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Photocatalytic Decomposition of Formic Acid on Mo_2C-Containing Catalyst

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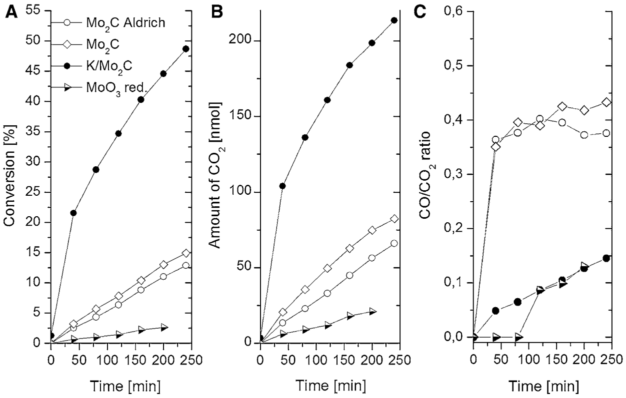
Abstract The photocatalytic behavior of pure and supported Mo_2C was investigated in the vapor-phase decomposition of formic acid. IR studies showed that illumination promoted the dissociation of molecularly adsorbed HCOOH and the decomposition of formate species formed on Mo_2C/TiO_2 sample. Mo_2C prepared on TiO_2 enhanced the extent of the photocatalytic decomposition exhibited by TiO_2. Both the dehydrogenation and dehydration reactions occurred. Interestingly, Mo_2C had photocatalytic properties even in unsupported state and also on an inert SiO_2 surface. Its photoactivity was dramatically increased by the presence of potassium prepared by the carburization of K_2MoO_4, when the dehydrogenation came into prominence. Pure and K-doped Mo_2C showed an appreciable photocatalytic effect in the visible light, which was attributed to their lower bandgap.

Graphical Abstract Photocatalytic decomposition of HCOOH on pure and K-doped Mo_2C at 300 K. (A) conversion of HCOOH; (B) Formation of CO_2; (C) CO/CO_2 ratio.



Keywords Photocatalytic decomposition of HCOOH · Supported and unsupported Mo_2C catalyst · Effect of potassium promotor · Photo-induced reaction in visible light

1 Introduction

There is a great effort to develop an effective and selective catalyst for the decomposition of organic materials to produce H_2, if possible, free of CO. Recently it was reported in several publications that the vapor phase decomposition of HCOOH catalyzed by supported Pt metals [1–7] and nanosize Au [8] is a suitable process for the generation of almost pure, CO-free H_2. In the following step an attempt was made to replace the expensive Pt metals with cheaper, but still powerful catalyst. As supported and unsupported Mo_2C was active in several catalytic reactions [9], and it also exhibited a unique catalytic behavior in the aromatization of CH_4 [10–12], it seemed reasonable to test its catalytic performance in the

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generation of hydrogen by the decomposition of organic compounds [13–17]. Mo_2C deposited on silica proved to be an effective catalyst for both the dehydrogenation and dehydration of HCOOH [15]. The extent of the decomposition approached 100 % at 623 K. Preparation of the Mo_2C catalyst by the reaction of MoO_3 with a multiwall carbon nanotube and carbon Norit, however, dramatically altered the product distribution. Dehydrogenation became the dominant process. In the optimum case, the selectivity for H_2 reached 98–99 %, even at the total conversion at 423–473 K. The addition of water to the formic acid completely eliminated CO formation and furnished CO-free H_2 on Mo_2C/carbon catalysts at 423–473 K.

In the present work we examine the photocatalytic behavior of unsupported and supported Mo_2C in the decomposition of HCOOH at room temperature. An attempt is made to induce the decomposition of HCOOH by visible light.

2 Experimental

2.1 Materials

The following materials were used as supports: TiO_2 (Hombikat, UV 100, 300 m^2/g, SiO_2 (Aerosil, 380 m^2/g). Supported Mo_2C was prepared by impregnating the supports with ammonium heptamolybdate. The suspension was dried and calcined at 873 K for 5 h. Afterwards, the MoO_3/support so obtained was heated under a 10 % (v/v) C_2H_6/H_2 gas mixture from room temperature to 1000–1050 K at a heating rate of 1.0 K/min. It was subsequently cooled down to room temperature in Ar. The Mo_2C samples were passivated in flowing 1 % O_2/N_2 gas mixture at 300 K and kept in air in a desiccator. A similar procedure was applied for the production of unsupported Mo_2C. In the case of preparation of K/Mo_2C the starting compound was K_2MoO_4. The surface area of Mo_2C samples used were as follows: Mo_2C (Aldrich) 5.1 m^2/g, Mo_2C prepared by us 20.0 m^2/g, K/Mo_2C 5.0 m^2/g. For the preparation of N-doped TiO_2 we adapted the method of Xu et al. [18]. Titanium tetrachloride was used as a precursor. After several steps the NH_3-treated TiO_2 slurry was vacuum dried at 353 K for 12 h, followed by calcination at 723 K in flowing air for 3 h. This sample was marked “SX”. The gases used were of commercial purity (Linde). HCOOH was a product of BDH, with a purity of 99.5 %.

2.2 Methods

The photocatalytic reaction was followed in a thermally controllable photoreactor equipped with a 15 W germicide lamp (type GCL 307T5L/CELL, Lighttech Ltd., Hungary) as light source [6, 19]. This lamp emits predominantly in the wavelength range of 250–440 nm. Its maximum intensity is at 254 nm. For the visible photocatalytic experiments another type of lamp was used (Lightech GCL 307T5L/GOLD) with 400–640 nm wavelength range and two maximum intensities at 453 and 545 nm. We note that this lamp also emits below 400 nm. The approximate light intensity at the catalyst films are 3.9 mW/cm^2 for the germicide lamp and 2.1 mW/cm^2 for the other lamp. The reactor (volume: 670 ml) consists of two concentric quartz glass tubes fitted one into the other and a centrally positioned lamp. It is connected to a gas-mixing unit serving for the adjustment of the composition of the gas or vapor mixtures to be photolyzed in situ. The length of the concentric tubes was 250 mm. The diameter of outer tube was 70 mm, and that of the inner tube was 28 mm. The catalyst sample (70–80 mg) was sprayed onto the outer side of the inner tube. The calculated thickness of the films was 0.86 μm. The height of the photocatalyst film was 89 mm. Formic acid (~1.3 %, 500–580 μmol) was introduced in the reactor through an externally heated tube avoiding condensation. The Ar carrier gas was bubbled through the formic acid at room temperature. The gas-mixture was circulated by a pump. The reaction products were analyzed with a HP 5890 gas chromatograph equipped with PORAPAK Q and PORAPAK S packed columns. The volume of the sampling loop of the GC was 500 μl. The amount of all products was related to this loop.

The XPS measurements were performed in a SPECS electron energy analyzer, using AlK_α radiation (hν = 1486.6 eV). The X-ray gun was operated at 210 W (14 kV, 15 mA). The pass energy was set to 20 eV. The takeoff angle of electrons was 20° with respect to surface normal. Typically five scans were summed to get a single spectrum. For data acquisition and evaluation both manufacturer’s (SpecsLab2) and commercial (CasaXPS, Origin) software were used. The pretreatments of the samples were performed in the preparation chamber attached to the UHV system. All binding energies were referenced to the C(1s) signal of adventitious carbon (285.1 eV). For FTIR studies a mobile IR cell housed in a metal chamber was used, which can be evacuated to 10^{-5} Torr using a turbo molecular pumping system. The samples were illuminated by the full arc of a Hg lamp (LPS-220, PTI) outside the IR sample compartment [6]. Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wavenumber accuracy of ±4 cm^{-1}. All the spectra presented in this study are difference spectra.

In the determination of the bandgap of Mo_2C, we tried to follow the method described before [6, 19]. Due to the low transparency of Mo_2C, however, we were not successful. Huang et al. [20] obtained a value of 2.0 eV for the bandgap of Mo_2C film using a novel technique involving the incorporation of two molybdenum screen grids embedded in an electron cyclotron resonance chemical vapor deposition system.

3 Results and Discussion

3.1 Carburization of MoO_3 with C_2H_6/H_2 Gas Mixture

The formation of Mo_2C in the MoO_3/TiO_2 samples was followed by XPS measurements. After treating MoO_3/TiO_2 with C_2H_6/H_2 (1:9) gas mixture, the Mo(3d) spectra showed the characteristic doublet of Mo(3d), which remained unchanged up to 600 K. At 700 K the peak maxima were detected at 229.3, 232.0 and 235.8 eV (Fig. 1a). At 850 K a Mo(3d) doublet at 228.0 and 231.2 eV characteristic of Mo_2C is displayed. These values remained practically constant during further treatment, including hydrogenation. The binding energy of C(1s) gradually shifted to lower values, reaching its minimum value, 283.3 eV at ~950 K. Hydrogenation in the final stage of the treatment caused no change in the C(1s) and Mo(3d) binding energies. Spectral changes in the carburization of MoO_3/SiO_2 have been described in our previous paper [15]. The final values for the doublet of Mo(3d) were ~227.8–227.9 and 230.7–230.9 eV. In the carburization of K_2MoO_4 the doublet at ~227.9–231.0 eV attributable to Mo(3d) appeared at higher temperatures as compared to the case of MoO_3. The BF values for K(2s) developed at 380.2 eV and for C(1s) at 285.1 eV [14]. The XP spectra of Mo_2C purchased form Aldrich and prepared by us show the charateristic binding energies of Mo_2C, 283.8 eV for C(1s) and 229.0 eV for Mo(3d) [21].

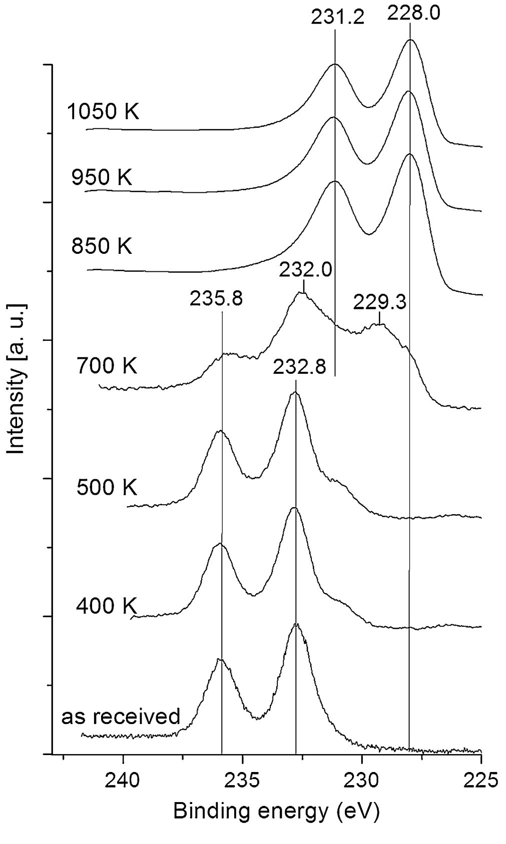


Fig. 1 XPS spectra of 1 % MoO_3/TiO_2 following its carburization with 10 % (v/v) C_2H_6/H_2 gas mixture at different temperatures

3.2 IR Spectroscopic Measurements

Figure 2a shows the FTIR spectra of 2 % Mo_2C/TiO_2 in the presence of HCOOH at 300 K. Intense absorption bands appeared at 1713, 1660, 1561 cm^{-1} and a weaker

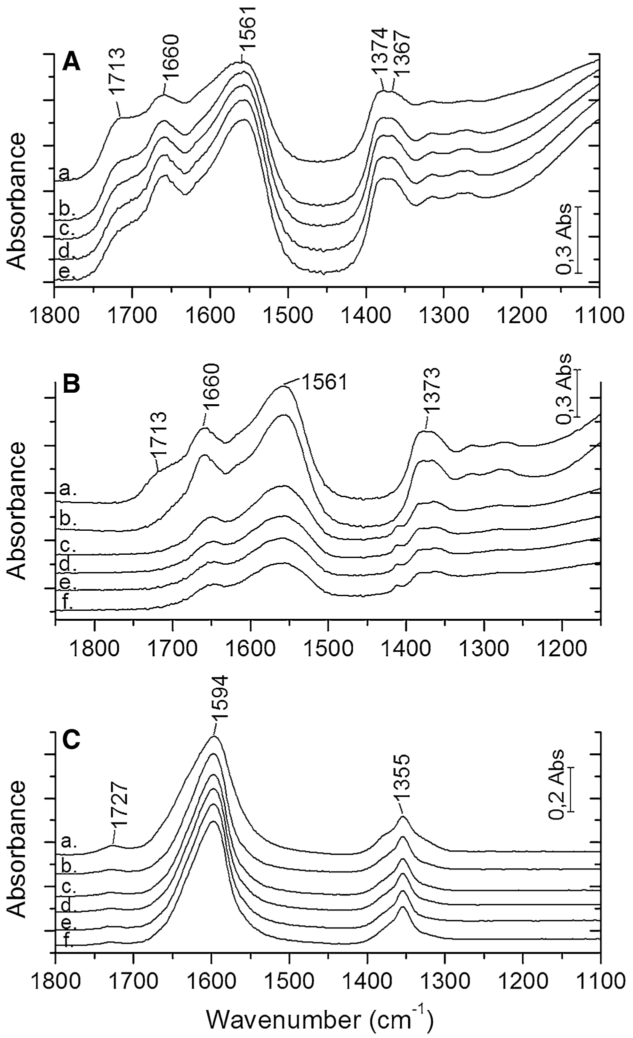


Fig. 2 Effects of illumination time on the FTIR spectra of 1 % Mo_2C/TiO_2 (**a**) and 1 % Mo_2C/SiO_2 (**c**) in the presence of HCOOH vapor; and after degassing of HCOOH on 1 % Mo_2C/TiO_2 (**b**). All experiments were carried out at 300 K

one at 1374 cm^{-1}. Illumination of the system led to a slight attenuation of the band at 1713 cm^{-1}. All the other bands became more intense with the length of the illumination. In contrast, the irradiation of adsorbed HCOOH (Fig. 2b) after degassing the sample for 30 min at 300 K caused a significant decrease of all absorption bands. We obtained a very similar picture for pure TiO_2 sample. Taking into account the large amount of IR spectroscopic studies concerning the adsorption of HCOOH [3, 6, 7, 22], the 1713 cm^{-1} band indicates the presence of molecularly adsorbed HCOOH. The appearance of the absorption features at 1561 and 1374 cm^{-1} suggests the occurrence of the dissociation of HCOOH:

$$HCOOH_{(a)} = HCOO_{(a)} + H_{(a)} \tag{1}$$

the first band is due to the asymmetric stretching, the second one is due to the symmetric stretching of formate species. The slow decline of the band at 1713 cm^{-1} and the strengthening of the other two absorption features in the presence of HCOOH vapour indicate that illumination promotes the dissociation of HCOOH into HCOO species (Fig. 2a). Note that without illumination such a spectral change was observed only very slowly. The photo-induced decomposition of formate species was only observed when HCOOH vapor was removed from the system (Fig. 2b). As we obtained a similar picture on pure TiO_2 of large surface area we can assume that most of the above species exist on TiO_2 surface. However, weak absorption features of formate species also appeared on Mo_2C/SiO_2 sample (Fig. 2c) suggesting that a small fraction of formate can be located on Mo_2C particles, as no formate exists on the silica surface [15].

3.3 Photocatalytic Studies

All photocatalytic measurements have been performed at room temperature. While the thermal decomposition of formic acid on pure Mo_2C starts only at or above 423 K [15], illumination induced the reaction even at 300 K. Both the dehydrogenation

$$HCOOH = H_2 + CO_2 \tag{2}$$

and dehydration process

$$HCOOH = H_2O + CO \tag{3}$$

occurred, but the dominant process is the first one. The activities of Mo_2C purchased from Aldrich and prepared by us were nearly the same. The conversion of formic acid reached 13–15 % in 240 min. The CO/CO_2 ratio varied around 0.4. The presence of K, however, drastically enhanced the photoactivity of Mo_2C: the conversion of HCOOH reached ~50 % in a given time. The dehydrogenation of HCOOH became the dominant process as indicated by the low CO/CO_2 ratio. Without illumination the conversion value was only 8–10 %. MoO_3 reduced at 700 K showed very little photoactivity. Results are presented in Fig. 3. When Mo_2C was synthetized on TiO_2 its photoactivity depended on the amount of Mo_2C. The highest conversion was measured for 0.5 % Mo_2C/TiO_2, which significantly exceeded that of pure TiO_2 treated in the same way (Fig. 4). A larger amount of Mo_2C, however, caused a decline in the activity of TiO_2. In the interpretation of the photocatalytic effect of Mo_2C samples, we assume the donation of photoelectrons formed in the photoexcitation process

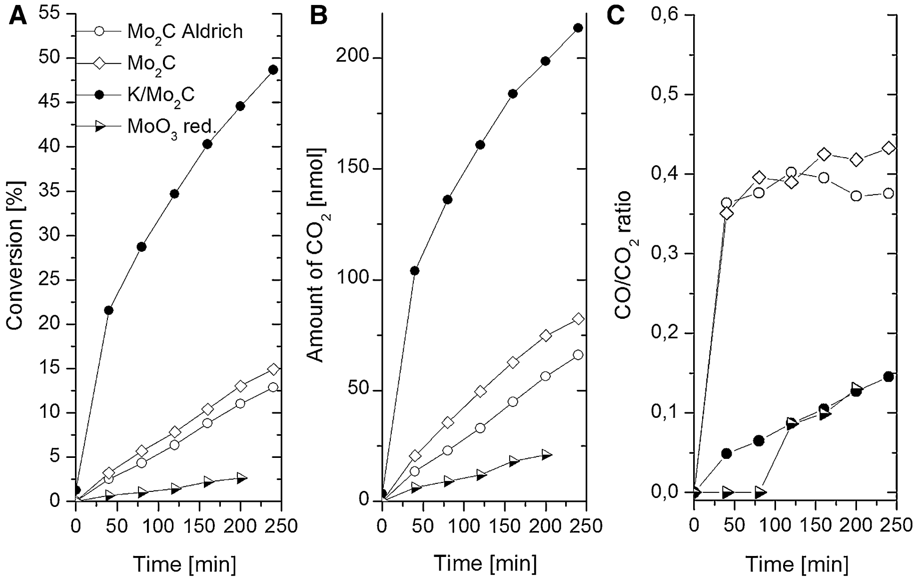


Fig. 3 Photocatalytic decomposition of HCOOH on pure and K-doped Mo_2C at 300 K. **a** Conversion of HCOOH; **b** formation of CO_2; **c** CO/CO_2 ratio

Fig. 4 Photocatalytic decomposition of HCOOH on TiO_2, Mo_2C/TiO_2 and Mo_2C/SiO_2 at 300 K. **a** Conversion of HCOOH; **b** formation of CO_2; **c** CO/CO_2 ratio

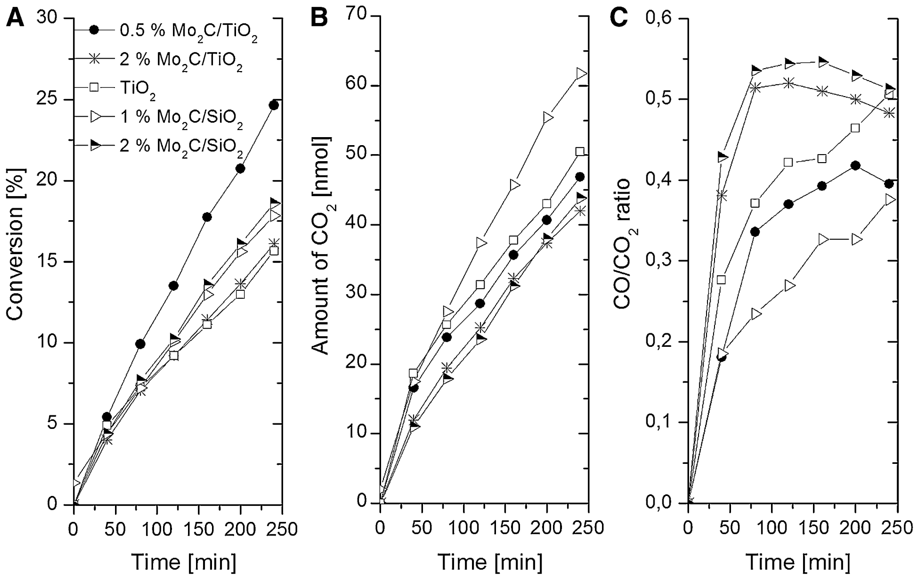
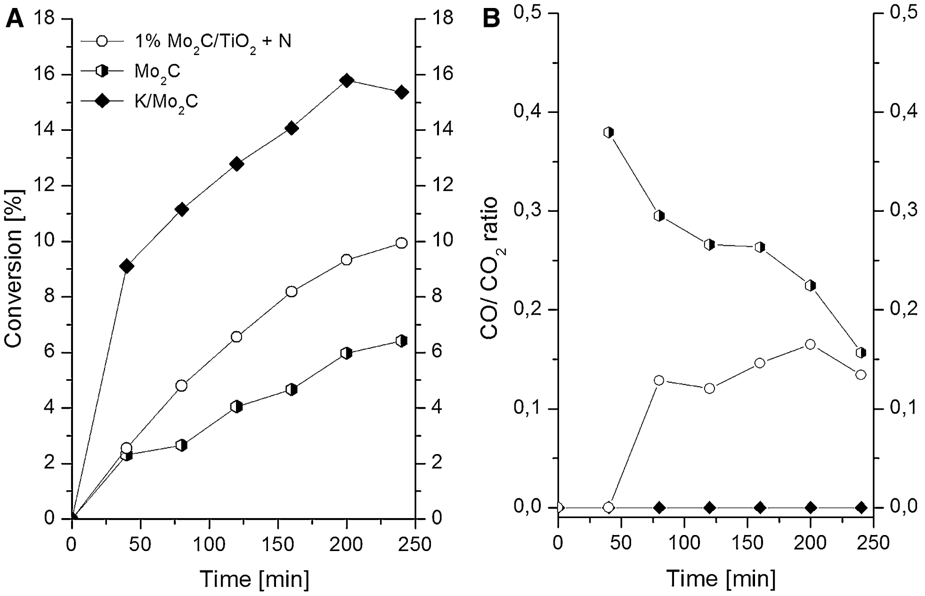


Fig. 5 Photocatalytic decomposition of HCOOH on Mo_2C, Mo_2C/TiO_2 doped with N, and K/Mo_2C in visible light at 300 K. **a** Conversion of HCOOH; **b** formation of CO_2; **c** CO/CO_2 ratio



$$Mo_2C + h\nu = h^+ + e^- \qquad (4)$$

to the HCOO

$$HCOO_{(a)} + e^- = HCOO^{\delta-} \qquad (5)$$

producing a more reactive charged species, which decomposes to H_2, CO_2 and CO.

$$2HCOO^{\delta-} = H_2 + 2CO^{\delta-}_{2(a)} \qquad (6)$$

$$CO^{\delta-}_{2(g)} + h^+ = CO_2 \qquad (7)$$

$$2HCOO^{\delta-}_{(a)} = 2CO_{(a)} + 2OH^{\delta-}_{(a)} \qquad (8)$$

Similarly to the metal/TiO_2 catalysts [4, 19, 23] we may assume the occurrence of an electronic interaction between n-type TiO_2 and Mo_2C. As the work function of Mo_2C is lower, 3.85 eV [24, 25], than that of TiO_2 (~4.6 eV), the electron transfer is expected to proceed from Mo_2C to the TiO_2. Illumination may enhance this charge transfer process. Accordingly Mo_2C can increase the photoactivity of TiO_2 at Mo_2C/TiO_2 interface. An alternative mechanism suggested by the referee is that hydrogen might evolve by the direct reduction of surface protons by conduction band electrons generated by bandgap excitation (no involvement of formate), while formate (or formic acid) is oxidized by the valence band holes to CO_2. Further studies are clearly required to obtain a deeper insight in the effect of illumination. In the explanation of the decline of the positive influence of Mo_2C at larger Mo_2C content we have to take into account that the preparation of Mo_2C on TiO_2 by C_2H_6/H_2 mixture at 900 K can cause a drastic change of TiO_2 surface leading to the loss of its active centers. The high photoactivity of K/Mo_2C prepared by the carburization of K_2MoO_4 can be attributed to the ability of K^+–O^{2-} overlayer to donate electrons. Praliaud et al. [26] showed that an electron donation can also occur from K^+–O^{2-} overlayers to the metal. The electron donating character of this overlayer was also considered by others as well [27, 28]. We may also mention that deposition of K on Rh(111) markedly enhanced the formation of formate species from adsorbed formic acid [29]. It also induces the rupture of C–O bond in the formate. Similar feature was observed by Jia et al. on Pd/C catalyst [5].

In order to establish the own photocatalytic behavior of highly dispersed Mo_2C independently of TiO_2, Mo_2C was prepared on silica surface. As it is seen in Fig. 4 Mo_2C/SiO_2 also exhibited an appreciable photocatalytic effect. To our best knowledge this was not observed in the case of Pt metals, which in highly dispersed state enhanced the photoactivity of TiO_2 [4, 6, 30, 31].

Experiments were also carried out in visible light. Previous studies indicated that lowering the band gap of TiO_2 with N doping resulted in an appreciable photoactivity of metal/TiO_2 catalysts in visible light. Preparation of Mo_2C on $TiO_2 + N$ sample exhibited the same behaviour (Fig. 5). More attractive results were obtained with unsupported Mo_2C. As shown in Fig. 5 Mo_2C catalyzes well the photo-induced decomposition of HCOOH even in visible light, which can be attributed to the low bandgap of Mo_2C, 2.0 eV, determined by Huang et al. [20]. As in UV, we measured a significantly higher extent of photocatalytic decomposition of HCOOH on K/Mo_2C catalyst, too. In this case only the dehydrogenation reaction occurred.

4 Conclusions

IR studies revealed that the dissociation of HCOOH proceeds on Mo_2C, and illumination leads to the decomposition of formate species.

Mo_2C in bulk or deposited on TiO_2 or SiO_2 induces the photocatalytic decomposition of formic acid.

Addition of potassium to Mo_2C markedly enhances the photoactivity of Mo_2C.

Mo_2C and particularly K/Mo_2C exhibited a high photoactivity even in visible light.

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