



Investigation of photochemical processes on TiO₂ supported catalysts

Ph. D. thesis

Gyula Halasi

Supervisor: Dr. Frigyes Solymosi

professor emeritus

Chemistry Doctoral School

University of Szeged

Department of Physical Chemistry and Material Science

Szeged

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PRECEDING WORKS AND AIMS OF THIS STUDY

Great efforts are currently being made to produce hydrogen for fuel and for various other applications. Oxygenated hydrocarbons (methanol, ethanol) are the most generally and conveniently used sources of hydrogen production. A number of effective materials have been developed for the catalysis of their decomposition and reforming. Unfortunately, even on the most effective and expensive Pt metals, the reactions of these oxygenated hydrocarbons occur at relatively high temperatures. Their photocatalytic decomposition may provide a solution, as in this way hydrogen might be generated even at ambient temperature. Taking into account the requirements of fuel cells, a growing attention is also paid to the production of hydrogen free of CO. TiO₂, as a semiconductor is applied frequently as a photocatalyst. One of the most promising and most popular photocatalyst as proved by the number of publications in heterogeneous photochemistry papers, approximately 80% involved TiO₂-based materials. However, its wide bandgap (3.0-3.2 eV) requires the use of UV light during the reactions, as only 4% of solar energy can be utilized for photoreactions. In contrast with heterogeneous catalysis, where the catalytic efficiency of TiO₂ can be varied appreciably by multivalent cations, in photocatalysis anionic dopants have been found to be effective due to the narrowing of the bandgap of TiO₂, leading to visible light photocatalysis.

During my work, the primary aim was to build a photocatalytic system and to produce hydrogen in this system with a selectivity as high as possible in the photo-induced vapour-phase decomposition of ethanol, methanol and formic acid on pure, N-doped and metal-promoted TiO₂. In addition, special attention was paid to studying the effect of anionic doping (nitrogen). In the case of formic acid the primary aim was to produce H₂ virtually free of CO at ambient temperature. CO-free H₂ was obtained only on a few catalysts at 423-473 K, mainly in the presence of water. Furthermore, the determination of the direction of photoinduced decomposition and mechanism formed an integral part of my job, particularly if this way was different from the thermal one. The photocatalytic vapour decomposition of methanol to methyl formate as a main product was not described. Methyl formate is mainly produced by dehydrogenation of methanol over Cu-based catalysts at higher temperatures. However, recent works

showed that it is also formed in the photo-oxidation of methanol at room temperature. Connected to the ethanol topic, we examined the photocatalytic reduction of nitrogen-oxide (as a model molecule) with ethanol on TiO₂ supported catalysts.

In the present work we attempted was to study - taking into account the results of previous studies - the photoinduced vapour decomposition of methanol, ethanol and formic acid on pure and N-doped metal promoted TiO₂ catalysts. Based on the results obtained the incorporation of nitrogen positively influenced the catalytic behaviour of TiO₂. The deposition of Pt metals on pure and N-doped TiO₂ markedly enhanced the photodecomposition of the studied compounds.

EXPERIMENTAL METHODS

In the experimental work Hombikat UV 100 TiO₂ was used as a support and catalyst as well. For the preparation of N-doped TiO₂ we applied three different methods: pyrolysis (urea treatment), sputtering technique (in flowing NH₃ gas) and sol-gel synthesis (NH₄OH).

High surface area (300 m²/g) nanocrystalline TiO₂ was modified by urea pyrolysis. Titania powder was placed into a Schlenk tube connected to a round bottom flask containing 1 g of urea and heated in an annealing-furnace for 30 min at different temperatures (573, 673, 723, 773 K), (this sample was denoted SK).

In another cases TiO₂ was treated with NH₃. Hombikat TiO₂ powder was heated in a flow reactor system in argon gas atmosphere up to 870 K. The heating rate was 7 K/min. For doping, after the target temperature had been reached, the argon flow was replaced by NH₃ for 30 min. Subsequently, the powder was kept in flowing argon for 1 h at 870 K and then cooled to room temperature in flowing argon over a time period of 2-3 h (SY).

Titanium tetrachloride was used as a precursor of the third kind of N-modified TiO₂ sample (SX). 25 ml of TiCl₄ (3.0 mol l⁻¹) was carefully added into Milli-Q water with gentle stirring in ice-water bath. Then the solution was heated to 323 K. After that, 4.5 ml of glacial acetic acid and 35 w/w % solution of ammonia was added dropwise with vigorous stirring until pH 8 was reached, then the mixed solution was quickly cooled down to ambient temperature (about 298 K). The samples were finally obtained after the residue was vacuum-dried at 353 K for 12 h, followed by calcination at 723 K in flowing air for 3 h.

Metal-promoted (Pt, Pd, Ir, Ru, Rh) TiO₂ samples were prepared by impregnation of pure and various N-doped titania in the solution of noble metal salts.

Preparations were characterized by specific surface area (BET), dispersion of metals and X-ray diffraction (XRD), furthermore by X-ray photoelectron spectroscopy (XPS), by diffuse reflexion spectroscopy (DRS), and Fourier-transform infrared spectroscopic (FTIR) methods. The possible structural modification of TiO₂ was examined by X-ray diffraction. The amount of incorporated N and its binding mode

were studied by XPS measurements. Based on DRS experiments the efficiency of N incorporation was connected to the decrease of TiO₂ bandgap in the case of prepared N-doped samples.

The surface species formed during the illumination were studied by IR spectroscopy while the reaction products were analyzed by HP 5890 gas chromatograph. Infrared spectra (4000-900 cm⁻¹) were recorded with a FTIR spectrometer with a wavenumber accuracy of ±4 cm⁻¹. Photocatalytic reactions were followed in a thermally controllable photoreactor equipped with a 15 W UV and visible lamp as light sources. The reactor was connected to a gas-mixing unit serving for the adjustment of the composition of the gas or vapour mixtures to be photolyzed in situ. The gas-mixture was circulated by a membrane pump. During the photocatalytic measurements special attention was paid to monitor and minimize the nitrogen content of the system. The amount of all products were related to the volume of the loop. For photocatalytic measurements the sample (~80 mg) was sprayed onto the outer side of the inner quartz tube of the catalytic reactor. The surface of the catalyst film was 168 cm². The catalysts were oxidized at 573 K for 30 minutes and when metal was also present it was reduced in H₂ stream for 60 minutes at 573 K in the IR cell or in the catalytic reactor.

NEW SCIENTIFIC RESULTS

We can conclude the following new scientific results:

T.1 Production of highly active nitrogen-doped TiO₂ catalysts

T1.1. We investigated thoroughly the effect of nitrogen doping in the studied photocatalytic processes. It was established that the bandgap of N-doped TiO₂ continuously decreased from 3.15 to 2.17 eV with elevation of the temperature of its modification. The photocatalytic activity increased in parallel with the decreasing of the bandgap in case of the photoinduced decomposition of the studied compounds.

T1.2. In the case of TiO₂ samples prepared with the sol-gel method ~1 eV bandgap decrease was achieved. This sample has shown the highest photoactivity in the visible light experiments. Incorporation of N was proved by characterization of the catalysts produced.

T1.3. It was shown that the deposition of Pt metals on pure and N-doped TiO₂ dramatically enhanced the photodecomposition of the compounds investigated.

T1.4. It was proved that the lowering of the bandgap of TiO₂ through N incorporation facilitated the photolysis on TiO₂ and metal deposited TiO₂ even in visible light.

T.2 Investigation of photocatalytic decomposition of ethanol, methanol and formic acid

T2.1. It was established that doping TiO₂ with N greatly increased its photoactivity in its reaction with ethanol to give acetaldehyde and hydrogen as primary products. The acetaldehyde formed subsequently underwent photolysis to methane and CO. The dehydrogenation of ethanol remained the main reaction pathway. The deposition of Rh on pure and doped TiO₂ significantly enhanced the extent of photodecomposition of ethanol, even in visible light.

T2.2. It was verified that the decomposition of formic acid proceeds through the formation and decomposition of formate species and H₂ and CO₂ were formed as major products. The small amount of CO in the products suggests that the dehydration of formic acid also occurs to a limited extent.

T2.3. With the exception of Pd/TiO₂, addition of water to formic acid completely eliminated the small amount of CO formed. We achieved the formation of practically CO free hydrogen on Pt-, Rh-, Ir-, Ru/TiO₂ samples.

T2.4. It was proved that the photoinduced decomposition mechanism of the methanol is different from the thermal one, as demonstrated by a very small amount of carbon monoxide. In the vapour phase photocatalytic decomposition of methanol we published among the first the formation of methyl-formate and hydrogen as major products. Based on experiences the mechanism of methyl-formate production is that the formaldehyde adsorbed reacts with a methoxy group derived from the decomposition of methanol but the methyl-formate formation can occur by recombination of adsorbed formaldehyde, too.

T2.5. Deposition of Pt metals on pure and N-doped TiO₂ radically enhanced the photoreaction of methanol to methyl formate, which formed with a selectivity of 85-90 %, in UV and in visible light photolysis.

T.3 Studying the effect of temperature in photoinduced processes

T3.1. We also examined the thermal reaction and the results of these control experiments lead us to exclude the contribution of thermal effects to the decomposition of investigated compounds induced by illumination. In the photoinduced decomposition of formic acid and methanol we succeeded to decrease the amount of carbon monoxide compared to the thermal way. These results are to be assigned that the decomposition of formic acid can be shifted toward the dehydrogenation step while the decomposition of methanol occurred in the direction of formation of methyl formate.

T.4 Photocatalytic reduction of nitrogen-monoxide with ethanol

T4.1. Photolysis of NO + C₂H₅OH gas mixture on Ag/TiO₂ led to the formation of an intense IR band that can be attributed to the vibration of Ag-NCO species verifying that in the reduction of NO with ethanol adsorbed isocyanate species were formed. It was proved that in this process acetaldehyde and N₂O were produced as major products.

LIST OF PUBLICATIONS

I. Publications

Impact factor

Publications relating to the Ph. D. thesis:

1. **Gy. Halasi**, A. Kecskeméti, F. Solymosi
Photocatalytic reduction of NO with ethanol on Ag/TiO₂
Catal. Letters **135** (2010) 16-20.
MTMT: [1323984]
1,907
2. **Gy. Halasi**, I. Ugrai, F. Solymosi
Photocatalytic decomposition of ethanol on TiO₂ modified by N and promoted by metals
Journal of Catalysis **281** (2011) 309-317.
MTMT: [1628678]
6,002
3. **Gy. Halasi**, G. Schubert, F. Solymosi
*Photolysis of HCOOH over Rh deposited on pure and N-modified TiO₂;
Production of pure H₂*
Catal. Letters **142** (2012) 218-223.
MTMT: [1838555]
2,244
4. **Gy. Halasi**, G. Schubert, F. Solymosi;
*Photodecomposition of Formic Acid on N-Doped and Metal-Promoted TiO₂
Production of CO-Free H₂*
J. Phys. Chem. C **116** (2012) 15396-15405.
MTMT: [2046778]
4,814
5. **Gy. Halasi**, G. Schubert, F. Solymosi
*Comparative study on the photocatalytic decomposition of methanol on TiO₂
modified by N and promoted by metals*
Journal of Catalysis **294** (2012) 199-206.
MTMT: [2050201]
5,787

Publications not relating to the thesis:

6. Z. Balogh, **Gy. Halasi**, B. Korbély, K. Hernádi;
CVD-synthesis of multiwall carbon nanotubes over potassium-doped supported catalysts
Appl. Catal. A: Gen. **344** (2008) 191-197.
MTMT: [1166579] **3,190**
7. **Gy. Halasi**, T. Bánsági, F. Solymosi;
Production of hydrogen from dimethyl ether over supported rhodium catalysts
ChemCatChem **1** (2009) 311-317.
MTMT: [113804] **3,345**
8. **Gy. Halasi**, G. Schubert, F. Solymosi
Photocatalytic decomposition of dimethyl ether on metal promoted TiO₂
Under publication, ACS catalysis (2013)

Cumulative impact factor: **Σ_{IF} : 27,289**
Number of full citations/independent: **46/34**

II. Performances

1. F. Solymosi, **Gy. Halasi**, A. Kecskeméti,
Photocatalytic reduction of NO with ethanol on pure, N-doped TiO₂ and Ag/TiO₂
Third International Conference on Semiconductor Photochemistry,
Glasgow, (Scotland) 2010.
2. **Halasi Gyula**, Solymosi Frigyes,
Photocatalytic reduction of NO with ethanol on TiO₂ supported catalysts
XXXIII. Kémiai Előadó Napok,
Szeged, 2010.
3. **Gy. Halasi**, G. Schubert, F. Solymosi,
Photodecomposition of formic acid on N-doped and metal-promoted TiO₂;
Production of CO-free H₂
15th International Congress on Catalysis
München, (Germany) 2012.
4. A. Gazsi, **Gy. Halasi**, G. Schubert, F. Solymosi,
Production of CO-free hydrogen in photocatalytic reactions
Gordon Research Conferences, Chemical Reactions at Surfaces
Les Diablerets, (Switzerland), 2013.
5. **Gy. Halasi**, G. Schubert, F. Solymosi,
Production of hydrogen. Photocatalytic decomposition of dimethyl ether on
N-doped and metal promoted TiO₂
3rd European Symposium on Photocatalysis, JEP 2013,
Portoroz, (Slovenia), 2013.
6. **Halasi Gyula**, Schubert Gábor, Solymosi Frigyes,
Investigation of photochemical processes on N-doped and TiO₂ supported
catalysts
MTA Felületkémiai és Nanoszerkezeti Munkabizottsági ülés
MTA TTK, Budapest, 2013.