KINETIC STUDIES ON BIMETALLIC Au CATALYSTS: INFLUENCE OF WATER

Markus Latschka[a], Andreas Nagl[a], Jenoff E. De Vrieze[b], Sotiria Mostrou-Moser[c], Jeroen A. van Bokhoven[c], Mark Saeys[b], Karin Föttinger[a,*]

[a] E165 - Institute of Materials Chemistry
[b] Laboratory for Chemical Technology, Technologiepark 914, B-9052 Gent, Belgium
[c] Institute of Chemical and Bioengineering, Vladimir-Prelog-Weg 1-5/10. 8093 Zürich, Switzerland

INTRODUCTION

Acetaldehyde is an important base chemical, at present it is mainly produced by the Wacker-Hoechst process, which requires petrochemical starting materials. Acetaldehyde can also be made by the oxidation of ethanol and ethanol can be produced renewably from biomass[1].

Normally gold is catalytically very inactive, but when the gold particles have a small diameter like below 30 nm, the catalytic activity is getting much better for a number of reactions. Then also oxygen can absorb on the gold surface even at room temperature. The catalytic activity of the gold catalyst per unit surface area for CO oxidation is about 100 times better when the gold is on a TiO_2 support as for the pure gold particles[2].

Therefore, supported gold nanoparticles have been studied as catalysts for the oxidation of alcohols to aldehydes with oxygen in the gas phase. When the reaction takes place in an aqueous solution the corresponding carbon acid is formed instead of the aldehyde[3]. The reason why the acetaldehyde is further oxidized to acetic acid only in the liquid phase reaction has not yet been determined.

When two metals are combined in a catalyst, the advantages of both individual metals can appear. However, also a synergistic effect can occur resulting in new functionalities of the catalyst[4].

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

Our group at the TU Wien synthesized gold nanoparticles on rutile wet-chemically via deposition-precipitation, while the silver was added via wetness impregnation. The bimetallic catalyst consists of 5 wt% gold and 1 wt% silver on rutile, the monometallics contain the same amount of the respective metals.

For the characterization of the catalysts, STEM-HAADF images were taken (FEI Tecnai F20 FEG-TEM). From these measurements a particle size distribution was obtained and thereby a quantification of the surface atoms of the precious metals.

Around 20 mg of the catalyst diluted with quartz sand were loaded into a continuous-flow fixed-bed quartz reactor to determine the reaction kinetics for ethanol oxidation to acetaldehyde. Prior to the reaction, the catalysts were pretreated with 20 % oxygen and 5 % hydrogen, both diluted in He, at 400 and 300 °C, respectively. The reaction took place with 1.1 mL/min of ethanol (introduced with a bubbler) and oxygen (total flow ~ 50 mL/min). In addition to the bimetallic catalyst, the monometallic Au and Ag references were tested as well.

The results obtained were compared with kinetic studies of ethanol oxidation in the liquid phase on the same catalysts, which were carried out by a collaborating group at the ETH Zurich. In the aqueous phase, the main product is acetic acid instead of acetaldehyde. To explore the reason for this and the influence of water, we added water during the gas phase ethanol oxidation.

The results of the catalytic studies in the gas and the liquid phase were compared with theoretical calculations, which were performed within a cooperation with the Saeys group at the University of Gent with the VdW-DF2 functional.

RESULTS AND DISCUSSION

In Figure 1 the TEM images of the pretreated Au and AuAg/TiO_2 catalysts can be seen. Both catalysts have a similar particle size distribution with small nanoparticles of around 3 nm. The monometallic silver catalyst showed the same result.

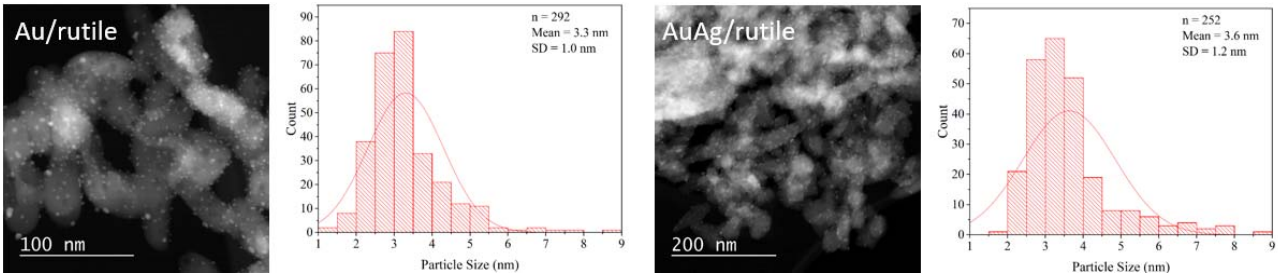

Figure 1: STEM-HAADF-Images and the resulting size distribution of the Au nanoparticles on rutile (left) and the AuAg nanoparticles on rutile (right).

Figure 2 shows the reaction rate of acetaldehyde formation on the three catalysts increasing with temperature. As expected, the monometallic gold catalyst had a better performance than the silver catalyst. The synergetic effect of the two precious metals in the bimetallic catalyst can be seen very well. The reaction rate is significantly higher than on the monometallic catalysts. Compared to reaction in liquid phase, an interesting behaviour occurred. Besides the fact that acetic acid is the main product in aqueous solution, the monometallic Au catalyst showed a higher conversion than the bimetallic AuAg one. In addition, other metal combinations like AuRu and AuPt were tested and the performance of these catalysts was completely reversed. For the gas phase the order by the activity was AuAg > Au > AuRu > AuPt and for the liquid phase it was AuAg < AuRu < Au < AuPt. The reason for the different behaviour might be related to the presence of water.

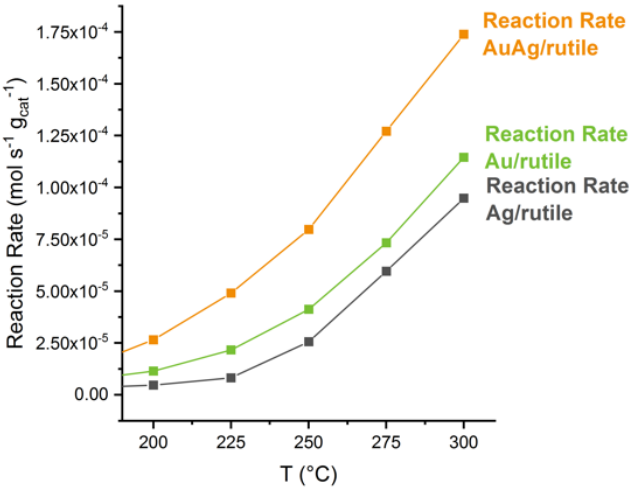

Figure 2: Reaction rate for acetaldehyde for both monometallic and the bimetallic catalyst.

CONCLUSION

The synergetic effect of silver and gold in the gas phase reaction of ethanol to acetaldehyde could has been proven. The influence of water on the catalysts during the reaction is still under investigation. Theoretical calculations should also help to elucidate the reaction pathways.

REFERENCES

[1] Baerns M. et al., Technische Chemie, 595-597, 2013

[2] Haruta M., Catalysis Today 36, 153-166, 1997

[3] Enache D. et al., Science VOL 311, 362-365, 2006

[4] Zaleska-Medynska A. et al., Advances in Colloid and Interface Science 229, 80-107, 2016