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. Thus many fundamental questions concerning the mechanism of the reaction remain controversial. 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.

Materials and Methods

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 more bulk located species. Copper-silver nanopowder (~100 nm, 2.5% Cu), was purchased from Sigma-Aldrich®. About 70 mg of the catalyst were pressed forming a ca 0.5 mm thick and 5 mm diameter pellet and placed on a sample holder. The catalyst was measured in a C_2H_4 to O_2 ratio of 1:2 and a total pressure of 0.5 mbar at 150 and 250° C. Production of ethylene oxide was measured using a Proton Transfer Reaction Mass Spectrometer (PTRMS) which allows differentiation between C_2H_4O and CO_2. C_2H_4O production was monitored simultaneously to the XPS characterization of the surface.

Results and Discussion

In fig. 1a the PTRMS signal of C_2H_4O as a function of temperature and time is presented. The rapid increase and decrease of the signal upon heating and cooling respectively, 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 agrees well with the corresponding reference spectra of a CuO sample, suggesting that copper is present mainly as Cu^{2+}. However, the small shoulder at 933.4 eV (marked with an arrow) denotes that copper at lower valences, most probably Cu^{1+}, is also present. This shoulder was more pronounced in Auger Electron Yield (AEY) NEXAFS spectra, indicating that reduced Cu states are surface located. From in situ photoelectron spectroscopy results two Cu 2p components, indicators of Cu^{1+} and Cu^{2+} were detected, in agreement with NEXAFS results. In fig. 1c O 1s spectrum recorded in-situ is shown. During reaction at least 3 oxygen components were found at 530.1 eV and 531.7 eV (surface located) and 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 [2], and to Cu_2O oxygen on Cu foil [3]. It should be noted that in the C 1s region there was no evidence of any carbon containing reaction intermediates. Measurements under pure H_2 and O_2 were also performed in order to investigate the redox properties of the catalyst. Post reaction Scanning Electron Microscopy results showed that the nanostructure morphology of Cu-Ag is practically unaffected under our reaction conditions (fig. 1d), while Transmission Electron Microscopy (HR-TEM) measurements are currently under way. XPS quantitative calculations showed the enrichment of catalyst surface with Cu. In addition valence band spectra with enhanced surface sensitivity were also employed in the analysis of the system. From aforementioned results no indications of an extended Cu-Ag alloy were found. The most reliable model of Cu-Ag surface arrangement consists of silver nano-aggregates *partly* decorated with a thin layer of oxidized copper. This prevents silver agglomeration leading to the long term catalytic stability demonstrated in fig. 1a. The discussion is also extended to the nature of copper promotion effect on silver.

Significance

This work provides significant information about the surface of Cu-Ag bimetallic catalyst under ethylene reaction conditions.

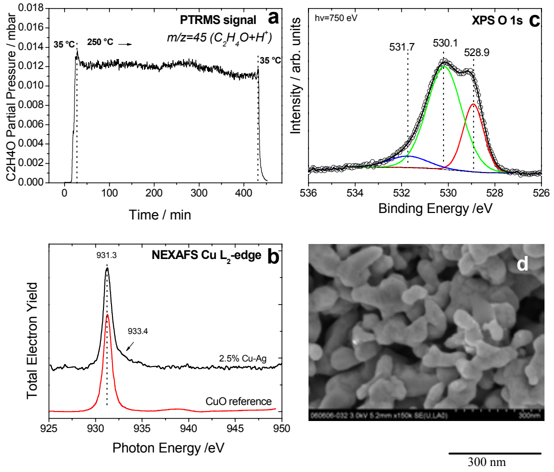

Figure 1. a) PTRMS signals from C_2H_4O with time and temperature b) in situ Cu L_2-edge NEXAFS c) O 1s photoelectron spectra measured under reaction conditions, d) Post-reaction SEM image of Cu-Ag catalyst.

References

1. J.T. Jankowiak, M.A. Barteau, J. Catal. 236 (2005) 366
2. V.I. Bukhtiyarov, A.I. Nizovskii, H. Bluhm, et. al. J.Catal. 238 (2006) 260.
3. H. Bluhm, M. Hävecker, A. Knop-Gericke, et. al. J.Phys. Chem. B (2004), 108 14340.