

# Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft

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## Heterogeneously catalyzed epoxidation of 1,3-butadiene to 3,4-epoxy-1-butene micro-reaction technology

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### Heterogeneously catalyzed epoxidation of 1,3-butadiene

to 3,4-epoxy-1-butene „EpB“ (fig. 1) in the gaseous phase is a very attractive process. EpB is a small multi-functional molecule and a potential intermediate for the production of other oxygen-containing products with large application potential. 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 butadiene. 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. Thus, the direct kinetically controlled oxidation to the corresponding epoxide is preferred.

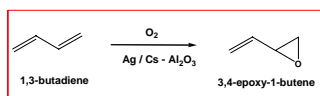


Figure 1 Direct epoxidation of 1,3-butadiene over Ag / Cs catalyst on  $Al_2O_3$  to 3,4-epoxy-1-butene.

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.<sup>[1]</sup> In recent years the influence of promoters (Cs / Rb / Ba, Tl) on this process was particularly investigated by combined theoretical and experimental investigations on catalyst surfaces.<sup>[2], [3]</sup>

### Motivation, intention and cooperation

Micro-structured modules for processes with rapid and exothermic reactions, e. g. epoxidation of 1,3-butadiene.

A micro structure reactor, developed and manufactured in the *Forschungszentrum Karlsruhe* <sup>[4]</sup> was set up to lab-scale to enable investigation. Additionally, our research considers the optimization and development of catalyst on the basis of different supporting materials and promoters.

Combination of chemical developments with micro-reactor technology shall offer alternative routes for important processes.

[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

### Preparation of catalysts

Preparation of catalysts takes place by sequential impregnation with  $AgNO_3$ /promoters on different types of  $\alpha-Al_2O_3$  (T60 / SLA 92, Almits). Particle size of support materials ranges between 0,045 mm and 0,063 mm, surface area is in the range of 0,8  $m^2 / g$  to 1.2  $m^2 / g$ .

The supported catalysts are analytically characterized by REM, BET, TPO and TPR. For sufficient EpB formation, homogeneous promoter distribution on the Ag surface is decisive.

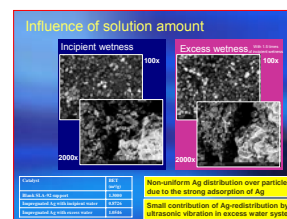


Figure 2. Influence of excess and incipient wetness.

### Mechanism of catalyzed epoxidation of 1,3-butadiene

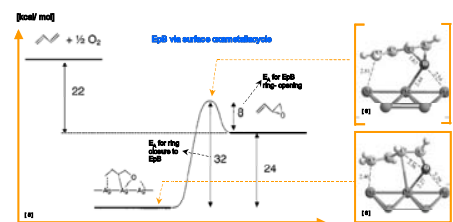


Figure 3.

Reaction coordinate for butadiene epoxidation. Heat of reaction and activation energy values are given in kcal/mol. The oxametallacycle intermediate is more thermodynamically stable than EpB by approx. 24 kcal / mol.

Moreover, the transition state for EpB formation from the oxametallacycle intermediate is actually lower in energy than the reactants, butadiene and oxygen.

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.<sup>[7]</sup>

### Lab-scale process

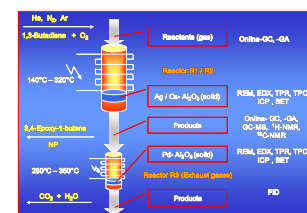


Figure 4. Schematic representation of the heterogeneously catalyzed EpB process (lab-scale).

A mixture of  $C_4H_6$ ,  $O_2$  and Ar ( $N_2$ ) is passed through a catalyst bed (fig.4) at an elevated temperature. Dosage, balance of the mass flows and analysis of the reactants take place completely automated.

R1 is the tubular fixed bed reactor, R2 is the micro-reactor. R3 serves for complete catalytic treatment of exhaust gases through oxidation over a catalyst ( $Pd / Al_2O_3$ ).

### Micro-reactor and tubular fixed bed reactor

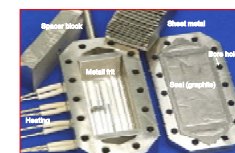


Figure 5. The micro structured reactor allows for highly defined flow conditions and high heat transfer rates compared to the tubular fixed bed reactor as depicted in fig. 6. In fig.5 (attached) the dimension of the micro reactor is visualized.

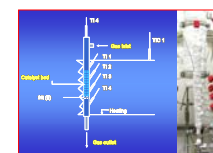


Figure 6. The glassy tubular fixed bed reactor is 18 cm in height and 0.8 cm in diameter.

### Initial process optimization

The limits of operation range were optimized by quantitative analyses of butadiene conversion, EpB yield and  $CO_2$  formation. From these data combined with the phase composition of the inlet gas flow (fig.7), appropriate operation conditions are chosen. Conversion curves are generated for constant space velocity (SV), constant inlet pressure and isothermal conditions.

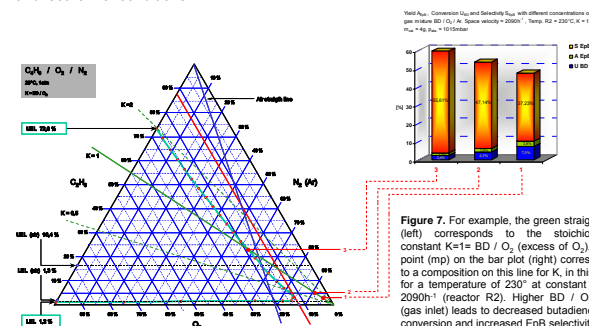


Figure 7. For example, the green straight line (left) corresponds to the stoichiometric constant  $K=1= BD / O_2$  (excess of  $O_2$ ). Each point (mp) on the bar plot (right) corresponds to a composition on this line for K, in this case for a temperature of 230° at constant SV of 2090h<sup>-1</sup> (reactor R2). Higher BD /  $O_2$  ratio (gas inlet) leads to decreased butadiene (BD) conversion and increased EpB selectivity.

### Results and conclusion

Butadiene epoxidation has been successfully carried out in micro structured and tubular fixed bed reactors. Up to now, an EpB selectivity of 95% at 5% BD conversion in the tubular fixed bed reactor (SV = of 2714h<sup>-1</sup>, Temp. 230°C) has been reached. So far, no better values have been achieved in the micro structured reactor, which is currently further optimized. Preliminary results also indicate, that stability of operating the epoxidation without total oxidation to  $CO_2$  is superior in the micro structured reactor. Optimization of the impregnation led to higher EpB yields in both reactor types.

Nano scaled silver particles on supporting materials are to be applied in future studies as well as testing additional micro reactor designs.