

Reaction Calorimetry: Exploring the state of Ag catalyst in ethylene epoxidation in-situ

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Introduction

The chemistry of oxygen and silver for the epoxidation of ethylene on the silver based catalyst has been a subject of extensive debates over many decades[1]. Development of *in-situ* methods and complementary techniques provided experimental evidences on the active state of the working catalyst. Herein, we report on the results and potential of *in-situ* reaction calorimetry technique together with adsorption microcalorimetry, temperature desorption spectroscopy (TDS) with support of DFT calculation in revealing the active state of the high performance catalyst. This study targets the quantitative assessment and thermochemical properties of reactive oxygen on supported silver catalysts (Ag/ α -Al₂O₃). The determination of the binding strength of lattice-, surface- and subsurface-oxygen is significant for understanding the chemistry of ethylene epoxidation reaction [2, 3].

Results

Figure 1 summarizes oxygen The reaction with oxygen of the catalyst surface in its active state is very favorable ($260 \pm 30 \text{ kJ/mol(O}_2\text{)}$). This effect is explained by the defect reach silver structure and presence of subsurface oxygen as suggested by theoretical calculations[4]. On the other hand, adsorption microcalorimetry showed decreasing energy of interaction with a lower total oxygen content in/on the catalyst. For the oxygen deficient, oxygen poor and pure silver surface the values of ~100, 25 and <20 kJ/mol(O₂), respectively, are measured. Our results unambiguously demonstrate that silver catalysts in its active state renders as oxygen reservoir.

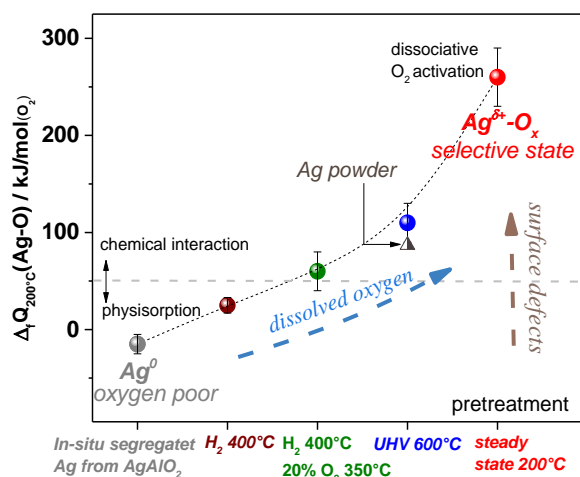


Figure 1. Silver-Oxygen interaction at 200°C for different catalyst's states. Specific pretreatment presumably affects the number of surface defects and amount of dissolved oxygen.

Figure 2A illustrates the results of isotope exchange pulse experiment in the reaction calorimetry setup [5]. A continuous 500ppm ethylene flow is interrupted with short pulses of $^{16}\text{O}_2$ or $^{18}\text{O}_2$. Each pulse results in 420kJ/mol(O_2) reaction heat, with $X(\text{C}_2\text{H}_4)$ 35% and $S(\text{EO})$ 10%. The prestored oxygen species (^{16}O) are gradually exchanged with the oxygen out of the gas phase ($^{18}\text{O}_2$) during the course of the reaction. The prestored oxygen ^{16}O diffuses out of the subsurface region to the surface and incorporates explicitly into the CO_2 ($\text{C}^{16}\text{O}^{18}\text{O}$ trace). EO in contrary contains only ^{18}O isotope. This experiment demonstrates unambiguously that the oxygen travels from the gas phase into the subsurface layer of the catalyst and diffuses back to the surface during the course of reaction. As follows from oxygen distribution in the gas products (Figure 2B), the product selectivity of prestored oxygen agrees well with the total oxygen selectivity (Figure 2C), indicating the crucial role of oxygen diffusion and counter diffusion on catalytic ethylene epoxidation.

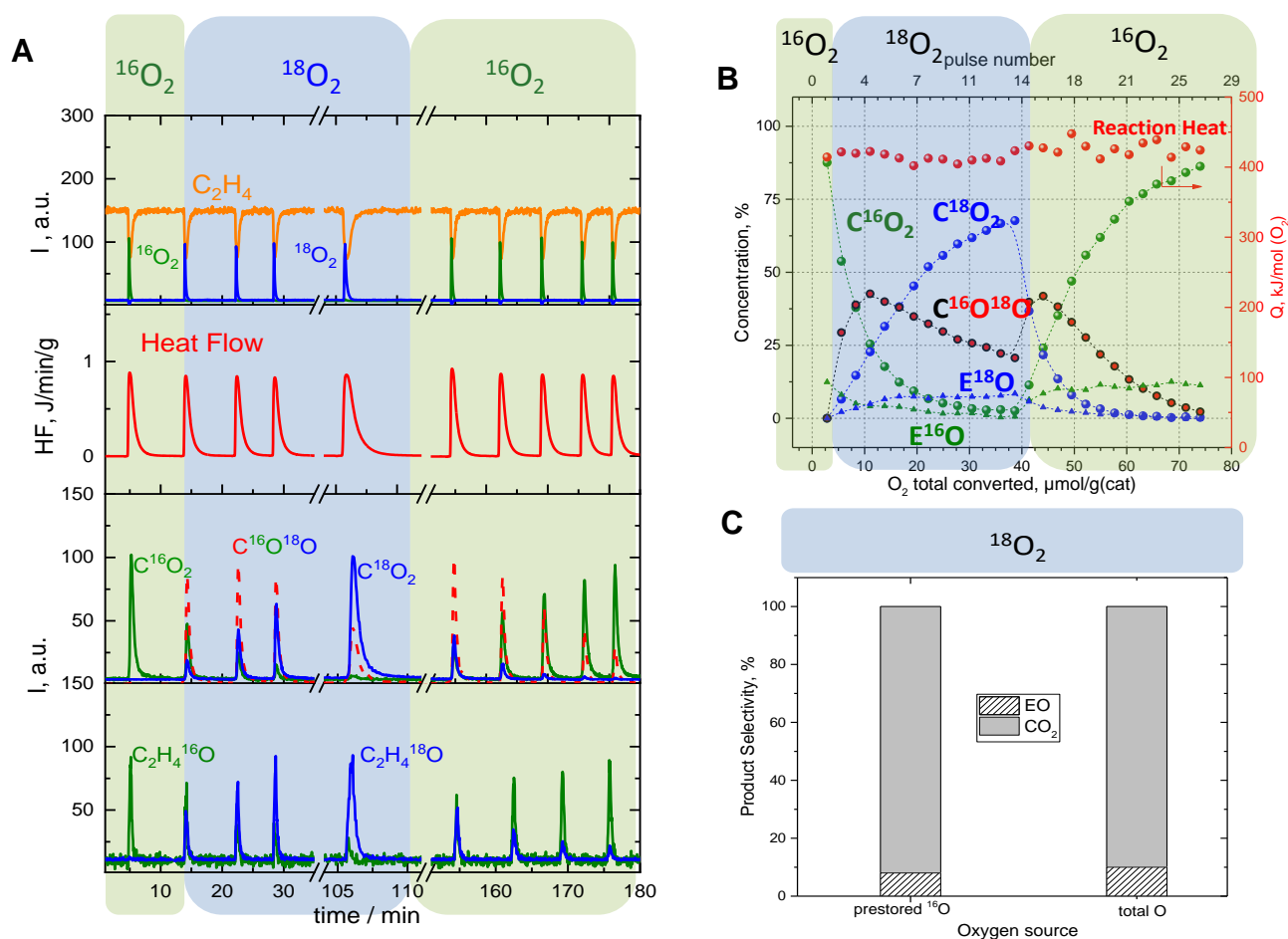


Figure 2. A and B) Product distribution during oxygen isotope exchange in ethylene epoxidation at 200°C C) product selectivity with prestored oxygen and total oxygen.

References

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