The Ag-O system in catalysis: New insights by ambient pressure XPS

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Introduction and Objectives

The oxygen interaction with silver has attracted great attention in the past years because silver based catalysts are used in two important large scale processes in the chemical industry, namely ethylene epoxidation and methanol oxidation[1]. These reactions produce highly valuable feedstock chemicals that are used in many applications. The economic importance of these processes motivated an extensive investigation of the Ag-O system in past years [2-4]. However the mechanisms behind the remarkable selectivity obtained with Ag catalysts for both reactions is still focus of debate in the literature [5]. In this work we applied the ambient pressure XPS technique to investigate the chemical state of the Ag catalyst surface in equilibrium with the gas phase with pure O_2 and reaction conditions in the mbar pressure range at industrially relevant temperatures.

Results and Discussion

Initially Ag catalysts under pure O_2 atmosphere were investigated in order to identify and characterize the O species formed at different temperatures. In the 150-500 C temperature range, five distinct features in the O 1s XP spectra were identified and assigned to different atomic O species on Ag, as shown in figure 1-a,b. Evidences for the distinct electronic structure of these species were obtained by comparing their binding energies (figure 1-a,b), amount of ionic Ag (figure1-c), temperature stability, valence band, O-K X-ray absorption near edge and O KVV Auger features [6].

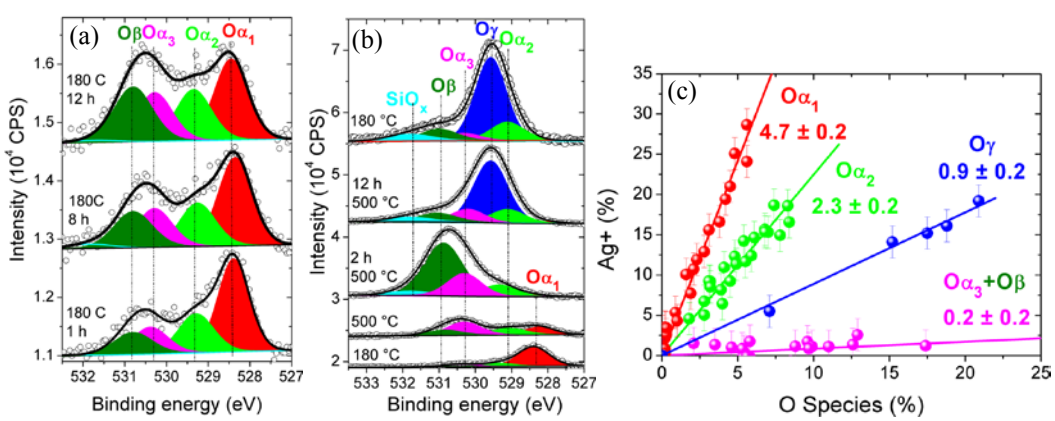

Figure 1. (a) O1s spectra showing the O species on Ag powder at 180 C. (b) O1s spectra showing the O species on Ag foil at 500 C. (c) Correlation of the abundance of different O species with the amount of $Ag^{\delta+}$

When methanol or ethylene is present together with O_2 in the gas phase, drastic changes in the O species distribution are observed, as a result of their different reactivity. Some of the species completely vanish, the abundance of others correlates with the hydrocarbon partial pressure. Simultaneous analysis of the gas phase composition by on-line mass-spectrometry and gas chromatography allows the direct correlation of surface spectroscpopy with catalytic performance. For the case of ethylene epoxidation running at steady state conditions, it was observed that the selectivity to the epoxide can be correlated to the ratio of different O species. A model of the role of the different O species in the frame of the oxidation reactions is suggested. Based on the electronic structure and reactivity data, it is proposed that while some species act as nucleophilic centers attacking C-H bonds ($O\alpha_1$ and $O\alpha_2$), which is the first step to total oxidation, other act as an electrophilic agent, attacking the C=C bonds and producing the epoxide ($O\alpha_3$).

Conclusions

The surface of unsupported Ag catalysts was characterized by XPS under working conditions for ethylene and methanol oxidation reactions. This analysis indicates that Ag is able to activate molecular oxygen into a number of distinct active forms with different chemical nature, which ultimately lead to different roles in the oxidation reactions. This new insights on the role of different O species can be used to better understand the mechanisms of selective oxidation reactions over silver and in the design of improved catalysts .

References

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