# Partial oxidation of butadiene to furan at bismuth molybdate catalysts

H.-G. Lintz and A. Quast

*Institut für Chemische Verfahrenstechnik, Universität Karlsruhe, Kaiserstrasse 12, D-76128 Karlsruhe, Germany*
E-mail: ic01@rz.uni-karlsruhe.de and andre.quast@ciw.uni-karlsruhe.de

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The partial oxidation of 1,3-butadiene to furan was investigated on pure phases of $\alpha$- and $\gamma$-bismuth molybdate (BiMo) as well as on a mixture of 50% $\alpha$-BiMo and $\gamma$-BiMo. The kinetic measurements were carried out in an isothermal tube reactor with plug flow assumed. Along the length of the catalyst bed the gas phase composition was analysed. The set-up of parallel and consecutive reactions with first-order kinetics made a mathematical modelling possible. Within a temperature range of 380 to 440°C butadiene conversions of up to 75% were achieved. Main organic product was furan with a maximum yield of 11%.

**Keywords:** partial oxidation, selective oxidation, butadiene, furan, reaction network, bismuth molybdates

## 1. Introduction

The different availability of organic raw materials and the development of modern catalysts may change typical routes in the transformation of organic substances. Butadiene for example was synthesized via the reduction of furan [1,2]. Nowadays butadiene is a typical by-product of the thermal cracking of naphta [1] to olefins. Thus it would be interesting to invert the synthesis route in order to obtain furan by the partial oxidation of butadiene. By now, however, only few authors have investigated this reaction [3–5], some of them actually being interested not in furan but in maleic anhydride production in the first place [6,7]. A single-pass yield of furan as high as 31% was reported in ref. [5], though we could not reproduce this value in preliminary experiments.

In the present work the partial oxidation of 1,3-butadiene has been studied using catalysts of $\alpha$- and $\gamma$-bismuth molybdate as well as a 1 : 1 mixture of both oxidic phases. Bismuth molybdates are employed very successfully as active compounds in oxidic catalysts for the oxidation and ammoxidation of lower olefins to the corresponding aldehyde or nitrile [8], but the performance of bismuth molybdates in oxidation reactions of $n$-$C_4$ unsaturated hydrocarbons changes completely.

By setting up a reaction network with first-order kinetics a mathematical description of the reactive system was achieved. Its purpose is not the elucidation of any elementary mechanism or reaction path, but the modelling of concentration profiles in the reactor in order to quantify the influence of operating parameters. In addition the fitting parameters enable us to compare different catalysts very easily. In order to discern any consecutive reaction of important intermediates, the measurements had to cover a large domain of conversion.

## 2. Experimental

### 2.1. Preparation of catalyst

In order to prepare these catalysts stoichiometrical amounts of ammonium heptamolybdate and bismuth nitrate were dissolved in water. The solution of molybdate was heated to 60°C, the solution of bismuth nitrate was added under heavy stirring and the resulting suspension was concentrated at 90°C. The residue was dried at 120°C and ground. After calcination at 600°C the catalyst powder has been extruded to cylinders of 5 mm in diameter and 10 mm in length.

The purity of the oxidic phases has been verified by X-ray diffraction. The BET surfaces of the catalysts were 0.7, 1.0 and 1.1 $m^2/g$ for the $\alpha$-, $\alpha/\gamma$- and $\gamma$-bismuth molybdate respectively.

### 2.2. Kinetic measurements

The experiments were run in an integrally operated fixed-bed reactor, containing between 430 and 480 g of catalyst. The reactor consists of a stainless steel tube, 15 mm in diameter and 1500 mm in length. As shown schematically in figure 1 the reactor is equipped with seven drawing ports distributed along the catalyst bed. Heated capillaries connect these ports to a multiposition valve (MPV) which feeds gas samples into the analysis section, consisting of nondispersive IR spectrometers for CO and $CO_2$, a magnetic device for $O_2$ and a gas

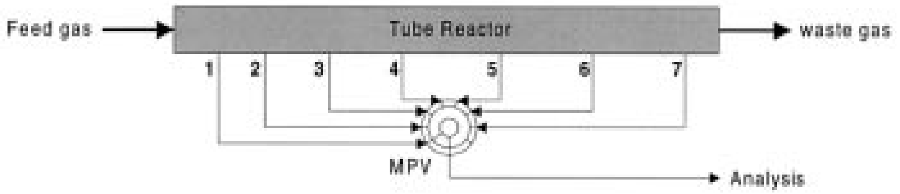


Figure 1. Experimental set-up.

chromatograph with capillary column and FID for the organic compounds.

### 2.3. *Experimental data and derived quantities*

The measurements were carried out in the open system at steady state. Each quantity can be determined at the location of each of the seven analytical ports distributed along the catalyst bed.

The modified residence time is related to the mass $m_{\mathrm{cat},z}$ of the catalytically active compound

$$t_{\mathrm{v},z} = \frac{m_{\mathrm{cat},z}}{\dot{V}}; \quad [t_\mathrm{v}] = \mathrm{g\ s/cm^3}$$

The gas composition at port $z$ is quantified by use of a normalized dimensionless concentration of species $i$,

$$y_{i,z} = \frac{\dot{n}_{i,z}}{\dot{n}_{\mathrm{bde,in}}}\varepsilon ,$$

relating the molar flux of species $i$ to the molar flux of butadiene at reactor inlet, $\varepsilon$ being the ratio of the number of carbon atoms in species $i$ and in butadiene.

Mass balancing between the reactor inlet and the drawing port $z$ additionally leads to the conversion of butadiene,

$$X_z = \frac{\dot{n}_{\mathrm{bde,in}} - \dot{n}_{\mathrm{bde},z}}{\dot{n}_{\mathrm{bde,in}}} .$$

For the reaction products the dimensionless concentration $y_i$ is equal to the yield $Y_i$ which is related to conversion and integral selectivity by

$$Y_i = XS_i .$$

## 3. Results

Typical results are shown in figure 2 for $\alpha$-bismuth molybdate. The dimensionless concentrations are plotted against the residence time. All oxygenated intermediates except for furan, i.e. acetaldehyde, acrolein, acrylic acid, maleic anhydride, benzene and benzaldehyde (the formation of crotonaldehyde was not observed), are lumped together as a pseudo species by-products (bp).

The dimensionless concentrations of furan and by-products pass through the typical maximum. The variation of the products of deep oxidation, CO and $CO_2$, shows an inflection point, indicating that both substances are formed by direct oxidation of butadiene as well as by consecutive oxidation of the intermediates, furan and by-products. The typical pattern of figure 2 has always been obtained, not dependent on the catalyst composition and water content in the feed gas, though there are of course some quantitative differences.

Comparing the dimensionless concentrations of butadiene and furan in figure 3 the poor performance of $\gamma$-bismuth molybdate becomes obvious, while the results are quite similar in case of $\alpha$- and $\alpha/\gamma$-bismuth molybdate. The yield of furan, however, is better at the mixed oxides catalyst – especially at higher residence times. For $\alpha$-bismuth molybdate more oxygenated by-products are formed: up to 3.5% maleic anhydride are found and the yield of acrolein is as high as that of furan.

The product distribution changes heavily with growing conversion of butadiene, as shown in the plot of integral selectivities against conversion for $\alpha$-bismuth molybdate in figure 4. The intermediates furan ($y_{\mathrm{Fur}}$) and the other oxygenated by-products ($y_{\mathrm{BP}}$) are converted into CO and $CO_2$. The maximum of furan yield was obtained at typical butadiene conversions of 55–60% throughout all measurements.

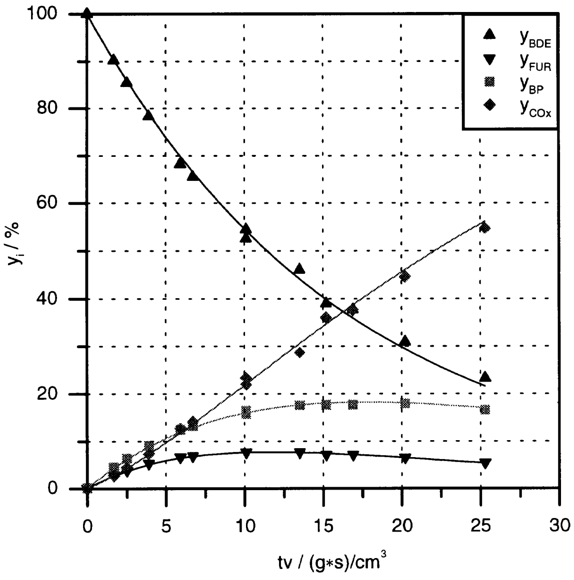


Figure 2. Dimensionless concentrations $y_i$ vs. residence time $t_\mathrm{v}$ ($\alpha$-BiMo; 400°C; feed: 2% $C_4H_6$, 7% $O_2$, 10% $H_2O$, 81% $N_2$).

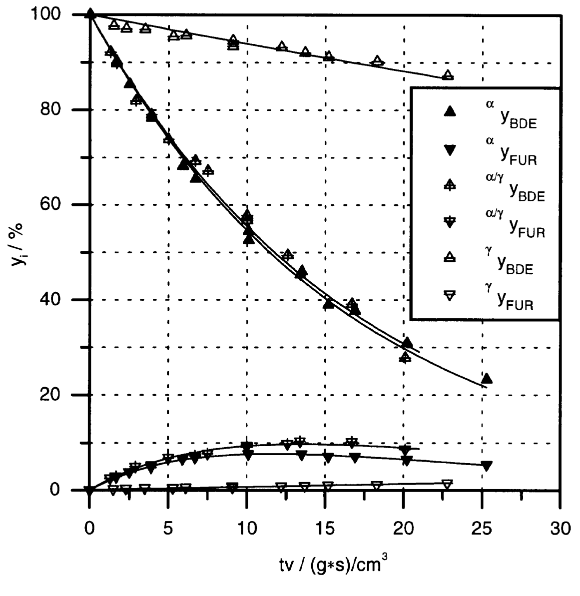


Figure 3. Dimensionless concentrations $y_{\mathrm{BDE}}$ and $y_{\mathrm{Fur}}$ vs. residence time $t_v$ ($\alpha$-, $\alpha/\gamma$-, $\gamma$-BiMo; 400°C; feed: 2% $C_4H_6$, 7% $O_2$, 10% $H_2O$, 81% $N_2$).

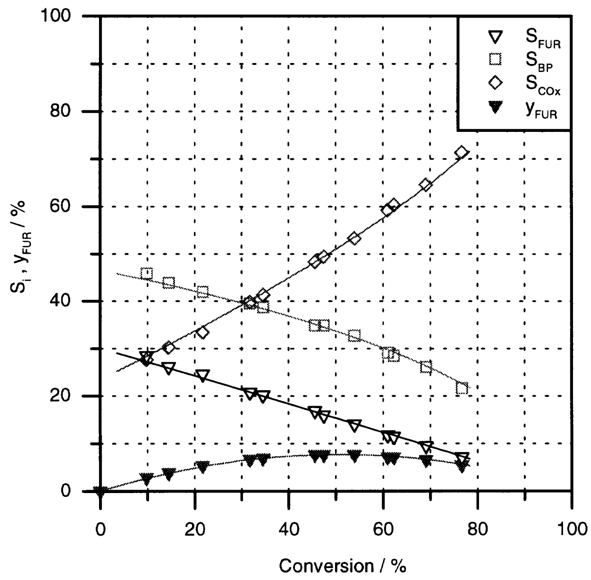
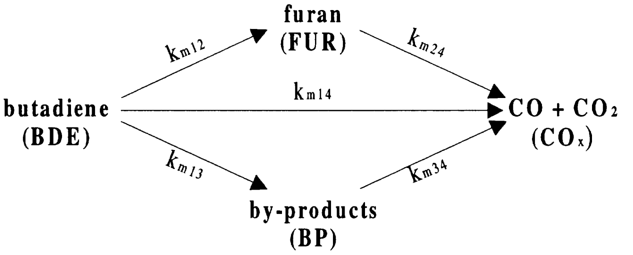


Figure 4. Selectivities and yield of furan vs. butadiene conversion ($\alpha$-BiMo; 400°C; feed: 2% $C_4H_6$, 7% $O_2$, 10% $H_2O$, 81% $N_2$).

## 4. Discussion

All results obtained can be described using the following network of three parallel and two consecutive reactions:



Mass related rates for the single reaction steps $k \to l$ are calculated by expressions of the type

$$r_{\mathrm{m},kl} = k_{\mathrm{m},kl} c_k .$$

In the whole temperature range investigated this first-order approximation is sufficiently precise within the experimental conditions given before, that is 2% butadiene, 7% oxygen and 10% water at reactor inlet. We thus need five kinetic coefficients $k_{\mathrm{m},kl}$ fitted to the experimentally determined concentration curves. The agreement between experiment and model calculation is surprisingly good. In fact, the solid lines in figures 2, 3 and 4, correlating the experimentally measured points, are the results of fitting. The different selectivities are equally well described by model calculations as shown in figure 4 in case of the same dataset. Thus we may safely use the kinetic coefficients in the comparison of the experimental results obtained from the catalysts investigated. We compare three derived quantities [9]:

– the global activity of catalyst in butadiene consumption,

$$k_{\mathrm{m1}} = k_{\mathrm{m12}} + k_{\mathrm{m13}} + k_{\mathrm{m14}} ;$$

– the grain selectivity to furan,

$$^{\mathrm{G}}S_{\mathrm{Fur}} = \frac{k_{\mathrm{m12}}}{k_{\mathrm{m1}}} ;$$

– the stability parameter of furan,

$$^{\mathrm{G}}\lambda_{\mathrm{Fur}} = \frac{k_{\mathrm{m12}}}{k_{\mathrm{m24}}} .$$

The parameters grain selectivity and stability determine the variation of the yield of furan along the tubular reactor and its maximum value. The grain selectivity can be obtained in figure 4 on the ordinate by extrapolation of the corresponding curve to zero conversion; it can be interpreted as the maximal possible reactor selectivity. The stability parameter is, on the other hand, a measure for the decrease of the selectivity curve.

Table 1 illustrates the positive influence of water in the feed gas for $\alpha$-bismuth molybdate. All parameters and the maximum yield of furan are somewhat increased thus justifying the use of 10% water at reactor inlet.

Table 1
Influence of water content in feed gas on kinetic quantities ($\alpha$-BiMo; 400°C; feed: 2% $C_4H_6$, 7% $O_2$)

| $H_2O$ in feed (%) | $k_{\mathrm{m1}}$ ($\mathrm{cm^3/(g\,s)}$) | $^{\mathrm{G}}S_{\mathrm{Fur}}$ (%) | $^{\mathrm{G}}\lambda_{\mathrm{Fur}}$ | $^{\mathrm{max}}Y_{\mathrm{Fur}}$ (%) |
|---|---|---|---|---|
| 0 | 0.049 | 27.6 | 0.138 | 6.8 |
| 10 | 0.061 | 30.0 | 0.156 | 7.6 |
| 20 | 0.062 | 29.1 | 0.176 | 8.2 |

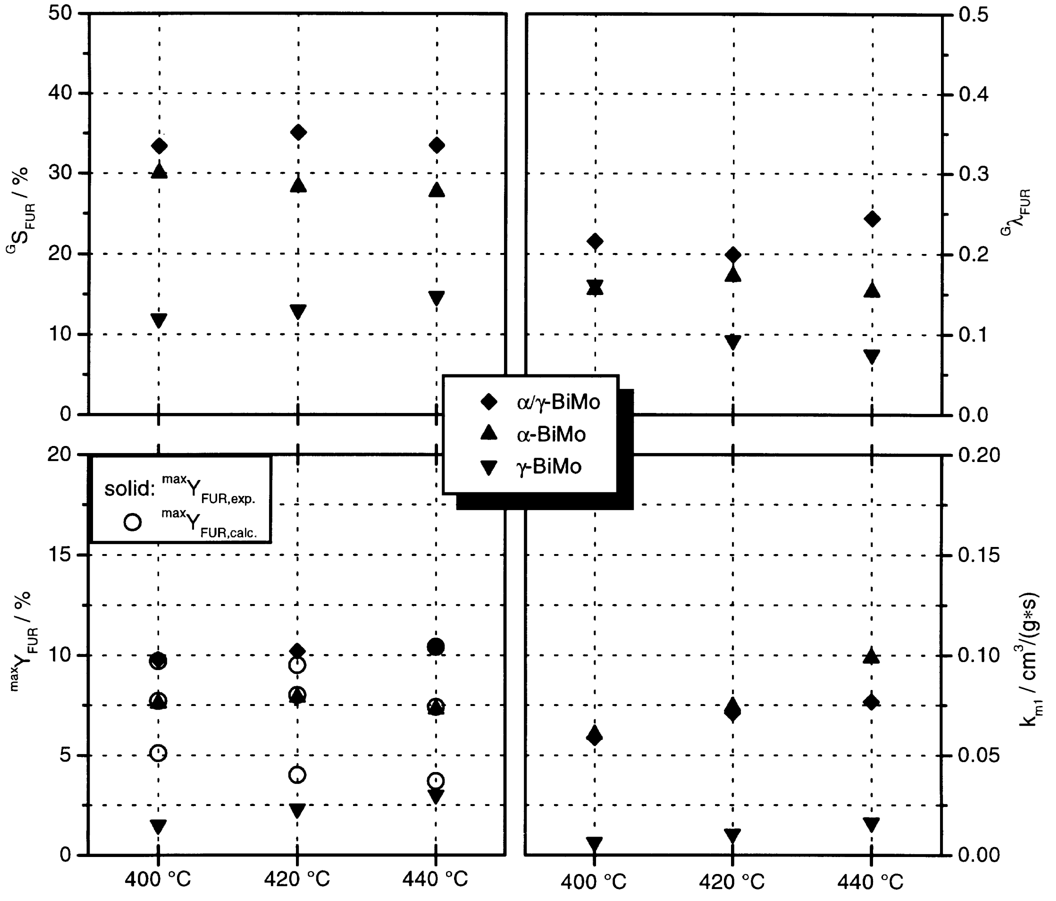


Figure 5. Kinetic quantities vs. temperature (feed: 2% $C_4H_6$, 7% $O_2$, 10% $H_2O$, 81% $N_2$).

Figure 5 shows the influence of reactor temperature for comparison of the different catalysts. We observe a rather small increase of the overall catalytic activity with raising temperature. The values of the selectivity to furan are only slightly changed, resulting in nearly constant maxima of furan yield. Because of the low activity of γ-bismuth molybdate the conversion was too poor to show the yield maximum in that case, as can be seen from the difference between calculated and experimental value in figure 5. The concentration curves had to be extrapolated using our model parameters in order to obtain that calculated value.

Additionally, there is some synergistic strengthening if one compares the mixture of oxides to the pure bismuth molybdate modifications. Both selectivity and stability are higher in case of the mixed catalyst and the highest value of maximum yield of furan – around 11% – is obtained. This synergy had already been observed for propene to acrolein oxidation in literature [10–12]. Therefore, one would assume that the active centres are the same in propene and in butadiene oxidation. This assumption may be reasonable, but the reaction mechanism itself must be a different one, because in case of butadiene there is no possibility of an α-methyl hydrogen abstraction, what is regarded as the rate-determining step in selective propene oxidation [13]. Centi and Trifirò [5] suggest (at VPO catalyst) a mechanism that first inserts an oxygen atom in 1,4-position before the abstraction of H atoms occurs.

## 5. Conclusions

The experimental results have shown that the partial oxidation of butadiene at bismuth molybdates can be described by a simplified reaction network of five first-order reactions. However, the relatively high yields of furan claimed in literature could not be reproduced. Therefore there is no economic interest to investigate the reaction further in order to elucidate mechanistic details.

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