Catalysis Letters Vol. 98, Nos. 2–3, November 2004 (© 2004)

Potentiometric measurements in the partial oxidation of propane at a Mo–V–Te–Nb oxide catalyst

I. Grißtede[1], H.-G. Lintz[1]*, and C. Renk[1]

[1]*Institut für Chemische Verfahrenstechnik, Universität Karlsruhe, Kaiserstraße 12, D-76128 Karlsruhe, Germany*

Received 19 July 2004; accepted 27 July 2004

Simultaneous kinetic and potentiometric measurements have been made in the partial oxidation of propane. The results show the principle applicability of the electrochemical method to characterize the catalyst under working conditions. This opens the perspective to derive guidelines for catalytic improvement.

KEY WORDS: solid electrolyte potentiometry; partial oxidation; multi-component oxide; propane; acrylic acid.

1. Introduction

Solid electrolyte potentiometry (SEP) is a valuable tool in the investigation of reactions on solid catalysts as it characterizes the catalyst under working conditions. Measurements on metallic catalysts were summarized recently [1]. The benefits and limits of simultaneous kinetic and potentiometric measurements on oxides have equally been discussed [2]. In course of the study of the partial oxidation of propane to acrylic acid on MoVTeNb mixed oxide catalyst, the results of the kinetic investigation have been published elsewhere [3,4], we have shown the principle applicability of SEP measurements in this system. The results obtained so far are of preliminary character but open interesting perspectives to further work.

2. Experimental

In SEP the catalyst forms one electrode of a galvanic cell which is separated from the reference electrode by an oxygen ion conducting solid electrolyte. The catalyst electrode is in contact with the reacting mixture, the reference electrode is normally in contact with air. Following Wagner [5] the potential difference ΔE measured under open-circuit conditions is related to the oxygen activity a_{O}^2 via the Nernst equation in the form

$$\Delta E = \frac{RT}{4F}\ln\frac{a_{\mathrm{O}}^2}{p_{\mathrm{O}_2,\mathrm{ref}}},$$

where $p_{\mathrm{O}_2,\mathrm{ref}}$, is the oxygen partial pressure at the reference electrode. This operational definition of a_{O}^2 is used throughout the study.

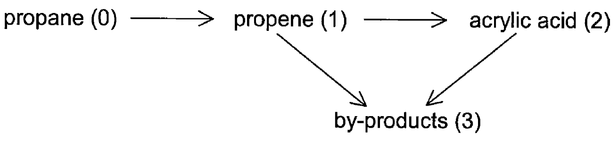
In a special device used in the present investigation the cell is operated in a simple flow-through mode and coupled with a fixed-bed reactor equipped with distributed local sampling ports. In that case the concentration profiles along the reactor axis and the corresponding activity profiles are simultaneously determined as the catalytic activity of the electrode is sufficiently low that the gas-phase composition is not altered during the potentiometric measurement. A detailed decription of the device, schematically shown in figure 1, is given elsewhere [6,7].

The oxidic catalyst has the bulk composition $\mathrm{MoV_{0.33}Te_{0.22}Nb_{0.11}O_x}$ and was used in the fixed-bed reactor and has catalytically active electrode in the galvanic cell. Its preparation has been described before [3], the special electrode preparation can be found elsewhere [8].

3. Results and discussion

Typical results of the combined kinetic and potentiometric study are shown in figure 2 as a function of a modified residence time. The normalized concentrations of the organic compounds y_i (left ordinate) and the oxygen partial pressure p_{O_2} (right ordinate) describe the concentration profiles along the tubular reactor. The corresponding profile of the oxygen activity a_{O}^2 (stars) at the same catalyst is equally given, the values being indicated on the right ordinate.

The reaction kinetics can be described by the following reaction network [4]. Propene is the primary product of the partial oxidation of propane. Propene reacts further to acrylic acid and by-products (CO, $\mathrm{CO_2}$ and acetic acid). Acrylic acid reacts also in a consecutive



Scheme 1.

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*To whom correspondence should be addressed.
E-mail: h-g.Lintz@ciw.uni-karlsruhe.de

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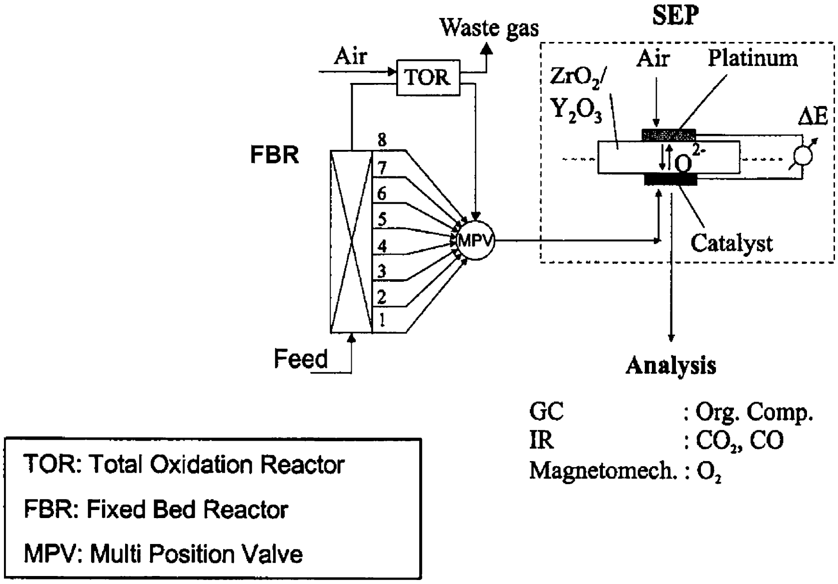

Figure 1. Schematic diagram of the experimental setup.

reaction to by-products. All reaction paths can be described by first order reactions (solid lines in figure 2) [4].

Wagner [9] has shown that the oxygen activity in a solid catalyst in contact with both an oxygen donor (e.g., oxygen) and an oxygen acceptor (e.g., an organic compound) is kinetically determined and results from the balance of the rate of oxygen uptake r_+ and oxygen removal r_- at the solid surface. This is shown schematically in figure 3. We consider that r_+ is a function of the concentrations of the oxygen donor, r_- a function of the oxygen acceptor, and both rates depend on the oxygen activity in the solid. It seems reasonable to admit that r_+ is decreasing and r_- increasing with growing values of a^2_{O}. The intersection represents the steady state value $a^2_{\mathrm{O,st}}$. In the absence of organic compounds and with O_2 as oxygen donor the oxygen activity would be given by the intersection of r_+ with the abscissa, determining the equilibrium value

$$a^{2*}_{\mathrm{O}} \equiv p_{\mathrm{O}_2}$$

The oxygen acceptor system is more complex, all oxidizable organic compounds–propane, propene, acrylic acid and by-products–have to be considered in the present case, but their relative influence is different. This determines the variation of the oxygen activity as a function of t_{m} shown in figure 2. For $t_{\mathrm{m}} = 0$ cm^3/(g s) and therefore with only propane as oxygen acceptor the highest oxygen activity is measured. As soon as propene is formed the oxygen activity decreases about one order of magnitude and then remains constant independently of the evolution of the gas-phase composition.

If propane alone were present one would expect the decrease of a^2_{O} with increasing propane concentration as the rate of oxygen uptake by the oxygen acceptor

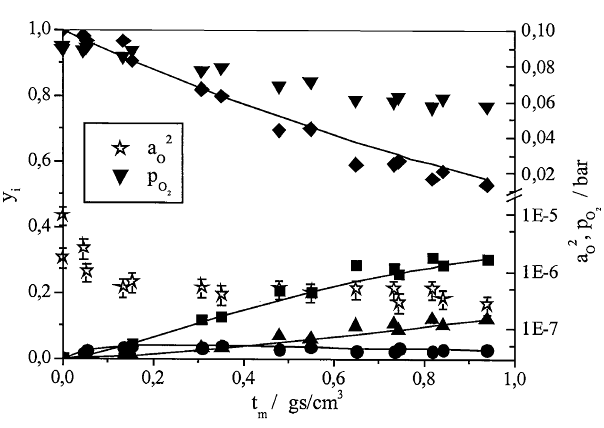

Figure 2. Product distribution and oxygen activity as a function of the modified residence time at 360 °C, $X_{\mathrm{C_3H_8,O}} = 0.02$, $X_{\mathrm{O_2,O}} = 0.06$, $X_{\mathrm{H_2O}}, O = 0.2$.

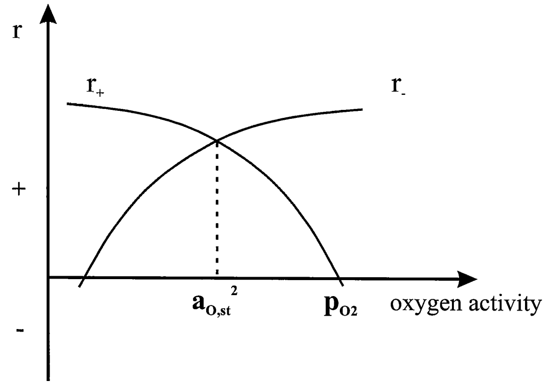

Figure 3. Rates of oxygen uptake (r_+) and oxygen release (r_-) as a function of the oxygen activity in the solid is shown schematically.

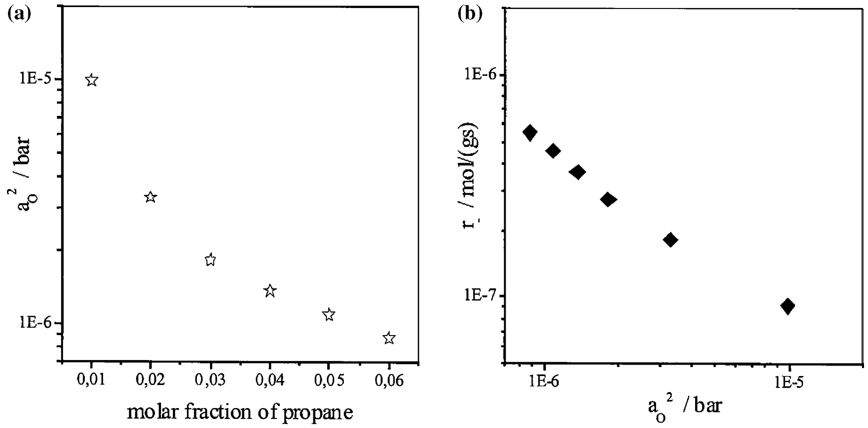

Figure 4. (a) Oxygen activity as a function of propane content and (b) Rate of oxygen release as a function of oxygen activity, $T = 360°C$, $X_{O_2} = 0.06$, and $X_{H_2O} = 0.2$.

increases. This is confirmed by the results represented in figure 4. The decrease is correlated with the rate r_- which can be calculated from the kinetic coefficients determined in the study [4,8]:

$$r_- = 0.5 \cdot k_{01} \cdot c_0 + (1.5 \cdot k_{12} + 3.3 \cdot k_{13}) \cdot c_1 + 1.8 \cdot k_{23} \cdot c_2$$

Similar calculations using the reaction network and the corresponding rate equations indicate that the variation of r_- and therefore, the oxygen activity along the reactor is largely dominated by the propene concentration. The results of the calculations are shown on figure 5. The calculations were done for the same conversion domain as the experimental results in figure 2. Figure 5 shows that r_- is largely determined by the propene concentration in spite of its small values. As the latter remains practically constant except for $X_{\text{propane}} < 0.1$ corresponding to $t_m < 0.2$ cm^3/(g s) the values of a_O^2 are nearly invariant in a large part of the catalyst bed. (In the limits of $0.1 < X_{\text{propane}} < 0.45$ the variation of r_- is between 0.55 and $0.75 \cdot 10^{-6}$ mol/(g s). This variation corresponds to a deviation of a_O^2 of about $\Delta a_O^2 = 2 \cdot 10^{-7}$ bar. Since this deviation is within the precision of the measurements, it doesn't invalidate the conclusions).

The dominant influence of the propene concentration is confirmed by the values obtained with pure hydrocarbons at constant oxygen concentration as shown below:

$X_{C_3H_8}$	$X_{C_3H_6}$	$r_- \cdot 10^6$/mol g^{-1} s^{-1}	a_O^2/bar
0.02	–	0.19	$3 \cdot 10^{-6}$
–	0.02	0.2	$5 \cdot 10^{-9}$

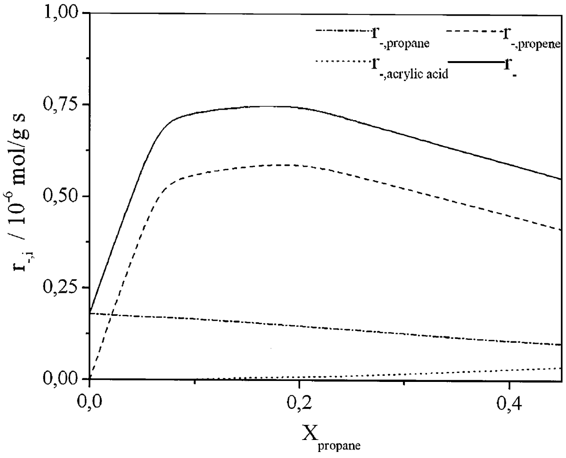

Figure 5. Rate of oxygen uptake by the different organic compounds $r_{-,i}$ and the sum r_- as a function of propane conversion.

The interaction of the catalyst with propene is stronger than with propane and thus the oxide is in a more reduced state. In the present case, the 1st product of the partial oxidation is strongly interacting and therefore less stable than the reactant propane. Similar measurements had been made in the partial oxidation of propene to acrolein and of acrolein to acrylic acid on industrial catalysts [2]. In both cases the partially oxidized products interact less with the catalyst than the reactant itself leading to the high product stability aimed at. It seems reasonable to admit from the kinetic results that in the present case acrylic acid is less interacting and more stable than propene but the measurements haven't been done yet. Anyhow, it is more interesting to compare the partial oxidation of propene on both the MoVTeNb oxide leading to acrylic acid and the industrial catalyst producing acrolein. At 360 °C the catalytic activity is identical in both cases. We observe 90% conversion at $t_m = 0.4$ cm^3/(g s). However, the oxygen activity in orders of magnitude lower in the industrial catalyst

$X_{C_3H_6}$	X_{O_2}	X_{H_2O}	a_O^2/bar	ref.
0.02	0.11	0.12	$5 \cdot 10^{-14}$	[10]
0.02	0.06	0.2	$5 \cdot 10^{-9}$	present work

Now, the weakness of $MoVTeNbO_x$ catalysts investigated so far is the relatively low grain selectivity [4]. In the partial oxidation of propene to acrylic acid almost 30% of by-products are formed, whereas the selectivity of acrolein formation on the industrial catalyst attains up to 99%.

In this context we may remember that the SEP aided study of propene oxidation on copper oxides had shown that at CuO (oxygen activities above 10^{-9} bar) mainly CO_x was formed and that the existence of CU_2O ($a_O^2 < 0^{-9}$ bar) was necessary to the formation of acrolein [2]. Thus, the question arises if these results are significant and if the selectivity to partially oxidized compounds and the oxygen activity in the catalyst are related.

In addition, the performance of the industrial catalyst is based on the synergism between two phases, iron cobalt molybdate and bismuth tungstate. SEP measurements have shown that the molybdate acts as an oxygen donor and the tungstate as an oxygen acceptor, following the terminology of Delmon and Weng [11]. In the case of MoVTeNb mixed oxide catalysts there are two equal phases present, commonly named M1 and M2 [12]. The addition of phase M2, inactive if alone, increases the selectivity from propane to acrylic acid. Thus, SEP measurements should indicate if the observed synergism is equally related to an oxygen transfer between both oxidic compounds.

4. Conclusions

The SEP measurements have shown that simultaneous kinetic and potentiometric measurements are possible in the investigation of propane oxidation on MoVTeNb mixed oxide catalysts. In further studies we propose to adjust a standard concentration profile in the tubular reactor as represented in figure 2 and compare the response of different catalysts (e.g., the pure phases M1 and M2) as working electrode in the galvanic cell. The results are expected to give an answer to the following questions

- Can we determine a domain of oxygen activity in the catalyst under working conditions in which high selectivity to acrylic acid is coupled with high stability of the latter?
- How is the difference of the oxygen activity in different phases as a driving force of oxygen transfer between solids related to high selectivity and stability of the partially oxidized product acrylic acid?

Hopefully the results should lead to guidelines in catalyst development.

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