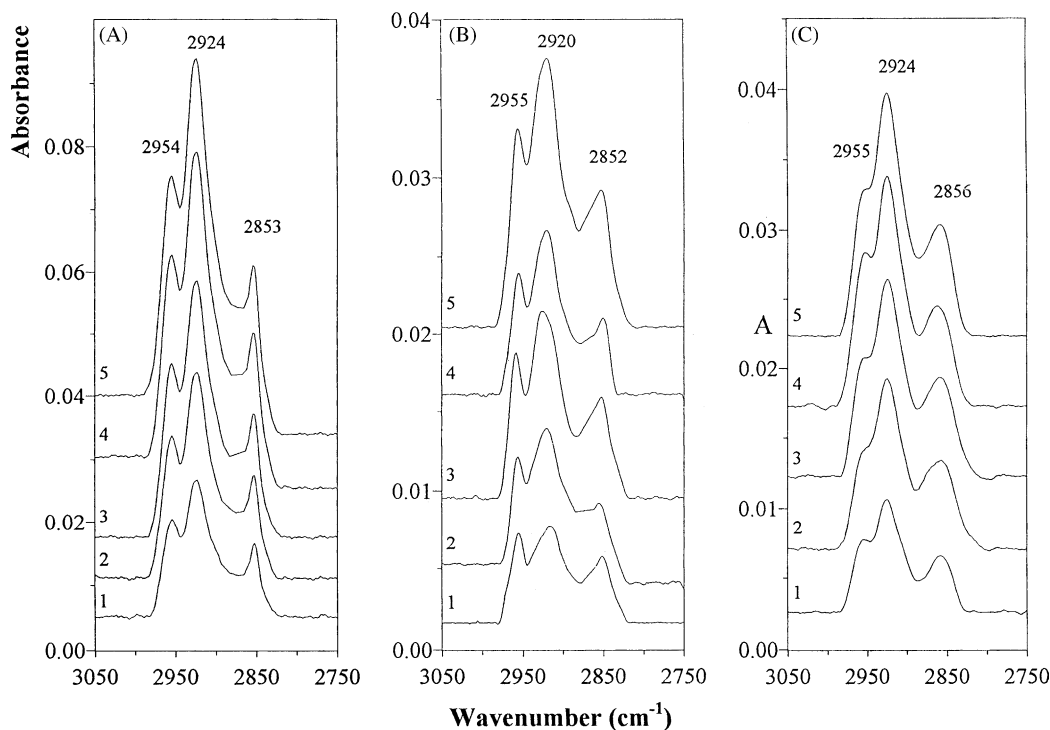
Fig. 3. Spectra taken during the interaction of CH_3 flux with the catalysts at 300 K in the function of time: (A) SiO_2; (B) 2% MoO_3/SiO_2 and (C) 2% Mo_2C/SiO_2; 1–1, 2–5, 3–15, 4–30 and 5–60 min.

3.4. Stability of $CH_{3(a)}$

The thermal stability of the surface species (with special attention to that of $CH_{3(a)}$) formed during a 30 min interaction between CH_3 and the catalysts at 300 K was investigated first by heating up the sample up to different temperatures and keeping it for 1 min at each temperatures. The thermal treatments was followed by cooling the sample to 300 K and the spectra were always taken at 300 K. The integrated absorbances of the $CH_{3(a)}$ band in the actual spectrum were ratioed by the starting integrated absorbances and the R values thus obtained were plotted in the function of temperature (Fig. 4B).

$CH_{3(a)}$ proved to be suprisingly unstable on SiO_2 (its pretreatment see in the previous chapter), as its characteristic band disappeared completely at 473 K. We note here that the band due to $CH_{3(a)}$ has formerly been detected even at 673 K on SiO_2, which was reduced at 673 K.

$CH_{3(a)}$ starts to disappear appreciably above 473 K, from 673 K its characteristic band could not be further observed on 2% MoO_3/SiO_2.

Similar experiments on 2% Mo_2C/SiO_2 catalyst revealed that the decay in the surface concentration of $CH_{3(a)}$ is enhanced above 373 K, and from 573 K its characteristic band disappears in the spectra.

Next the stability of the surface species was investigated isothermally on the catalysts at 373 and 423 K, respectively. After producing the surface species in an interaction between CH_3 and the catalysts at 300 K, the samples were heated up to 373 and 423 K for different time. The changes of R values (see above) for $CH_{3(a)}$ on SiO_2 revealed that the surface concentration of $CH_{3(a)}$ decreased to about 30% (at 373 K) and to about 10% (at 423 K) of its original value after 120 min vacuum treatment (Fig. 5A and B).

The R versus time curves for 2% MoO_3/SiO_2 and 2% Mo_2C/SiO_2 show that the loss of surface concentration of $CH_{3(a)}$ is about 40% at 373 K after 120 min
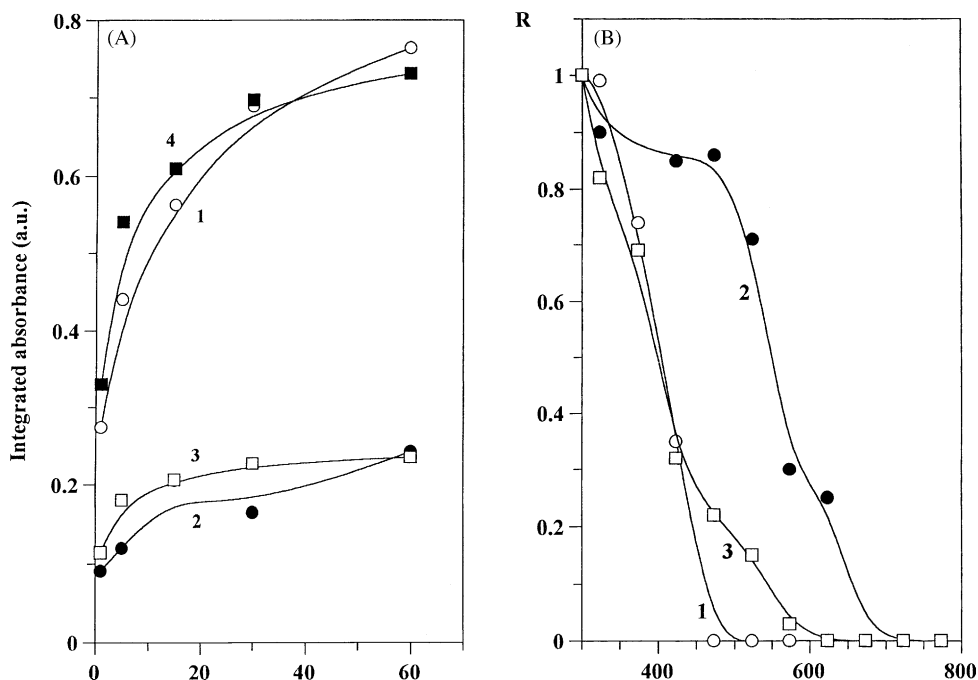
Fig. 4. (A) Change of the integrated absorbance of the $CH_{3(a)}$ band during the interaction between CH_3 flux and the catalysts at 300 K in the function of time: 1% SiO_2; 2–2% MoO_3/SiO_2; 3–2% Mo_2C/SiO_2 and 4–10% MoO_3/SiO_2. (B) Changes of R values (see text) for the $CH_{3(a)}$ band due to the effect of thermal treatment in vacuum: 1% SiO_2; 2–2% MoO_3/SiO_2 and 3–2% Mo_2C/SiO_2.

vacuum treatment on both surfaces. At 423 K, however, the extent of $CH_{3(a)}$ disappearance is 1.5–2 times higher on Mo_2C/SiO_2, than on MoO_3/SiO_2 (Fig. 5A and B).

3.5. Mass spectrometric analysis of the gas phase during vacuum treatments

During heating up of the adsorbed layer ($CH_{3(a)}$ and $CH_3O_{(a)}$) to different temperatures (see above) MS data characteristics for the gas phase products were collected on the catalysts.

A significant difference was observed in H_2 evolution: while the amount of gas phase H_2 starts to increase slightly from 723 K on SiO_2 and from 673 K on 2% MoO_3SiO_2, H_2 evolution can be observed already from 423 on 2% Mo_2C/SiO_2 (Fig. 6A).

The MS intensity versus temperature curves for CH_4 formation were similar on all surfaces: the amount of gas phase CH_4 was increased in the temperature range of 300–473 K, it remained constant between 473 and 673 K, and then a small decay was observed. Although the amount of CO evolved on

SiO_2 was constant in the whole temperature range, the amount of CO showed a maximum at 423 K on 2% MoO_3/SiO_2 and 2% Mo_2C/SiO_2 catalysts.

Basic difference was observed in the formation of ethylene: the intensity of amu 27 (C_2H_4) did not change on SiO_2 and 2% MoO_3/SiO_2, on 2% Mo_2C/SiO_2, however, a maximum at 623 K was observed (Fig. 6B).

Amu 30 (C_2H_6) changed insignificantly in the whole temperature range on all surfaces. Special care was taken to the changes of amu 51, amu 52 and amu 78 (characteristics to benzene), without any positive results. No H_2O and CO_2 formation was observed in the temperature range on different catalysts investigated in these experiments.

4. Discussion

4.1. On the nature of the 2282 cm^{-1} band

An unexpected finding was the detection of the 2282 cm^{-1} band on the base spectrum of the $Mo_2C/$
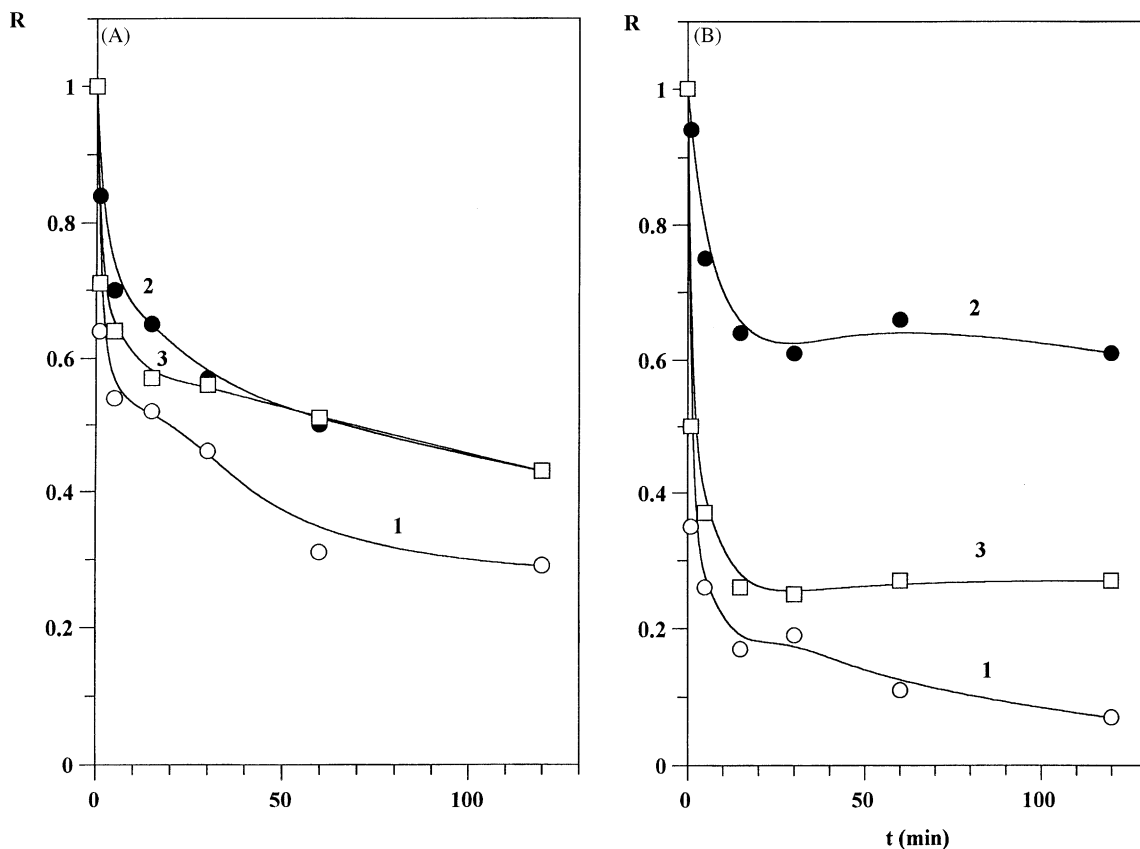
Fig. 5. Changes of R values for $CH_{3(a)}$ band due to the isothermal vacuum treatment: (A) at 373 K and (B) at 423 K; 1% SiO_2; 2–2% MoO_3/SiO_2 and 3–2% Mo_2C/SiO_2.

SiO_2. MS analysis during TPD of the Mo_2C/SiO_2 catalyst revealed the high-temperature formation of H_2, H_2O, C_2H_4 and CO; all these products suggest that surface species causing the appearance of the $2282\,cm^{-1}$ band contain carbon and hydrogen. These species formed during the preparation of Mo_2C/SiO_2 in CH_4–H_2 mixture at high-temperature.

Based on CO/H_2 adsorption data Lee et al. [18] concluded that polymeric carbon on their Mo_2C/Al_2O_3 samples appeared to block ca. 30% of the surface Mo atoms. We think that the $2282\,cm^{-1}$ band observed here is due to this polymeric carbon. For better approaching of the nature of polymeric carbon we mention that disubstituted acetylene (R–CC–R) causes a band at around $2280\,cm^{-1}$ [19]. The other possible candidates, the surface fullerenes, can be disregarded, as no such band was detected in the spectra of different fullerenes [20].

We may suppose that the polymeric carbon localizes strongly on the support, as its intensity seems to be unchanged during the high-temperature H_2 treatment and its presence does not affect the CO adsorption on Mo_2C (see below).

4.2. CO adsorption

The IR data presented here show that CO adsorption on MoO_3/SiO_2 (evacuated and reduced at 773 K) causes the appearance of the bands at 2195, 2128 and $2084\,cm^{-1}$, which can be eliminated by a short evacuation at 300 K. The spectra of Mo_2C/SiO_2 in CO atmosphere exhibit bands at 2127, 2079 and $2055\,cm^{-1}$, and in contrary with MoO_3/SiO_2, bands at 2089 and $2032\,cm^{-1}$ remained on the spectra after evacuation of gaseous CO. To our knowledge, these are the first IR spectra for CO adsorbed on
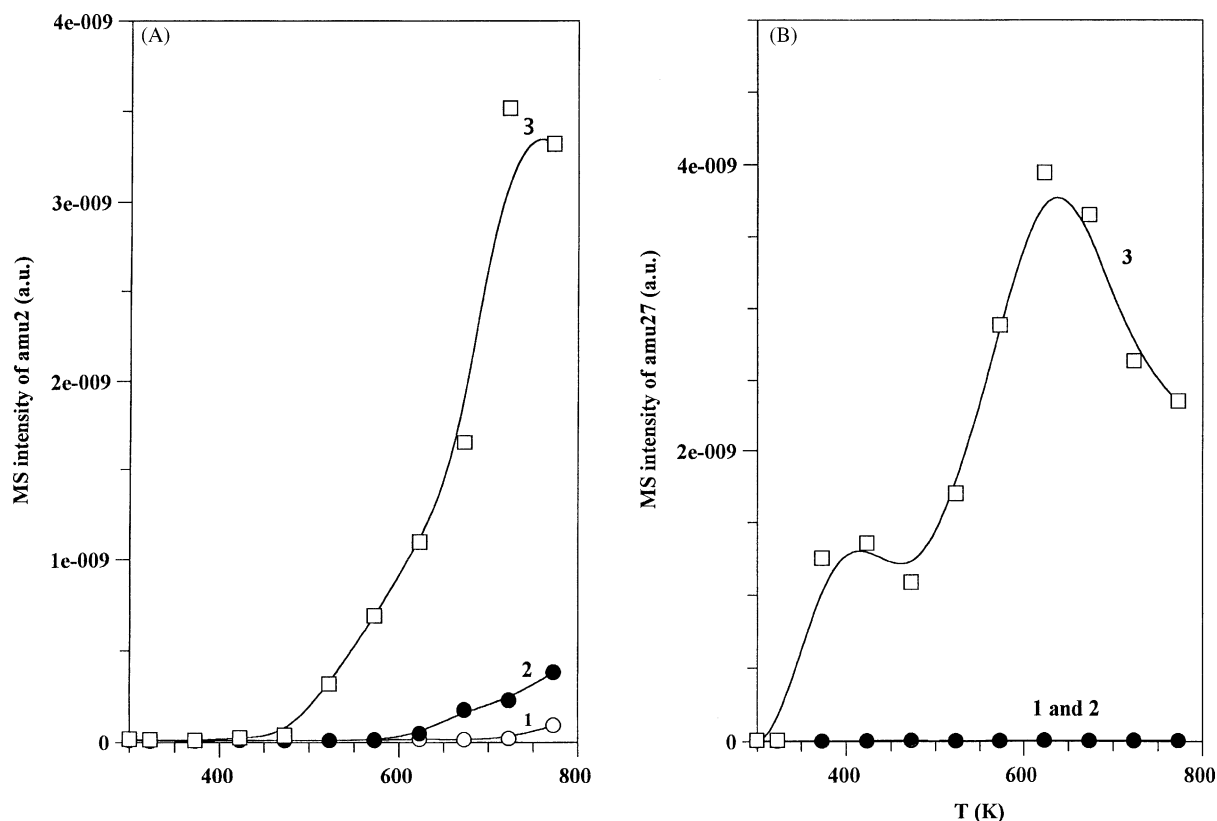
Fig. 6. MS intensity changes of gas phase products during the thermal treatment of adsorbed layer formed in the interaction between CH_3 flux and the catalysts at 300 K: (A) hydrogen (amu 2) and (B) ethylene (amu 27); 1% SiO_2; 2–2% MoO_3/SiO_2 and 3–2% Mo_2C/SiO_2.

MoO_3/SiO_2 and Mo_2C/SiO_2, respectively, but informations to aid the assignment of the observed IR bands available from a number of related studies.

Früberger and Chen [21] observed three adsorbed CO species on a Mo (1 1 0) single crystal with a surface carbide layer by HREELS. The bands at 2015 and 1850 cm^{-1} were assigned to terminally and bridge bonded CO species, respectively, while a very weak band at 1150 cm^{-1} was assigned to a "side-on" CO species. Wang et al. [22] using RAIRS detected one band due to CO adsorbed on a β-Mo_2C foil at 104 K. The position of this band found to be coverage dependent and shifted from 2054 cm^{-1} at low CO coverage to 2069 cm^{-1} at saturation coverage. The authors assigned this ν_{CO} band to a terminally bound CO species and noted that its stretching frequency is characteristic of terminally bound CO on group VIII metals.

Additional informations concerning the assignment of CO bands on MoO_3/SiO_2 and Mo_2C/SiO_2 can also be obtained from transmission IR studies of adsorbed CO on Mo/Al_2O_3 [23] and on Mo_2C/Al_2O_3 [24] catalysts. DeCanio and Storm [23] investigated the adsorption of CO on mildly reduced Mo/Al_2O_3. IR band positions of the CO bands were found to be dependent upon both the CO coverage and how recently the catalyst had been calcined prior to place it into the IR cell. The authors assigned the bands at 2175 and 2050 cm^{-1} to CO bonded to *cus* Mo^{4+} and *cus* Mo^{2+} species, respectively, and the band at 2130 cm^{-1} was assigned to physisorbed CO. Aegerter et al. [24] observed two bands on the IR spectra of CO on activated Mo_2C/Al_2O_3 catalyst; the band at 2178 cm^{-1} was assigned to CO bonded to *cus* Mo^{4+}, and the 2060 cm^{-1} band was attributed to CO adsorbed on *cus* Mo^{2+} species.

Considering the above assignments, in the case of MoO_3/SiO_2 sample we tentatively assign the $2195 \, cm^{-1}$ band to CO adsorbed on *cus* Mo^{4+}, and the band at $2084 \, cm^{-1}$ to CO adsorbed on *cus* Mo^{2+}. The $2128 \, cm^{-1}$ band is due to physisorbed CO. We note that all these bands could be eliminated by a mild evacuation at $300 \, K$.

The position and the stability of the bands due to CO adsorbed on Mo_2C/SiO_2 resemble well to that of terminally bonded CO on β-Mo_2C foil [22]. We agree with the statement [22] that the characteristics of CO adsorbed on Mo_2C are very close to that of terminally bound CO on group VIII metals. From the comparison of the data for Mo_2C/Al_2O_3 [24] and for Mo_2C/SiO_2 presented here it can be inferred that more "metallic-like" Mo_2C is produced on SiO_2, than on Al_2O_3. This might be the consequence of a stronger "metal"-support interaction occurring on Al_2O_3.

4.3. Adsorption of CH3 and its reactions

The interaction between CH_3 flux and the catalysts led to the formation of CH_3O and CH_3 on the surfaces. $CH_3O_{(a)}$ species were mainly formed on SiO_2, as it has recently been postulated [25]. As the surface concentration (integrated absorbances) of $CH_{3(a)}$ (characteristic band at $2920 \, cm^{-1}$) depended on the MoO_3 content of the MoO_3/SiO_2 catalysts (Fig. 4), it can be stated that CH_3 adsorbs rather on MoO_3, than on silica. Its adsorption place are very probably the *cus* Mo-ions of different oxidation states, which are the consequence of high-temperature oxygen lost of MoO_3. It is noteworthy that the position of the $CH_{3(a)}$ band on Mo_2C/SiO_2 is the same, as that on metal single crystals and silica-supported transition metals [25].

The thermal stability of $CH_{3(a)}$ shows marked differences on MoO_3/SiO_2 and Mo_2C/SiO_2, respectively. The band due to $CH_{3(a)}$ started to disappear at $373 \, K$ on Mo_2C/SiO_2, while on MoO_3/SiO_2 appreciable disappearance of this band could be observed only from $473 \, K$. The temperatures of complete elimination of the band due to $CH_{3(a)}$ were $573 \, K$ on Mo_2C/SiO_2 and $673 \, K$ on MoO_3/SiO_2. Isotherm experiments performed at $423 \, K$ revealed that the extent of $CH_{3(a)}$ disappearance is 1.5–2 times higher on Mo_2C/SiO_2, than on MoO_3/SiO_2. From the above findings we can state that $CH_{3(a)}$ species are less stable (more reactive) on Mo_2C/SiO_2.

As concerns the products of the surface reactions of $CH_{3(a)}$, we did not observe differences in the formations of CH_4 and CO on SiO_2, MoO_3/SiO_2 and Mo_2C/SiO_2, respectively. We may speculate that CO emerges from the decomposition of $CH_3O_{(a)}$ possibly formed on silica. The self-hydrogenation of $CH_{3(a)}$ (formation of CH_4) may occur mainly with the help of protons in surface OH groups of silica.

There is, however, a marked difference between dehydrogenation of $CH_{3(a)}$ (hydrogen evolution):

$$CH_{3(a)} \rightarrow CH_{2(a)} + \tfrac{1}{2}H_2$$

which took place already at $423 \, K$ on Mo_2C/SiO_2 and it could be observed only above $673 \, K$ on MoO_3/SiO_2. We think that this difference is the origin of C_2H_4 formation on Mo_2C/SiO_2 and the absence of ethylene on MoO_3/SiO_2. The formation of $CH_{2(a)}$ is the prerequisite of the production of ethylene via its dimerization:

$$2CH_{2(a)} \rightarrow C_2H_{4(g)}$$
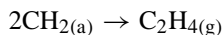
Similarly to the above results ethylene formation ($T_p = 520 \, K$) was experienced from $Mo_2C/Mo(1\,1\,1)$ single crystal surface after adsorption of CH_3I at $300 \, K$ [26]. Ethylene was not evolved from $CH_{2(a)}$ produced by CH_2I_2 adsorption on $Mo(1\,0\,0)$ and oxygen-covered $Mo(1\,0\,0)$ [27], and on MoO_x thin film [28].

Ethylene formation from the surface reaction of $CH_{3(a)}$ (without surface additives) was not observed on several metal surfaces [29–33].

The clear observation of ethylene among the gas phase products on Mo_2C/SiO_2 strengthens the former suggestion [16] that Mo_2C is the active surface component in the Mo-containing catalysts, which converts methane into ethylene. According to the present data Mo_2C itself does not produce benzene, the benzene formation needs the presence of active support, like ZSM-5 [15].

5. Conclusions

1. The stable band at $2282 \, cm^{-1}$ on the spectrum of Mo_2C/SiO_2 shows that polymeric carbon (presumably of disubstituted acethylene type) was formed on the catalyst's surface during its preparation.
2. The spectrum of CO adsorbed on Mo_2C/SiO_2 is very similar to that obtained on supported group

VIII metals. This can be accepted as an indication for noble metal-like character of silica-supported Mo_2C.

3. In the surface reaction of $CH_{3(a)}$ on Mo_2C, ethylene is detected among the gas phase products. This observation strengthens the suggestion that Mo_2C is the active surface component on Mo-containing catalysts in converting of methane into ethylene.

Acknowledgements

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