Selective oxidation for the production of chemicals

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Content of my lecture

• Example of catalytic heterogeneous vapor-phase oxidation of alkanes: n-butane to maleic anhydride

• Example of catalytic oxidation of biomass: the production of acrylic acid
What we mean for oxidation reactions?

1) **Insertion of oxygen** in organic molecules with formation selectively of aldehydes, ketones, peroxides, epoxides and acids and in inorganic molecules and CH\textsubscript{4} to produce oxides(NO\textsubscript{2},SO\textsubscript{2},CO ).

2) **Dehydrogenation** reactions with formation of olefins and water

- Ex CH\textsubscript{3}-CH\textsubscript{2}-CH\textsubscript{3} +1/2O\textsubscript{2}→CH\textsubscript{2}=CH-CH\textsubscript{3} +H\textsubscript{2}O

3) **Insertion of N, Cl and F** in organic molecules with NH\textsubscript{3}, HCl, HF and O\textsubscript{2} and formation of o nitryles, oximes, organic chlorine and organic fluorine compounds.
TYPES OF OXIDATION INDUSTRIAL PROCESSES

• 1) Oxidation in vapor phase with heterogeneous catalysts with oxygen or air.

• 2) Oxidation in liquid phase with homogenous catalysts with oxygen, air, hydrogen peroxide or hydroperoxides.

• 3) Oxidation in liquid phase with heterogeneous catalysts with oxygen, air or hydrogen peroxide.

• In conclusions four oxidants are used: Oxygen, Air, H₂O₂, and Hydroperoxides
To operate at low or at high temperature?

- Low temperature – liquid phase

  - 1.1 **Unstable products**: aldehydes, acids, hydroperoxides, epoxides and ketones must be synthesized at low temperature with the exception of formaldehyde and ethylene oxide.

  - 1.2 **Unstable reagents** (products of fine chemicals) molecules with more functional groups.

- High temperature vapour phase

  - 2.1) **Stable products**: anhydrides, nitriles, acids and aldehyde alfa insature with heterogeneous catalyst.

  - 2.2) **Unstable products** can be obtained in vapour phase with very low contact time (milliseconds).

    \[
    \text{Styrene} + \frac{1}{2}\text{O}_2 \rightarrow \text{styrene epoxide at } 280^\circ\text{C}
    \]
Raw materials in catalytic oxidation reactions

- Olefins
- Alcohol
- Aromatics
- Alkanes
- Biomass (sugar, glycerol)
Commercial and under development processes with alkanes

- Methane to syngas
- Methane to formaldehyde
- Ethane to acetic acid
- Ethane to vinyl chloride
- n-Butane to maleic anhydride
- Propane to acrylonitrile
Processes under research

- Propane to acrylic acid
- Isobutane to methacrylic acid
- n-Pentane to maleic and phthalic anhydride
- Alkanes oxidative dehydrogenation to olefins
- n-Hexane or cy-Hexane to adipic acid
Advantages in the use of alkanes as alternatives to the use of olefins or aromatics

- Lower cost
- Less toxic or noxious reactants: example: n-butane alternative to benzene
- Replacement of energy-intensive processes
  Example: oxidative dehydrogenation: alternative to dehydrogenation or steam-cracking for the production of olefins
Discovery of new crystalline phases

• The most important advancements in light alkanes oxidation have been achieved with the discovery of new crystalline structures, exhibiting the specific ability to activate alkanes and selectively transform them. These structures have the following features:

• Site isolation
• Multifunctionality
• Acid sites
How to face transformation of an alkane?

Site isolation
specific crystalline structures

Multifunctionality
cooperation of sites

Acid-base properties

alkane

[alkane] → [olefin] → [oxygenated]

CO_x
The most important properties of catalysts

1) **multifunctional properties**, with cooperation between elements playing different roles in the complex mechanism of alkane transformation;

- 2) *site isolation*, or isolated ensembles of sites, to perform selective oxidation and avoid overoxidation;

- 3) **specific acid** properties to let more easy the desorption of products (in some cases at least)
THE KEYS PROPERTIES OF A CATALYST

1. in general the presence of vanadium
2. isolation of the active sites
3. stability of the reaction products
4. multifunctionality of the catalyst
5. formation of alkenes as reaction intermediates
6. control of the relative rates of surface H-abstraction and O-insertion, and of redox versus acid sites reactivity
7. absence of desorption of intermediates

n-Butane selective oxidation to maleic anhydride
The active and selective catalyst: 
(VO)$_2$P$_2$O$_7$

The first successful "multifunctional" catalyst for alkanes transformation

development of the precursor, VOHPO$_4$0.5H$_2$O
thermal treatment (air, nitrogen, mixed feeds)

2 (VO)HPO$_4$0.5H$_2$O $\rightarrow$ (VO)$_2$P$_2$O$_7$ + 2H$_2$O

Morphology: tablets, microspheroidal particles
Dopants
oxidative dehydrogenation

allylic H-abstraction

1,4-O-insertion

allylic H-abstraction or O insertion

allylic O insertion or electrophilic O insertion
The multifunctional properties of the vanadyl pyrophosphate

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>isobutyric acid</td>
<td>methacrylic acid</td>
<td>oxidehydrogenation</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>benzene</td>
<td>oxidehydrogenation</td>
</tr>
<tr>
<td>hexahydrophthalic anhydride</td>
<td>phthalic anhydride</td>
<td>oxidehydrogenation</td>
</tr>
<tr>
<td>paraffin</td>
<td>olefin</td>
<td>oxidehydrogenation</td>
</tr>
<tr>
<td>olefin</td>
<td>diolefin</td>
<td>allylic oxidation (H–abstraction)</td>
</tr>
<tr>
<td>2,5–dihydrofuran</td>
<td>furan</td>
<td>allylic oxidation (H–abstraction)</td>
</tr>
<tr>
<td>tetrahydrophthalic anhydride</td>
<td>phthalic anhydride</td>
<td>allylic oxidation (H–abstraction)</td>
</tr>
<tr>
<td>benzene</td>
<td>maleic anhydride</td>
<td>electrophilic oxygen–insertion</td>
</tr>
<tr>
<td>butadiene</td>
<td>furan</td>
<td>electrophilic oxygen–insertion</td>
</tr>
<tr>
<td>naphthalene</td>
<td>naphthoquinone</td>
<td>electrophilic oxygen–insertion</td>
</tr>
<tr>
<td>furan</td>
<td>maleic anhydride</td>
<td>electrophilic oxygen–insertion</td>
</tr>
</tbody>
</table>

The structure of (VO)$_2$P$_2$O$_7$
Some reviews on V/P

• Anatomy of a catalyst: vanadyl pyrophosphate, \((\text{VO})_2\text{P}_2\text{O}_7\), for the selective oxidation of n-butane to maleic anhydride

• By Centi, Gabriele; Trifirò, Ferruccio

• From Chimica e l'Industria (Milan, Italy) (1986), 68(12), 74-81.

• A review with 62 references
Some reviews on V/P

- Mechanistic aspects of maleic anhydride synthesis from C4 hydrocarbons over phosphorus vanadium oxide
- By: Centi, Gabriele; Trifiro, Ferruccio; Ebner, Jerry R.; Franchetti, Victoria M. Chemical Reviews (1988), 88(1), 55-80
- (together with Monsanto)
- A review with 188 references.
Some reviews on V/P

• VPO catalyst for n-butane oxidation to maleic anhydride: A goal achieved, or a still open challenge?

• Topics in Catalysis Vol. 38, Nos. 1–3, July 2006 (2006) 147

• N. Ballarini, F. Cavani,*, C. Cortelli, S. Ligi, F. Pierelli, F. Trifiro`, C. Fumagalli, G. Mazzoni, and T. Monti

• (together with Lonza)

• a review with 156 references
Some reviews on V/P

- Vanadium Phosphate Materials as Selective Oxidation Catalysts
  - N. F. Dummer, J. K. Bartley, and G. J. Hutchings
  - Advances in Catalysis, Vol. 54 2011
  - a review with 309 references
How was the yield in maleic anhydride improved, over the years?

1) I shall speak on some parameters which influence the catalytic behavior of V/P mixed oxides in the oxidation of n-butane to maleic anhydride.

2) I shall not use informations from scientifical literature.

3) I shall take only data from patents.
The reasons of my choice

1) In the patents there is lesser contradictions of the role of the several parameters important for the preparation of an optimal catalyst

2) In the industry, the driving forces for innovation are due to factors not easy to evidence in academic laboratories and therefore in scientific papers and therefore reported in the patents such as:

- the life of catalyst
- the pressure drop and density of catalyst
The reasons of my choice

- the environmental problems
- the safety problems
- the quick time on stream of the catalyst
- the short time of preparation of the catalyst
- innovation claimed for 1 or 2 points of increase of yield
What is considered as “Prior art” in the recent patents

• Method of preparation of the active catalyst in two stages

• 1) Preparation of (VO)HPO$_4$ 0.5 H$_2$O the precursor, isolation of precipitate and drying and shaping

• 2) Transformation of the precursor to VO$_2$P$_2$O$_7$ (the active phase) by thermal treatment (calcination) and formation as coproducts VO(P0$_3$)$_2$ and/ or VOPO$_4$
How the yield in maleic anhydride was increased in Monsanto

1) In Monsanto patent Appl. B (1975), US 330354 15 from a yield of 30% they arrived at a yield of 43% by pelletizing the precursor (the innovation) not the active phase as previously with change of internal porosity from 30% to 53%
2) Second improvement in Monsanto patent

Eur. Pat. (1981), Appl EP 39537 A1 they arrived from 44% to a yield of 54% by reducing $V_2O_5$ in the preparation of precursor with isobuthanol (the innovation) instead with HCl
Other well agreed points in n butane oxidation

1) Nowadays due to other further innovations the yields are arrived from 54 to 65% at n-butane conversion of 80–85 mol%].

2) The presence of parallel reactions of n-butane combustion and of oxidative degradation to acetic and acrylic acids. These are characterized by higher activation energies with respect to the main reaction.

3) The presence of consecutive reactions of combustion, which lower the selectivity to MA when the alkane conversion is increased after 70%
Evolutions of patents in Lonza (Polynt)
Catalyst 1 reference 1990
Catalyst 2 E pat 804963 (1997)
hydrothermal preparations: optimization of the transformation of the precursor to the active phase.

• Catalyst 3 WO pat 6072963 (2000) reduction with alcohol and poliol: avoiding the residues of organic compounds inside the catalyst.

• Catalyst 4 E pat 1914398 (2005) addition of Nb as promoter.
Development of catalyst along the years in Lonza (Polynt)
Problems in calcination of the precursor

• One of the most critical steps in the catalyst preparation is the calcination procedure i.e. the transformation of the vanadyl hydrogen phosphate precursor into the active catalyst substantially containing vanadyl pyrophosphate
Calcination of the precursor in prior art Catalyst 1

- a) preparation of the precursor
- b) transformation of the vanadyl hydrogen phosphate precursor into the active catalyst substantially containing vanadyl pyrophosphate by calcination realized in air at 350°C and after in nitrogen a 550°C
- c) and finally ageing of the active catalyst under reaction conditions
Innovation in Cata 2 (1997)

- Hydrothermal activation
- The activation takes place in a fluidized bed with a precursor jet with optimal size
- by the following steps:
  - (a) initial heating of the precursor;
  - (b) further heating and isothermal stage heating steam/air and in steam/nitrogen
  - (c) cooling the activated catalyst.
Innovation in calcination

- $V_2O_5$ (in isobuthanol) was added to $H_3PO_4$ (in isobuthanol), water is removed in reaction, to form precursor.
- Calcination of the precursor in hydrothermal condition in fluid bed,
- precursor was heated 25-180° in air at 4°/ min,
- heated 180-425° in air/steam at 1.5°/min,
- heated at 425° for 2 h,
- heated at 425° for 3 h in $N_2$/steam,
- and cooled in $N_2$/steam at 2°/min to ambient to give an activated catalyst.
Development of catalyst along the years in Lonza (Polynt)
A process for the preparation of the precursor is described, comprising the reaction of a vanadium source in selected org. media in the presence of a phosphorus source. The organic medium comprises:

(a) iso-Bu alc. or a mixt. of iso-Bu alc. and benzyl alc.
and (b) a polyol in the wt. ratio (a) to (b) of 99:1 to 5:95.
Optimal Composition of alcohols

Most preferred polyols are the C2-4 alkanediols 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol. The preferred mixture of alcohols contains 5 to 30 mol% of polyol with respect to isobutyl alcohol.
A major disadvantage of the prior art

(i) strongly adsorbed organic compounds at the solid surface, and therefore not easily removable by the washing and drying treatment,

or (ii) physically trapped in between the crystals of the precursor,

or (iii) physically or chemically trapped ("intercalated") in the crystalline structure of the precursor
Major disadvantages of the prior art method

It has been found that this percentage of organic compound which remains trapped in the precursor is a fundamental parameter which can adversely affect the performance characteristics of the active catalyst obtained after the thermal treatment.
Advantages of addition of polyol

Advantages of this new activation procedure is better control of ratio V4+ /V5+. The catalyst is yet activated and does not require period of aging during the oxidation process, and this is an advantage for catalyst introduced as make-up in fluid bed. And therefore the catalysts present minor variation of catalytic performances and it is stable for the beginning. Beside the catalyst presents higher crystallinity with higher exposure of the 100 crystal face.
Niobium as promoter

- The catalyst comprises niobium as a promoter element in an amount corresponding to an atomic ratio of vanadium to niobium in the range of 300:1 to 10:1. The catalyst exhibits improved activity, improved yield of maleic anhydride, and optimal performance from the very beginning of its catalytic lifetime.
addition of Nb as promoter

1) providing a reaction mixture comprising a vanadium source, a niobium source, a phosphorus source, an organic medium capable of acting as a solvent and a reducing agent, and an additive selected from the group consisting of benzyl alcohol and a polyol

2) Calcination realized in hydrothermal conditions
Nature of invention

• They found that a positive effect both on the activity of the catalyst and on its selectivity to maleic anhydride can be obtained by promoting the VPO catalyst with very low amounts of Nb. The positive effect is obtained by combining a specific method of preparation of the precursor. The niobium is added to the precursor with a specific thermal treatment to transform it into the active catalyst vanadyl pyrophosphate.
Results

• Comparative NoNiobium 424°C Conv 80% yield sel 59%

• Example of innovation with Niobium V/Nb 160

• 404°C conv 81% yield % select 67%
Silver vanadium phosphates and their use in as catalysts in butane oxidation to maleic anhydride

The invention relates to a silver vanadium phosphate of formula $\text{Ag}_a \text{V}_1 \text{P}_b \text{M}_c \text{O}_d$, where M is at least one element selected from the group consisting of Li, Na, K, Rb, Cs, Mg, Ca, Al, Ga, Si, Nb, Co, Cu and Zn;
$\text{Ag}_a \text{V}_1 \text{P}_b \text{M}_c \text{O}_d$, the new catalysts

- $a$ is 0.7-1.3;
- $b$ is 0.8-2.0;
- $c$ is <0.25;
- $d$ is 3.85-8.375 and indicates the no. of O$^{2-}$ ions in the formula which are required to achieve elec. neutrality given the oxidn. state and abundance of the elements other than oxygen.
A new compound

• The calcined crushed material had an average oxidation state of vanadium of +4.17. An X-ray powder diffraction pattern was recorded on the powder obtained, with the strongest reflections of AgVPO$_{5.05}$.
Parameters of preparation which influence the catalytic behaviour

1) The method of preparation of the precursor \((\text{VO})\text{HPO}_4 \cdot 0.5\text{H}_2\text{O}\)
2) The method of transformation of the precursor to the active phase \((\text{VO}_2\text{P}_2\text{O}_7)\)
3) The presence of promoters
4) The methodology of insertions of promoters
5) The use of a support
6) The ratio P/V
7) The composition of reaction mixture
8) The type of reactor used (the morphology of the catalyst)
Factors which influence the catalytic behaviours

Data present in the patents

• Surface area, porosity, density, thermal conductivity
• Presence of other phosphate together with VO$_2$P$_2$O$_7$
• The ratio V$^{4+}$/V$^{5+}$

Data not present in the patents but in scientifical literature

• Acidity (Bronsted and/ or Lewis)
• Redox properties
• Presence of amorphous species
The several routes from biomass to acrylic acid

In one or more steps
Main objectives

• To produce products with the prefix bio
  To decrease greenhouse gas emission
• To reduce toxic wastes and by-products
• To use renewable raw materials
• To use wastes and coproducts from biorefineries
• To have an additional gain for the agriculture
The mechanism of formation of acrylic acid

- Propylene
- Acrolein
- Glycerol
- Acrylic acid
- Polyacrylic acid
- Acrylate esters
From glycerol to acrylic acid

• It is necessary to have a dehydration and a redox catalyst.

Glycerol -------> Acrolein ---> Acrylic acid

• The different solutions
• 1) A multifunctional catalyst in one reactor
• 2) Two beds of different catalysts in series in the same reactor
• 3) Two reactors with different catalysts in series (in tandem)
From Acrolein to Acrylic Acid

- Well established industrial process
- Exothermic
- Redox catalyzed
- 90% selectivity
- THE ACTUAL INDUSTRIAL CATALYST

\[(\text{MoWV})_5\text{O}_{14}\]
Oxydehydration of glycerol to acrylic acid in one step

- At 280°C N<sub>2</sub>/ O<sub>2</sub>/ H<sub>2</sub>O /Glycerol 72/6/19/3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Yield %</th>
<th>Acrolein</th>
<th>Acrylic Acid</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo&lt;sub&gt;3&lt;/sub&gt;VO</td>
<td>100%</td>
<td>3</td>
<td>26.3</td>
<td>23.5</td>
<td></td>
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<tr>
<td>MoVNbTe</td>
<td>99.6</td>
<td>1.7</td>
<td>28.4</td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>W&lt;sub&gt;3&lt;/sub&gt;VO</td>
<td>100</td>
<td>0.1</td>
<td>23.7</td>
<td>23.2</td>
<td></td>
</tr>
</tbody>
</table>

- They observed after 30 hours a slight deactivation of the catalysts

- J. Deleplanque, J.L Dubois, W Ueda and others, Catalysis Today 2011 157, 351-358
Glycerol to acrylic acid-in one step with a multifunctional catalyst

Catalyst Mo/ W/ V/ Nb with an hexagonal tungsten bronze structure prepared hydrothermally

- At 290° C, with 2% glycerol, 4% O₂, 40% H₂O 54%He.
- Conversion glycerol 100%
- Selectivity acrylic acid 34%
- Selectivity acrolein 18%
- From 5 to 100 h on stream the catalyst presented only small deactivation of acrylic acid yield and a small increase of acrolein yield.

Hexagonal Tungsten Bronzes (HTB): Synthesis and W-substitution

Hydrothermal synthesis

\[(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O\]

\[ VOSO_4 \cdot xH_2O \]

\[ Nb \text{ oxalate} \]

\[(NH_4)_6Mo_7O_{24} \cdot 4H_2O\]

Heat-treatment 600°C (-NH$_3$)

**Substitution of W-atoms for:**

1. Vanadium
2. Niobium & Vanadium
3. Molybdenum & Vanadium

Tungsten

Acid-sites (B)

Oxygen

H$^+$
Properties of the catalyst for one pot synthesis of acrylic acid from glycerol

- Acid and redox sites are in the same structure
- Defective W creates acid sites and Niobium increases the number of strong acid sites which favors acrolein formation but they are also active in polymerization of acrolein
- Lewis sites are negative leads to by-products and later to heavy compounds'
- Vanadium creates redox sites for oxidation of acrolein to acrylic acid
Improvements of one pot synthesis with multifunctional catalyst

- By increasing the oxygen and the glycerol concentration increases the yield in acrylic acid
- At 265 °C 6% glycerol, 12% oxygen, 40% H₂O, 42% helium
- Catalyst Mo/V/W/Nb tungsten bronze
- Conversion glycerol 100%
- Yield acrylic acid 50.5%
- Yield acrolein 5%

A Cherigato F Cavani, J Lopez Nieto et al. Applied Cataysis B Environmental 2014 150-151, 37
Glycerol to acrylic acid in one step

• Glycerol transformation to acrolein W NbO catalyst with addition phosphoric acid acrolein yield of 81.8%,

• Direct transformation of glycerol to acrylic acid with WVNbO catalyst activated with phosphoric acid gave acrylic acid yield of 59.2%.

• S. Ishikawa W. Ueda Chemistry Letters 2014 4
Two catalysts in one reactor
From glycerol to acrylic acid in two reactors in tandem

- Nippon Skokubai in 2009 has realized a pilot plant to produce acrolein from glycerol with a new acid catalyst and as second step the conventional oxidation catalyst of acrolein to acrylic acid that they had.

- The plant had to be built together with Arkema in 2010 but it is not yet builded.

- The yield in acrylic acid they obtained was from 80 to 90%.

- Chemical Engineering 2009 116,10,14
Two catalysts in series in one reactor

• 10% glycerol concentration in water and air at 300 °C

• First step  Conversion 100% selectivity to acrolein 81 % medium pore zeolites (HZSM-5).

• Second step  The catalyst V–Mo–O (45% V) with yield 48% acrylic acid, selectivity 98% at 300°C.

• A Witsuthammakul et al. Applied Catalyisi A 2012, 413-414, 109
Glycerol to acrylic acid in two steps in one reactor

• At 305 °C 3mml gycerol, 3mml 02, and water
• First step dehydratation: WOx/ZrO₂ (one monolayer) conversion glycerol 99.8 %yield acrolein 77.4%
• Two consecutive catalysts in one reactor :: W/Zr + WVMo(Commercial) conversion100 % acrylic acid 44.1 % acrolein 7.8%
• Massa, A Anderson G Busca et al .J Catal 2013, 297,93
Two catalysts beds in the same reactor

- **Acid catalyst** $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ supported on $\text{Nb}_2\text{O}_5$
- **Oxidation catalyst** V-Mo mixed oxide supported on CSi
- The catalyst is stable for 70h
- Coke can be eliminated by calcination at 500°C without deactivation of the catalyst

Two beds in the same reactor

1) In two separate beds in series
   - At 300 °C with H₂O/glycerol = 23
   - O₂/glycerol = 12.5
   - 100% conversion with 75% yield in acrylic acid after 25 hours (time on stream)

2) In one bed with the catalysts mixed yield
   - acrylic acid 25% yield acrolein 13%

Two different beds of catalysts in one reactor from glycerol to acrylic acid

First step
- Dehydration catalyst: \((H_4SiW_{12}O_{40}/Al_2O_3)\)

Second step
- Oxidation catalyst: \((Mo_3VOx)\)
  - calcined at 450°C

L. Liu et al. Applied Catalysis Environmental 2015, 174-175, 1
Two catalysts in one reactor

At 300°C and N₂/ O₂/ H₂O/ glycerol mola ratio of 59/4.2/35.1/1.7

• 1) Only Dehydratation catalysts: SiW/Al₂O₃
  • Conversion 100% Selectivity acrolein 54.3%

• 2) Two consecutive steps in one reactor
  • Conversion 100% selectivity to acrolein 3%,
  • Selectivity acrylic acid 62%

• Liu Applied Catalysis Environmental 2015 174 - 175
From glycerol to acrylic acid in three steps, in two reactors

• Preparation in three steps

• 1) **Dehydratation of glycerol** at 320° C with WO₃ - ZrO₂
  – Inlet 34.5% glycerol, 34.5%H₂O, 23.7% N₂, 7.2%O₂
  – Outlet 47.5%H₂O 23.7%N₂ 5%O₂ 16.4% acrolein

• 2) **Purification of acrolein** at low temperature

J-L Dubois and G- Patience to Arkema US 8.2012070 B2
From glycerol to acrylic acid in three steps reactors

3) Oxidation of acrolein to acrylic acid
   – At 245°C with W-M.V.O based catalyst
   – Inlet 39.9%N₂ 27.2 acrolein, 8.4 %O₂
     16.2H₂O
   – Outlet 59.1%N₂ 13.1%H₂O 14.7% acrylic acid,
     2.8 % O₂  Yield about 80%

• J-L Dubois and G- Patience to Arkema US
  8.2012070 B2
From glycerol to acrylic acid in three steps reactors

3) Oxidation of acrolein to acrylic acid
   – At 245 with W-M.V.O based catalyst
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• J-L Dubois and G- Patience to Arkema US 8.212070 B2
From 3 hydroxypropionic acid to acrylic acid

• Previous purification of the acid from fermentation brod
• Dehydration of 3-hydroxypropionic acid to acrylic acid at 300° C with bentonite activated (F-24 from Basf/) (Si Al Mg H )
• 89 % yield in acrylic acid

• D Decoster et al  OPX Biotechnologies Inc
• WO 2013192451 A1
Dehydration of lactic acid to acrylic acid

- With calcium hydroxyapatite with Ca/P 1.3
- At 375°C 50% lactic acid in water in N2
- Conversion 100% selectivity 60%
- Selectivity high with strong acid sites and low with basic sites. Side reaction decarboxylation of lactic acid to acetaldehyde

V.C. Ghantani et al Greem Chem 2013 15, 1211
Conclusions acrylic acid from biomass

One step yield 59% WVNb (H3PO4) Ueda
One step yield MoV W Nb 50% Cavani-Lopez Nieto
Two steps yield 75% Cs H PW + VMo Liu
Two steps yield 44% WZr+WVMo Anderson
Two reactors yield 80-90% acid cata + (VWMO) Nippon Skokubai

From 3-hydroxypropionic acid yield 89% OPX Biotec
From lactic acid yield 60% Ghantani
Conclusions

• 1) Oxidation catalysis is always important also in the transformation of biomass feedstock's.
• 2) It is possible to use the similar catalysts but with different promoters and/or supports,
• 3) but also some time with different structure where is necessary to have acid site near oxidation sites
• 4) but also it is necessary to have sites lesser reactive
• 6) and very likely it is necessary to use different reactors owing to the deactivation problems.