

The Influence of water and catalyst leach process toward propane oxidation on MoVTenb catalyst

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Abstract. The effect of water stream to the propane oxidation on diluted MoVTenb catalyst has been investigated. The present work has elucidated that careful operation of high throughput instrumentation can be used in various beneficial ways to speed up the discovery process of improved catalysts in other forms than enabling efficient trial-and error testing of compositional variations of a given catalyst system. The result show that the addition of massive amounts of water to the feed should have a negative influence on the kinetics, as water will compete with all other polar molecules in the system for adsorption sites. This work also investigated the effect of catalyst leach process toward propane oxidation. From the result, it can be described that catalyst leach process tends to reduce the phase of the catalyst that responsible to the total oxidation of propane. This work also proposed the reaction network and gave the comparison between the propane oxidation reaction kinetic using leached and un-leached catalyst. The result showed that the activation energy of the acrylic acid formation on leached catalyst was slightly higher than that of on un-leached catalyst. On the other hand, the activation energy of the carbon dioxide formation on leached catalyst was much higher than that of on un-leached catalyst. It can be described that leaching process to the catalyst can reduce the phase of the catalyst that responsible for the total oxidation of propane.

Keywords: *MoVTenb catalyst, propane, oxidation, water, leach process*

1. Introduction

The oxidation process using a catalyst has developed into a very important technology in the modern chemical industry. One of the important processes that utilize this technology is the functionalization of aromatics and alkanes, due to advantageous economy and the easy processing. Acrylic acid is one of the most important catalytic oxidation products, which its consumption in 2020 is expected 8,000 kilo tons. One of the most widely used acrylic acids in the industry is as intermediate for polyacrylates and methacrylate esters production. These products can be used for various purposes, such as super adsorbents. Acrylic acid is presently factory-made from propylene in two steps via acrolein in a gas phase using special catalysts which the yield up to 80% [1]. Despite the promising yield of the product, the price of propylene has seen attention being drawn to develop a method for producing acrylic acid alternatively by direct oxidation of propane in the presence of catalyst. One of the promising catalysts that are widely studied is mixed metal oxide, such as MoVTenb catalyst [2-7].

The problem that is still faced in the utilization of this catalyst is the control of the complexity of the reaction network consisting of consecutive reactions and parallel reactions [3, 8-10]. The phase in Movtenb which is responsible for the production of acrylic acid from direct oxidation of propane is

referred to as “M1” phase [2, 4, 11-13]. Mo and V are very suitable for the oxidation of alkanes via alkenes to carboxylic acids [14, 15].

Some results of previous studies have reported the proposed reaction mechanism [3, 9, 16], as well as the structure of the catalyst during the reaction [4, 17-21].

The presence of water in this oxidation reaction provides a reaction advantage as has been reported by previous researchers [3, 22-25].

In this paper we will discuss the effect of the presence of water on catalytic reactions and the effect of the leaching process on diluted MoVTeNb oxide catalyst.

2. Experimental

2.1. Materials

The materials used for catalyst synthesis were Telluric acid (Aldrich), Ammonium metavanadate (Riedel-de Haën), Niobium ammonium oxalate (Aldrich), Ammonium heptamolybdate tetrahydrate (Merck), Aerosil300 (Degussa). The gases used for reactants were oxygen, nitrogen, and propane (MOX).

2.2. Instrumentation

Nanoflow catalytic reactor is one of the equipments that are used for this high throughput experimentation study.

2.3. Procedure

Preparation of MoVTeNb oxide catalysts and kinetic studies was carried out according to the procedure described previously, and some kinetics data were also reported previously [4, 5, 7]. The catalytic reaction was done by presenting small quantity of catalyst (0.1 g) mixed in SiO₂ to a total volume of 0.5 ml. The high total flow rates (15 mlN/min, GHSV = 1800 h⁻¹). The reaction rate (rate of propane disappearance and rate of formation of products) is calculated by Equations presented below:

$$\text{Reaction rate (mol/h. gcat)} = \frac{\%vol \times \text{total flow} \times d \times 60}{Mr \times \text{catalyst weight}}$$

where, Mr is molecular weight and d is density.

To study the effects of water dependence, the concentration of water varies and other concentrations are fixed. To determine activation energy, the oxidation reaction was studied at four different temperatures, namely, 653, 663, 673 and 683 K. After taking the natural logarithm of equation, 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.

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

3. Result and Discussion

3.1. Effect of Water

There are several opinions about how water affects the performance of the catalyst and the distribution of products, such as by facilitating the desorption of oxygenate from the catalyst or modifying the catalyst structure. The present study has substantiated that the modification of the catalyst surface required for partial oxidation by water concentration in the feed is a fact for the systems studied here. The beneficial effect of water in helping to wash off the partial oxidation products and to protect them from over-oxidation by blocking sites next to the adsorption site of the freshly formed products and so inhibiting the access of activated oxygen from neighbouring sites have also been identified in the present study.

To interpret this point, kinetic investigations were lead with water as the varied feed component. The rate of propane disappearance and acrylic acid formation were calculated and plotted against the water concentration (see Figure 1 and 2).

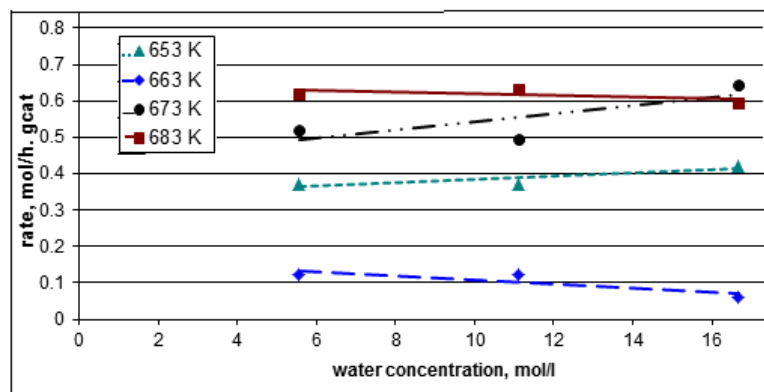


Figure 1. Rate of propane disappearance with respect to water concentration at 653, 663, 673, and 683 K

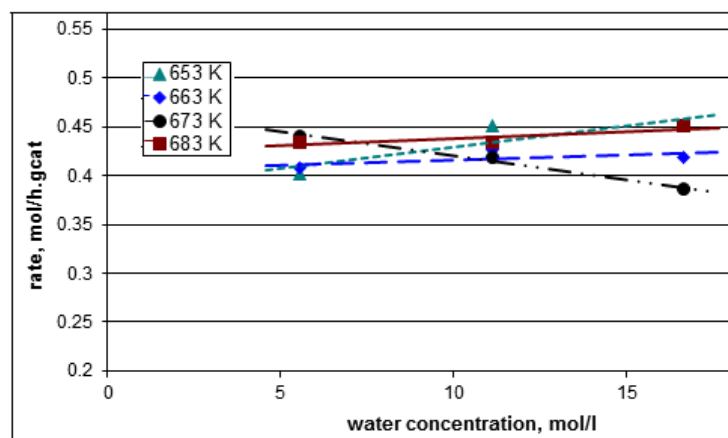


Figure 2. Rate of acrylic acid formation with respect to water concentration at 653, 663, 673, and 683 K

In all cases a small value of the reaction order with respect to water was obtained. This is unexpected taking into account that water is a reaction product in all processes considered here and that it will control the processes of C-H activation leading to (intermediate) OH groups. The addition of massive amounts of water to the feed should have a negative influence on the kinetics, as water will compete with all other polar molecules in the system for adsorption sites. It has to be assumed that the integrity of the catalysts requires its surface to be covered to a substantial extent with water. On such a surface the additional water created during reaction of propane will not affect greatly the coverage and hence will not lead to a significant reaction order detectable by formal kinetics. In contrast to current opinion the low values of reaction order do not imply that water cannot interfere with the reaction kinetics.

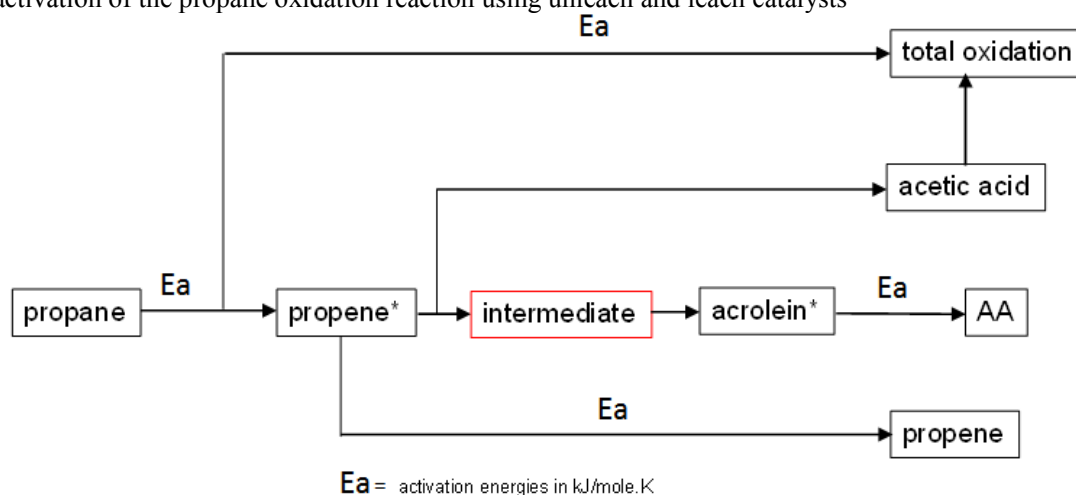
For acrylic acid a strong dependence of the reaction order on temperature is observed, showing at low temperatures a slightly beneficial and for high temperatures a slightly inhibiting effect of water. As the C-H chemistry should not be relevant, it may be concluded that at low temperatures the beneficial washing off effect is at work whereas at high temperatures the site competition effect prevents the optimisation of the surface coverage with other species than water indicating that water desorption must be a strongly activated process.

In summary, the effects of water in the propane oxidation are fourfold, i.e. (i) water equilibrates the surface with respect to its coverage with OH and molecular species and hence contributes to the equilibration of the C-H activation steps, (ii) water stabilises the integrity of the active sites responsible for partial oxidation, (iii) water supports the desorption of carboxylic acids from the catalyst surface at relatively low temperatures, (iv) water blocks active sites required for propane oxidation at relatively high temperatures. This is beneficial in suppressing the strongly activated total oxidation reaction channel and in contributing to site isolation. It is detrimental as it supports the premature desorption of the reaction intermediate propene at high temperatures.

The present work has elucidated that careful operation of high throughput instrumentation can be used in various beneficial ways to speed up the discovery process of improved catalysts in other forms than enabling efficient trial-and error testing of compositional variations of a given catalyst system.

3.2. Effect of leach process

For further development of the catalyst system two conclusions can be drawn. It is very important to design the dilution of the active phase in such a way as to maximize the hydrothermal stability and to optimise the heat management of the entire catalyst. With respect to the active phase it became evident that a single phase is essential as then the chances to bring about a single type of active sites, capable to perform minimum consecutive total oxidation the selective oxidation of propane. To this end leaching and nanostructuring of the surface are suitable concepts. To clarify this point, a reaction mechanism has been proposed (scheme 1, [7]) and then it will be compared the amount of energy activation of the propane oxidation reaction using unleach and leach catalysts



Scheme 1: Schematic representation of the reaction network

Overall, this propane oxidation reaction consists of three parallel processes paths. These processes are one main path that produces the desired product, acrylic acid. The other pathway is the total oxidation of propane to carbon dioxide, and another pathway is the process of desorption of propene. One thing that is quite good in this reaction process is that the total oxidation pathway of propane requires a fairly large activation process, so it is technically quite difficult to occur. The proposed reaction mechanism is in accordance with the presence of 2 types of active catalyst sites referred to as M1 for the partial oxidation pathway to produce acrylic acid, and M2 for the total oxidation pathway.

To further understand the effect of washing or leaching the catalyst on the presence of phases responsible for the formation of acrylic acid, activation energy calculations for each process are presented in table 1. This washing is intended to reduce the M2 phase which leads to a total oxidation reaction. It is expected that the reduction of M2 phase in total in the catalyst material will be dominated by M1 phase which pushes towards selective oxidation, so that the desired product will be produced more.

Table 1. Comparison of activation energy in each process of selective propane oxidation using leached and unleached MoVTeNb

Processes	Activation Energy (kJ mol ⁻¹)	
	Unleached catalyst	Leached catalyst
Propane disappearance	21,8	27,3
Propene formation	62,7	40,9
CO _x formation	123,2	177,3
Acetic acid formation	46,9	91,6
Acrylic acid formation	32,9	30,3

From table 1, it can be described that the process of removal (conversion) of propane requires a slightly higher energy in the reaction using leached catalysts. It can be logically explained that the washing process causes several active catalytic sites both M1 and M2 phases to be washed away. The reduced active site will complicate the process of propane removal/conversion. However, in the process of using leached catalysts, it appears that the formation of propene is easier. Propene is an intermediate product which will immediately turn into the next oxidation product, acetic acid and acrylic acid. The formation of acetic acid which is a by-product requires higher energy, while the formation of acrylic acid as a product of the main reaction pathway requires lower energy. This proves that the washing process is quite successful in eliminating the M2 phase which is responsible for the total combustion of propane. This is confirmed by the fact that the activation energy of CO_x formation increases very high. This means that the formation of CO_x is increasingly difficult to occur. On the other hand, converting propane towards propene and continuing towards acrylic acid is even easier. Obviously this confirms that the washing process succeeded in reducing the M2 phase responsible for the total oxidation reaction of propane towards CO_x, and at the same time managed to maintain the M1 phase responsible for the propane selective oxidation reaction to acrylic acid.

4. Conclusion

In general, this study has provided a phenomenological framework for understanding the action of MoVTeNb in propane oxidation catalysis. It was found that there are two types of reaction sites present, one of which requires the presence of excess water to function. The extent to which these sites will be present depends on the details of the bulk material nanostructuring and can be modified by synthetic and post-synthetic steps. One of these steps is the washing process. Parallel reaction pathways for partial oxidation need to be treated more carefully so that acrylic acid can be produced optimally.

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