

# Adsorption and reactions of butyl species over Mo<sub>2</sub>C catalyst

Frigyes Solymosi<sup>a,b,\*</sup>, Tamás Bánsági<sup>b</sup>, Tímea Süli Zakar<sup>a</sup>

<sup>a</sup> Institute of Solid State and Radiochemistry, University of Szeged, P.O. Box 168, Dom sqr 7, H-6701 Szeged, Hungary

<sup>b</sup> Reaction Kinetics Research Group, Hungarian Academy of Sciences, P.O. Box 168, Dom sqr 7, H-6701 Szeged, Hungary

Received 4 June 2004; accepted 1 August 2004

Available online 13 October 2004

## Abstract

The adsorption and reactions of butyl iodide on Mo<sub>2</sub>C/ZSM-5 and Mo<sub>2</sub>C/SiO<sub>2</sub> have been investigated by means of FTIR spectroscopy and mass spectrometry. Adsorption bands were observed following the adsorption of butyl iodide at 200–230 K that corresponds well to the vibrations of molecularly adsorbed C<sub>4</sub>H<sub>9</sub>I. At higher adsorption temperatures, bands due to the adsorbed butene and butylidyne also appeared. From the comparison of the adsorption and desorption characteristics determined on pure and Mo<sub>2</sub>C-containing ZSM-5, it was concluded that the majority of butyl iodide is attached to ZSM-5. The presence of Mo<sub>2</sub>C on ZSM-5 and SiO<sub>2</sub>, however, enhanced the rate of the decomposition, promoted the coupling of butyl species and catalyzed the formation of xylene and benzene. It was assumed that Mo<sub>2</sub>C interacting with the acidic sites of the support is the active center for the latter processes.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Adsorption; Benzene; Butane

## 1. Introduction

In an effort to convert methane into more valuable compounds, extensive research has been performed in the last decades to develop an effective catalyst for its processes [1–3]. The finding that Mo<sub>2</sub>C on ZSM-5 is capable of converting methane into benzene with 80% selectivity at 10–15% conversion is meant a significant achievement in this area [4–11]. Mo<sub>2</sub>C/ZSM-5 also catalyzed the aromatization of ethane and propane [12–14]. Recently it was found that while *n*-butane undergoes dehydrogenation and cracking on pure ZSM-5 with the formation of a small amount of benzene, the deposition of Mo<sub>2</sub>C markedly enhanced the yield and the selectivity of aromatics [15–18]. This observation suggested that Mo<sub>2</sub>C opened a new route for the activation of butane, namely the generation of butyl species from the adsorbed butane molecule, which is effectively transformed into compounds leading to aromatics.

In order to establish the role of Mo<sub>2</sub>C in the activation and reactions of alkanes, hydrocarbon fragments (CH<sub>3</sub>, CH<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>5</sub>, etc.) were prepared on Mo<sub>2</sub>C/Mo(100) by the adsorption and dissociation of the corresponding iodo compounds [19–23]. As appeared from previous studies on metal single crystal surfaces, alkyl iodides dissociate on metals at 100–300 K resulting in alkyl species, which, depending on the nature of the metals, undergo various reactions [24–27]. While this approach provided valuable informations on the bonding and reaction pathways of C<sub>x</sub>H<sub>y</sub> fragments on Mo<sub>2</sub>C/Mo(100) surface under UHV conditions, a caution is needed to use the results in establishing the mechanism of the catalytic reactions occurring under different experimental conditions, namely on highly dispersed catalysts and at the atmospheric pressure. Another difference is that in the real catalyst, Mo<sub>2</sub>C is deposited on ZSM-5, which also promotes some steps leading to aromatic compounds. To overcome this drawback, the adsorptions and reactions of butyl species formed in the dissociation of butyl iodide is examined on real catalysts, Mo<sub>2</sub>C/ZSM-5, Mo<sub>2</sub>C/SiO<sub>2</sub> and ZSM-5, under almost the same conditions as applied in the catalytic studies.

\* Corresponding author. Fax: +36 62 420 678.

E-mail address: [fsolym@chem.u-szeged.hu](mailto:fsolym@chem.u-szeged.hu) (F. Solymosi).

## 2. Experimental

Two ZSM-5 samples were used with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 80 and 280. The starting material was  $\text{NH}_4\text{-ZSM-5}$  (Zeolite International), which was calcined to produce H-ZSM-5 in air at 863 K for 5 h. Silica was the product of Aerosil. Butyl iodide (Fluka) was cleaned by several freeze-pump-thaw cycles.  $\text{MoO}_3$ -containing catalysts were prepared by impregnating H-ZSM-5 or  $\text{SiO}_2$  with a basic solution of ammonium heptamolybdate to yield different wt% of  $\text{MoO}_3$ . The suspension was dried at 373 K and calcined at 863 K for 5 h. Supported  $\text{Mo}_2\text{C}$  catalysts were produced by the carburization of calcined  $\text{MoO}_3/\text{ZSM-5}$  or  $\text{MoO}_3/\text{SiO}_2$  by ethane following the description of Green et al. [28]: the  $\text{MoO}_3$ -containing sample was heated under 10% (v/v)  $\text{C}_2\text{H}_6/\text{H}_2$ , from room temperature to 900 K at a heating rate of 0.8 K/min. After preparation, the catalysts were cooled down to room temperature under argon. The carbides were passivated in flowing 1%  $\text{O}_2/\text{Ar}$  at 300 K. Before most of the catalytic experiments, the samples were treated with  $\text{H}_2$  at 873 K for 60 min to remove the excess carbon. Unsupported  $\text{Mo}_2\text{C}$  was also prepared by carburization of  $\text{MoO}_3$  with ethane.

The catalysts have been characterized by XPS measurements. The binding energies for  $\text{Mo}(3d_{5/2})$  and  $\text{Mo}(3d_{3/2})$  were 227.8–228.2 and 230.7–231.1 eV, respectively, and for  $\text{C}(1s)$  283.8 eV. These values are consistent with those attributed to  $\text{Mo}_2\text{C}$  [8,11,29]. Infrared transmission spectra were recorded with a FTIR spectrometer (Bio-Rad, 155) with a wavenumber accuracy of  $\pm 4 \text{ cm}^{-1}$ . Typically 16 scans were recorded. All the spectra presented are different. Subtractions of the spectra were taken without use of a scaling factor ( $f=1.0000$ ). The reaction of butyl iodide was followed in a closed circulation system; the amount of catalyst was 0.2 g. The products were analyzed by a quadruple mass spectrometer.

## 3. Results

### 3.1. Infrared studies

First, the adsorption of butyl iodide was investigated by means of FTIR spectroscopy. Fig. 1A shows the IR spectra of  $\text{Mo}_2\text{C}/\text{SiO}_2$  sample following the adsorption of  $\text{C}_4\text{H}_9\text{I}$  (1.0 Torr) at 200–230 K, and after subsequent evacuation, major bands appeared at 2966, 2937, 2879, 2841, 1466, 1430, 1383, 1370 and  $1356 \text{ cm}^{-1}$ . Heating the adsorbed layer to higher temperature, the bands gradually attenuated, but it did not lead to any spectral changes. The bands completely disappeared above 300 K.

In the next experiments, the  $\text{Mo}_2\text{C}/\text{SiO}_2$  sample was heated in the presence of  $\text{C}_4\text{H}_9\text{I}$  (1.0 Torr) at different temperatures, and after 20 min the cell was evacuated for 10 min at the temperature of the adsorption. Spectra obtained are displayed in Fig. 1B. New bands, not observed previously,

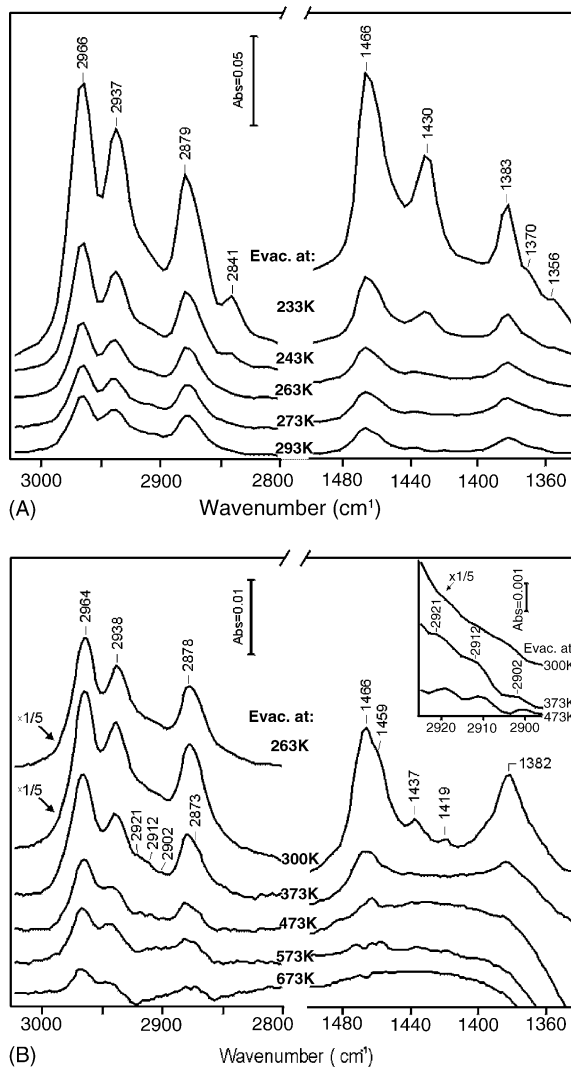


Fig. 1. (A) FTIR spectra of 1.4%  $\text{Mo}_2\text{C}/\text{SiO}_2$  following the adsorption of butyl iodide (1.0 Torr) at 200 K and subsequent evacuation at different temperatures. (B) FTIR spectra of 1.4%  $\text{Mo}_2\text{C}/\text{SiO}_2$  following the adsorption of butyl iodide (1 Torr) at different temperatures. The samples were degassed at the temperature of the adsorption before registering the spectra.

appeared at 2921, 2912, 2902, 2873, 1459 and  $1419 \text{ cm}^{-1}$  at 300–373 K. Raising the adsorption temperature led to an intensification of these bands up to 473 K, and then to their attenuation. Similar measurements were carried out with the  $\text{SiO}_2$  support alone. We detected the characteristic absorption bands of adsorbed  $\text{C}_4\text{H}_9\text{I}$ , which disappeared after evacuation at 373 K.

Adsorption of 1.0 Torr of  $\text{C}_4\text{H}_9\text{I}$  on  $\text{Mo}_2\text{C}/\text{ZSM-5}(80)$  at 200–230 K gave similar spectral features as observed for  $\text{Mo}_2\text{C}/\text{SiO}_2$  samples with only small alterations (Fig. 2A). Spectra obtained after heating the  $\text{Mo}_2\text{C}/\text{ZSM-5}(80)$  with  $\text{C}_4\text{H}_9\text{I}$  (1 Torr) at 263 K caused a slight shift in the position of the bands registered at lower temperature and produced only new weak bands at 2909, 2905 and  $2864 \text{ cm}^{-1}$ . Adsorption at higher temperature led to attenuation of all spectral features (Fig. 2B).

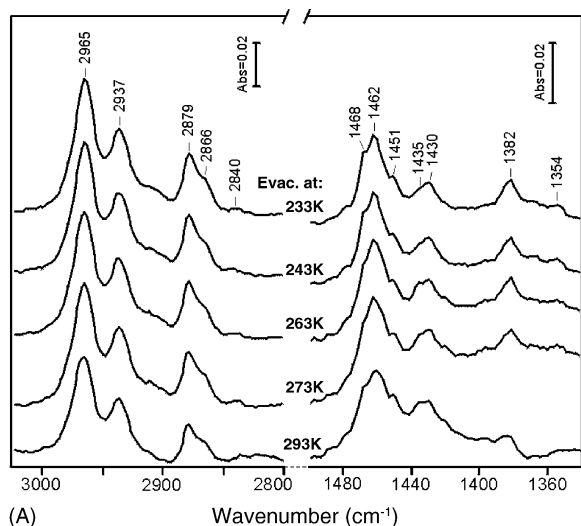
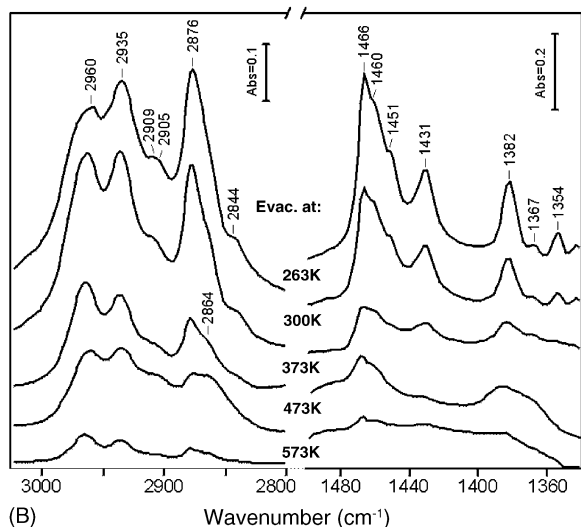
(A) Wavenumber ( $\text{cm}^{-1}$ )(B) Wavenumber ( $\text{cm}^{-1}$ )

Fig. 2. (A) FTIR spectra of 1.4%  $\text{Mo}_2\text{C}/\text{ZSM-5}(80)$  following the adsorption of butyl iodide (1.0 Torr) at 200 K and subsequent evacuation at different temperatures. (B) FTIR spectra of 1.4%  $\text{Mo}_2\text{C}/\text{ZSM-5}(80)$  following the adsorption of butyl iodide (1 Torr) at different temperatures. The samples were degassed at the temperature of the adsorption before registering the spectra.

In order to facilitate the assignments of the above bands, the IR spectra of the adsorbed 1-butene have been also registered under the same experimental conditions. At low temperature, 173–206 K, intense absorption bands appeared at 2972, 2966, 2941, 2918, 2902, 2879, 2848, 1465, 1443, 1417 and  $1380\text{ cm}^{-1}$ , the intensity of which decreased with the rise in evacuation temperature (Fig. 3). No development of new bands were experienced between 200–250 K. Adsorbing 1-butene at higher temperatures, 300–373 K, produced weak bands at 2933, 2926, 2865 and  $2857\text{ cm}^{-1}$  (Fig. 3).

### 3.2. Thermal desorption measurements

In the following experiments, we determined the product desorbed after  $\text{C}_4\text{H}_9\text{I}$  adsorption on various catalysts. Ad-

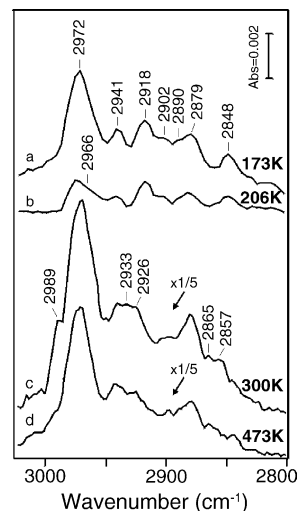


Fig. 3. FTIR spectra of 1.4%  $\text{Mo}_2\text{C}/\text{SiO}_2$  following the adsorption of 1-butene (1.0 Torr) at different temperatures. Spectra of (a) and (b) were obtained after evacuation at 173 and 206 K, respectively.

mitting 10 Torr of  $\text{C}_4\text{H}_9\text{I}$  onto  $\text{Mo}_2\text{C}/\text{ZSM-5}$  at 300 K the mass spectrum of the  $\text{C}_4\text{H}_9\text{I}$  showed only a slight change compared to that observed in the absence of the catalyst. After degassing the reactor for 10 min, the catalyst has been heated up with approx. 35 K/min. As shown in Fig. 4, the desorption of butyl iodide (57 amu) started at  $\sim 360\text{ K}$  with  $T_p \approx 412\text{ K}$  followed by butene (43 amu)  $T_p = 416\text{ K}$ , and bu-

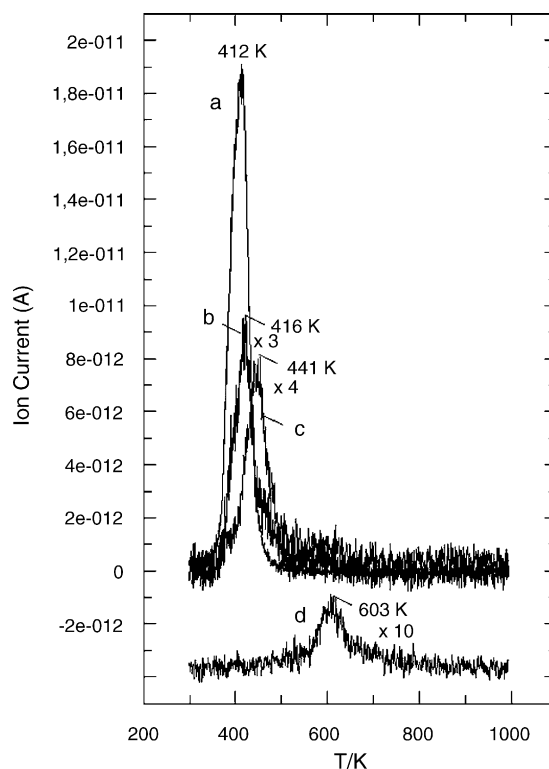


Fig. 4. Desorption products formed following the heating of 1.4%  $\text{Mo}_2\text{C}/\text{ZSM-5}(80)$  after adsorption of butyl iodide (10 Torr) at 300 K. (a) butyl iodide; (b) butene; (c) butane; (d) xylene.

tane (58 amu)  $T_p = 441$  K. In addition, the release of xylene (91 amu)  $T_p = 603$  K also occurred. Taking into account the calibration of our MS to various products we came to the conclusion that the intensities of butene, butane and xylene are 15, 10 and  $\sim 100$  times, respectively, higher than those calculated from the fragmentation of butyl iodide. Very similar TPD curves were obtained for pure ZSM-5(80), but the amount of desorbed butane and butene was somewhat lower.

### 3.3. Decomposition of $C_4H_9I$

The decomposition of  $C_4H_9I$  (10 Torr) was next, followed by stepwise increase of the temperature. On ZSM-5(80) a decrease in the pressure of  $C_4H_9I$  started at 373 K together with the formation of hydrogen, butene and propane (44 amu). At 473 K the evolution of xylene, and at 573 K that of benzene was observed. This was accompanied with the decay of the butene. Above 373 K, the formation of octanes (71 amu) was also detected. The other products were methane and ethane. The rise of the temperature was clearly favorable for the formation of xylene and benzene. The deposition of 2%  $Mo_2C$  on ZSM-5(80) enhanced the rate of the reaction of butyl iodide, and particularly that of the  $H_2$  production. Its favorable effect was clearly exhibited in the formation of xylene and benzene, which occurred at lower temperature and to a greater extent. In addition,  $Mo_2C$  also promoted the production of octane, octene and octadiene.

A particular attention was paid to the catalytic effect of  $Mo_2C/SiO_2$  samples, as silica, in contrast to ZSM-5, is practically inactive in the aromatization of *n*-butane [18]. Pure silica exerted no or only a very slight influence on the decomposition of  $C_4H_9I$ . On  $Mo_2C/SiO_2$  catalyst, however, we registered a well-measurable reaction from 423 K and besides butene and butane, the formation of xylene, benzene and octane was also observed at higher temperatures. They were

produced, however, in much less concentrations compared to ZSM-5-based catalysts. Relevant data for the comparison of the effects of different catalysts on the production of aromatics and octane are presented in Fig. 5.

Some experiments have been performed under isotherm conditions at 773 K. At this temperature the decomposition of butyl iodide is relatively fast, even the homogeneous reaction is well-measurable, but aromatics are not formed in the absence of catalysts. The promoting effect of  $Mo_2C$  is well-exhibited in this case, too. As regards the catalytic efficiency, the ZSM-5(80) samples were always superior to ZSM-5(280)-based catalysts. Aromatics and  $C_8$  compounds were produced on  $Mo_2C/SiO_2$  too, but the amount was almost one order of magnitude less compared to that measured on ZSM-5 type catalysts. Some data are shown in Fig. 6.

## 4. Discussion

### 4.1. Infrared spectroscopic measurements

The absorption bands observed following the adsorption of butyl iodide on  $Mo_2C$ -containing catalysts at 200–230 K correspond very well to the different vibrations of adsorbed  $C_4H_9I$  (Table 1). On heating the adsorbed layer under continuous evacuation up to 275–293 K caused a gradual attenuation of the absorption bands without any shift in their position and the development of new absorption features. This behaviour may suggest that no dissociation or reactions occurred on the catalyst. This conclusion is probably not right as recent XPS measurements on  $Mo_2C/Mo(100)$  surface that disclosed the dissociation of  $C_4H_9I$  at 200–300 K, which was not accompanied with any detectable spectral changes in the HREEL spectra [33]. The failure of the detection of the dissociation by HREELS was attributed to the low resolution of

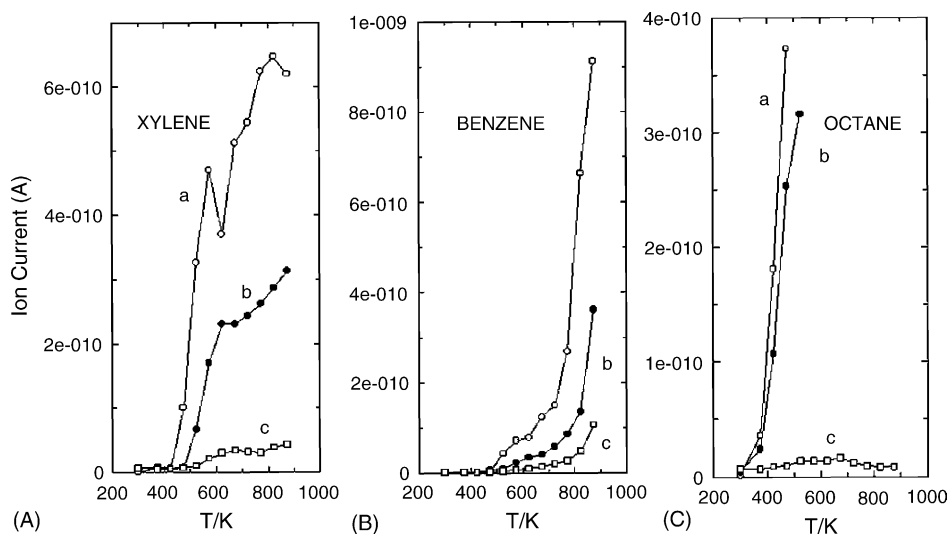


Fig. 5. Formation of xylene (A), benzene (B) and octane (C) in the reaction of butyl iodide (10 Torr) on (a) 1.4%  $Mo_2C/ZSM-5(80)$ , (b) ZSM-5(80) and (c) 1.4%  $Mo_2C/SiO_2$  during the gradual increase of the temperature.

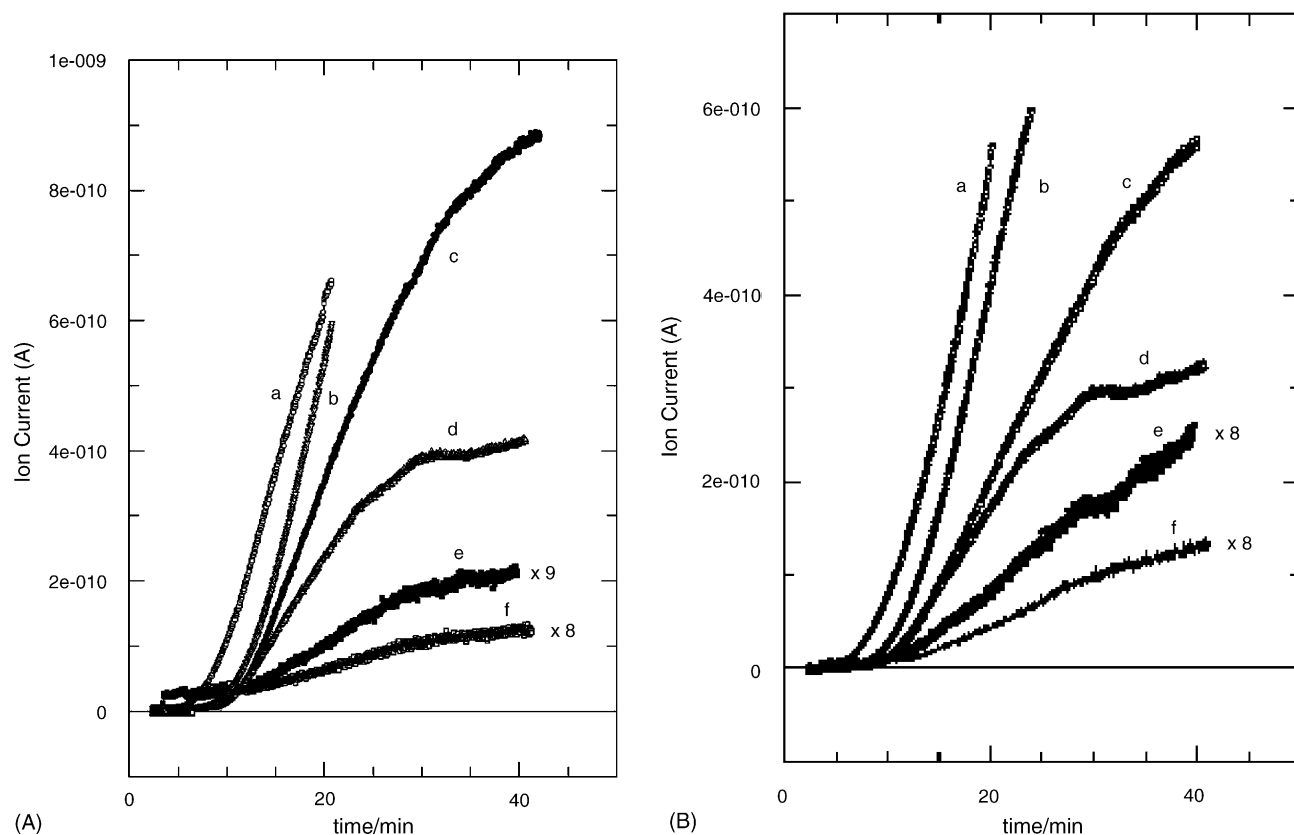


Fig. 6. Formation of xylene (A) and benzene (B) on (a) 1.4% Mo<sub>2</sub>C/ZSM-5(80), (b) ZSM-5(80), (c) 1.4% Mo<sub>2</sub>C/ZSM-5(280), (d) ZSM-5(280), (e) 15% Mo<sub>2</sub>C/SiO<sub>2</sub> and (f) 1.4% Mo<sub>2</sub>C/SiO<sub>2</sub> in the reaction of butyl iodide (10 Torr) at 773 K.

Table 1  
Characteristic absorption bands and vibration losses of various C<sub>4</sub> compounds

| Approximate mode description                        | Ar-matrix/<br>C <sub>4</sub> H <sub>9</sub> I IR,<br>20 K [30] | SiO <sub>2</sub> /C <sub>4</sub> H <sub>9</sub> I<br>IR, 200 K<br>(this work) | Mo <sub>2</sub> C/SiO <sub>2</sub> /<br>C <sub>4</sub> H <sub>9</sub> I IR,<br>200–233 K<br>(this work) | Pt/SiO <sub>2</sub> /1-butene<br>IR, 300 K [31] | (4 × 4)-C/Mo(1 1 0)/<br>isobutene HREELS,<br>150 K [32] | Pt(1 1 1)<br>trans-butylidyne<br>RAIRS, 270 K [31] | (4 × 4)-C/Mo(1 1 0)/<br>butylidyne HREELS,<br>300 K [32] |
|---|--|---|---|---|---|--|--|
| CH <sub>3</sub> and CH <sub>2</sub> asym. stretches | 2972 (vs)  | 2964  | 2965  | 2960  | 2943  |  |  |
| CH <sub>2</sub> sym. stretch                        | 2943 (vs)  | 2937  | 2937, 2911  | 2932, 2920                                      |   |  |  |
| CH <sub>2</sub> sym. stretch                        | 2884 (s)   | 2879  | 2879  | 2890  |   |  |  |
| CH <sub>2</sub> sym. stretch                        | 2872 (s)   | 2868  | 2871  | 2875  | 2874  | 2934   | 2936   |
| CH <sub>3</sub> sym. stretch                        | 2847 (s)   | 2840  | 2841  |   |   | 2874   | 2875   |
| CH <sub>3</sub> asym. deformation                   | 1469 (s)   | 1466  | 1466  | 1480  |   |  |  |
| CH <sub>3</sub> asym. deformation                   |  | 1461  | 1461  |   |   |  |  |
| CH <sub>2</sub> deformation                         | 1445 (w)   |   |   | 1450  |   |  | 1441   |
| CH <sub>2</sub> deformation                         | 1435 (w)   | 1430  | 1430  |   | 1434  |  |  |
| CH <sub>2</sub> deformation                         | 1430 (s)   |   |   | 1408  |   |  |  |
| CH <sub>3</sub> sym. deformation                    |  | 1382  | 1383, 1369,<br>1355   | 1380, 1352                                      | 1353  | 1377   | 1366   |
| CH <sub>2</sub> twist                               | 1288 (s)   |   |   |   |   | 1331   |  |
| CH <sub>2</sub> twist                               | 1260 (m)   |   |   |   |   |  | 1238   |
| CH <sub>2</sub> wag                                 | 1250 (vs)  |   | 1200  | 1330  |   | 1110   | 1035   |
| CC stretch  | 1014 (w)   |   | 1033  |   | 1035  |  |  |
| CC stretch  | 992 (w)  |   |   |   |   |  | 852  |
| CC stretch  | 966 (w)  |   |   |   | 960   |  |  |



the spectrometer, which does not make it possible to distinguish between them. The fact that we could not find any spectral differences of the annealed layer at 220–300 K even by sensitive FTIR spectroscopy indicates that the vibration characteristics of the adsorbed  $C_4H_9I$  and  $C_4H_9$  are very similar, e.g., undistinguishable. This is in contrast to the other alkyl iodides with lower C number, where this distinction can be easily achieved [19–23].

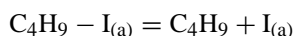
A well-observable spectral changes occurred, however, when the  $Mo_2C$  catalyst was kept in the presence of  $C_4H_9I$  at 275–300 K for 20–30 min. New bands appeared at 2902 and 2912  $cm^{-1}$ , which can be likely attributed to the vibrations of adsorbed butene species (Figs. 1 and 2). The bands at 2921 and 2864–2870  $cm^{-1}$  developed at 373 K are probably due to adsorbed butylidene. These features were also observed when 1-butene interacted with  $Mo_2C$  catalyst.

#### 4.2. Reactions of butyl iodide

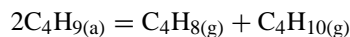
Studies performed under UHV conditions on  $Mo_2C$  prepared on  $Mo(1\ 0\ 0)$  single crystal surfaces revealed that the weakly adsorbed  $C_4H_9I$  ( $T_a \approx 100$  K) desorbs in two peaks,  $T_p = 160$  and 280 K [33]. The more strongly adsorbed fraction dissociates at 140–300 K, and the butyl species formed undergoes dehydrogenation and hydrogenation to give butene ( $T_a = 246$  and 322 K) and butane ( $T_p = 246$ –290 K). Higher hydrocarbons or aromatic compounds, benzene, toluene and xylene, were not identified in the desorbing gases. The product of the coupling of butyl species,  $C_8$  compound was detected only in the trace amounts. When the adsorption temperature was higher ( $T_a = 300$  K), the gaseous products formed were the same, but the desorption of butyl iodide was not observed. A very stable  $C_xH_y$  fragments also formed in the reaction of  $C_4H_9$  on the surface, however, as indicated by HREEL spectra and the release of hydrogen above 550–600 K.

The situation in the present case using supported  $Mo_2C$  and working of higher pressures is different from many respects. TPD measurements revealed the presence of adsorbed  $C_4H_9I$  which desorbs in a peak,  $T_p = 412$  K. In the light of the results obtained for  $Mo_2C/Mo(1\ 0\ 0)$  we cannot expect the existence of undissociated  $C_4H_9I$  on the  $Mo_2C$  surface at and above 300 K. It is more likely that most part of this butyl iodide is bonded to the ZSM-5, as we obtained the same peak for  $C_4H_9I$  desorption using pure ZSM-5 surface. This conclusion is supported by the results for  $Mo_2C/SiO_2$  when the amount of desorbed  $C_4H_9I$  was significantly less. Note that on pure silica practically no  $C_4H_9I$  remained adsorbed after evacuation at 300 K. This is in harmony with the FTIR measurements.

The release of butene and butane above 400 K in TPD measurements suggests the occurrence of the dissociation of adsorbed  $C_4H_9I$ , e.g., the formation butyl species



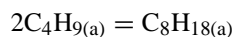
a fraction of which may undergo disproportionation



to yield butene and butane. In addition, we may count with the dehydrogenation step



and also with the decomposition of  $C_4H_9$  to  $C_xH_y$  and  $H_2$ . Octane, the product of the coupling of  $C_4H_9$



was detected only in a trace amount. In contrast, the formation of xylene was well-measurable even by TPD experiment (Fig. 4).

The promoting effect of  $Mo_2C$  on the above processes came into fore when gaseous  $C_4H_9I$  was contacted with  $Mo_2C$ -containing catalyst (Figs. 5 and 6). This was primarily exhibited in the enhanced formation of aromatics, xylene and benzene. This implies that  $Mo_2C$ , besides facilitating the cleavage of C–I bond, promotes the coupling of hydrocarbon fragments and the reactions leading to aromatics. As concerns the production of xylene and benzene, the results presented in Fig. 6 show that the ZSM-5-based catalysts with low Si/Al ratio is more active compared to the zeolite with high silica content. The total acidic sites/unit cell determined by  $NH_3$  adsorption is 9.79 for ZSM-5(80), and only 1.32 for ZSM-5(280). This strongly supports the idea that the acidic sites play an important role in the aromatization of lower hydrocarbons. We may also conclude that these processes proceed more easily at the  $Mo_2C/ZSM-5$  interface, e.g., on the  $Mo_2C$  particles interacting with Brönsted centers of ZSM-5.

When  $Mo_2C$  was deposited on silica, most of the reaction products were identified, but their formation occurred to a limited extent even using higher loading of  $Mo_2C$  (Figs. 5 and 6). This is particularly true for the xylene and benzene. In the study of the reaction of *n*-butane, we found that the aromatization processes occur to less extent even over  $Mo_2C/SiO_2$  [18]. As silica does not contain Brönsted centers, and this acidic site is not generated during the carburization of  $MoO_3$  [34], we may infer that the aromatization processes are facilitated by the  $Mo_2C$  particles interacting with the Lewis sites of the silica.

## 5. Conclusions

- (i) In harmony with the HREELS measurements performed on  $Mo_2C/Mo(1\ 0\ 0)$  [33], there was no spectral indication of the formation of butyl species in the dissociation of butyl iodide on  $Mo_2C$ -containing catalysts.
- (ii) Butyl iodide adsorbed on ZSM-5 at 300 K desorbs with  $T_p = 412$  K. Another fraction disproportionate through the possible formation butyl species into butene and butane.

- (iii) Mo<sub>2</sub>C deposited on ZSM-5 promotes the decomposition of butyl iodide, and the formation of xylene, benzene and different C<sub>8</sub> compounds.
- (iv) The catalytic effect of Mo<sub>2</sub>C towards the coupling of butyl groups and formation of aromatics was well-exhibited on inactive SiO<sub>2</sub> support.

## Acknowledgements

The work was supported by the Hungarian Academy of Sciences and by Grant OTKA T 38233 and TS 40877.

## References

- [1] D.M. Bibby, C.D. Chang, R.F. Howe, S. Yurchak (Eds.), *Stud. Surf. Sci. Catal.* — Methane conversion, vol. 36, Elsevier, Amsterdam, 1988.
- [2] Y. Ono, *Catal. Rev. - Sci. Eng.* 34 (1992) 179.
- [3] J.H. Lunsford, in: L. Guzzi, F. Solymosi, P. Tétényi (Eds.), *Proceedings of the 10th International Congress in Catalysis*, Akadémiai Kiadó, Budapest, 1993, p. 103.
- [4] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, *Catal. Lett.* 21 (1993) 35.
- [5] Y. Xu, L. Wang, M. Xie, X. Gou, *Catal. Lett.* 30 (1995) 135.
- [6] F. Solymosi, A. Erdőhelyi, A. Szőke, *Catal. Lett.* 32 (1995) 43.
- [7] F. Solymosi, A. Szőke, J. Cserényi, *Catal. Lett.* 39 (1996) 157.
- [8] F. Solymosi, J. Cserényi, A. Szőke, T. Bánsági, A. Oszkó, *J. Catal.* 165 (1997) 150.
- [9] D.W. Wang, J.H. Lunsford, M.P. Rosynek, *Top. Catal.* 3 (4) (1996) 299.
- [10] J.H. Lunsford, M.P. Rosynek, D.W. Wang, *Stud. Surf. Sci. Catal.* 107 (1997) 257.
- [11] D.W. Wang, J.H. Lunsford, M.P. Rosynek, *J. Catal.* 169 (1997) 347.
- [12] F. Solymosi, A. Szőke, *Appl. Catal. A* 166 (1998) 225.
- [13] F. Solymosi, R. Németh, *Catal. Lett.* 62 (1999) 197.
- [14] F. Solymosi, R. Németh, L. Óvári, L. Egri, *J. Catal.* 195 (2000) 316.
- [15] S. Yuan, S.B. Derouane-Abd Hamid, Y. Li, P. Ying, Q. Xin, E.G. Derouane, C. Li, *J. Mol. Catal. A: Chem.* 180 (2002) 245.
- [16] F. Solymosi, R. Németh, A. Széchenyi, *Catal. Lett.* 82 (2002) 213.
- [17] S. Yuan, S.B. Derouane-Abd Hamid, Y. Li, P. Ying, Q. Xin, E.G. Derouane, C. Li, *J. Mol. Catal. A: Chem.* 184 (2002) 257.
- [18] F. Solymosi, A. Széchenyi, *J. Catal.* 223 (2004) 221.
- [19] F. Solymosi, L. Bugyi, A. Oszkó, I. Horváth, *J. Catal.* 185 (1999) 160.
- [20] F. Solymosi, L. Bugyi, A. Oszkó, *Catal. Lett.* 57 (1999) 103.
- [21] L. Bugyi, A. Oszkó, F. Solymosi, *Surf. Sci.* 516 (2002) 74.
- [22] L. Bugyi, A. Oszkó, F. Solymosi, *Surf. Sci.* 519 (2002) 139.
- [23] L. Bugyi, A. Oszkó, F. Solymosi, *Surf. Sci.* 539 (2003) 1.
- [24] B.E. Bent, *Chem. Rev.* 96 (1996) 1361.
- [25] F. Zaera, *Acc. Chem. Res.* 25 (1992) 260.
- [26] F. Solymosi, *J. Mol. Catal. A* 131 (1998) 121.
- [27] F. Zaera, *Catal. Lett.* 91 (2003) 1.
- [28] A.J. Brungs, A.P.E. York, J.B. Claridge, C. Márquez-Alvarez, M.L.H. Green, *Catal. Lett.* 70 (2000) 117.
- [29] L. Leclercq, M. Provost, H. Pastor, J. Grimblot, A.M. Hardy, L. Gengembre, G. Leclercq, *J. Catal.* 117 (1989) 371.
- [30] A.J. Barnes, H.E. Hallam, J.D.R. Howells, G.F. Scrimshaw, *J. Chem. Soc., Faraday Trans. II* 69 (1973) 738.
- [31] M.A. Chesters, C. De La Cruz, P. Gardner, E.M. McCash, P. Pudney, G. Shahid, N. Sheppard, *J. Chem. Soc., Faraday Trans.* 86 (1990) 2757.
- [32] J. Eng Jr., B. Fruhberger, J.G. Chen, B.E. Bent, *Catal. Lett.* 54 (1998) 133.
- [33] L. Bugyi, A. Oszkó, F. Solymosi, *Surf. Sci.* 561 (2004) 57.
- [34] L. Óvári, F. Solymosi, *J. Catal. A: Chem.* 207 (2004) 35.