Partial oxidation of propane and propene to acrylic acid over a Mo–V–Te–Nb oxide catalyst

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The partial oxidation of propane and propene is investigated over a multi-component oxidic catalyst. Kinetic measurements were carried out in an integrally operated fixed-bed reactor with distributed local sampling. The selectivities to acrylic acid are above 60%. In the case of propane oxidation the highest yield obtained so far compares favorably with the values given in the open literature. In both cases the results can be described quantitatively by a network of parallel and consecutive first-order reactions.

KEY WORDS: partial oxidation; multi-component oxide; propane; propene; acrylic acid.

1. Introduction

Acrylic acid is commercially produced in a two-step process starting from propene. An alternative route could be the partial oxidation of propane. The economic importance of this possibility and the successful manufacture of maleic anhydride by selective oxidation of *n*-butane have stimulated various research efforts in this field. However, for a long period all efforts remained futile and the yields reported in the literature were very low [1,2]. Very recently the use of multi-component oxidic catalysts based on molybdenum, vanadium, niobium and tellurium seems to be a major breakthrough leading to promising developments. The actual state of the art of the selective oxidation of propane to acrylic acid has been reviewed by Lin [3].

Most of the applications of the catalytic system mentioned above are discussed in the patent literature. Some of the results are listed in table 6 of Lin's review [3]. The activities and selectivities reported are strongly related to the mode of preparation of the catalyst and, as Grasselli [2] has already pointed out, it has been rather difficult to reproduce independently the claimed performance. Therefore the open literature is mainly restricted to the study of catalyst preparation and structure and the comparison with other catalytically active systems [3–5]. By contrast, in the following the results of a kinetic study are presented which lead to a quantitative description of the reaction by use of a simple reaction sequence. As we merely observe the evolution of the gas phase, the investigation is not aimed at the elucidation of mechanistic details but at the derivation of a sufficiently precise reaction network in order to give guidelines for improved engineering measures and future catalyst developments.

2. Experimental

2.1. Catalyst

The oxidic catalyst has the global composition $MoV_{0.33}Te_{0.22}Nb_{0.11}O_x$. It was synthesized according to the patent literature [6]: 55.51 g ammonium metavanadate, 73.16 g telluric acid and 253.2 g ammonium heptamolybdate were dissolved in 1782 ml water at 80 °C. Separately, 72.53 g ammonium niobium oxalate were dissolved in 300 ml water at 60 °C. Both solutions were then mixed at 60 °C and the resulting suspension was spray dried ($T_{\mathrm{in}} = 240\,^{\circ}\mathrm{C}$, $T_{\mathrm{out}} = 110\,^{\circ}\mathrm{C}$). The catalyst precursor was precalcined in air (275 °C, 1 h) and then for 2 h at 600 °C under nitrogen. It is of the eggshell type and contains 10 or 20 wt% active compound on spherical steatite. The mean diameter is 3 mm.

2.2. Kinetic measurements

The experiments were run in an integrally operated fixed-bed reactor, containing between 215 and 340 g of catalyst at flow rates between 30 and 60 N cm^3/s. The reactor consisted 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 sampling ports distributed along the catalyst bed. Heated capillaries connect these ports to a multi-position valve (MPV) which feeds gas samples into the analysis section, consisting of nondispersive IR spectrometers for CO and

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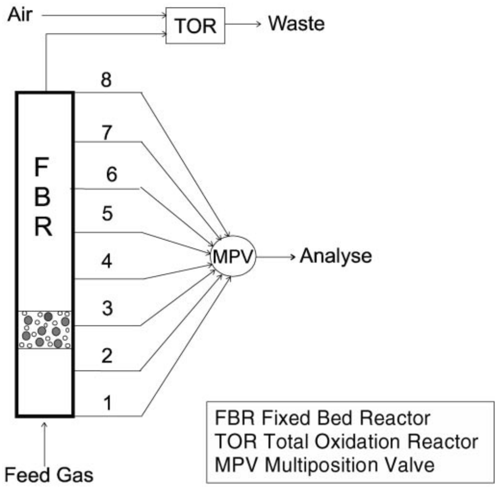

Figure 1. Experimental set-up.

CO_2, a magnetomechanical device for O_2 and a gas chromatograph with capillary column and FID for the organic compounds. Automatic continuous operation of the unit was possible as all functions are controlled and recorded by computer.

The feed contained the hydrocarbon, oxygen and water in nitrogen. The measurements were made at a pressure of 1.5 bar, the temperature being varied in the case of propane in the range 360–420 °C and in the case of propene between 310 and 360 °C.

The reactor is considered as an isothermal plug flow system; the results obtained at the same residence time but different flow rates agree accordingly.

2.3. *Experimental data and derived quantities*

The measurements were carried out in the open system at steady state. Each quantity could 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:

$$\tau_{\mathrm{m},z} = \frac{m_{\mathrm{Cat},z}}{\dot{V}}; \qquad [\tau_{\mathrm{m}}] = \mathrm{g\,s/cm^3}$$

where $\dot{V}$ is the volume flow rate under operational conditions.

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

$$y_{i,z} = \frac{\dot{n}_{i,z} \cdot \varepsilon_i}{\dot{n}_{\mathrm{hc,in}} \cdot 3}$$

relating the molar flux of species i to molar flux of the hydrocarbon (propane or propene) at the reactor inlet. The parameter ε_i is the number of carbon atoms of species i.

Mass balancing between the reactor inlet and the sampling port z additionally leads to the conversion of the hydrocarbon:

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

and the integral selectivity of formation of species i at this location:

$${}^{\mathrm{R}}S_{i,z} = \frac{\dot{n}_{i,z} \cdot \varepsilon_i}{(\dot{n}_{\mathrm{hc,in}} - \dot{n}_{\mathrm{hc},z}) \cdot 3}.$$

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

$$Y_{i,z} = X_z \cdot {}^{\mathrm{R}}S_{i,z}.$$

3. Results

Typical results obtained in the partial oxidation of propane are shown in figures 2 and 3. Interesting products of the reaction are propene and acrylic acid; only traces of acrolein are found. The species by-products consist of CO_x and acetic acid. No acetone could be detected by online gas chromatography. Figure 2 shows the decrease of propane concentration and the steady increase of the concentrations of acrylic acid and by-products with the residence time in the reactor. The concentration of propene passes through a maximum and the values remain low under the conditions used. They are even less at higher temperature.

The corresponding values of the integral selectivities are represented in figure 3 as a function of propane conversion. Measurements at low conversion confirm that the intrinsic selectivity of propene formation is close to unity. The shape of the curves for acrylic acid and by-products indicate that these species are formed in consecutive reactions.

Analogous measurements in the case of propene oxidation are represented in figures 4 and 5. In this case the activity of the catalyst is much higher. A conversion of 40% of the hydrocarbon is already attained at a residence time about seven times smaller than in the oxidation of propane. This is consistent with the low values of propene concentration observed in the latter case. By-products consist of CO_x and acetic acid. Again acetone has not been detected. The concentration of acrolein is higher at lower temperatures and reaches 10% at 310 °C.

The variation of the selectivities as a function of conversion indicates the simultaneous formation of the three species acrolein, acrylic acid and by-products. This is confirmed by measurements at lower temperature, e.g. at 310 °C, where propene conversions as low as 10% could be measured and thus the gap of extrapolation was considerably reduced.

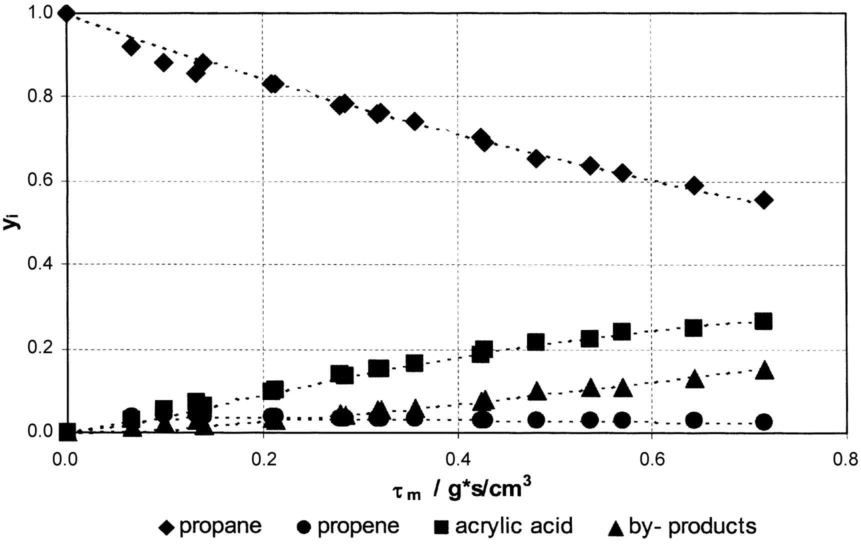

Figure 2. Dimensionless concentrations y_i *versus* residence time at 360 °C. Feed: 2% C_3H_8, 6% O_2, 20% H_2O, balance N_2.

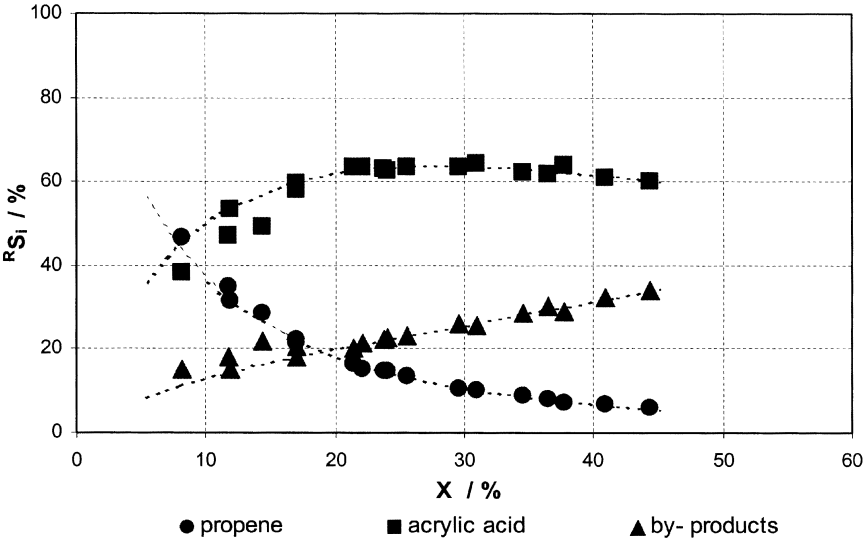

Figure 3. Selectivities *versus* propane conversion at 360 °C. Feed: 2% C_3H_8, 6% O_2, 20% H_2O, balance N_2.

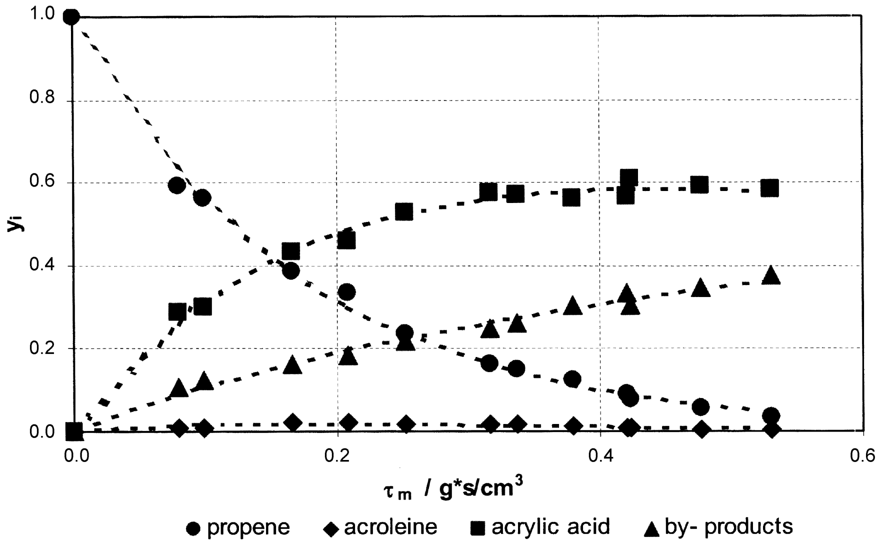

Figure 4. Dimensionless concentrations y_i *versus* residence time at 360 °C. Feed: 3% C_3H_6, 9% O_2, 20% H_2O, balance N_2.

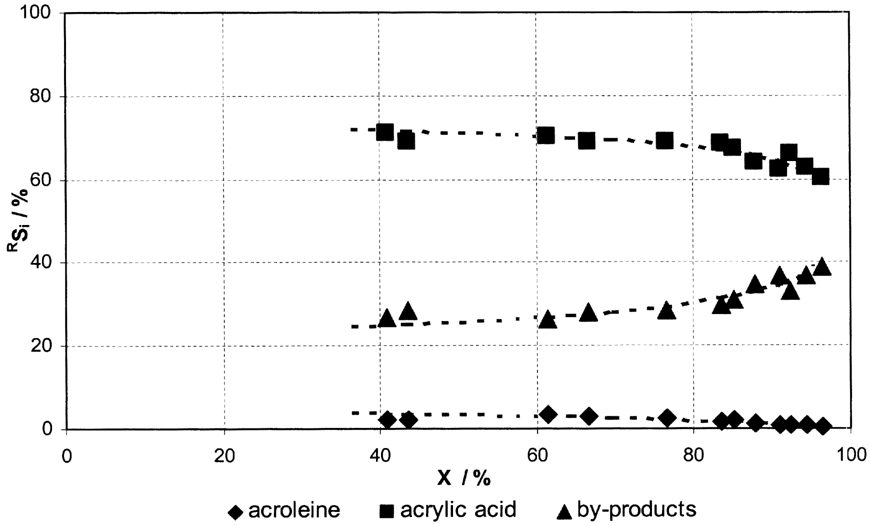

Figure 5. Selectivities *versus* propene conversion at 360 °C. Feed: 3% C_3H_6, 9% O_2, 20% H_2O, balance N_2.

4. Discussion

The partial oxidation of propane can be described using the following network:

$$\begin{tikzcd}
\text{propane}\,(0) \arrow[rr] & & \text{propene}\,(1) \arrow[rr] \arrow[dr] & & \text{acrylic acid}\,(2) \arrow[dl] \\
 & & & \text{by-products}\,(3) &
\end{tikzcd}$$

Mass-related rates for the single reactions k → l are calculated by expressions of the type

$$r_{\mathrm{m,kl}} = k_{\mathrm{m,kl}} \cdot c_{\mathrm{k}}.$$

In fact, the first-order approximation is sufficiently precise in the whole temperature range investigated. The lines in figure 2 correlating the experimentally determined points are the results of the model calculations after fitting of the four kinetic coefficients $k_{\mathrm{m,kl}}$ of the network. The agreement is good. The numerical values of the kinetic coefficients are given in table 1.

The network is justified by the evolution of the selectivities shown in figure 3 and by its simplicity. There is no need to include more single reactions to model quantitatively the concentration profiles along the reactor. Therefore we do not consider the main pathway by comparison with the schemes proposed in the literature [3–5]. The exclusive formation of propene from propane is in agreement with the work of Luo *et al.* [5], who report an intrinsic selectivity to propene of 100%.

The reaction scheme needs to be more complex in the case of propene oxidation. We now detect acrylic acid, acrolein and by-products, the latter being composed of CO_x and acetic acid as before in the oxidation of propane. The existence of acrolein as an intermediate can no longer be neglected as its concentration reaches 10% at 310 °C. Based on these observations and the measured selectivities three parallel reactions of propene are taken into account as shown below:

$$\begin{tikzcd}
 & \text{acrolein}\,(4) \arrow[dr] & \\
\text{propene}\,(1) \arrow[ur] \arrow[rr] \arrow[dr] & & \text{acrylic acid}\,(2) \arrow[dl] \\
 & \text{by-products}\,(3) &
\end{tikzcd}$$

Once more the first-order approximation is sufficiently precise as shown by the good agreement between the calculated curves and experimental data in figures 4 and 5. The numerical values of the kinetic coefficients obtained after curve fitting are given in table 2. The consideration of the additional path of acrolein to by-products did not show any improvement.

It must be mentioned that the catalyst is evolving. If one switches from propane to propene then the catalyst needs nearly 72 h to attain a new steady state. Therefore the propene oxidation scheme may safely be inserted in the simpler propane network but one cannot expect to use the separately determined values of the kinetic

Table 1
Numerical values of the kinetic coefficients for the partial oxidation of propane

T (°C)	k_{01} ($cm^3/(g\,s)$)	k_{12} ($cm^3/(g\,s)$)	k_{13} ($cm^3/(g\,s)$)	k_{23} ($cm^3/(g\,s)$)
360	0.84	17	3.4	0.75

Table 2
Numerical values of the kinetic coefficients for the partial oxidation of propene

T (°C)	k_{12} ($cm^3/(g\,s)$)	k_{13} ($cm^3/(g\,s)$)	k_{14} ($cm^3/(g\,s)$)	k_{23} ($cm^3/(g\,s)$)	k_{42} ($cm^3/(g\,s)$)
360	4.0	1.3	0.45	0.63	5.5

coefficients in the latter case. However, the intrinsic selectivities remain at the same order of magnitude, e.g. 18% to by-products from propane and 22% to by-products from propene.

Comparing both networks we observe that due to the low stability of the intermediate acrolein the pathway $1 \rightarrow 4 \rightarrow 2$ can be merged with the direct formation of acrylic acid from propene ($1 \rightarrow 2$) without loss of precision in the modeling of propane oxidation.

The fact that we can neglect the acetone pathway in both cases by no means implies that this route does not exist as acetic acid may attain up to 25% of the grouped species by-products. However, we do not detect acetone in the gas phase and the quantitative description of the evolution of the concentration profiles is not improved by a further complication of the reaction network.

It has already been mentioned that the characteristics of the multi-component oxide are strongly dependent on the preparation mode. Additionally our measurements have shown that the catalyst is modified under reaction conditions responding to the composition of the gas phase. Therefore any comparison must be treated with caution and the numerical values obtained in different investigations cannot be considered as generally valid for a catalyst of the global composition $MoV_{0.33}Te_{0.22}Nb_{0.11}O_x$.

Nevertheless, it is interesting to look at the performance of the catalyst in view of the one-step production of acrylic acid from propane. The highest yield we obtained so far (32.5% at 370 °C) compares favorably to the value of 17.6% given in the open literature at 350 °C [5] and 380 °C [4]. It is still far below the highest value, 48%, claimed in the patent literature [7].

Taking the reaction networks as a guideline for further developments it appears that the major drawback seems to be the rather high selectivity of formation of by-products from propene. Additionally, if we calculate the stability parameter λ for the partially oxidized species as proposed by Riekert [8], we observe a very low value in the case of acrolein ($\lambda = k_{14}/k_{42} = 0.037$) but a high value for acrylic acid. As the typical catalyst in the classical process shows a high selectivity from propene to acrolein [9], while being rather inactive in propane oxidation [10], it seems interesting to investigate either a mixed catalyst or a structured catalyst bed for a further increase of the acrylic acid yield in the one-step process.

5. Conclusions

The present investigation has to be considered as an attempt to quantify the evolution of the reacting system based on the observation of the gas phase. This attempt had been successful for the oxidation of both propane and propene on a multi-component oxide. It must be emphasized that no mechanistic consideration is necessary for the establishment of the reaction network proposed and that no direct link to a surface mechanism can be derived from it.

As our main interest lies in the description of the behavior of the system in the range of higher conversions we consider that the observed data are fitted adequately by the approach chosen. The utility and limits of this kind of approach in oxidation reactions has been discussed recently [11].

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