



Ethylene epoxidation over copper-silver bimetallic catalyst : surface characterization under reaction conditions

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Introduction

The unique ability of silver to selectively catalyze the partial oxidation of ethylene to ethylene oxide has attracted scientific interest in this system for several decades. Although the selectivity of this reaction in industrial processes has exceeded 80 %, research is still continuing in the field since there is no thermodynamic limit for further increasing selectivity. Recently Barteau et al. found that copper-silver bimetallic catalysts offer improved selectivities compared to pure silver in the direct epoxidation of ethylene [1]. Due to the low adsorption enthalpy, ethylene epoxidation is impossible to study under UHV conditions. This limits the information regarding the chemical state of the surface and adsorbents under reaction conditions. Recent development of a photoelectron spectroscopy apparatus, which is able to operate in the mbar pressure range, allows monitoring of the chemical status of the surface under working catalytic conditions.

Experimental

In situ XPS and NEXAFS experiments were performed at beamline U49/2-PGM1 and PGM2 at BESSY II in Berlin. All spectra were recorded using two excitation energies in order to distinguish between surface and bulk located species. Copper-silver nanopowder (~100 nm, 2.5% Cu), was purchased from Sigma-Aldrich[®]. The catalyst was measured in a C₂H₄ to O₂ ratio of 1:2 and a total pressure of 0.5 mbar at 250° C. Production of ethylene oxide was measured using a Proton Transfer Reaction Mass Spectrometer (PTRMS) which allows differentiation between C₂H₄O and CO₂. Post reaction Scanning Electron Microscopy results showed that the nanostructure morphology of Cu-Ag is practically unaffected during reaction (fig. 1d).

Results and Discussion

In fig. 1a the PTRMS signal of C₂H₄O as a function of temperature and time is presented. The rapid increase and decrease of the signal upon heating at 250° C and cooling respectively,

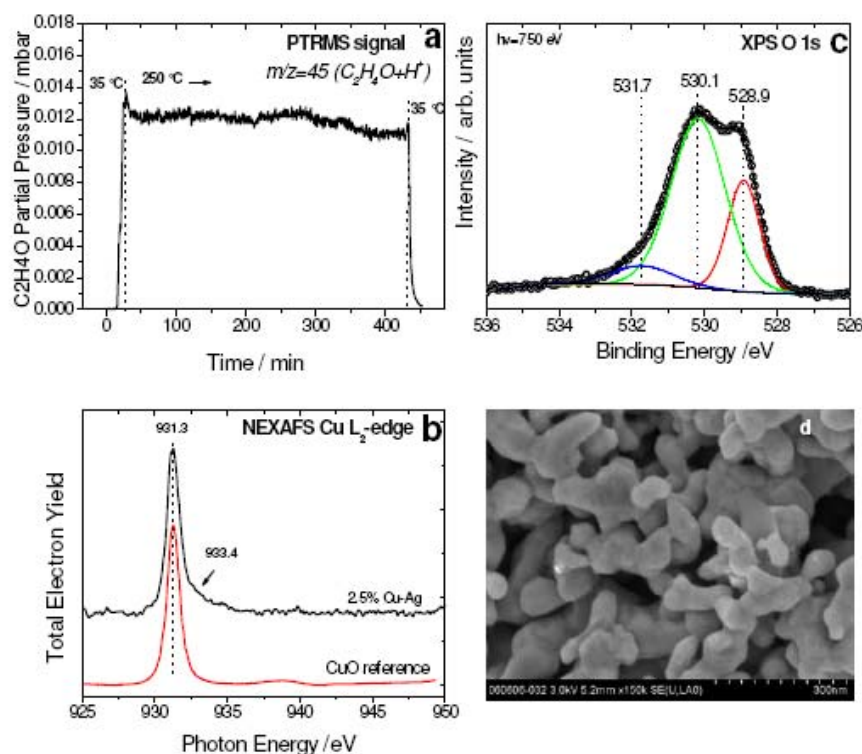


Figure 1. a) PTRMS signals from C_2H_4O with time and temperature b) in situ Cu L_2 -edge NEXAFS c) in situ O 1s photoelectron spectra, d) Post-reaction SEM image of Cu-Ag catalyst.

highlights the catalytic activity and long term stability of the catalyst. In situ Total Electron Yield (TEY) NEXAFS spectra measured simultaneously with the PTRMS data shows that copper is mainly Cu^{2+} . However, the small shoulder at 933.4 eV (marked with an arrow) indicates that copper at lower valences, most probably as Cu^{1+} , is also present. From in situ photoelectron spectroscopy results of Cu $2p_{3/2}$ transition (data not shown) the main peak is accompanied by a satellite feature ca. 9 eV at higher BEs characteristic of CuO [2]. Comparison with reference spectra recorded in H_2 atmosphere reveals an additional component at low BE site. This component is an indication of co-existence more than one Cu oxidation states in agreement with NEXAFS spectra.

In fig. 1c the O 1s spectrum recorded in-situ is shown. During reaction 3 oxygen components were used to fit the overall spectrum. Two broad components (~ 1.8 eV) at 530.1 eV and 531.7 eV (surface located) and a narrow (1.1 eV) at 528.9 (predominantly in the bulk). The peak at 530.1 eV was previously assigned both to: electrophilic oxygen linked with the epoxidation path of ethylene on silver foil [3], and to Cu_2O oxygen on Cu foils [4]. The distinction of the origin of this peak in our spectra is difficult; however the case of Cu_2O oxygen is less likely due to the minor contribution of Cu^{1+} in the Cu 2p and NEXAFS spectra. Peaks at 528.9 and 531.7 eV are nicely correlated with oxygen in CuO and hydroxyl groups, respectively

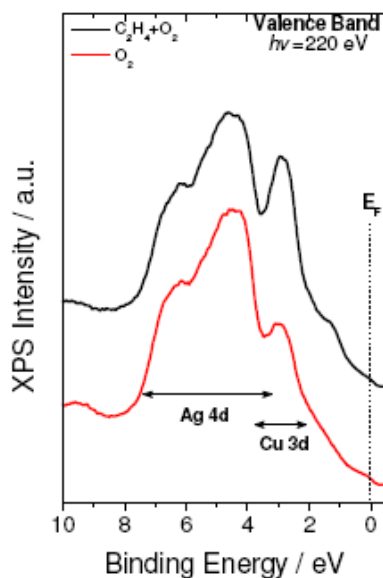


Figure 2. Valence band spectra of Ag-Cu catalyst recorded in situ at 250° under 0.5 mbar (C₂H₄+O₂) and O₂

[2]. The Ag 3d_{5/2} region (data not shown) is dominated by a metallic silver peak at 368.15 eV. Spectra subtraction using Ag 3d_{5/2} peak recorded in hydrogen atmosphere as a reference, revealed an additional Ag 3d_{5/2} component in the low BE site (367.7 eV). This peak is an indication of ionic silver which is probably formed during the reaction [3].

Valence band spectra recorded during ethylene oxidation and pure O₂ atmosphere (0.5 mbar, 250° C) are presented in Figure 2. The valence band region is mainly dominated by Ag 4d (4-8 eV) and Cu 3d (2-4 eV) intensities. After subtraction it was evident that extra features at 1.5 and 3.1 eV exist under reaction conditions. These extra features can be induced both,

from new Ag and Cu oxidized states, and/or changes of the Ag-Cu surface stoichiometry. Since core level spectra did not reveal additional oxidized species compared to O₂ atmosphere, enhanced Cu surface segregation during reaction is the most probable cause of these features. The most reliable model of Cu-Ag surface arrangement consists of silver nano-aggregates *partly* decorated with a thin layer of oxidized copper in +2 and +1 valence. This prevents silver agglomeration leading to the long term catalytic stability demonstrated in fig. 1a. It should be noted that experiments performed on monometallic silver nanoparticles showed that very fast particles agglomeration take place upon heating at 250° C which leading to the decrease of the catalytic activity.

Acknowledgment

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References

1. J.T. Jankowiak, M.A. Barteau, *J. Catal.* 236 (2005) 366
2. J. Chijsen, L.H. Tjeng, J. Van Elp., *Phys. Rev. B.* 38 (1988) 11322
3. V.I. Bukhtiyarov, A.I. Nizovskii, H. Bluhm, et. al. *J.Catal.* 238 (2006) 260.
4. H. Bluhm, M. Hävecker, A. Knop-Gericke, et. al. *J.Phys. Chem. B* (2004), 108 14340.