Effect of support specific surface area on the selectivity in the Ag catalyzed epoxidation of ethylene

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Effect of support specific surface area on the selectivity in the Ag-catalyzed epoxidation of ethylene

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Introduction

Ethylene epoxide (EO) is produced at a large scale, and is the starting point for the production of ethylene glycol and a range of polymer precursors. Industrial ethylene epoxidation catalysts consist of α-alumina supported silver particles. The silver catalyzes selective ethylene oxidation, minimizing the side reaction leading to full combustion. Silver is the only commercially feasible catalyst for this process, with promoters like rhenium, cesium and chlorine being added to enhance its performance. Industrial catalysts are supported on low surface area materials like α-alumina. Conversions are low (<5%) to suppress the EO partial pressure in the reactor and hence subsequent side reactions. We use catalytic data over a wide range of conversion levels to investigate the effect of support specific surface area on the catalytic performance of supported silver catalysts.

Materials and Methods

Commercial α-alumina was obtained from Sigma-Aldrich (1 m²/g) and BASF (8 m²/g), commercial silica was obtained from NECARBO BV (Aerosil 380, Evonik). High surface area α-alumina was synthesized using an optimized synthesis procedure from Stein et. al. Supports were impregnated with a solution of Ag₂C₂O₄ in ethylene diamine (0.42 g/g solvent) and water (0.58 g/g solvent). The concentration of Ag₂C₂O₄ in the impregnation solution was chosen such that the resulting catalyst yielded a 15 wt% Ag/α-Al₂O₃ or Ag/SiO₂ after heat treatment. Heat treatment was performed in a glass tubular reactor in a flow of O₂ or N₂ for 2 hours at 215 or 300°C in order to obtain particle sizes in the range of 20 to 200 nm.

Catalysts were tested in a flow setup described earlier. Typically 150 mg catalyst was loaded in quartz reactor and a 15 ml/min flow was applied, consisting of 30% ethylene and 8.5% O₂ and helium. Different conversions were obtained in a temperature range of 180 - 260°C. Effluent gasses were analyzed using an online Interscience Compact GC system.

Results and Discussion

As can be seen in figure 1 the selectivity towards ethylene oxide decreases with increasing conversion. For Ag/α-Al₂O₃ with a range of silver particle sizes on an 8 m²/g support the selectivity decreases roughly linearly with conversion, independent of particle size (left frame). This trend is highly dependent on the specific surface area of the support (right frame).

The data obtained from catalysts on supports with different specific surface areas and similar silver particle sizes (60 – 100 nm) were explained by considering three possible reactions. Two of these reactions, the epoxidation of ethylene (1) and the complete oxidation of ethylene (2) were taken as independent of EO partial pressure, while the subsequent oxidation of ethylene oxide (3) was taken as first order in EO. This third reaction occurs via surface group catalyzed ring opening of ethylene oxide as rate-determining step and is therefore expected to be surface area dependent. The selectivity for all surface areas converges at a conversion close to 0%. At this conversion the EO partial pressure equals zero and the full oxidation of ethylene oxide (reaction 3) cannot occur. The selectivity at this point is therefore determined by the ratio of the reaction rates for reactions 1 and 2.

With increasing conversion, the difference between the different catalysts becomes more pronounced. The selectivity for the high surface area catalysts drops off fast with conversion compared to low surface area catalysts. This effect is attributed to ethylene oxide reacting with the support surface followed by an oxidation step on silver forming CO₂ and H₂O. This decreases the overall observed selectivity with specific surface area and EO partial pressure, for which the latter scales with conversion. The surface area independent selectivity at 0% conversion shows that reaction 1 and 2 are support independent and the observed trends with support specific surface area originate from reaction 3.

Figure 1. Selectivity of Ag/α-Al₂O₃ (8 m²/g) catalysts with a range of particle sizes at different conversions (left) and selectivity of silver catalysts on different supports with silver particle size ranging in 60 – 100 nm (right).

Significance

The primary role of the support is to stabilize the silver particles during preparation and reaction. Unfortunately, in this reaction the support material is not inert. The surface groups on the support are reported to catalyze the ring opening reaction of the ethylene oxide product thus decreasing the selectivity at higher conversions. We clearly show the effect of support specific surface area on selectivity experimentally, and are able to explain and fit the observations with a simple first order reaction model.

References