2. Literature Review on Catalysts Systems

2.1 Overview on Catalyst Technology for Selective Oxidation of Propane to Acrylic Acid.

The economic advantages of switching to a propane feedback in the production of acrylic acid have been a motivating force for extensive research studies focusing on developing alkane partial oxidation catalysts. Due to the abundance and low cost of light alkanes, the selective oxidation of methane, ethane, propane and butane to oxygenates has economic and environmental implications (S.Albonetti, F.Cavani et al. 1996). In the industry, acrylic acid and its esters are important monomers for the manufacture of homo- and co-polymers such as paints adhesives, textile finishing, leather processing, and superabsorbents (M.Aounine, J.L.Dubois et al. 2001).

The most important industrial process for the synthesis of acrylic acids involves two steps, which consist of propene oxidation to acrolein followed by the oxidation of acrolein to acrylic acid (H.H.Voge 1967). However, the one-step partial oxidation of propane could be an alternative route. In the literatures, various catalysts systems such as mixed oxide catalyst (Ushikubu T, Nakamura H *et al*. 1995; Ushikubu T, Oshima K *et al.* 1997; Lin M and W 1999; Botella P., Solsona B. *et al.* 2001; Li H, Tong J *et al.* 2002; Lin M 2002; Ushikubu 2003; Tu , Furuta N *et al.* 2006; Solsona B, Vazquez M I *et al.* 2007), heteropoly acid (Centi and F 1991; Cavani F, Etienne E et al. 1995; Ueda and Y 1995; Mizuno, Suh D J et al. 1996; Ueda, Suzuki Y et al. 1996) and VPO type catalysts (Ai 1986; Misono 1987; Ai 1992; Volta 1996; Ai 1998) have been reported for the oxidative conversion of propane to acrylic acid.

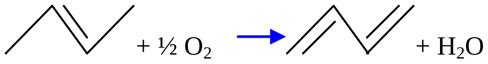
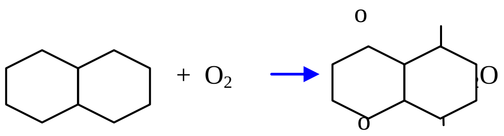
Selective catalytic oxidation and ammoxidation processes of hydrocarbon comprise approximately one quarter of the value produced by all catalytic processes worldwide. They contribute significantly to the gross national product of industrial countries and offer future opportunities for developing countries. These processes are not only important from a commercial standpoint and their contribution to the well-being of modern mankind, but they also present the opportunity for significant fundamental be the most efficient for the selective oxidation and ammoxidation of hydrocarbons and organic oxygenates. Different hypotheses have been proposed to explain the enhancement in both catalytic activity and selectivity (Vedrine, Novakova et al. 2003). Many factors play a role in selective oxidation reactions on metal oxide catalysts and the complexity of such catalysts is widely recognised. Many catalytic systems are based on molybdenum and vanadium oxide. Common reactions from these catalytic reactions are partial oxidation of propane, propylene and also acrolein. The design and synthesis of multi metal oxide catalysts are currently a main focus for both industrial and academic laboratories that are pursuing the goal of selective alkane oxidation.

Catalytic oxidation of light alkanes is attractive from an industrial perspective due to the economic implications of using a globally abundant raw material. The combination of low cost and abundance supply of propane is the driving force in developing a commercially attractive catalyst based on propane.

The use of mixed metal oxides for oxidative dehydrogenation of olefins is already well established, with highly selective processes for the production of butadiene, isopropene and acrolein reported almost 40 years ago. Even though propylene is commercially used as the starting material,acrylic acid production by propane oxidation is an alternative process.

These include morphology changes under catalytic conditions, interaction between phases, and contamination/wetting of one phase by the other under catalytic conditions or remote control (oxygen spill-over) process. In this approach, large libraries of materials are synthesized as potential catalysts and examined by microanalysis techniques, and the results are evaluated statistically. This methodology permits an efficient material screening in the case of multi-parameter problems such as the development of solid catalysts. It seems that potential catalyst formulations can be determined by the combinatorial approach; while technologically important parameters such as catalyst morphology, texture and forms, mechanical and thermal properties, long-time stability, environmental friendliness, regenerability and disposal of spent catalysts will still have to be tested independently. The oxidation reaction has been studied in the last 30 years and the main components of multimetal oxide catalyst used in many types of reaction are listed in Table 2.1 (Ertl G. 1997).

Table 2.1: Selective oxidation reaction of hydrocarbon (Ertl G. 1997)

Catalyst	Reaction	Product
Mo-V-Te-Nb Mo-V-Sb-Nb	$CH_2=CH-CH_3 + O_2 \rightarrow CH_2=CH-CHO + H_2O$	Acrylic Acid
Mo-Bi-Fe-O Mo-V-O	$CH_2=CHCH_3 + O_2 \rightarrow CH_2=CHCHO + H_2O$	Acrolein
Pd/CH_3COONa	$CH_2=CH-CH_3 + O_2 \rightarrow CH_2=CH-CHO + H_2O$	Ethylene Oxide
Pd/CH_3COONa	$CH_2=CH_2 + CH_3COOH + ½ O_2 \rightarrow CH_2=CH-O-CO-CH_3$	Vinyl Acetate
$(VO)_2P_2O_7$	$CH_3CH_2CH_2CH_3 + 7/2O_2 \rightarrow CH_4H_2O_3 + 4H_2O$	Maleic Anhydride
Fe_2O_3, Cr_2O_3, $Cu (Ni)_3(PO_4)_2$		Butadiene
V_2O_5+promoter		Naphthoquinone

2.2 Acrylic Acid

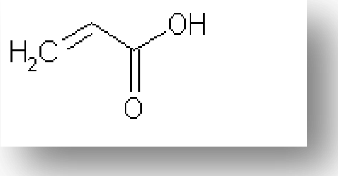
Petrochemical is any chemical derived from fossil fuel. These includes purified fossil fuels such as methane, propane, butane, gasoline, diesel fuel or fuel oil and also include many agricultural chemical such as pesticides, herbicides and fertilizers and also others items ie; plastics and synthetic fibres. The most variety of industrial chemicals is petrochemicals. Many petrochemicals have been produced because they have two common characteristics: they are simple and also reactive. One of the simplest organic acids containing double bond and highly reactive is acrylic acid. It can readily undergo polymerization (reacts by itself because of the double bond) and esterification (reacts with alcohol). Due to the tendency for acrylic acid to polymerize easily when exposed at low temperature, heat, light or metals, therefore polymerization inhibitor (such as hydroquinone derivatives) is added to commercial products to prevent the strong exothermic polymerization.

Malaysia has a well-developed oil and gas sector and a growing petrochemical industry. The industry covers petroleum products, natural gas and petrochemicals. A wide range of petrochemicals resins are produced in Malaysia such as olefins, polyolefins, aromatics, ethylene oxides, glycols, oxo-alcohols, ethoxylates, acrylic acids, phthalic anhydride, acetic acid, styrene monomer, polystyrene, ethylbenzene, vinyl chloride monomer and polyvinyl chloride. Five major types of petrochemical resins produced locally are polyethylene, polypropylene, polyvinyl chloride, polystyrene and acrylonitrile butadiene styrene. Other major petrochemical products include styrene monomer, vinyl chloride monomer, urea/ammonia, acetic acid, ethylene oxide/ ethylene glycol and derivatives, acrylic acid and esters, and terephthalic acid.

2.2.1 Physical and Chemical Properties of Acrylic Acid

Physical Properties

Acrylic acid is a clear, colourless liquid with a sharp, sweet and acrid odour at room temperature and pressure. It is miscible in water and most organic solvents. It can emit into atmosphere and react with photo chemically produced hydroxyl radicals and ozone, resulting in rapid degradation. Acrylic acid is rapidly oxidised in water and can therefore it potentially decreases oxygen concentration if discharge in large quantities into a body of water. It has been shown to degrade under both aerobic and anaerobic conditions.



Acrylic Acid
Formula: $C_3H_4O_2$
Molecular Weight: 72.0

Figure 2.1: Structure and formula molecule of acrylic acid

Table 2.2: Chemical properties of acrylic acid

Properties	**Info**
Common Name	Acrylic Acid
CAS Name	2-propenoic acid
CAS registry number	79-10-7
Molecular formula	$C_3H_4O_2$ (CH_2=$CHCO_2H$)
Molecular mass	72.06 g/mol
Melting point	13-14 ^oC
Boiling point	141- 142 ^oC
Solubility in water	soluble in all proportions
Solubility in solvents	soluble in all proportions in ethanol, diethyl ether, and chloroform; soluble in acetone and benzene.
pH value	2.63 (0.1M solution)
Vapor pressure	2.5 (air = 1)
Relative density	1.06 (20/20^oC)
Synonyms	acroleic acid, 2-propenoic acid, vinyl formic acid, propene acid, ethylene

Chemical Properties

Acrylic acid and its esters undergo reactions characteristic of both unsaturated compounds and aliphatic carboxylic acids or esters. The high reactivity of these compounds stems from the two unsaturated centres situated in a conjugated position. The β carbon atom, polarized by the carbonyl group, behaves as an electrophile.This favours the addition of a large variety of nucleophiles and active hydrogen compounds to the vinyl group. Moreover, the carbon double bond undergoes radical-initiated addition reactions, Diels-Alder reactions with dienes, and polymerization reactions. Acrylic acid and its esters polymerize very easily. The polymerization is catalyzed by heat, light, and peroxides and inhibited by stabilizers, such as the monomethyl ether of hydroquinone or hydroquinone itself. These phenolic inhibitors are effective only in the presence of oxygen. The highly exothermic, spontaneous polymerization of acrylic acid is extremely violent.

Acrylic acid reacts readily with free radicals and electrophilic or nucleophilic agents (Kirk-Othmer, 1984). It may polymerize in the presence of acids (sulfuric acid, chlorosulfonic acid), alkalis (ammonium hydroxide), amines (ethylenediamine, ethyleneimine, 2-aminoethanol), iron salts, elevated temperature, light, peroxides, and other compounds that form peroxides or free radicals. In the absence of an inhibitor, peroxides are formed when oxygen is mixed with acrylic acid. This mixture can undergo violent polymerization if heated to 323 K (Chris, 1989). The mechanism of auto-accelerating polymerization of acrylic acid in hexane-methanol solution, which can become explosive, has been studied by Bretherick (1985). Acrylic acid rapidly decomposes in the atmosphere by photochemical attack on the double bond. Acrylic acid is corrosive to many metals but not to stainless steel or aluminum (Kirk-Othmer, 1984).

2.2.2 Application of Acrylic Acid

Commercial scale synthesis of acrylic acid began in 1930s and has grown to a world market in excess of two million tonnes per year. Acrylic acid is commercially available in two grades; technical grade and glacial grade. Acrylic acid is a versatile chemical that can be esterified, aminated or otherwise modified and polymerised to complex molecular arrangements to suit requirements. The esters are produced by reacting acrylic acid with alcohols especially ethanol, methanol and butanol that may be saponified, converted to other esters or amides by aminolysis. Acrylates are derivatives of acrylic acid (such as methyl and ethyl acrylate) whose properties have been sufficiently modified to enable acrylic acid to be used in different media as emulsion and solution polymers. Approximately two-third of the acrylic acid manufactured is used to produce acrylic ester-methyl acrylate, butyl acrylate, ethyl acrylate and 2-ethylexyl acrylate as coatings, finishes and binders for application in paints, adhesives, and polishes with solutions used for industrial coatings. Acrylic acid and acrylate ester processes are shown in Figure 2.2.

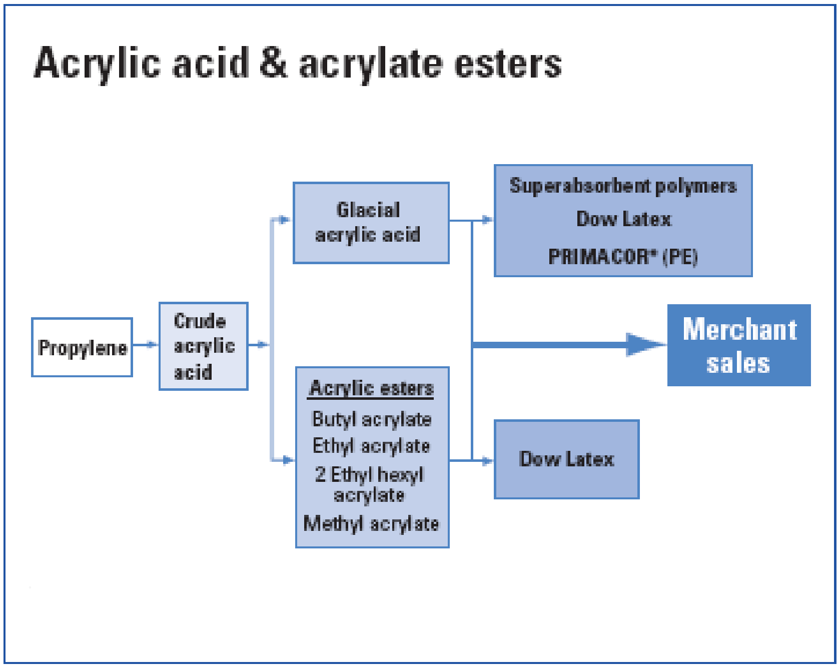


Figure 2.2: Acrylic acid & acrylates esters process by Dow Celanese Chemicals (www.ebcohost.com/acrylic acid).

Two-third of the world's production of acrylic acid is used to produce acrylic esters (acrylates) primarily for use in emulsions and solution polymers for latex-based paints, coatings, adhesives and textiles. Polymers of acrylic acid can be produced as superabsorbent materials, and as a replacement for phosphates in detergents. Both of these represent fast growing applications for acrylic acid.

The chemical and physical properties of the polymers can be modified through controlled variation in the selection and balance of the monomers, the extent of cross-linking and molecular mass. High resistance to chemical and environmental degradation, strength, clarity, and being readily available in high purity forms complements this flexibility. The remaining one-third of the acrylic acid is used to produce polyacrylic acid, or cross-linked polyacrylic acid compound d as superabsorbent materials in hygiene products, and soluble as a replacement for phosphates in detergents and also waste water treatment chemicals *[http://www.chemlink.com.au/acryful.htm]*.The following pie chart in Figure 2.3 shows world consumption of crude acrylic acid: While Figure 2.4 shows the pie chart for world consumption of acrylate esters until 2010.

Figure 2.3: World consumption of crude acrylic acid until 2010

(http://www.sriconsulting.com/CEH/Public/Reports/606.4000/25 july 2011)

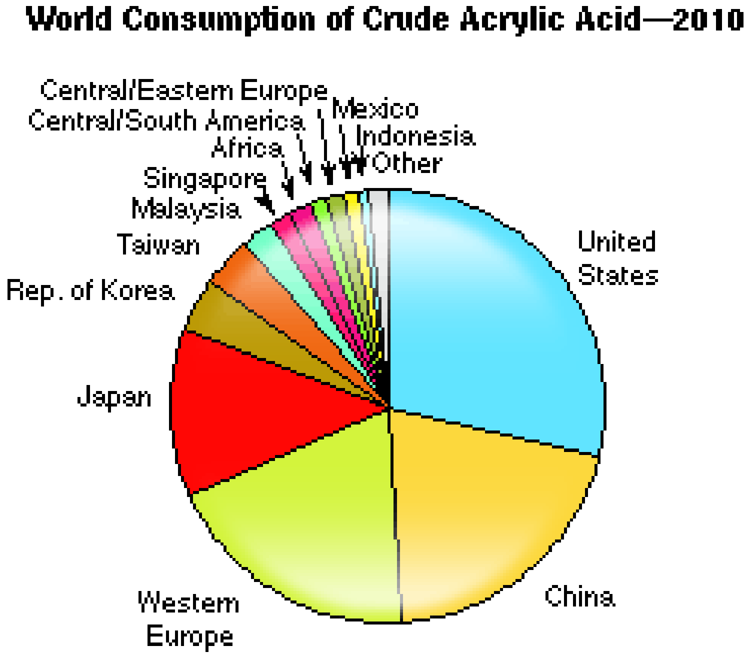
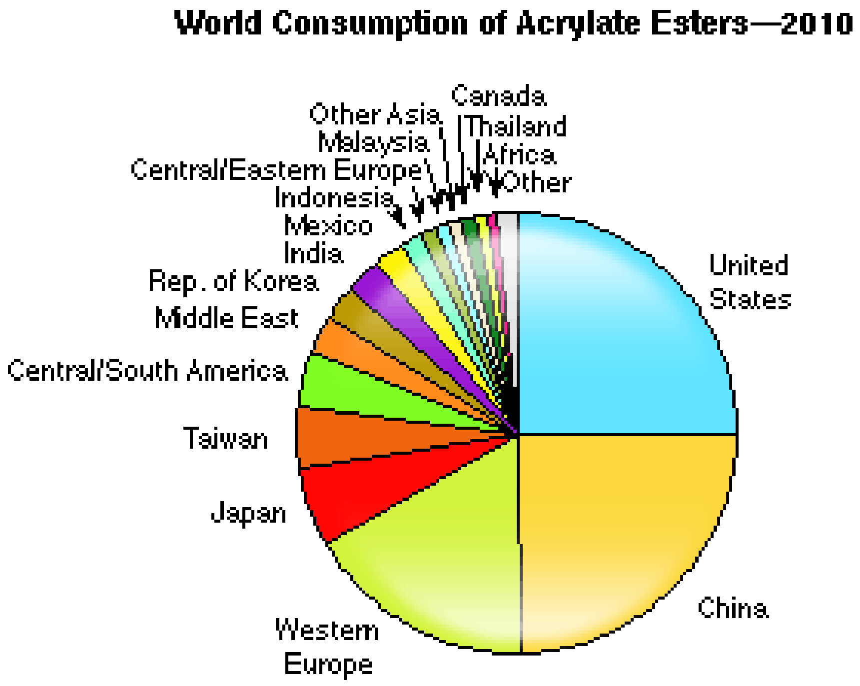


Figure 2.4: World consumption of crude acrylate esters until 2010 (http://www.sriconsulting.com/CEH/Public/Reports/606.4000/25 july 2011)



Chemically, it can be explained that acrylic acid is a versatile. It can enter into common reactions with a large number of organic and inorganic compounds and intermediates for the synthesis of many low and high-molecular weight compounds. These are some products derived from acrylic acid (see also Figure 2.5):

- As a vinyl compound in addition reactions.
- As a carboxylic acid — acrylic esters, acrylamide, N-substitute amides and acrylic acid chloride.
- Copolymers with acrylic esters, methacrylic esters, acrylonitrite maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene and ethylene.
- Homopolymers of acrylic acid and copolymers form water-soluble compounds in acid form or their alkali/ammonium salts. Uses include thickening agents; dispersing agents; protective colloids for stabilizing emulsions and polymer

dispersions wetting agents. AAG is used to produce very high molecular weight polymers for flocculents and viscosity control in oil-well drilling mud.

- Superabsorbant polymers are lightly crosslinked polyacrylic acid salts. They are used for fluid retention, largely in baby diapers, but also in products for feminine hygeine, adult incontinence and agriculture.
- Copolymers with less than 50% acrylic acid produce polymers only slightly soluble or even insoluble in water. Their alkali or ammonium salts are used in sizes, adhesive intermediates, and binders for printing inks and coatings.
- Copolymers with small amounts of acrylic acid improve adhesions and improve resistance to oil and solvents. In polymer dispersions, acrylic acid addition improves stability and compatibility with pigments (Sittig 1965).

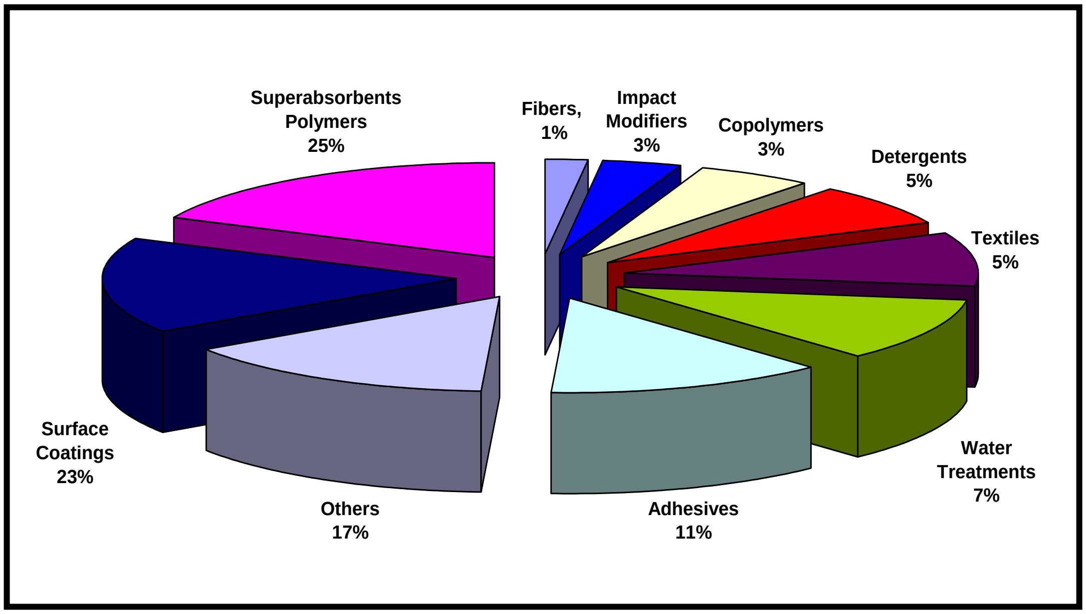


Figure 2.5: Products derived from acrylic acid (Widi 2004)

2.2.3 Worldwide Demand

The economy of Malaysia is largely built on their vast natural resources of palm oil and natural gas. With Malaysia strategically positioned as a global supplier of raw materials to the industrial sector, it would be more economical to convert these raw materials into higher value added products for trading. The profit for the Malaysian economy could be substantially increased if suitable catalyst material, (*i.e*. a material that increases the rate and the selectivity of chemical reaction where it is not consumed by the reaction) could be developed, that would turn them into products of higher value, e.g. acrolein or acrylic acid. The success of meeting this objective requires the most advanced technology in catalysis and chemical processes. Thus, this mission has led to the focus to upgrade these relative economic low valued raw materials.

Many researches are now focusing on the development of catalysts and optimal process conditions, and the identification of new product synthesis routes. The petrochemical industry is an important sector in Malaysia with investment totaling RM 28 billion (US $ 7.4 billion) as at the end of 2004. From being an importer of petrochemicals, Malaysia is the major exporter of petrochemicals products. In 2005, the petroleum products and petrochemicals industry contributed with RM 56 billion to the country’s export earnings, compared with RM49 billion in 2004.The main exports market were China, ASEAN, the USA and Japan. Imports totaled RM 37 billion in 2005 compared with RM 32 billion in 2004. Imports were mainly from Singapore, Saudi Arabia and the USA.

Overall, Malaysian investments in the industry amounted to RM 34.8 billion (63%), with PETRONAS being the major investor. Foreign investments, mainly from the USA and Japan, accounted for 36.7% of the total investments in the industry. The main domestic investor in the petrochemical sector is PETRONAS. The USA is the largest source of foreign investments, contributing 40% of the foreign investments. Among the global petroleum and petrochemical companies that have invested in the Petronas Petrochemical Integrated Complex (PPIC) are ExxonMobil, Dow Chemical, BASF, BP, Amoco, Shell, BASF, Eastern Chemicals, Toray, Mitshubishi, Idemitsu, Polyplastic, Kaneka, Dairen and Titan Petchem Group. Petronas has made significant contributions to the development of support infrastructure utilities and services. This has created an investment environment, which is conducive to the petroleum and petrochemical industry to expand, particularly in Kerteh, Terengganu and Gebeng, Pahang.

PETRONAS, the multinational petrochemical company, is embarking on the development of petrochemical business in an integrated manner has succeeded in attracting renowned joint venture partners to set-up world scale plants. The development of world class centralized utility facilities that offer a ready and reliable supply of crucial utilities such as power, steam, as well as services such as primary waste water treatment, further enhances the efficiency of the integrated petrochemical zone concept, making as competitive as similar site in the Asia Pacific region.

The main driver for the glacial acrylic acid market is superabsorbent polymers (SAP), which are used to produce disposable baby diapers and detergent polymers in washing powder formulations. From the mid-1980s, two new applications - superabsorbent polymers (SAPs) and detergent polymers - have emerged. SAPs are cross-linked polyacrylates with the ability to absorb and retain more than 100 times their own weight in liquid. They have experienced very strong growth, primarily in baby diapers (nappies), although the US and West European markets have now matured. However, forecasts show that over the next few years, this will account for a lower proportion of acrylic acid consumption, falling from 33 percent in 2001 to 30.5 percent in 2011, owing to the very high penetration of SAP into most applications in the developed world. SAPs account for over 30% of world acrylic acid consumption. Growth in the acrylate esters and acrylic acid polymers markets is the main driver for acrylic demand (*Chemical Weeks, Aug 1-14, 2005, pg. 11).*

Global demand for crude acrylic acid is forecast to grow at 4.8% annually during 2010–2015, driven by growth in superabsorbent polymers (SAPs) at 5.6% and acrylate esters at 4.3%. Glacial acrylic acid (GAA) is forecast to grow at 5.4% annually during 2010–2015 (http://www.sriconsulting.com/CEH/Public/Reports/606.4000/25 july 2011).Nearly half of the acrylic acid produced is consumed in polymer form for use in diapers and hygiene products. But gains in the acrylic acid polymers market were beginning to decelerate. Virtually all brands of baby diapers, adult incontinence products, and hygiene products already incorporate high loadings of super absorbent polymers. However, an aging population will slightly accelerate growth in that area. Demand for acrylate esters—used in a wide range of coatings, adhesive finishes for paper, and wood—will increase by 3.5%/year through 2005 *(Chemical Weeks, Jan 1/8, 2003, pg. 36).*A new application for SAPs is soaker pads used in food packaging. In 2007, the US Food and Drug Adminstration authorised SAPs in packaging with indirect food contact for poultry, meat, fish, fruit and vegetables.

World demand for crude acrylic acid is forecast by US-based consultants SRI Consulting to grow at 3.7%/year during the 2006-2011 period. Demand for glacial acrylic acid is forecast to increase at about 4%/year in this period, primarily due to the growth in SAPs. SRI Consulting estimates demand for commodity acrylates to grow at 3.7%/year. In western Europe, growth is much slower at just 1.6%/year but new capacity has been added. In 2006, StoHaas and Arkema increased the capacity of their plants in Germany and France. BASF is carrying out a 160,000 tonnes/year expansion in Antwerp, Belgium, due for completion in late 2008.

In the US, consumption of acrylic acid grew by 3.4%/year in the 2002-2007 period, buoyed by peak growth years in 2002 and 2003. However, growth slowed to about 2%/year in the following three years and is now only predicted to grow at 1.6%/year through to 2011. US demand is therefore predicted to grow from 1.17m tonnes in 2007 to 1.24m tonnes in 2011, according to *ICIS Chemical Business* (*ICB*). Exports in 2007 were 61,000 tonnes in 2007 while imports were negligible. With the downturn in the US construction industry in 2008, demand for architectural coatings and other acrylic acid-based products used by the building trades will be down by perhaps 5-10%. Recovery in this sector is not anticipated until 2011. *(http://www.icis.com/v2/chemicals/9074870/acrylic-acid/uses.html/25 July 2011)*

According to the chemical weeks, world demand for crude acrylic acid is forecast to grow at 3.7%/year for the next six years, following an 8.1%/year jump from 2004 to 2005, to 3.4 million m.t. Demand from bulk acrylates is expected to grow at 3.7%/year, and from glacial acrylic acid into superabsorbent polymers (SAP) at 4.1%/year over the same period A highly penetrated SAP market and demand growth of 0.5%/year from the acrylates market is expected to keep North American consumption growth at 1.6%/year from 2007 to 2013. .BASF closed its 70,000-m.t./year Freeport, TX plant in 2003 and restarted it in 2005 in response to global acid shortages. Dow Chemical has pulled out of feasibility studies on a planned acrylic acid plant at Betim, Brazil with Brazil's state oil company Petrobras (Rio de Janeiro) and Elekeiroz (Sao Paolo) *(Chemical Weeks, Dec. 14, 2005, pg. 4)*

The west European market is expected to grow at 0.7%/ year in the next six years. StoHaas Monomer, a 50-50 jv of Degussa and Rohm and Haas, is bringing onstream 65,000 m.t./year of acid at Marl, Germany. Arkema has announced that it would debottleneck its 240,000-m.t./year plant at St. Avoid, France by 15% by the end of the year (Chemical Weeks, 2005). BASF is building a new l60,000-m.t./year acrylic acid plant at Antwerp for startup in 2008 (Chemical Weeks, 2006). The major growth market is China, where growth rates surpassed expectations. Acrylic acid consumption jumped from 232,000 m.t. in 2003, to 378,000 m.t. last year, or 27.6%/year. Whilst, acrylates accounted for 63% of Chinese demand, but demand from SAP is growing fast. Figure 2.6 has shown the global supply of crude acrylic acid over the world from 1990 to 2010. The acrylic acid and acrylates esters merchant market exhibits a strong demand growth rate of 4 to 5 % with limited capacity *(Chemical Weeks, Feb. 15, 2005, pg. 10).*

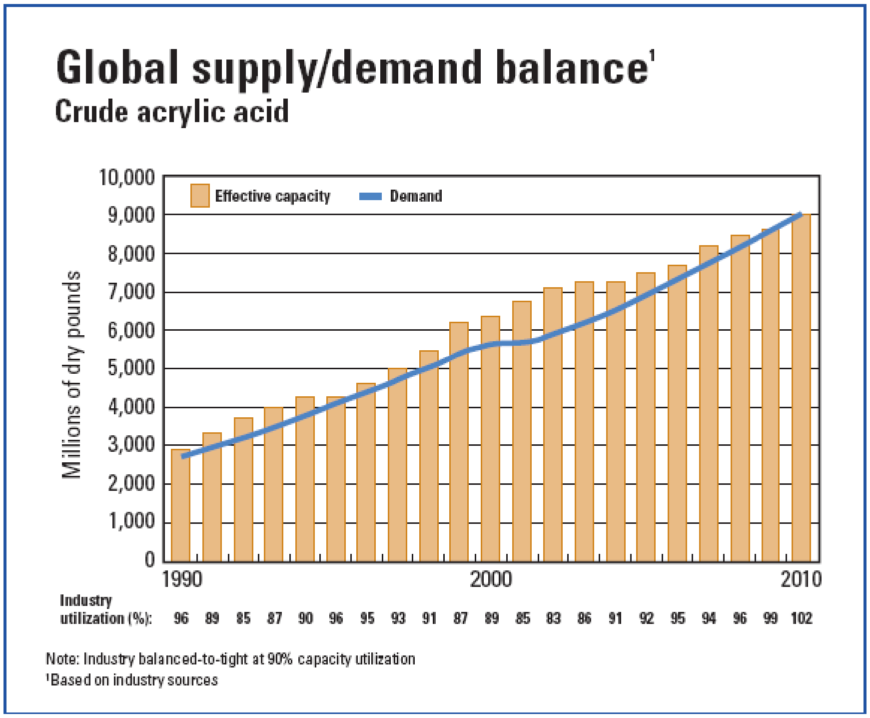


Figure 2.6: Global supply/ demand of crude acrylic acid

BASF announced its intention to build SAP capacity at its Nanjing, China site, where acrylic acid and acrylates production started in mid-2005. New acrylic acid plants and additions are expected on-stream in China between this year and 2008 to meet fast-growing demand in China. Formosa Plastics started a 160,000-m.t./year acrylic acid plant at Ningbo, China this year. Nippon Shokubai is testing its new 160,000- m.t./year unit at its Himeji, Japan plant. LG Chem is also planning to build an 80,000- m.t./year acrylic acid plant at Yeosu, Korea for startup in late 2007 to supply China *(Chemical Weeks*, *April 12/19, 2005, pg. 18.*

Tight propylene supply and expensive propylene is hampering acrylic acid production, particularly in Asia. A tightening world oxo-alcohols market has also restricted acrylates output. Rising propylene feedstock costs have prompted producers to seek global price increases of 8%-10% in North America, about 5% in Europe, and around 15% in Asia/ Pacific for the fourth quarter. Figure 2.7 shows the global demand for production of acrylic acid until 2010.

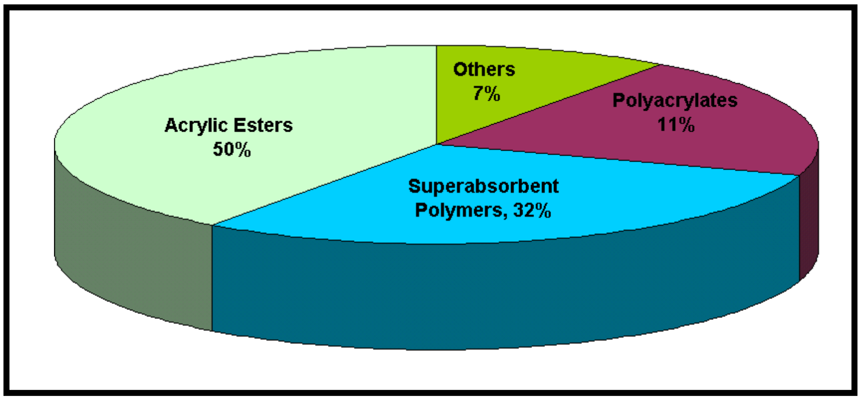


Figure 2.7: Global demand for production of acrylic acid until 2010

(Source: Tecnom Orbichem (London)

Supply Conditions

Acrylates are traded as technical grade (99% purity), inhibited ors, which have been successfully to require a hazardous shipping label, but butyl-, isobutyl-, and 2-ethyl hexyl-acrylates have high enough flash points to be considered safe. Acrylic acid is highly corrosive to many metals and must be stored in stainless steel, glass, aluminium or polyethylene lined equipment. It is commonly supplied in 200kg plastic drums. Acrylic acid must be used within about three months of manufacture as it degrades by polymerisation by at least 0.5 per cent per month even faster if not held in a narrow temperature range during transport and storage. This instability requires more frequent and hence costly turnover of inventories.

2.2.4 Production of Acrylic Acid

Acrylic acid is commercially produced in two steps process starting from propene. An alternative route could be the partial oxidation of propene. Recently, the use of multi-component metal oxide catalysts based on molybdenum, vanadium, tellurium and niobium seems to be a major breakthrough leading to promising developments. The actual state of the art of the selective oxidation of propane to acrylic acid has been reviewed by Lin (Lin 2001). The direct oxidation of propane to acrylic acid has attracted a lot of attention in past two decade. Progress has been made with the discovery of new active and selective oxide-based catalysts, and it's reasonable to change the existing industrial two-step process via propene to single step which is directly from propane. Thus, replacing propene to with the much cheaper propane as the starting material to produce acrylic acid will provide a huge cost saving.

Furthermore, the direct utilization of propane in chemical productions can also provide additional energy and environmental benefits to the society. Among selective alkane oxidation, the conversion of propane to acrylic acid has been focus of extensive research worldwide since the early 1990s. With highly reactive double bond and carboxyl moiety, acrylic acid is especially suited for use as a monomer or co-monomer for various commercially important polymers.

Acrylic acid is also useful as a starting material to produce various commercially important acrylates, which are also important building blocks for any polymer materials, such as plastics, paints, adhesives, caulks, sealants, and detergent, etc. In 2004, the global merchant sales showed the increment of crude acrylic acid. There are 9 participants which active in global merchant of crude acrylic acid such as Dow, BASF, Rohm & Haas, NSKL, FPC, AtoFina, Mitshubishi, LG and others (see Figure 2.8). Based from the sales, Dow is the largest participant in the profitable of acrylic acid and esters.

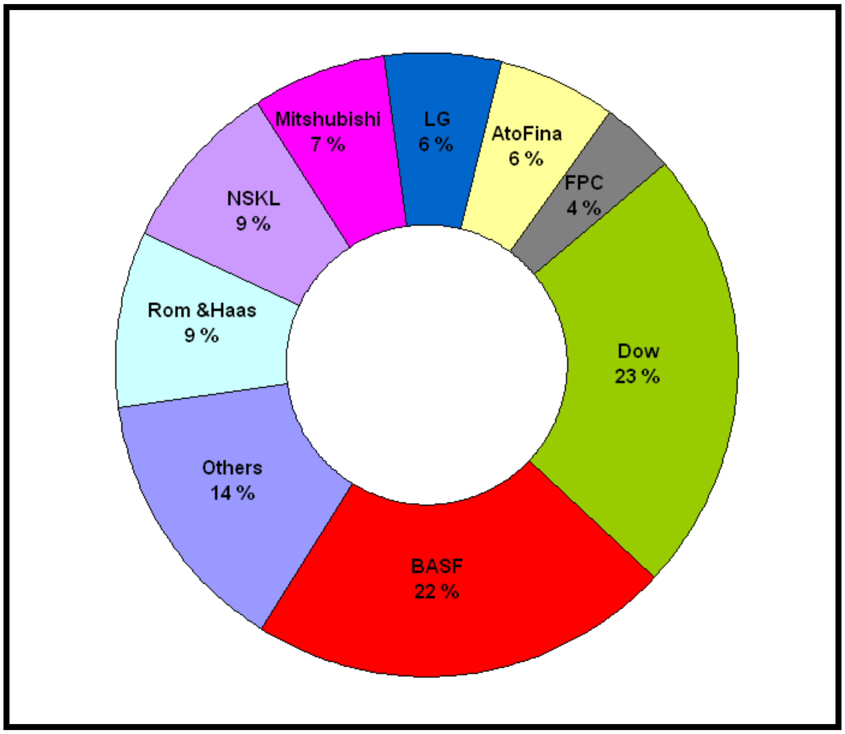


Figure 2.8: Global merchant sales of crude acrylic acid basis in 2007

2.2.4.1 Historical Production of Acrylic Acid

Acrylic acid has been begun to produce commercially in 1930s *(Chemical Market Reporter, 2002)*. BASF, the largest scale manufacturer of acrylic acid, started produce acrylic acid using the Reppe process, which synthesizes acrylic acid from acetylene, carbon monoxide, and water over a nickel catalyst. However, BASF has discontinued use of this Reppe process. Currently, most plants produce acrylic acid via a two-step oxidation process in which propylene is oxidized to make acrylic acid. The process also generates acrolein, which can be further oxidized at high temperatures to form more acrylic acid.

2.2.4.2 Process and Technology of Acrylic Acid

Most of the produce acrylic acid via a two-step oxidation process in which propylene is oxidized to make acrylic acid using special catalyst. The process also generates acrolein, which can be further oxidized at high temperatures to form more acrylic acid. Though just an oxidation process, the limited life of the catalyst has promoted the two stage manufacturing process via acrolein using two catalysts.

1. The first stage is the oxidation of propylene to arolein using bismuth molybdate catalyst in a strongly exothermic reaction at 370°C.

   - **$CH_2 = CHCH_3$ (propylene) + O_2 $CH_2 = CHCHO$ (acrolein) + H_2O**

2. The second stage is the reaction of gas acrolein passed over to molybdenum vanadium oxide catalyst at 270°C in exothermic process.

   - **$CH_2 = CHCHO + 1/2\ O_2$ $CH_2 = CHCO_2H$ (acrylic acid)**

Conversion rates up to 90 percent are achievable at commercial scales of production depending on the technology, catalysts and conditions. Acrolein is immediately passed through a second oxidation reactor to form acrylic acid. A few side products form, namely formic acid, acetic acid, carbon monoxide and dioxide. The crude acrylic acid is cooled to about 80°C, absorbed in water (30-60 % the concentration). Acrylic acid is either purified by distillation from the solvent or removed from water with added inhibitors to minimise the formation of polymers.

Overall yields of propylene to acrylic acid are high 85-90%. Most manufacturing plants use the Japanese Nippon Shokubai process (including Rohm and Haas) and another licensor is Mitsubishi Yuka. BASF however, is still the largest scale manufacturer of acrylic acid and esters (www.chemlink.com.au/acryful.htm).

Most production is based on the gas phase catalytic oxidation of propylene via acrolein. The reaction can be carried out in single or two-step processes, but the latter is favoured because of higher yields. The oxidation of propylene produces acrolein, ***acrylic acid***, acetaldehyde and carbon oxides. ***Acrylic*** acid from the primary oxidation can be recovered while the acrolein is fed to a second step to make ***acrylic acid***. Purification can be carried out by azeotropic distillation.

LG's process uses a new reactor design and purification technique that gives enhanced production efficiency and stability. Supported by Engelhard, Rohm & Haas is developing a process that uses propane instead of propylene, which could offer significant cost savings. Table 2.3 shows the reaction parameters for propene oxidation to produce acrylic acid.

Table 2.3: Reaction Parameters for Propene Oxidation

Propylene Oxidation

Feed:		**Product:**	
Propylene:	642 lbs	Acrylic acid:	1000 lbs
Oxygen:	735 lbs	Water:	250 lbs
Catalyst:	small amount	By-products:	127 lbs

A technical grade of acrylic acid may be produced by a simple distillation to produce a grade of acid that is suitable for the manufacture of acrylic esters, but unsuitable for polymerisation. A high purity form (often referred to as glacial acid) is produced by a second distillation or crystallization that reduces aldehyde impurities which inhibit polymerisation. Different grades of glacial acrylic acid are available with flocculants requiring higher purity levels than dispersants and some other applications.

It is worth noting that technical difficulties have been reported as for example during 1995, Idemetsu Petrochemical Company, and the Sumitomo Chemical Company failed to operate above two-thirds capacity after adding to plant capacity. Table 2.4 show some of the active players and process conditions to produce acrylic acid.

Table 2.4: Producers, catalysts, processors and reactors to produce acrylic acid

Producers /Inventors	Year/ Patent No	Technology/Process	Catalyst	Process Condition	Output
ExxonMobil Research & Engineering Company/ Wang; Kun ; et al.	2011/7,910,772	• Gas phase oxidation of propylene • Two step reaction process: i) oxidation of propylene to acrolein using mixed metal oxides ii) oxidation of acrolein to acrylic acid • The catalyst produced 2 phases which are M1called orthorhombic (60-90%) and pseudo-hexagonal called M2 • Catalyst prepared via sol gel technique	$Mo_1V_{0.01-1}Te_{0.01-1}Sb_{0.01-1}O_{0\cdot01-1}$	• Fixed bed or fluidised bed system • Catalyst was pre-conditioned at 200^oC in N2 150 ml/min • Feed composition: C3: O2: N2: H2O 5: 9: 67: 17 • Temp: 380 oC • Pressure: 1 atm • GHSV = 2672h^{-1}	• Yield of acrylic acid is 50 %
BASF SE/ Dieterle, et.al	2010/ 7,795,470	• Gas phase partial oxidation of n-propane to acrylic acid • Separation liquid between acrylic acid and water by crystalisation • Oxidation of n-propane to acrylic acid using metal oxide catalyst	$Mo_1V_{0.33}Te_{0.15-1}Nb_{0.11}O_x$	• Tubular reactor • Feed composition: C3: O2: CO: H2O 3.3: 10: 5 : 41.7 • Catalyst was pre-conditioned at 200^oC • Temp: 350 ^oC • Pressure : 2 bar • GHSV:	• Conversion of propane: 27 mol % • Selectivity to acrylic acid : 60 mol %
Rohm and Haas Company/ Gaffney , et al.	2010/7,718,568	• Gas phase oxidation of alkane/mixture of alkane and alkenes • Catalyst prepared by hydrothermal technique	$Mo_1V_{0.3}Te_{0.23}Nb_{0.11}O_x$	• Fluidised bed system • Feed composition: C3: O2: Steam 1: 96 : 3 • Temp: 300-400 oC • Pressure: 1 atm • GHSV : 300-2000h^{-1}	• Propane conversion : 75 % • Yield of Acrylic acid : 52 %

Producers /Inventors	Year/ Patent No	Technology/Process	Catalyst	Process Condition	Output
Rohm and Haas Company/ Benderly , et al.	2011/ 8,049,036	• Steam cracking to oxygenates • Two steps oxidation: i) Dehydrogenation of propane to acrolein ii) Oxidation of propylene to acrolein and acrylic acid	$Mo_1V_{0.3}Te_{0.23}Nb_{0.17}Pd_{0.01}O_x$ impregnated with Pt 0.01M washed coated onto an alumina foam	• Fixed bed system • Temperature : 700 -1000 °C	• Multi stage method produced CO2, wate vapor and unreated alkanes at 5-30 % weight of C3-C8 alkanes
Rohm and Haas Company/ Lemonds , et al.	2010/7,820,854	• Gas phase partial oxidation of propane to acrylic acid	$Mo_1V_{0.285}Te_{0.21-1}Nb_{0.17}Pd_{0.01}O_x$	• Fixed bed system or a fluidized bed system • Feed composition: C3: O2: Steam: N2 7.1 : 10 : 23: 59.9 • Temperature : 300-342 °C • Pressure : 1 atm	Yield of acrylic acid more than 50 %
Arkema France/ Dubois , et al.	2010/ 7,732,639 B2	• Gas phase partial oxidation of propane to propylene	$Mo_1V_{0.33}Te_{0.22}Nb_{0.11}Si_{0.95}O_x$	• Fixed bed reactor • Feed composition: C3: O2: Steam: He/Krypton 0.829 : 0.877 : 4.234 : 8.44 (NL/h) • Temp: 300-450 °C • Catalyst volume : 0.5 and 1 g • GHSV : 10000 h^{-1}	• Yield of propylene and acrylic acid increases when 50 % of partial oxidation of propane reached.

Strength

Most acrylic acid is consumed in the form of a polymer. Previously, the dominant share of acrylic acid was converted to esters. Today, however, the growth in demand for superabsorbents (used in diapers and hygienic products) has increased consumption for acrylic acid homopolymers. Acrylic acid is also used directly as a component for various copolymers. Consumption of acrylic acid grew at an average annual rate of 6.4 percent between 1995 and 2000. Demand for acrylic acid is forecast to increase four percent per anum through the year 2005. The largest contributors to this growth were polyacrylic acid (PAA) and n-butyl acrylate. Consumption of PAA for superabsorbent polymers is expected to grow at an average annual rate of 5.5 percent; most of its increase was due to strong demand for superabsorbent polymers (SAPs). Super absorbent polymers (SAP) are used to produce disposable baby nappies and detergent polymers in washing powder formulations. However, forecasts show that over the next few years this will account for a lower proportion of ***acrylic acid*** consumption, falling from 33% in 2001 to 30.5% in 2011. This is due to the very high penetration of SAP into most applications in the developed world. Acrylic acid accounts for about 80-85% of the raw materials in the manufacture of SAPs.

Weakness

The general market condition has been that of oversupply as the growth rate of this sector transitioned from more than 6 percent annually to something closer to 4 percent, due to the depressed economy. Although prices increased about 5 percent last year, feed stock propylene prices increased by 15 percent. Thus, margins have also been depressed. The production of acrylic acid will decrease from 33% in 2001 to 30 % in 2010 about 3 percent less from previous years.

2.3 Reviews on Development of Catalyst for Selective Oxidation Reaction

Selective oxidation of propane is highly attractive because it would bypass the energy intensive endothermic steam cracking or dehydrogenation reactions currently employed to manufacture olefin intermediates from natural gas and petroleum feedstocks for subsequent oxidation. Catalytic selective oxidation of propane is motivated by both the potential economic and environmental advantages. It has recently attracted great attention in both academia and industry.

During the last decade, the MoVTeNb oxide catalysts developed by Mitsubishi Chemical Corporation have received a lot of attention (Ushikubu, Oshima *et al.* 1993; Ushikubu, Koyasu *et al*. 1994; Ushikubu, Oshima *et al*. 1997). An exception appears to be the Mitsubishi reported catalyst of the empirical composition $MoV_{0.3}Te_{0.23}Nb_{0.12}Ox$ which is claimed by the patentees to yield 48% acrylic acid with 80.1% conversion and 60.5% selectivity. These catalysts have shown high efficiency in selective oxidation and ammoxidation of propane. It is debatably suggested that their unique catalytic properties are due to the presence of two major structures, called orthorhombic M1 phase ($Te_2Mo_{20}O_{57}$, M=Mo,V.Nb), which is responsible for activation of propene. Another phase is called hexagonal M2 phase, $Te_{0.33}MO_{3.33}$ (M=Mo,V,Nb). Formation of the active phases responsible for selective catalytic transformation of propane is determined by synthesis conditions and post synthesis thermal treatment of the material.

Graselli and Albonetti reported that the selective oxidation of light alkanes into oxygenated products is very attractive path toward the chemical utilization of large natural resources. The one step direct conversion to acrylic acid has attracted much research interest as a possible replacement for the current two- step propene- acrolein and acrolein-acrylic acid process. Several systems for catalyzing this reaction have been reported such as Te-V-P-O

[Ai. M, 1986; Han *et.al,* 1999], heteropoly compound [Lin, 2001; Ueda *et.al,* 1996; Mizuno *et.al.* 1995], Mo-V-O based complex metal oxides [Lin, 2001; Ueda *et.al,* 1999; Ushikubo *et.al,* 1997; Botella *et.al,* 2001], and Te-Ni-Mo-O [Fujikawa *et.al,* 2001]. None of these catalysts give acrylic acid yields in excess of about 10%.

Tu *et al* reported bulk mixed Mo-V-Te-Nb-O system, which exhibited a 48% acrylic acid yield and 63.4% propane conversion at a reaction temperature of 380 ^{o}C. Despite the promise of the results obtained, few papers have reported about the fundamental information (Tu , Furuta N *et al.* 2006).

Beato et.al reported that preparation parameters of MoVTeNb mixed oxide have a significant effect on the catalytic activity. The interaction between molybdenum,vanadium, and tellurium resulted in favored formation of an Anderson-type anions $[TeM_6O_{24}]^{n-}$, M=Mo,V;n $\geq$ 6 and protonated decavanadate species $[H_xV_{10}O_{28}]^{(6-x)}$.Raman analysis showed that the monomeric motif of the Anderson-type tellurate is preserved after addition of the Nb precursor and the crystallinity effect can be controlled by spray-drying process and heat treatment.

Several approaches have been implies to improve preparation of MoVTeNb oxide catalyst. A. Celaya Sanfiz et.al studied the role of the (011) crystallographic plane of M1 phase for selective oxidation of propane to acrylic acid by investigating phase- pure of M1 material. A model catalyst was prepared by complete silylation of M1, followed by breakage of the SiO2-covered needles. Using this approach, the reactivity of the M1 (001) surface was investigated by combining a microreactor study of propane oxidation with high-sensitivity low-energy ion scattering (HS-LEIS).SEM and TEM were used to study the shape and microstructure of the model system and verify the surface exposure of the model catalyst. The specific rate of formation of acrylic acid on the model catalyst was found to be similar to that on the phase-pure M1 reference material, indicating that the (001) plane of the M1 crystal structure did not have better catalytic properties compared with the lateral surface of M1 needles in propane oxidation (Celaya Sanfiz, Hansen *et al.* 2008).

Restu and his group studied the effect of diluents and reaction parameter on selective oxidation of propane to acrylic acid using high throughput nanoflow reactor. The effects of catalyst dilution and reaction parameters such as gas hourly space velocity (GHSV) and reaction temperature on the catalytic performance of the MoVTeNb mixed oxide catalyst in selective oxidation of propane to acrylic acid were also investigated. Based on the result, acrylic acid exhibited about 32.0 % and 14.5 % propane conversion at temperature 673 K. The results obtained provided very good reproducibility and it showed that preparation methods as well as reaction parameters can play significant roles in catalytic performance of these catalysts (Widi, Abdul Hamid *et al.* 2008).

Yu et.al reveal that proper chemical composition, calcination atmosphere and water content affect greatly the catalysts in many ways including structure, chemical composition, which are related to their catalytic performances; and 51.0% propane conversion and 30.5% one-pass yield to acrylic acid can be achieved (Yu, Zheng *et al.* 2009).

Alkaline earth (Mg, Ca, Sr and Ba)-doped Mo-V-Sb-Ox catalysts, prepared by a dry-up method, showed a good catalytic activity and selectivity to oxygenated products, particularly to acetic acid and acrylic acid, in the oxidation of propane. Among the alkaline earth metal doped catalysts, Mg (25.6 % AA) and Sr (34.4 % AA) doped catalysts showed promising catalytic performance in the oxidation of propane with good activity and selectivity to oxygenated compounds. The catalytic activity and product selectivities were found to be influenced by the reaction temperature, C_3H_8/O2 ratio and space velocity. A significant improvement in the selectivity to acrylic acid has also been observed by the addition of water vapor in the feed of propane and oxygen in the oxidation of propane (Chaudhari, Sable *et al.* 2010).

Work has been done by Frederik N.N and his groups which claimed that the performance of selective oxidation propane to acrylic acid have significant effect on concentration vanadium, tellurium and niobium. Catalysts containing M1 phase were obtained over the compositional range of $MoV_{0.14–0.22}Te_{0.1–0.2}Nb_{0.1–0.2}Ox$. Vanadium containing sites in the M1 phase are drastically more active for propane activation than in other materials studied. The catalytic activity is directly correlated to its fraction in the overall material and in particular the M1 phase. High concentrations of tellurium induce the formation of the M2 phase decreasing so the overall activity of the catalysts. The intrinsic activity of the M1 phase is, however, independent of the tellurium concentration. Although the presence of the M1 phase is not a stringent requirement for the oxidative dehydrogenation of propane to propene, it is required to oxidize the intermediately formed propene with high selectivity to acrylic acid. The active sites for propane activation and propene oxidation are structurally coupled, because the ratio between the rates of the two reactions was always 1:25. Oxygen defect sites in mixed oxides seem to enhance interaction with acrylic acid and lead to decarboxylation and total oxidation (Naraschewski, Praveen Kumar *et al.* 2011).

2.4 Catalyst Preparation of MoVTeNb mixed oxide catalyst.

2.4.1 Precipitation Method

The typical preparation of catalysts and support of complex metal oxides (CMO) is precipitation to obtain an aqueous precursor –slurry. Unfortunately, precipitation is usually more demanding than several other preparation techniques, due to the necessity of product separation after precipitation and the large volumes of salt-containing solutions generated in precipitation processes. Molybdenum oxide based catalyst is one of the examples for major synthesis using precipitation method. It is because low cost and it can be carried out industrially in large scale. Most of the precipitation processes are carried out above room temperature often close to 373K. With increasing the temperature, the energy of activation, the nucleation induction period and the critical supersaturation decrease. It is probable that the surface tension between the solution and the nucleus formed and hence the energy requirement of nucleation also decreases with increasing temperature. Therefore, a temperature increase might lead to decrease in crystal size as was observed in molybdate system.

Nevertheless, for several catalytically relevant materials, especially for support materials, precipitation is the most frequently applied method of preparation. However, in many cases not enough attention is drawn to the fact that the process of precipitation is crucially affected by a multitude of parameters, such as temperature, precursor and acid concentration or the nature of the counter cation. Reproducible results are only obtained if all these parameters are fully controlled. A large study recently showed that four different families of product can be obtained by just altering the parameters mentioned. Precipitation processes are not only relevant for catalysis, but also for other industries such as the production of pigments. However in spite of the tremendous importance of precipitation from solution, many basic questions in this field are still unsolved and the production of a precipitate with properties that can be adjusted at will is still rather more an art than a science. This is primarily due to the fact that the key step, nucleation of the solid from homogeneous solution, is a very elusive one, and is difficult to study using the analytical tools currently available. Thus, investigations of crystallization and precipitation processes from solution often have to rely on indirect and theoretical methods (Ertl G. 1997) . Figure 2.9 depict a general flow scheme for the preparation of a precipitated catalyst.

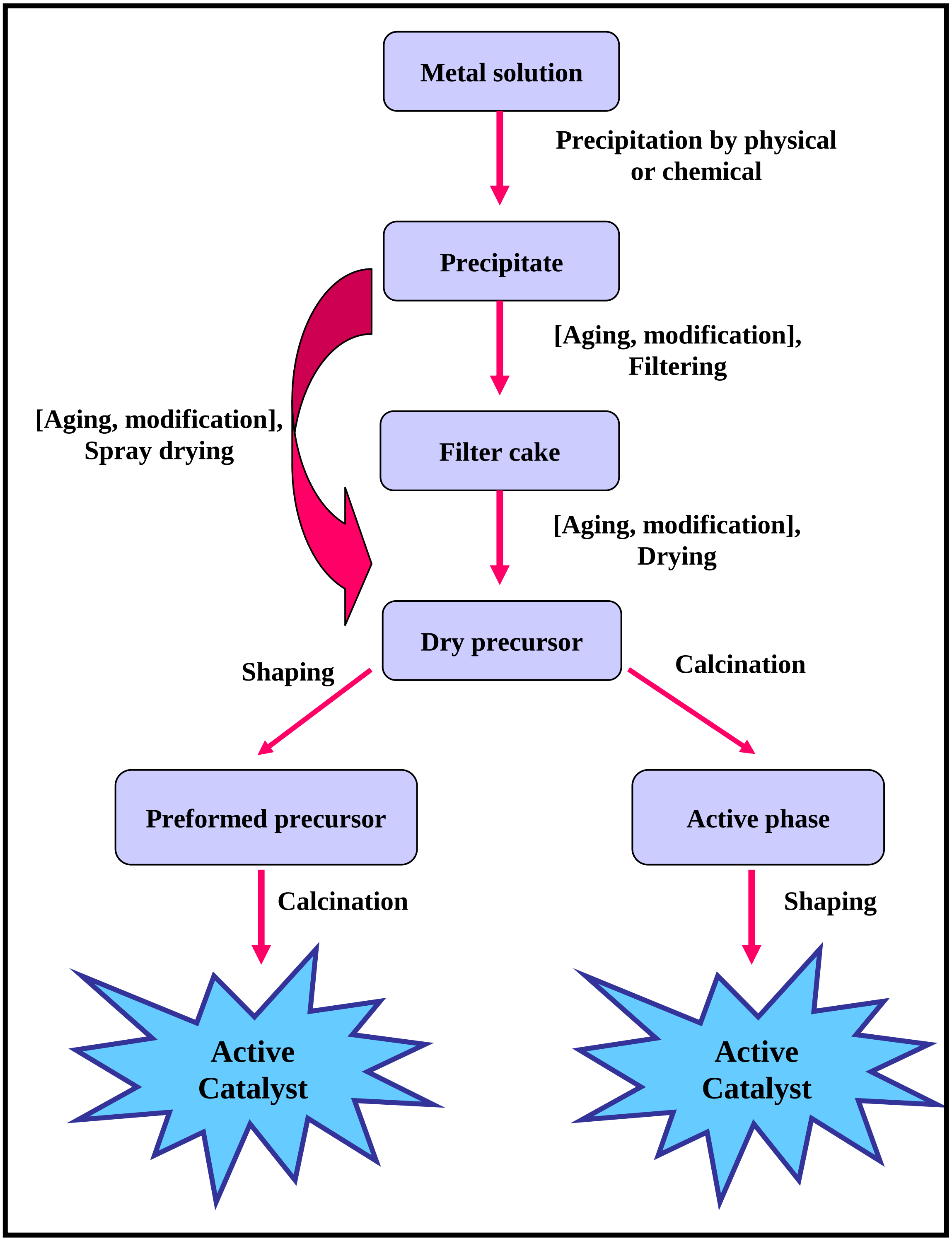


Figure 2.9: Preparation scheme for precipitated catalysts. Optional preparation steps are indicated by square brackets (Ertl G. 1997)

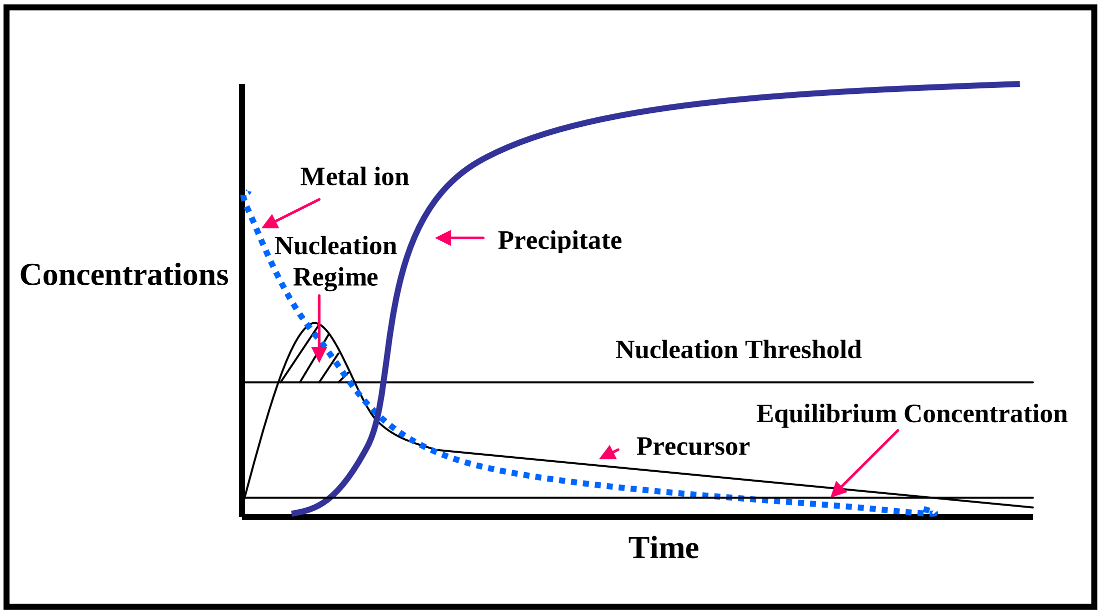


Figure 2.10: Simplified scheme for the formation of a solid product from solution (Ertl G. 1997)

The general process of the formation of a solid from a solution can be described in a simplified form as indicated in Figure 2.10. The most important curve is the nucleation curve which is described the development of the precursor concentration with time. The precipitation begins when the precursor concentration exceeds a critical threshold concentration will a nucleus form. The nucleus is defined as the “smallest solid-phase aggregate of atoms, molecules or ions which is formed during precipitation and capable growth in spontaneously. As long as the concentration of precursor species stays above the nucleation threshold, new particles are formed. As soon as the concentration falls below the critical concentration due to the consumption of precursors by nucleation or by the growth process, only particle growth of existing particles prevails. The size of the particles finally resulting from a precipitation process will be dependent on the area of the shaded area between the nucleation curve and the nucleation threshold. The larger the area, the more particles nucleate and the smaller resulting particles will be. The nucleation process is strongly temperature dependent. The uniformity in the final particle size distribution can be reached by size dependent aggregations rate. The supersaturation of the solution is one of the key factors of the precipitation process. It can be reached either by physical which is usually cooling down the reaction mixture, or evaporation of the solvent or by the chemicals means which is addition of a precipitating agent. The precipitating agent either changes the pH, thus leading to condensation of precursors to form the hydroxides or the oxides, or the additional ions into the system by which the solubility product for a certain precipitate is exceeded.

The ***nature of solvent*** also has considerable effect on the rate of re-crystalization. The solvent dissolves the amorphous parts of the precipitate, while deposition occurs on the nearest crystals. Hence, the more powerful the solvent for the given precipitate, the more rapidly the recrystalization may occur. For economic reasons water is the almost exclusively used as the solvent for precipitation processes (Omar 2005).

The current preparation routine for MoVTeNb oxide is the "slurry method" in which a mixture of solid and liquid phases (slurry) is dried and calcined. Such procedure is extremely undefined and will therefore lead to inhomogeneous material. Precipitation however, is a method that is much more understood and can be carried out in a much more controlled way. Basically all process parameters, some which are fixed and some are variable, influence the quality of the final product of the precipitation. These properties could be the nature of the phase formed, chemical composition, purity, particle size, surface area, pore sizes, pore volumes, separability from mother liquor, including the demands whish are imposed by the requirements of downstream processes like drying, palletizing or calcinations. It is necessary to optimize in order to produce the desired material. Figure 2.11 summarizes the parameters and its properties which are influenced in precipitation process.

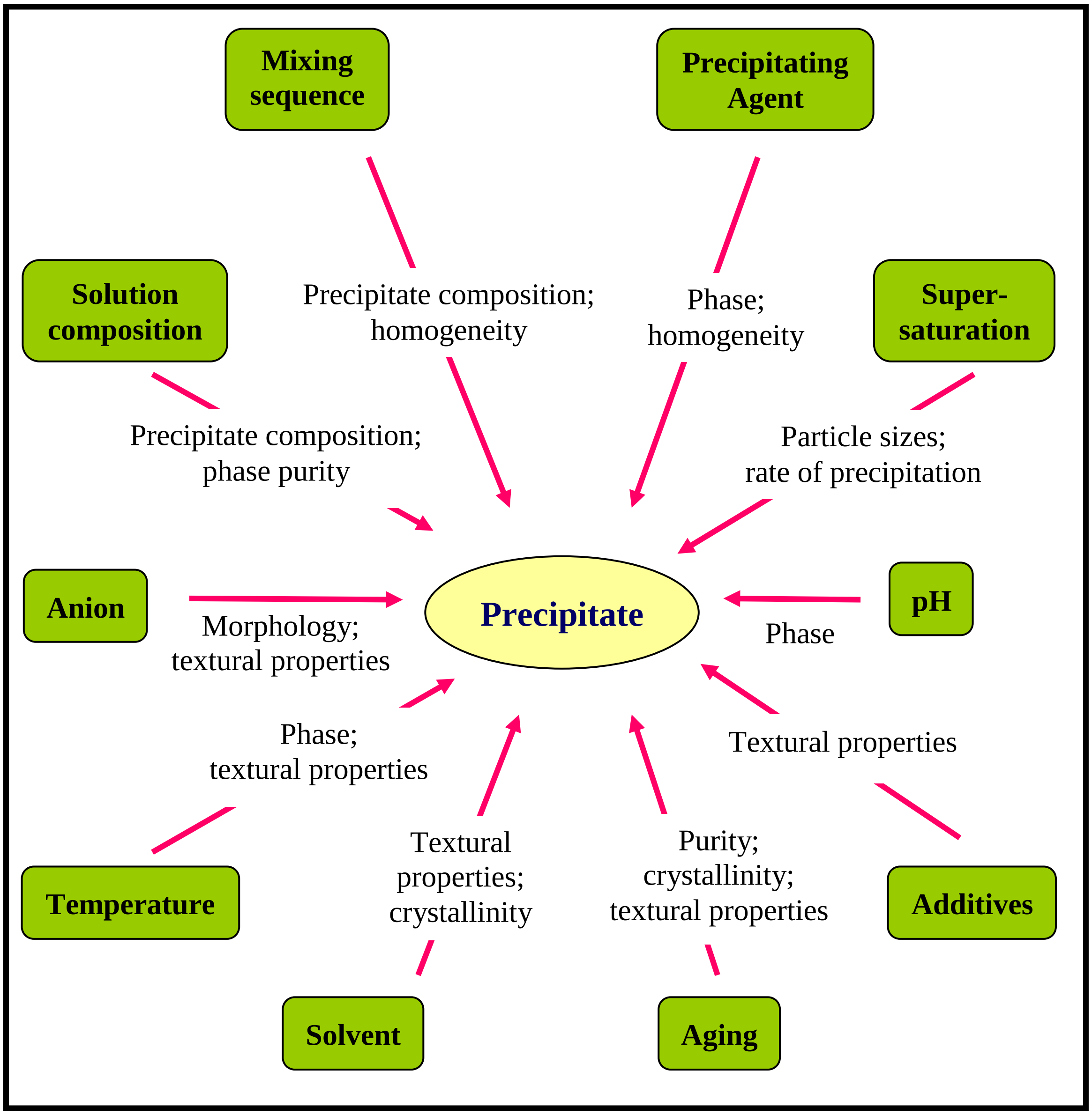


Figure 2.11: Parameters affecting the properties of the precipitate and main properties influenced (Ertl G. 1997)

F. Ivars and his group members have studied the influence of gel composition in the synthesis of MoVTeNb oxide catalyst. Chemical analysis indicates that the composition of samples before and after the heat-treatment changes, especially the Te-content, since a significant amount of Te is lost during the heat-treatment step when the amount of oxalate (from niobium oxalate) increases in the synthesis gel. Thus, the nature of the crystalline phases and the catalytic performance of heat-treated materials will be related to the final chemical composition. The catalysts active presenting as so called M1 phase, were active and selective in the partial oxidation of propane to acrylic acid (Ivars, Solsona *et al.* 2010).

Despite the effort expended in synthesizing and characterizing mixed metal oxides, only a few methods have been used to synthesize the MoVTeNb oxide catalysts. Many researchers proposed slurry (Ushikubu T, Nakamura H *et al.* 1995; Lin M and W 1999; P. Botella, B. Solsona *et al.* 2001; Botella, López Nieto *et al.* 2002; F. Ivars, B. Solsona *et al.* 2009) and hydrothermal (P. Botella, B. Solsona et al. 2001; J.M. Oliver, J.M. López Nieto *et al.* 2004; R. Feng, X.J. Yang *et al.* 2007; B. Deniau, J.M.M. Millet *et al.* 2008; F. Ivars, B. Solsona *et al.* 2009) methods are the most common options, microwave-assisted hydrothermal synthesis has been also proposed (N.R. Shiju and V.V. Guliants 2007). Ramli and coworkers reports the applicability of reflux to the synthesis of Mo–V–Te–Nb–O metal oxide catalysts. The well-formed and defined orthorhombic M1 phase, i.e. $Te_2M_{20}O_{57}$ (M= Mo, V, Nb), was found to be better developed when a longer time was used to reflux the mixed metal clusters. The catalysts efficient for propane selective oxidation to acrylic acid, reaching ca. 60% of selectivity to acrylic acid at propane conversion of ca. 50% and at a reaction temperature of 693 K. In addition, there is a clear parallel between redox and catalytic properties, suggesting that the reducibility of crystalline phases is a key factor in the partial oxidation of propane (Ramli, Botella *et al.* 2011).

2.4.2 Solidification on aqueous slurry solution

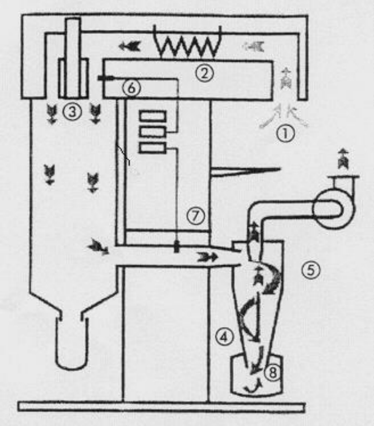
Drying of industrial catalysts is often a difficult and complicated procedure, during which both the physical structure and the catalytic properties may change considerably. Drying is usually performed with air between 60 and 200 ^{o}C. At higher temperatures gel particles undergo fragmentation and it may therefore become necessary to apply a further step. In many cases the desired pore structure and mechanical strength are achieved during drying. The drying procedure requires great care, technological precision, and in most cases, continuous and automatic control, in order to ensure the reproducibility of the prescribed physical and chemicals properties.

In preparation of MoVTeNb mixed oxide catalyst, several drying methods of removing water from the precursors mixture can be applied to form catalyst presursors such as freeze-dry, rotavap, rapidvap, spray dry and heat evaporation. For instance, in the freeze drying method, the aqueous mixture was turned under liquid nitrogen temperatures into a frozen solid coated onto the wall of a fast-freeze flask, which then dried under vacuum at 25-133 mbar to obtain a dry solid. In the rotavap method, water was removed in a rotary evaporator, generally performed at a bath temperature of about 40-60 ^{o} C and at reduced pressure of 10-40 mmHg. For rapidvap method, the aqueous was added to the flask in the Rapidvap apparatus and evaporated with agitation under a reduced pressure ~260 mmHg at 50 ^{o}C to obtain a dry solid. In the spray-dry procedure, a small lab spray-dryer with nitrogen as the carrier was used with an inlet temperature of 162 ^{o}C and outlet of 100-10 ^{o}C to result the powdery precursor solid. The last method is heat evaporation; the aqueous mixture was stirred in an open beaker while slowly heated in a water bath or on a hot plate until dry to obtain a precursor solid (Lin 2003).

Spray Drying Method

Drying method is very crucial in preparation of the solid precursor catalyst. From all method that mentioned above, spray dryer is the best method to obtain a homogeneous precursor catalyst. Because of the ability of the spray drying process to produce a free-flowing powder consist a spherical particle with a well-defined size distribution and the rapid drying times for heat-sensitive materials, spray drying is an attractive for a wide range of applications.

Spray drying is an established method that is initiated by atomizing/spraying a suspension of droplets followed by a drying process, resulting in the production of solid particles (K. Masters 1991). It is an efficient drying method due to the large surface area available for heat and mass transfer as a result of atomizing the liquid into very small droplets of the order of tens to hundreds of micrometers (M. Fareed 2003). Spray drying is successfully used in the pharmaceutical industry to produce products with defined physical and chemical properties. Spray drying produces particles by atomizing a solution or slurry and evaporating moisture from the resulting droplets by suspending in a hot gas. The production of dry, spherical particles from a liquid feed in single processing steps makes spray drying a unique and important unit operation. Figure 2.12 is a schematic of a spray dryer.



No	Function
1	Suction opening
2	Heating
3	Flow stabilized inlet to the drying chamber
4	Cyclone, the product is separated from the air current here
5	Aspirator
6	Temperature probe air inlet
7	Temperature probe air outlet
8	Collecting vessel for the finished product

Figure 2.12: Schematic diagram of spray dryer.

In a first step the solution or suspension is sprayed into a hot air stream. The formed droplets have a large surface in comparison to their volume. Since the heat transfer from the hot air to the liquid phase is proportional to the surface area, the temperature of the small droplets is raising much faster than it would do in one large drop of the same volume. This fact is important for the evaporation process: The higher the droplet temperature the faster the evaporation of the solvent takes place. Considering the droplet phase we will find an increasing temperature due to the heat transfer from the hot air over the phase boundary. As a consequence the evaporation rate will increase, too. On the other hand the energy for the evaporation of the solvent comes from the liquid drop. The drop temperature is decreasing and heat from the hot air is transferred to the droplet by convection due to temperature gradients. Finally the temperature of the gas phase is decreasing proportional to the mass of evaporated solvent.

2.4 Surface Modification Method on MoVTeNb Oxide Catalyst

2.4.1 Leaching

Leaching is one of the methods to remove of materials by dissolving them away from the solids. The separation usually involves selective dissolution, with or without diffusion, but in the extreme case of simple washing it consists merely of the displacement (with some mixing) of one interstitial liquid by another with which it is miscible. It can be omitted with many impregnated catalysts, but it is usually important with precipitates and gels . Leaching of precipitates is generally performed by stirring a suspension of the precipitate with water or even organic solvent with different time of leaching, temperature or concentration of the solvent. More specifically, a method for this preparation is by treating a calcined catalyst with an organic treating agent, and the use of the above catalyst as an oxidation catalyst in the preparation of oxidized hydrocarbons especially of acrylic acid. In this work, it will discuss the effect of the leaching with solvent to the MoVTeNbOx catalyst in order to see the catalytic performance of the catalyst.

2.4.2 Solvents Properties

The vast majority of chemical reactions are performed in solution. The solvent fulfills several functions during a chemical reaction. A solvent is a liquid that dissolves a solid, liquid or gases solute, resulting in a solution. The most common solvent in everyday life is water. The solvent provides a means temperature control, either to increase the energy of the colliding particles so that it will react more quickly, or to absorb heat which is generated during an exothermic reaction.

Generally a good solvent should meet the following criteria:

- It should be inert to the reaction conditions
- It should dissolve the reactants and reagents
- It should have an appropriate boiling point
- It should be easily removed at the end of the reaction.

2.4.2.1 Water

Protic refers to a hydrogen atom attached to an electronegative atom. In other words, polar protic solvents are compounds that can be represented by the general formula ROH. The polarity of the polar protic solvents stems from the bond dipole of the O-H bond. Examples of polar protic solvents are water (H_2O), methanol (CH_3OH) and acetic acid (CH_3CO_2H).

Water is relatively stable chemically. It ionizes only slightly, but will hydrolyze or react with a number of materials. It is stable at very high temperatures. Many reactions are catalysed by the addition of very small amounts of water, with corrosion or rust being an outstanding example. The water molecules in the liquid state are so strongly associated that a large amount of energy in the form of heat is needed to break loose a molecule into the gas state. As a result, the boiling point and heat of vaporization of water are very high for this low molecular weight material. Another property related to this internal attraction or association of molecules in a liquid is called surface tension. These properties are based on water being strongly associated and polar in nature. The polar nature of water is attributed to any non-symmetrical molecule schematically.

Water itself has only a slight tendency to ionize or split into oppositely charged particles. Many acids, bases and salts, however, ionize readily in water solution. Neutralization is the reaction of ions of acids and bases generating a salt and usually water. The process of ionization is important in the preparation and classification of surfactants. A positively charged particle is called a cation and a negatively charged particle is called an anion.

2.4.2.2 Nitric Acid

Nitric acid (HNO_3), also known as aqua fortis and **spirit of niter**, is a highly corrosive strong mineral acid. The pure compound is colorless, but older samples tend to acquire a yellow cast due to the accumulation of oxides of nitrogen. Most commercially available nitric acid has a concentration of 68%. When the solution contains more than 86% HNO_3, it is referred to as **fuming nitric acid**. Depending on the amount of nitrogen dioxide present, fuming nitric acid is further characterized as white fuming nitric acid or red fuming nitric acid, at concentrations above 95%. Nitric acid is also commonly used as a strong oxidizing agent.

A commercial grade of fuming nitric acid, referred to in the trade as "strong nitric acid" contains 90% HNO_3 and has a density of 1.50 g/mL. This grade is much used in the explosives industry. It is not as volatile nor as corrosive as the anhydrous acid and has the approximate concentration of 21.4 molar. Nitric acid reacts with most metals but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals. Magnesium, manganese and zinc liberate H_2. Others give the nitrogen oxides.[6]

It can oxidize non-active metals such as copper and silver. With these non-active or less electropositive metals the products depend on temperature and the acid concentration. For example, copper reacts with dilute nitric acid at ambient temperatures with a 3:8 stoichiometry.

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu^{2+} + 2\ NO + 4\ H_2O + 6\ NO_3^-$$

The nitric oxide produced may react with atmospheric oxygen to give nitrogen dioxide. With more concentrated nitric acid, nitrogen dioxide is produced directly in a reaction with 1:4 stoichiometry.

$$Cu + 4\ H^+ + 2\ NO_3^- \rightarrow Cu^{2+} + 2\ NO_2 + 2\ H_2O$$

Upon reaction with nitric acid, most metals give the corresponding nitrates. Some metalloids and metals give the oxides, for instance,Sn, As, Sb, Ti are oxidized into SnO_2, As_2O_5, Sb_2O_5 and TiO_2 respectively. Some precious metals, such as pure gold and platinum group metals do not react with nitric acid, though pure gold does react with aqua regia, a mixture of concentrated nitric acid and hydrochloric acid.

Being a powerful oxidizing agent, nitric acid reacts violently with many non-metallic compounds and the reactions may be explosive. Depending on the acid concentration, temperature and the reducing agent involved, the end products can be variable. Reaction takes place with all metals except the noble metals series and certain alloys. As a general rule, oxidizing reactions occur primarily with the concentrated acid, favoring the formation of nitrogen dioxide (NO_2). However, the powerful oxidizing properties of nitric acid are thermodynamic in nature, but sometimes its oxidation reactions are rather kinetically non-favored. The presence of small amounts of nitrous acid (HNO_2) can greatly enhance the rate of reaction.

2.4.2.3 Ammonia

Ammonia solution, also known as **ammonium hydroxide, ammonia water, ammonical liquor, ammonia liquor, aqua ammonia, aqueous ammonia,** or **simply ammonia**, is a solution of ammonia in water. It can be denoted by the symbols $NH_3(aq)$. Although the name ammonium hydroxide suggests a base with composition $[NH_4^+][OH^−]$, it is actually impossible to isolate samples of NH_4OH, as these ions do not comprise a significant fraction of the total amount of ammonia except in extremely dilute solutions.

In aqueous solution, ammonia deprotonates a small fraction of the water to give ammonium and hydroxide according to the following equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^−.$$

In a 1M ammonia solution, about 0.42% of the ammonia is converted to ammonium, equivalent to a pH of 11.63. The base ionization constant is

$$K_b = [NH_4^+][OH^-]/[NH_3] = 1.8×10^{−5}$$

Ammonia solution is also use as cleaning agent in household products. In industry, ammonium hydroxide is used as a precursor to some alkyl amines, although anhydrous ammonia is usually preferred.

In addition, ammonium hydroxide is also use in food additive as an antimicrobial. In the United States, ammonium hydroxide is classified by the Food and Drug Administration as generally recognized as safe (GRAS). Furthermore aqueous ammonia is used in traditional qualitative inorganic analysis as a complexant and base.