

# SELECTIVE ETHANOL OXIDATION ON SUPPORTED BIMETALLIC GOLD CATALYSTS: BASE CHEMICALS FROM “GREEN” PROCESSES

Andreas Nagl<sup>a</sup>, Sotiria Mostrou-Moser<sup>b</sup>, Jenoff De Vrieze<sup>c</sup>, Mark Saeys<sup>c</sup>, Goran Dražić<sup>d</sup>, Jeroen van Bokhoven<sup>b</sup>, Karin Föttinger<sup>a</sup>

<sup>a</sup>E165 - Institute of Materials Chemistry

<sup>b</sup>Institute for Chemical and Bioengineering, ETH Zürich, Zürich, Switzerland

<sup>c</sup>Department of Materials, Textiles and Chemical Engineering, Ghent University, Ghent, Belgium

<sup>d</sup>Department for Environmental Sciences and Engineering, National Institute of Chemistry, Ljubljana, Slovenia

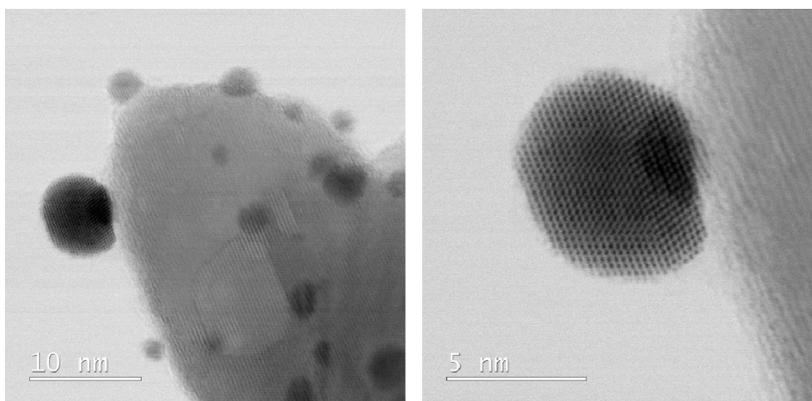
## INTRODUCTION

Both acetaldehyde and acetic acid are important base chemicals produced on large scale. Thus, a “green” heterogeneous process accessing renewable feedstocks such as (bio-)ethanol is highly desirable. Bimetallic catalysts have gained much interest as they offer a wide range of possibilities to tune catalytic properties by the choice of the second metal component. We study the selective oxidation of ethanol to acetaldehyde or acetic acid using highly performant bimetallic gold catalysts supported on titania with Ag and Ru as promoters, both of which have a high affinity towards O<sub>2</sub><sup>[1-3]</sup> (relevant for the activation of molecular oxygen as “mild” reactant).

## EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

Catalysts are prepared with Deposition Precipitation (Au catalysts) and Incipient Wetness Impregnation (AuAg prepared from the Au catalysts): 5 wt.% Au and 1 wt.% Ag/Ru on titania. Rutile, Anatase and (commercial) mixtures of Rutile and Anatase were evaluated as support materials. The samples underwent thorough evaluation of their catalytic properties in gas-phase as well as in (aqueous) liquid phase (at the ETH Zurich<sup>[4]</sup>). In gas-phase, the influence of H<sub>2</sub>O (on the reaction rate as well as the product distribution) was investigated.

However, the mechanism of oxygen activation (and the role of the catalyst support in it) as well as the structure of the of the bimetallic metal particles (segregation effects, alloy formation, surface oxides, eg. AgO<sub>x</sub>) are still poorly understood. Catalyst materials were characterized by HR-(S)TEM (see Picture 1), STEM-EDX as well as XRD and XPS (to determine the surface composition and the oxidation states of the metal nanoparticles and the Ti(III)/Ti(IV) ratio). Moreover, operando studies were performed: DR-UV-Vis spectroscopy was used to monitor the evolution plasmon bands of the bimetallic nanoparticles and reactive species on the catalyst surface were monitored using DRIFTS, thus giving insight into the reaction mechanism. Experiments were backed by DFT calculations from our project partners at the Ghent University.



**Picture 1:** HR-STEM micrographs of the AuAg nanoparticles on TiO<sub>2</sub>.

## RESULTS AND DISCUSSION

Both Ag and Ru show a strong synergistic effect with Au: AuAg and AuRu show high-conversion and long-term stability of at least 72 hours in combination with a high resistance against sintering. In gas-phase, selectivity is throughout > 95% with acetaldehyde as the main product and mainly methyl-acetate and acetic acid as side products. In contrast to that, in (aqueous) liquid phase acetic acid is the dominant product (and pure Au or AuPt is more beneficial than AuAg or AuRu). Even with an EtOH/H<sub>2</sub>O ratio of 1:2, this shift from acetaldehyde to acetic acid cannot be achieved in gas-phase.

Rutile is by far the best catalyst support, outperforming both Anatase and mixtures of Anatase/Rutile (probably also because of the less beneficial distribution of the metal nanoparticles between Anatase/Rutile as reported in<sup>[5]</sup>). Differences in oxygen vacancies/mobility between Rutile and Anatase are suspected and are to be confirmed by operando XPS studies.

Preliminary XAS as well as (ex-situ) HR-STEM-EDX measurements show evidence for alloy formation. Operando DRIFTS measurements revealed a relatively clean surface of the catalyst, which is in alignment with DFT calculations (clean surface for Au(111) and an alkoxy-covered surface for Ag(111)). The exact role of (possible) Ag/Ru surface segregation (and its possible influence on sintering as reported for AuIr systems<sup>[6]</sup>) and alloy formation under dynamic conditions will be studied in future operando XAS and XPS beamtimes in the first half of 2018.

## CONCLUSION

AuAg as well as AuRu have proven to be performant catalysts for the oxidation of ethanol to acetaldehyde with high selectivities (> 95%) and excellent long-term stability. In gas-phase, the main product is acetaldehyde, whereas in aqueous solution in liquid phase acetic acid is formed.

Alloy formation was observed for AuAg and evidence for the oxidation of Ag and Ru was found. For AuRu, we show irreversible storage damage due to Ru(IV) formation.

Operando XAS and (near ambient pressure) XPS (first preliminary results to be presented at the VSS) will shed light on the electronic structure, possible (surface) segregation of Ag/Ru, and alloy formation of the catalyst under dynamic reaction conditions.

Thus, bimetallic Au supported on titania is a promising catalyst for a green heterogeneous ethanol oxidation under mild conditions (best operating conditions at approx. 250°C) with molecular oxygen as oxidant.

## REFERENCES

- [1] R. Blume, M. Hävecker, S. Zafeirotos, D. Teschner, E. Vass, P. Schnorch, A. Knop-Gericke, R. Schlögl, S. Lizzit, P. Dudin, A. Barinov, M. Kiskinova, *Phys Chem Chem Phys*, 3648 (2007)
- [2] X. Bao, M. Muhler, T. Schedel-Niedrig, R. Schlögl, *Phys. Rev. B*, 2249 (1996)
- [3] M. Schmid, A. Reicho, A. Stierle, I. Costina, J. Klikovits, P. Kostelnik, O. Dubay, G. Kresse, J. Gustafson, E. Lundgren, J. N. Andersen, H. Dosch, P. Varga, *Phys. Rev. Lett.*, 146102 (2006)
- [4] S. Mostrou-Moser, T. Sipőcz, B. Fődi, F. Darvas, A. Nagl, K. Föttinger, J. A. v. Bokhoven, submitted in *Green Chemistry*, (2018)
- [5] D. Tsukamoto, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, *J. Am. Chem. Soc.*, 6309 (2012)
- [6] C. W. Han, P. Majumdar, E. E. Marinero, A. Aguilar-Tapia, R. Zanella, J. Greeley, V. Ortolan, *Nano Lett.*, 8141 (2015)