

Production of CO-Free H₂ by Formic Acid Decomposition over Mo₂C/Carbon Catalysts

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Abstract The vapor phase decomposition of formic acid was studied over supported Mo₂C catalysts in a flow system. Mo₂C deposited on silica is an effective catalyst for both the dehydrogenation of formic acid to yield H₂ and CO₂, and its dehydration to yield H₂O and CO. The extent of the decomposition approached 100% at 623 K. Preparation of the Mo₂C catalyst by the reaction of MoO₃ with a multiwall carbon nanotube and carbon Norit, however, dramatically altered the product distribution. Dehydrogenation became the dominant process. In optimum case, the selectivity for H₂, expressed in terms of the ratio CO₂/CO + CO₂, was 98–99%, even on total conversion at 423–473 K. The addition of water to the formic acid completely eliminated CO formation and furnished CO-free H₂ on Mo₂C/carbon catalysts at 373–473 K. Another feature of the Mo₂C catalyst is its high stability. No changes in activity or selectivity were observed within 10 h.

Keywords Pure hydrogen production · Formic acid decomposition · Mo₂C catalyst · Multiwall carbon nanotube support · Carbon Norit support

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1 Introduction

The increasing demand for pure, CO-free H₂ for various applications, including fuel cells, led to extensive research on the generation of H₂ from various compounds [1, 2]. The direct decomposition of CH₄, which is effectively catalyzed by supported Pt metals, is an attractive route for the production of CO/CO₂-free H₂ [3–7]. Early poisoning of the catalyst by carbon deposition, however, hampers the application of this method. The decomposition and reforming of oxygen-containing hydrocarbons, such as C₂H₅OH, CH₃OH and (CH₃)₂O, afford H₂ in high yields, but the unavoidable formation of CO and its complete elimination cause great problems [8–10]. It is somewhat surprising that the use of HCOOH, which is also a potential source of H₂ for fuel cells [11, 12], has received very little attention, though considerable information is available on this process on metals [13, 14], oxides [15–17], and supported metals [13, 14, 18, 19]. This reaction proceeds in two directions:



and



It was earlier used to test the roles of the electronic properties of metals, alloys and oxides in heterogeneous catalysis [13–19]. It was found that the semiconducting oxides mainly catalyzed the dehydrogenation reaction, whereas on insulating materials the dehydrogenation process comes into prominence. The first experimental evidence that electronic interactions between a metal and its support may play an important role in the support effect was demonstrated by the decomposition of HCOOH on Ni supported by pure or doped n-type TiO₂ [18, 19]. Interest in

the catalytic decomposition of HCOOH was later renewed, when the efficiencies of supported metals were compared on the basis of the turnover frequencies, without special attention to improvement of the production of H₂ [20–22]. The use of metal single-crystals and various electron spectroscopic methods provided deeper insight into the interactions of HCOOH with metals on an atomic scale [23, 24].

In the present work, we report that Mo₂C prepared by the reaction of MoO₃ with a multiwall carbon nanotube and carbon Norit is an excellent and stable catalyst for the production of H₂ virtually free of CO. Mo₂C has the interesting property that, when it is deposited on a ZSM-5 support, it catalyzes the aromatization of CH₃OH, C₂H₅OH and (CH₃)₂O with high efficiencies [27]. In contrast, the reaction pathways of these compounds on Mo₂C are dramatically altered when Mo₂C is prepared on carbon supports: instead of the formation of aromatics, degradation of these compounds to H₂, CO, CO₂ and CH₄ becomes prominent [25].

2 Experimental

Catalytic reactions were carried out at a pressure of 1 atm in a fixed-bed, continuous flow reactor consisting of a quartz tube (8 mm id) connected to a capillary tube [25]. The flow rate was 40 mL/min. The carrier gas was Ar, which was bubbled through the formic acid at room temperature: its content was ~5–6.0%. In general, 0.3 g of loosely compressed catalyst sample was used. The reaction products were analyzed with a HP 4890 gas chromatograph equipped with PORAPAQ Q + S and 30-m long HP-PLOT Al₂O₃ column. The conversion of formic acid was determined by taking into account the amount consumed. The selectivity of hydrogen was calculated from the ratio of CO₂ concentration to the sum of CO₂ + CO. Multiplying this value with the conversion gave the hydrogen yield. Fourier Transformed Infra Red (FTIR) spectra of adsorbed formic acid were recorded with a BioRad FTS-155 spectrometer with a wavenumber accuracy of ±4 cm⁻¹. X-ray photon electron energy spectra (XPS) were taken with a Kratos XSAM 800 instrument using non-monochromatic Al K_α radiation (hν = 1,486.6 eV) and a 180° hemispherical analyzer at a base pressure of 1 × 10⁻⁹ mbar.

The following materials were used as supports: SiO₂ (Aerosil, 300 m²/g), carbon Norit (1,175 m²/g) and a multiwall carbon nanotube (labeled as CNT) (170 m²/g). The preparation of the carbon nanotube has been described elsewhere [26]. Both carbon supports were purified by treatment with aqueous HCl (10%) for 12 h at room temperature. After this treatment, the metal impurities, mainly

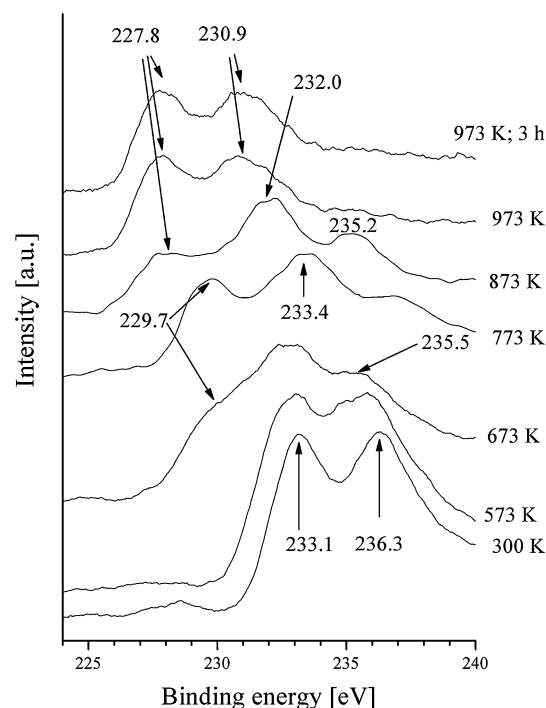
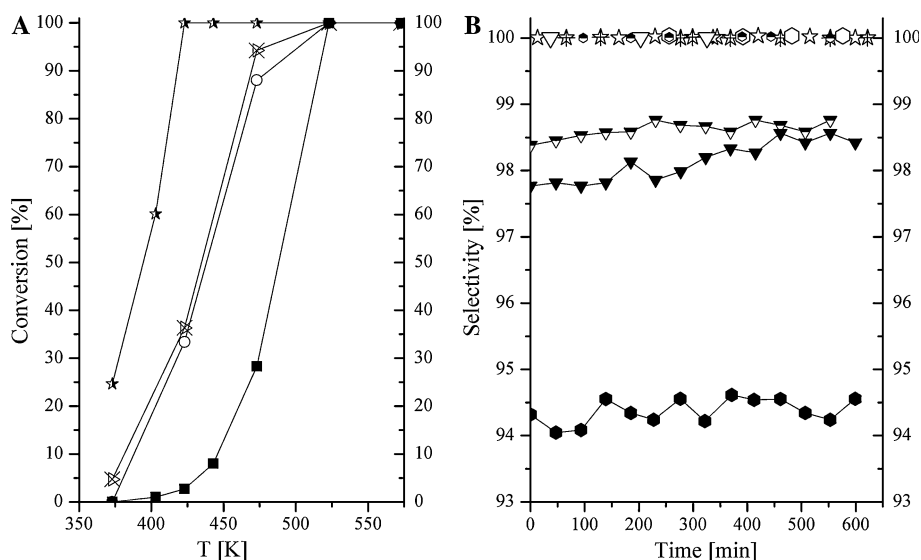


Fig. 1 XPS spectra of MoO₃ in the course of the formation of 1% Mo₂C on carbon Norit in the flow of H₂ at different temperatures

Fe, determined by the ICP-AES method, amounted to less than 0.002%. Mo₂C on a multiwall carbon nanotube and carbon Norit was prepared by impregnating the carbon support with ammonium heptamolybdate to yield 1, 2 or 5 wt% of Mo₂C, and the dried suspension was treated in air at 673 K for 3 h [25, 27]. Afterwards, the sample was heated up to 973 K in a H₂ flow, with a temperature ramp of 3 K/min. The Mo₂C/SiO₂ catalyst was prepared by the carburization of MoO₃/SiO₂ in the C₂H₆/H₂ gas mixture [27]. The sample was heated under a 10% v/v C₂H₆/H₂ gas mixture from room temperature to 900 K at a heating rate of 0.8 K/min. It was subsequently cooled down to room temperature under Ar. MoO₃/SiO₂ was produced by impregnating SiO₂ with a basic solution of ammonium heptamolybdate. The suspension was dried and calcined at 863 K for 5 h. Following the method of Boudart et al. [28], the Mo₂C samples were passivated in flowing 1% O₂/H₂ at 300 K and kept in air in a desiccator. Before use, the catalysts were reduced in a H₂ flow at 673 K for 1 h in situ. The gases used were of commercial purity (Linde). HCOOH was a product of BDH, with a purity of 99.5%.

The formation of Mo₂C in the samples used was followed by XPS measurements. The XP spectrum of the MoO₃/Norit shows the characteristic Mo(3d_{3/2})–Mo(3d_{5/2}) doublet at 233.1 and 236.3 eV (Fig. 1a). The O 1s binding energy (BE) was measured at 530.8, and that of C 1s at 285.0 eV (not shown). Upon heating the sample in H₂ flow the first spectral change was observed at 673 K, when a

Fig. 2 a The conversion of the decomposition of HCOOH on various catalysts as a function of temperature, 1% Mo₂C/CNT (■); 1% Mo₂C/Norit (★); 2% Mo₂C/Norit (○); 5% Mo₂C/Norit (⊗) (b) and the selectivity of hydrogen formation in the reforming of HCOOH on various catalysts at different temperatures. 1% Mo₂C/CNT (○) 373 K, (●) 423 K, (●) 473 K; 1% Mo₂C/Norit (☆) 443 K, (★) 473 K; 5% Mo₂C/Norit (▽) 373 K, (▼) 423 K, (▼) 523 K

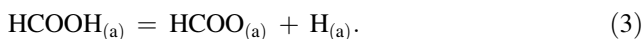


shoulder developed at 229.7 eV due to the partial reduction of MoO₃. At 773 K the BE values for Mo appeared at 229.7, 233.4 and 236.3 eV, which can be regarded as an indication of the formation of Mo₂C. The final values for the doublet, 227.8 and 230.9 eV measured at 973 K, agree well with those characteristic for Mo₂C [29, 30] suggesting that MoO_x reacted with carbon to give Mo₂C. In the course of this process a significant reduction in the intensity of O 1s peak also occurred. Its complete elimination, however, was not achieved even upon treating the sample with H₂ at 973 K for 3 h. The final value of C 1s was registered at 285.1 eV. We performed XPS measurements for 1% MoO₃/CNT catalyst, when similar spectral changes were experienced. In this case the final BE values measured for Mo(3d_{3/2})–Mo(3d_{5/2}) of Mo₂C were 227.8 and 230.8 eV. This result indicates that MoO₃ is converted into Mo₂C on the surface of multiwall carbon nanotube, too. Previous XPS studies showed that the carburization of MoO₃ deposited on silica by C₂H₆/H₂ mixture is complete using the method described [27].

3 Results and Discussion

3.1 FTIR Spectroscopic Studies

Previous IR studies clearly showed that HCOOH undergoes dissociation on metals to give formate species [17, 21]:



As Mo₂C on a carbon support is not transparent, IR measurements were performed with a 2% Mo₂C/SiO₂ sample. We first examined the adsorption of HCOOH on pure SiO₂. In harmony with our previous studies, HCOOH adsorbs only weakly on SiO₂, without any detectable

dissociation, e.g. the formation of formate species [21]. The situation is different on Mo₂C/SiO₂: the adsorption of HCOOH at 300 K gave well-defined absorption bands at 1,575 and ~1,370 cm⁻¹. These peaks are tentatively attributed to the vibrations of formate species [14, 17, 21].

3.2 Decomposition of Formic Acid

We first examined the reactions of HCOOH on 2% Mo₂C/SiO₂ catalysts. Decomposition started above 450 K yielding H₂, CO₂, CO and H₂O. Total conversion of HCOOH was approached at 623 K. At lower temperatures, the selectivity of H₂ formation was below 70% and it reached 80% only at 723 K. A very small amount of CH₄ (~1%) was also detected at 723 K, which suggests the occurrence of the hydrogenation of CO or CO₂.

A different picture was obtained when Mo₂C was prepared on a carbon nanotube, which does not contain OH groups. Measurable decomposition was already observed at ~373 K, and was complete at 523 K. The selectivity for H₂ formation varied in the interval 80–70%. A much better catalytic performance was exhibited by Mo₂C prepared on carbon Norit with a very high surface area. On 1% Mo₂C/Norit the decomposition began by ~350 K, and was complete at 423 K. The selectivity for H₂ formation was 95–98% even at a very high conversion of HCOOH. When the Mo₂C content was increased to 2 or 5% the onset of the reaction shifted to higher temperature. Data for conversion are displayed in Fig. 2a. Following the reaction in time on stream at 423 and 523 K, we experienced no deactivation and the product distribution remained practically constant in ~10 h.

In the subsequent measurements we examined the effects of H₂O on the product distribution over Mo₂C catalysts. The addition of H₂O exerted positive influence

Table 1 Some characteristic data for production of H₂ in steam reforming of HCOOH over supported Mo₂C catalysts

Catalyst	Temp. (K)	Conv. (%)	H ₂ sel. (%)	H ₂ yield
1% Mo ₂ C/CNT	373	7–8	100	7.0–8.0
1% Mo ₂ C/CNT	423	30–40	100	30.0–40.0
1% Mo ₂ C/CNT	473	100	94.5	94.5
1% Mo ₂ C/Norit ^a	423–473	100	~98.0	~98.0
1% Mo ₂ C/Norit	443	100	100	100
1% Mo ₂ C/Norit	473	100	100	100.0
1% Mo ₂ C/Norit	573	100	95.5	95.5
5% Mo ₂ C/Norit	373	~27	100	27.0
5% Mo ₂ C/Norit	403	89–90	98.0	87.2–88.2
5% Mo ₂ C/Norit	423	100	98.5	98.5
5% Mo ₂ C/Norit	523	100	98.0	98.0

^a Without H₂O

on the extent of decomposition and diminished the CO content, even eliminating the CO completely from the products under some conditions. This feature can be attributed to the occurrence of the water–gas shift reaction. As shown in Fig. 2b on 1% Mo₂C/CNT catalyst the selectivity for H₂ attained 100% at 373 and 423 K and subsequently decreased to 94.5% by 473 K. In the case of 1% Mo₂C/Norit, the selectivity for H₂ production remained 100% up to 473 K, when the conversion was 100%. It decreased to ~95.7% at 573 K. On 5% Mo₂C/Norit, pure hydrogen was obtained at 373 K. At 423–523 K the selectivity for H₂ varied between 97.5 and 98.5%. As in the absence of H₂O, no deterioration of the catalyst occurred in ~10 h at 403–473 K. To demonstrate the efficiency of the Mo₂C catalysts we calculated the yield of the formation of H₂. Data are listed in Table 1. It appears that the highest yield for the production of H₂ is obtained on 1% Mo₂C/Norit at 443–473 K.

We explain the behavior of HCOOH on this catalyst as follows. On the basis of previous studies [25, 27], we assume that the active centers of the catalyst are carbon deficient sites on the Mo₂C surface. The first reaction step is very probably the dissociation of HCOOH to a formate species (Eq. 3), which is bonded via its oxygen end to the active sites of Mo₂C. This is followed by the decomposition of the adsorbed formate to H and CO₂. We presume that the rate-determining step is the cleavage of the C–H bond in the formate species. A remarkable feature of the Mo₂C catalyst is the absence of deactivation. XPS studies in a reactor combined with the XPS system demonstrated no enhancement of the O (1s) signal of the Mo₂C/Norit catalyst (on reaction for 5 h at 423 and 523 K) relative to that measured for the starting sample. This is in harmony with the results obtained in the study of the interactions of CO and CO₂ with the Mo₂C/Mo(100) model system in

UHV showing that the dissociation of both compounds on Mo₂C is very limited [31, 32]. Further investigations are in progress to obtain a deeper insight in the reaction and to enhance the catalytic efficiency of the Mo₂C.

4 Conclusions

In conclusions, we were able to demonstrate that supported Mo₂C prepared by the reaction of MoO₃ with carbon supports is an active catalyst for the decomposition of HCOOH. The product distribution and the selectivity of hydrogen formation depended on the nature of the supports and on the reaction temperature. In the absence of water the highest yield for hydrogen was achieved on 1% Mo₂C/carbon Norit. The addition of H₂O to HCOOH eliminated CO completely from the products on carbon supported Mo₂C even at the total decomposition of formic acid up to 473 K.

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