Available online at www.sciencedirect.com
SCIENCE DIRECT®
Vacuum 80 (2005) 64–68
VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY
www.elsevier.com/locate/vacuum

New reaction route of HCOOH catalytic decomposition

T. Kecskés, R. Németh, J. Raskó, J. Kiss*

Reaction Kinetics Research Group of the Hungarian Academy of Sciences, Institute of Solid State and Radiochemistry of the University of Szeged, Dom square 7, P.O. Box 168, H-6701 Szeged, Hungary

Abstract

The adsorption of HCOOH and the further reactions of adsorbed species formed on TiO_2(1 1 0) and on TiO_2-supported noble metals (Rh, Pt, Au) has been studied by RAIRS, FTIR and mass spectrometry. Besides molecularly adsorbed HCOOH and surface formate species, adsorbed formaldehyde was detected. MS measurements showed formaldehyde in the gas phase, too. The amount of formaldehyde (formed both in the adsorbed layer and in the gas phase) depended on the pre-treatment, the metal content of the samples and on the reaction temperature. The formations of formaldehyde and CO were to be complementary, from which it was concluded that CO forms mainly in the decomposition of formaldehyde during HCOOH catalytic decomposition. Studies of formaldehyde surface reactions strengthened the above statement. A new reaction route for HCOOH catalytic decomposition has been proposed, which consists of the de-oxygenation of HCOOH on oxygen vacancies and/or on the metallic sites, and the decomposition of the resultant HCHO into H_2 and CO on metallic sites.

1. Introduction

The adsorption and surface reactions of formic acid on TiO_2 and TiO_2-supported metals are important in many respects. Formic acid can easily dissociate producing formate and hydrogen on these surfaces [1,2]. Formate decomposes further to a variety of products, the dominant of which are CO, CO_2, H_2O and H_2. Taking into account these products, the decomposition of formic acid on TiO_2 surfaces has been described in terms of dehydration (to CO and H_2O) and dehydrogenation (to CO_2 and H_2) mechanisms [3–8]. Recent studies on single-crystal TiO_2 surfaces revealed that the production of H_2O and CO could not be directly linked, thus the dehydration reaction can be excluded [9]. It was also stated that oxygen vacancies should play a decisive role in the decomposition processes. The interaction of formate with oxygen vacancies led to the formation of gas phase formaldehyde [9,10]. Two routes of formaldehyde formation were proposed: the first, on reduced surfaces, involves the reduction of HCOOH to formaldehyde accompanied by the oxidation of surface Ti cations, while a second route for formaldehyde formation, operative on

*Corresponding author. Tel.: +36 62 544 803; fax: +36 62 420 678.
E-mail address: jkiss@chem.u-szeged.hu (J. Kiss).

0042-207X/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2005.07.014

fully oxidized surfaces, involves bimolecular coupling of two formats [10]. The above conclusions have been stated mostly for well-defined TiO_2 single-crystal surfaces and $Pd/TiO_2(1\,1\,0)$ model catalyst [11].

In the present work an attempt was made to study formic acid adsorption on model systems ($TiO_2(1\,1\,0)$ and $Rh/TiO_2(1\,1\,0)$) and on powdered TiO_2 and noble metal/TiO_2 catalysts. The formation of surface species was monitored by FTIR spectroscopy and the changes in the gas phase were registered by mass spectrometry. Special attention has been paid to the possible link between the products of HCOOH catalytic decomposition and the formation of formaldehyde.

2. Experimental

The catalysts were prepared by impregnating TiO_2 (anatase, Degussa P25, $50\,m^2/g$) with the solutions of $H_2PtCl_6 \times 3\ H_2O$ (Reanal) and $RhCl_3 \times 3\ H_2O$ (Johnson Matthey), respectively. TiO_2-supported Au catalysts were made by a deposition-precipitation method [12] using $HAuCl_4 \times aq$ (Fluka). The metal contents were 1 and 5 wt%. The impregnated powders were dried at 383 K in air overnight. The model system $TiO_2(1\,1\,0)$ was used (Crystal Tec.). Rh deposition was produced using a metal evaporator (Oxford Applied Research).

For FTIR studies the catalyst powders were pressed onto a Ta mesh (30×10 mm, $5\,mg/cm^2$),

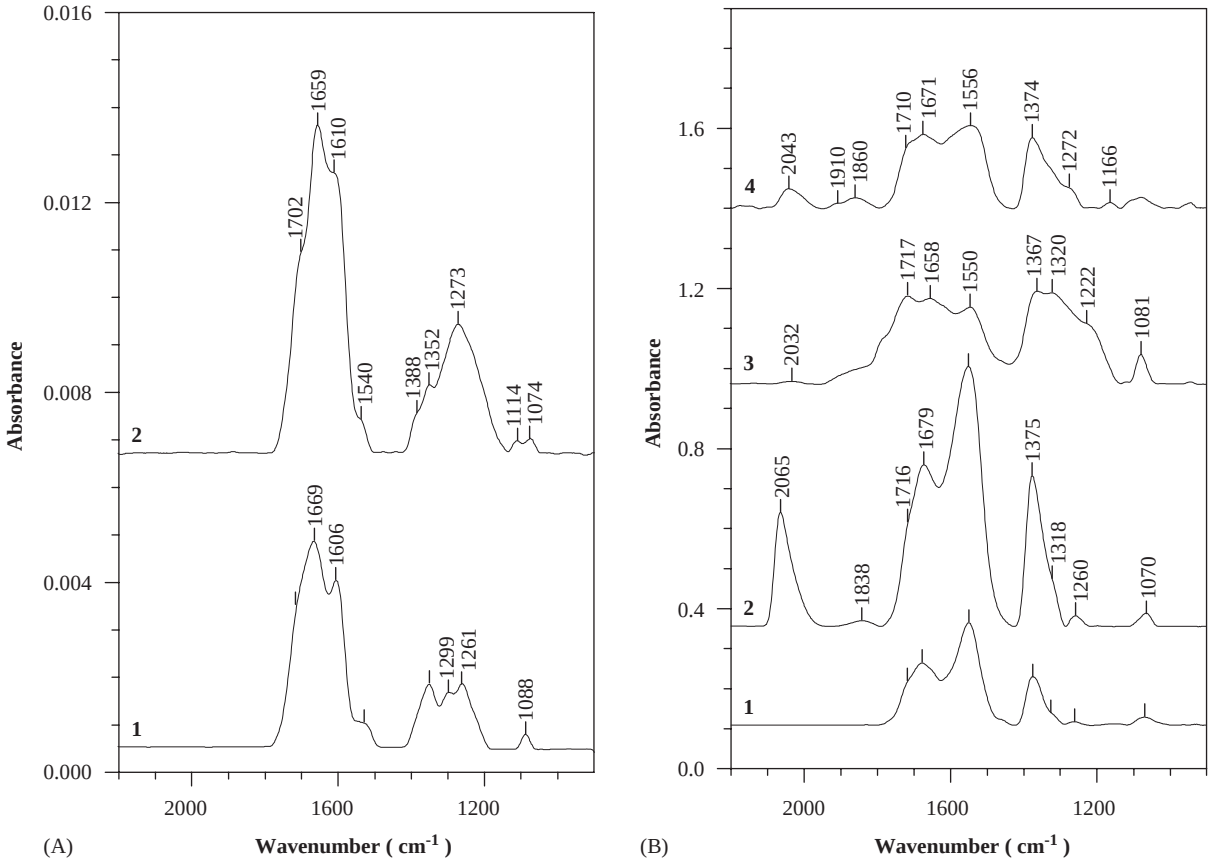

Fig. 1. IR spectra taken in the adsorption of HCOOH (1.33 hPa) at 300 K for 60 min on reduced catalysts (A) 1-$TiO_2(1\,1\,0)$; 2-$Rh/TiO_2(1\,1\,0)$; (B) 1-TiO_2; 2–1% Pt/TiO_2; 3–1% Au/TiO_2 and 4–1% Rh/TiO_2. (Background spectrum and the spectrum of gas phase HCOOH were subtracted.)

which was fixed to the bottom of a conventional UHV sample manipulator. Before measurements, the samples were kept either in 1.33 hPa O_2 (oxidized surface) or in 1.33 hPa H_2 (reduced surface) at 573 K for 1 h. After a 30 min evacuation at 573 K, the samples were cooled to the adsorption temperature. Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of $\pm 4\,cm^{-1}$. Typically 136 scans were collected. The spectrum of the pretreated sample (background spectrum) and the actual vapour spectrum were subtracted from the spectrum registered in the presence of vapour. RAIRS spectra of well-defined TiO_2(1 1 0) and Rh/TiO_2(1 1 0) were recorded in UHV system the Mattson FTIR spectrometer. The system was equipped with Auger electron spectroscopy (AES) for controlling the purity and the metal content. The structure of TiO_2(1 1 0) was determined by STM. It exhibited a (1×1) structure. The surfaces were cleaned by Ar^+ bombardment.

In parallel with the FTIR experiments the changes in the signal intensity of the main fragments of formic acid and the possible products were monitored by a QMS 200 (Balzers) quadrupole mass spectrometer.

3. Results and discussion

The adsorption of HCOOH (1.33 hPa) at 300 K caused similar spectra on well-defined surfaces and

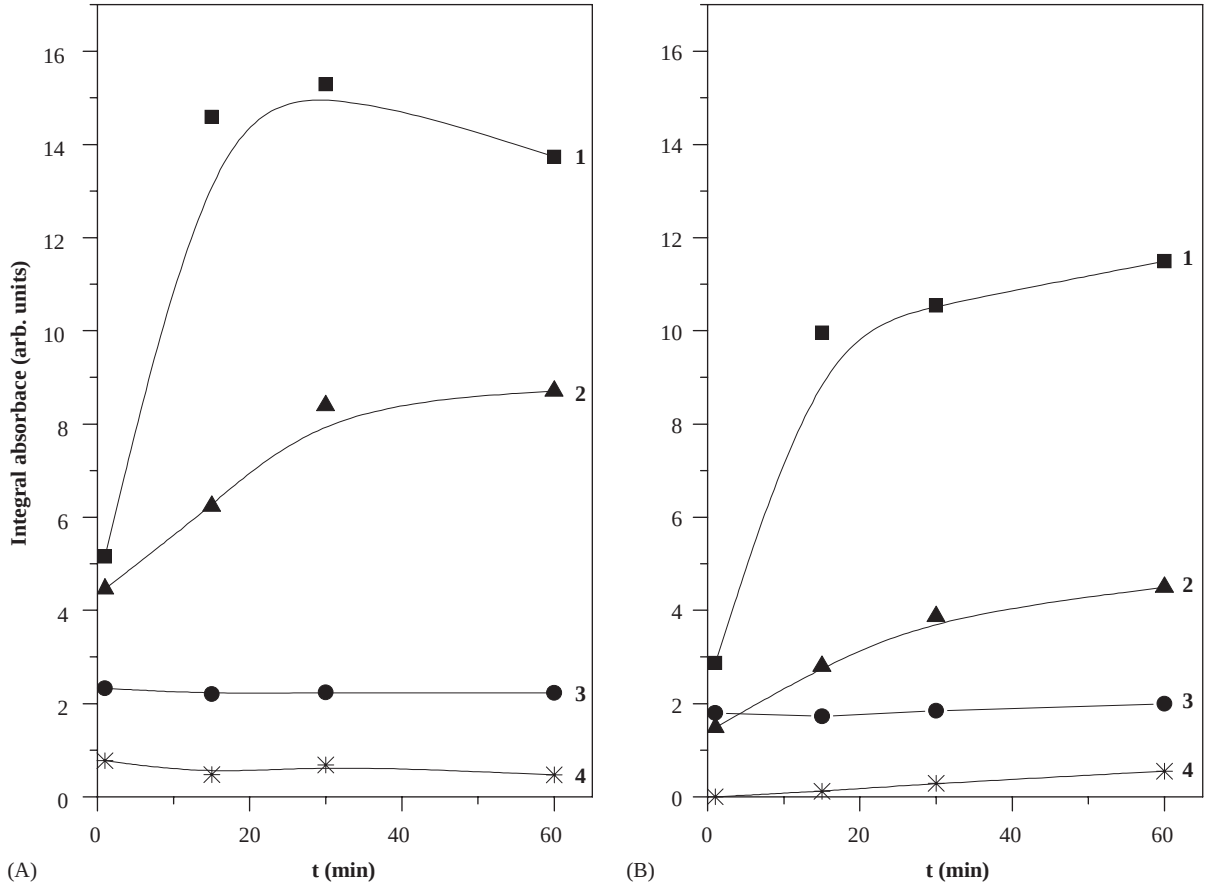

Fig. 2. The changes of surface concentration of adsorbed formaldehyde during the adsorption of HCOOH (1.33 hPa) at 300 K on oxidized (A) and on reduced (B) catalysts: 1–5% Pt/TiO_2; 2–5% Au/TiO_2; 3-TiO_2 and 4–5% Rh/TiO_2.

on powdered catalysts (Fig. 1). In the present case of the model catalyst one monolayer of Rh was studied. The bands due to molecularly adsorbed HCOOH [9] (1671–1658 and 1072–1081 cm^{-1}), and due to the dissociation of HCOOH to adsorbed formate species [9] (1556–1550 and 1374–1367 cm^{-1}) were registered on the spectra; the bands at 1712–1717, 1272–1278 and 1166 cm^{-1} are assigned to the adsorbed formaldehyde [10,11] (Fig. 1). We suppose that oxygen vacancies on the TiO_2 surface and/or the metal sites may act as surface centres for de-oxygenation of HCOOH:

$$HCOOH + Ti^{3+} - \square \rightarrow CH_2O_{(a)} + Ti^{4+} - O,$$

where $\square$ denotes oxygen vacancy and/or

$$HCOOH_{(a)} + Me \rightarrow CH_2O_{(a)} + Me{-}O,$$

where Me denotes Pt, Au, Rh.

The amount of formaldehyde in the adsorbed layer depends on the metal content and the pretreatment of the catalysts. It was the highest on 5% Pt/TiO_2 and it decreased in the order of $Au/TiO_2 > TiO_2 > Rh/TiO_2$ (Fig. 2). This order can be connected with the ability of different metals (catalysts) to extract oxygen from HCOOH.

Some formaldehyde desorbs from the catalyst surfaces: its quantity in the gas phase depends on the nature of the metals and on the adsorption temperature (Fig. 3). The highest amount of gas phase formaldehyde was observed on TiO_2 at all temperatures. While H_2 and CO_2 (products of dehydrogenation) formed in parallel in any experimental conditions, there was no direct correlation between the formation of H_2O and CO (products of dehydration). As the reaction temperature increased, the surface concentration of $CH_2O_{(a)}$

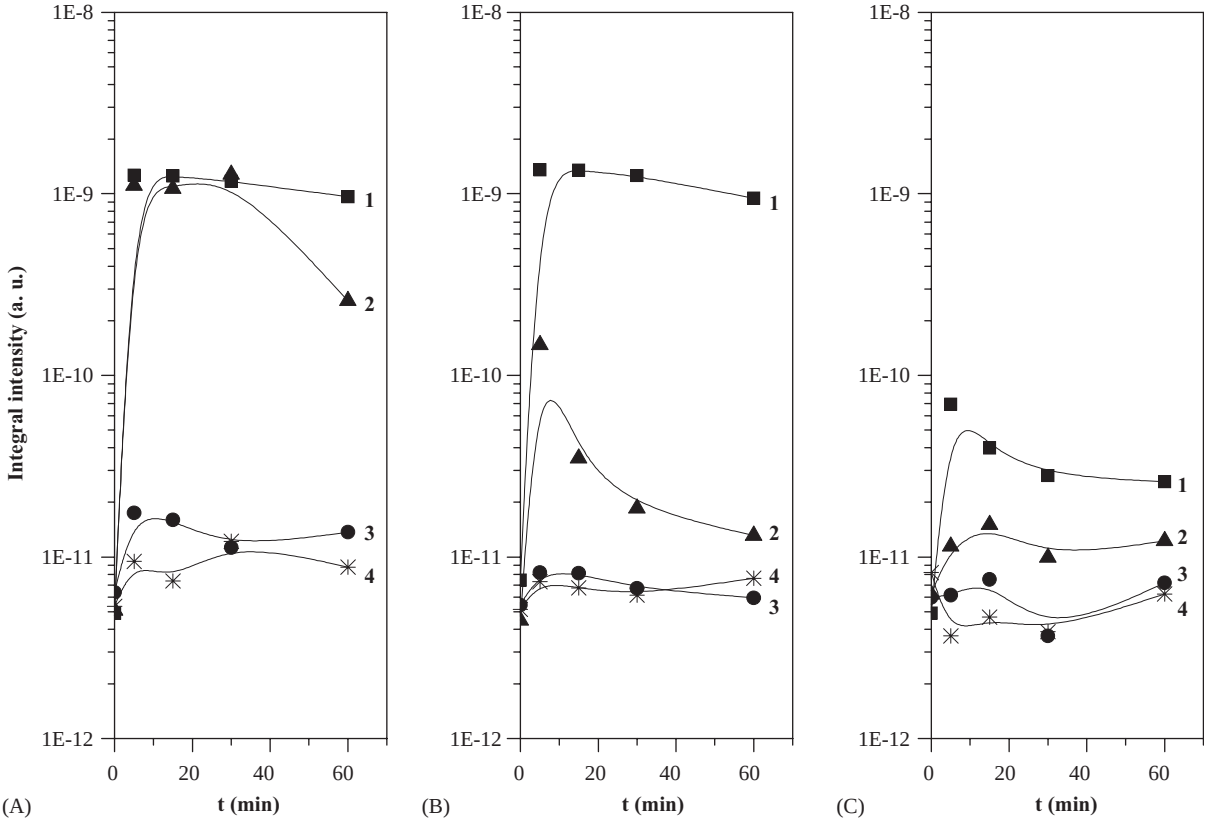

Fig. 3. The amounts of gas phase formaldehyde in the decomposition of HCOOH (1.33 hPa) on reduced catalysts at 300 K (A), at 383 K (B) and at 473 K (C): 1-TiO_2; 2–5% Pt/TiO_2; 3–5% Au/TiO2 and 4–5% Rh/TiO_2.

and the amount of formaldehyde in the gas phase decreased, while CO appeared among the gas phase products. These findings suggest that the main source of CO gas during HCOOH decomposition would be the decomposition of formaldehyde into H_2 and CO. Indeed, the main gas-phase products of formaldehyde decomposition on the same catalysts are H_2 and CO:

$$CH_2O_{(a)} \rightarrow CO_{(g)} + H_{2(g)}.$$

The appearance of the bands between 1800 and 2100 cm^{-1} on the spectra of Pt/TiO_2 and Rh/TiO_2 (Fig. 1) due to different modes (linear and bridge) of adsorbed CO can be accepted as an indirect proof of the de-oxygenation of HCOOH causing the oxidation of the originally reduced metal sites. In the case of Au/TiO_2 the band characteristic of adsorbed CO was not observed, or it was hardly detected. It should be taken into account that CO adsorbs very weakly on oxide-supported Au [13]. On the $Rh/TiO_2(1\,1\,0)$ model system adsorbed CO could not be detected at 300 K. This means that the formate of formaldehyde species exhibited more stability on this system. Work to established the stabilities of formate and formaldehyde on nano size Rh supported by $TiO_2(1\,1\,0)$ (1×1) is in progress.

4. Conclusions

Formaldehyde forms both in the adsorbed layer and in the gas phase in the interaction between HCOOH and the catalysts. The changes in the amounts of formaldehyde and CO were found to be complementary. Instead of the traditional dehydration mechanism it is suggested that in the HCOOH decomposition, the main source of CO gas is the decomposition of formaldehyde formed by the de-oxygenation of HCOOH.

Acknowledgements

This work was supported by the Hungarian Scientific Research Foundation Grant OTKA, TO46351 and TO43057.

References

[1] Munuera G. J Catal 1970;18:19.
[2] Groff RP, Manogue WH. J Catal 1983;79:462.
[3] Kim KS, Barteau MA. Langmuir 1990;6:1485.
[4] Onishi H, Aruga T, Iwasawa Y. J Am Chem Soc 1993;115:10460.
[5] Onishi H, Aruga T, Iwasawa Y. J Catal 1994;146:557.
[6] Onishi H, Iwasawa Y. Chem Phys Lett 1994;226:111.
[7] Trillo JM, Munuera G, Criado JM. Catal Rev 1972;7:51.
[8] Kim KS, Barteau MA. Langmuir 1988;4:945.
[9] Henderson MA. J Phys Chem B 1997;101:221.
[10] Idriss H, Lusvardi VS, Barteau MA. Surf Sci 1996; 348:39.
[11] Bowker M, Stone P, Bennett R, Perkins N. Surf Sci 2002;511:435.
[12] Solymosi F, Bánsági T, Süli Zakar T. Phys Chem Chem Phys 2003;5:4724.
[13] Shastri AG, Datye AK, Schwank Y. J Catal 1994;87:265.