Heterogeneously catalyzed epoxidation of 1,3-butadiene to 3,4-epoxy-1-butene

**Micro-reactor technology**

**Motivation, intention and cooperation**

Combination of chemical developments with micro-reactor technology shall offer alternative routes for important processes. A micro-reactor, developed and manufactured in the Forschungszentrum Karlsruhe, was set up to lab-scale to enable investigation. Furthermore, a conventional tubular fixed bed reactor with catalyst bed serves the comparison with the industrially used procedure. From the results of the attempt alternative technical and economic procedure possibilities are to be derived. Additionally, our research considers the optimization and development of catalysts on the basis of different supporting materials and promoters.

**Direct Epoxidation**

to 3,4-epoxy-1-butene EpB (fig. 1) in the gaseous phase is a very attractive process. EpB is a multi-functional molecule and a potential intermediate for the production of other oxygen-containing products. The reason for the efficiency of EpB formation in comparison to propylene epoxidation is caused from the fact that splitting of an allylic methyl group is not possible with 1,3-butadiene. Thus, the direct kinetically controlled oxidation to the corresponding epoxide is preferred. Whether one considers homolytic or heterolytic C-H bond strength, it is clear that allylic hydrogens are vulnerable to abstraction by reactive oxygen atoms on the catalyst.

**Lab-scale process**

A mixture of C₄H₆, O₂ and Ar (N₂) is passed through a catalyst bed (fig.2) at an elevated temperature, pressure and space velocity. R1 represents the tubular fixed bed reactor. R2 represents the micro-reactor (fig.4). R3 serves for complete catalytic treatment of exhaust gases through oxidation over a catalyst (Pd / Al₂O₃). Fig. 3 shows the lab equipment which make the parallel investigation possible at both reactor types.

**Experiments**

The realization of the experiments is based on different space velocities (SV), different gas compositions (fig. 5) and catalysts formed by a variety of methods. With these parameters the efficiency of the epoxidation, as well as thermal and kinetic behavior in the micro-reactor is to be examined. The limits of operation range were optimized by quantitative analyses of BD-conversion, EpB yield and CO₂ formation. From these data conversion curves are generated as depicted in fig. 6.

**Mechanism of catalyzed epoxidation**

The guiding hypothesis is that surface oxametallacycles are key intermediate for epoxidation on Ag / Cs catalyst. The intermediate EpB, finally leading to molecular EpB, is probably strongly adsorbed on the catalyst surface indicated by theoretically calculations which also support its identity as an oxametallacycle. The oxametallacycle intermediate is more thermodynamically stable than EpB by approx. 24 kcal / mol (fig.7). Moreover, the transition state for EpB formation from the oxametallacycle intermediate is actually lower in energy than the reactants, butadiene and oxygen.²¹,²²

**Preparation of catalysts**

Preparation of catalysts takes place by sequential impregnation with AgNO₃ promoters on different types of α-Al₂O₃ supports (TiO₂ / Sb₂O₃, Alumina, Particle size 0.045 - 0.063 mm, BET-surface 0.8 m² / g to 1.2 m² / g). Ag loading is 10 w % and Cs 0.1% ppm. The catalysts are analytically characterized by SEM (fig.8, fig.9), TPO and TPR. For sufficient EpB formation, homogeneous promoter distribution on the Ag surface is decisive.

**Results and conclusion**

The heterogeneously catalyzed epoxidation of butadiene has been successfully carried out in the micro-reactor. EpB selectivity of max. 46% and 8% CO₂ conversion (SV = 506h⁻¹), Temp. 235°C, Space time yield = 0.9 kg m⁻³ h⁻¹ has been reached. It should be pointed out that EpB and CO₂ are produced from a common surface intermediate. So far, no better EpB selectivity have been achieved in the micro-reactor, which is currently further optimized. Optimization of the catalyst impregnation method led to higher EpB yields. Nano-scaled silver particles on supporting materials are to be applied in future studies as well as testing additional micro-reactor designs.

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**Reference**

[1] U.S. Patent No. 6,455,713, Reactivation of Cs-Promoted, Ag Catalysts for the Selective Epoxidation of Butadiene to 3,4-epoxy-1-butene, J. R. Mannier, September 24, 2002

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**Figure 1.** Direct epoxidation of 1,3-butadiene over Ag / Cs catalyst on Al₂O₃

**Figure 2.** Schematic representation of the heterogeneously catalyzed EpB process (lab-scale)

**Figure 3.** Lab equipment with control unit and gas analyzers. On the left side one can see the micro-reactor. Right of the tubular fixed bed reactors is to be seen (blue frame)

**Figure 4.** Micro-reactor and its components.

**Figure 5.** Phase plot of 1,3-Butadiene, O₂, N₂ (Ar). The green dashed lines corresponds to the BD / O₂ relation.

**Figure 6.** 1,3 BD conversion, yield of EpB (measured) and EpB Selectivity calculated. The micro-reactor (R1), lab-scale (R2) and industrial reactor (R3).

**Figure 7.** Heat of formation and activation energy for EpB formation from the oxametallacycle intermediate.

**Figure 8.** Evaluation of the metal distribution on the catalyst. SEM; electron emission; volume ration 10K:1. Bright spots show Ag. Dark areas show Al₂O₃

**Figure 9.** Element-specific quantification by EDS of the catalysts (KEA Energy, Oxford).