World Chemicals Sales (2010)

Source: Cefic Chemdata International
Chemical Industry Sales (2010)
Sectoral Breakdown (Europe)

- Basic inorganics: 13.6%
- Petrochemicals: 24.0%
- Polymers: 24.0%
- Specialties: 25.6%
- Consumer chemicals: 12.8%

Source: Cefic Chemdata International
<table>
<thead>
<tr>
<th>Year</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1888</td>
<td>Sulfuric acid production by the contact process</td>
</tr>
<tr>
<td>1913</td>
<td>Ammonia synthesis (Haber-Bosch process)</td>
</tr>
<tr>
<td>1922</td>
<td>High pressure process for production of methanol</td>
</tr>
<tr>
<td>1926–1945</td>
<td>Coal liquefaction process for fuel production</td>
</tr>
<tr>
<td>1930</td>
<td>Production of synthesis gas for ammonia and methanol</td>
</tr>
<tr>
<td>1977</td>
<td>Acrylic acid process</td>
</tr>
<tr>
<td>1988</td>
<td>Low pressure production of methanol on the basis of lean gas</td>
</tr>
<tr>
<td>1997</td>
<td>Process for decomposition of N$_2$O (greenhouse gas)</td>
</tr>
<tr>
<td>2003</td>
<td>High-load process for production of phthalic anhydride</td>
</tr>
<tr>
<td>2008</td>
<td>Propylene oxide from propylene and hydrogen peroxide</td>
</tr>
</tbody>
</table>
Heterogeneous Catalysts Global Market 2010

- Chemicals € 3,0 bn
- Polyolefins € 1,0 bn
- Chemical Industry € 4,0 bn 35,4%
- Refinery € 3,1 bn 27,4%
- Mobile Emissions € 3,7 bn
- Stationary Emissions € 0,5 bn

∑ € 11,3 bn

Source: BASF estimates
SRI Consulting 2011
Process Research and Chemical Engineering (GC)
Research Organization

Heterogeneous Catalysis (GCC)
New Technologies (GCN)
Chemical and Process Engineering (GCP)
Organic Synthesis and Homogeneous Catalysis (GCS)
Major Research Sites for Heterogeneous Catalysis (BASF Group)

- Beachwood, OH
- Iselin, NJ
- Union, NJ
- Huntsville, AL
- Savannah, GA
- Attapulgus, GA
- Vidalia, LA
- Nienburg, Germany
- Hannover, Germany
- Ludwigshafen, Germany
- Heidelberg, Germany (hte)
- DeMeern, Netherlands
- Shihwa, Korea (HCC)
- Shanghai, China
- Numazu, Japan (NECC)
- Güilin, China
Process Research and Chemical Engineering (GC)
Research Focus

- Product innovation
- Process innovation
- Process optimization

- Extension of the value chains
- Development of new technologies
- Raw material change
Process Research and Chemical Engineering
Propylene Oxide
HPPO Process

\[ \text{Propylene + H}_2\text{O}_2 \rightarrow \text{Propylene Oxide} \]
Polyurethanes
Propylene Oxide Product Life Cycle Technologies

Propylene oxide capacity [kt/a]

Year


Total
Chlorohydrin
SM/PO
MTBE/PO
Cumene
HPPO
Propylene Oxide
State-of-the-Art Technologies at BASF

Chlorohydrin
1930

\[
\text{Propene} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{Cl} \text{OH} \rightarrow \text{CH}_2\text{O} \text{H}
\]

\[+ \text{Ca(OH)}_2 \rightarrow \text{O}
\]

- \[\text{CaCl}_2\]

2.2 t salt/t PO

SM/PO
1975

\[
\text{Phenol} + \text{O}_2 \rightarrow \text{PhenolOOH}
\]

\[- \text{H}_2\text{O}\]

2.3 t SM/t PO

BASF-HPPO
JDA with DOW
2008

\[
\text{Propene} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_2\text{O} \text{H}
\]

- \[\text{H}_2\text{O}\]

water only
Propylene Oxide (HPPO Process)
BASF Catalyst

Macroscopic catalyst

Microscopic catalytic site

\[ \text{CH}_3\text{O} + \text{H}_2\text{O}_2 \xrightarrow{\text{Ti-zeolite system}} + \text{CH}_3\text{OH} \]

Proprietary Ti-zeolite System
Propylene Oxide (HPPO Process) Simplified Process Flowsheet

- Epoxidation using fixed-bed catalyst arrangement

- Full $\text{H}_2\text{O}_2$ conversion and solvent methanol recycle, PO distillation for final purification
HPPO
Pilot Plant Ludwigshafen
HPPO
Production Plant Antwerp
HPPO
Economic and ecological advantages
300 kt/a Plant in Antwerp

- 75% reduction of waste water
- 35% lower energy consumption
- 25% lower capital investment
- Only water as co-product
Recognition of HPPO Technology

IChemE Award 2009
York, GB, Nov. 2009

40th Kirkpatrick Honor Award 2009
New York, Nov. 2009

US Presidential Green Chemistry Award
Washington, June 2010
Process Research and Chemical Engineering (GC)
Research Focus

- Product innovation
- Process innovation
- Process optimization

Extension of the value chains
Development of new technologies
Raw material change
Acrylic Acid

\[ \text{CH}_2\text{CH} = \text{C} = \text{O} \]

Colourless liquid with perceptible odour \((T_m = 13°C, T_b = 141°C)\)
- corrosive
- flammable (flash point ~ 49°C)
Polyacrylates
Acrylic Acid from Propene

**Step 1:**

\[ \text{CH}_2\text{=CH--CH}_3 + \text{O}_2 \xrightarrow{\text{Bi-Fe-Mo-O}} \text{CH}_2\text{=CH--C=O} + \text{H}_2\text{O} \]

Propene

\[ \Delta H = -341 \text{ kJ/mol} \]

**Step 2:**

\[ \text{CH}_2\text{=CH--C=O} + 0.5 \text{ O}_2 \xrightarrow{\text{Mo-V-O}} \text{CH}_2\text{=CH--C=O} + \text{H}_2\text{O} \]

Acrolein

\[ \Delta H = -254 \text{ kJ/mol} \]

- Process developed by SOHIO and Nippon Shokubai
- Since 1977 at BASF
Improvement of Acrylic Acid (AA) Catalysts

- **AA Yield [Index]**
- **CO₂ Emission / t AA [%]**
- **Propene load [Index]**

<table>
<thead>
<tr>
<th>Year</th>
<th>AA Yield</th>
<th>CO₂ Emission</th>
<th>Propene Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>1976</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
</tr>
<tr>
<td>1981</td>
<td>100 %</td>
<td>67 %</td>
<td>150</td>
</tr>
<tr>
<td>1986</td>
<td>110</td>
<td>50 %</td>
<td>200</td>
</tr>
<tr>
<td>1991</td>
<td>120</td>
<td>33 %</td>
<td>30 %</td>
</tr>
<tr>
<td>1996</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Electricity**

City with 275,000 two persons households
Light Duty Engine Production (Million)

Year | Gasoline | Diesel | Others | Total
--- | --- | --- | --- | ---
2008 | 51 | 15 |  | 66
2009 | 45 | 12 |  | 57
2010 | 56 | 16 |  | 72
2011 | 57 | 17 |  | 74
2012 | 60 | 17 |  | 77
2013 | 66 | 18 | 1 | 85
2014 | 71 | 20 |  | 92
2015 | 75 | 22 | 1 | 98
2016 | 78 | 23 | 1 | 102

Source: JD Power, Engine & Transmission Forecast, Q4/2011
# Engine out emissions

## Passenger Cars

<table>
<thead>
<tr>
<th></th>
<th>NEDC</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/km</td>
<td>“g/km”</td>
<td>g/kWh</td>
</tr>
<tr>
<td><strong>Gasoline</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Audi / 2,0 l)</td>
<td>5.15</td>
<td>0.95</td>
<td>2.79</td>
</tr>
<tr>
<td><strong>Diesel</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(BMW / 2,0 l)</td>
<td>0.95</td>
<td>0.16</td>
<td>0.20</td>
</tr>
</tbody>
</table>

## Trucks

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diesel</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MAN / 12,4 l)</td>
<td>6.78</td>
<td>3.50</td>
</tr>
</tbody>
</table>

### Emissions

- **CO**
  - Gasoline: 5.15 g/km
  - Diesel: 0.95 g/km
- **Hydrocarbons**
  - Gasoline: 1.05 g/km
  - Diesel: 0.16 g/km
- **NO\(_x\)**
  - Gasoline: 1.35 g/km
  - Diesel: 0.13 g/km
- **Soot**
  - Gasoline: Insign.
  - Diesel: 0.05 g/km

### Efficiency

- Gasoline: 2.79 g/km
- Diesel: 1.40 g/kWh
- Hydrocarbons: 0.20 g/km
- NO\(_x\): 3.50 g/kWh
- Soot: 0.06 g/km
### Worldwide Emission Regulations

#### Current regulations

- **Europe**: Euro 3, Euro 5, Euro 5, Global, 4a, Euro 4, Euro 6, Global, 4b
- **Brazil**: Euro 3, Euro 4
- **Russia**: Euro 3, Euro 4, Euro 5
- **India**: Euro 3, Euro 4
- **China**: Euro 3, Euro 4, Euro 5
- **South Korea**: Euro 5
- **Japan**: Euro 6, Global, 4a, Global, 4b
- **Vietnam**: Euro 3
- **Thailand**: Euro 3

#### Future regulations

- **Phase in**: CA LEV III
- **2016**: Euro 7 - to be decided in 2016

<table>
<thead>
<tr>
<th>Year</th>
<th>Light-duty</th>
<th>Heavy-duty</th>
<th>Motorcycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>2008</td>
<td>2009</td>
<td>2010</td>
</tr>
<tr>
<td>2011</td>
<td>2012</td>
<td>2013</td>
<td>2014</td>
</tr>
<tr>
<td>2015</td>
<td>2016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Legend:
- Light-duty
- Heavy-duty
- Motorcycle
Transition State Motorcycle
Main Reactions in Vehicle Exhaust Gas Treatment

Gasoline engines:

(1) $\text{CO} + \text{O}_2 \xrightarrow{\text{Pt} / \text{Pd}} \text{CO}_2$

(2) Hydrocarbons + $\text{O}_2$ \(\xrightarrow{\text{Pt} / \text{Pd}}\) $\text{CO}_2 + \text{H}_2\text{O}$

(3) $\text{NO}_x + \text{CO} \xrightarrow{\text{Rh} / (\text{Pd})} \text{CO}_2 + \text{N}_2$

Diesel engines:

(4) $\text{NO} + \text{O}_2 \xrightarrow{\text{Pt}} \text{NO}_2$

(5) $\text{C} + \text{NO}_2 \xrightarrow{\text{Cu} / \text{Fe} / \text{V}} \text{CO} + \text{NO}$

(6) $\text{C} + \text{O}_2 \xrightarrow{} \text{CO}_2$

(7) $\text{NO} + \text{NO}_2 + \text{O}_2 + \text{NH}_3 \xrightarrow{\text{Cu} / \text{Fe} / \text{V}} \text{N}_2 + \text{H}_2\text{O}$

(8) $\text{NH}_3 + \text{O}_2 \xrightarrow{\text{Pt}} \text{N}_2 + \text{H}_2\text{O}$
# Vehicles and Catalyst Families

<table>
<thead>
<tr>
<th>Vehicles Type</th>
<th>Catalysts</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gasoline Engine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDG</td>
<td>TWC</td>
<td></td>
</tr>
<tr>
<td><strong>Diesel Engines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDD</td>
<td>DOC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DOC + CSF</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DOC + CSF + SCR</td>
<td></td>
</tr>
<tr>
<td>HDD</td>
<td>DOC + CSF + SCR + AMOX</td>
<td></td>
</tr>
<tr>
<td><strong>Motorcycles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TWC</td>
<td></td>
</tr>
</tbody>
</table>
Emission Control in Trucks (Euro VI)

**Diesel Oxidation Catalyst (DOC)**
- Oxidation of carbon monoxide
- Oxidation of NO to NO₂

**Catalyzed Soot Filter (CSF)**
- Soot filtration
- Soot burn off
- Oxidation of CO and hydrocarbons
- Oxidation of NO to NO₂

**Selective Catalytic Reduction (SCR)**
- Reduction of NOx to nitrogen
- Hydrolysis of urea

**Ammonia Oxidation Catalyst (AMOX)**
- Oxidation of ammonia to nitrogen
General Structure of Automotive Catalysts

- Coatings on honeycomb
- Catalyst
  - Exhaust gas from engine
  - Top coat
  - Middle coat
  - Bottom coat
  - Honeycomb
General Structure of Catalytic Soot Filters (CSF)

- **Inlet channel**
- **Outlet channel**
- **Soot layer**
- **Porous Filter Wall**
- **Plug**
- **Catalyst**

Soot-laden gas flows through the inlet channel, filters through the porous wall, and reacts with the catalyst. The soot is converted to soot-free gas, which exits through the outlet channel.
Fluctuation of Precious Metal Prices
(Average prices p.a.)
Emission Limits and Precious Metal Content of Light Duty Gasoline Catalysts

Ford, Engine displacement ≤ 2 l

- CO
- Total Hydrocarbons + NOx
- None Methane Hydrocarbons

<table>
<thead>
<tr>
<th>Year</th>
<th>CO (g/km)</th>
<th>Total Hydrocarbons + NOx (g/km)</th>
<th>None Methane Hydrocarbons (g/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EURO 1 1992</td>
<td>3.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>EURO 2 1996</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>EURO 3 2000</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>EURO 4 2005</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>EURO 5 2009</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

- Pt + Pd + Rh
- Rh
Key Features of Automotive Catalysts

Automotive catalysts have:

- To manage different chemical reactions at the same time (oxidation and reduction)

- To work under varying reaction conditions
  - Low feed concentrations from 100 to 3 500 v ppm but high conversions and selectivities needed
  - Rapid oscillations between lean and rich atmospheres
  - Temperatures from ambient to 1000 °C
  - Space velocities from 10 000 h⁻¹ to 200 000 h⁻¹

- To cope with “other challenges”
Operator of Chemical Catalysts
Operator of Automotive Catalysts
Process Research and Chemical Engineering (GC)
Research Focus

- Product innovation
- Process innovation
- Process optimization

Extension of the value chains
Development of new technologies
Raw material change
Primary Energy Share

Source: Royal Dutch/Shell Group, "Energy Needs, Choices and Possibilities"
Syngas to Olefins

Reaktion: \[ \text{CO} + 2 \text{H}_2 \xrightarrow{\text{Katalysator}} \text{Kohlenwasserstoffe} + \text{H}_2\text{O} \]

Mechanismus:

Produkte: Breite Produktverteilung: C1 (Methan) – C100 (Wachse)
Benzene from Methane

\[ \text{CH}_4 \rightarrow \text{CH}_x \rightarrow \text{C}_2\text{H}_y \rightarrow \text{C}_2\text{H}_z \rightarrow \text{C}_6\text{H}_6 \]

HZSM-5

Zeolite (HZSM-5)
Process Research and Chemical Engineering (GC)
Research Focus

- Product innovation
- Process innovation
- Process optimization

- Extension of the value chains
- Development of new technologies
- Raw material change
PEM Fuel Cell
Proton Exchange Membrane

Air
Cathode
Electrolyte (Cell division)
Anode
Hydrogen

Electrons
Protons

Water

$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
Cost Target for Fuel Cell Systems

- **Mobile**
  - Submarine - PEM
  - Bus - PEM
  - APU - PEM
  - Car - PEM

- **Portable**
  - Laptop - DMFC

- **Stationary**
  - BHPP - MCFC
  - Home PEM
  - SOFC

Cost Targets:
- < 1,500 €/kW
- < 750 €/kW
- < 500 €/kW
- < 75 €/kW
PEM Fuel Cell
Proton Exchange Membrane

Air

Hydrogen

Electrolyte (Cell division)

Cathode

Anode

Water

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$H_2 \rightarrow 2H^+ + 2e^-$
Metal Organic Framework (MOF)

ZnO + COOH → MOF-5
World record values in surface areas

typ. 1 500 - 3 000 m²/g
MOF
Milestones by Prof. O. Yaghi (Berkeley)

Surface

World record
MOF-210
10,000 m²/g

MOF-200
8,000 m²/g

MOF-177
5,000 m²/g

MOF-5
3,000 m²/g

Zeolite 13X
600 m²/g

1950
1999
2004
2009
2010
Year
MOF
Unique Properties

World record values in surface areas
typ. 1 500 - 3 000 m²/g

Dead-volume-free structures
in contrast to zeolites and activated carbons

Low solid densities
300 - 500 g/l
MOF
Unique Properties

World record values in surface areas
  typ. 1 500 - 3 000 m²/g

Dead-volume-free structures
  in contrast to zeolites and activated carbons

Low solid densities
  300 - 500 g/l

High thermal stability
  decomposition only at 350 - 500 °C

Variable design
  more than 2 000 structures annually
MOF
Hydrogen Storage Capacities (50 bar, 77K)
MOF
Natural Gas Storage

Basolite™ A520

Metal: Aluminum

Linker: Fumaric acid

Properties: water-stable, thermally stable up to 350 °C
MOF
Natural Gas Storage (Mercedes Sprinter, 295 K)

Customer value: higher distance or lower pressure
MOF Natural Gas Storage

Cooperation with Agility: US manufacturer of alternative fuel systems

- 1 Truck equipped with MOF A520 pellets to store natural gas
- Successful operation since summer 2010