



A study of thermal reactions on catalysts containing gold nanoparticles

Ph.D. thesis

Gazsi Andrea

Supervisor:
Dr. Frigyes Solymosi
(Professor Emeritus)

Chemical Doctoral School

Department of Physical Chemistry and Materials Science
Faculty of Natural Sciences and Informatics
University of Szeged

2015

Szeged

Background and aims

One of the most important current tasks is the search for alternative energy sources and their development for industrial utilization. Hydrogen (H_2) is an obvious such energy source, and great efforts are being made to extend the use of hydrogen energy. H_2 can be used directly as a fuel in internal combustion engines, or indirectly in fuel cells. Operations with H_2 , however, involve a number of problems, especially as concerns its transport, storage and safety aspects. A potential solution might be the use of organic compounds which have a high H/C ratio, contain relatively few C-C bonds and can readily be transported as liquids. The platinum group metals are generally used as catalysts in the decomposition and reforming of such compounds, though these metals are active only at elevated temperatures, are expensive and can easily be poisoned by by-products formed in the reactions.

One of our aims, therefore, was the preparation of H_2 as an energy carrier. For this, starting compounds were chosen in which the C/H ratio was low, in order to achieve greater selectivity. Important points in the choice of the reactants were their ready availability or the possibility of their comparatively cheap preparation, and their lack of harmful effects on the environment. The most important compounds which met these criteria were formic acid, methanol, ethanol and dimethyl ether.

In order to enhance the H_2 selectivity, a gold (Au) catalyst impregnated on various supports was used in every case. The true catalytic application of Au as a catalyst began when it was discovered that Au in the form of 2-10 nm nanoparticles displays outstanding activity. One of the pioneers in the field was Haruta, who demonstrated in the early 1990s that CO undergoes oxidation at room temperature if Au nanoparticles dispersed on the surface of a variable valency oxide is used as catalyst. Extremely active catalyst samples were obtained with combined precipitation and separation-precipitation methods and during the past 20 years there has been a considerable increase in the interest in Au-containing catalysts, as reflected by an almost exponential rise in the number of publications.

One of the greatest challenges in the research on Au catalysis is the preparation of stable catalysts with long lifetimes, which is a precondition for industrial application. One of the keys to stability is the prevention of aggregation of the Au particles.

Besides H_2 , CO formed as by-product can poison the catalyst extensively, even in trace amounts, through adsorption to the metal particles of the catalyst, thereby giving rise to

great difficulties. This phenomenon can be avoided effectively if Au is used as catalyst as it readily oxidizes CO and prevents deactivation.

Mention should be made of the high activity of Au catalysts in the water-gas reaction (which plays a part in fuel cells), Au/Fe₂O₃ catalysts, for instance, remove CO from water-gas (as one of the components of fuel cells). The reaction proceeds more economically at lower temperature than on currently known catalysts.

Overall, the above facts led to the idea that the dispersion of Au particles on an oxide support might yield a catalyst with which CO-free H₂ can be prepared. We therefore set out to investigate the catalytic behaviour of Au nanoparticles on CeO₂, Al₂O₃, MgO, TiO₂, SiO₂, H-ZSM-5 and norite supports under thermal conditions in the decompositions of methanol, ethanol, formic acid and dimethyl ether from the aspects of the possibilities of increasing the conversion and the selectivity.

Methods applied

The catalysts applied contained Au nanoparticles in quantities in the range between 1 and 5% on the various supports. The catalysts were prepared in every case by impregnation. The necessary amount of a stock solution of HAuCl_4 was diluted with triply distilled (milli Q) water, and the pH was then adjusted to 7.5 with aqueous NH_3 solution. The calculated quantity of carrier was next added to the solution, and the mixture was stirred with a magnetic stirrer at 353 K, then filtered with a vacuum-filter, washed Cl^- -free, and dried under an infrared lamp. The resulting catalyst was heated in the air in a furnace at 573 K for 4-5 h (the two known oxides of Au decompose to Au and O_2 at 523 K). Before the thermal measurements, the catalyst obtained at this stage was oxidized with O_2 at 573 K for 30 min, and reduced with H_2 *in situ* at 673 K for 60 min, in a gas flow of 40 ml/min.

The norite support was pretreated before the preparation of the catalyst: it was treated with 10% HCl solution for 12 h, and then washed Cl^- -free. The metal contaminants (predominantly Fe) were next determined by an ICP-AES method.

The materials used as catalysts were CeO_2 (50 m^2/g), Al_2O_3 (100 m^2/g), MgO (170 m^2/g), TiO_2 (50 or 100 m^2/g), SiO_2 (198 m^2/g), norite (859 m^2/g) and H-ZSM-5 (425 m^2/g).

The reactants methanol, ethanol and formic acid were admitted to the system via a saturator, whereas dimethyl ether was added via a mass-flow regulator.

The dimensions of the Au particles impregnated on the surface of the catalysts were measured by transmission electron microscopy (TEM) (Philips CM 20 and Morgani 258 D instrumentation) at 300 K. Approximately 1 mg catalyst was placed on the TEM grid.

Changes in the oxidation state of the Au particles on the surface of the catalysts during the reactions were followed by means of X-ray photoelectron spectroscopic measurements with a Kratos XSAM 800 instrument operating without a monochromator. An Al $K\alpha$ ($h\nu = 1486.6$ eV) anode was used as X-ray photon source, and the spectroscope was fitted with a 180° hemispherical analyser. With the exception of Au/ SiO_2 , where the Si2p energy (103.4 eV) was used, the C1s bonding energy (285.1 eV) was the reference for the energies observed.

Infrared measurements to detect compounds formed on the surface of the catalysts were made with a Bio-Rad FTS 155 infrared spectrometer, in part with temperature increase during suction following the adsorption, and in part in response to illumination or high temperature during the reforming reaction of the reactant + water mixture. In the first case, the

reactant or the reactant + water-gas mixture was admitted to the reduced catalyst at room temperature for 30 min, after which the sample was heated under continuous suction to higher temperatures, where the spectra were recorded. In the other series of experiments, the infrared spectra were recorded *in situ* at high temperature. The spectra of the samples obtained after the reduction step served as background.

The courses of the thermal reactions, the formation of the products and their quantities were followed in every case with an HP 5890 Series II gas chromatograph. The various compounds were separated on PORAPAK Q and PORAPAK S columns, and were analysed with thermal conductivity and flame ionization detectors. The reactions proceeded at a pressure of 1 atm, in continuous flow, in a quartz-bed reactor tube (internal diameter 8 mm, length 25 cm). 0.3 g of catalyst was compressed into a pastille (exposed to 20 bar for several seconds), and the pastille was then placed at the centre of the reactor, stabilized by quartz wool on both sides so as to prevent movement of the particles in response to the flow. The dead-space of the reactor was decreased to the minimum through the use of quartz debris. The reactor tube was surrounded by a furnace (the temperature of which could be regulated), which ensured a constant reaction temperature during the experiment. Through the use of a room-temperature saturator containing the reactants in the liquid state, with the aid of Ar/N₂ as carrier gas, the reaction mixture was passed into the reactor, or the product mixture was passed into the gas chromatograph. The N₂ content of the carrier gas was determined for every sample, thereby ensuring the continuity of the feed. The flow rate was 60 ml/min. The reactant content of the gas mixture was 7% in the case of formic acid, and 9-10% in the cases of methanol, ethanol and dimethyl ether. In every case, the catalysts were pretreated *in situ* before the reactions. They were oxidized in a 40 ml/min stream of O₂ for 30 min at 573 K, then flushed with Ar for 15 min, reduced in a stream of H₂ for 60 min at 673 K, again flushed with Ar for 15 min, and finally cooled to the lowest reaction temperature. The Ar gas atmosphere was next replaced by the reactant gas mixture and the reactor temperature was progressively raised in 50 K steps from 473 K to 773 K, with analysis of the gases present at each temperature after equilibrium had been established. For study of the stability of the catalysts, the system was maintained at 773 K for 10 h and measurements were made at 40-min intervals.

For investigation of the reactions of mixtures of reactant and water in ratios of 1:1 and 1:3, the mixture in question was transferred to a vaporizer at a rate of 1.0 ml liquid/h with the aid of an infusion pump (Medicor Assistor PCI), and the gas was passed in an Ar/N₂ stream from the vaporizer into the reactor via a heated tube, condensation thereby being prevented.

Thermal desorption measurements were also made in the catalytic reactor. The catalyst was pretreated as described above, and the reactant was then adsorbed on its surface for 30 min at 333 K. This was followed by flushing of the system with Ar. Detection was carried out at 6-min intervals at a heating rate of 5 K/min up to 873 K in a 20 ml/min Ar flow.

In order to study the deposition of C formed in the course of the reactions, temperature-programmed reduction measurements were carried out. Following the reaction, the catalysts was heated from 300 K to 1100 K at 5 K/min in a 20 ml/min stream of pure H₂, and the products formed were analysed at 5-min intervals.

In the investigations of the reactions of the various reactants, the most active catalysts were applied and a 60-K temperature interval was selected in which the conversion lay in the range ~ 2–15%. At constant temperatures within this interval, measurements were made to detect the products formed, and the activation energies relating to the reactions were determined.

In the measurement of the reaction orders, the partial pressure of the fed-in reactant was varied, while the overall flow rate was maintained constant. The products formed at temperatures corresponding to low conversions were therefore detected on a given catalyst.

New scientific results

T1. Preparation and characterization of catalysts containing Au nanoparticles

T1.1. The preparation of catalysts containing Au nanoparticles was optimized. Detailed investigations revealed that the catalysts contained Au particles of the desired size (2–10 nm), were stable and demonstrated effective and reproducible catalytic action. It was confirmed that the impregnation of the oxide carriers with the Au nanoparticles significantly enhanced the conversions and H₂ selectivities of the examined reactions. Whereas the conversions on the pure supports were found to be 1–15%, those on the catalysts containing the Au nanoparticles under the same reaction conditions were 55–100%, depending on the Au content.

T1.2. The Au in the oxidized 1% Au/CeO₂ sample was predominantly in the oxidation states +1 and +3. Reduction of the catalyst at 673 K led to the reduction of the Au(III), but only partial reduction of the Au(I) to Au(0), probably because Au(I) is stabilized in the nanoparticles by the support. The binding energy of Ce(III) appeared when the support was impregnated with the Au nanoparticles, suggesting that the strong interaction between the Au and the CeO₂ led to the partial reduction of the Ce(IV).

T1.3. As expected, the Au catalysts proved to be stable in the reactions of CO formation. As evidence of this, the addition of CO to the system in the case of formic acid did not influence (or merely extremely slightly) the rate or the direction of the decomposition. This was in contrast with the results obtained with Rh-containing catalysts, when the decomposition was blocked practically completely by the presence of CO. Our measurements revealed that the CO formed in the course of the decomposition does not bind strongly to the Au particles, and therefore does not decrease the number of free sites important for the occurrence of the reaction.

T1.4. We assume that Au/CeO₂ contains highly active centres, presumably on the boundary surface between the Au and the partially reduced CeO_x, where an electrical interaction develops between the Au and the n-type semiconductor CeO₂. The favourable catalytic properties of the Au catalysts may be ascribed to the Au/oxide boundary surface.

T2. Decomposition of reactants

T2.1. The catalytic properties (selectivity and activity) of the Au nanoparticles in the decomposition and reforming of the reactants were found to depend sensitively on the nature of the support. The highest activity was achieved with the Au/CeO₂ catalyst. The characteristic reaction pathway on Au/Al₂O₃ was dehydration, the ability of Al₂O₃ to induce dehydration being so strong that the Au could not exert its effect.

T2.2. The results obtained during the investigations of the adsorption of methanol on a solid surface and its subsequent reactions confirmed that the rate-determining step in the decomposition of methanol is the rupture of a single C–H bond in the readily formed methoxy group. Infrared measurements clearly showed the formation of the methoxy group on both the Au and the CeO₂ support.

T2.3. Our Fourier transformation infrared (FTIR) and thermal desorption (TPD) investigations on pure SiO₂ and on Au/SiO₂ demonstrated that the ethyl radical is formed on the Au particles during the decomposition of ethanol at 300 K. At temperatures above 400 K, the ethyl radical undergoes further decomposition to acetaldehyde, H₂, ethylene and methane.

T2.4. The acetaldehyde formed in the course of the dehydrogenation of ethanol on Au/CeO₂ was shown to be transformed to ketones containing 5 C atoms (2-pentanone and 3-penten-2-one) in amounts which increased with increase of the Au content of the catalyst. The formation of these compounds was observed only in the case of CeO₂ as support.

T2.5. The Au nanoparticles proved to promote cleavage of a C–O bond in dimethyl ether, affording a surface complex AuOCH₃. The slowest step in the H₂-producing reaction was the splitting of a single C–H bond in the methoxy groups.

T2.6. The decomposition of dimethyl ether on the Au/CeO₂ catalyst resulted in the formation of H₂, whereas the main process that occurs on Au/Al₂O₃ is the hydrolysis of dimethyl ether. Accordingly, we made use of both these properties and utilized Au nanoparticles on a mixed oxide, CeO₂/Al₂O₃, under appropriate conditions. This turned out to be highly effective from the aspect of H₂ formation in the decomposition and reforming of dimethyl ether. The high

activity was attributed to the ready formation of methanol on the Al_2O_3 surface and to the high activity of the Au/CeO_2 surface in the decomposition of methanol.

T3. Reforming reactions

T3.1. It proved possible to decrease the quantity of CO formed in the reactions and hence to increase the selectivity of H_2 formation (to 100% in the case of formic acid) through the addition of water to the reactants. The result achieved can be attributed to the effectivity of the Au/oxide catalysts in the water-gas reaction. The presence of water was much less effective as concerns the formation of H_2 on Au/norite, probably as a consequence of the lack of active OH groups, which are necessary for the water-gas reaction to occur.

T3.2. The addition of K to the $\text{Au/CeO}_2\text{-Al}_2\text{O}_3$ catalyst further accelerated the formation of H_2 during the reforming of dimethyl ether, which is probably a result of the promoting action of K in the water-gas reaction. The methane content was also demonstrated to be decreased in the case of the K-doped samples, as confirmed by the enhanced rate of methane reforming. The K was found to behave as an electron donor with the adsorbed water and the CO, activating them and hence resulting in a higher H_2 yield.

List of publications

Publications serving as the basis of the Ph.D. thesis

Hydrogen Formation in the Reactions of Methanol on Supported Au Catalysts

Gazsi, A.; Bansagi, T.; Solymosi, F.

Catal Lett. 131 (2009) 33.

MTMT identification no.: 113805

IF: 2.021

No. of independent citations: 13

No. of self-citations: 4

Adsorption and decomposition of ethanol on supported Au catalysts

Gazsi, A.; Koos, A.; Bansagi, T.

Catalysis Today 160 (2011) 70.

MTMT identification no.: 1422942

IF: 3.407

No. of independent citations: 17

No. of self-citations: 3

Production of hydrogen from dimethyl ether on supported Au catalysts

Gazsi, A.; Ugrai, I.; Solymosi, F.

Applied Catalysis A: General 391 (2011) 360.

MTMT identification no.: 1413930

IF: 3.903

No. of independent citations: 15

No. of self-citations: 3

Decomposition and Reforming of Formic Acid on Supported Au Catalysts: Production of CO-Free H₂

Gazsi, A.; Bansagi, T.; Solymosi, F.

J. Phys. Chem. 115 (2011) 15459.

MTMT identification no.: 1680533

IF: 4.805

No. of independent citations: 18

No. of self-citations: 6

Publications not directly related to the Ph.D. thesis

Decomposition and reforming of methanol on Pt metals supported by carbon Norit

Tolmacsov, P.; Gazsi, A.; Solymosi, F.

Applied Catalysis A: General 362 (2009) 58.

MTMT identification no.: 113800

IF: 3.564

No. of independent citations: 13

No. of self-citations: -

A Comparative Study of the Decomposition of Ethanol on Pt Metals Supported by Carbon

Gazsi, A.; Tolmacsov, P.; Solymosi, F.

Catal Lett. 130 (2009) 386.

MTMT identification no.: 1241673

IF: 2.021

No. of independent citations: 4

No. of self-citations: 2

Photocatalytic decomposition of formic acid and methyl formate on TiO₂ doped with N and promoted with Au. Production of H₂

Gazsi, A.; Schubert, G.; Pusztai, P.; Solymosi, F.

J. Hydrogen Energy 38 (2013) 7756.

MTMT identification no.: 2399301

IF: 2.930

No. of independent citations: 3

No. of self-citations: 3

Photocatalytic decomposition of methanol and ethanol on Au supported by pure or N-doped TiO₂

Gazsi, A.; Schubert, G.; Bansagi, T.; Solymosi, F.

Journal of Photochemistry and Photobiology A: Chemistry 271 (2013) 45.

MTMT identification no.: 2399279

IF: 2.291

No. of independent citations: -

No. of self-citations: 1

Photocatalytic decomposition and oxidation of dimethyl ether over Au/TiO₂

G. Schubert, A. Gazsi, F. Solymosi

Journal of Catalysis 313 (2014) 127-134

MTMT identification no.: 2577685

IF: 6.073

No. of independent citations: -

No. of self-citations: -

Overall impact factor: 31.015

No. of independent citations: 83

No. of self-citations: 22

Lectures relating to the Ph.D. thesis

Metanol bomlásának vizsgálata különböző hordozós Au katalizátorokon

Gazsi A.

Kémiai Előadói Napok

Szeged, 2010.

Preparation of carbides effective for the production of CO-free H₂

Solymosi F.; Gazsi A.;

17th International Symposium on the Reactivity of Solids

Bordeaux, 2011.

Lectures not directly related to the Ph.D. thesis

Hydrogenation activity of Pt/SBA-15 catalysts in the conversion of cyclohexene to cyclohexane

Rémiás R.; Gazsi A.; Molnár É.; Tóth T.; Kukovecz Á.; Kónya Z.; Kiricsi I.

Pannon Conferences

Szeged, 2006

Photodecomposition of formic acid on N-doped and Au-promoted TiO₂. Production of CO-free H₂

Solymosi F.; Gazsi A.;

10th Natural Gas Conversion Symposium

Doha, 2013.

Poszter: Production of CO-free hydrogen in photocatalytic reactions

Solymosi F.; Gazsi A.;

Gordon Research Conferences, Chemical Reactions at Surfaces

Les Diablerets,

Switzerland, 2013.