Formation and reactions of CH_3 species over Mo_2C/Mo(111) surface

F. Solymosi *, L. Bugyi and A. Oszkó

*Institute of Solid State and Radiochemistry, A. József University, and Reaction Kinetics Research Group of the Hungarian Academy of Sciences, PO Box 168, H-6701 Szeged, Hungary***

E-mail: Frigyes.Solymosi@chem.u-szeged.hu

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The reaction pathways of adsorbed CH_3 on the Mo_2C/Mo(111) surface were investigated by means of temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). CH_3 fragments were produced by the dissociation of the corresponding iodo-compound. CH_3I adsorbs molecularly on Mo_2C at 90 K and dissociates at and above 140 K. The main products of the reaction of adsorbed CH_3 are hydrogen, methane and ethylene. The coupling into ethane was not observed. The results are discussed in relevance to the conversion of methane into benzene on Mo_2C deposited on ZSM-5.

Keywords: methyl iodide, methyl, Mo_2C, C–H bond activation, CH_2 coupling, aromatization of methane, reaction pathway

1. Introduction

The study of the chemistry of CH_3 species on Mo_2C is in strong relevance to the better understanding of the activation of CH_4 by Mo_2C, and to the reaction pathways of the primary product of its decomposition. Recently, it was found that Mo_2C on ZSM-5 support (which is formed in the high-temperature reaction between MoO_3 and CH_4), is an excellent catalyst in the conversion of CH_4 into benzene [1–7]. The favourable effect of Mo_2C was attributed to the mild activation of the C–H bond, which provides a sufficient lifetime to CH_x species to undergo dimerization on Mo_2C and/or to migrate onto ZSM-5, where the further reactions proceed to give benzene [4–7].

As a source of CH_3 species we use CH_3I, which was successfully applied in our laboratory to produce CH_3 species on Pd(100) [8,9], Rh(111) [10] and on supported metal surfaces [11,12]. The chemistry of CH_3 over other metals has been summarized in several recent reviews [13–15].

2. Experimental

The Mo(111) crystal used in this work was a product of Materials Research Corporation, purity 99.99%. Initially, the sample was cleaned by cycled heating in oxygen. This was followed by cycles of argon-ion bombardment (typically 1–2 kV, 1×10^{-7} Torr Ar, 1000 K, 10 μA for 10–30 min) and annealing at 1270 K for several minutes. Mo_2C over Mo(111) surface was prepared by the method of Schöberl [16], but instead of ethylene we used propylene. The Mo(111) surface was exposed to 200 L of propylene at 900 K. The partial pressure of propylene near the sample was about 10^{-7} Torr. The resulting surface as checked by XPS and AES turned out to be carbidic showing the characteristic three-lobe line shape of carbidic carbon in AES at 255.6, 262.1 and 272.7 eV, and the C(1s) peak at 282.7 eV in the XPS [16]. CH_3I was a product of Merck. It was degassed and purified by freeze–pump–thaw cycles.

The experiments were performed in two separate UHV chambers with a routine base pressure of 2×10^{-10} Torr produced by turbomolecular, ion-getter and titanium sublimation pumps. One chamber was equipped with facilities for AES, HREELS and TPD. The heating rate for TPD measurements was ca. 10 K/s. The HREEL spectrometer (VSW, type HA-50) was situated in the lower level of the chamber and has a resolution of 70–100 cm^{-1}. All HREEL spectra were recorded with a primary energy of 5.0 eV and at an incident angle of 45°. The second system was a Kratos XSAM 800 instrument, where XPS measurements were performed using Al K_α radiation (14 kV, 10 mA). All binding energies are referred to the Fermi level which places the $Mo(3d_{5/2})$ photoelectron line at 227.2 eV.

3. Results and discussion

3.1. XPS measurements

Previous studies clearly demonstrated that XPS is a suitable method in the study of the dissociation of iodo-compounds on metal surfaces, as the binding energy of $I(3d_{5/2})$ in the atomically adsorbed state is about l.0–l.5 eV lower than that for molecularly adsorbed iodo-compounds [8–15]. Following the adsorption of CH_3I on a Mo_2C/Mo

* To whom correspondence should be addressed.

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

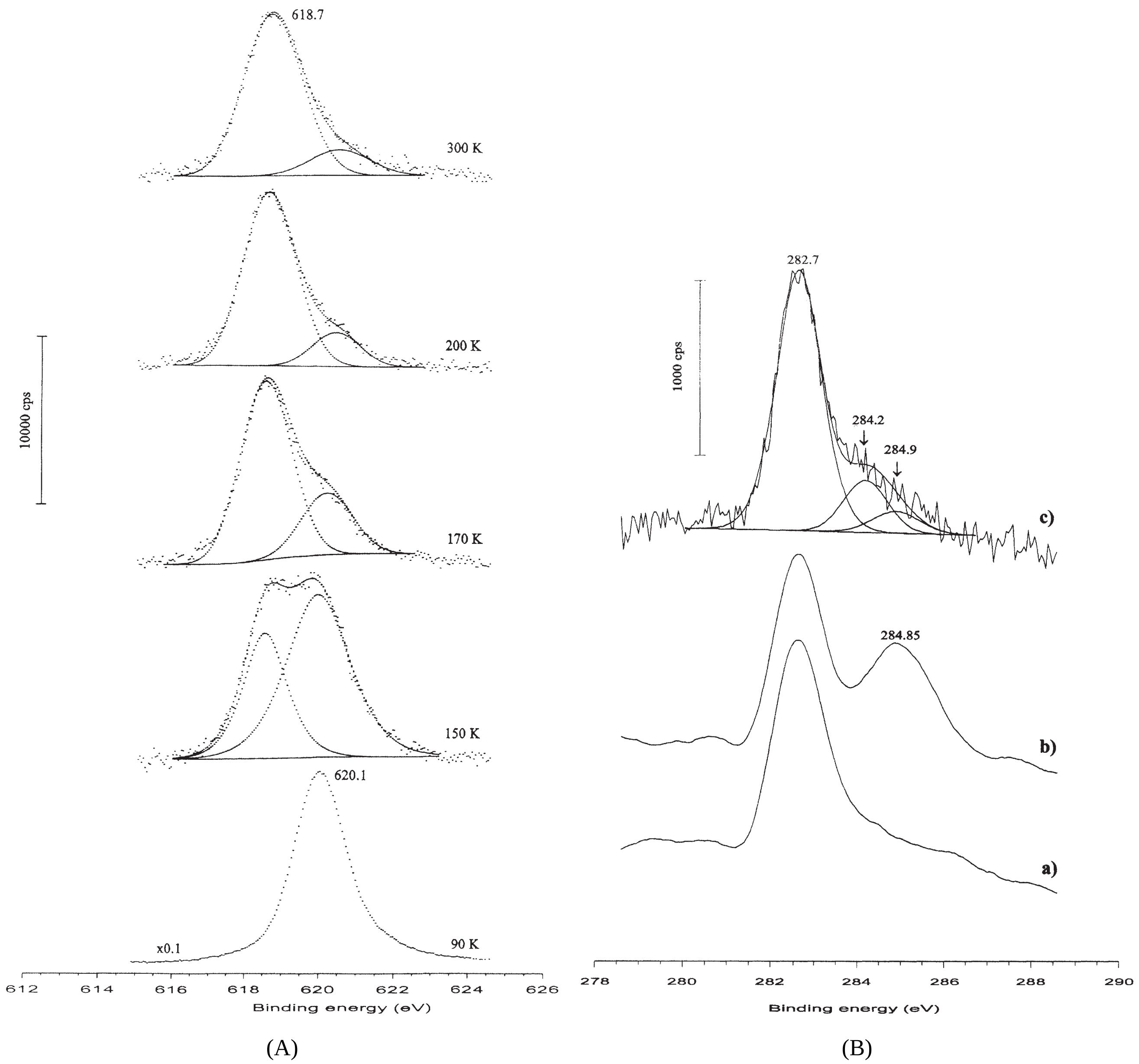


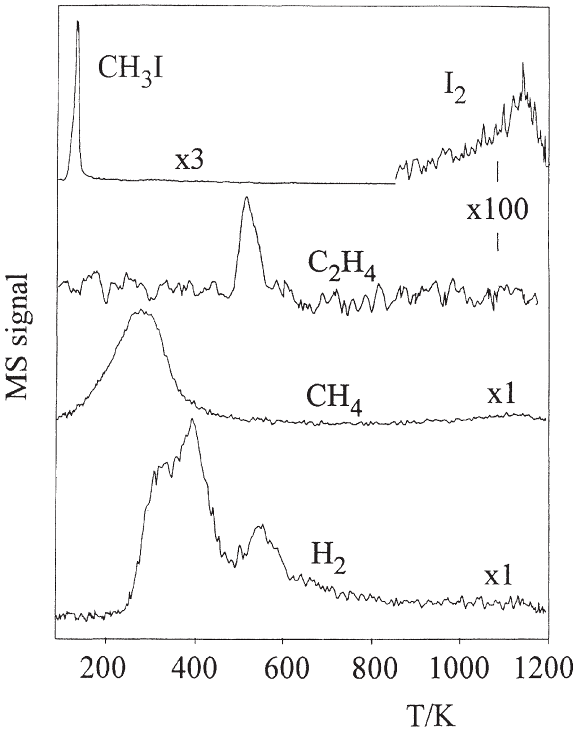
Figure 1. (A) Effects of annealing on the $I(3d_{5/2})$ peaks in the XP spectra of CH_3I adsorbed on $Mo_2C/Mo(111)$ at 90 K. (B) C(1s) peaks of $Mo_2C/Mo(111)$ (a) before CH_3I adsorption, (b) after CH_3I adsorption at 90 K, and (c) after annealing at 200 K.

sample at 90 K, the binding energy of $I(3d_{5/2})$ appeared at 620.1 eV. The position of the peak was practically independent of the coverage. In the region of the binding energy of C(1s), a new C(1s) signal developed at 284.85 eV. No appreciable changes occurred in the position of the C(1s) peak of Mo_2C.

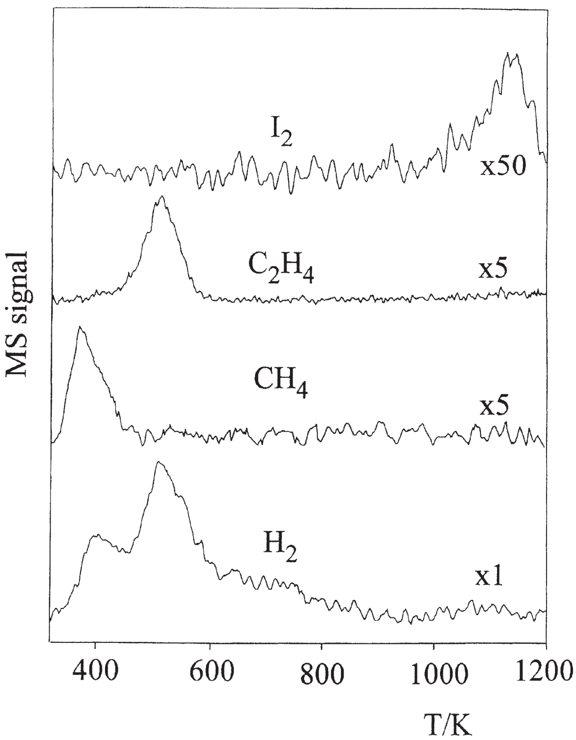
XP spectra of adsorbed layers annealed at different temperatures are presented in figure 1. A significant attenuation in the intensity of the I peak at 620.1 eV occurred above 130–140 K accompanied with an appearance of a low binding energy of the $I(3d_{5/2})$ state at 618.6–618.7 eV. This latter peak corresponds to atomically adsorbed I formed in the dissociation process. Further increase in the annealing temperature caused the diminution of the peak at 620.1 eV and a slight intensification of the peak at 618.7 eV. The complete disappearance of the first peak occurred at 300–350 K, whereas the other was eliminated above 1100 K. The new C(1s) peak also underwent a marked reduction above 150 K. Careful analysis and deconvolution of the remaining C signals revealed two minor peaks at 284.2 and 284.9 eV. The results of the XPS measurements suggest that CH_3I adsorbs molecularly on the Mo_2C surface at 90–100 K, and its dissociation starts at 140–150 K. The detection of the high energy I peak up to 300–350 K suggests that a fraction of CH_3I is bonded more strongly on the surface.

3.2. Thermal desorption measurements

The TPD spectra obtained are presented in figure 2. Molecularly adsorbed CH_3I desorbs from Mo_2C above 100 K with a peak temperature of 126 K. As this peak cannot be saturated, it is attributed to a condensed phase. No desorption of other I-containing compounds was observed below 1000 K, where the atomically bonded I desorbed. As regards the formation of other compounds, we detected the desorption of H_2 ($T_p = 380$ and 540 K), CH_4 ($T_p = 270$ K), and C_2H_4 ($T_p = 530$ K). The amount of C_2H_4 is about 1–3% of that of CH_4. It is important that we could not identify the formation of ethane. This is in complete contrast with the behavior of adsorbed CH_3 on Pt metals, where ethylene was not produced from CH_3 species [14,15].



(A)



(B)

Figure 2. TPD spectra following the adsorption of CH_3I on Mo_2C/Mo(111) (A) at 100 K and (B) at 300 K.

Some TPD experiments have been performed following the adsorption of CH_3I at 300 K. In this case the desorption of methyl iodide was not observed (figure 2(B)). A considerable increase, by a factor of 5, was experienced, however, in the amount of ethylene released with $T_p = 520$ K. A new methane peak also developed with a $T_p = 395$ K, and a high-temperature peak for H_2, $T_p = 515$ K, became more pronounced. Ethane formation was not observed at any exposures. It is important that the amount of I desorbed agreed with the value observed following the adsorption of CH_3I at 90 K. This indicates that the enhanced C_2H_4 formation is not due to the more extended decomposition of CH_3I, but rather to a change of the reaction pathway of CH_x species with the temperature. As most of the methane formed was released during the adsorption of CH_3I, the ratio of CH_4/C_2H_4 cannot be determined.

3.3. HREELS measurements

In a search for surface intermediates formed in the dissociation of CH_3I, HREELS measurements were carried out under similar conditions. Spectra are displayed in fig-

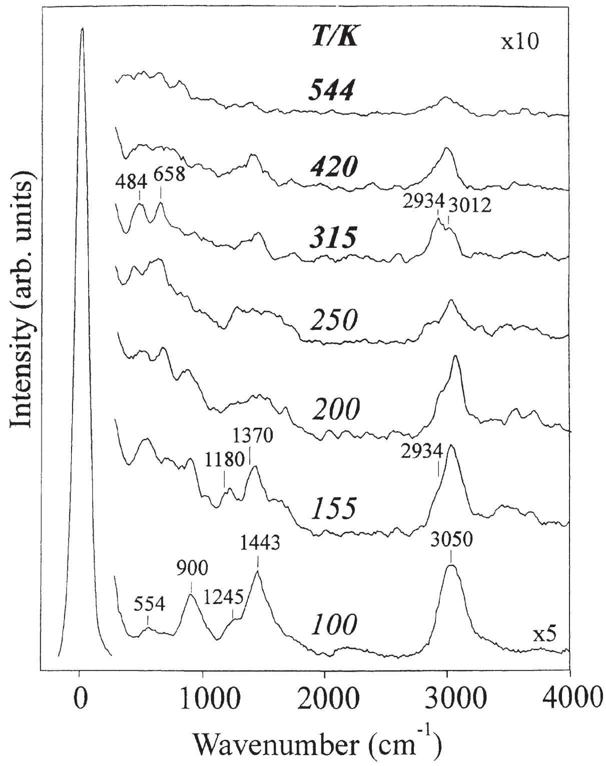


Figure 3. Effects of annealing on the HREEL spectra of CH_3I adsorbed on Mo_2C/Mo(111) at 100 and 315 K. Spectra marked by 155–250 K were taken after adsorption at 100 K. Spectra marked by 420–544 K were taken after adsorption at 315 K.

Table 1
Characteristic vibrations of adsorbed CH_3I, CH_3 and C_2H_4.

Vibrational assignment	$CH_3I + Rh(111)$ [10]	$CH_3I + Mo_2C/Mo(111)$ [this study]	$CH_3 + Rh(111)$ [10]	di-σ-$C_2H_4 + Mo_2C/Mo(110)$ [18]	$CH_3I + Mo_2C/Mo(111)$ at 310 K [this study]
$\nu_s CH_3$	3044	3065	-	–	–
$\nu_{as} CH_3$	–	–	2920	–	–
$\nu_{as} CH_2$	–	–	–	3010	3012
$\nu_s CH_2$	–	–	–	2935	2934
CH_2-scissor	–	–	–	1395	1390–1430
$\delta_a CH_3$	1430	1443	1350	–	–
$\delta_s CH_3$	1230	1245	1185	–	–
CH_2-wag (s)	–	–	–	1180	(1200)
νCC	–	–	–	1035	(1010)
CH_2-twist (s)	–	–	–	905	–
ρCH_3	900	900	760	–	–
CH_2-rock	–	–	–	635	658
ν(C–I)	522	554	–	–	484
$\nu_s MC$	–	–	–	380	–
$\nu(Rh–CH_3)$	–	–	–	–	–

ure 3. At low exposures we obtained only very weak signals. More pronounced vibration losses appeared at 3050, 1443, 1245, 900 and 554 cm^{-1} at higher exposures. With the increase of the exposure, the position of these peaks remained practically unchanged. The losses obtained corresponded well to the molecularly adsorbed CH_3I, which – together with their assignments – are listed in table 1. The features are consistent with the conclusion drawn from the XPS studies, namely that CH_3I adsorbs molecularly on Mo_2C at 90–100 K.

On warming the adsorbed layer all the losses underwent a significant attenuation at 155 K, but the characteristic losses of adsorbed CH_3I can be clearly seen at least up to 250 K. New weak peaks or shoulders at 2930, 1370 and 1180 cm^{-1} already appeared at 155 K, which we attribute to the vibrations of CH_3 species (see its characteristic vibrations and their assignments in table 1) formed in the partial dissociation of CH_3I:

$$CH_3I_{(a)} \rightleftharpoons CH_{3(a)} + I_{(a)}$$

Above 200–250 K, the vibration losses due to CH_3 are less detectable, but several new weak features can be seen in the spectra.

In order to increase the surface concentration of adsorbed species the sample has been exposed to CH_3I at 300–315 K. Spectra obtained are also shown in figure 3. Vibrational features were observed at 3012, 2934, 1434, 658 and 484 cm^{-1}. At 420 K, the shoulder at 2934 cm^{-1} was less detectable, but no other spectral changes occurred up to 544 K, where weak peaks were discernible at 3000, 1330, 815, 645 and 480 cm^{-1}. At 664 K, only a broad feature remained at 632 cm^{-1}.

The lack of the most intense loss of CH_3 above 250 K can be explained by decomposition, or self-hydrogenation, or coupling of this adsorbed species. TPD measurements revealed the formation of methane, but indicated no production of ethane at all. This means that the coupling of adsorbed CH_3 can be excluded on Mo_2C.

Taking into account the characteristic vibrations of adsorbed ethylene (table 1), it appears certain that a fraction of CH_3 underwent dissociation to CH_2 species:

$$CH_{3(a)} \rightleftharpoons CH_{2(a)} + H_{(a)}$$

and the CH_2 formed dimerized into ethylene:

$$2CH_{2(a)} \rightleftharpoons C_2H_{4(a)}$$

The study of the surface reaction of ethylene on carbide-modified Mo(110) has been recently carried out using HREELS [18]. It was found that ethylene molecules bond to the $Mo_2C/Mo(110)$ surface in the di-σ-bonded configuration, and ethylidyne species is formed from this kind of ethylene at 260–350 K [18]. Although in the present case we can count with the coexistence of several adsorbed species, which makes the vibrational assignment somewhat ambiguous, the intense loss features at 3012 and 2934 cm^{-1} in the spectrum of the adsorbed layer produced at 315 K correspond very well to the vibration, $\nu_{as}CH_2$ and $\nu_s CH_2$ of di-σ-bonded ethylene [18–24]. The spectral changes caused by annealing the adsorbed layer to higher temperature are in harmony with the transformation of strongly bonded ethylene into ethylidyne [19–24].

These results suggest that in the high-temperature conversion of methane into benzene on Mo_2C/ZSM-5 catalyst there is a high probability that not only the activation of methane occurs on Mo_2C, but the subsequent reactions, decomposition of CH_3 to CH_2 and coupling of CH_2 may also proceed on Mo_2C. The role of ZSM-5 is very likely to promote the reactions of ethylene (oligomerization and aromatization) migrated from Mo_2C onto ZSM-5.

4. Conclusions

(i) Methyl iodide dissociates on Mo_2C at and above 140 K.

(ii) Adsorbed CH_3 species is not stable on the surface, but dehydrogenates to CH_2, a fraction of which dimerizes into ethylene.

(iii) The chemistry of ethylene is similar to that occurring on metal surfaces, i.e., a strongly bonded di-σ-ethylene is formed, which transforms into ethylidyne at higher temperature.

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