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The Epoxidation of Ethylene on Silver – A TAP Reactor Study at Atmospheric Pressure.

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Highlights

- TAP experiments at atmospheric pressure
- Mechanistic insight into ethylene epoxidation on Ag by pulse titration experiments

1. Introduction

The well known and powerful temporal analysis of products (TAP) approach as pioneered by Gleaves in the 1980s [1] was adapted by the authors to study catalytic reactions in a plug flow reactor at atmospheric pressure and conditions of viscous flow – as opposed to Knudsen diffusion in the conventional TAP.
As a pilot experiment we have chosen the catalytic epoxidation of ethylene on elemental silver. We are going to show how versatile, simple and economic the method is and how it can be used to shed light on the reaction mechanism and the catalyst properties under practically relevant reaction conditions.

2. Methods

Fig. 1 shows the experimental setup [2]. A tubular reactor (OD 8 mm, ID 6 mm, glass) is filled with approx. 1g of elemental silver powder as catalyst. In the idle state a constant flow of helium passes through the reactor. The outlet of the reactor is at atmospheric pressure and the pressure drop is on the order of a few mbar. In order to probe the catalyst material, the reagents ethylene, oxygen or carbon dioxide can be added to the feed in a pulse-like fashion, i.e. as rectangular functions of arbitrary length but with a minimum duration of 0.2 seconds. All reagents can be switched independently; the total volumetric flow at the reactor entrance is always constant and is on the order of 100 sccm, resulting in a space velocity of about 1 Hz. The reactant concentrations are kept small (<1%$_{mol}$) so that the change of the volumetric flow rate due the reaction can be neglected. As a result, the reactor behaves like a plug flow reactor with a constant contact time at any conversion and selectivity. We note that in general, the setup does allow operation under conditions of higher concentrations at constant total volumetric inflow and with arbitrary superposition of reagent step functions – and hence also steady state operation. The response of the catalyst to a given sequence of pulses is monitored by a molecular beam mass spectrometer. Threshold ionization is used to distinguish ethylene oxide from CO_2 at m/z=44amu.

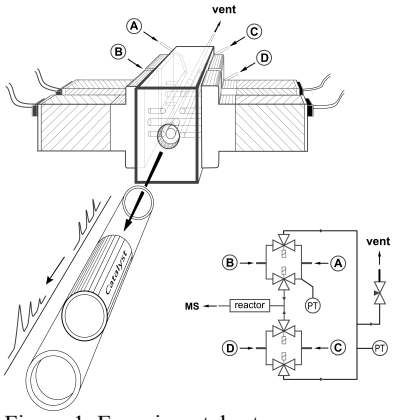

Figure 1. Experimental setup.

3. Results and discussion

Figure 2 shows a typical pulse sequence to interrogate the mechanism of ethylene epoxidation on silver.

It is a well-known fact that silver binds and stores oxygen in different forms (atomic, molecular and subsurface). The oxygen can react with ethylene to form ethylene oxide and also carbon dioxide and water. By reducing the surface step by step using pulses of ethylene, it is possible to probe the activity of the catalyst as a function of oxygen loading. The results of such an experiment are shown in Figure 3 and Figure 4. No gas

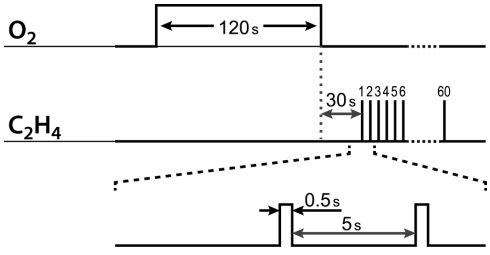

Figure 2. Typical pulse sequence.

phase oxygen is present during this pulse sequence. We find that the conversion goes through a pronounced maximum as the catalyst is being reduced and that more ethylene oxide is produced per pulse as oxygen vacancies develop on the surface. As the oxygen is depleted further, the activity drops until no reactive oxygen remains. Selectivity to ethylene oxide does not depend on the oxygen loading of the catalyst.

A TAP reactor study by Gleaves et al. from 1990 [3] actually revealed a similar trend. Further experimental findings will be discussed which illuminate the reaction mechanism and which also yield physico-chemical data about the catalytic system.

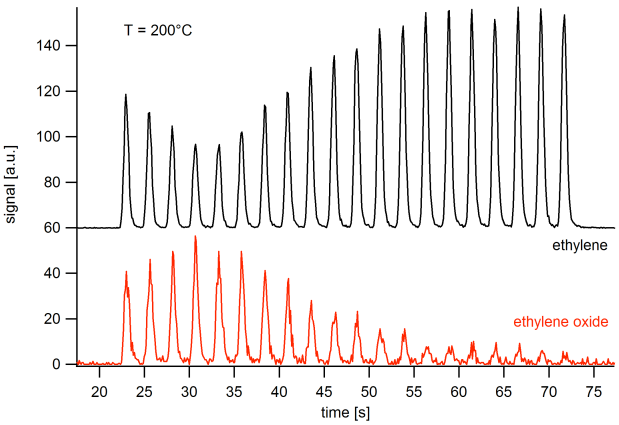

Figure 2. Response of oxidized elemental silver powder to 20 ethylene pulses of 0.5 s duration, each separated by 2 s of pure helium at 200°C; top: ethylene, bottom: ethylene oxide

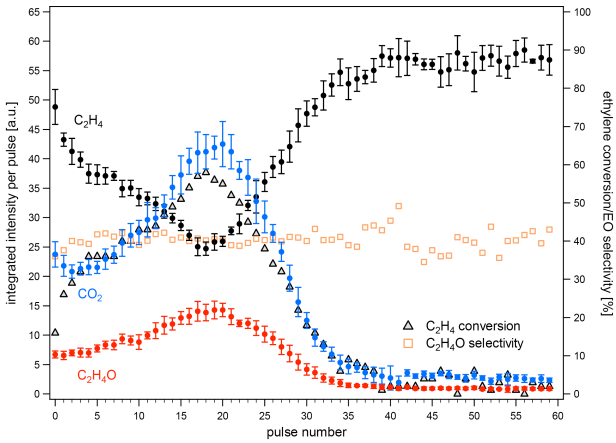

Figure 3. Peak area, ethylene conversion and ethylene oxide selectivity as function of the pulse number.

4. Conclusions

The atmospheric TAP method described in this contribution is a powerful tool to study mechanism and kinetics of catalytic reactions under atmospheric pressure conditions using well-defined pulse surface titration experiments. The catalyst surface can be prepared in a defined state by exposing it to pulses of a reactant or promoter and the response of the surface prepared in this way to pulses of reactants can be studied.

References

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Keywords
atmospheric pressure TAP, ethylene epoxidation, silver, mechanism, kinetics