

Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft

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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*^[4], 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 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.

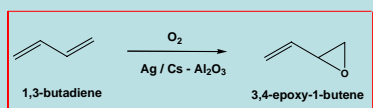


Figure 1. Direct epoxidation of 1,3-butadiene over Ag / Cs catalyst on Al₂O₃ to 3,4-epoxy-1-butene.

EpB was so far industrially produced by Eastman (Texas) by means of gaseous phase oxidation of 1,3-butadiene with air at Ag / Cs catalyst.^[1] In recent years the influence of promoters (Cs / Rb / Ba, Ti) on this process was particularly investigated by combined theoretical and experimental investigations on catalyst surfaces.^{[2], [3]}

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.

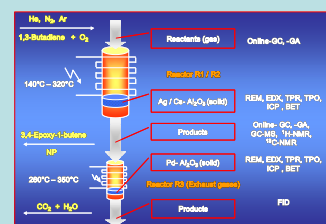


Figure 2. Schematic representation of the heterogeneously catalyzed EpB process (lab-scale).

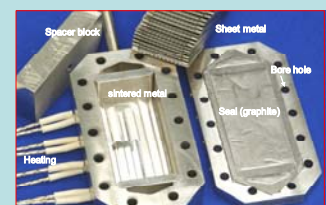


Figure 4. Micro-reactor and its components.

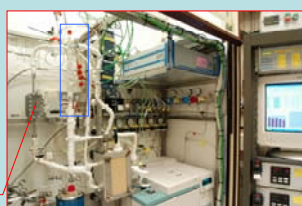


Figure 3. Lab equipment with control unit and gas analyzers. On the left side one can see the micro-reactor. Right of it the tubular fixed bed reactor is to be seen (blue frame).

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. Monnier, September 24, 2002.
- [2] John R. Monnier, Jerome L. Stavinoha Jr., Robin L. Mingaa, *Journal of Catalysis* 226 (2004) 401–409
- [3] John R. Monnier, Prepr. Pap. - Am. Chem. Soc., Div. Petr. Chem. 2007, 52 (2), 163
- [4] P. Pfeifer et al., *chimica oggi (Chemistry Today)* 25 (2007) 42-46
- [5] John R. Monnier *Journal of Catalysis* 203, 362–368 (2001)
- [6] Mark A. Barteau, *Topics in Catalysis* Vol. 22, Nos. 1/2, January 2003
- [7] Mark A. Barteau, *Topics in Catalysis* Vol. 22, Nos. 1/2, January 2003

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.

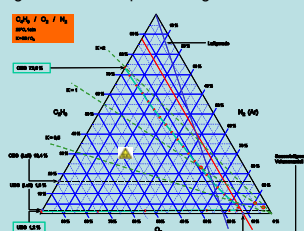


Figure 5. Phase plot of 1,3-Butadiene, O₂, N₂ (Ar). The green dashed lines corresponds to the BD / O₂ relation.

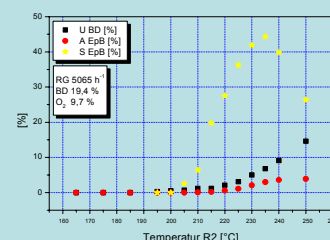


Figure 6. 1,3-BD conversion, yield of EpB (measured) and EpB Selectivity (calculated) in the micro-reactor (R2), gas temp. = 160°C – 250°C, gas inlet BD = 19.4%, O₂ = 9.7%, Ar = 80.9%, K=2, SV= 5065h⁻¹, Ag = 10wt%, Cs = 0.1wt%, S_{max} EpB = 235°C, P_{gas inlet} = 1040 mbar.

Mechanism of catalyzed epoxidation

The guiding hypothesis is that surface oxametallacycles are key intermediate for epoxidation on Ag / Cs catalyst. The intermediate EpB_(ads), finally leading to molecular EpB, is probably strongly adsorbed on the catalyst surface indicated by theoretical 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.^[7]

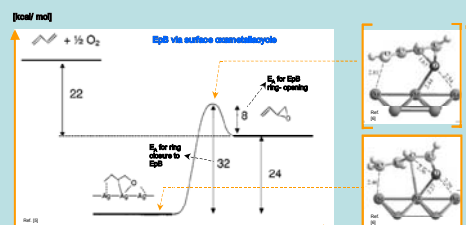


Figure 7. Heat of formation and activation energy for EpB formation from the oxametallacycle intermediate.

Preparation of catalysts

Preparation of catalysts takes place by sequential impregnation with AgNO₃/ promoters on different types of α-Al₂O₃ supports (T60 / SLA 92, Almatris, 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.

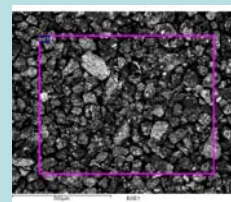


Figure 8. Evaluation of the metal distribution on the catalyst (BSE detector, excitation volume-meet 10kV). Bright spots show Ag. Dark areas show Al₂O₃.

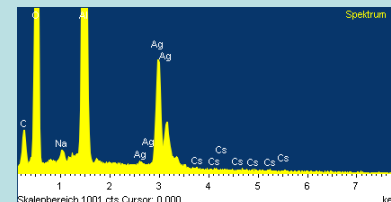


Figure 9. Element-specific quantification by EDX of the catalysts (INCA Energy, Oxford).

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% BD conversion (SV = of 5065h⁻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.