

Kinetic investigation of propane oxidation on diluted $\text{Mo}_1\text{-V}_{0.3}\text{-Te}_{0.23}\text{-Nb}_{0.125}\text{-O}_x$ mixed-oxide catalysts

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Abstract Reaction kinetics and proposed mechanism for the oxidation of propane over diluted $\text{Mo}_1\text{-V}_{0.3}\text{-Te}_{0.23}\text{-Nb}_{0.125}\text{-O}_x$ are described. The kinetic study allowed determination of the orders of propane disappearance, propene formation, CO_x formation, and acids formation. The results show that selective oxidation of propane to propylene over this catalyst follows the Langmuir-Hinshelwood mechanism. Deep oxidation of propane to carbon dioxide is first order with respect to hydrocarbon, and partial order (0.21) with respect to oxygen. The selective oxidation of propane to acrylic acid is half order with respect to hydrocarbon and partial order (0.11) with respect to oxygen, while water does not participate directly in propane transformation. The result also shows that the overall reaction consists of three parallel process channels. One main sequence of consecutive reactions leads to the desired product.

Keywords Propane oxidation · Acrylic acid · Kinetic · Reaction pathways

Introduction

Currently, most plants produce acrylic acid via a two-step oxidation process in which propylene is oxidized over multi-component Mo–Bi–Co–Fe-based oxide

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catalysts at 320–330 °C to make an intermediate compound. The process generates acrolein, which can be further oxidized at 210–255 °C over Mo–V-based oxide catalysts to form more acrylic acid. Overall selectivities to acrylic acid based on propene of 85–90% are obtained at conversions above 95% [1]. Alternatively, acrylic acid can also be produced from a one-step oxidation of propane. The economic importance of this possibility and the successful manufacture of maleic anhydride by selective oxidation of *n*-butane has stimulated various research. In parallel, investigations on the catalytic oxidative dehydrogenation of propane have been undertaken since this route is expected to lead to lower costs of propylene production as compared to the non-catalytic and non-oxidative processes [2]. Another reason to pay specific attention to use propane is that the behaviour of light alkanes (C₁–C₆) in catalytic partial oxidation reactions is different from the one to another [3–7].

Reactions involving selective oxidation of propane to acrylic acid have been heavily studied [8–10]. Propane partial oxidation to acrylic acid over vanadium pyrophosphate (VPO) catalysts has been reported [11, 12]. Propane oxidation to acrylic acid with heteropolyacids or with their corresponding salts has also been reported [13, 14]. In the last years, the use of multi-component oxidic catalysts based on molybdenum, vanadium, niobium and tellurium seems to lead to a major breakthrough and promising developments. The actual state of the art of the selective oxidation of propane to acrylic acid has been reviewed by Lin [15]. Unfortunately, until now, no catalyst system has been reported for the direct oxidation of propane that is active and selective enough to substitute the existing industrial process; this is mainly due to the higher reaction temperatures required for the activation of the paraffin, which results in the enhancement of total oxidation reactions.

So far the open literature is mainly restricted to the study of catalyst preparation, its structure and the comparison with other catalytically active systems [9, 15–17]. Selective oxidation of propane is an important reaction type as an alternative route for the production of acrylic acid. The reaction is difficult to perform with a very high yield since the product is easily further oxidized [18]. The detailed expression for apparent rate (kinetics) will permit the chemical engineer to make a rigorous extrapolation of experimental results to the industrial scale. Also, those expressions will be useful to the chemist, who is not always interested in the apparent rate so much as in the rate of chemical action whose mechanism he searches to clarify, because they will permit the chemist to identify adequate experimental conditions.

It is shown in the literature that the reaction network and products distribution are very sensitive toward the catalyst used. Significant differences in the reaction pathways are observed when the reaction is carried out over, Te–P/NiMoO catalysts [19], Mo–V–Sb–Nb catalysts [10], and Mo–V–Te–Nb catalysts [9]. This article deals with the reaction kinetics and mechanism of propane partial oxidation to acrylic acid on diluted MoVTeNbO_x mixed-oxide catalysts using high-throughput system (nanoflow reactor).

Experimental

Diluted $\text{Mo}_1\text{V}_{0.30}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_x$ has been prepared according to the method described in the previous literature. These preparations and the catalysts characterizations have been described in more detail before [20, 21].

The kinetic studies were conducted by analysis of the products at low propane and oxygen concentrations (lower than 10%), which is required for operating the reactor in a differential mode. This was achieved by introducing small amount of catalyst (0.09 g) diluted in SiO_2 to a total volume of 0.5 mL and using high total flow rates (15 mLN/min, GHSV = 1800 h^{-1}). Only one of the reactants was varied at the time and the rest were chosen to be in excess and outside of the explosive limits for the mixture of propane and oxygen. The feed composition was propane, oxygen, and steam (water) balance in nitrogen. The study of the kinetic dependence on propane was performed by varying the propane concentration and maintaining the others. For the oxygen dependence, oxygen concentration was varied and concentrations of the others were maintained. Finally, for the water dependence, water concentration was varied and concentrations of the others were maintained. The effect of reactant concentration was studied at four different temperatures, i.e., 653, 663, 673, and 683 K. Particle size of catalytic material was 212–425 μm or less. The reaction was carried out in a nanoflow catalytic reactor [21]. For all experimental results, the reaction rate (rate of reactant disappearance and rate of products formation) and the concentration of reactants are calculated using Equations shown below:

$$\text{Reaction rate (mol/h gcat)} = \frac{\% \text{vol} * \text{total_flow} * d * 60}{\text{Mr} * \text{catalyst_weight}}$$
$$\text{Concentration (mol/L)} = (\% \text{vol} * d * 1000) / \text{Mr}$$

where %vol is concentration of product in %v/v; total_flow is the total flow of product stream from the reactor in mLN/min; Mr and d are molecular weight and density of the product; and catalyst_weight is the weight of catalyst in gram

Result and discussion

The structure and surface texturing of Mo–V–Te–Nb oxide catalyst particles composed of two phases referred to in the literature as M1 and M2 is revealed by high-resolution transmission electron microscopy of high performing catalysts. The chemical composition of the catalyst surface is modified by treatment in water to obtain a significant increment in yield of acrylic acid. A chemical realization of the site isolation concept recurring on a supramolecular arrangement of catalyst and reactant rather than on atomic site isolation is suggested. A complex Mo–V–Te–Nb– O_x precursor phase carries nanoparticles made from a network of oxoclusters active as catalyst for the conversion of propane to acrylic acid. The structure and surface of this catalyst have been described in more detail before [20]. The reproducibility of catalytic activity test has been carried out by repeated the

experiments under the same condition and showed very good reproducibility in terms of both the propane conversion and acrylic acid selectivity [21].

Kinetic description of the oxidation reaction

The kinetic parameters for the propane oxidation were determined by following the product formation as a function of propane, oxygen, and water concentrations under reaction conditions required for a differential operating regime (reactants conversion lower than 10–15% at any temperatures used). The obtained products comprised of propene (propylene), acrolein, isopropyl alcohol, acetic and acrylic acids, and carbon oxides. Due to the very low selectivities to acrolein and isopropyl alcohol (lower than 1%), the formation of these products was not further investigated in this kinetic study. In these experiments, carbon oxide is referred to only carbon dioxide, since there is no carbon monoxide detected during the reaction at any reaction temperatures.

A blank reaction (SiO_2 only, 0.5 mL) was carried out prior to conducting the kinetic study and did not show any activity, nor did homogeneous combustion of propane occur. The diagnostic test of external and internal mass transfer limitations were also carried out prior to conducting the kinetic study and show that the reaction was free of external and internal mass transfer limitations.

The observed products of propane oxidation were propene, acrylic acid, carbon dioxide, and acetic acid. From Fig. 1, it is observed that the selectivity to propene decreases as propane conversion is increased, on the other hand, the selectivity to acrylic acid increases as propane conversion is increased, while selectivities to carbon dioxide and acetic acid are relatively constant at all propane conversions. These data indicate that propene as an intermediate product is relatively easily

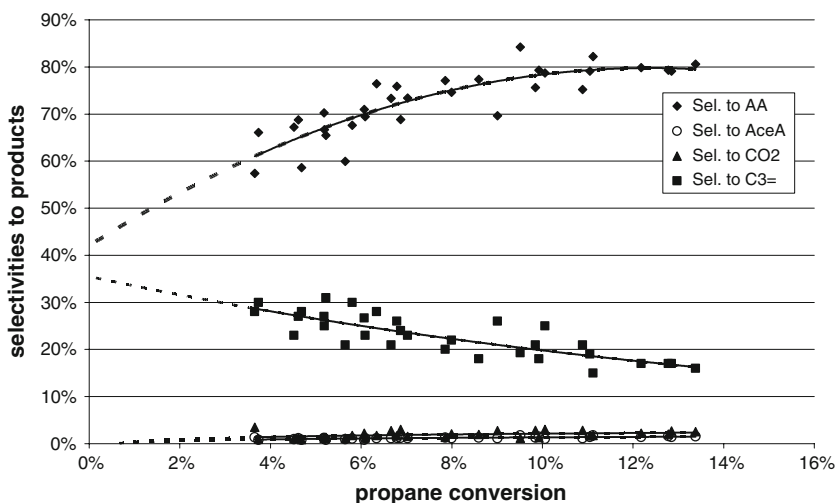


Fig. 1 Product selectivity profiles for propane oxidation over diluted MoVTaNb oxide catalyst (under reactor differential mode)

converted to acrylic acid, while carbon dioxide must be formed by at least one subsequent reaction step, or being produced by a reaction channel different from that of the partial oxidation (dehydrogenation) channel. However, it also indicates that the acrylic acid produced is quite stable under the reaction conditions used in this study, since carbon dioxide is obtained only in very low amount. According to these data, the reaction can be proposed by the following reaction $C_3H_8 + O_2 \rightarrow$ products, where the products are propene, acrylic acid, acetic acid, and carbon dioxide.

Figs. 2 and 3 describe that the propane disappearance observed is a linear function of propane concentration, but it is a logarithmic function of oxygen concentration. For the experiments on oxygen dependence, the oxygen concentration was varied whereas the concentrations of the other constituents of the gas phase were maintained.

From kinetic theory, it is known that reaction orders indicate the surface coverage with the respective species. These coverages vary strongly with partial pressures if we assume that no transport limitations render the kinetic analysis “apparent”. Reaction orders are not constants but variables over the range of surface coverages occurring under the given partial pressures in a heterogeneous reaction. Hence it is clear that the rate determining step does involve a reaction between propane, or an activated complex thereof, and activated atomic oxygen. Thus neither the Eley-Rideal (ER) nor the Mars van Krevelen (MvK) mechanisms are consistent with the process being the rate determining for the disappearance of propane. In this case, it is very difficult to interpret the numerical value of the fractional reaction order with respect to oxygen.

This is expected as the propane sticks to the surface directly from the gas phase whereas oxygen needs to be dissociatively pre-activated before it can be a reactant. It is now a matter of semantics if pre-adsorbed atomic oxygen is called “lattice oxygen” or simply adsorbed oxygen as the adsorption site of atomic oxygen must

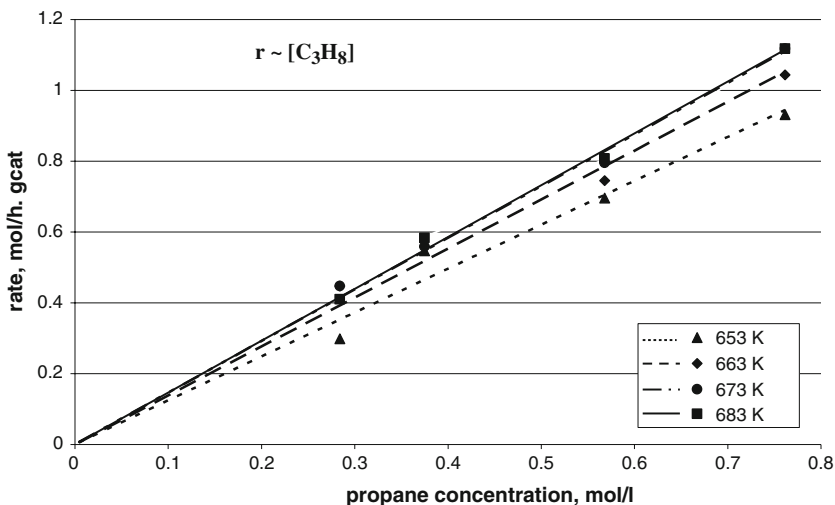


Fig. 2 Rate of propane disappearance as a function of propane concentration at 653, 663, 673, and 683 K

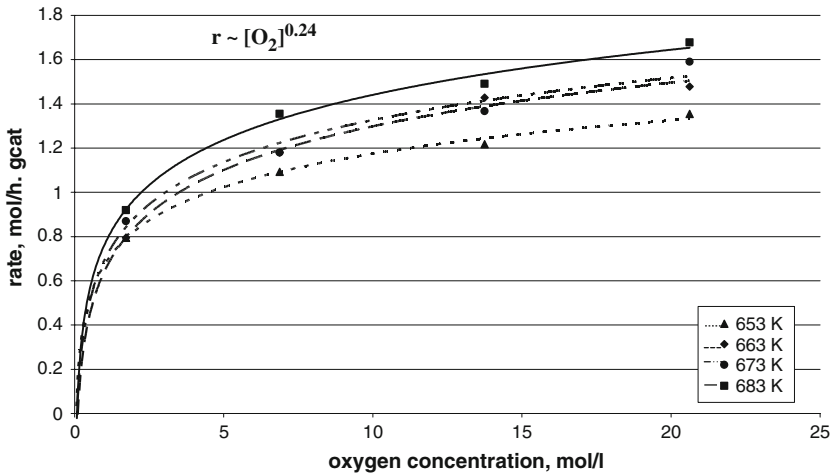


Fig. 3 Rate of propane disappearance as a function of oxygen concentration at 653, 663, 673, and 683 K

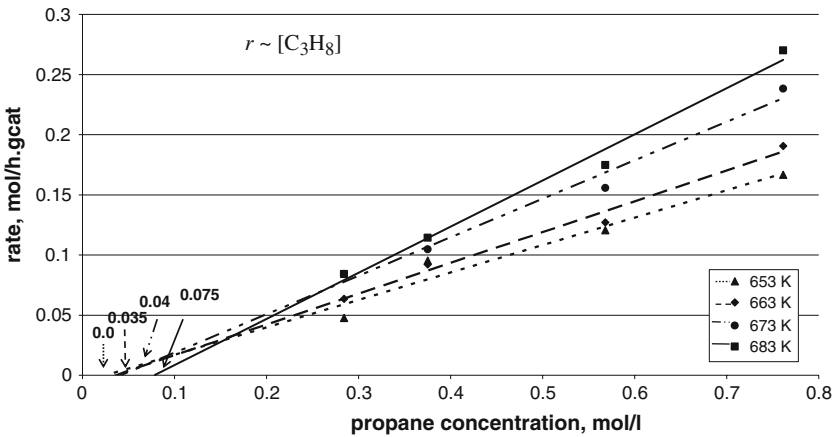


Fig. 4 Rate of propene formation as a function of propane concentration at 653, 663, 673, and 683 K

have been a defect in the catalyst surface and the geometric location of the adsorbed oxygen is thus a lattice position. There is, in contrast to general belief, no justification for the assumption of a special mechanism of a selective oxidation. The description terms of a Langmuir-Hinshelwood (LH) mechanism involving a lattice defect in the oxide catalyst surface, as active site is perfectly consistent with the present kinetic findings. Fig. 4 illustrates that the rate of partial oxidation of propane to propene is first order with respect to propane concentration in the whole range of temperatures.

It is widely believed that propene is the only primary product of propane oxidation and, therefore, is directly dependent on propane concentration. However, the straight lines do not pass through the origin of the graphs; their rate of

appearance is zero at a propane concentration of 0.03 mol/L at 653 K, 0.035 mol/L at 663 K, 0.04 mol/L at 673 K, and 0.075 mol/L at 683 K. The reason for this is that the rate found experimentally for a product intermediate is the difference between the true rate of formation and the rate of product disappearance in the next step of the reaction. Thus, it is indicative that at low propane concentration, the propene formed is entirely converted to other products. This result also indicates that increasing the reaction temperature will affect the intermediate product (i.e. propene) to convert to other products. It means that at higher reaction temperature, the intermediate product (namely propene) easily converts to other products.

Fig. 5 shows that the rate of partial oxidation of propane to propene is zero order with respect to oxygen; which contradicts a previous report mentioning a non-zero order with respect to oxygen [10].

The statement is in line with the assumed LH mechanism of the propane conversion derived above. It is apparent that propene is the first intermediate on the path of selective oxidation and hence should carry the kinetic signature of the overall reaction. Considering however, the principle of the MvK mechanism, the first explanation is not likely to apply except in the case of gas-phase reaction. However, the present results (Fig. 5) are consistent with observations reported by Stern and Grasselli [22], which were interpreted by the authors in terms of the MvK [23] paradigm. In this mechanistic scenario, if the rate of replenishment of lattice oxygen by gaseous molecular oxygen is rapid compared to the rate of removal, then the concentration of lattice oxygen at the catalyst surface is essentially constant and independent of the oxygen partial pressure in the gas phase, and the rate of hydrocarbon (i.e. propane) oxidation becomes zero order with respect to oxygen. This notion is also fully consistent with the derived LH mechanism stating a pre-equilibrium of formation of dissociated oxygen over pre-existing defects in the oxygen-terminated catalyst surface. The partial or selective oxidation of propane to propene is first order with respect to propane (Fig. 4) and hence, consistent with a

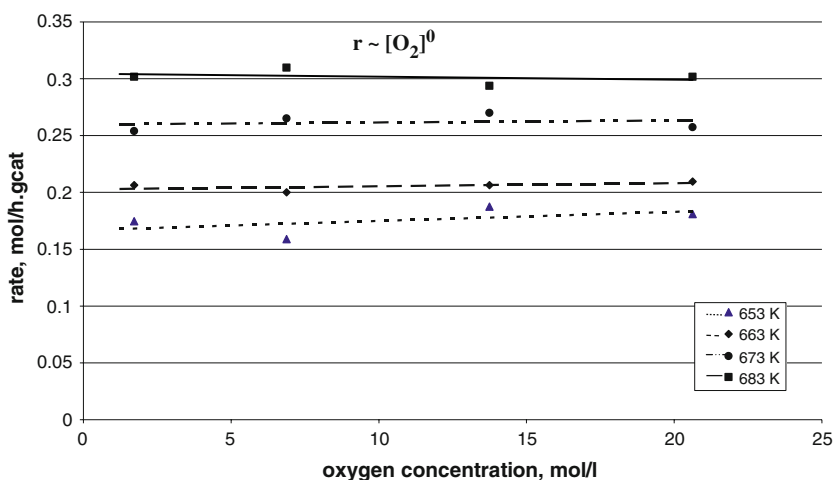


Fig. 5 Rate of propene formation as a function of oxygen concentration at 653, 663, 673, and 683 K

rate limiting reaction between propane and a site on the catalyst surface. If we consider that oxygen is not a constituent of the product but rather required to capture the electrons and protons from the propane educts, it is clear that no solid derivation of the rate-determining step with respect to oxygen can be made. The data only indicate that the elementary steps of propene formation and of hydrogen oxidation are decoupled such that no temporal interference occurs between both reactions. This is in line with the general function of a catalyst that should facilitate chemical transformations by spatio-temporal decoupling of individual reaction processes. Table 1 shows the apparent activation energy. The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of equation:

$$\ln k = \ln A - \frac{Ea}{R} \left(\frac{1}{T} \right)$$

it can be seen that a plot of $\ln k$ versus $1/T$ should be a straight line whose slope is proportional to the activation energy. In this kinetic study (Figs. 4, 5, and Table 1), it can be shown that this intermediate product (propene) is easily oxidized further to other products, such as acetic and acrylic acids. Its liberation as a stable by-product is with an activation energy significantly higher than that of the overall propane reaction, a not very effective side channel of the main reaction path. This is confirmed by the very low selectivity to propene during the reaction. In other words, the catalyst used in this study is very active to convert the intermediate product to other products.

The first order with respect to propane (Fig. 6) indicates that these are formed via surface-catalysed reaction and do not originate from a gas-phase reaction. It can be seen that carbon dioxide formation in the selective oxidation reaction of propane over diluted MoVTeNb oxide catalyst (Figs. 6, 7) is found to be a linear function with temperature.

This implies that the high activation energy (123.2 kJ/mol) is required for the formation of carbon dioxide over this catalyst. It clearly shows that carbon dioxide originates from a direct combustion of propane or over-oxidation of acetic acid. The total oxidation of the desired product acrylic acid is a less likely contribution as its formation and desorption requires smaller activation energies. This property of MoVTeNb is a key to the understanding of its function. Apparently, the specialised sites detected [20, 21] for total oxidations are not very active and as shown in the kinetic survey study require a significantly higher thermal activation than the

Table 1 Apparent activation energies

Process	Slope	Activation energy (kJ mol ⁻¹)
Propane disappearance	-2623.2	21.8
Propene formation	-7538.2	62.7
CO _x formation	-1481.5	123.2
Acetic acid formation	-5645.3	46.9
Acrylic acid formation	-3955.1	32.9

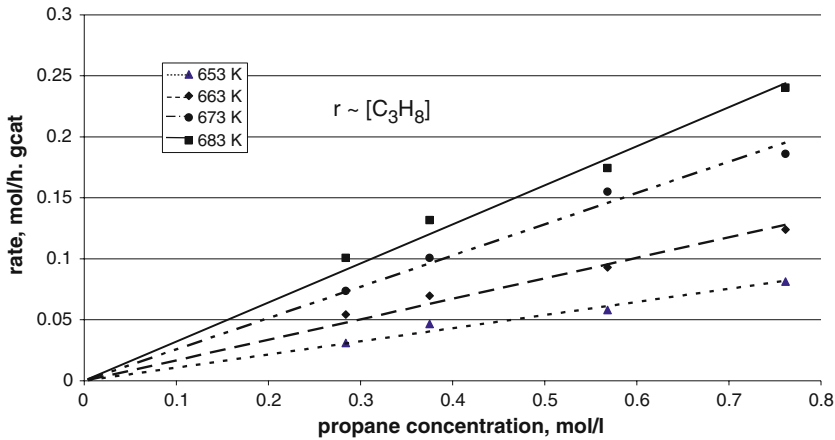


Fig. 6 Rate of carbon dioxide formation as a function of propane concentration at 653, 663, 673, and 683 K

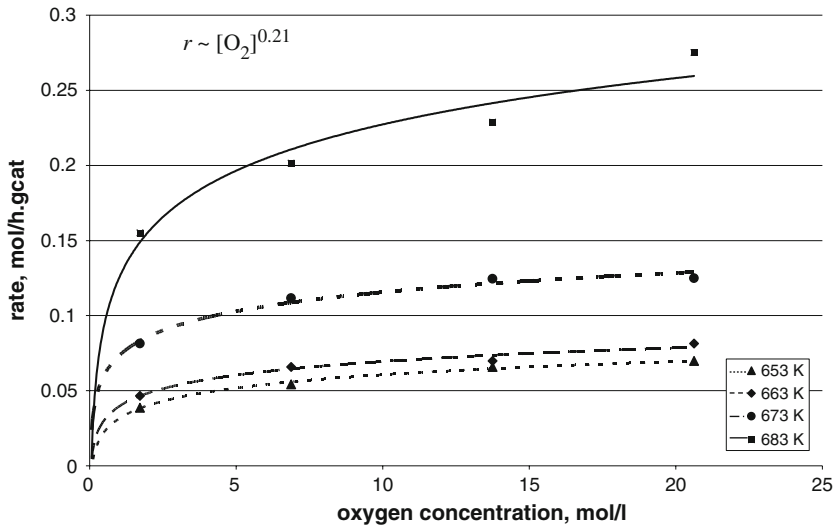


Fig. 7 Rate of carbon dioxide formation as a function of oxygen concentration at 653, 663, 673, and 683 K

complex partial oxidation. The nanostructuring of the surface preventing large patches of such sites to be present may as atomistic origin hamper the combustion reaction requiring 10 oxygen atoms to be involved in the turnover of one propane molecule. The provision of so many activated atoms to one adsorption site will require substantial transport of oxygen across the surface, which is a significantly activated process, as it requires cooperative defect migration.

In this kinetic study, acid products refer to acetic acid and acrylic acid. Acetic acid is believed to result from isopropyl alcohol in a parallel reaction from an allylic

intermediate after addition of a molecule of water whereas acrylic acid will result from addition of oxygen instead of water onto the same common intermediate. The potential intermediates of isopropyl alcohol and acrolein are too reactive to be detected as side products indicating that low thermal barriers must exist for their further oxidation to the stable carboxylic acids. Hence, these products are structurally amenable to facile total oxidation (one molecule of CO_2 already performed), very stable against total oxidation and in the presence of water find sufficient time to desorb before they are further oxidized. The addition of water competing with activated oxygen and with the organic products for surface sites helps to “wash off” the carboxylic acids.

Figs. 8 and 9 show the typical behavior of a surface process being rate-determining again in agreement with the concept of an overall LH reaction scenario developed with the overall formation of acetic acid. These data imply that the formal kinetic parameters are, despite of the shape of the partial pressure dependencies, not related to the elementary reaction steps. The reaction orders are small, as the surface coverage seems to be high at steady state. It may be concluded that desorption of the polar acid may severely hamper the kinetic of its formation. The alternative explanation of the combustion of one carbon atom to CO_2 , being a difficult step, can be checked by comparing the kinetic data to those for the acrylic acid (AA) formation.

Figs. 10 and 11 show that the rate of acrylic acid (AA) formation is not a linear function with respect to propane concentration and oxygen concentration at all temperatures. In addition, extrapolation to zero propane concentration indicates that the curve does not pass through the origin of the graph; their rate of appearance is zero at a propane concentration of about 0.05–0.075 mol/L. The reasons for this are that (a) the experimentally determined rate for a product (i.e. AA) is the difference between the true rate of formation and the rate of product disappearance in deep oxidation of this product or (b) at low propane concentration (0.05–0.075 mol/L), an intermediate product does not convert to AA but it converts to other products. Thus,

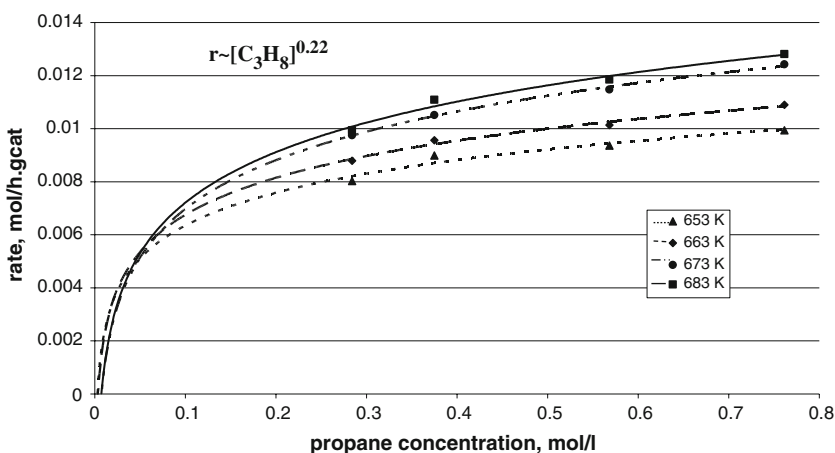


Fig. 8 Rate of acetic acid formation as a function of propane concentration at 653, 663, 673, and 683 K

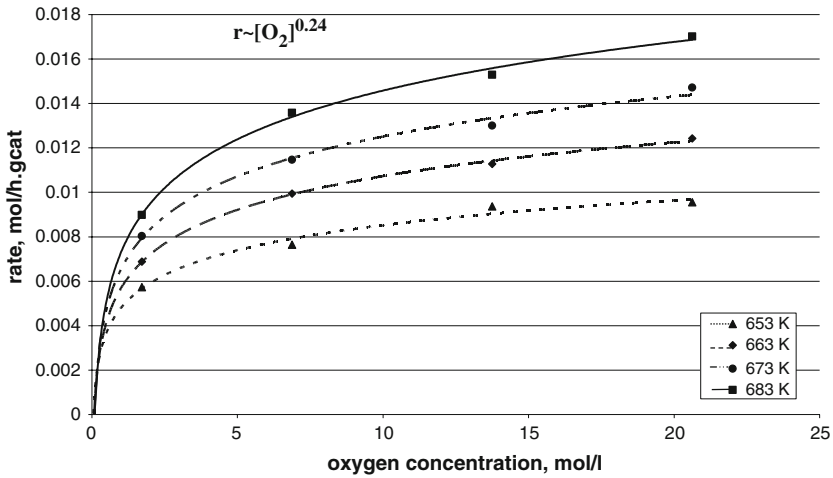


Fig. 9 Rate of acetic acid formation as a function of oxygen concentration at 653, 663, 673, and 683 K

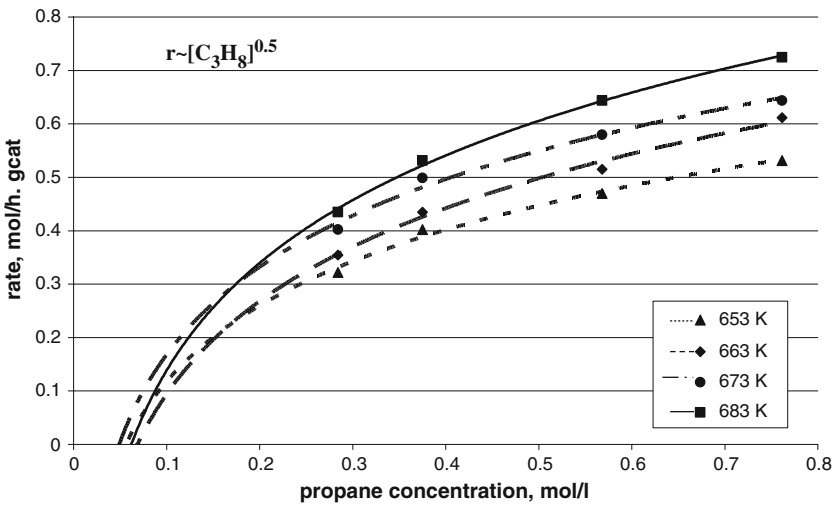


Fig. 10 Rate of acrylic acid formation as a function of propane concentration at 653, 663, 673, and 683 K

it is indicative that at low propane concentration, the AA cannot be obtained. The data imply that a kinetically demanding intermediate must exist before the formation of AA can be achieved. As the activation energy for total combustion is so high, it is assumed that the possibility of a fast consecutive total oxidation seems less likely than the existence of a difficult-to-form intermediate before the formation of AA.

The formation of AA from the selective oxidation of propane over the diluted MoVTenb oxide catalyst requires the minimum energy of 32.9 kJ/mol. In comparison to the data for acetic acid formation, it is now clear that the reactions

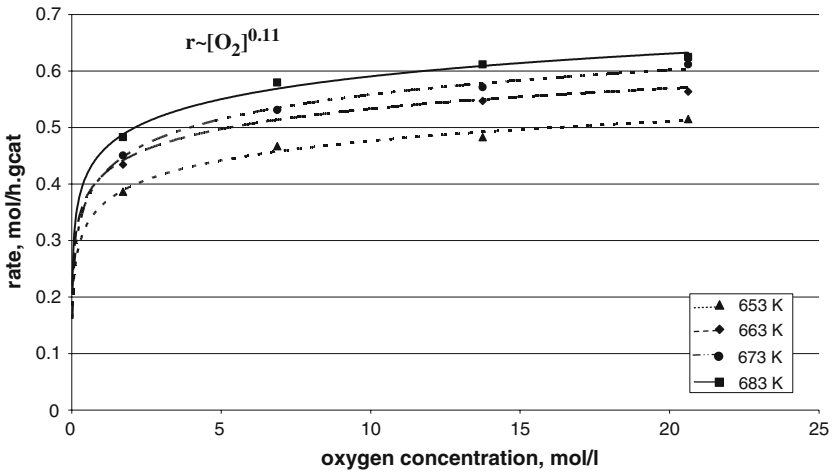


Fig. 11 Rate of acrylic acid formation as a function of oxygen concentration at 653, 663, 673, and 683 K

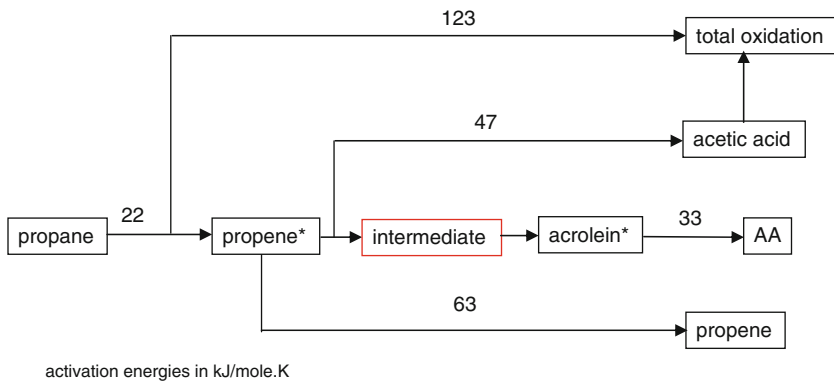


Fig. 12 Proposed oxidation pathway on diluted Mo-V-Te-Nb mixed-oxide catalyst

to carboxylic acids are strongly hindered by desorption from the catalyst, explaining also the fractional apparent reaction order with respect to propane for the AA formation. For the same reason of a high fractional surface coverage of the product, the reaction order with respect to oxygen is low and even lower than for the other oxidation processes analyzed. There is again no reason to invoke the lattice oxygen concept in the analysis of the numerical values of the kinetic constants of the desired product formation.

Reaction networks

It is possible to derive from the summary of the results the following schematic representation of the reaction network (see Fig. 12).

The overall reaction consists of three parallel process channels. One main sequence of consecutive reactions leads to the desired product. There is one very difficult reaction step that may be the oxidation of the activated hydrocarbon. This is concluded from the detection of a small amount of propene in the effluents composition, which might be further activated propene (allylic intermediate). The desorption of propene will be in competition with allylic intermediate to the further consecutive reaction, which should be the formation of an activated acrolein species. This oxidation must have a barrier equal or higher than the 63 kJ/mole found for propene formation. The other parallel reaction channel is the total combustion, which is the highest activated process in the network. This is an excellent property of an oxidation catalyst, rendering the direct deep oxidation of the feed a highly unlikely process. The formation of acetic acid arises from a branching of the consecutive reaction in parallel to the desorption of propene: excess water can be added to the unsaturated activated hydrocarbon forming 2-propanol from which acetic acid is a known product of carbon-carbon bond scission. The appearance of acetic acid is another indication of the height of the barrier of oxygen addition to the activated hydrocarbon.

This reaction network is in agreement with the existence of several different sites on the active catalyst. The network would require two sites, one for total oxidation and one for partial oxidation, as the other products are side chains of the partial oxidation channel. The fact that in the screening study the preferential washing off of molybdenum oxide was beneficial for the performance renders it plausible to assume that a pure Mo-oxide is the site for total oxidation and a Mo–V mixed oxide may be the active material for partial oxidation. This is inferred from the function of pure Mo–V oxides in the generation of AA from propene. The addition of Nb and of Te to the system may merely serve the purpose of structuring or stabilizing the active site in a better way than on the technical propene oxidation systems. A special function for propane oxidation seems not to be required according to present kinetic results finding no great barrier for initial activation of the propane.

Conclusion

In conclusion, this work has given a phenomenological frame to understand the action of Mo–V–Te–Nb mixed-oxide in propane oxidation catalysis. It was found that two independent reaction networks following the LH mechanistic scenario are adequate to rationalise the complex experimental observations. From this study, it is viewed unnecessary to invoke a special oxidation chemistry reaction mechanism such as the participation of lattice oxygen or of remote control. In addition, it could be misleading to assume phase cooperation is necessary and in place in this selective oxidation of propane to AA. There is a single active site responsible for the activation and subsequent transformation to AA.

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