

4 CATALYST SCREENING

4.1 The procedure of catalyst screening using High Throughput System

In most cases, the rate of a chemical reaction is neither dependent on the reactants nor the products. Therefore, a good catalytic plays a very important role in speed up the rate of a chemical reaction. A good and highly active catalytic system can speeding up a reaction by a factor of tenor million. Nevertheless, an unsuitable catalytic system (negative catalyst) might results in a decreased rate of chemical reaction. If a variety of side reactions are encountered in a process, the most important issue that needed to be considered would be the ability of the catalyst used in controlling the selectivity of the reactions in the particular process. Thus, in the presence of an appropriate catalyst, the desired products can be obtained predominantly from a given feed (Levenspiel 1999).

The application of combinatorial methodologies in heterogeneous catalysis is continuously increasing at a rapid pace in both academic and industrial academics. Combinatorial method allows the exploration of very large and diverse compositional, structural and process spaces much of which would otherwise go unexplored, but from which new and unexpected discoveries often arise (Bergh S. 2003). This leads to increased probability of discovering new catalytic materials that facilitated process optimization, and the availability of large amounts of information to aid the chemist in the development of new heterogeneous catalysts. The high-throughput experimental process in heterogeneous catalysis involves the design, synthesis, as well as testing of high-density libraries which aimed at efficiently exploring very large numbers of diverse materials. In this chapter, our studies aim at demonstrating the influence of different preparation method which involves

the addition of support as well as surface modification on the catalysts by introducing high-throughput combinatorial technology in the experimentation.

In our standard high throughput workflow, we can divide our methodology into two different sections, namely primary and secondary screening. Primary screening is semi-quantitative and most often focused on discovering the good catalytic material. This stage requires an effective parallel testing method as often several ten thousands of samples are being evaluated.

Secondary screening is utilized for confirmation of primary screening results, optimization, or discovery of good catalytic material. The aim in this stage would be to optimize the pre-existing catalyst system which is defined by their cationic composition without the necessity of excluding the discovery of new materials. The most important part of this methodology would be the association of preparation and evaluation of materials under the most ideal conditions with a rational approach that orients the investigation among predetermined paths. The initial discovery phase of the identification of MoVTaNb has been shown in Chapter 3 where *de novo* screening of the chemical composition is no longer promising.

Secondary screening can be achieved by employing continuous flow parallel micro reactors with a complete identification of reaction products. An additional target also envisaged in the present work is the kinetic investigation to develop a working hypothesis of the mode of operation of the system that can be used as guidelines for further optimisation of the successful systems coming out of the stage two. The distinction between primary and secondary screening is obviously somewhat arbitrary, and not necessarily appropriate for each type of catalysis (Holtzwarth 1999).

Direct oxidation of propane to acrylic acid using molecular oxygen as an oxidant has recently attracted the great attention in both academia and industry. Multi metal oxide

catalysts are commonly considered to have a possibility to substitute the traditional catalysts in the existing industrial twostep process via propylene. An appropriate MoVTaNb metal oxide ratio is critical in formulating the catalyst active phase, according to the two patents of Ushikubo and Lin (Ushikubo 1994, Lin M. 1999) which had shown excellent catalytic performance for selective oxidation of propane to acrylic acid.

4.1.1 Definitions and formula for determination of the catalytic performance towards acrylic acid product.

The catalytic performance of the multi metal oxide catalyst for selective oxidation of propane to acrylic acid was evaluated using high-throughput fixed bed reactor systems called COMBICAT Nanoflow. The mixture of propane-oxygen-nitrogen and steam were fed in from the top of the reactor. The off- gas was condensed and the liquid phase was separated from the gas phase using a cold trap. Both of the gas and liquid phases of the product streams were analyzed with online GC to determine the values of propane. Conversion is defined as the ratio of consumed hydrocarbon over the feed hydrocarbon for the reaction. Selectivity of product defined as the fraction of consumed hydrocarbon converted to each product. The formulas are defined as below:

Conversion of propane ($X_{C_3H_8}$)

$$X_{C_3H_8} = \frac{(C_3H_8)_{in} - (C_3H_8)_{out}}{(C_3H_8)_{in}} \quad (\text{e.q. 4.1})$$

Selectivity of product ($S_{product}$)

$$S_{product} = \frac{\frac{1}{stc} \times (\text{product})}{(C_3H_8)_{out} \times X_{C_3H_8}} \quad (\text{e.q. 4.2})$$

Yield of product ($Y_{product}$)

$$Y_{product} = X_{C_3H_8} \times S_{product} \quad (\text{e.q.4.3})$$

Note : (C_3H_8) in % volume concentration

stc = stoichiometric coefficient to propane

4.1.2 Calculations of conversion and selectivity using carbon balance

The propane conversion and product selectivity (acrylic acid) are calculated on the basis of the components in the effluent gas. Since the carbon source in the feed is propane, the calculation of propane conversion thus would be based on the carbon balance.

i) Carbon balance $(C_3H_8)_{CB}$:

$$(C_3H_8)_{cb} = \sum \frac{(\text{carbon_products})}{stc} + (C_3H_8)_{out} \quad (\text{Eq 4.4})$$

ii) Material balance (MB) based on carbon balance:

$$MB = 1 - \left(\frac{(C_3H_8)_i - (C_3H_8)_{cb}}{(C_3H_8)_i} \right) \text{ in } \% \quad (\text{Eq 4.5})$$

iii) Conversion calculated by carbon balance :

$$X(\text{C3H8})_{cb} = \frac{\sum \frac{(\text{carbon_products})}{stc}}{\sum \frac{(\text{carbon_product})}{stc} + (\text{C3H8})_{out}} \quad (\text{Eq 4.6})$$

Or

$$X(\text{C3H8})_{cb} = \frac{(\text{C3H8})_{cb} - (\text{C3H8})_{out}}{(\text{C3H8})_{cb}} \quad (\text{Eq 4.7})$$

iv) Selectivity and yield can be calculated as:

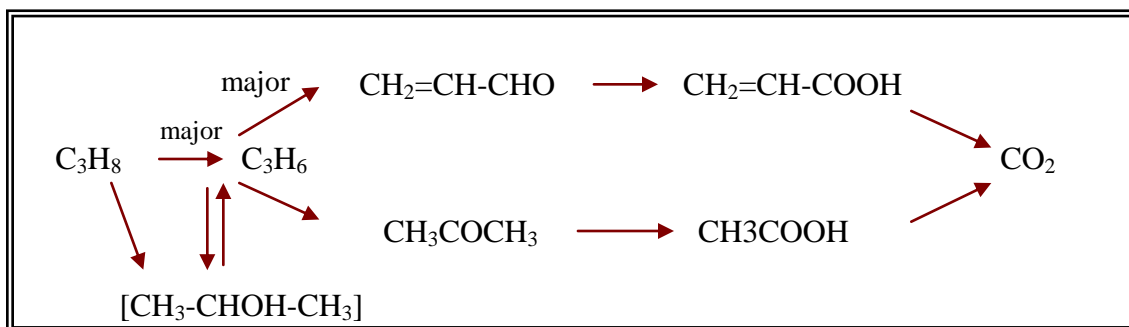
$$S(\text{product})_{cb} = \frac{\sum \frac{(\text{product})_{out}}{stc}}{(\text{C3H8})_{cb} \times X(\text{C3H8})_{cb}} \quad (\text{Eq 4.8})$$

Or

$$Y(\text{product})_{cb} = X(\text{C3H8})_{cb} \times S(\text{product})_{cb} \quad (\text{Eq. 4.9})$$

4.13 Reaction Stoichiometry and Reaction Pathways

The selective oxidation reaction pathway of propane oxidation over a Mo-V-Te-Nb-O catalyst was recently proposed is given in Scheme 1 (Lin 1999, Lin 2000). Oxidative dehydrogenation of propane to propylene and allylic oxidation of propylene to acrylic acid are the two important steps which determine the selectivity of propane conversion to acrylic acid. In this viewpoint, propane is regarded partially oxidized to acrylic acid via propylene and acrolein as intermediates. Other than carbon dioxides, acetic acid would be the major by-product, which is formed mostly through an undesirable pathway with acetone as intermediate. Further oxidation of acrylic acid and undesirable acetone pathway are the two major factors that decrease the selectivity of the catalytic material in converting propane to acrylic acid. In addition, direct C-C breakage of acrolein to propylene which finally converted to C1 and C2 molecules without going through acrylic acid may also decreased the selectivity of the catalytic material in converting propane to acrylic acid.



Scheme 4.1: Proposed oxidation pathway over Mo-V-Te-Nb-O catalyst (Lin 1999, Lin 2000)

The selective oxidation of propane to acrylic acid and its side product can be described using the following stoichiometric reactions:

I. Propane to acrylic acid



II. Propane to carbon monoxide



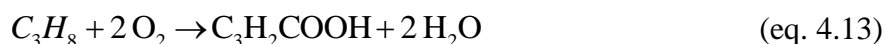
III. Propane to carbon dioxide



IV. Propane to propene/propylene



The overall reaction equation of propane to acrylic acid follows:



With the heat of reaction, $\Delta H = -715 \text{ kJ/mol}$

The most important side reaction is the parallel and sequential reaction to COx. In case of complete combustion to CO₂, the overall reaction is:



With the heat of reaction, $\Delta H = -2043 \text{ kJ/mol}$

The conversion of propane to CO_x would generate large amount of heat that elevate the catalyst bed temperature. In return, this favors a higher selectivity towards the formation of CO_x . Currently, the commercial production of acrylic acid involves a twostep process. The process starts with oxidation of propane to propylene, goes through the formation of acrolein as the intermediate, and finally leads to the formation of acrylic acid. The optimal process temperatures ranged approximately 598 – 613 K for the first step and 483 – 528 K for the second step. Apparently, the activation of propylene requires a higher reaction temperature than that of acrolein formation. In case of one step reaction using propane as a feedstock, it is expected that propane activation requires an even higher temperature to produce acrylic acid (Lin 2001).

The most important part in this Chapter would be the association of preparation and evaluation of the material under realistic condition with an idea to aid the investigation along predetermined paths. Therefore the success of this work is carried out from the previous logical consequence of preceding COMBICAT's member such as one preceding PhD. Thesis by Restu K.W (Widi 2004) and the other by Emmy (Omar 2005) which achieved the optimization of the reaction conditions via high-throughput fixed bed reactor (COMBICAT Nanoflow). From their proceeding, many tests were found to be adequate with standard parameter settings being: space velocity (GHSV) of 1200 h^{-1} , the standard volume catalytic bed of 0.5 ml and a set of feed composition as shown in Table 4.1.

Table 4.1: Feed gas ratio

Component	Normalized Concentration	Concentration (vol %)
Propane	1	3.3
Oxygen	2	6.7
Nitrogen	18	60
Steam	9	30

4.2 Blank experiment and reproducibility of performance for catalytic materials in nanoflow system

The blank experiment was carried out in prior to the reaction study on selective oxidation of propane to acrylic acid. The blank experiment was done to check the cleanliness of the reactor tube by continuously injecting the feed (propane, oxygen, nitrogen and steam) into the reactor tube at temperature 673 K. If no propane conversion or other by-product were detected, the reactor tube is confirmed to be free from any contamination.

. The reproducibility test has been conducted by our co-worker in his previous work (Widi 2004). In the testing, one of the reactor tube was left empty as a blank reference. Same catalytic materials were loaded into two or three of the reactor tubes, i.e., the inert material (Aerosil 300) was loaded into two reactors tubes while benchmark catalyst (422-undiluted) was loaded into another three reactor tubes. The catalysts Mo was loaded into two reactor tubes. The material balance (based on carbon balance) for all the reaction analyses were always about 90 % and above, which indicate that material loss during the reaction was acceptable (see Figure 4.1).

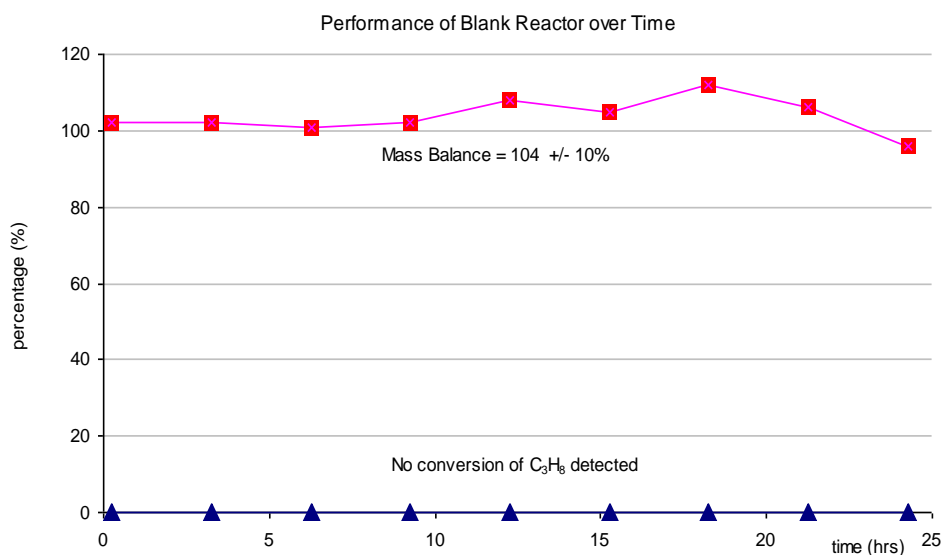


Figure 4.1: The material balance during reproducibility testing using COMBICAT nanoflow

4.3 Effect of reaction temperature for undiluted MoVTeNb oxide catalyst

The effect of different reaction temperature was studied using two undiluted samples. The addition of oxalic acid in one of the sample has been set as a variable. The results are summarized in Table 4.2. The preparation methods and reaction temperature have been shown to affect strongly on the phase composition of the catalyst and its characteristics in the propane oxidation to acrylic acid.

Table 4.2: Catalytic performance of different preparation method on undiluted $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$ catalyst

Catalyst ID	Type of method	Temperature (K)	C_3H_8 Conversion (%)	AA Selectivity (%)	AA Yield (%)	BET Surface area (m^3/g)
792	Undiluted without oxalic acid	653	6	47	3	3.3
		663	7	43	3	
		673	8	41	3	
		683	9	38	3	
		693	10	35	3	
2307	Undiluted with oxalic acid	653	33	60	19	5.9
		663	36	55	19	
		673	39	51	19	
		683	42	48	19	
		693	43	42	17	

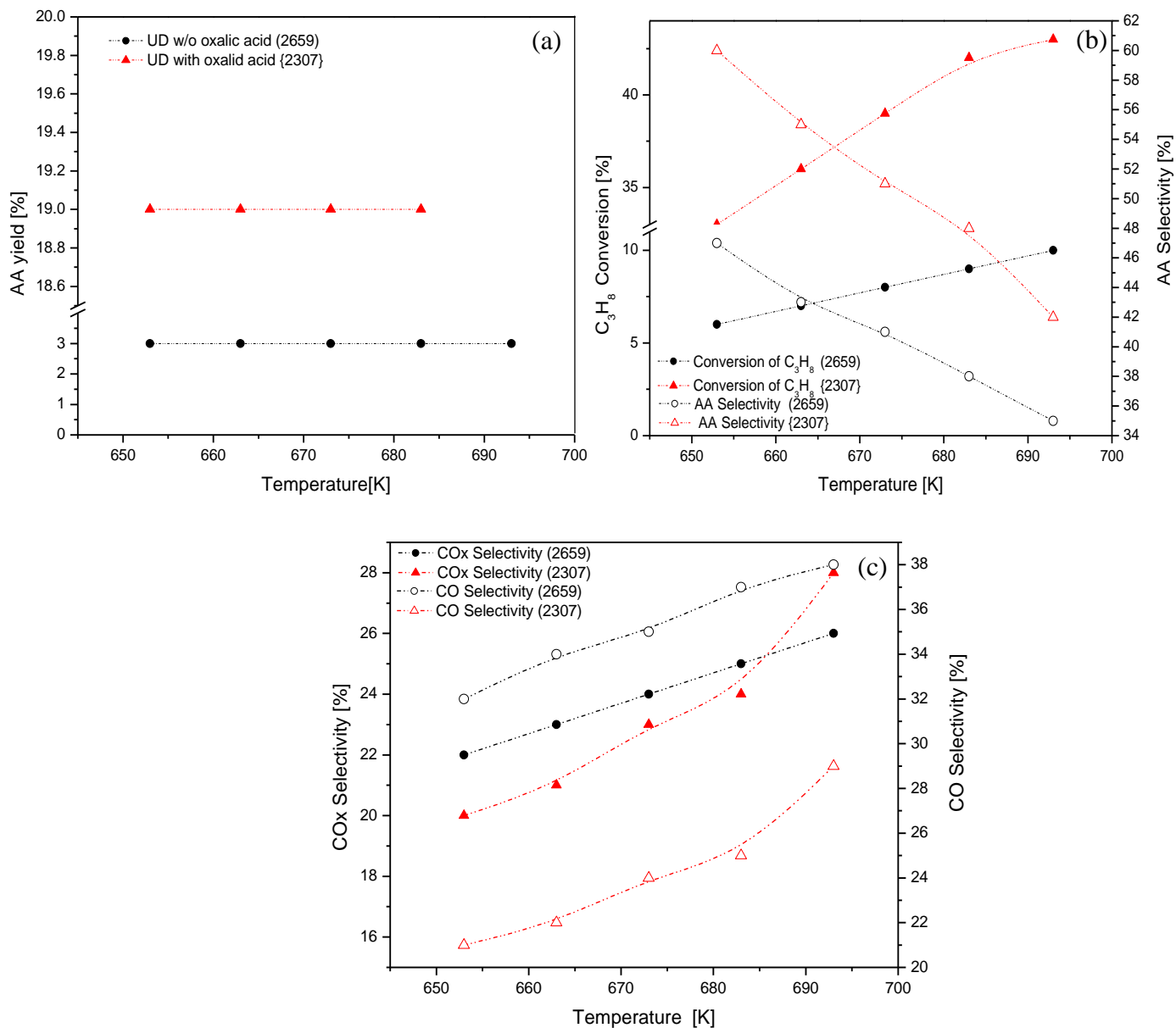


Figure 4.2: Propane oxidation over undiluted MoVTenbOx catalysts at different methods.

(a) Acrylic acid yield as a function of the reaction temperature.

(b) The conversion of propane and selectivity of acrylic acid towards reaction temperature 653, 663, 673, 683 and 693 K.

(c) The corresponding selectivity of COx and CO in different reaction time

The catalytic testing has been carried out under feed composition of propane/oxygen/nitrogen/steam = 1/2/18/9 with GHSV of 1200 h⁻¹ at STP, volume catalyst bed is 0.5 ml and different temperature from 653 to 693 K. The results are shown in Figure 4.2. The catalytic performance of Mo₁V_{0.3}Te_{0.23}Nb_{0.12} catalyst was evaluated for the selective oxidation of propane to acrylic acid in a high-throughput fixed bed reactor at atmospheric pressure. To ensure the data acquisition from gas chromatography was stable, the analysis was repeated up to three times for each sample. In the reaction, the acrylic acid and CO_x are the major product; while acetic acid is the by-product in a small amount. Meanwhile, acetone and acrolein are also formed in a trace amount. It is clear that the reaction temperatures have strong effects on the products distribution. As the temperature elevated from 653 to 693 K, the conversion of propane increases from 6 to 10 %. On the other hand, the selectivity of acrylic acid decreases from 47 to 35 % at the expense of a relative increase of the selectivity to CO_x from 22 to 26 %. For the undiluted MoVTeNb oxide with addition of oxalic acid, the conversion of propane is slightly higher than undiluted without addition of oxalic acid from 88 to 90 %. The selectivity of acrylic acid also decreases from 60 to 42 % with relative increase of selectivity to CO_x from 20 to 28 %. It has been reported that the introduction of oxalic acid into the preparation of MoVTeNb precursor changes the catalyst activity and selectivity of the propane oxidation to acrylic acid (Popova 2007).

Due to the high saturation of C-H bonding, propane has low reactivity in low reaction temperatures. Nevertheless, higher temperatures are useful in propane activation, the conversion of propane can therefore be increased significantly with increasing the temperature.

Results were calculated with 3 points data analysis. This means that each one of the analysis was taken after 15 minutes of catalytic reaction. Furthermore, prior to the analysis started, 15 minutes stabilization on the reaction has been done. For the whole analysis (1, 2 and 3), 45 minutes was allocated for each reactor tubes. The loss of conversion would be roughly consistent with the surface area factor that decreased in undiluted without addition of oxalic acid which is $3.3 \text{ m}^2\text{g}^{-1}$ compared to undiluted with oxalic acid which is increased about $5.9 \text{ m}^2\text{g}^{-1}$. Anderson *et.al.* stated that the surface area s of MoVTenb oxides catalyts could be in the range of 1.0 to $11.0 \text{ m}^2\text{g}^{-1}$ (Andesron A 2003).There are some assumption on how catalyst works suggested by Grzybowska (Grzybowska 1995).

1. Propane is oxidized at the surface of the catalyst whereby
 - a. propane adsorbs at the catalyst surface
 - b. oxygen is transferred from metal oxide to propane to form reactive propylene or propane oxide intermediate species, and
 - c. a metal is reduced to a lower oxidation state

2. The reactive propane or propylene intermediate is further oxidized to acrylic acid, presumably while being chemisorbed on the catalyst surface, by
 - a. chemisorbed, activated oxygen species
 - b. oxygen transfer from a metal oxide
 - c. gas phase oxygen

3. The reduced metal(s) are reoxidized by oxygen from the gas phase

According to Lin's results on MoVTeNbO catalysts, the order of relative reactivity of reactants was propane \ll acetic acid = acrylic acid, propylene, acetone, acrolein = isopropanol. That is, acrylic acid is more reactive than propane. So, increasing temperatures would accelerate the overoxidation of acrylic acid and other intermediate to CO_x which leads to a decrease in the selectivity. A rapid increase in the selectivity towards CO_x (CO₂ and CO) would be expected.

Due to the negative contribution of reaction temperatures towards acrylic acid selectivity and propane conversion, the yield of acrylic acid is consistent at all temperature investigated. Considering the selectivity to acrylic acid, the suitable reaction temperature is in the range 673-693 K. From the previous work (Salim 2007), the suitable reaction temperature for selective oxidation propane to acrylic acid is 673 K. Therefore the suitable temperature for this reaction has been decided at 673 K.

4.4 Effect of different reaction temperature for diluted MoVTeNb oxide catalyst.

The effect of dilution of the catalyst using Aerosil300 as a support toward the catalytic performance of selective oxidation of propane to acrylic acid has been carried out under feed gas composition of propane/oxygen/nitrogen/steam = 1/2/18/9, gas space velocity of 1200h⁻¹, volume catalytic bed of 0.5 ml and temperature from 653 to 693 K using Nanoflow catalytic reactor. Many practical catalysts consist of one or several catalytically active components deposited on a high-surface-area support. The main purpose of using a support is to achieve an optimal dispersion of the active components and to stabilize it against sintering. In addition, the support can also be used as a way of tailoring the

performance of a catalyst, particularly if the active phase consists of small diameter particles. The surface area of the support affects strongly on the dispersion of the active phase. If low surface area support is used, low surface area of active site would be resulted.

Different supported MoVTeNb oxide catalyst has been synthesized using spray drying techniques. Since oxalic acid is an excellent ligand for metal ions, the effect of oxalic acid loading on supported MoVTeNb oxide will be an important parameter to understand the structure-activity relationship of the catalyst towards propane oxidation. The general procedure which is described in detail in Chapter 3 was to prepare a solution of ammonium heptamolybdate, ammonium metavanadate and telluric acid as Solution 1. A second solution was prepared as ammonium niobium oxalate to which oxalic acid was added (Solution 2). Solutions 1 and 2 were mixed and the support powder was added to form a slurry. At high temperature (473 K), spray drying is used to eliminate the solvent from the precursor slurry. Apparently, the methods of drying and activation play an important role in directing the final structures of the resulting catalysts, which, in turn, determines the catalytic performance. This fact will be confirmed by structural analysis i.e XRD technique in which it is postulated to favor the formation of an effective crystal phase and suppress the formation of impurities.

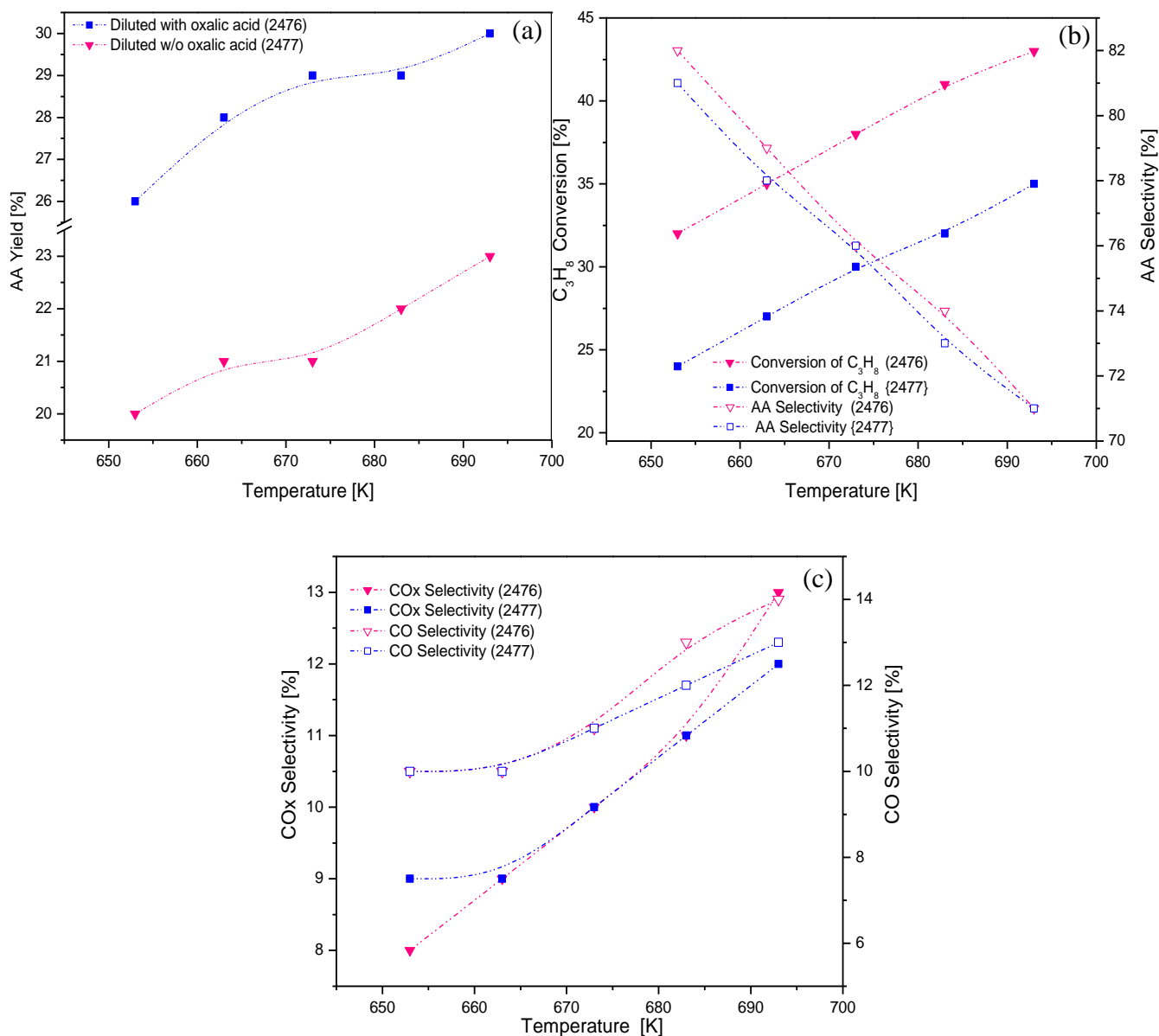


Figure 4.3: Propane oxidation over diluted MoVTenbOx catalysts at different methods.

(a) Acrylic acid yield as a function of the reaction temperature.

(b) The conversion of propane and selectivity of acrylic acid towards reaction temperature 653, 663, 673, 683 and 693 K.

(c) The corresponding selectivity of COx and CO in different reaction time

Figure 4.3 shows the results of catalytic performance for selective oxidation of propane to acrylic acid over diluted with and without addition of oxalic acid (catalyst _2476 and

catalyst_2477, respectively). The effect of reaction temperatures was studied in a range of 653 to 693 K. It is clear that the temperatures affects strongly on the catalytic performance. In the reaction, acrylic acid and CO_x (CO₂ and CO) are the major products; while acetic acid and propylene are in a small amount. As the temperature is elevated from 653 to 693 K, the conversion of propane increases from 24 to 35 % for diluted sample without addition of oxalic acid and slightly increases from 32 to 43 % with addition of oxalic acid. The decreased propane conversion observed would be roughly consistent with the geometric dilution factor as per volume unit of catalyst where the diluted system contains only about half of the active site when neglecting the difference in bulk densities. Nevertheless, both catalysts are also selective to acrylic acid, but diluted catalyst with addition of oxalic acid presents much higher acrylic acid from 26 to 30 % than that (20-23 %) diluted without addition of oxalic acid. Both catalysts show consistent decrease towards the selectivity to acrylic acid from 82-71 % (for catalyst 2476) and 81 to 71 % (for catalyst 2477) at the expense of relative increase of the selectivity towards CO_x from 8 to 13 % (for catalysts 2476) and 9 to 12 % (catalyst 2477). Saturated hydrocarbon like propane has low reactivity under lower temperature. Apparently, higher temperatures are suitable for propane activation, whereby the propane conversion increases with increasing reaction temperature. The effect of different preparation method for diluted system was summarized in Table 4.3. The diluted catalyst with the addition of oxalic acid exhibits a higher surface area compared to diluted sample.

Table 4.3: Catalytic performance of different preparation method on diluted $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$ oxide catalyst

Catalyst ID	Type of method	Temperature (K)	C_3H_8 Conversion (%)	AA Selectivity (%)	AA Yield (%)	BET Surface area (m^3/g)
2477	Diluted without oxalic acid	653	24	81	20	26.7
		663	27	78	21	
		673	30	76	21	
		683	32	73	22	
		693	35	71	23	
2476	Diluted with oxalic acid	653	32	82	26	37.0
		663	35	79	28	
		673	38	76	29	
		683	41	74	29	
		693	43	71	30	

It has been well known that most of the heterogeneous catalysts experience certain degree of sintering after usage. Sintering of the active component decreases the surface area, and thus reduces the activity of the catalyst. Generally, sintering in gas phase reaction occurs at high temperature by atomic species (Flynn 1974, Flynn 1974, Flynn 1975) or/and crystallites migration on the support surface (Ruckenstein 1973, Ruckenstein 1974, Ruckenstein 1975, Ruckenstein 1977). Processes of sintering by crystallite migration and by atomic species migration operate on two completely different mechanisms: first involving the migration of crystallites resulting in collision with stationary or mobile particles leading to their coalescence on the support surface; the second mechanism involves a dissociation of metal crystallites to metal atoms that then diffuse and associate with larger particles. However, the last mechanism might also explain the inverse phenomenon of sintering which is the re-dispersion of the metallic phase rather than particle-particle association. The sintering processes are complex in which the mechanisms are highly activated processes and might be expected to occur only at relatively high temperature (Doudah A. 2002).

The term “dilution” is used to discriminate the addition of a mineralic component to the catalyst from the usual supporting effect in which is normally used for dispersion of active component, whereby is clearly not the case in the present system. To be effective, the diluent should be at least as finely divided as the dispersed metal.

The diluent acts as a physical “spacer” between the metal crystallites, and if there is adequate support available it will inhibit sintering of the metal crystallites (Ertl 1979, Ertl 1979, Pearce 1981).

There are several functions of diluents in catalyst system which are:

- (a) Maintain the surface area for the active component
- (b) A stable surface over which the active component is dispersed in such a way that sintering is reduced
- (c) Mechanical strength of catalyst particles
- (d) Thermal stability of catalyst particle
- (e) Enable or enhance the accessibility of the gas phase to maximum surface area per volume of active catalyst (an important factor for bulk catalyst exposing essentially the geometric surface area without any porosity suitable for gas transport).

The low reactivity of the substrate propane is traditionally understood in view high strength of C-H bonds especially of those in the terminal methyl group. As a result, substantial amount of energy (normally from reaction temperature) is required to selectively activate the methylene C-H bonds, and even more is needed for the methyl C-H bonds of propane, since the former is weaker than the latter (Lin 2001). In addition, at high temperature the oxygenated product (such as acrylic acid) from the oxidation of propane is less stable and tends to oxidize further to decompose (Fujikawa 2001).