SURFACE SPECIES AND GASPHASE PRODUCTS IN THE CATALYTIC DECOMPOSITION OF FORMIC ACID

Ph. D. Thesis

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1. INTRODUCTION

The study of catalytic decomposition of formic acid has a real past, almost a decade. It was investigated on numerous catalysts so in TiO_2 and in other TiO_2 supported metals, too. The formic acid easily dissociates to hydrogen and formate on the surface of the latest one. The formate continues the disintegration to different products from which the most important are the following: CO, CO_2, H_2O ad H_2. Taking into account the dominant 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 in spite of the peak of desorption temperature of H_2O and CO was not the same either on single crystals or policrystals. Later it has been proven that the desorption of water and carbon dioxide are not parallel processes therefore the unimolecular process can be excluded. During the interaction between HCOOH and the single crystal surfaces of TiO_2 only the formation of gasphase formaldehyde has been previously observed.

In the present work our attempt was to study formic acid catalytic decomposition on powdered TiO_2, 1% and 5% Rh/TiO_2, Pt/TiO_2, Au/TiO_2 and on $TiO_2(110)$-(1×1) and $Rh/TiO_2(110)$-(1×1) single crystals. Differently pretreated catalysts were used, and the gas pressure, the adsorption temperature and adsorption time were varied in our experiments in order to understand the reaction mechanism more correctly.

The formation of surface species was monitored by FTIR spectroscopy and the changes in the gas phase were registered by mass spectroscopy.

On the basis of the results until now we expended additional care in studying the potential connection between dehydration, dehydrogenation processes and the formation of formaldehyde. Relying upon our findings it was reasonable to study the adsorption and reaction of formaldehyde on TiO_2 and TiO_2-supported metal catalysts, too.

2. EXPERIMENTAL METHODS

The policrystalline TiO_2 was a product of Degussa. 1% and 5% Rh-, Pt- and Au/TiO_2 catalysts were prepared by impregnating of TiO_2 with an aqueous solution of $RhCl_3 \times 3\ H_2O$ or $H_2PtCl_6 \times 3\ H_2O$ salt, or by a deposition-precipitation method with $HAuCl_4 \cdot aq$.

For IR studies the catalysts powders were pressed onto a Ta-mesh which was fixed to the bottom of a conventional UHV sample manipulator. It was resistively heated and the temperature of the sample was measured by NiCr-Ni thermocouple spot-welded directly to the mesh. The pretreatments (oxidation or reduction) of the samples were performed in a stainless steel HV-IR cell, and were followed by degassing and by cooling the sample to the temperature of the experiment.

The dispersity of metal/TiO_2 was determined by H_2 adsorption (Rh, Pt) or by CO adsorption (Au) at room temperature.

The experiments with policrystalline were carried out in a HV chamber. Infrared spectra (4000-900 cm^{-1}) were recorded with a FTIR spectrometer with a wavenumber accuracy of $\pm$ 4 cm^{-1}. The spectrum of the pretreated sample (background spectrum) and the actual vapour spectrum were subtracted from the spectrum registered in the presence of vapour. Parallel with FTIR experiments the changes in the signal intensity of the main fragments of formic acid, formaldehyde and the possible products were monitored by a mass spectrometer.

The typical cleaning procedure of the TiO_2 (110) single crystal (Crystal Tec.) consisted of 15 min Ar^+-bombardment, 30 min annealnig at 900 K and cooling in oxygen in an UHV chamber. This procedure ensured us a clean, (1×1) surface structure. Rh was deposited on the $TiO_2(110)$-(1×1) by resistive heating of a Rh filament. The cleanness of the sample surface and the ultrathin metal adlayer was checked by Auger electron spectroscopy. RAIRS spectra of HCOOH adsorption on well-defined and clean TiO_2 (110) -(1×1) and Rh/TiO_2 (110)-(1×1) were recorded in UHV system with FTIR spectrometer.

Formic acid was of 99.9 % purity, formaldehyde was prepared by thermal decomposition of paraformaldehyde at 453 – 473 K.

3. NEW SCIENTIFIC RESULTS

1. The formation of formaldehyde was detected in the adsorbed layer on $TiO_2(110)$-(1×1) and $Rh/TiO_2(110)$-(1×1) surface and both in the gas phase and adsorbed layer on the TiO_2, 1% and 5% Pt-, Rh- and Au/TiO_2 powder catalysts.

2. It was proved, that the amount of formaldehyde depended on the pretreatment, the metal content of the catalysts and on the temperature of the interaction.

3. The amount of formaldehyde depended on the character of the supported metal too. The formaldehyde formed in the highest concentration on Pt/TiO_2, and its amount in the adsorbed layer decreased in the order of $Au/TiO_2 > TiO_2 > Rh/TiO_2$.

4. It was established that the formation of formaldehyde through the deoxygenation of formic acid took place at oxygen vacancies of TiO_2 and/or metal sites.

5. It was shown that the development of water and carbon monoxide was not directly linked thus the simple unimolecular reaction proposed for the H_2O and CO formation could be excluded.

6. It was presumed that CO originated not from the dehydration of formic acid but from the decomposition of formic acid through formaldehyde.

7. It was established that molecularly adsorbed formaldehyde, formic acid, formate, dioxymethylene and polyoxymethylene surface species formed during the interaction of formaldehyde with the investigated catalysts.

8. At higher temperatures the decomposition of molecularly adsorbed formaldehyde and dioxymethylene resulted in mainly H_2 and CO in the gas phase.

9. It was more than likely that the forming of H_2 and CO through the decomposition of formaldehyde took place at the surface metal sites.

10. It was shown that the formation of gasphase ethylene, acetylene and formic acid depended on the concentration of oxygen vacancies of the catalysts: by the increase of the metal content of the catalysts the amount of these products decreased.

11. It was proved that the main source of CO in the catalytic transformation of HCOOH could be the thermal decomposition of formaldehyde produced by the deoxygenation of HCOOH.

4. APPLICATION OF THE RESULTS

Results of this work have importance mainly in the field of fundamental studies, the main application of these are noteworthy for theoretical purposes. In our measurements formaldehyde can be detected both in the adsorbed layer and in the gas phase. The presence of formaldehyde in the adsorbed layer may give a new approach in the explanation of formic acid decomposition reactions. This presumption opens up a new prospect to producing more effective catalysts. The results gained during the study of surface chemistry of formaldehyde can give supplement information to the catalytic transformation of aldehydes, too.

5. PUBLICATIONS

Impact Factors

1. A. Berkó, T. Bíró, **T. Kecskés,** F. Solymosi: Thermal induced selforganization of oxide nanodots produced by low energy Ar^+ sputtering on TiO_2 (110)-(1×2) surface.
   Vacuum **61** (2001) 317-322.   **0.541**

2. **T. Kecskés**, R. Barthos, J. Raskó, J. Kiss: The effect of adsorbed CO on the surface chemistry of CH_3 on Rh(111).
   Vacuum **71** (2003) 107-111.   **0.541**

List of publications on which the thesis is based:

3. J. Raskó, **T. Kecskés**, J. Kiss: Formaldehyde formation in the interaction of HCOOH with Pt supported on TiO_2.
   Journal of Catalysis **224** (2004) 261-268.   **3.293**

4. **T. Kecskés**, J. Raskó, J. Kiss: FTIR and mass spectrometric study of HCOOH interaction with TiO_2 supported Rh and Au catalysts.
   Applied Catalysis **268** (2004) 9-16.   **2.258**

5. J. Raskó, **T. Kecskés**, J. Kiss: Adsorption and reaction of formaldehyde on TiO_2 supported Rh catalysts studied by FTIR and mass spectrometry.
   Journal of Catalysis **226** (2004) 183-191.   **3.293**

6. **T. Kecskés**, J. Raskó, J. Kiss: FTIR and mass spectrometric studies on the interaction of formaldehyde with TiO_2 supported Pt and Au catalysts.
   Applied Catalysis: **273** (2004) 55-62.   **2.258**

7. **T. Kecskés**, R. Németh, J. Raskó, J. Kiss New reaction route of HCOOH catalytic decomposition
   Vacuum:

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6. CONFERENCES

1. A. Berkó, T. Bíró, **T. Kecskés**, F. Solymosi: Thermal induced selforganization of oxide nanodots produced by low energy Ar^+ sputtering on TiO_2 (110)-(1×2) surface.
   8th *Joint Vacuum Conference,* Pula (Croatia), 06. 4-9.

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6. Kiss J., Solymosi F., Erdőhelyi A., Berkó A., Deák L., Raskó J., Novákné Hajdú É., Óvári L., Barthos R., Németh R., Hancz A., **Kecskés T.**, Szökő J., Farkas A.: Új típusú nanoszerkezetű katalizátorok előállítása és spektroszkópiai jellemzése.
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