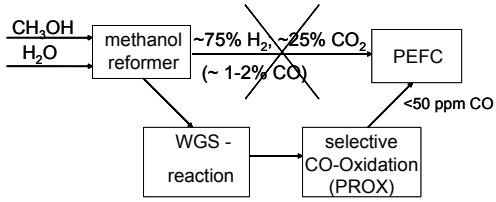
Deactivation of Au/CeO_2 catalysts in watergas-shift reaction from idealized to realistic conditions

A. Karpenko, V. Plzak** A. Chuvilin*, B. Schumacher, U. Kaiser* und R. J. Behm

Abteilung Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm
*Zentrale Einrichtung Elektronenmikroskopie Materialwissenschaftliche Elektronenmikroskopie, D-89069 Ulm
**Zentrum für Sonnenenergie- und Wasserstoff-Forschung, Helmholtzstr. 8, D-89081 Ulm

Motivation

CO removal from H_2-rich feed gases for polymer electrolyte fuel cell (PEFC) systems

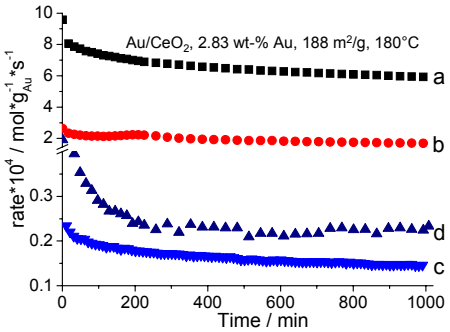


WGS reaction: $CO + H_2O \rightarrow H_2 + CO_2$

- Understanding of the deactivation mechanism of Au/CeO_2 catalysts
- Optimization of activity and stability of Au/CeO_2 catalysts for watergas shift (WGS) reaction

Results

1. Influence of the Reaction atmosphere



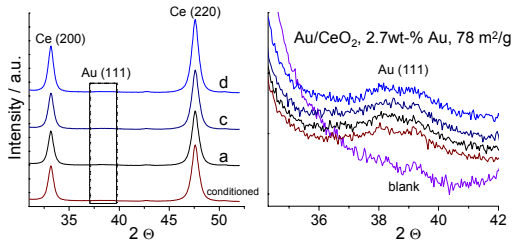
Deactivation during 1000 min reaction

a	26.3%
b	27.7%
c	37.5%
d	57.6%

- Negative influence of both products (H_2 and CO_2) on the catalyst activity
- Deactivation behavior depends strongly on the amount of CO_2 and is independent from the presence of H_2

a) Pure watergas: 1 kPa CO, rest N_2 ; + 2 kPa H_2O pure watergas
b) Idealized reformate: 1 kPa CO, rest H_2 ;+ 2 kPa H_2O – idealized reformate
c) Semi-realistic reformate: 1 kPa CO,1 kPa CO_2, rest H_2; + 2 kPa H_2O
d) Realistic reformate: 4 kPa CO, 1 kPa CH_4, 16.75 kPa CO_2, rest H_2; + 20 kPa H_2O

2. CeO_2 particle size distribution (XRD)

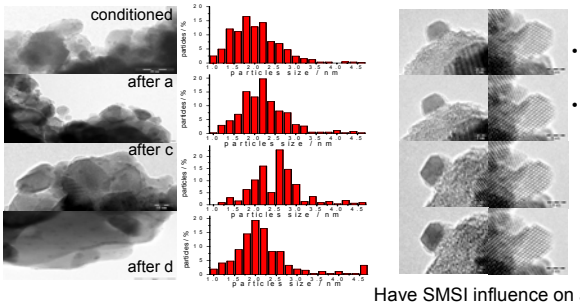


- Ceria does not sinter during WGS reaction under different gas mixtures
- Gold particles size is stable

sample	Au(111)* nm	Ce(200)* nm	Ce(220)* nm	Au(111)** nm	Ce(200)** nm	Ce(220)** nm
a	1.7	13.4	10.8	2.0	7.2	5.3
b	2.0	13.4	10.9	1.8	7.2	5.4
c	1.8	13.4	10.9	1.8	7.3	5.4
d	1.9	13.4	11.0	1.8	7.1	5.6

* Au/CeO_2 with 78 m²/g, ** Au/CeO_2 with 188 m²/g

3. Gold particle size distribution (TEM)

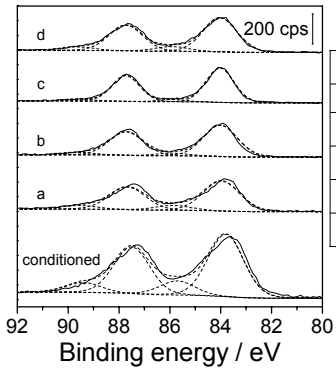


- Broad distribution of gold particle sizes
- Increase gold particles with diameter more than 3 nm from freshly conditioned to realistic reformate

Have SMSI influence on activity and stability of Au/CeO_2?

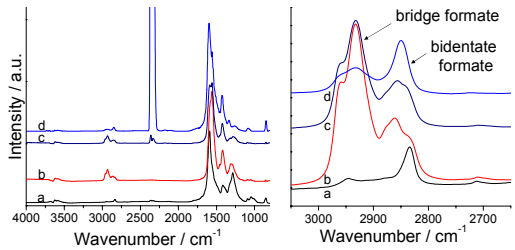
- TEM+XRD: No significant particle size modifications

4. Reaction atmosphere ↔ Reaction intermediates ↔ ↔Au^{n+} formation



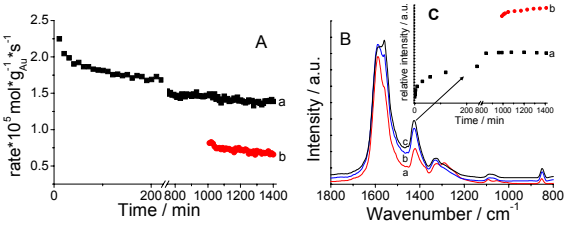
Reaction atmosphere	Au^{n+}	Ce^{3+}	Au/Ce
e) realistic	12.8	~44.0	0.048
c) Semi-realistic	7.0	23.6	0.039
b) Idealized reformate	8.7	24.9	0.044
a) Pure watergas	14.1	26.7	0.049
Reductive treatment	19.7	20.9	0.096

- Correlation between reaction rate and Au^{n+} and Au/Ce ratio



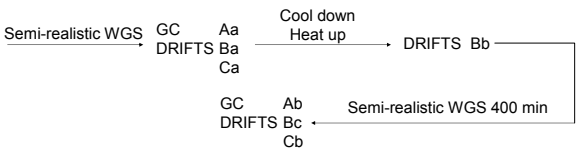
- Change of bidentate formate to bridge formate species a)→d)
- Correlation between H_2 concentration and bridge formate amount
- Strong increase of carbonate concentration from pure watergas to realistic reformate. Is carbonate a reason for deactivation?

5. Reversible deactivation



- Strong decrease of activity after reaction transients experiment
- Deactivation correlates well with increase of carbonate peak at 1423 cm^{-1}

Reaction transients experiment:



Conclusion

- Irreversible Au and CeO_2 particle sintering during reaction is small, but increasing amount of gold particles with sizes more than 3 nm by watergas-shift reaction
- Increase of deactivation from pure watergas to realistic reformate
- Substitution of bidentate formate by bridge formate upon changing from watergas to realistic reformate
- Strong deactivation of Au/CeO_2 through carbonate deposition on the catalyst surface

Acknowledgment

We acknowledge financial support by DFG (Graduiertenkolleg of Ulm „Molekulare Organisation und Dynamik an Grenz- und Oberflächen“ GRK 328) and Landesstiftung Baden-Württemberg („Selektive CO Entfernung aus H_2-reichem Reformat mit einem kostengünstigen Reaktorkonzept auf der Grundlage neuartiger Gold-Katalysatoren“).