REACTION NETWORK AND PRODUCT DISTRIBUTION OF THE VAPOUR PHASE EPOXIDATION OF PROPENE

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Introduction

Propylene oxide (PO) is an important intermediate for the chemical industry with an annual worldwide production capacity of more than 5 megatons [1]. However, PO production technology is dominated by disadvantageous, liquid phase processes containing multiple reaction steps, namely the chlorhydrin process and several peroxidation routes [1-3]. Particularly in the last ten years, different approaches led to progress concerning a direct epoxidation of propene. However, a high amount of organic solvent reacting both with the feed and the products, catalyst deactivation and mass transfer limitations may still be problems for liquid phase processes using H_2O_2 as oxidant [2-5]. Due to the disadvantages, a direct, vapour phase route is still in the focus of research because of simpler reactor technology, absence of mass transfer limitations and more convenient catalyst handling.

One promising route in the vapour phase could be the use of nitrous oxide (N_2O) as an oxidant, which was firstly demonstrated by Duma and Hönicke using silica supported iron oxide promoted with Na [6]. An improvement of the catalyst led to a promising silica supported iron oxide system promoted with cesium ions and –oxides ($CsO_x/FeO_y/SiO_2$), which provides at 375 °C a maximum selectivity to PO of ~75% among the vapour phase products at a propene conversion of ~10% [7]. Other research groups claimed to obtain even higher PO selectivities using similar catalysts with KCl or Rb_2SO_4 as promoters [8-11], underlining the potential of this route. However, a strong deactivation was always observed, probably due to coking. As a consequence, real product selectivities obtained from the carbon balance must be lower in the above mentioned investigations.

The present study focuses on the reaction network of the catalytic epoxidation of propene using nitrous oxide and a $CsO_x/FeO_y/SiO_2$-catalyst under the condition of a proper carbon-balance. The residence time was varied in a broad range, and propylene oxide and propionaldehyde were added to the reactor feed to determine the importance of different side reactions.

Experimental

Reaction Unit and Catalyst. Experiments were carried out in a fixed bed reactor with plug-flow characteristics. Reactants and products were analysed by means of gas chromatography (Varian CP 3800, equipped with a PoraPlotQ column, TCD, and FID). The carbon balance was monitored on-line through a combination of a total oxidation reactor downflow and a NDIR detector for CO_x measurements. Reaction experiments were typically performed at 375 °C with a reactor feed containing 1 vol.-% propene and 15 vol.-% N_2O in helium. The volume flow was adjusted to reveal modified residence times ($t_{mod} = m_{catalyst}/\dot{V}$) of 10 – 2000 kg s m^{-3}.

Catalysts were prepared through impregnation of silica gel (Silica Gel 60, Merck) with iron acetylacetonate and caesium acetate in toluene and water, respectively, followed by calcination in air at 600 °C. Thereafter, the catalysts were shaped by extrusion (l=5 mm, d=2 mm) using a mixture of catalyst powder, colloidal silica (Ludox AS40, Du Pont), and a solution of hydroxyethyl-cellulose in water (8.5 wt.-%).

Mass transfer effects both inside and outside the catalyst particle can be neglected for propene, propylene oxide, and propionaldehyde conversion indicated by values for Wheeler–Weisz modulus and Carberry number smaller than 1×10^{-4}.

Analysis of Experimental Data. Conversion and selectivity were defined as

$$X = \frac{\dot{n}_{r,in} - \dot{n}_{r,out}}{\dot{n}_{r,in}}, \qquad (1)$$

$$S_{i,r} = \frac{\alpha_i \dot{n}_i}{\alpha_r (\dot{n}_{r,in} - \dot{n}_{r,out})}. \qquad (2)$$

Therein $\dot{n}$ denotes the molar flow of either a reactant r or a product i, and α is the number of carbon atoms in the respective substance.

Plotting the selectivity of each product as function of the reactant's conversion is a valuable tool for evaluating the functional properties of the catalyst. Furthermore, if mass transport effects can be neglected, information on the reaction network can be gained from this plot [7, 12, 13]: the value obtained from extrapolating the selectivity trend of a certain product to zero conversion shows how this product is intrinsically formed. When the extrapolated selectivity differs from zero then the respective product is formed directly from the reactant, whereas if it equals zero then the product is formed via a consecutive pathway.

The carbon balance was defined as

$$\dot{n}_{C,in} = \dot{n}_{C,out} + \dot{n}_{C,accumulated}, \qquad (3)$$

leading directly to the mass of coke accumulating on the catalyst surface, if the carbon flows entering and leaving the reactor are known. The methods applied to measure and calculate these flows, and how to determine the absolute mass and the selectivity to coke is described in detail in [14].

Results and Discussion

Deactivation of the Catalyst and Carbon Balance. Deactivation of the catalyst was observed in all experiments. The reason for the deactivation is the formation of carbonaceous deposits (coke) on the catalyst surface. This becomes clear because of two reasons: firstly, the colour of the catalyst changed from white to black during operation and, secondly, the activity of a fresh sample can be restored by catalyst regeneration in air at temperatures of 773 K for 2 h. During regeneration, the coke species were burned off to CO_2 and H_2O.

Monitoring the carbon balance by means of measuring the CO_2 concentration after the catalytic total oxidation reactor
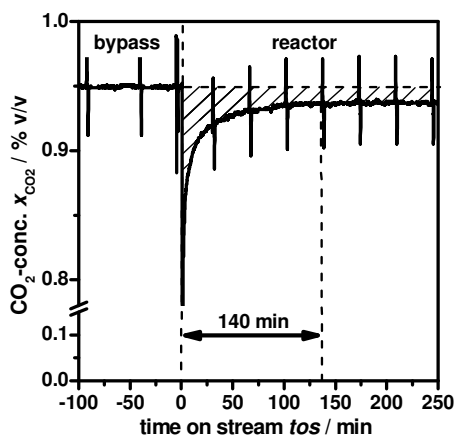
Figure 1. Trend of the CO_2 concentration in the effluent of the catalytic total oxidation reactor during an experimental run (peaks indicate the drawing of a sample for gas chromatography).

(CTOR) was used as a tool to observe the formation of coke species during propene epoxidation (Fig. 1): after switching from bypass to reactor mode, it took about 140 min until the CO_2 concentration was stationary but at that time only 90–95% of the CO_2 concentration measured in bypass mode was reached. The missing CO_2 can be correlated to the deficit in the carbon balance as shown in [14]. The area between the CO_2 concentrations measured in bypass and reactor mode denotes the amount of carbon remaining inside the reactor (hatched area in Fig. 1). In the following, steady-state conditions have been defined at 140 min (''pseudo-steady-state''), because the deficit in the carbon balance is constant after that time.

In all experiments, the sum of selectivities to the reaction products obtained from the gas chromatographic analysis did never reach 100%. As solid products like coke cannot be detected by gas chromatography, at least a part of this deficit must be caused by coke. Fig. 2 shows the selectivity to coke as
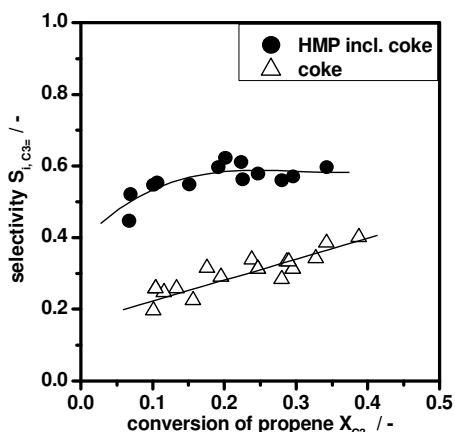

Figure 2. Selectivity to HMP determined by gas chromatography (filled circles) and coke obtained through monitoring the CO2-concentration after the total oxidation reactor (blank triangles) vs. propene conversion ($x_{C3=}$=1% v/v, x_{N2O}=15% v/v).

a function of propene conversion, compared to the selectivity to products not detectable in the GC calculated as

$$S_{HMP,C3=} = 1 - \sum_i S_{i,C3=} .$$ (4)

The comparison of both trends reveals that coke formation can only account for about half of the products not detectable in the GC. Thus, other high molecular products must be formed during the conversion of propene, PO, and PA. These products likely consist of higher alkenes and alkyl aromatics, but also high molecular oxygenates are possible. In the following, carbonaceous deposits and unidentified products are merged in one chemical species designated as ''higher molecular weight products'' (HMP).

Product Spectra and Reaction Network. A deep insight into the network of reactions proceeding during the epoxidation of propene using N2O was gained by converting not only propene but also two of the major products: propylene oxide and propionaldehyde. Both substances were fed into the reactor under the same reaction conditions, but in the range of the low concentrations formed during propene epoxidation (0.1–0.4% v/v). Table 2 shows the rate coefficients for the conversion of these reactants under the presumption of a first order rate law and ideal plug flow behaviour:

$$\frac{dc_r}{dt_{mod}} = -k_m c_r .$$ (5)

The estimated rate coefficients show that the products of propene conversion, PO and PA, are converted more than 10 times faster than propene itself. This displays that PO and PA are highly reactive intermediate products and that short residence times are necessary to obtain high PO selectivities.

From the obtained trends of the selectivities as functions of the conversions of propene, PO, and PA, the reaction network presented in Fig. 3 was revealed. In the following, the reaction paths will be discussed in detail by means of interpreting the selectivity plots obtained from the conversion of propene, PO, and PA.

Propene Conversion. The main products of propene conversion in the presence of N₂O were PO and HMP. Fig. 4 shows a selectivity plot for both substances. A steep decrease in selectivity to PO with increasing propene conversion was observed and the PO selectivity extrapolated to zero conversion was about 0.3–0.4. This indicates that PO is a primary product of propene conversion which is rapidly converted to consecutive products. In the same way, HMP can be identified as a primary product, but in contrast, selectivity to HMP increased with increasing propene conversion up to a limit of 60%.

Other products of propene conversion were propionaldehyde (PA), allyl alcohol (AA), acetone, light alkanes and alkenes (C_1, C_2, and C_4), and CO_2, as well as trace

Table 1. First Order Rate Constants k_m for the Conversion of Propene, PO, and PA

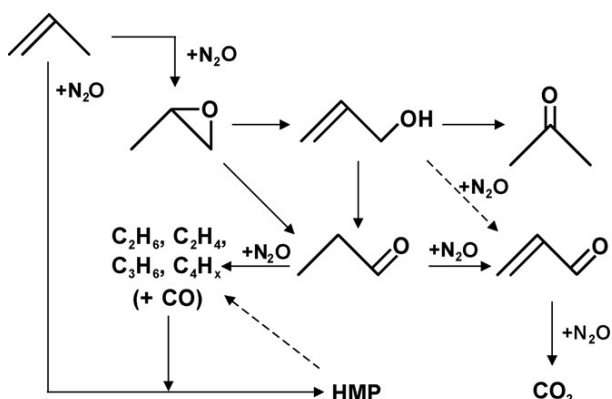| Reactant	k_m (m³ kg⁻¹ s⁻¹)
Propene	3.1×10^{-4}
PO	5.6×10^{-3}
PA	9.6×10^{-3}

Figure 3. Proposed reaction network of the catalytic propene epoxidation (stoichiometry was disregarded, HMP = higher molecular weight products).

amounts (S<1%) of acrolein and acetaldehyde. All these products were identified as consecutive products, which is discussed in detail in [14].

PO Conversion. The conversion of PO mainly proceeded to AA, PA, and HMP, which is shown in the selectivity plot in Fig. 5. As the selectivities to AA and PA extrapolated to zero conversion reveal values of ≈0.5 and ≈0.35, respectively, it is clearly indicated that both products are formed directly through PO isomerisation. Both products are highly reactive intermediates shown by the steep decrease in selectivity down to zero with increasing PO conversion. In contrast, the selectivity to HMP increased with increasing PO conversion from 0 up to over 50%. Thus, HMP are formed as consecutive products.

Other products of PO conversion were CO_2, light alkanes and alkenes (C_1–C_4), acetone, acrolein, and acetaldehyde, all of them showing selectivities of zero at zero conversion (not shown). Selectivities to all of these consecutive products, except acrolein and acetaldehyde, increased with increasing PO conversion over the investigated interval. The selectivity trends of acrolein and acetaldehyde both pass trough a maximum at around 30% conversion. Thus, among the consecutive products of PO conversion, only acrolein and
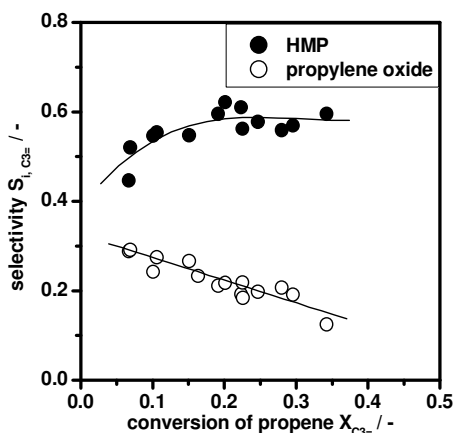

Figure 4. Propene conversion: selectivity to propylene oxide and higher molecular weight products (HMP) vs. propene conversion ($x_{C3=}$=1% v/v, x_{N2O}=15% v/v).
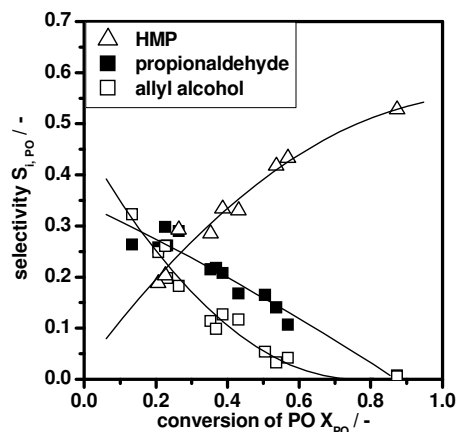

Figure 5. PO conversion: selectivity to higher molecular weight products (HMP), propionaldehyde aldehyde, and allyl alcohol vs. PO conversion (x_{PO}=0.1-0.4% v/v, x_{N2O}=15% v/v).

acetaldehyde are further converted.

Studies on the influence of acid–base properties on the isomerisation of PO [15-18], allow some statements about the active sites of our catalyst. It was reported that PA and acetone are produced on acidic and basic sites, respectively, whereas AA is formed on acid–base bifunctional sites. The comparison between their results and ours indicates that our catalyst still provides a high density of acid sites, although their strength must be quite low. This explains why no acetone is directly formed through isomerisation.

PA Conversion. When PA was converted in the presence of N_2O, the main products were HMP, ethane, ethene, and acrolein. As shown in Fig. 6, a steep increase in selectivity to HMP was observed between 15 and 30% conversion, and at higher conversions a limit of 55–60% selectivity was reached. Thus, the consecutive formation of HMP is definitely faster than a primary formation from PA and HMP seem to be not converted to consecutive products.

In contrast to HMP, the selectivities to ethane and ethene steeply decreased with increasing conversion until at X=30% constant selectivities were reached (Fig. 6). A similar trend was observed for the other hydrocarbons (not shown). Thus, all the C_1–C_4 hydrocarbons seem to be formed as primary products from PA. These species are assumed to be the result of cracking and oxidative C–C bond cleavage.

Due to the complementary selectivity trends of HMP and C_1–C_4 hydrocarbons, we can conclude that the first are formed at least partially from the latter. The fact that both substance classes reach a stationary selectivity at X>30% allows the assumption that the reaction from C_1–C_4 hydrocarbons to HMP can also run in the opposite direction. This means that on acidic surface sites both HMP cracking and formation take place.

Acrolein is formed directly from PA through oxidative dehydrogenation with N_2O and is fast converted to consecutive products, most likely to CO_2.

Note that no acetone was formed in the PA conversion. Since acetone is no primary product of propene and PO conversion, we assume that it is formed through the conversion
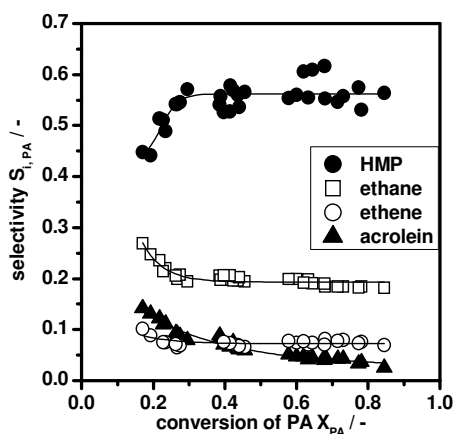
Figure 6. PA conversion: selectivity to higher molecular weight products (HMP), acrolein, ethane, and ethene vs. PA conversion (x_{PA}=0.1-0.4% v/v, x_{N2O}=15% v/v).

of AA. This seems to be reasonable because AA was identified as a highly reactive intermediate product.

Conclusions

Allyl alcohol and acrolein were found only in traces when converting propene. According to Duma and Hönicke [6], the conclusion from these results is that the applied catalyst strongly favours the path of vinylic oxidation to PO as compared to the path of allylic oxidation. However, our results show that allylic alcohol and acrolein in the product spectra are not necessarily an indicator for the existence of the allylic oxidation pathway, because allyl alcohol is a product of PO isomerisation and acrolein is formed through oxidative dehydrogenation of PA.

The epoxidation reaction proceeds in a complex reaction network. This was revealed by the trends of the selectivities as functions of the conversions of propene, PO, and PA. Important side reactions are the PO isomerisation and the formation of high molecular weight products (HMP).

Although HMP cannot be exactly specified at the moment, we can distinguish between two species: carbonaceous deposits (coke) on the catalyst surface and other high molecular weight products in the vapour phase. Coke is assumed to be mainly formed from the reactant propene and other light alkanes and alkenes formed as cracking products of PA conversion. Coking is held responsible for the catalyst deactivation. Other HMP must be formed as primary or consecutive products during the conversion of propene, PO, and PA. These products likely consist of higher alkenes, alkyl aromatics, and higher oxygenates.

When HMP in general are regarded as products of the propene epoxidation, the PO selectivity is decreased by more than half compared to when only substances detected in the GC are taken into account. The formation of HMP was not reported by other research groups [6, 8–11] and therefore not taken into account for the calculation of conversion and/or selectivities. This seems inconsistent as other research groups consider carbonaceous deposits as responsible for catalyst deactivation. Note, that neglecting the significant formation of

HMP makes it impossible to correctly determine the conversion of propene via the concentrations of the products detected by GC analysis and the remaining propene, because then not all products are considered. Consequently, it is not possible to determine correct product selectivities with this method.

It was shown that catalyst deactivation by coking and the formation of higher molecular weight products are the main problems of this propene epoxidation route. Thus, further development of the catalyst should concentrate on the tuning of the acid–base properties, which will directly influence the consecutive conversion of PO, rather than the activation of N_2O and the generation of an appropriate oxygen species. Then, not only higher PO selectivities can be obtained, but also the long term stability of the catalyst can be improved.

References
(1) Haas, Th.; Hofen, W.; Thiele, G.; Kampeis, P. in: *Proceedings of the DGMKConference 2001-4*, Hamburg, Germany, 2001, 127.
(2) Nijhuis, T.A.; Makkee, M.; Moulijn, J.A.; Weckhuysen, B.M. *Ind. Eng. Chem. Res.* **2006**, 45, 3447.
(3) McCoy, M. *Chem. Eng. News* **2001,** 79, 19.
(4) Clerici, M.; Ingallina, P. *Catal. Today* **1998,** 41, 351.
(5) Perego, C.; Carati, A.; Ingallina, P.; Mantegazza, M.A.; Belussi, G. *Appl. Catal. A* **2001**, 221, 63.
(6) Duma, V.; Hönicke, D. *J. Catal.* **2000**, 191, 93.
(7) Ananieva, E.; Reitzmann, A. *Chem. Eng. Sci.* **2004**, 59, 5509.
(8) Wang, X.; Zhang, Q.; Guo, Q.; Lou, Y.; Yang, Y.; Wang, Y. *Chem. Commun.* **2004**, 1396.
(9) Wang, X.; Zhang, Q.; Yang, S.; Wang, Y. *J. Phys. Chem. B* **2005**, 109, 23500.
(10) Zhang, Q.; Guo, Q.; Wang, X.; Shishido, T.; Wang, Y. *J. Catal.* **2006,** 239, 105.
(11) Moens, B.; De Winne, H.; Corthals, S.; Poelman, H.; De Gryse, R.; Meynen, V.; Cool, P.; Sels, B.F.; Jacobs, P.A. *J. Catal.* **2007**, 271, 86.
(12) Riekert, L. *Appl. Catal.* **1985**, 15, 89.
(13) Lintz, H.G. *Oil Gas Sci. Technol.* **2002**, 57, 653.
(14) Thömmes, T.; Zürcher, S.; Wix, A.; Reitzmann, A.; Kraushaar-Czarnetzki, B. *Appl. Catal. A* **2007**, 318, 160.
(15) Imanaka, T.; Okamoto, Y.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1972**, 45, 1353.
(16) Imanaka, T.; Okamoto, Y.; Teranishi, S. *Bull.Chem. Soc. Jpn.* **1972**, 45, 3251.
(17) Okamoto, Y.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, 46, 4.
(18) Fási, A.; Gömöry, A.; Pálinkó , I.; Kiricsi, I. *J. Catal.* **2001**, 200, 340.