1st Spain-Japan Joint Workshop on "Nanoscience and New Materials"

Ordered Porous Materials as heterogenous catalysts and adsorbents

Fernando Rey

Institute of Chemical Technology ITQ - Valencia

Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

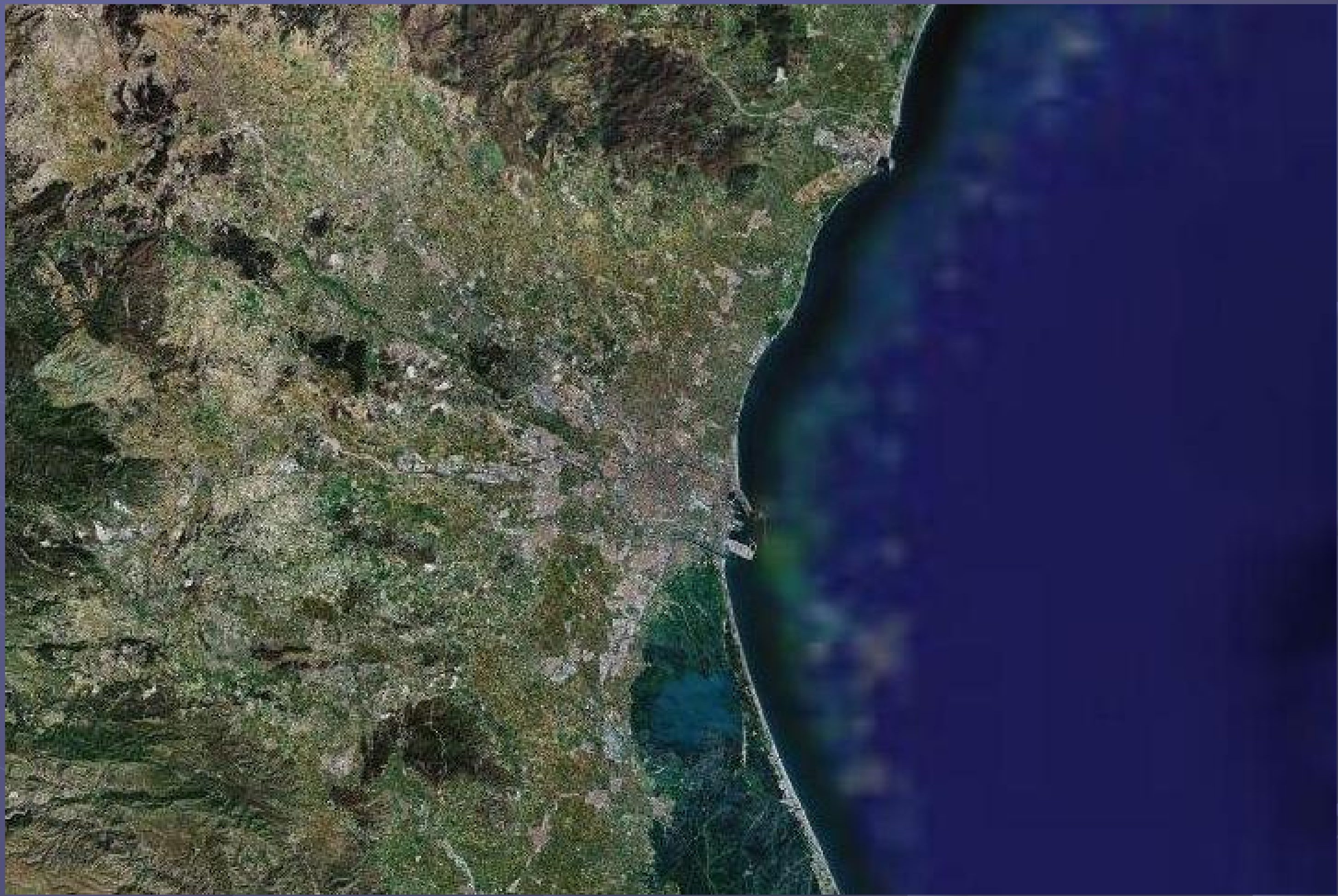
Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials



Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

Spanish Groups Working on Ordered Porous Materials

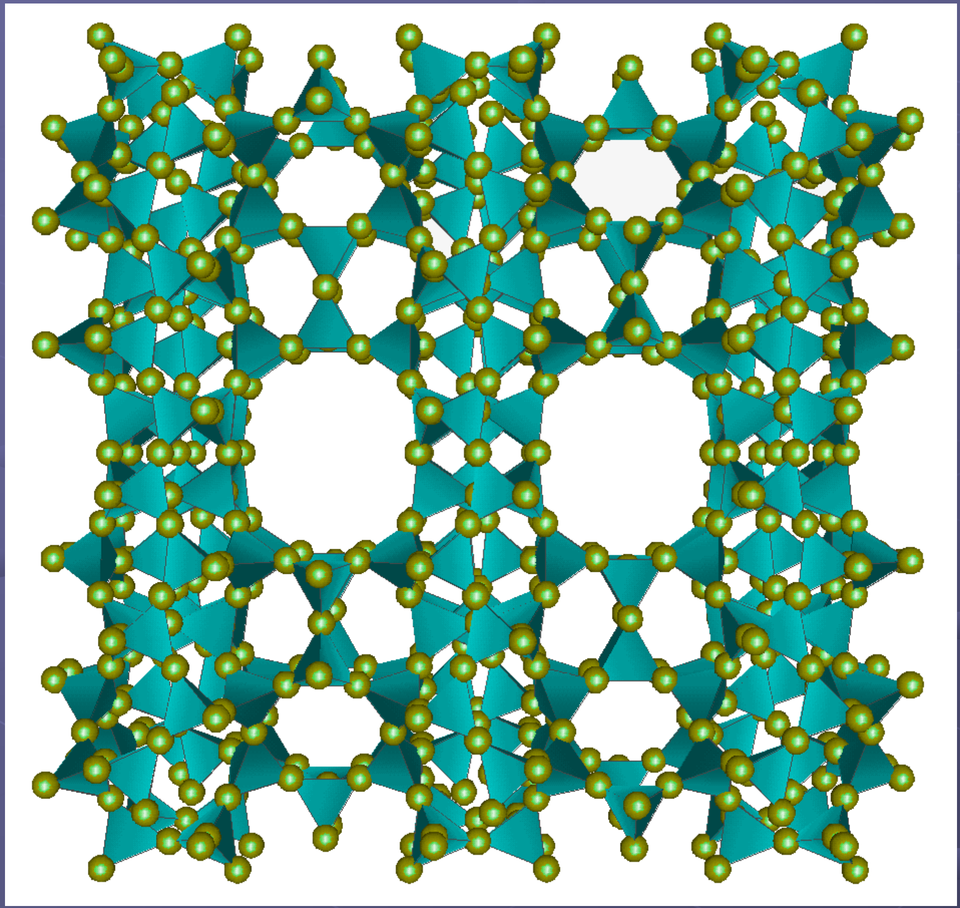
Outline of the Presentation

- **Zeolites**
- **Natural Gas Upgrading**
- **Olefin Production**

Outline of the Presentation

- **Zeolites**
- **Natural Gas Upgrading**
- **Olefin Production**

Zeolites

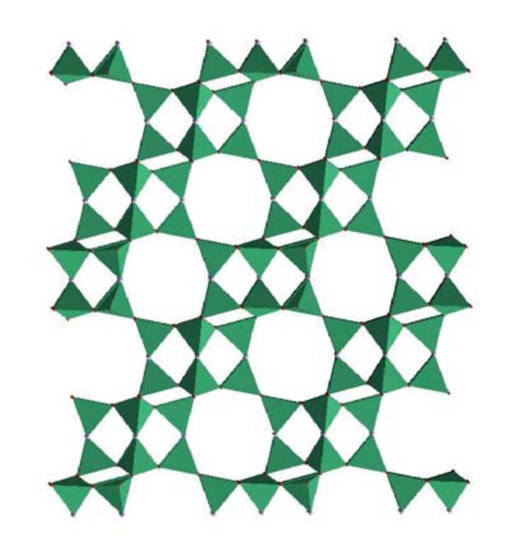
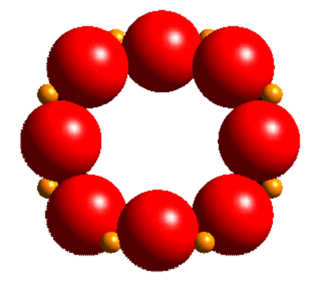


Structure of Zeolite EU-1

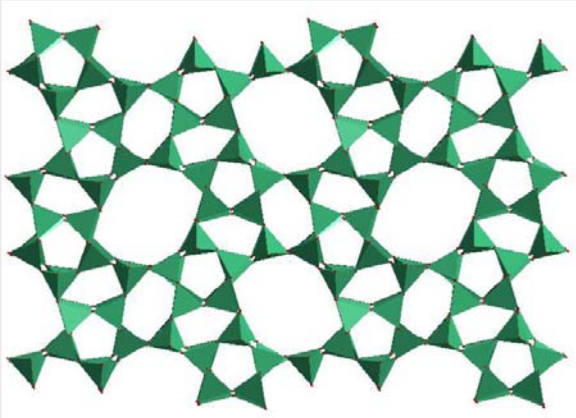
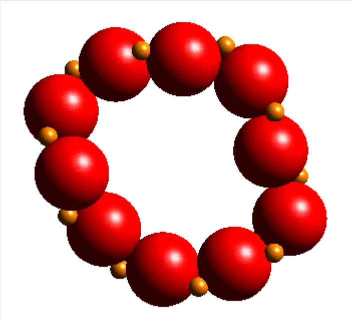
Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves."

The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter, formed or get out of the pores of a zeolite is controlled by the dimensions of the channels

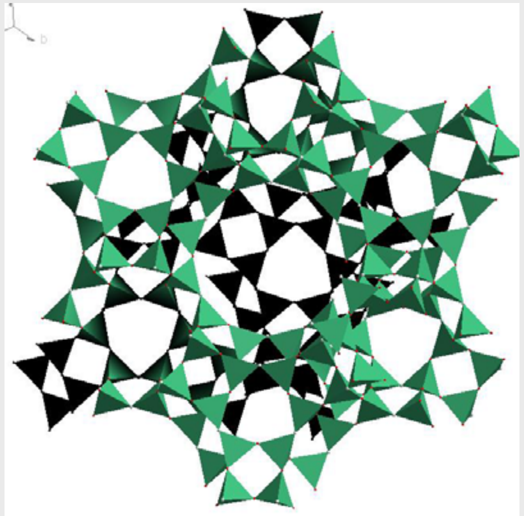
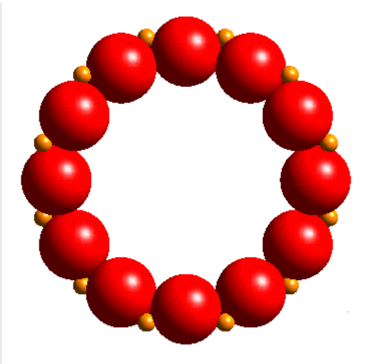
Zeolites

Chabazite
8 TO_2
3.8 x 3.8 Å

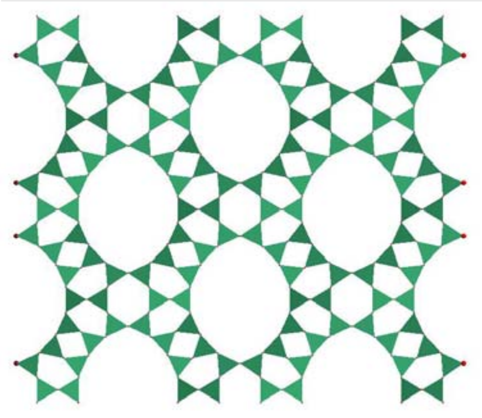



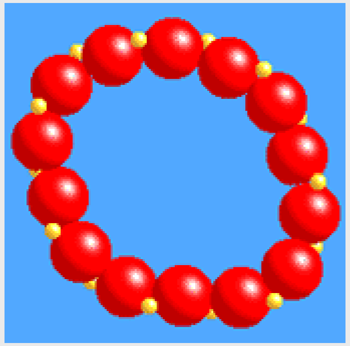
ZSM-5
10 TO_2
5.5 x 5.1 Å

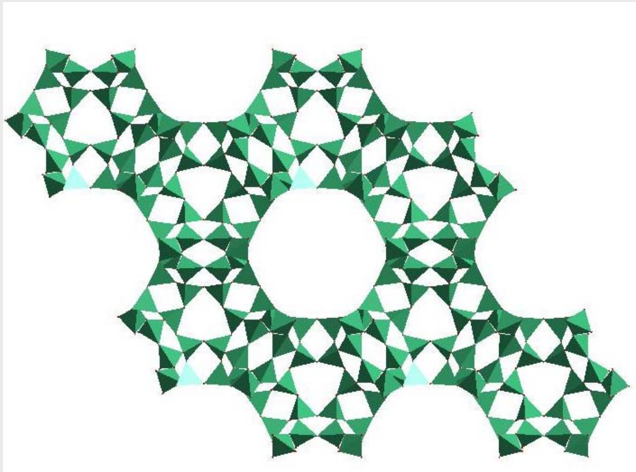
Faujasite
12 TO_2
7.4 x 7.4 Å

Zeolites

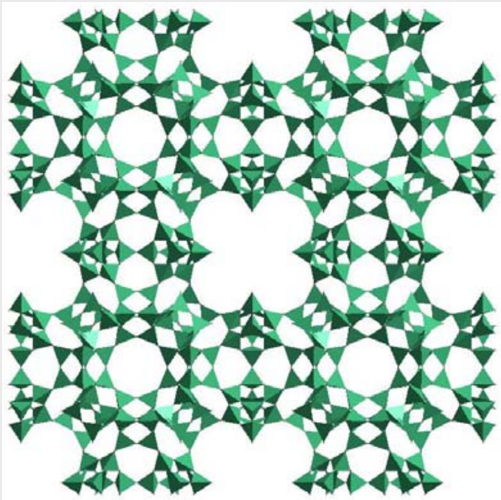


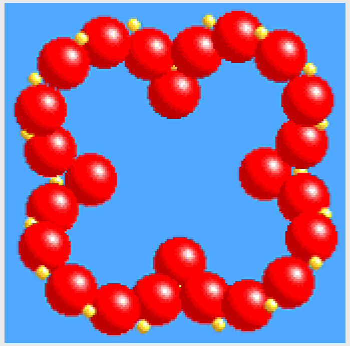


UTD-1
14 TO_2
8.2 x 8.1 Å



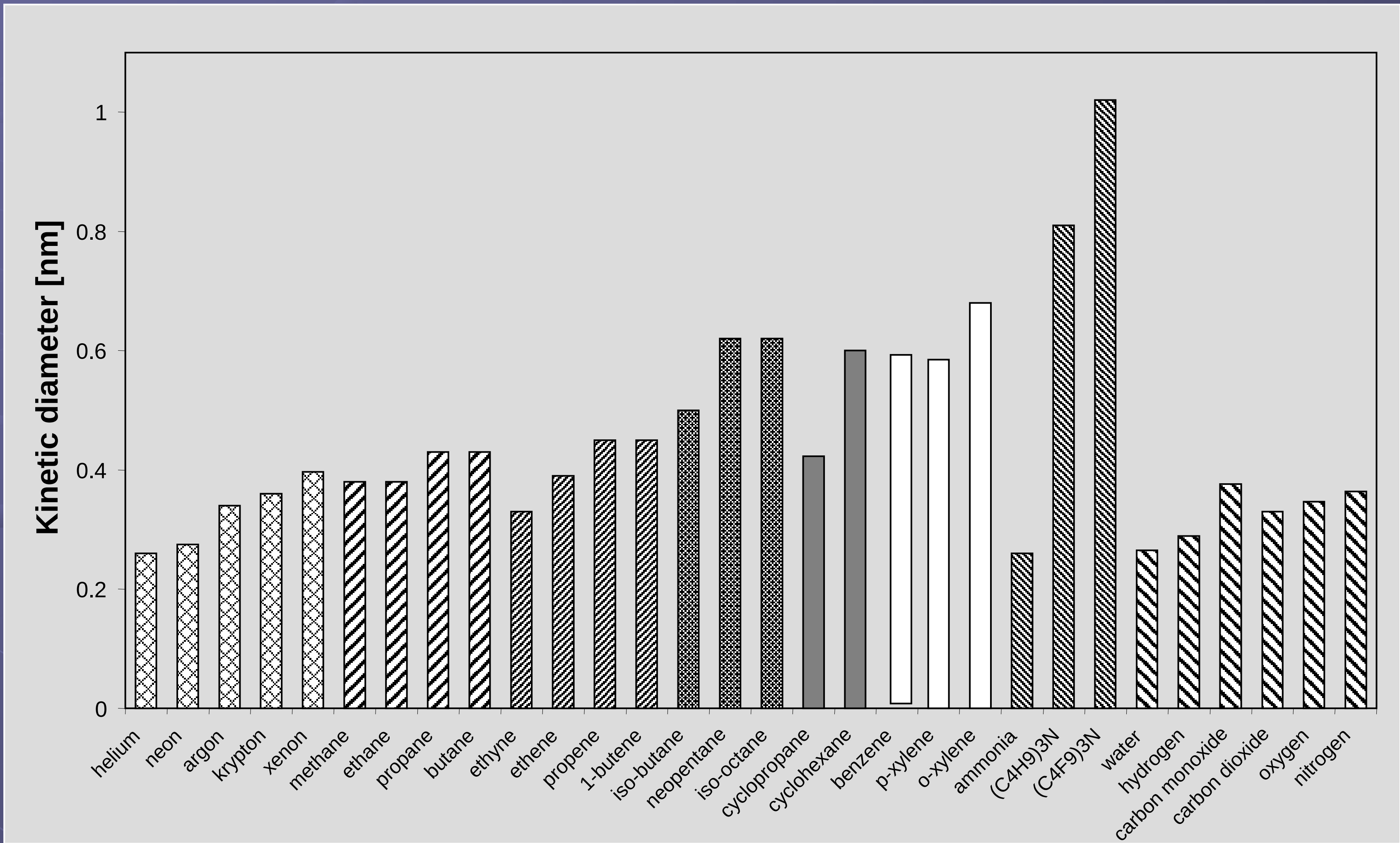
ECR-34
18 TO_2
10.1 x 10.1 Å





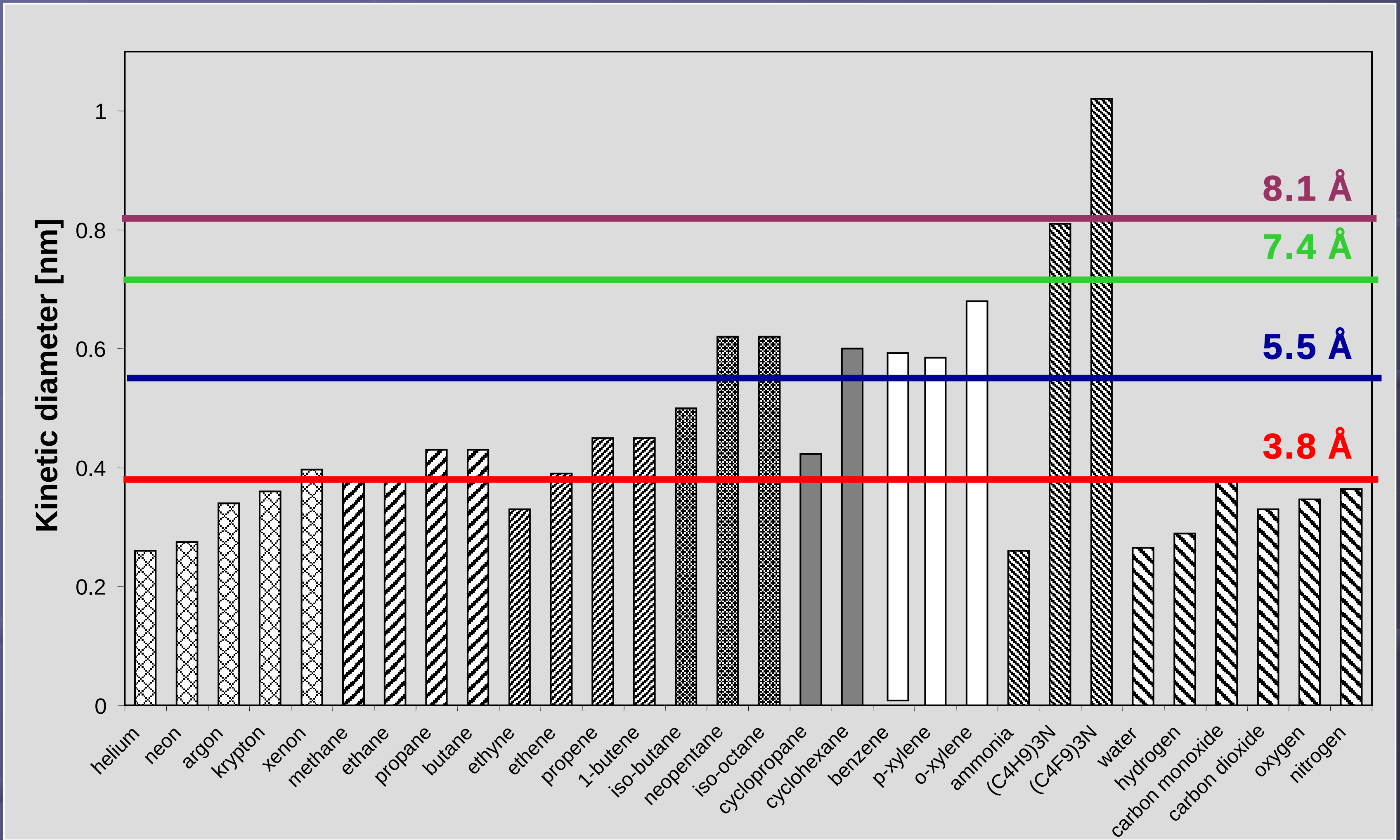
Cloverite
20 TO_2
13.2 x 6.0 x 3.5 Å

Zeolites

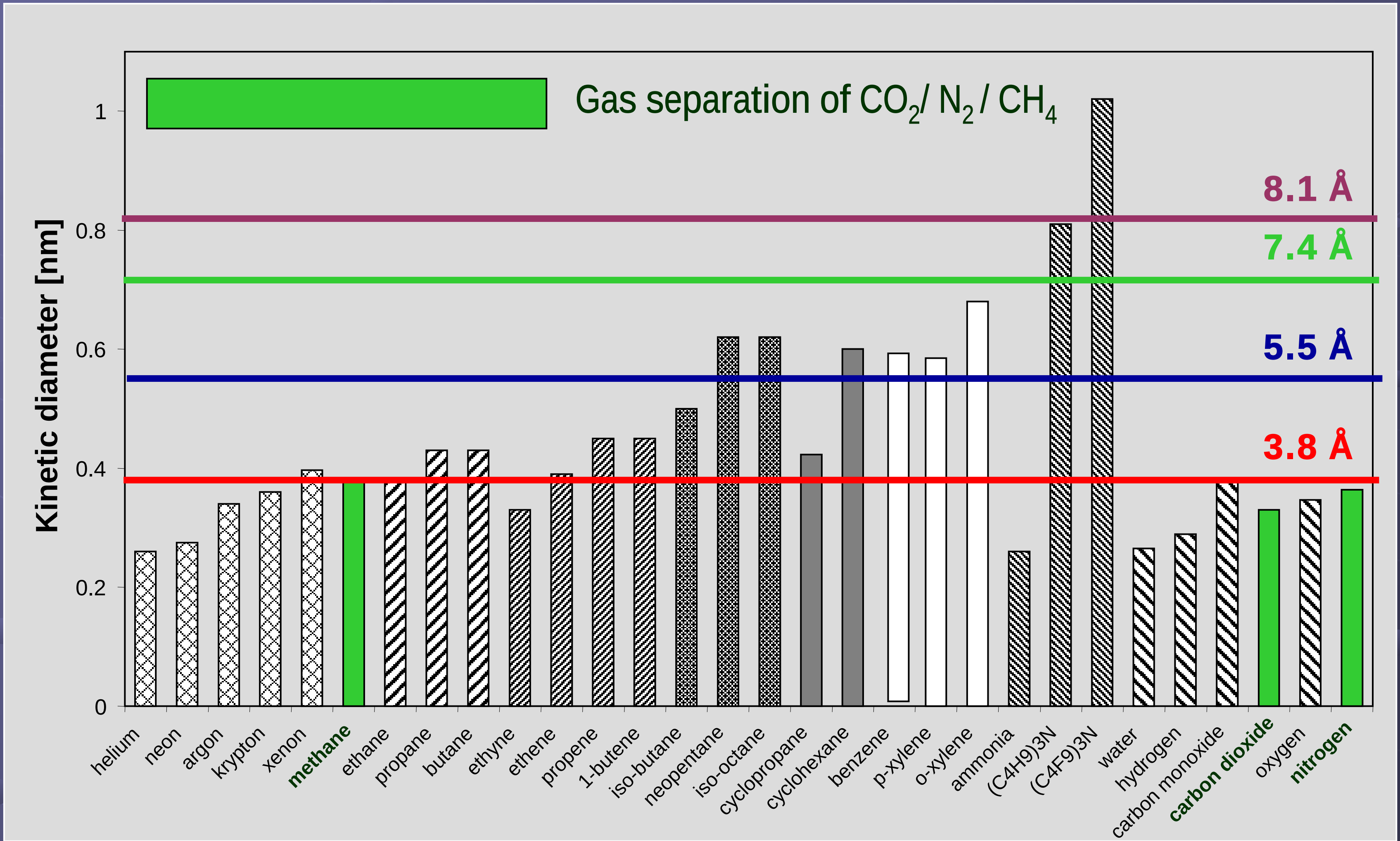


Kinetic diameter [nm]
0
0.2
0.4
0.6
0.8
1
helium
neon
argon
krypton
xenon
methane
ethane
propane
butane
ethyne
ethene
propene
1-butene
iso-butane
neopentane
iso-octane
cyclopropane
cyclohexane
benzene
p-xylene
o-xylene
ammonia
(C4H9)3N
(C4F9)3N
water
hydrogen
carbon monoxide
carbon dioxide
oxygen
nitrogen

Zeolites


Kinetic diameter [nm]
0
0.2
0.4
0.6
0.8
1
8.1 Å
7.4 Å
5.5 Å
3.8 Å
helium
neon
argon
krypton
xenon
methane
ethane
propane
butane
ethyne
ethene
propene
1-butene
iso-butane
neopentane
iso-octane
cyclopropane
cyclohexane
benzene
p-xylene
o-xylene
ammonia
(C4H9)3N
(C4F9)3N
water
hydrogen
carbon monoxide
carbon dioxide
oxygen
nitrogen

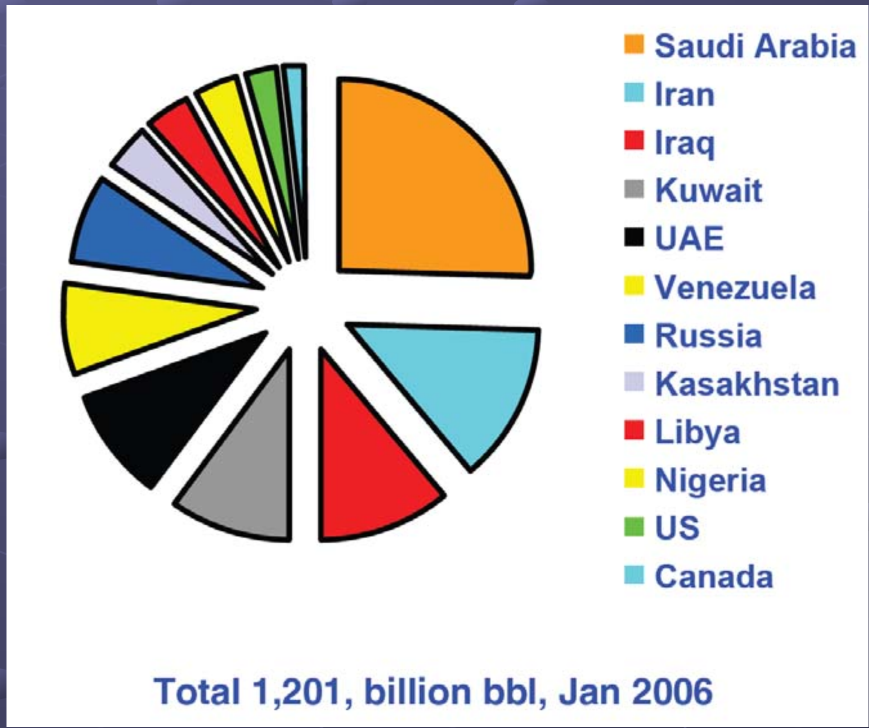
Natural Gas Upgrading



Natural Gas Upgrading

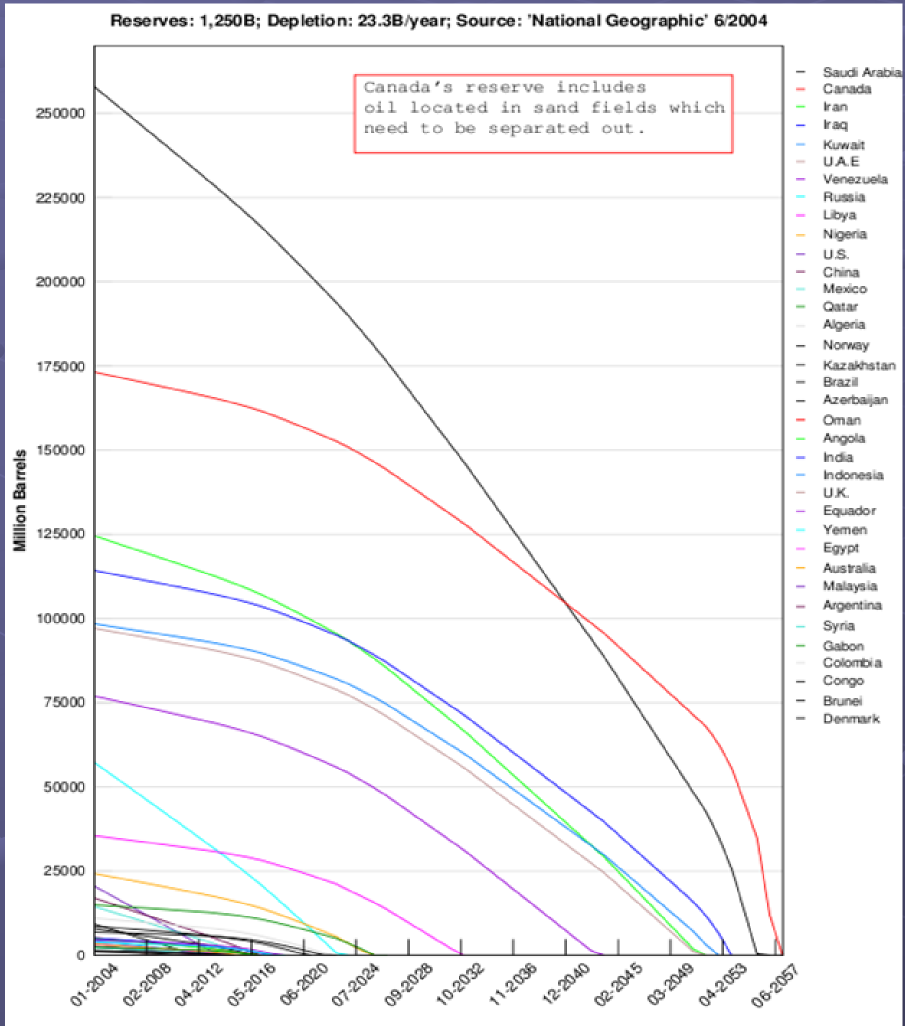
To understand the aiming of the Natural Gas Upgrading, it is needed to spend some time looking at the energy landscape for the near future

World Oil reserves



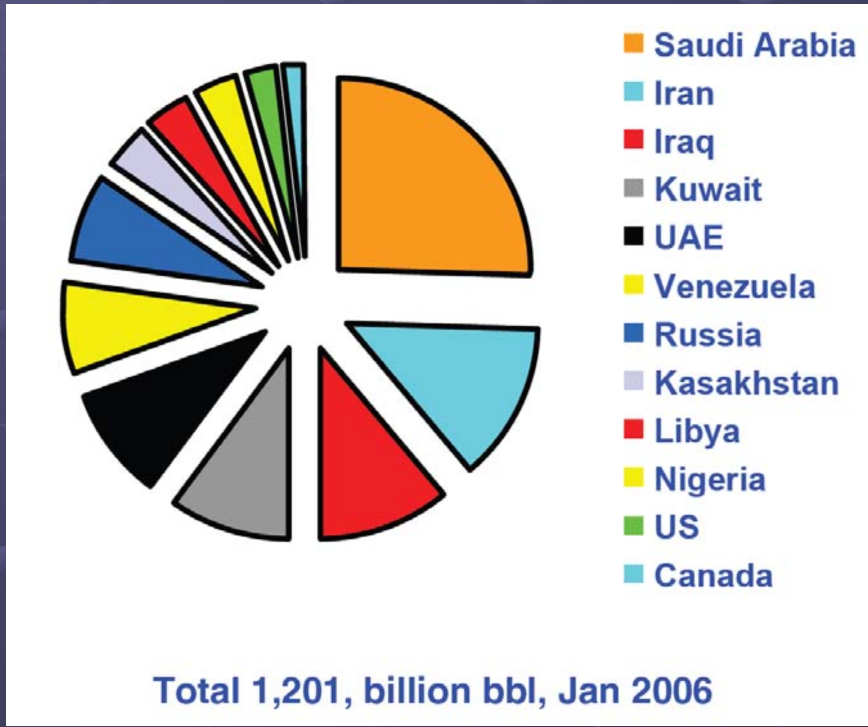
Natural Gas Upgrading

World Oil depletion



World Oil reserves

1.200 billion bbl

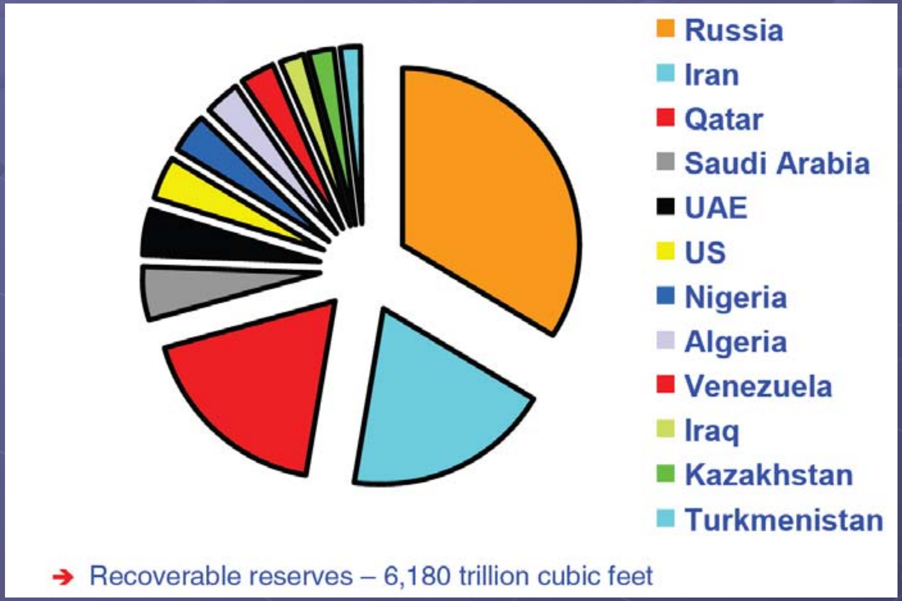


CSIC

Natural Gas Upgrading

World Natural Gas Reserves

6.180 trillion cubic feet

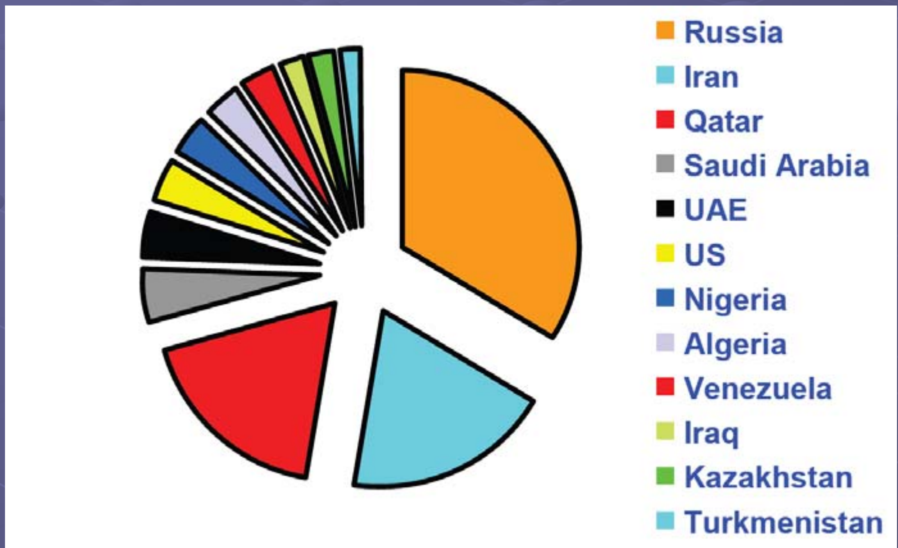


About 80% of the proven reserves are small and/or far from final markets.

Natural Gas Upgrading

World Natural Gas Reserves

6.180 trillion cubic feet



- Recoverable reserves – 6,180 trillion cubic feet
- 80% of the proven natural gas reserves are stranded

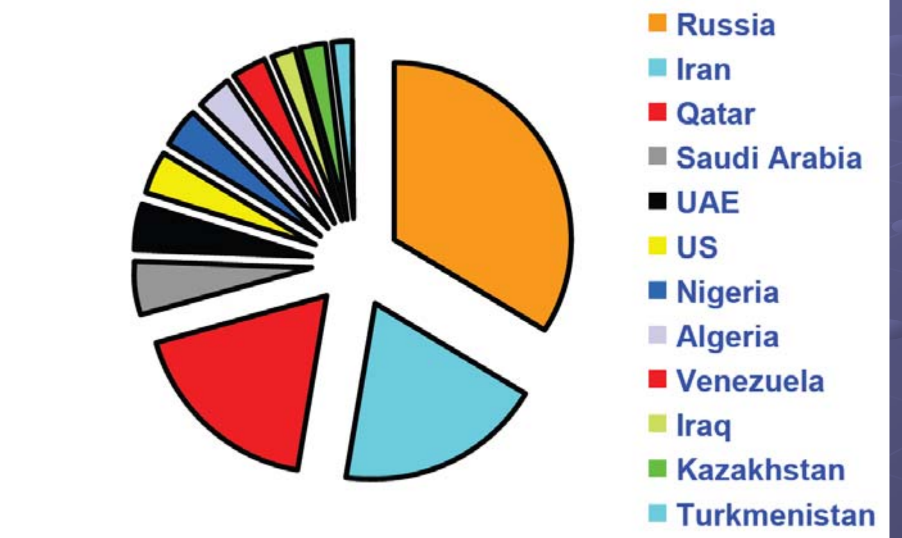
Their exploitation is not economically profitable

Proved Reserves → **Profiteable Reserves**

6.180 trillion cubic feet → **1.236 trillion cubic feet**

CSIC

Natural Gas Upgrading

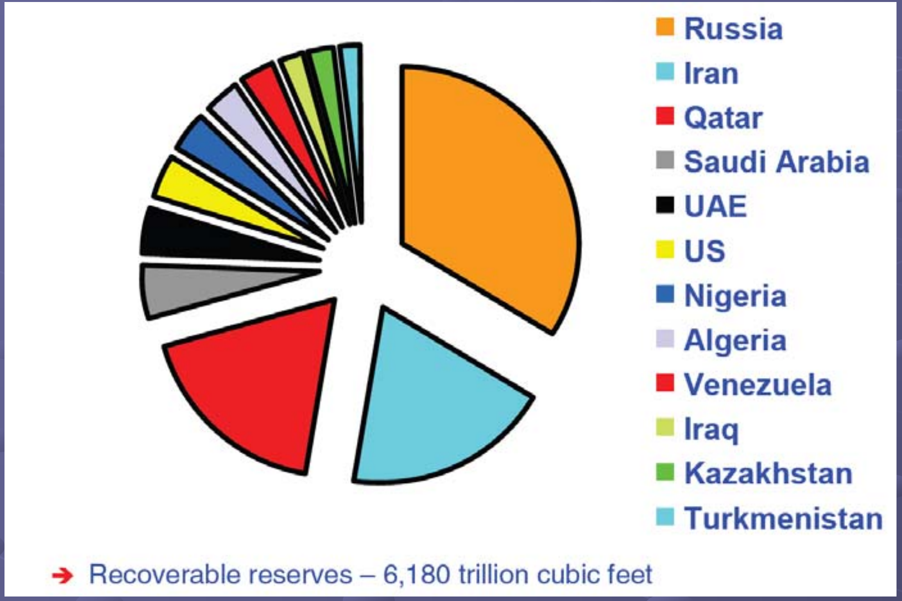


➔ Recoverable reserves – 6,180 trillion cubic feet

➔ 80% of the proven natural gas reserves are stranded

Why ?

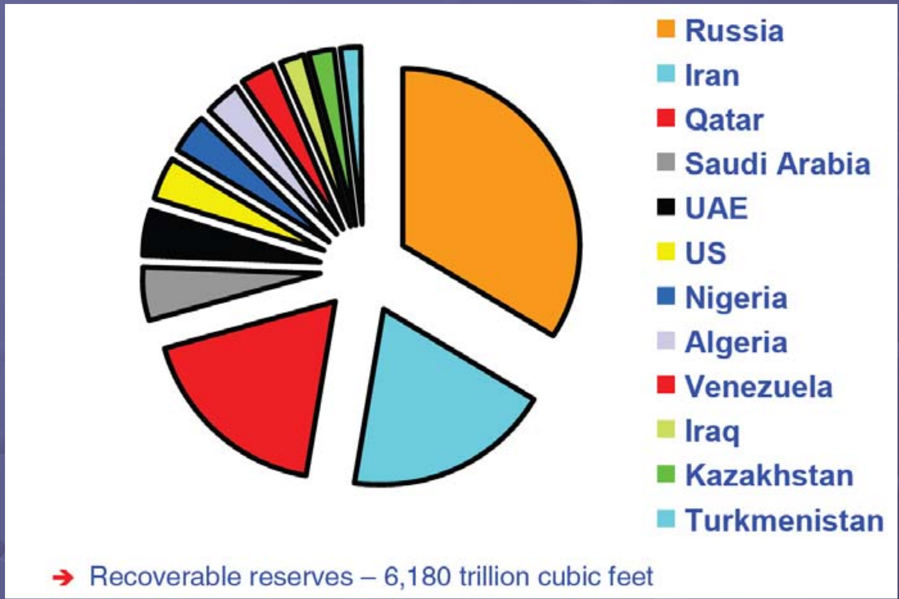
Natural Gas Upgrading



Natural Gas is transported through pipelines or as cryogen liquid to final markets

Contaminat	Level (vol %)	Problem
CO_2	0.5 – 10.0 , peak 70	Corrosion, no heating value,
SH_2	0 – 1, peak 10	Corrosion, toxicity
N_2	0.5 – 5.0, peak 25	No heating value
Water	0.5 – 1.0	plugging of transmission lines
C2+	1 – 5 %	Pipeline blocking, heating value

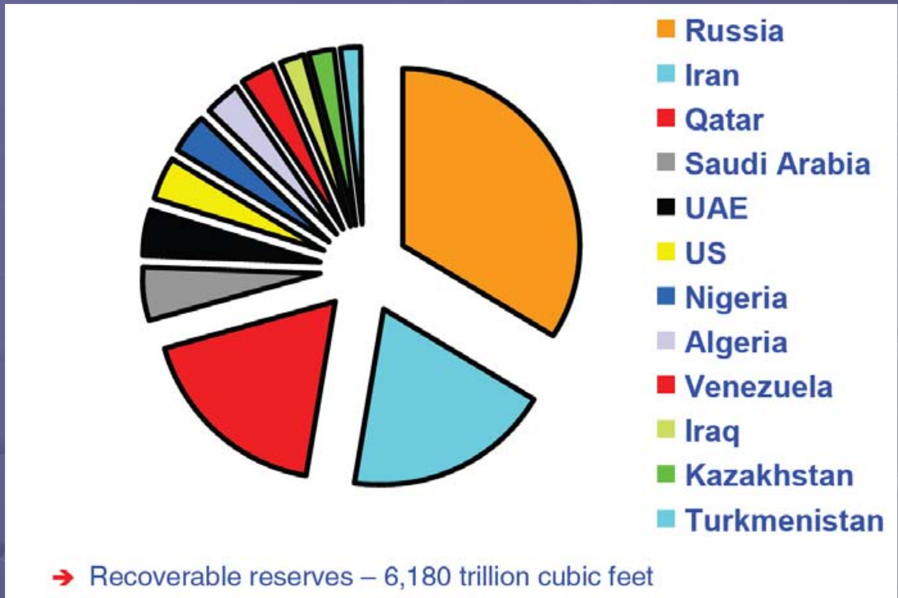
Natural Gas Upgrading



Natural Gas is transported through pipelines needs a huge investment, only affordable in large landfills.

Impurity	Initial value	Pipeline Gas
CO_2	0.5 vol%	3 – 4 vol.%
H_2S	10 vol%	5.7 – 22.9 mg/m^3
N_2	3 vol%	3 vol.%
H_2O	0.5 vol%	150 ppmv
C_{2+}	4 vol%	4 vol%

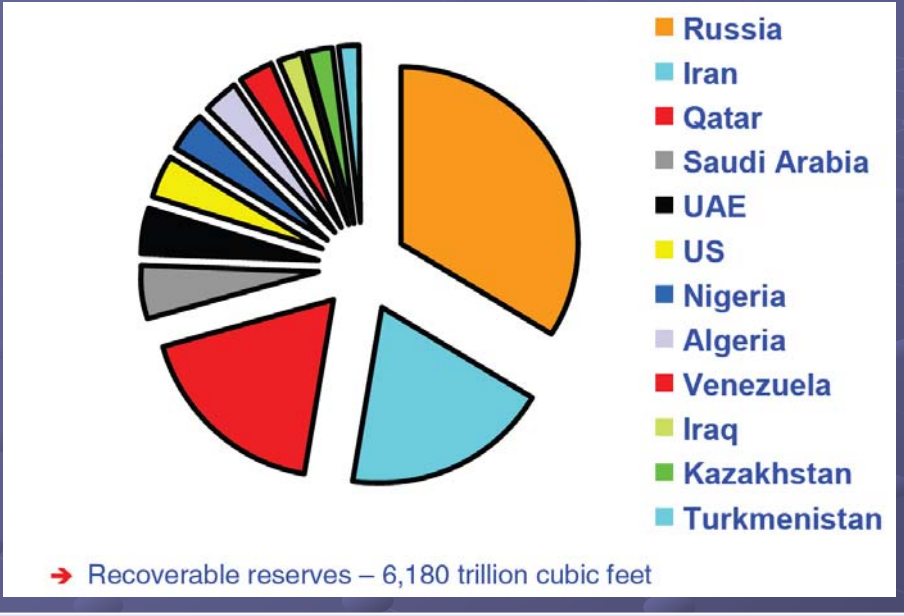
Natural Gas Upgrading



The optimum situation is the in-situ production of liquefied Natural Gas.

Impurity	Initial value	Pipeline Gas	Feed to LNG Plant
CO_2	0.5 vol%	3 – 4 vol.%	< 50 ppmv
H_2S	10 vol%	5.7 – 22.9 mg/m^3	< 4 ppmv
N_2	3 vol%	3 vol.%	< 1 vol.%
H_2O	0.5 vol%	150 ppmv	< 0.1 ppmv
C_{2+}	4 vol%	4 vol%	< 2 vol.%

Natural Gas Upgrading



The actual technologies do not allow their easy installation and maintenance in remote places.

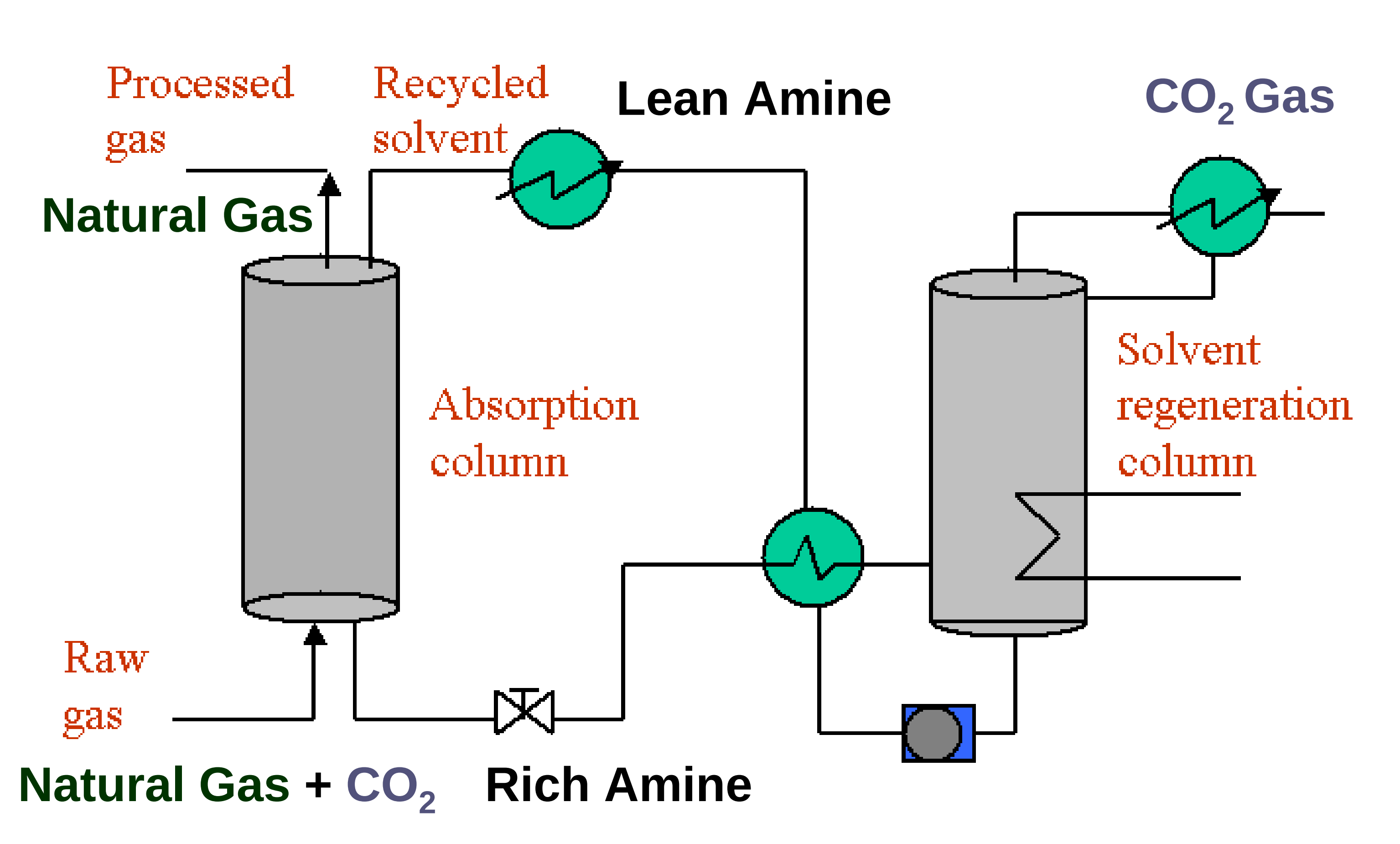
Particularly difficult is the removal of CO_2 and N_2 from raw Natural Gas streams.

Impurity	Initial value	Pipeline Gas	Feed to LNG Plant
CO_2	0.5 vol%	3 – 4 vol.%	< 50 ppmv
H_2S	10 vol%	5.7 – 22.9 mg/m^3	< 4 ppmv
N_2	3 vol%	3 vol.%	< 1 vol.%
H_2O	0.5 vol%	150 ppmv	< 0.1 ppmv
C_{2+}	4 vol%	4 vol%	< 2 vol.%

CSIC

Natural Gas Upgrading

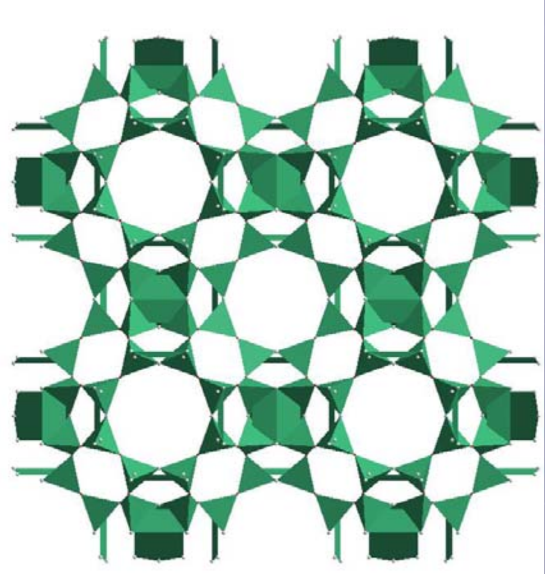
Aqueous amine or organic solvent scrubbing



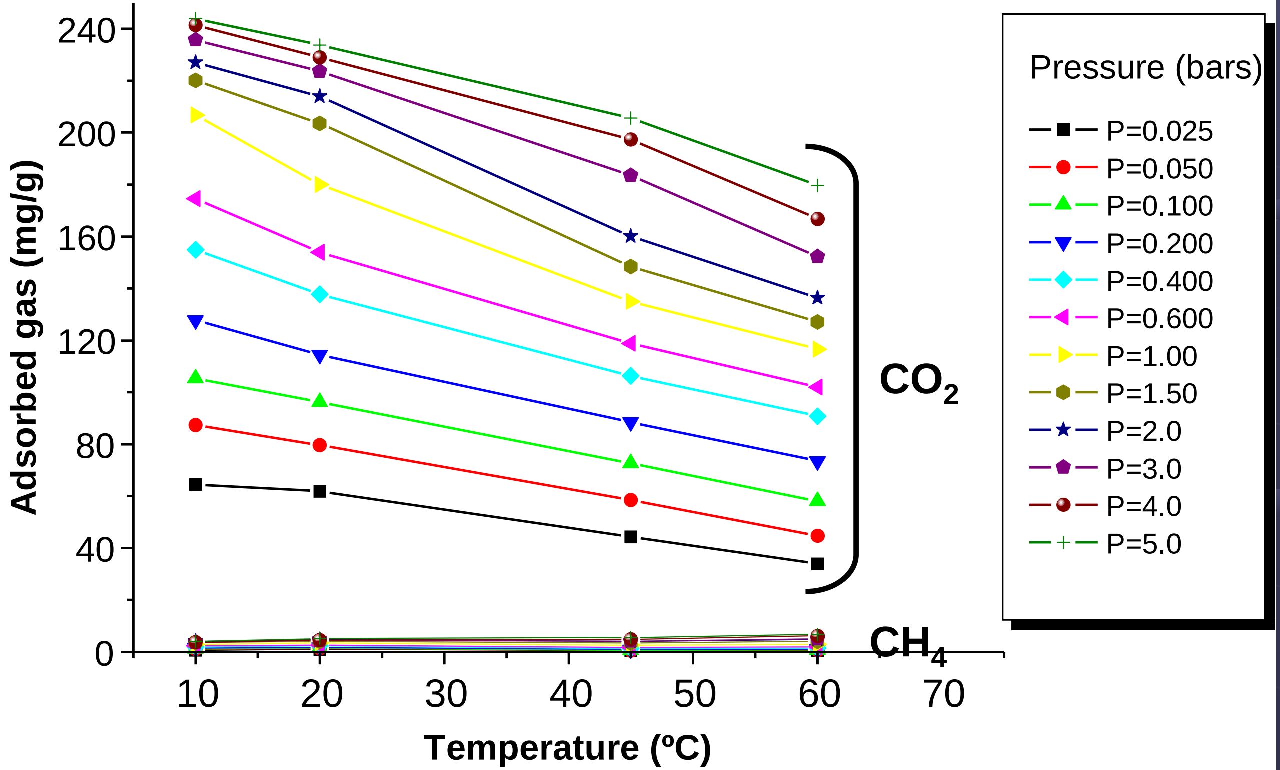
Natural Gas Upgrading

Can help zeolites in upgrading CO_2?

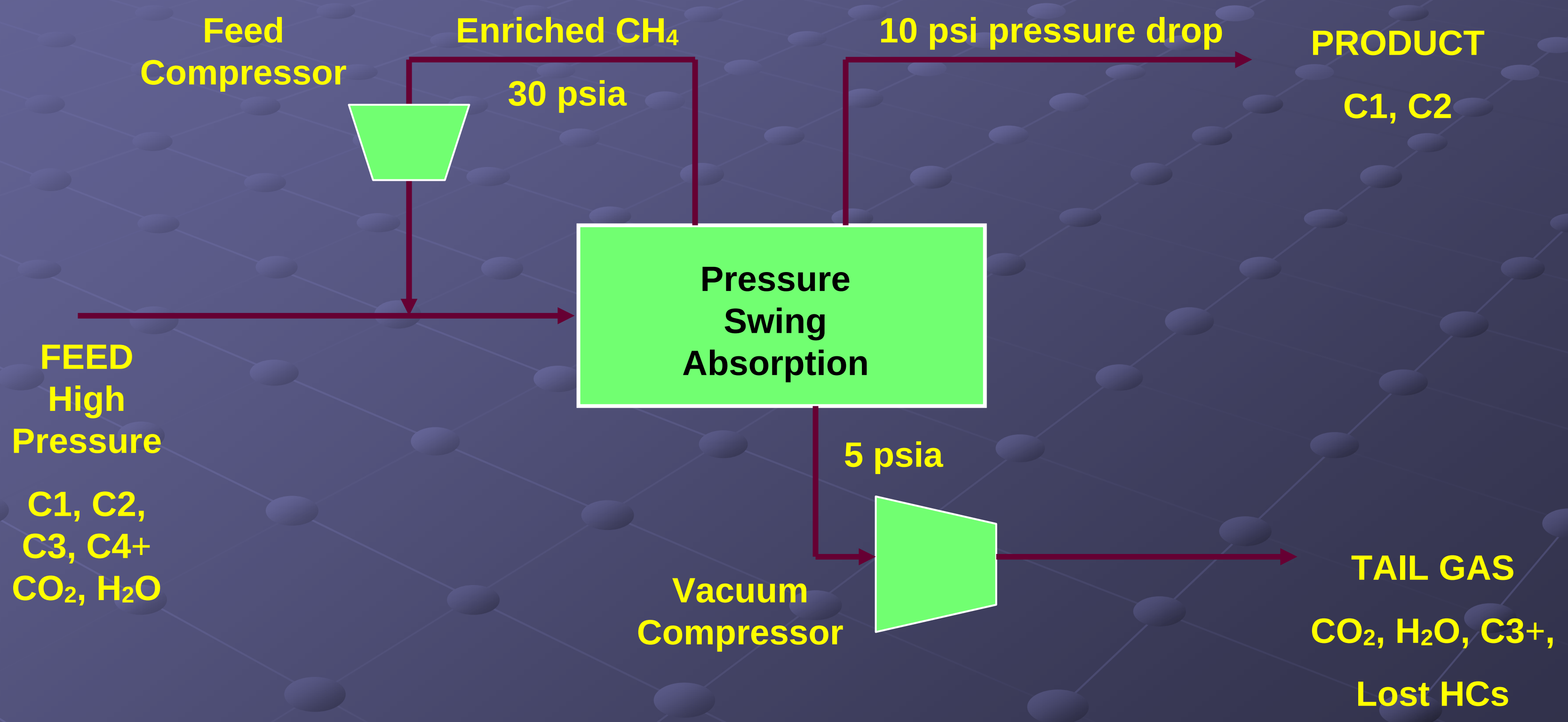
Natural Gas Upgrading



New zeolite
8 TO_2
3.7 x 3.7 Å

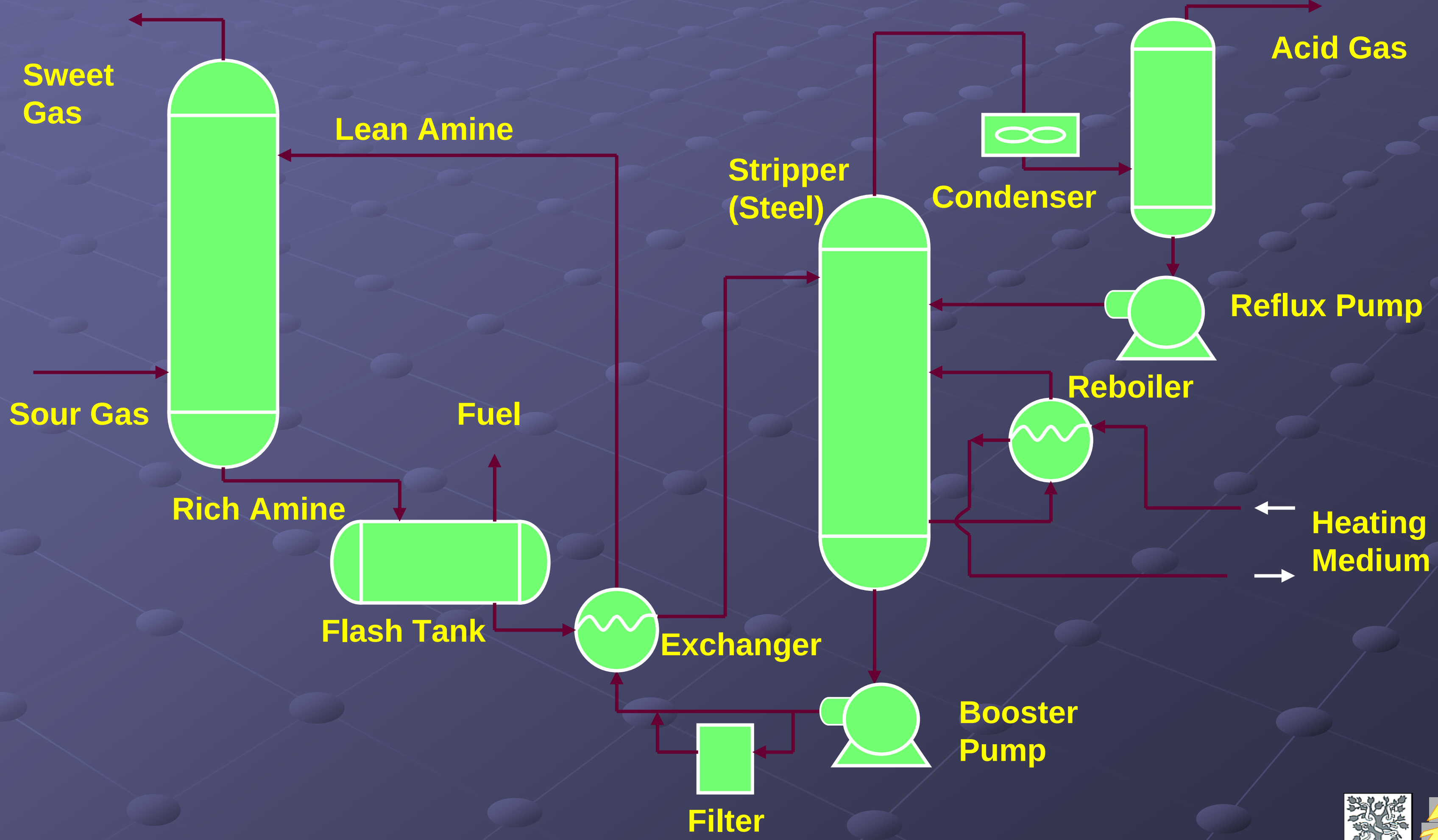


Molecular Sieve Technology for CO_2 capture



Natural Gas Upgrading

Typical amine Process



Natural Gas Upgrading

ACHIEVEMENTS

- Raw Natural Gas con be upgraded to Methane of quality enough to be transported as Liquid Methane with a simpler technology.
- The use and transportation of amines is overcome by using this new sequestration model.

OBJECTIVES

- To increase the selectivity for the elective adsorption of N_2 versus CO_2.
- To tailor the hydrophobic properties of the zeolite in order to increase the regenerability of the adsorbent.

CSIC

Natural Gas Upgrading

ACHIEVEMENTS

- Raw Natural Gas con be upgraded to Methane of quality enough to be transported as Liquid Methane with a simpler technology.
- The use and transportation of amines is overcome by using this new sequestration model.

OBJECTIVES

- To increase the selectivity for the elective adsorption of N_2 versus CO_2.
- To tailor the hydrophobic properties of the zeolite in order to increase the regenerability of the adsorbent.

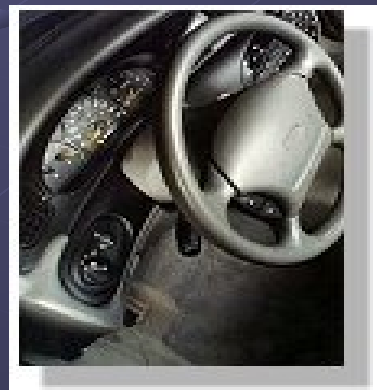
Profiteable reserves		**Profiteable Reserves**
1.236 trillion cubic feet	→	**< 4.000 trillion cubic feet.**
Amine technology		**ZEOLITE TECHNOLOGY**

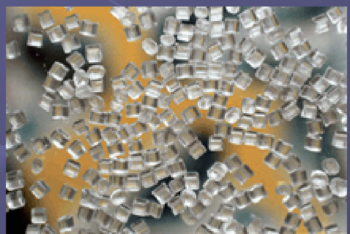
CSIC

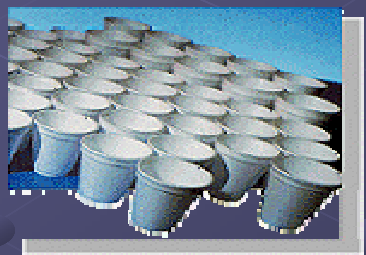
ETHYLENE AND PROPYLENE PRODUCTION

Olefin production

Olefins are employed as very primary chemical building blocks of most of the goods we found in our life: plastics, fibers, lubricants, films, textiles, pharmaceuticals, etc. ---even chewing gum!

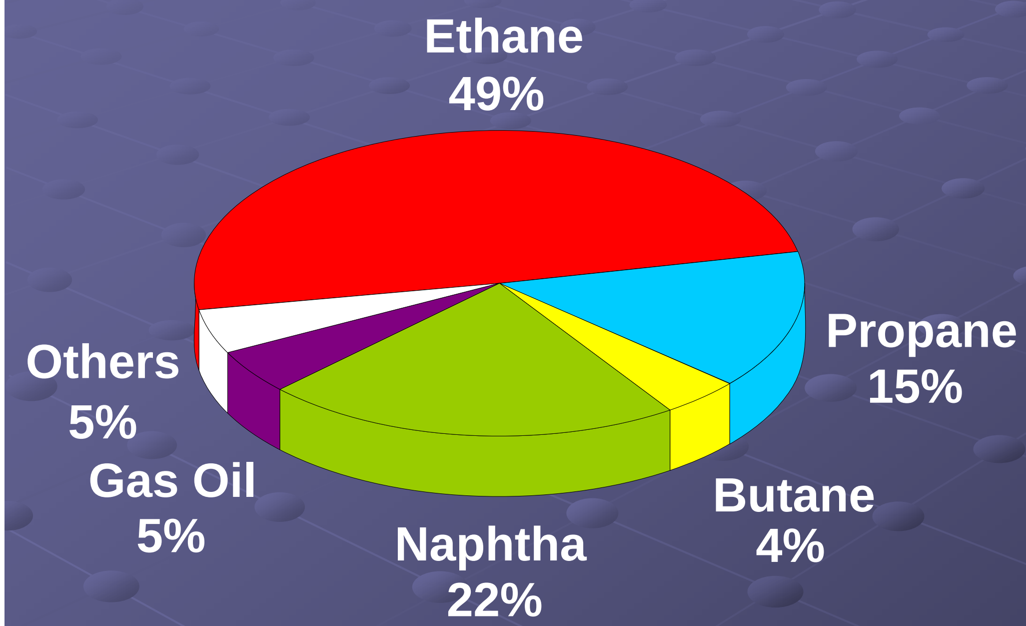




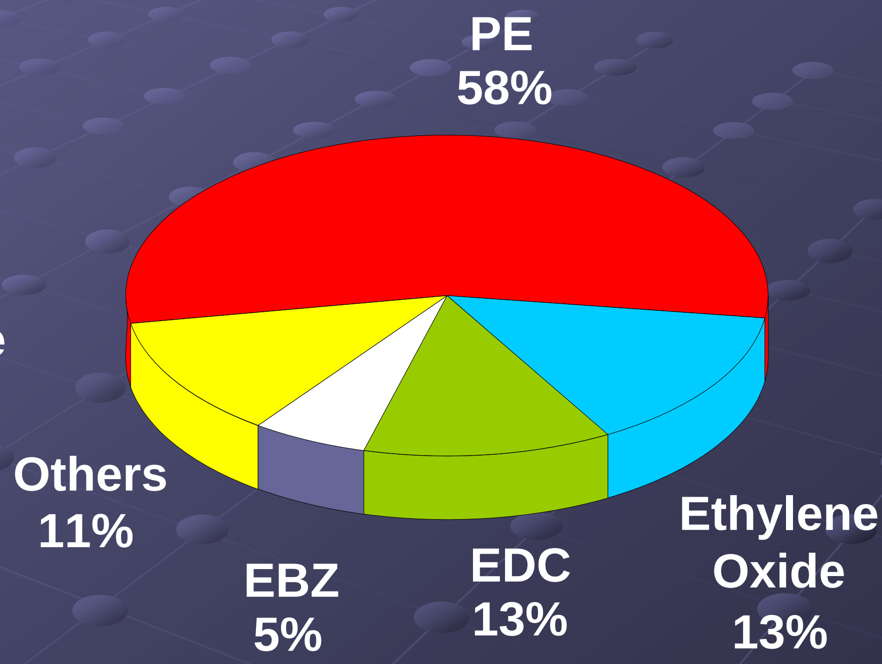


North America
2006 Ethylene Supply/Demand

Production by Feedstock

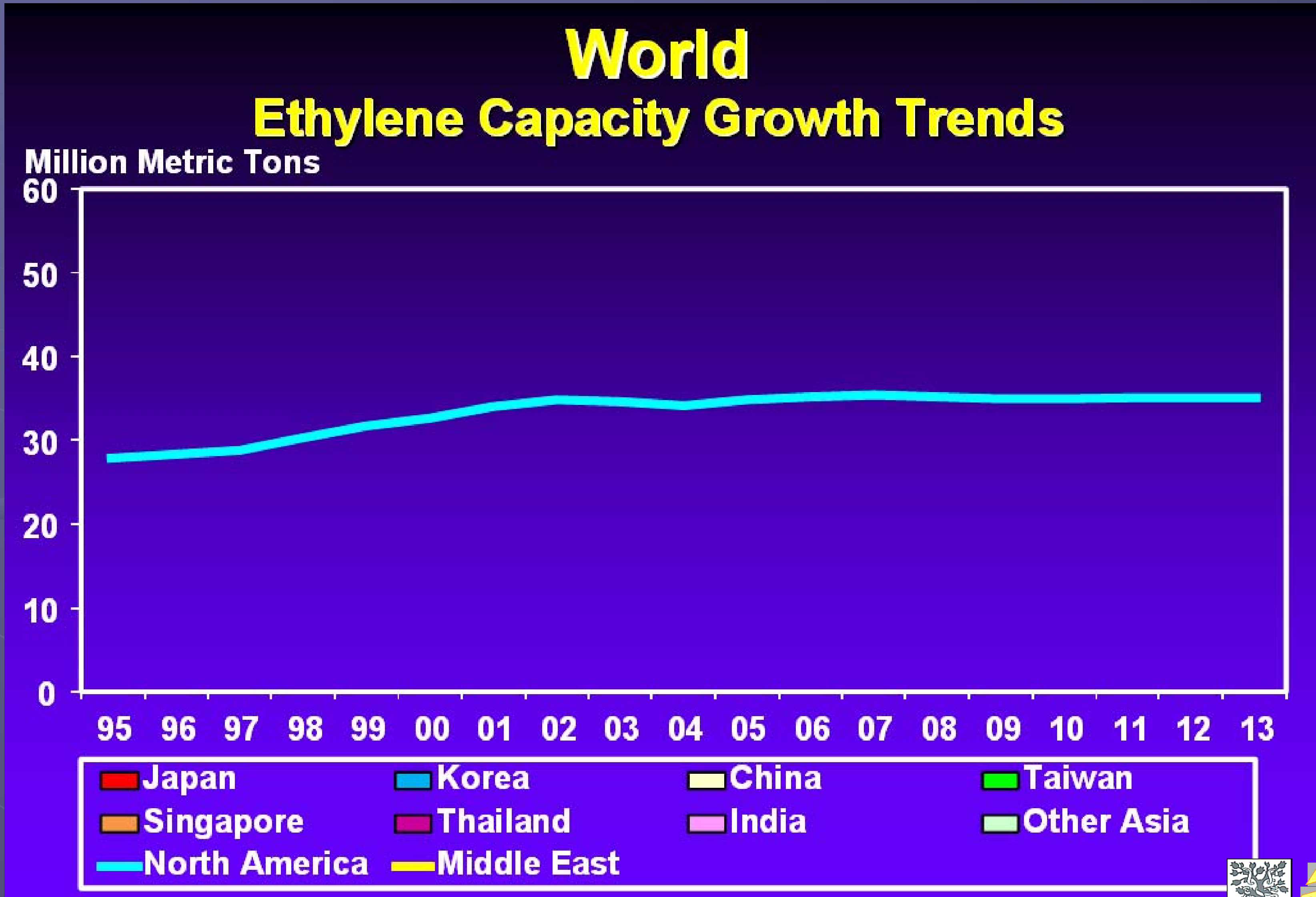


Demand by End-Use

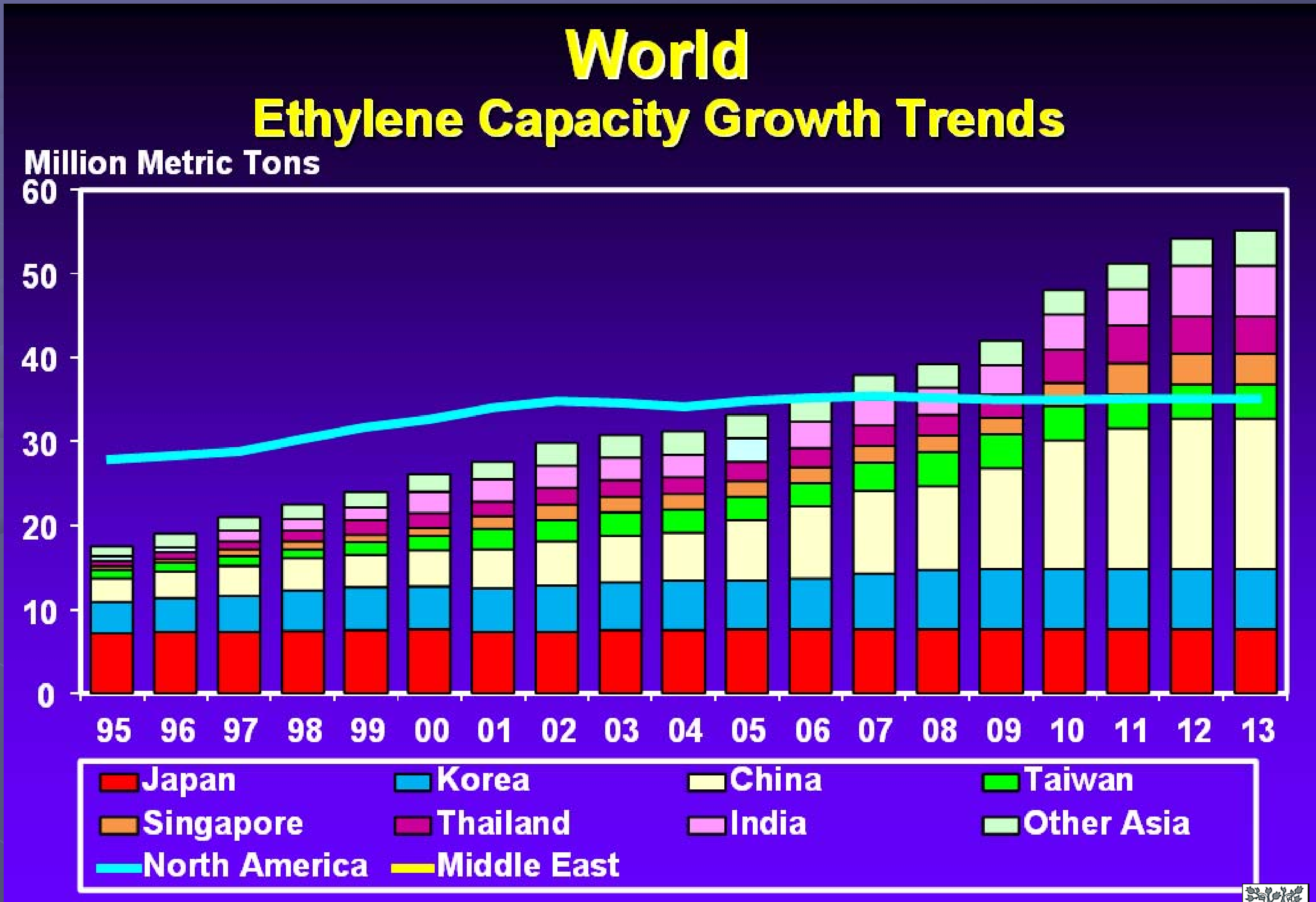


Domestic Demand = 31 Million Metric Tons

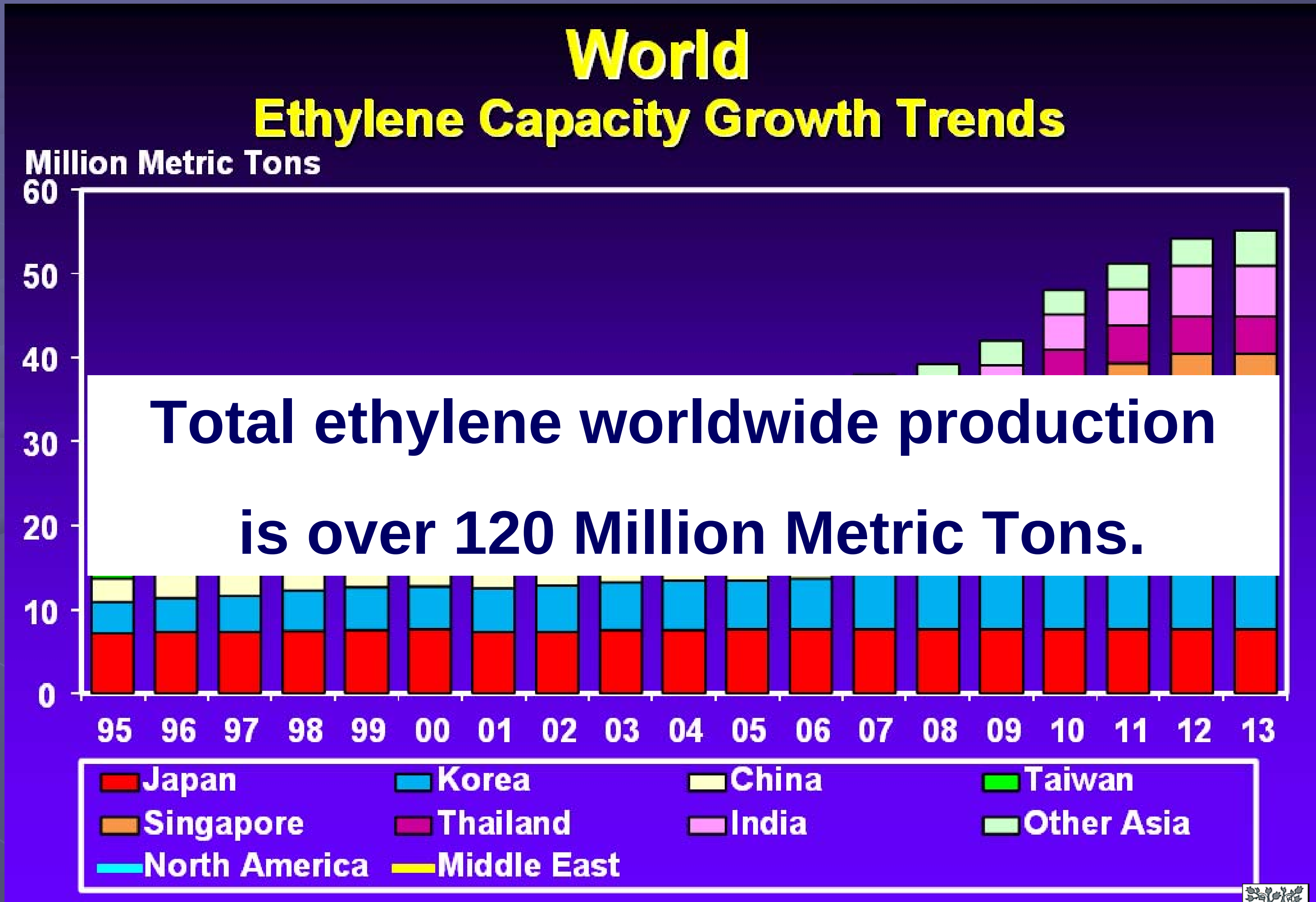
North America
2006 Ethylene Supply/Demand



North America
2006 Ethylene Supply/Demand



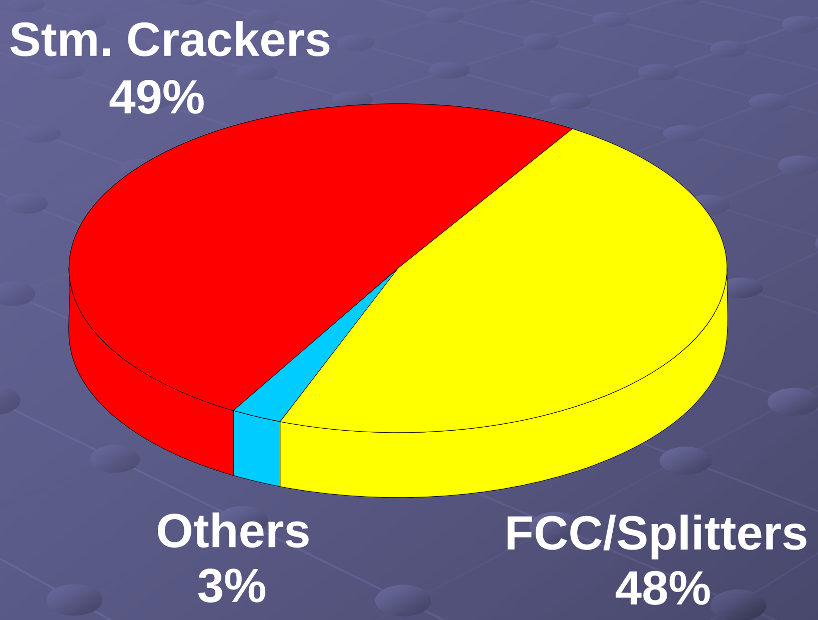
North America
2006 Ethylene Supply/Demand



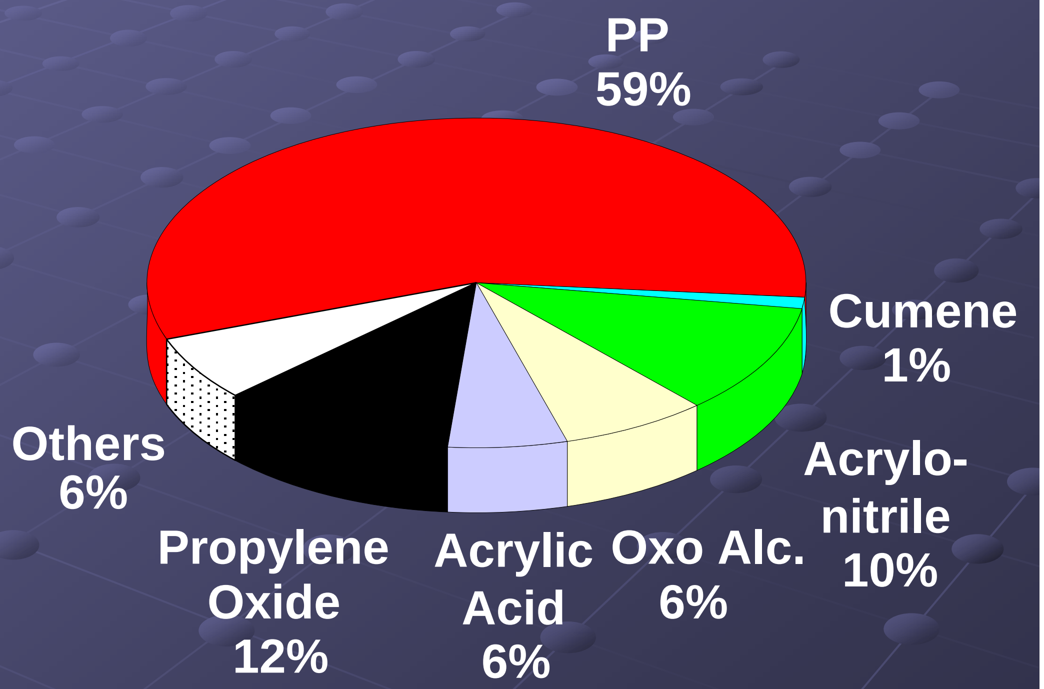
Total ethylene worldwide production is over 120 Million Metric Tons.

North America
2006 PG/CG Propylene Supply/Demand

Production by Source

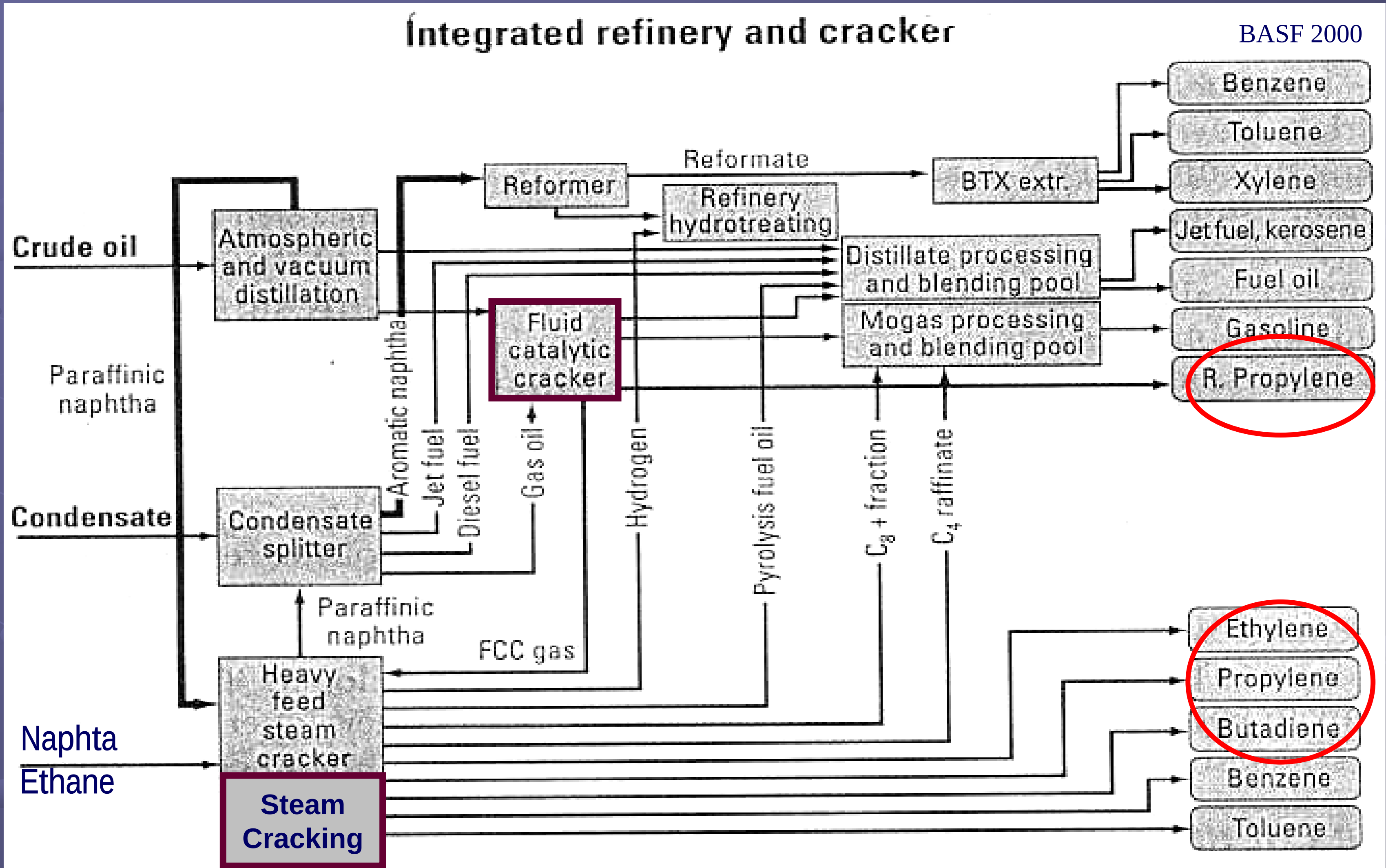


Demand by End-Use



Domestic Demand = 16 Million Metric Tons

Olefin production



Olefin production

- Steam cracking process :
  - Operates at very high temperature (800 -900 ºC)
  - High water content in the stream (H_2O /C = 1 - 3)
  - Very short contact time
  - Selectivity towards valuable olefins is approx. 85%
  - The reaction is highly endothermic

Huge needing of energy

Olefin production

Steam cracking is the single **most energy consuming process** in the chemical industry

ca. 30% of the sector's total final energy use and ca. 180 millions tons of CO_2 in 2004

Another reason for innovation:

over 35% of European crackers are over 25 years old

Olefin production

An attractive alternative to steam cracking is the selective oxidative dehydrogenation of low value paraffins (ODH).

Paraffin + O_2 → Olefin + Water

$$C_nH_{(2n+2)} + O_2 \rightarrow C_nH_{2n} + H_2O$$

- Exothermic process
- Low temperature reaction (approx. 400ºC)

Profesor Ueda is leadering this field

Olefin production

An attractive alternative to steam cracking is the selective oxidative dehydrogenation of low value paraffins (ODH).

Paraffin + O_2 → Olefin + Water

$C_nH_{(2n+2)} + O_2$ → $C_nH_{2n} + H_2O$

CO_2 + Water

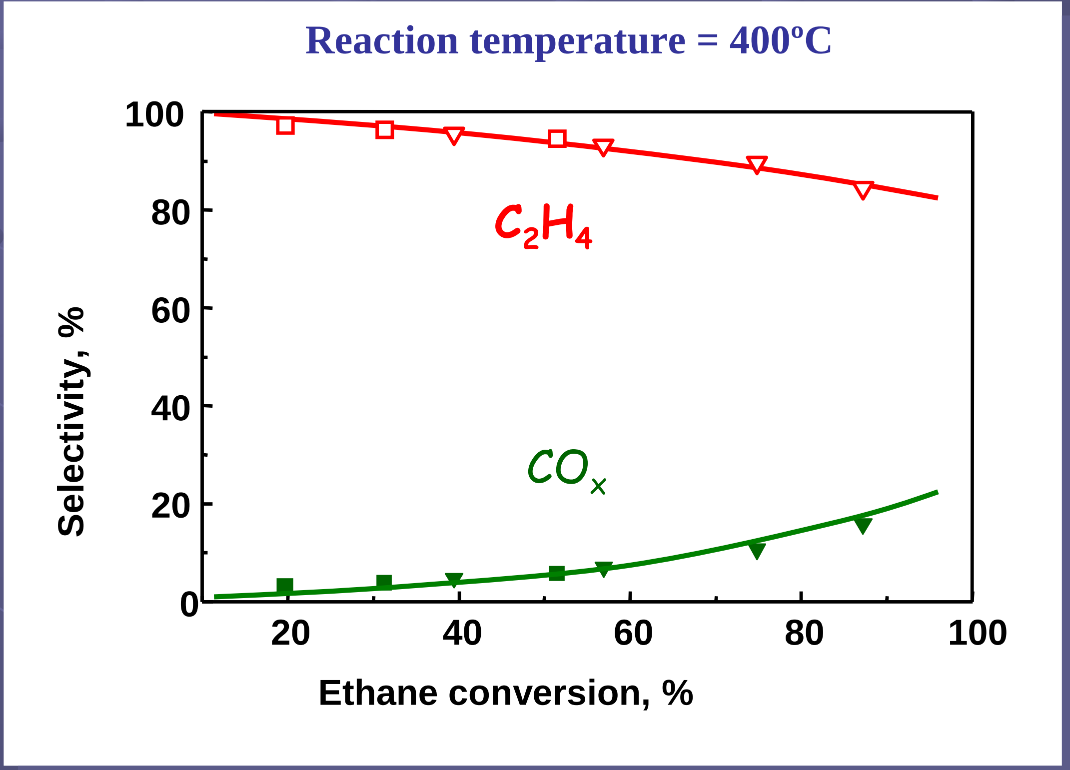
Combustion must be minimized!!

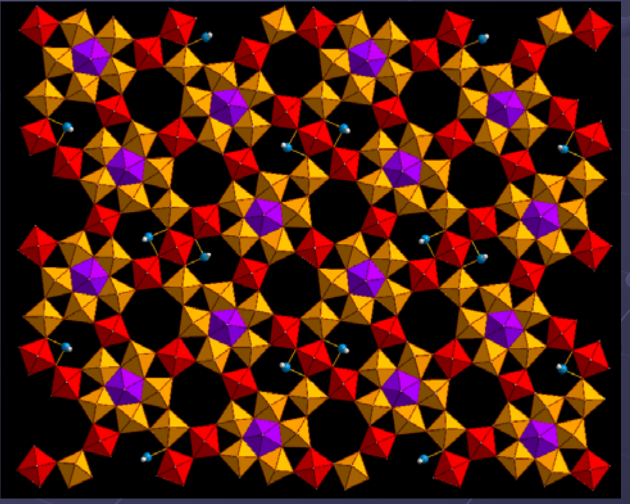
Olefin production

Ethane to ethylene by ODH process

Ethane + O_2 → Ethene + Water

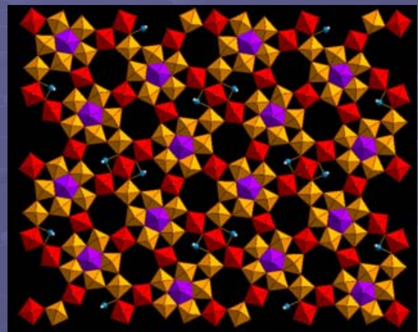
$C_2H_6 + O_2$ → $C_2H_4 + H_2O$





Porous mixed oxide MoVTeNbO

Olefin production



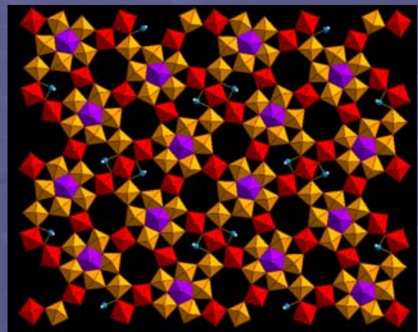
Ethane + O_2 → Ethene + Water

$C_2H_6 + O_2$ → $C_2H_4 + H_2O$

CO_2 + Water

•

Olefin production



Ethane + O_2 → Ethene + Water

$C_2H_6 + O_2$ → $C_2H_4 + H_2O$

CO_2 + Water

Combustion is minimized!!

J.M. López Nieto et al
Chem.l Comm. (2002) 1906-1907.

Olefin production

Propane to propylene by ODH process

Propane + O_2 → Propene + Water

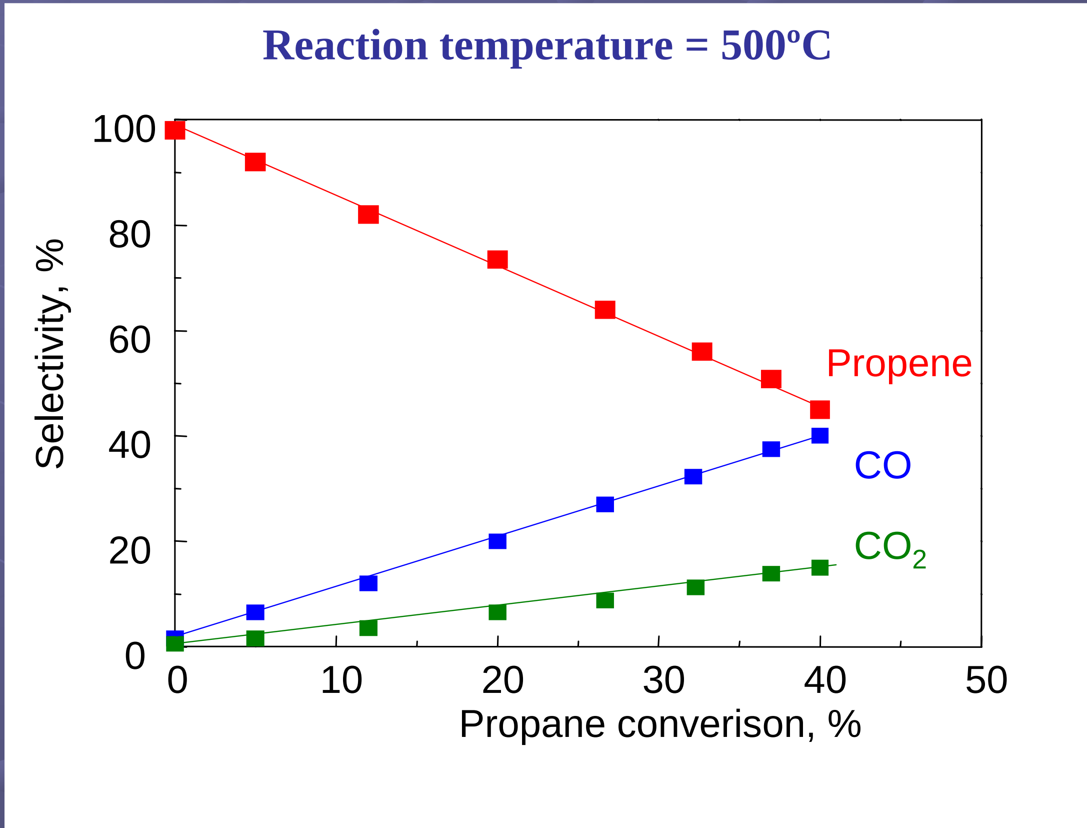
$C_3H_8 + O_2$ → $C_3H_6 + H_2O$

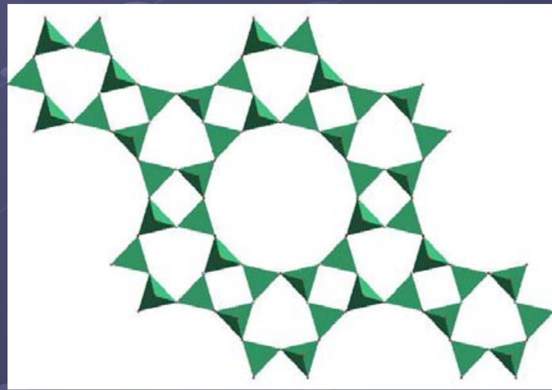
Olefin production

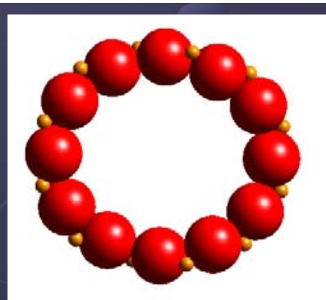
Propane to propylene by ODH process

Propane + O_2 → Propene + Water

$C_3H_8 + O_2$ → $C_3H_6 + H_2O$





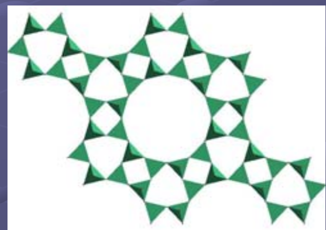


Vanadium-AlPO-5

T. Blasco; J.M. Lopez-Nieto et al
J. Catal., 152 (1995) 1-17.

Olefin production

Propane to propylene by ODH process



Propane + O_2 → Propene + Water

$C_3H_8 + O_2$ → $C_3H_6 + H_2O$

CO_2 + Water

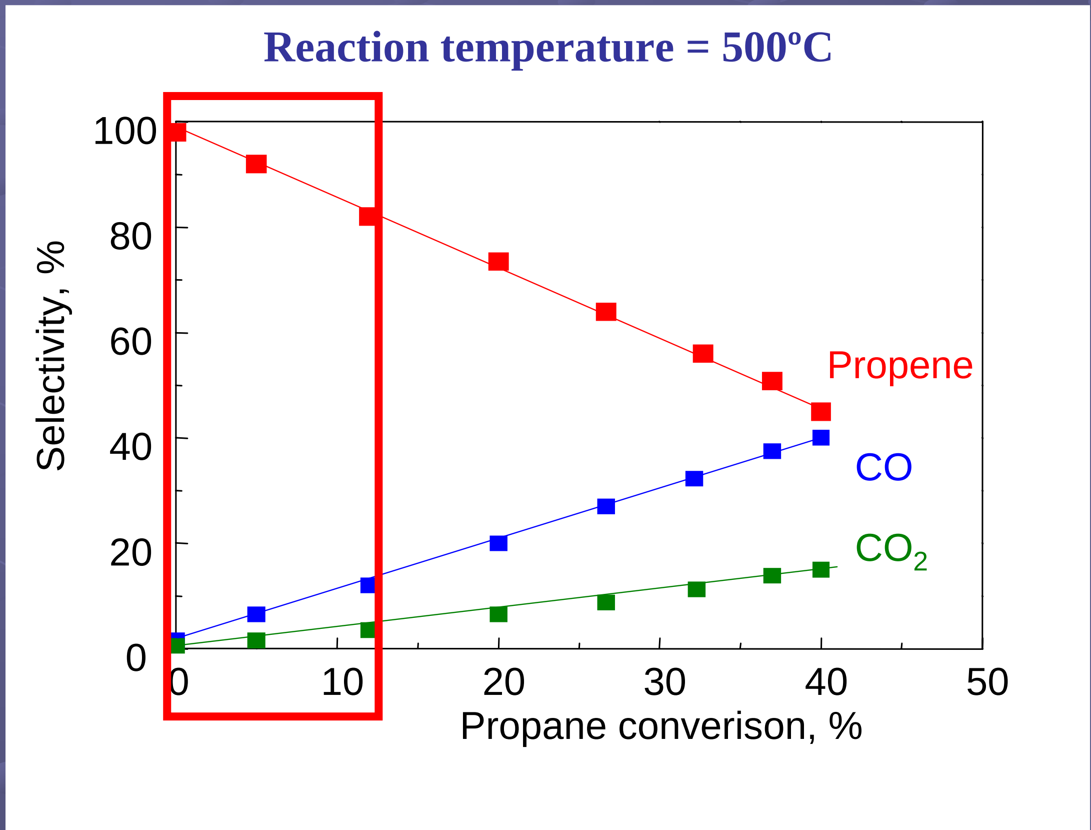
•

Olefin production

Propane to propylene by ODH process

Propane + O_2 → Propene + Water

$C_3H_8 + O_2$ → $C_3H_6 + H_2O$



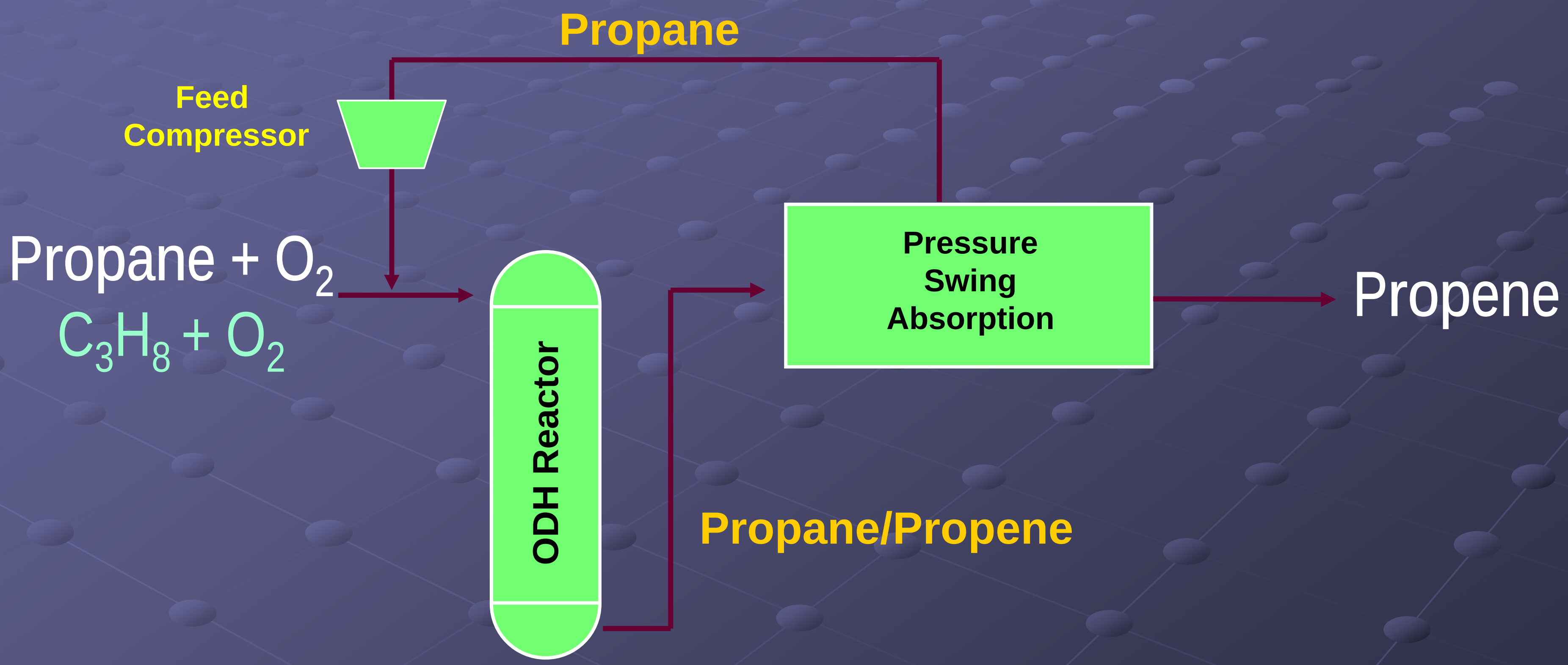
At low conversion the propylene selectivity is very high.

COMBINED PROCESS REACTION-ADSORPTION

T. Blasco; J.M. Lopez-Nieto et al
J. Catal., 152 (1995) 1-17.

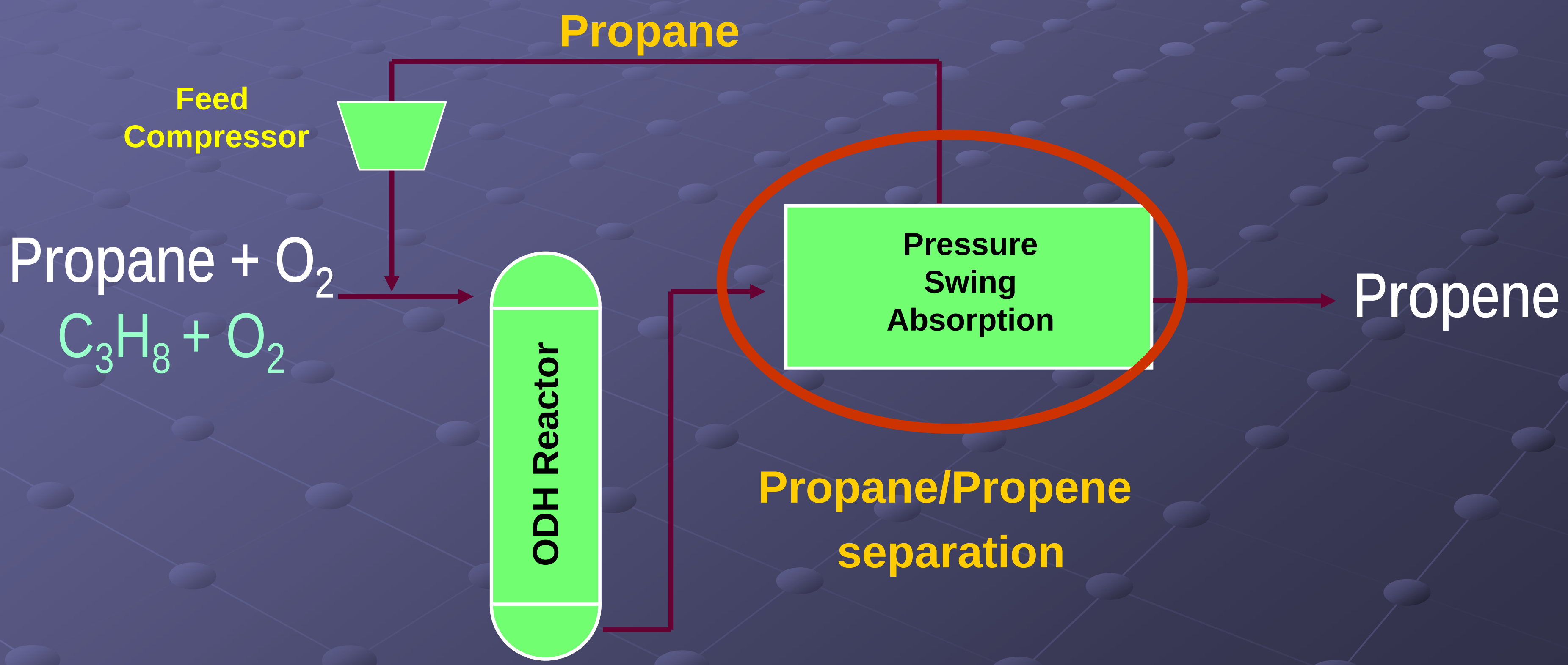
Olefin production

Propane to propylene by ODH/separation process



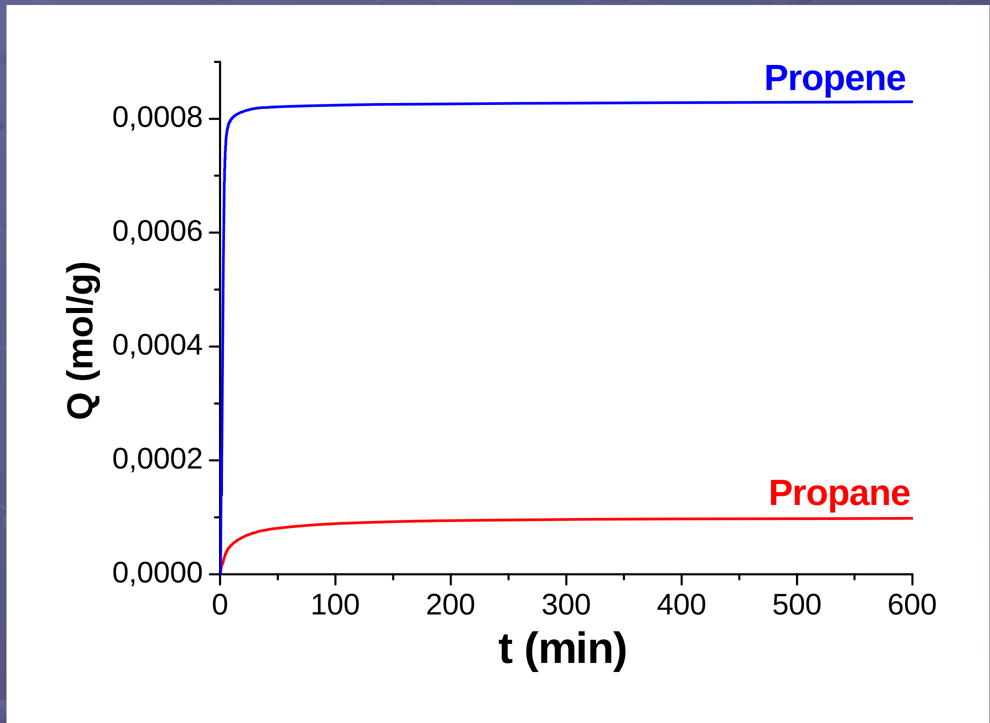
Olefin production

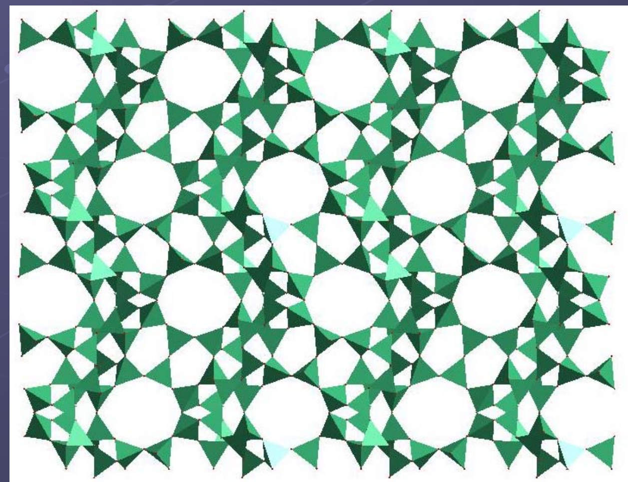
Propane to propylene by ODH/separation process



Olefin production

Promising results on
Propane/propylene separation process





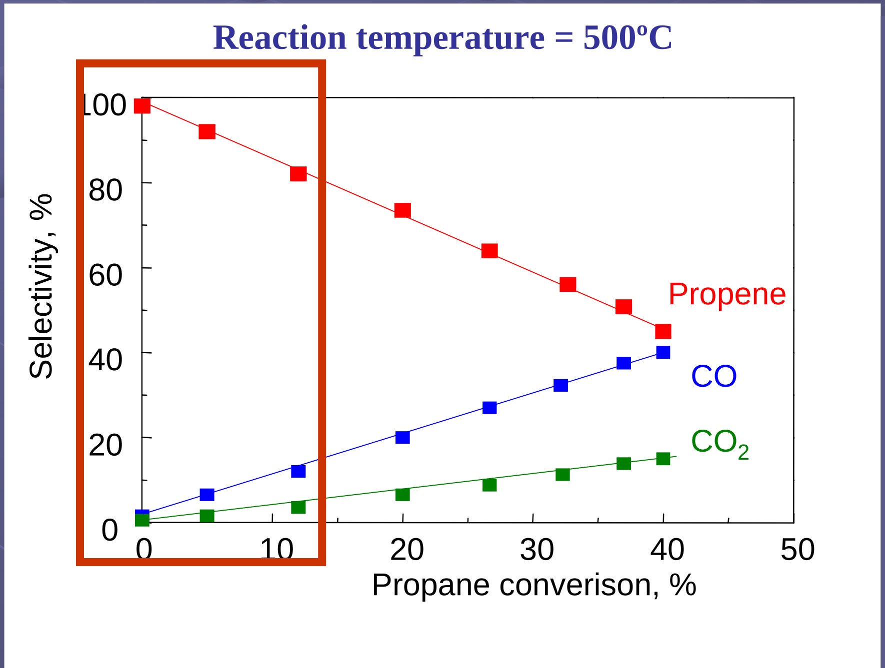
ITQ-32
8 TO_2
3.8 x 3.6 Å

Kinetic separation

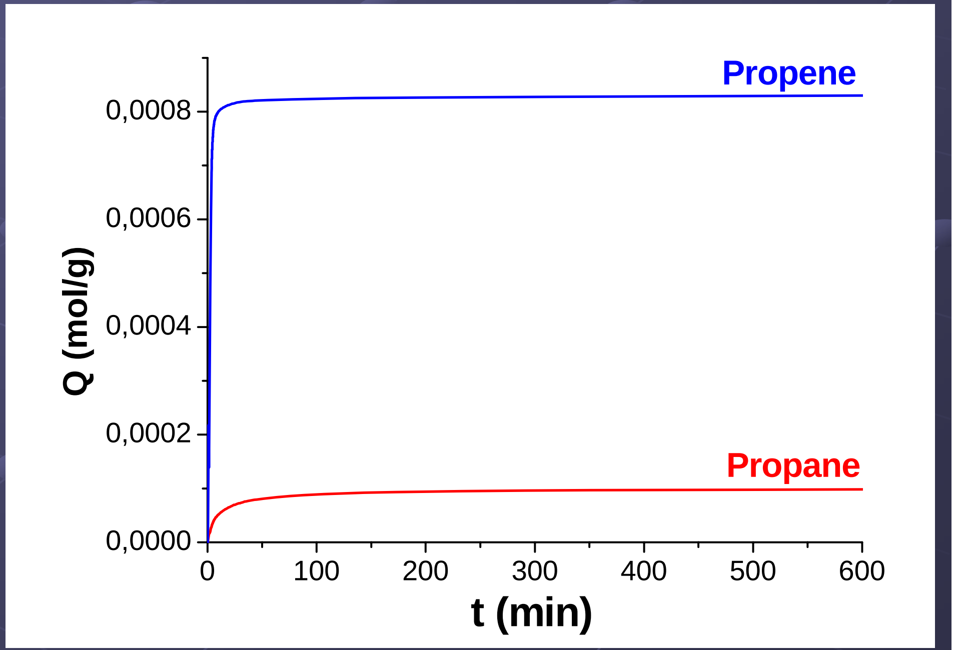
Olefin production

Propane to propylene by ODH/separation process

Propane ODH reaction on vanadium-AlPO-5



Propane/propene separation on ITQ-12 or ITQ-32



Olefin production

ACHIEVEMENTS

- Very selective catalyst for Ethylene production by ODH of ethane.
- Modest selectivities in propane ODH reaction, but promising expectatives in combined ODH/separation processes.

OBJECTIVES

- Increase the selectivity of current propane ODH catalysts.
- To increase the selectivity for the selective adsorption of propylene versus propane (THERMODYNAMIC SEPARATION)
- To tailor the hydrophillicity properties of the zeolite in order to increase the water retention capacity, without penalty of the propene adsorption.

Many application of zeolites in energy related processes

- **Fischer-Tropsch process to Diesel**
- **Modified Fischer-Tropsch to gasoline**
- **Modified Fischer-Tropsch to olefins**

- **Biomass to fuels and/or olefins**
- **Biomass to chemicals**

THANKS FOR YOUR ATTENTION

CSIC