Gold Catalysis: New Routes to Key Commodity Chemicals

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Introduction

Gold has always been a fascinating element among chemists, and recently it has been found to be catalytically active in several reactions. To date gold catalysis has mainly been focusing on CO oxidation, [1] but lately, several reports concerned with selective oxidation of alcohols have also emerged [2].

Presently, acetic acid and other carbonaceous commodity chemicals are mainly produced from petrochemical sources, but due to the diminishing amount of fossil fuels it is important to investigate new routes. One possibility is to use renewable feedstocks such as bioethanol. The production of bioethanol is growing, and it could be economically feasible to convert the ethanol into acetic acid. Today, bioethanol is mainly used as a fuel or fuel additive, but it has also attracted interest as a source for hydrogen [3]. However, it appears much more feasible to use ethanol as a feedstock for chemical production from both an economical and green perspective. In addition, the demand for acetic acid is increasing, which further indicates that it is time to find useful alternatives to the fossil fuels. Furthermore the price of renewable feedstocks is decreasing, whereas the price of fossil fuels is increasing making the ethanol route even more interesting.

Many methyl esters are industrially important chemicals, both as products in *e.g.* the perfume industry as solvents, extractants, diluents and as intermediates. An environmentally friendly route to such chemicals could be an important step forward towards a more green chemical industry.

Materials and Methods

Experiments were conducted in stirred autoclaves at elevated pressures and temperatures. Two different gold catalysts were used, one reference catalysts Au/TiO_2 acquired from the World Gold Council and one prepared by deposition precipitation, Au/ $MgAl_2O_4$. The oxidation of ethanol was performed in aqueous solution. By changing the solvent from water to methanol primary alcohols can selectively be oxidized by dioxygen to the corresponding methyl esters using Au/TiO_2 and base. The products were analyzed by gas chromatography (GC) and combined gas chromatography and mass spectroscopy (GC-MS). Atmospheric air or pure dioxygen were used as oxidant.

Results and Discussion

The results for oxidation of ethanol showed ethanol conversions above 90 % and selectivities toward acetic acid of around 80 %. Importantly, the activities of the catalysts seem apparently independent of pH, in contrast to present catalysts based on Pt and Pd [4].

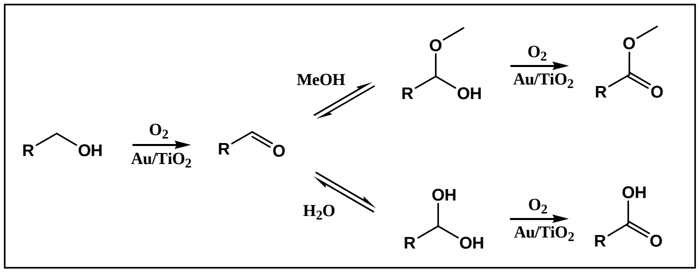

Figure 1. Reaction scheme for oxidation of alcohols with gold catalyst

The result concerning ester formation gave conversions in the vicinity of 99 % and yields of the methyl esters in the same range as the conversion [5].

The two oxidation pathways give possible alternatives for a greener production of commodity chemicals, which utilize other feedstock than the fossil fuels.

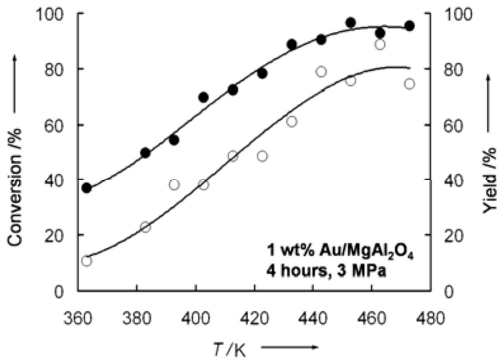

Figure 2. Conversion of ethanol (closed circles) and yield of acetic acid (open circles) as a function of temperature.

References

1. Haruta, M. and Daté, M. *Appl. Catal. A: General* 222, 427 (2001).
2. Prati, L. and Porta, F. *Appl. Catal. A: General* 291, 199 (2005).
3. Deluga, G.A., Salge, J.R., Schmidt, L.D. and Verykios, X.E. *Science* 303, 993 (2004).
4. Christensen, C.H., Jørgensen, B., Rass-Hansen, J., Egeblad, K., Madsen, R., Klitgaard, S.K., Hansen, S.M., Hansen, M.R., Andersen, H.C. and Riisager, A. *Angew. Chem. Int. Ed.* 45, 4648 (2006).
5. Nielsen, I.S., Taarning, E., Egeblad, K., Madsen, R. and Christensen, C.H. submitted (2006).