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New Insights in the Scope of Heterogeneously Catalyzed Epoxidation of 1,3-Butadiene to 3,4-Epoxy-1-butene

Introduction

Combination of chemical developments with microreactor technology is expected to give rise to alternative routes for important processes. 3,4-epoxy-1-butene „EpB“ has so far been industrially produced by Eastman (Texas) by means of gas-phase oxidation of 1,3-butadiene with air on an Ag / Cs catalyst [1]. The influence of promoters (Cs / Rb / Ba, TI) on this process was studied in particular by investigations on catalyst surfaces [2],[3].

A microreactor developed at Forschungszentrum Karlsruhe [4] is used on the laboratory scale. A conventional tubular fixed-bed reactor serves for comparison with the industrial process. For epoxidation, an Ag catalyst is applied. This catalyst is produced by simultaneous wet impregnation (incipient wetness method) of an α -Al₂O₃ carrier with an aqueous active component solution (AgNO₃, CsNO₃, Ba(NO₃)₂). The principal purpose is to reach a high silver dispersion on the surface.

Direct Epoxidation

Epoxidation to 3,4-epoxy-1-butene „EpB“ (fig. 1) in the gaseous phase is the electrophilic addition of oxygen across the carbon-carbon double bond of 1,3-butadiene, resulting in a three-member ring structure that can undergo further chemical transformations to oxygenated products, such as ketones, alcohols, and ethers. Supported silver catalysts are known to epoxidize olefins with nonallylic hydrogen when an alkali promotor is doped on the surface. Thus, the direct kinetically controlled oxidation to the corresponding epoxide is preferred.

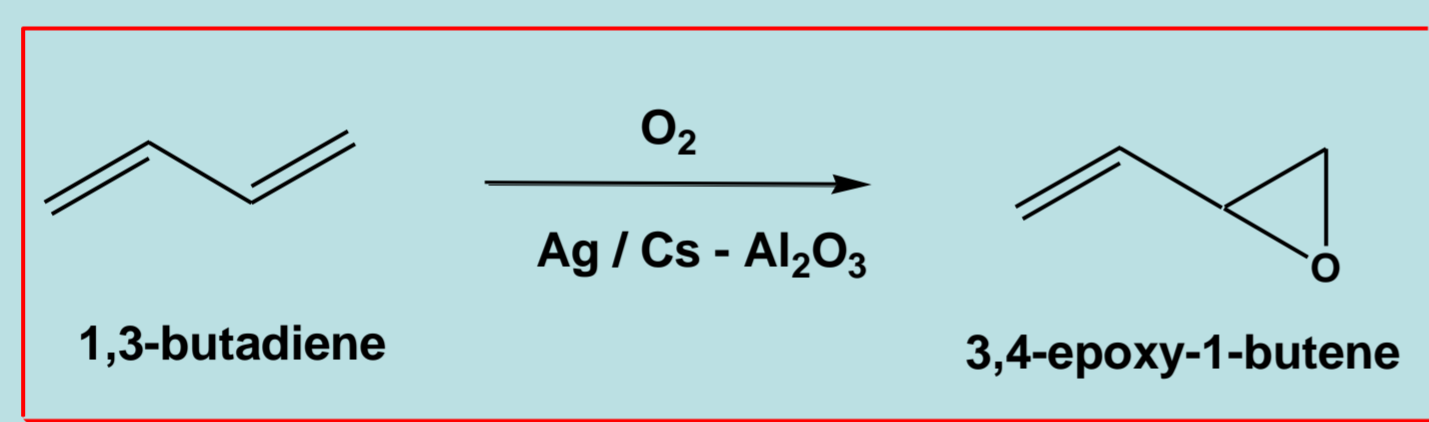


Figure 1. Direct epoxidation of 1,3-butadiene on an Al₂O₃-based Ag / Cs catalyst to 3,4-epoxy-1-butene.

Lab-scale Process

Figure 2 represents the microreactor, figure 3 the tubular reactor. A mixture of C₄H₆, O₂, and Ar is passed through the catalyst in the reactor at elevated temperatures (130-320°C), ambient pressure, and a space velocity of about 5900 h⁻¹. From these data, conversion curves are generated. Based on these parameters, the epoxidation efficiency as well as the thermal and kinetic behavior in the microreactor are examined [5].

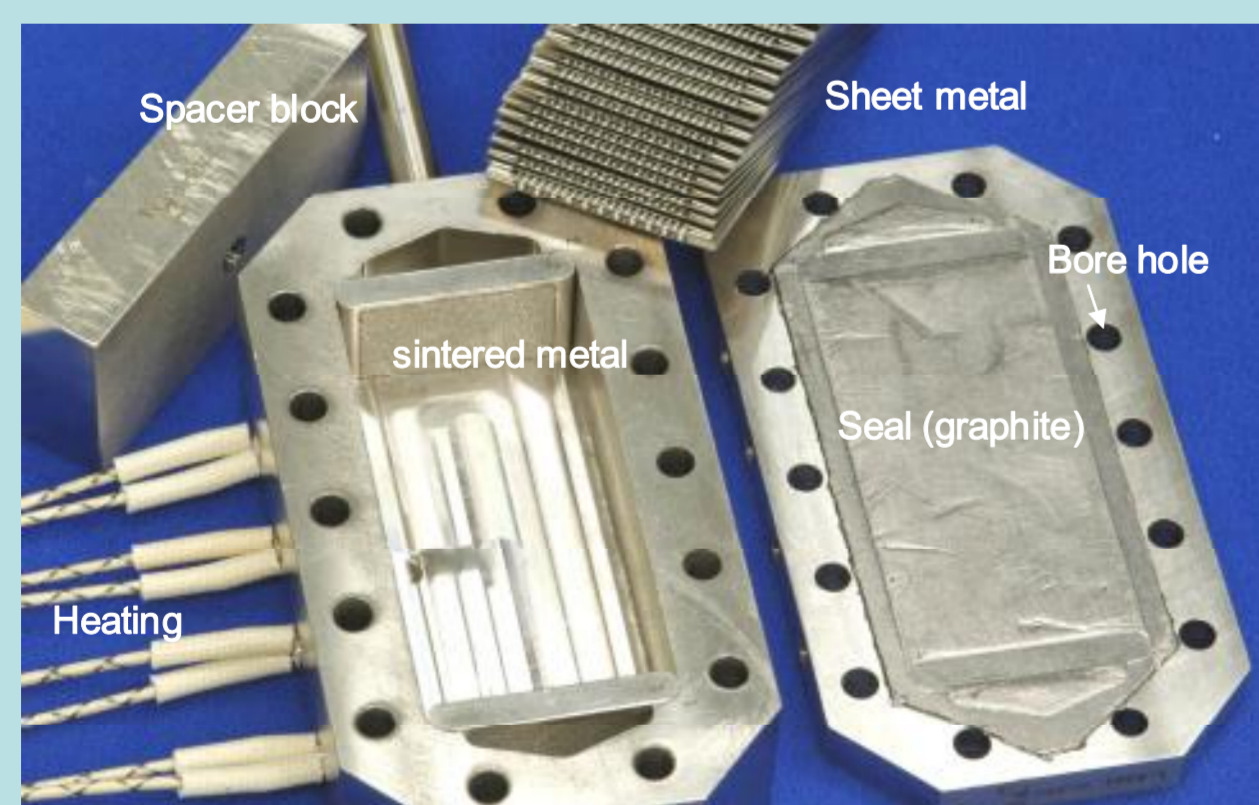


Figure 2. Microreactor and its components.

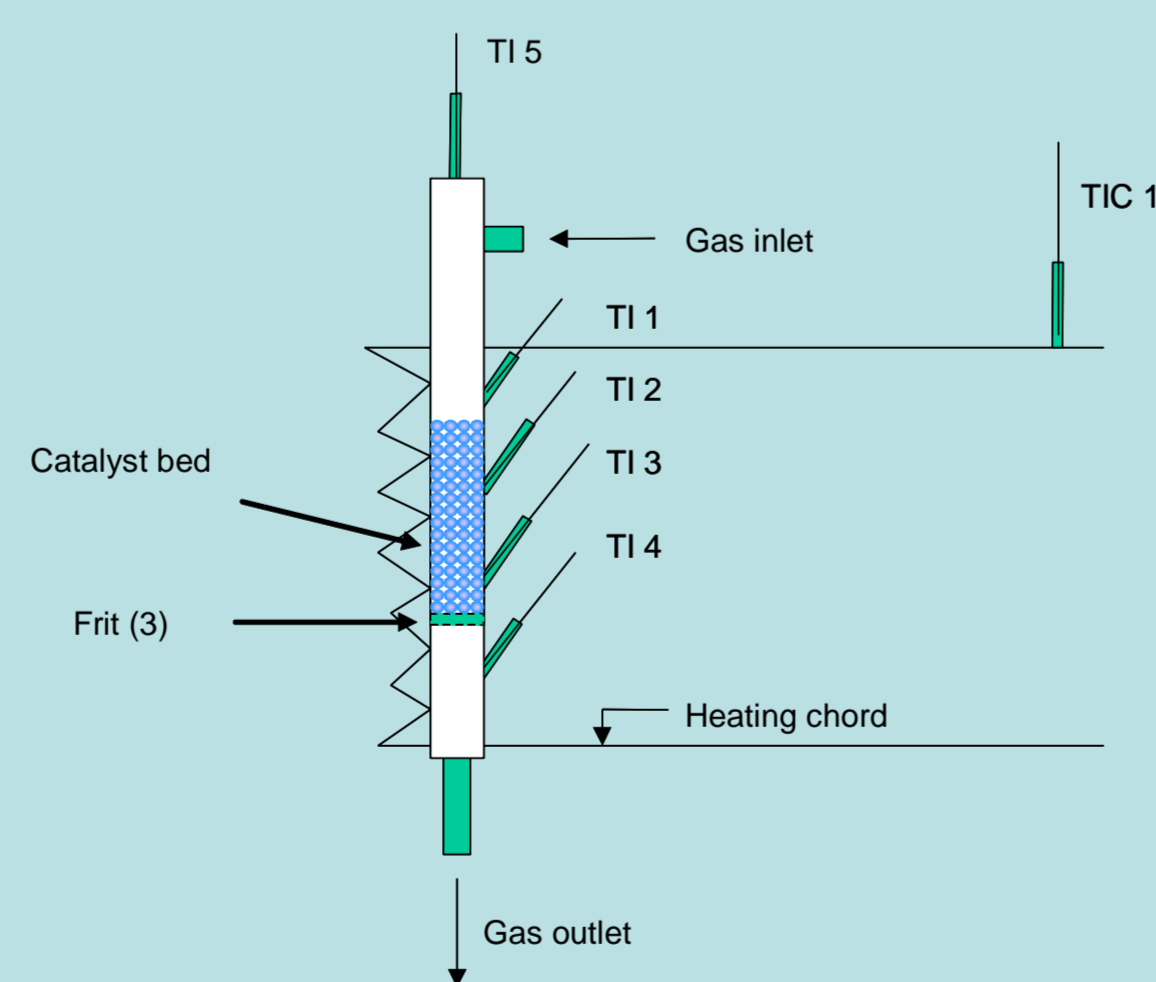


Figure 3. Tubular fixed-bed reactor.

References

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Mechanism of Catalyzed Epoxidation

The guiding hypothesis is that surface oxametalla cycles are key intermediates for epoxidation on an Ag / Cs catalyst. The intermediate EpB_(ads) (see fig. 4) finally leads to molecular EpB. The oxametalla cycle intermediate is thermodynamically more stable than EpB. Moreover, the transition state for EpB formation from the oxametalla cycle intermediate is lower in energy than the reactants, butadiene and oxygen [6]. Figure 5 represents the mechanism of catalyzed epoxidation.

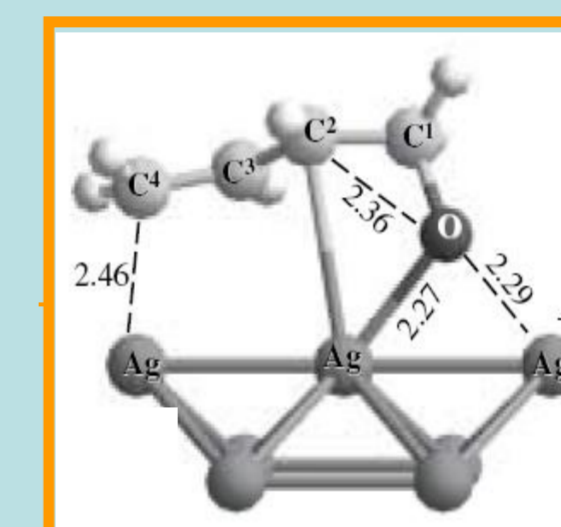


Figure 4. Formation from the oxametalla cycle intermediate [7].

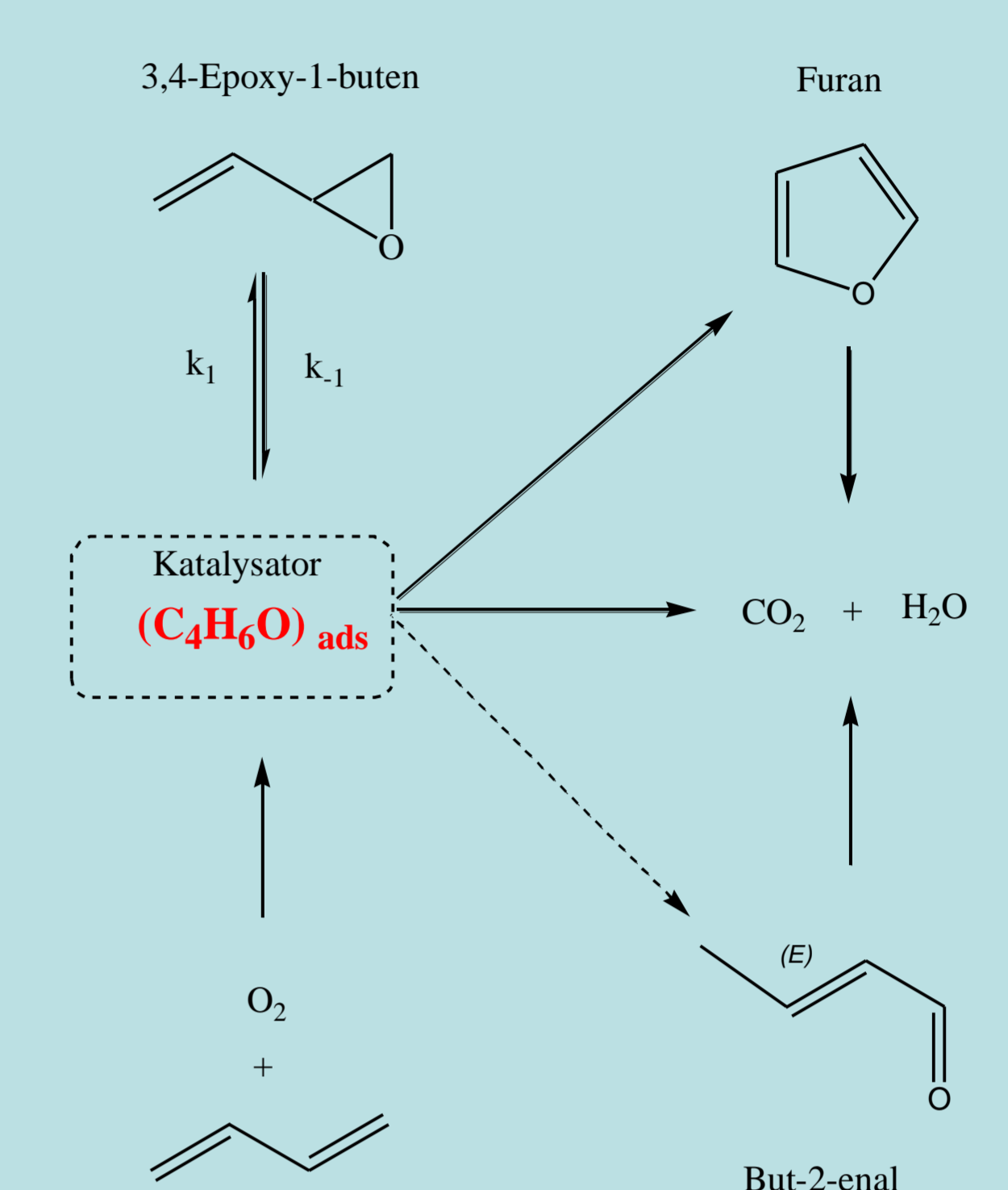


Figure 5. Mechanism of heterogeneously catalyzed epoxidation of 1,3-butadiene [8].

Results

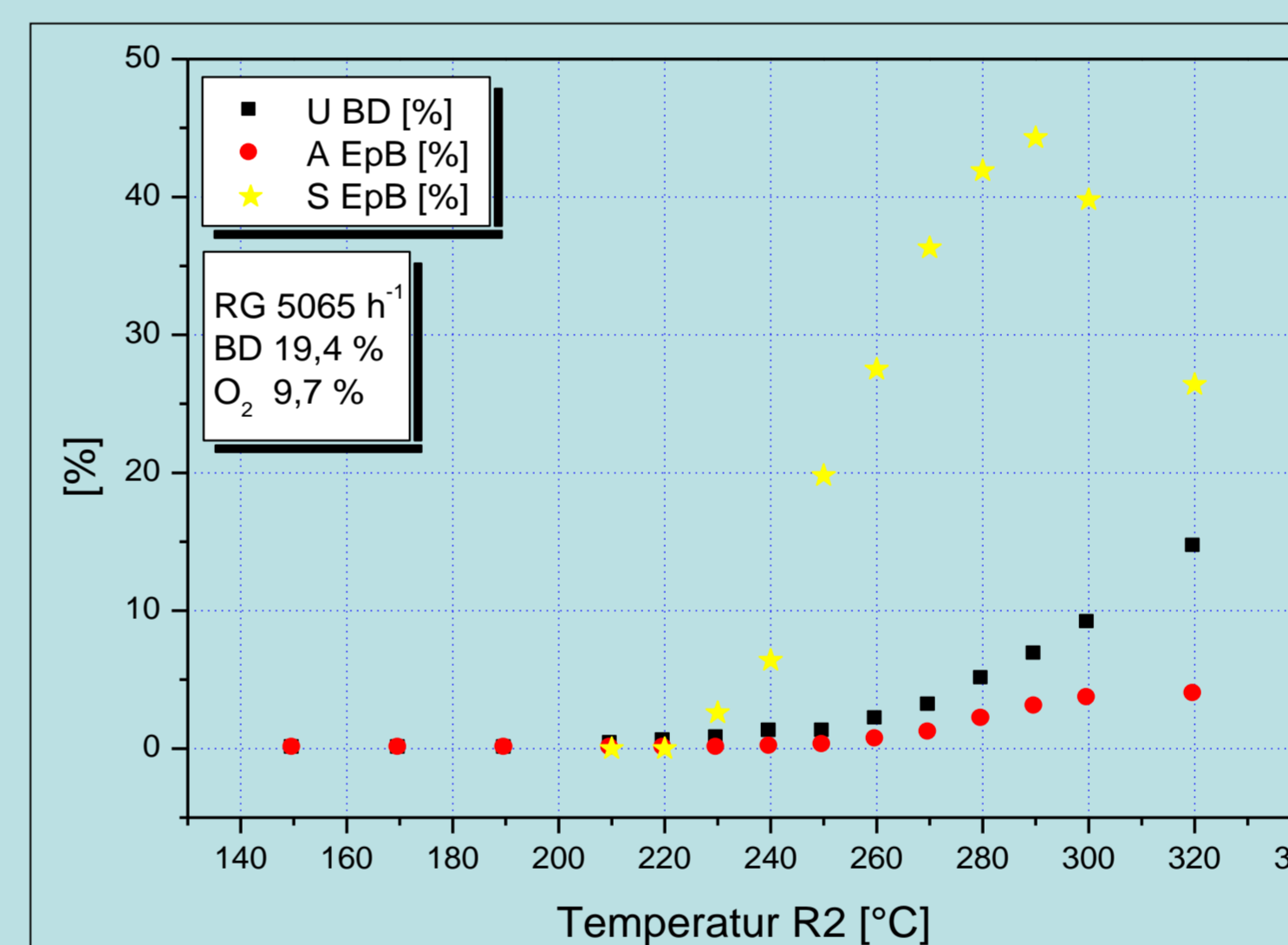


Figure 6. 1,3-BD conversion, yield of EpB (measured), and EpB selectivity (calculated) in the microreactor (R2), gas temp. = 160°C – 260°C, gas_{inlet} BD = 19.4%, O₂ = 9.7%, Ar = 80.9%, SV = 5900h⁻¹, Ag = 10 wt%, Cs = 0.1 wt%. S_{max} EpB = 235°C, p_{gas inlet} = 1040 mbar.

The limits of the operation range are optimized by analyses of 1,3-BD conversion, EpB yield, and CO₂ formation. From these data, conversion curves are generated, as depicted in fig. 6.

Furthermore, a mathematical model is generated to study the heterogeneously catalyzed epoxidation of 1,3-butadiene on the Ag catalyst in the laboratory-scale tubular reactor. For this purpose, the reaction mechanism is transformed into a system of 29 coupled differential equations [9].

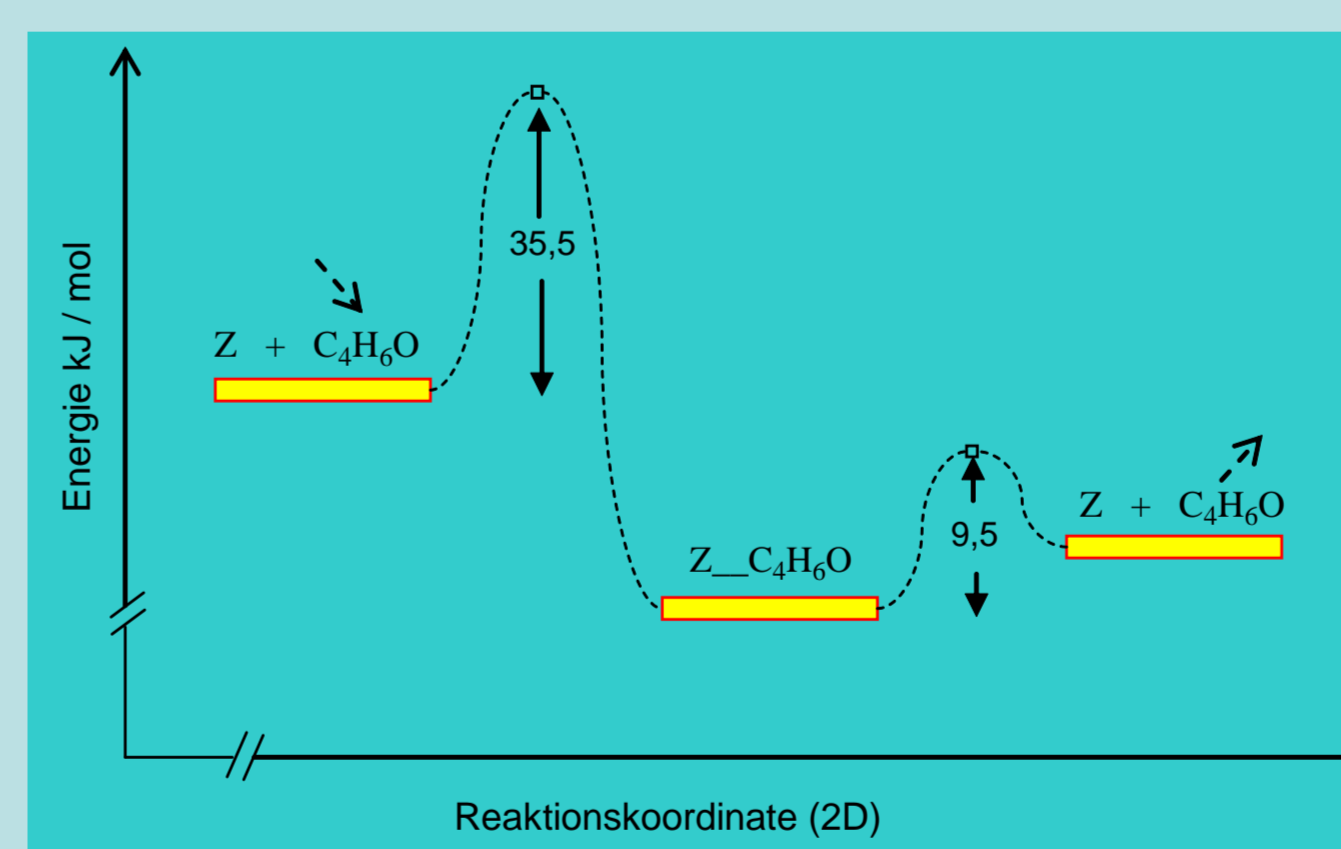


Figure 7. Possible interpretation of the modeled E_a. The arrow above the C₄H₆O species represents adsorption (downward arrow) and desorption (upward arrow).

The model results obtained for the most significant products of 3,4-epoxy-1-butene, CO₂, and CO are in good agreement with the experimental values. An activation energy of 26.02 kJ/mol results for the generation of the molecular target product of 3,4-epoxy-1-butene from the complex surface center (Z), as depicted in fig.7

Conclusion

Heterogeneously catalyzed epoxidation of butadiene has been carried out successfully in the microreactor. Maximum EpB selectivity reached 46%, a 1,3-BD conversion of 8% was achieved (SV = 5900 h⁻¹, temp. 235°C, space-time yield = 0.9 kg m⁻³ h⁻¹). For comparison, the 1,3-BD conversion rate in the tubular reactor with the same catalyst system and under the same conditions is about 18%. EpB selectivity amounts to about 60%. It should be pointed out that EpB and CO₂ are produced from a common surface intermediate. So far, no better EpB selectivities have been achieved in the micro-reactor, which is currently being further optimized. Optimization of the catalyst impregnation method led to higher EpB yields. In future studies, nanoscaled silver particles on supporting materials will be applied and additional microreactor designs will be tested.