

KINETIC INVESTIGATION OF PROPANE DISAPPEARANCE AND PROPENE FORMATION IN PROPANE OXIDATION ON DILUTED AND LEACHED MoVTenb CATALYST

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ABSTRACT

Reaction kinetics for the oxidation of propane over diluted-leached MoVTenb is described. This paper is focused on the study of products selectivity profile and determination of the orders of propane disappearance and propene formation. The result shows that selective oxidation of propane to propene over this catalyst follows the Langmuir-Hinshelwood mechanism. The disappearance of propane is first order with respect to hydrocarbon and partial order (0.21) with respect to oxygen. The propene formation is first order with respect to hydrocarbon and not depending on oxygen concentration.

Keywords: propane oxidation, propane disappearance, propene formation, kinetic, reaction order

INTRODUCTION

Nowadays, most industrial processes produce acrylic acid via a two-step oxidation reaction. This two steps including propene oxidation over multi-component Mo-Bi-Co-Fe-based oxide catalysts at 320-330 °C to make an intermediate compound, 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]. Currently, the development of acrylic acid production from one-step oxidation of propane has been conducted. The economic importance of this possibility and the successful manufacture of maleic anhydride by selective oxidation of n-butane have stimulated various researches. In parallel, investigations on 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]. In addition, the behaviour of light alkanes (C₁-C₆) in catalytic partial oxidation reactions is different from the one to another [3-7].

The involvement of selective oxidation reaction of propane to acrylic acid has been heavily studied [8-10]. Partial oxidation of propane to acrylic acid over vanadium pyrophosphate (VPO) catalysts [11-12] and heteropolyacids [13-14] has been reported. 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 [15]. 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]. The Selective oxidation reaction of propane is difficult to perform for a very high yield since the product is easily further oxidized. The detailed expression for apparent rate (kinetics) will permit the chemical engineer and chemist to make a rigorous extrapolation of experimental results to the industrial scale and 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, metal oxides catalysts [18], Mo-V-Sb-Nb catalysts [10], and Mo-V-Te-Nb catalysts [9]. In the previous article, it has been described the reaction kinetics and mechanism of propane partial oxidation to acrylic acid on diluted MoVTenbOx mixed-oxide catalysts using high-throughput system (nanoflow reactor) [19]. This article more focus and deals with the similar reaction oxidation over diluted and leached MoVTenbOx mixed-oxide catalysts. The paper is divided into two parts. Part one is focused on the profile of products selectivity, the rate of propane disappearance and the rate of propene formation.

EXPERIMENTAL SECTION

Materials

Ammonium Heptamolybdate tetrahydrat (Merck), Ammonium Metavanadate (Riedel-de Haen), Telluric acid (Aldrich), Niobium Ammonium Oxalate (Aldrich), Water, Nitrogen, Propane, Oxygen.

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Instrumentation

Calcinatory set, spray drier, nanoflow catalytic reactor on-line with gas chromatography (Agilent).

Procedure

The preparation of Diluted $\text{Mo}_1\text{V}_{0.30}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_x$ and its characterization have been described in more detail before [20-21]. In addition, in this article the catalyst preparation is followed by leaching process using water for 1 h, and then it is dried and calcined according to the method described in the previous literature.

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 [19,21]. For all experimental results, the reaction rate and the concentration of reactants are calculated using Equations shown below:

$$\text{Reaction rate (mol/h.g}_{\text{cat}}) = \frac{\% \text{vol} \times \text{total gas flow} \times d \times 60}{M_r \times \text{catalyst weight}} \quad (1)$$

$$\text{Concentration (mol/L)} = \frac{(\% \text{vol} \times d \times 1000)}{M_r} \quad (2)$$

where, % vol is concentration of product in % (v/v); total gas flow is the total flow of product stream from the reactor in mLN/min; M_r 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. The M1 phase is the cluster that active as catalyst for the conversion of

propane to acrylic acid [15]. Chemical composition of the catalyst surface is modified by treatment in water to obtain a significant increment in yield of acrylic acid. The process is called as leaching. It means the leaching process using water for 1 h support to release the M2 phase from the catalyst. It can be expected that the catalyst more active since only M1 phase stay in the catalyst [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]. The kinetic investigation of partial oxidation of propane to acrylic acid on diluted MoVTeNb (without leached) has been reported [19].

Product selectivity profiles

The propane oxidation kinetic parameters were determined by following the products formation as a function of propane and oxygen concentrations under reaction conditions required for a differential operating regime (reactants conversion lower than 15% at any temperatures used). The obtained products consisted of propene, acrolein, acetic and acrylic acids, and carbon dioxides. Due to the very low selectivity to acrolein, the formation of this product was not further investigated in this kinetic study.

A blank reaction using SiO_2 (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 showed that the reaction was free of external and internal mass transfer limitations.

Fig.1 observed that the increasing of propane conversion is followed by decreasing of selectivity to propene and on the other hand is followed by increasing of selectivity to acrylic acid, while selectivity to carbon dioxide and acetic acid are relatively constant at all propane conversions. These data indicate that propene as an intermediate product is relatively easy converted to acrylic acid, while carbon dioxide must be formed by at least one subsequent reaction step, or being produced by a different reaction channel, i.e. total combustion 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. This data also indicates that propene might be further oxidized via two different channels, i.e. via acetic acid formation or via acrylic acid formation. According to these data, the reaction can be proposed by the following reaction $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{products}$, where the products are propene, acrylic acid, acetic acid, and carbon dioxide.

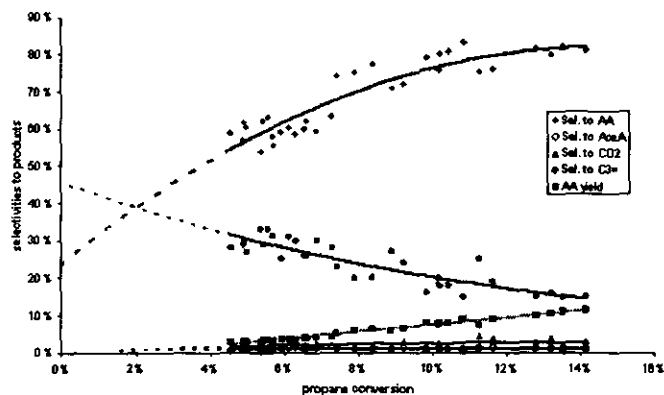


Fig 1. Product selectivity profiles for propane oxidation over diluted and leached MoVTenb oxide catalyst under reactor differential mode

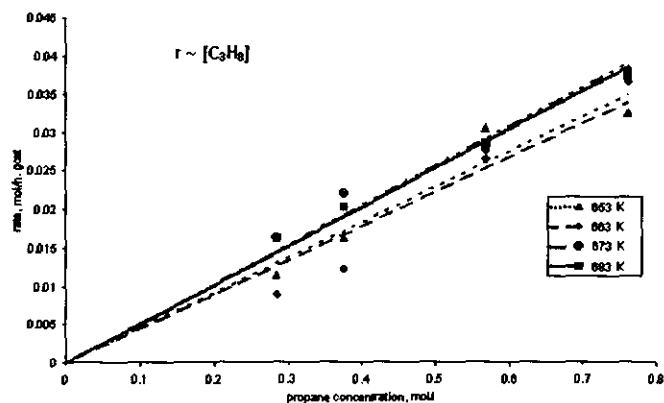


Fig 2. Rate of propane disappearance with respect to propane concentration at 653, 663, 673, and 683 K

Rate of propane disappearance

Fig. 2 and Fig. 3 describe that propane disappearance observed is a linear function of propane concentration, but it is a logarithmic function of oxygen concentration. The reaction is first order with respect to propane and partial order (0.21) with respect to oxygen concentration.

Based on the kinetic theory, it can be described that reaction involves the surface coverage with the respective species (propane). The coverage varies strongly with the reactant partial pressures. Hence it is clear that the rate determining step involves a reaction between propane, or an activated complex thereof, and activated atomic oxygen. It might be explained that propane sticks to the catalyst surface directly from the gas phase whereas oxygen needs to be dissociative pre-activated before it can be a reactant. So that, propane molecules interacted with the active side on the catalyst surface to form propane-catalyst complex, whereas oxygen molecules dissociated resulting oxygen atom

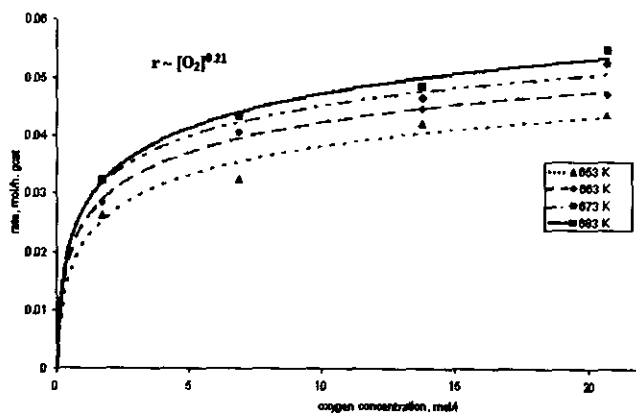


Fig 3. Rate of propane disappearance with respect to oxygen concentration at 653, 663, 673, and 683 K

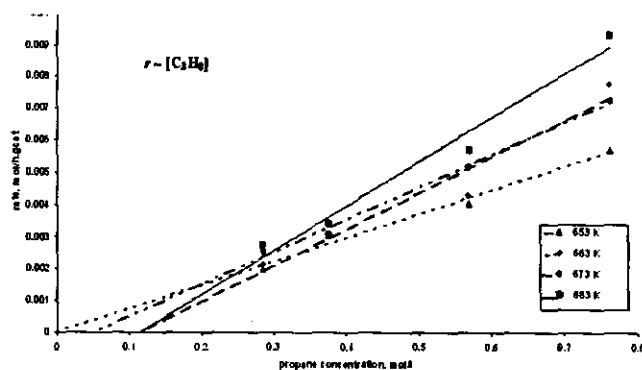


Fig. 4. Rate of propene formation with respect to propane concentration at 653, 663, 673, and 683 K

and then it interacted with active side on the catalyst surface to form oxygen-catalyst complex. The next step is the activated-propane and oxygen react to form intermediate product. This mechanism is agreed with the Langmuir-Hinshelwood (LH) mechanism.

Rate of propene formation

Fig. 4 showed that the rate of propane oxidation to propene is first order with respect to propane concentration at all reaction 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. This is because of the rate of intermediate (propane) formation is difference with the rate of intermediate disappearance in the next step of the reaction. Thus, at low propane concentration, the propene formed is entirely converted to other products. This result also indicates that increasing the reaction temperature will affect

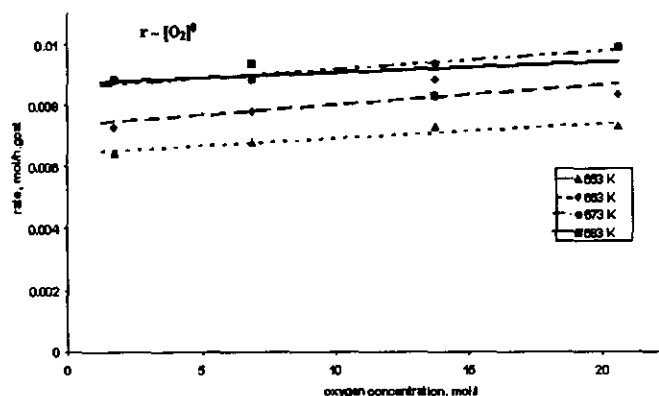


Fig 5. Rate of propene formation with respect to oxygen concentration at 653, 663, 673, and 683 K

Table 1. Apparent activation energy

Process	Activation energy (kJ. mol ⁻¹)
Propane disappearance	27.3
Propene formation	40.9

the intermediate product (i.e. propene) to convert to other products more easily.

Fig. 5 shows that the rate of partial oxidation of propane to propene is zero order with respect to oxygen concentration; contradict to previous report mentioning a non-zero order with respect to oxygen [10], but consistent with the result reported by Stern and Grasselli [22] which is interpreted using Mars van Kravelen mechanism paradigm [23] and also agree with our previous observation [19].

It is obvious that propene is the first intermediate on the path of selective oxidation and hence should carry the kinetic signature of the overall reaction. If the rate of replacement 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 becomes zero order with respect to oxygen. This is consistent with the derived LH mechanism stating oxygen dissociate before formation of the oxygen-catalyst surface complex. Table 1 depicts the activation energy which is needed in the reaction. It is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of equation:

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (3)$$

From Table 1, it can be shown that propene is easily further oxidized to other products since the activation energy is quite low. 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 word, the catalyst used in this study is very active to convert the intermediate product to other products.

CONCLUSION

The result showed that MoVTeNb catalyst is active for oxidation of propane. The rate of propane disappearance is consistent with Langmuir-Hinshelwood mechanism. In this scenario propane molecules interact with active site on the catalyst surface to form propane-catalyst complex and then react with the gaseous oxygen. This reaction gives the intermediate product, propene. The activation energy of propene formation is quite low, therefore propene is easily further oxidized to other products.

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