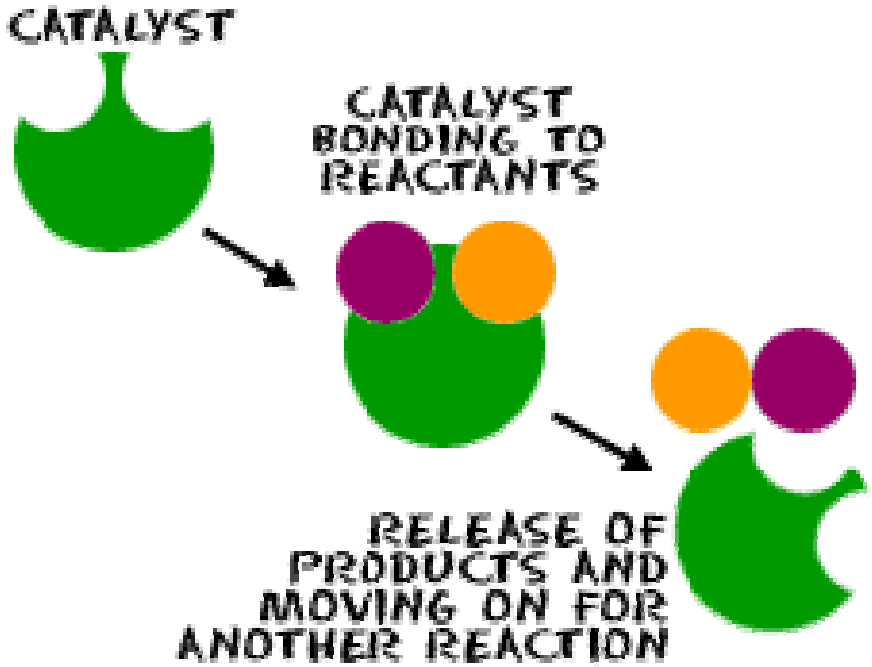
CATALYSTS IN COMBUSTION TECHNOLOGY AND FLUE GAS CLEANING

COMBUSTION AND FUELS

CATALYSIS AND CATALYSTS



Catalytic reactions

Catalysts influence a chemical reaction by changing its mechanism:

Reaction without catalyst: A + B = AB (final product)

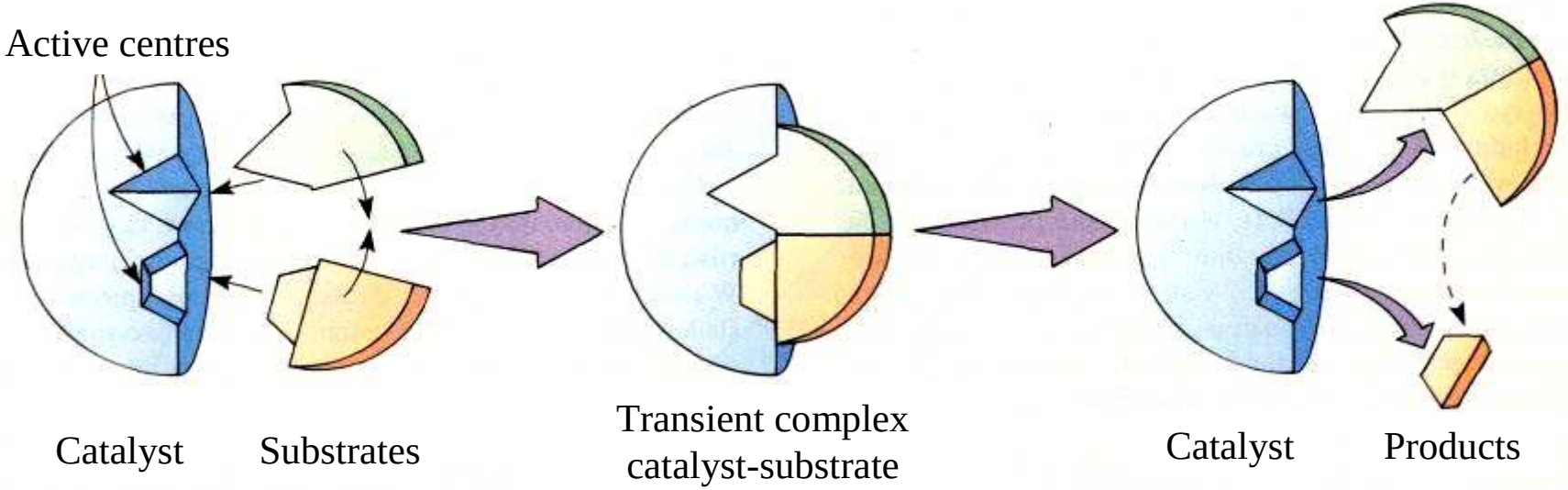
Reaction with catalyst: A + K = AK (transient product)

AK + B = AB + K

K – catalyst

Catalyst K is preserved in the chemical reaction.

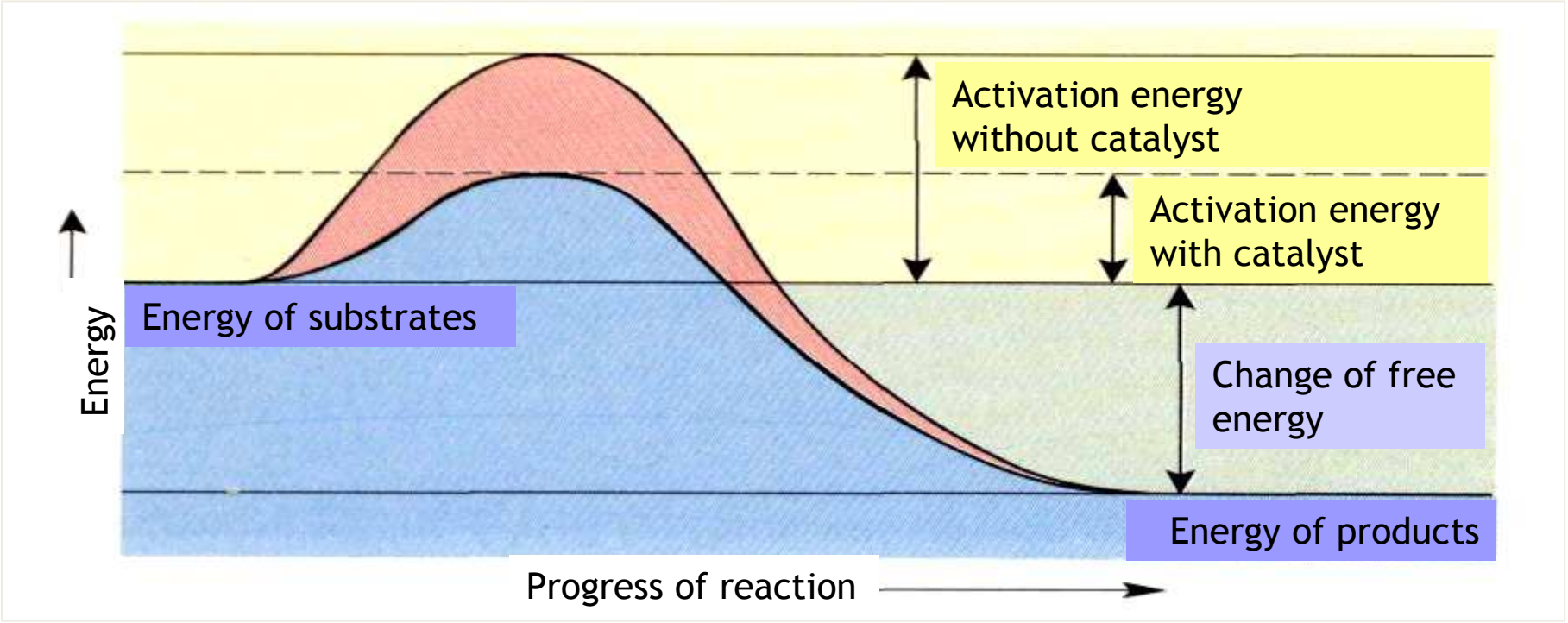
Operation of catalyst



Mechanism of catalyst operation. Reagents reacts with active centres of catalyst and together. After removal of products of reaction the catalyst may operate and catalyse of chemical reaction of new subtracts.

Catalysts

Catalysts is a chemical compound which influence the rate of chemical reaction by lowering its activation energy, i.e. the initial energy necessary to initiate the chemical reaction. Catalyst is a reagent, which amount before and after the chemical reaction doesn't change.



Types of catalyse reactions

Homogeneous catalysis – in gas phase.

Heterogeneous catalysis – on the surface of solid body.

In combustion processes and environment protection methods heterogeneous catalysis is in use.

Mechanism of Heterogeneous Catalysis

Heterogeneous catalyst catalyse chemical reactions in gas phase on the surface of solid body.

The mechanism of heterogeneous catalysis is as follows:

adsorption

↓

reaction in active centres

↓

desorption

Heterogeneous Catalysis

Adsorption – reaction in active centres – desorption

Adsorption – densification of gas phase on surface of on a solid body (chemisorption – adsorption with chemical reaction of gas- and solid-phase).

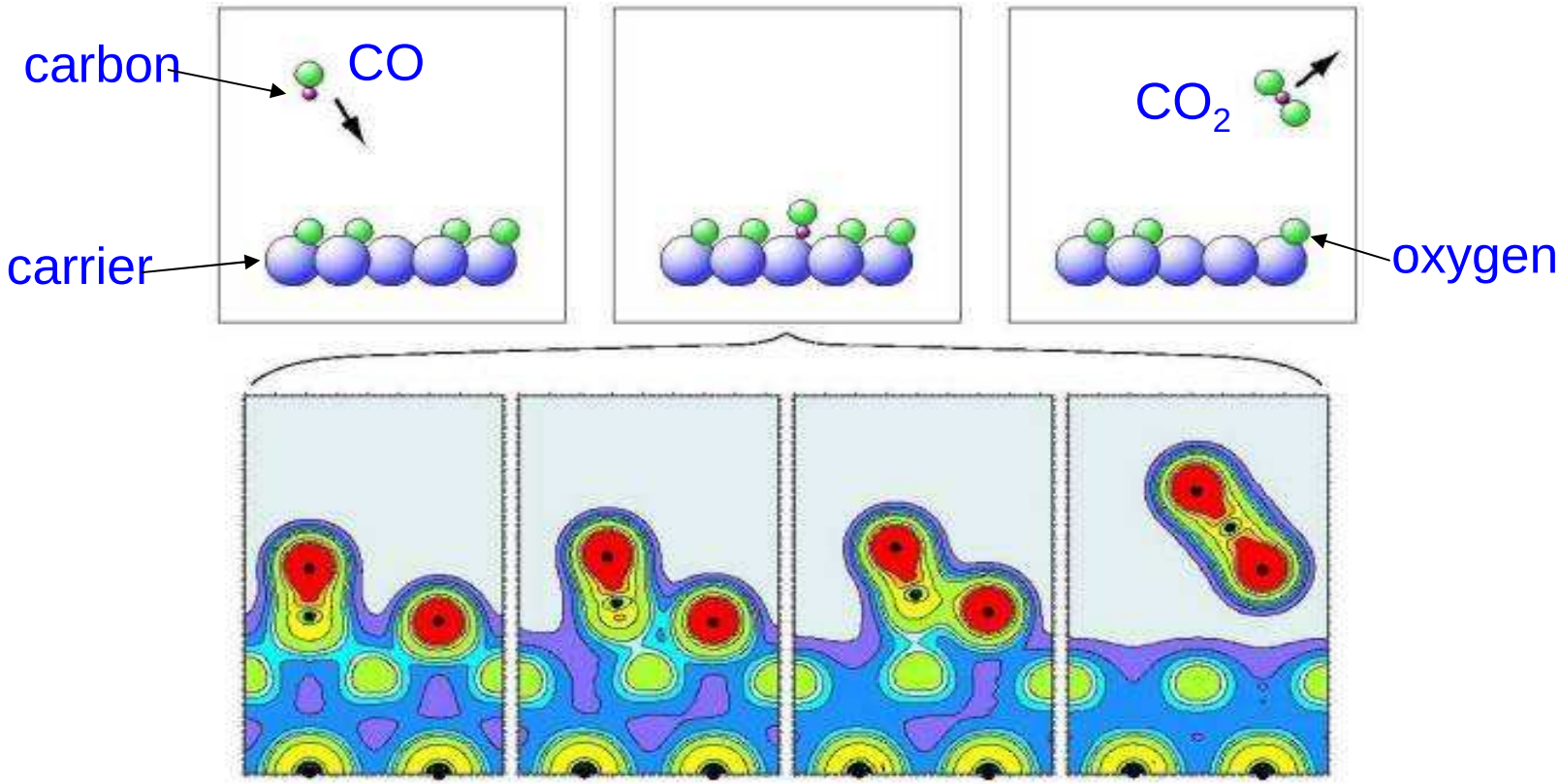
Active center – chemically active defects of crystal structure on the surface of a solid body.

Catalytic active centres – active centres having catalytic properties, i.e.:

Pt- O, Pt – H, Pd – H, Ni – O

Example: catalytic oxidation of CO

$$CO + O \rightarrow CO_2$$



Catalysts and catalytic reactions

Oxidation

Metals: mainly (platinum group): platinum, palladium, rhodium

Oxides: Ag_2O, Fe_2O_3, CuO, V_2O_5, Cr_2O_3, TiO_2, MnO_2

Reduction

Metals : platinum group, gold, iridium, chromium

Oxides: Cr_2O_3

Hydrogenation and de-hydrogenation:

Platinum group, cobalt, nickel, cuprum, zinc

ZEOLITES

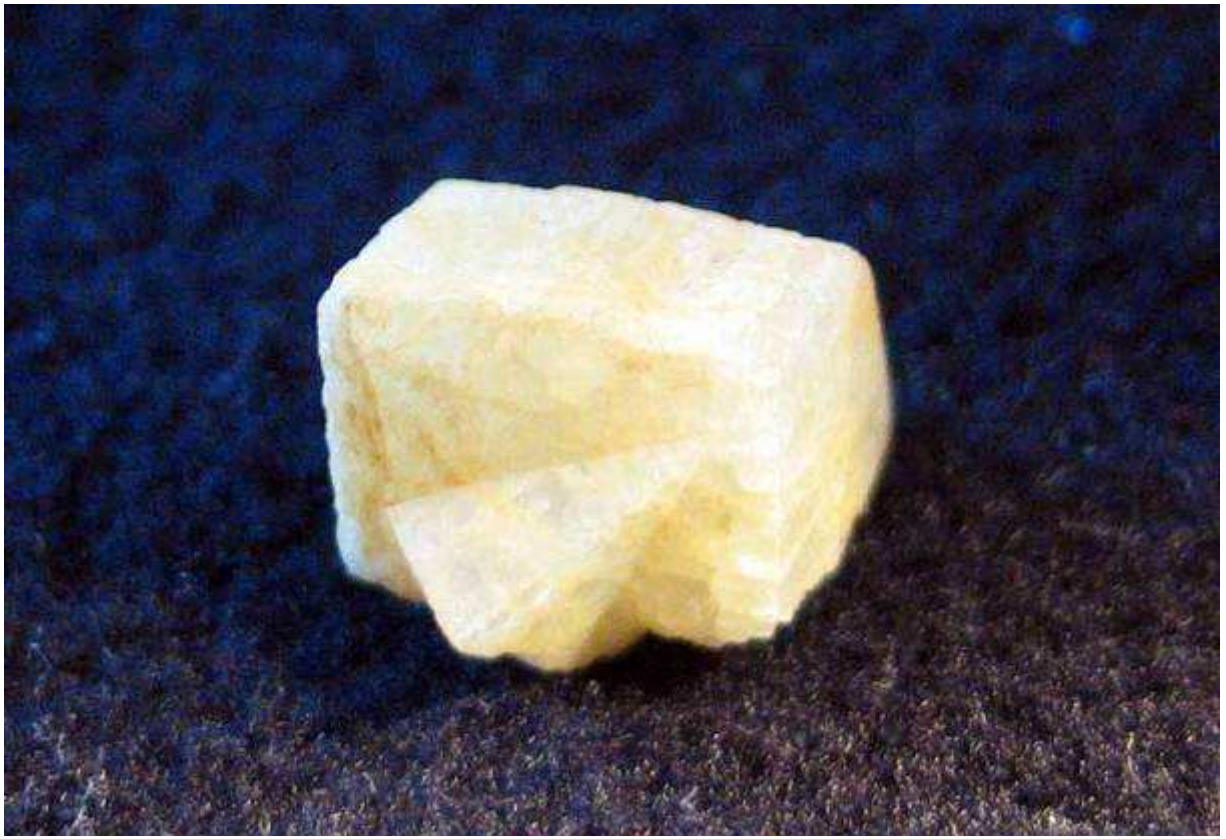
ZEOLITES

Zeolites are mineral catalysts of crystal structure. They are silicates of high porosity.

As catalysts are in use:

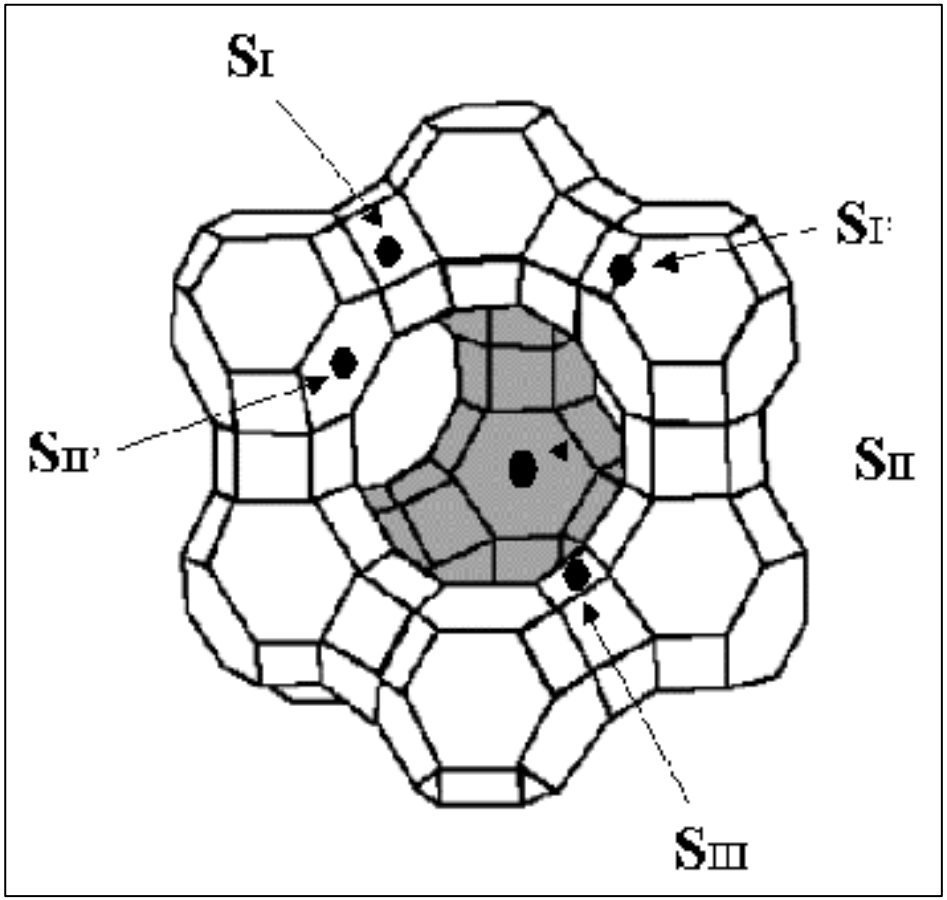
- natural zeolites (chabazyt, erionit, gmelinit, mordenit, fojazyt) and
- synthetic zeolites.

Chabazite



$(Ca, Na_2)[Al_2 Si_4 O_{12}] \times 6 H_2O$ – aluminiumsilica of calcium and sodium

STRUCTURE OF ZEOLITE



Deactivation of catalysts

In theory catalysts are not wear out in chemical reactions.

In fact their time of activity is limited due to the phenomenon called deactivation.

Deactivation is reduction of catalyst activity due to the chemical adsorption of some chemical elements or compounds, which form stable connections eliminating active centres.

Deactivation of catalysts

Heterogeneous catalysts are deactivated by chemical elements:

chlorines (J_2, Cl_2, Br_2), mercury (Hg), lead (Pb), phosphorus (P), arsenic (Ar)

and chemical compounds:

sulfur compounds, like: H_2S, CS_2, tiofen, HCN, CO, mercury salts, compounds of phosphorus, arsenic and lead.

TYPES OF CATALYST CARRIERS

- Ceramic
- Metallic

How do we understand ‘catalyst’?

Catalyst – rather catalytic reactor is a technical device, in which catalysis is in use.

A catalytic active substance covers directly the carrier or indirectly the intermediate layer on a carrier.

Ceramic carriers

Material: oxides (Al_2O_3, TiO_2)

Advantages:

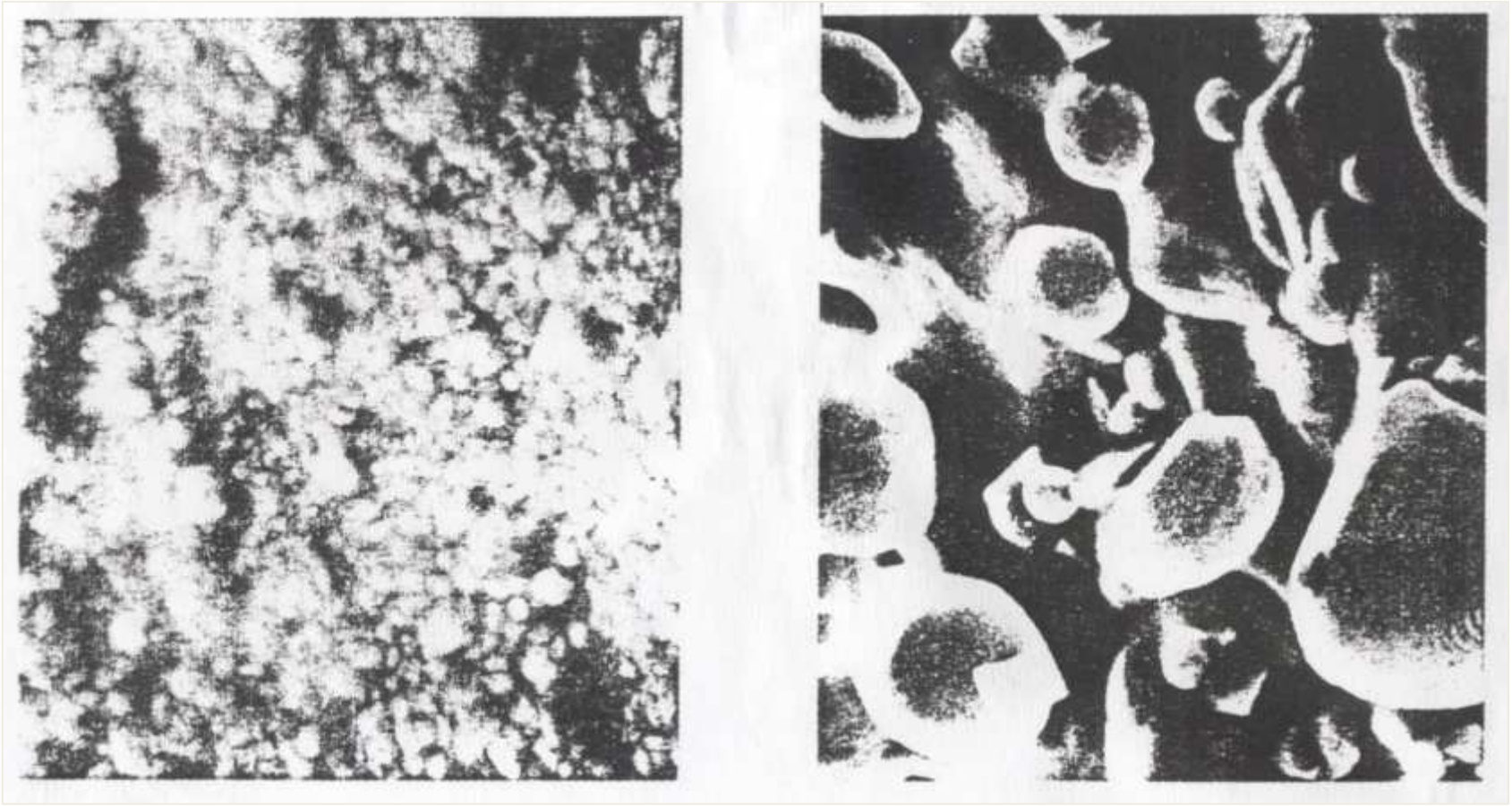
- Low costs of manufacture; easy formation
- Large inner surface
- Resistance to corrosion;
- Strong adhesion of active substance;
- High temperature of melting;

Disadvantages:

- Low resistance for vibrations;
- Low resistance for temperature variations.

Ceramic catalysts: monoliths and granulates

Surface of ceramic carriers

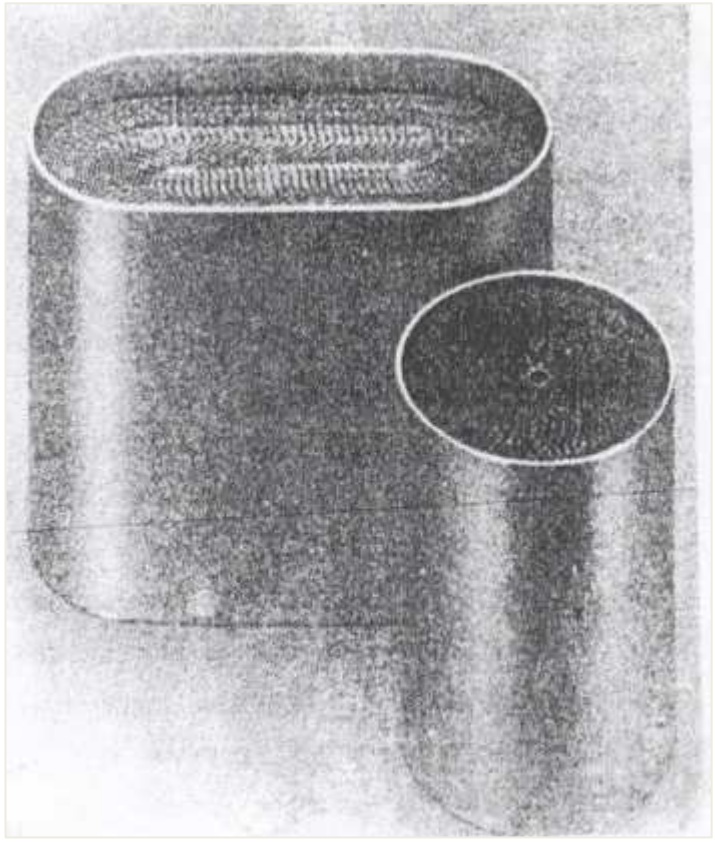


Metallic carriers

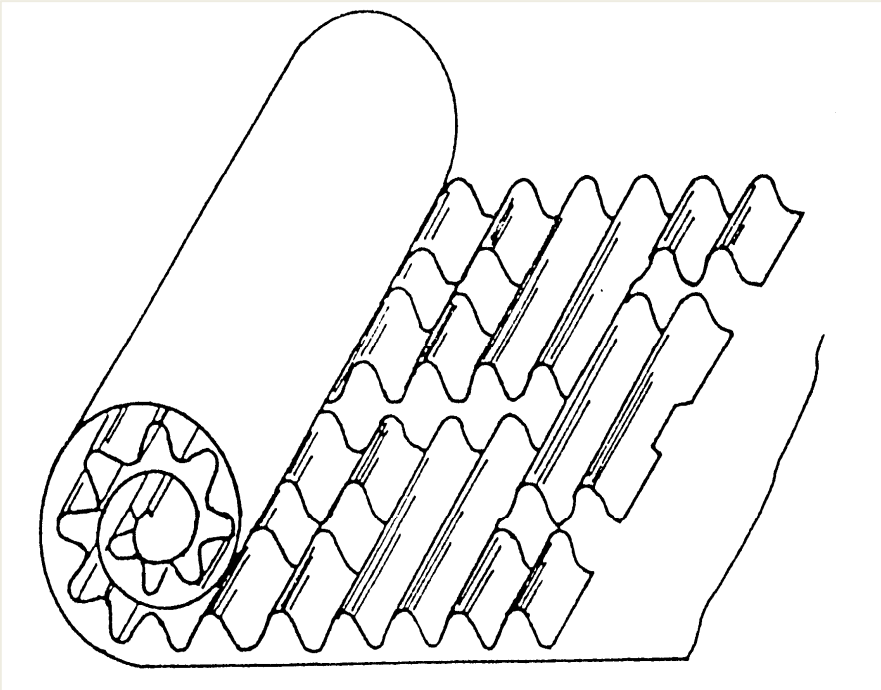
Advantages:

- Efficient heat transfer (resistance to local overheating);
- Low hydraulic resistance;
- High resistance to mechanical stresses;
- Low weight.

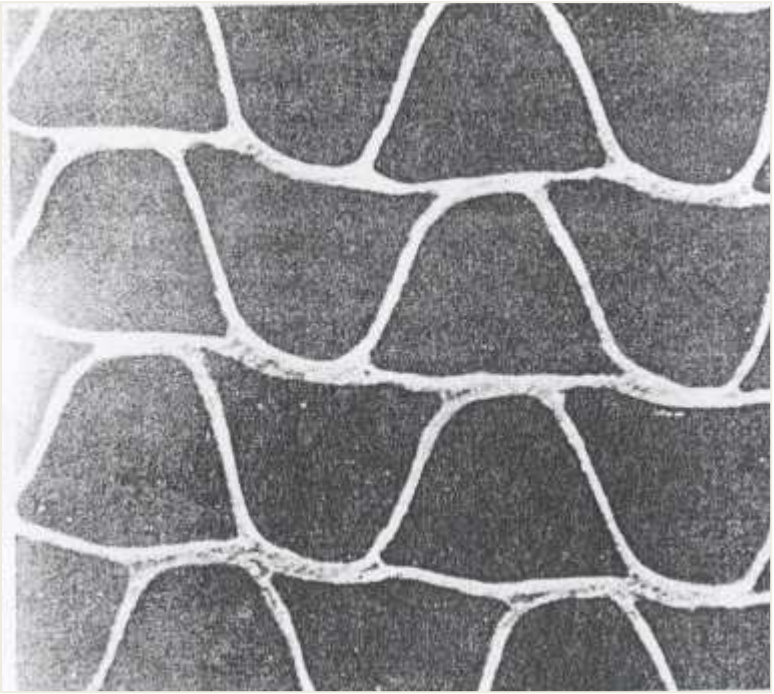
Metallic carriers usually are made in the form of steel tapes, wire or wire-net.



Structure of metallic carriers

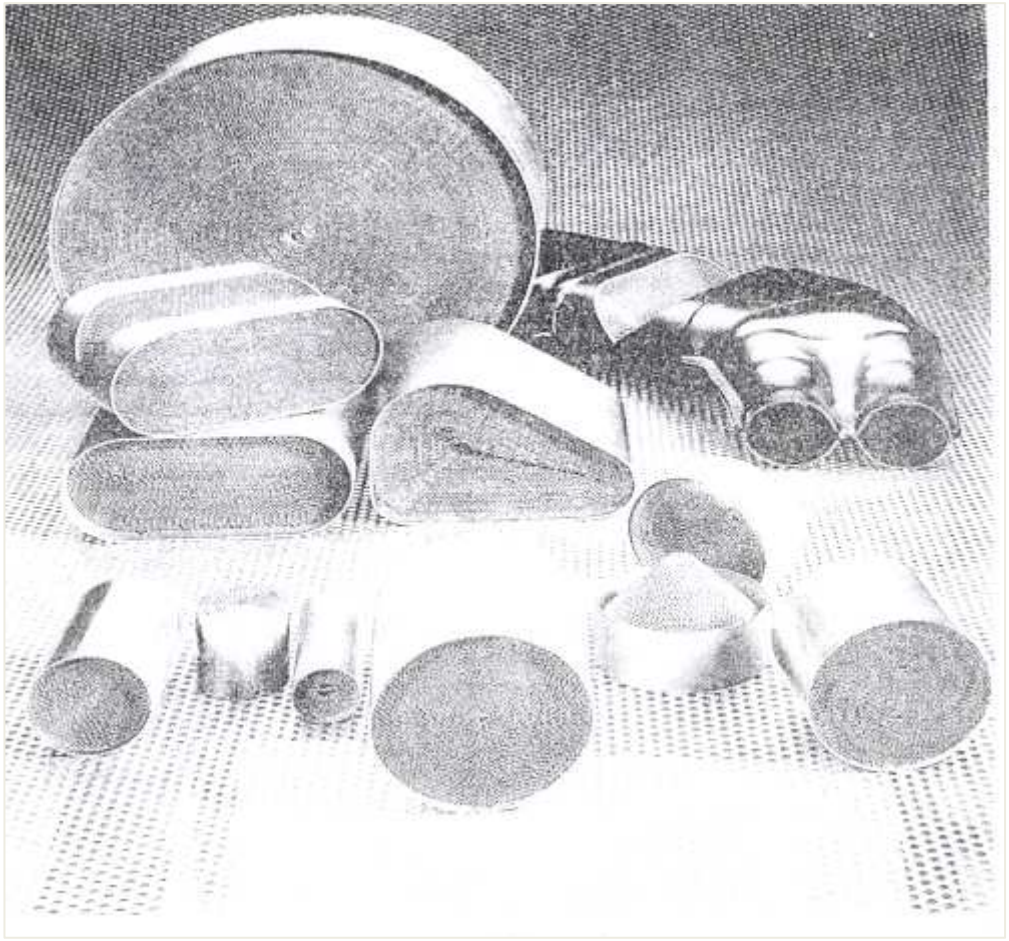


Structure of metallic carrier



Cross section of metallic carrier

„Metallic” catalysts



„Metallic” catalysts in car industry

APPLICATIONS OF CATALYSTS IN COMBUSTION TECHNOLOGY

The most important applications of catalysts in combustion and related technologies

- Removal of NO_x i SO_2 from flue gas (car industry).
- Reburning of CO and CH in flue gas.
- Burning of low-caloric waste gases and oxidation of odours (food industry, chemical technology, painting).
- Low-temperature combustion.
- Selective catalytic reduction of NO_x with ammonia.

Advantages and disadvantages of catalytic combustion

Advantages:

- Combustion with substantial air excess ($\lambda > > 1$).
- Combustion at low temperature.
- Low NO_x emission.

Disadvantages:

- Low thermal resistance of catalysts.
- Low mechanical resistance of catalysts.
- Temperature of catalytic combustion limited to 800 ^{o}C.

CATALYTIC COMBUSTION OF LOW-CALORIC GASES AND NEUTRALIZATION OF ODOURS

Combustion of low-caloric gases

Catalytic combustion of low-caloric waste gases:

•Catalysts make possible the neutralization of organic compounds in waste gases by their oxidation and utilization of thermal energy.

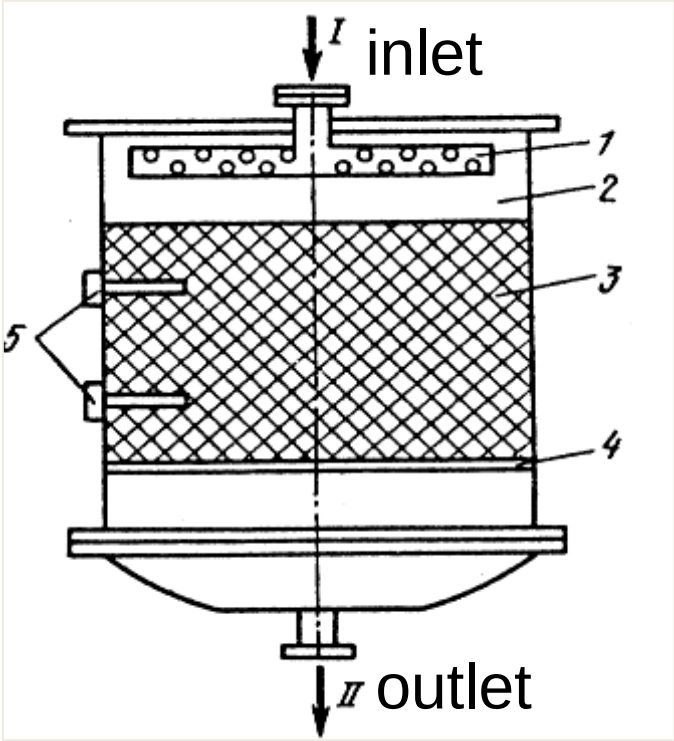
•Low temperature of the process: 250 – 450 ^{o}C;

Catalyst used

•The carrier are pellets or monoliths of Al_2O_3;

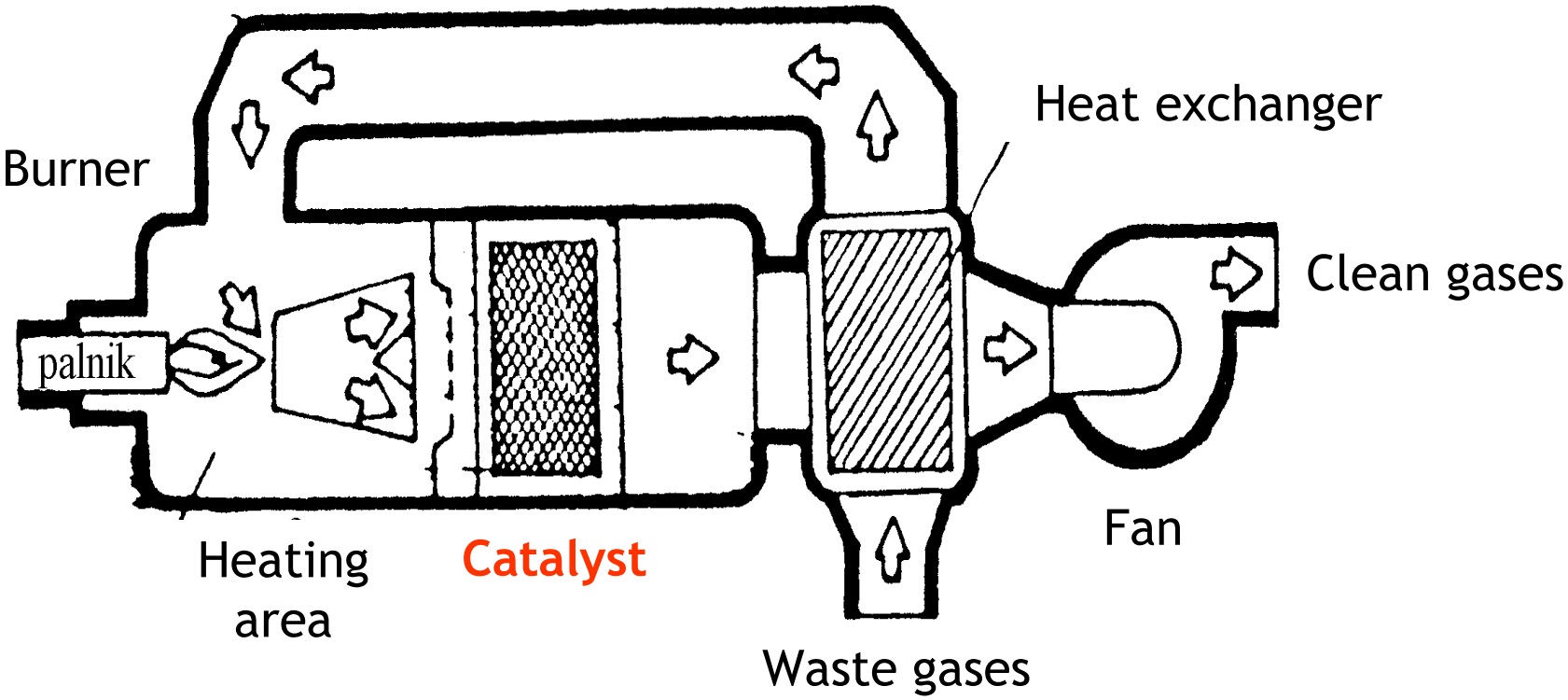
•Active material: platinum.

Simple catalytic reactors



Examples of catalytic reactors for combustion of low-caloric waste gases:
1 – gas distributor, 2 – mixing chamber, 3 – catalyst, 4 – wire net,
5 – thermocouples, I i II – inlet and outlet of gases

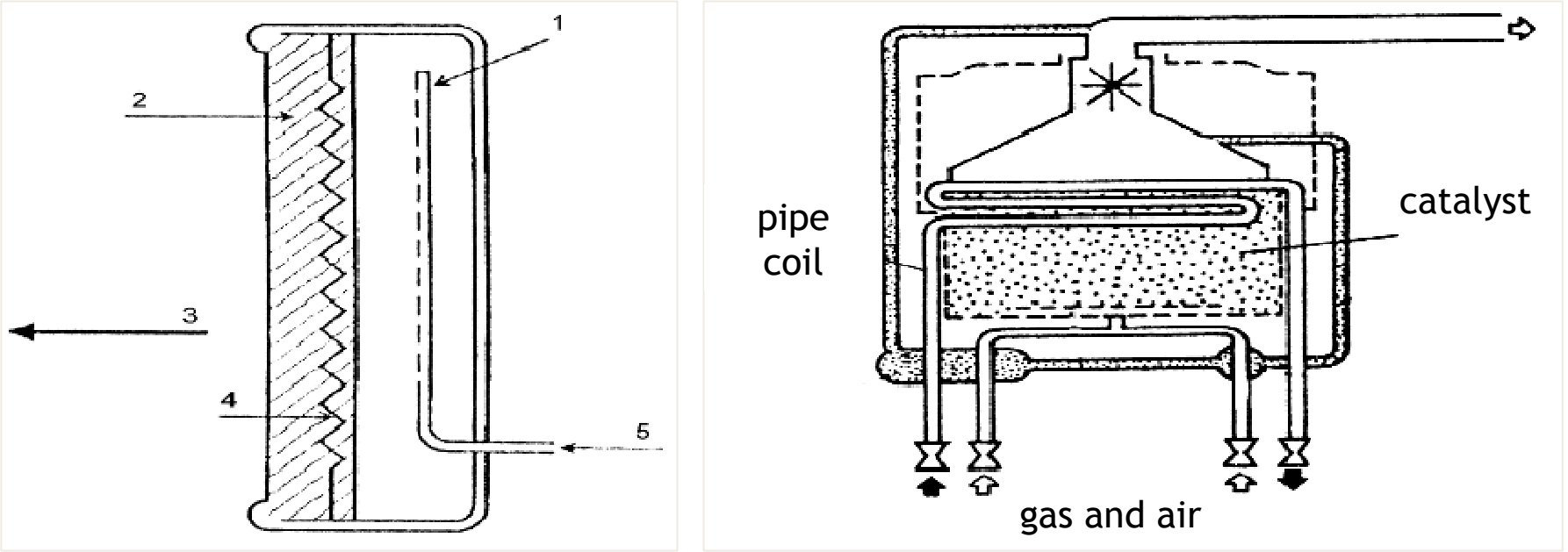
Installation of catalytic combustion of waste gases with heat exchanger



APPLICATIONS OF CATALYSTS IN HEAT ENGINEERING

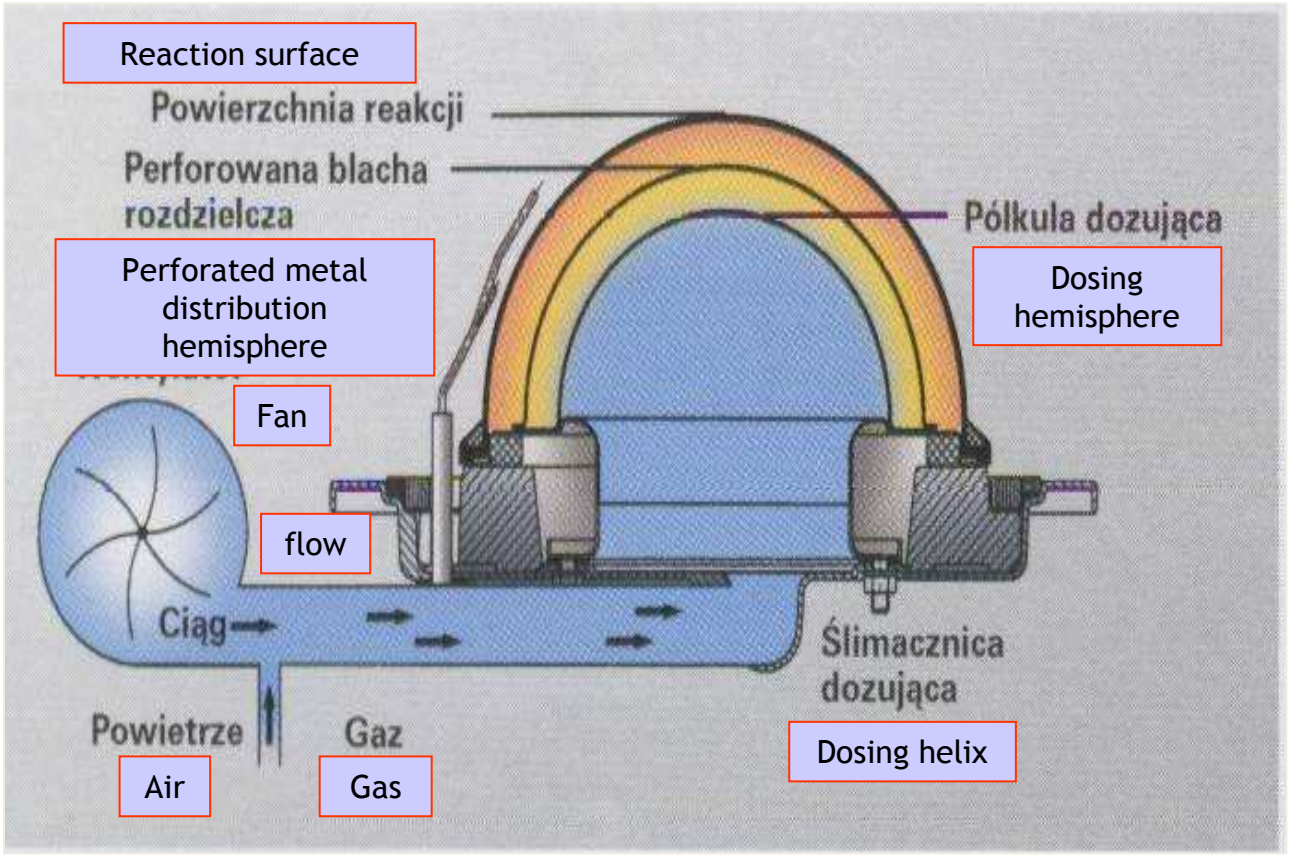
Applications of catalysts in low power heating devices

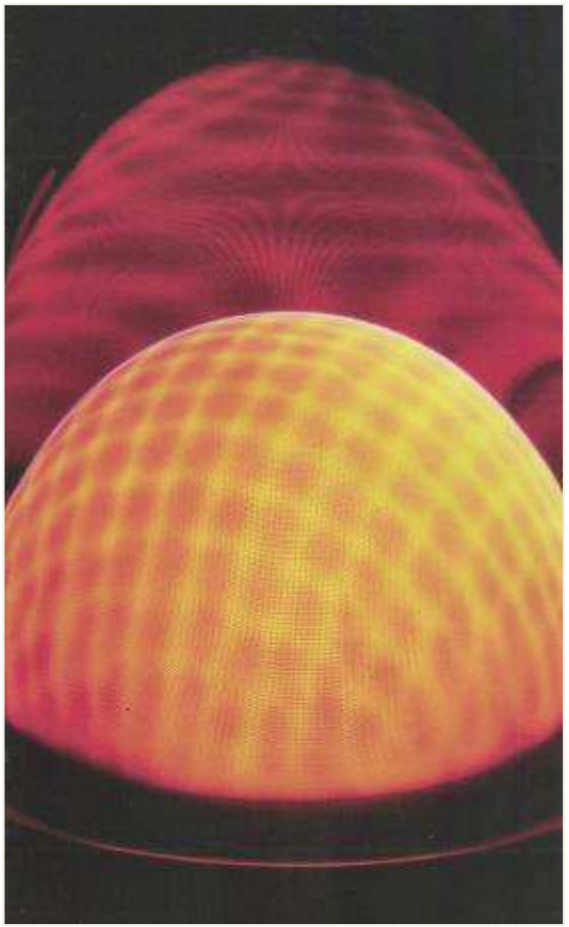
Domestic heating device – limitation of pollutants emission: NO_x, CO, CH in devices burning gas (natural gas or propane-butane).



(a) Radiant catalytic heater [1 – gas distributor, 2 – catalyst, 3 – radiation, 4 – electrical heater, 5 – gas inlet], (b) catalytic water heater

Radiant burner Matrix - design





Advantages of the burner Matrix

- Low pollutant emissions: NOx (9mg/kWh), CO (17mg/kWh);
- High safety exploitation and long durability, due to low load of the burner.
- Safe burning of natural gas in range of its parameters E and L.
- Reduced costs of heating.

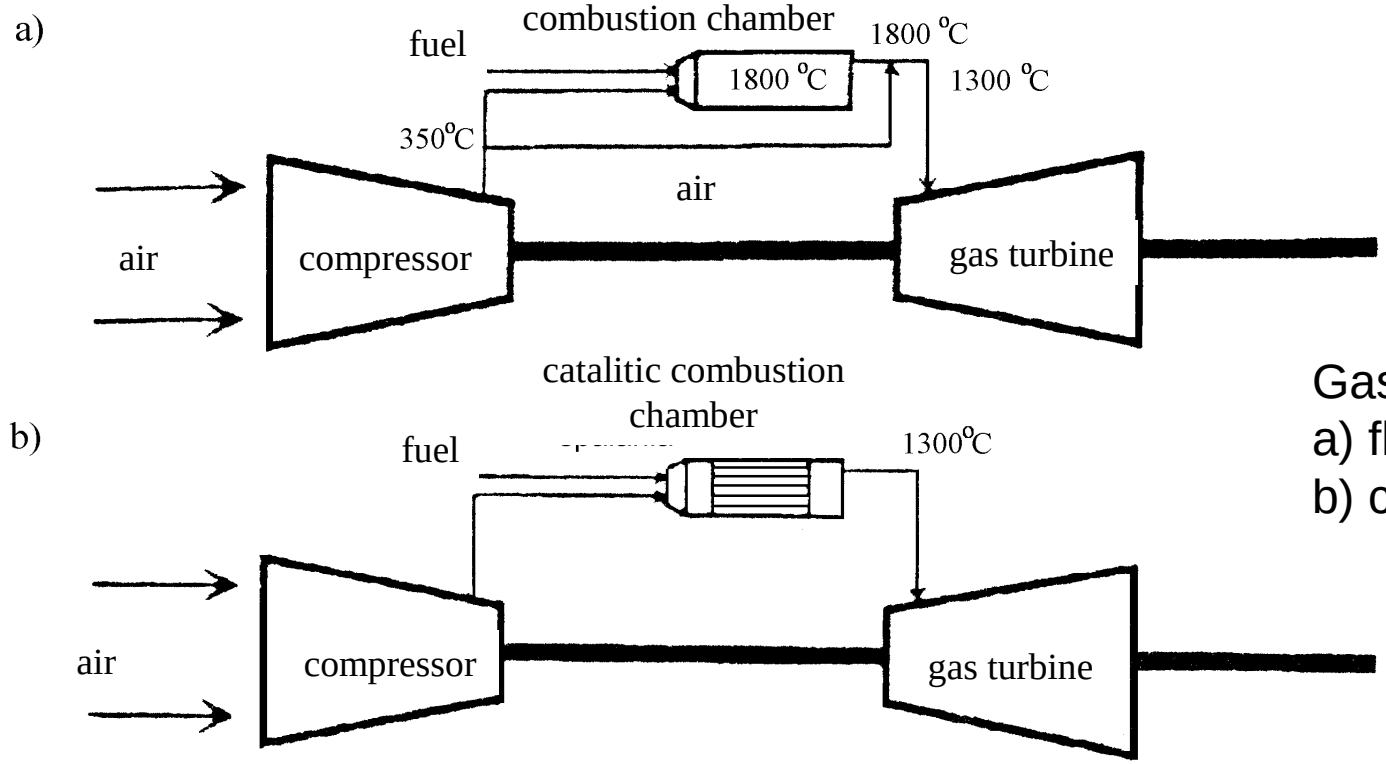
Radiant burner Matrix – how does it work

The net of stainless steel is glowing and transfers a lot of heat into the reaction zone by radiation. The burner surface is made without welding. The temperature of combustion is much lower than in comparison to diffusion flame.

Large half-sphere surface of burning makes of thermal load of the burner low,which caused that NO_x emission is low (below 8mg/kWh).

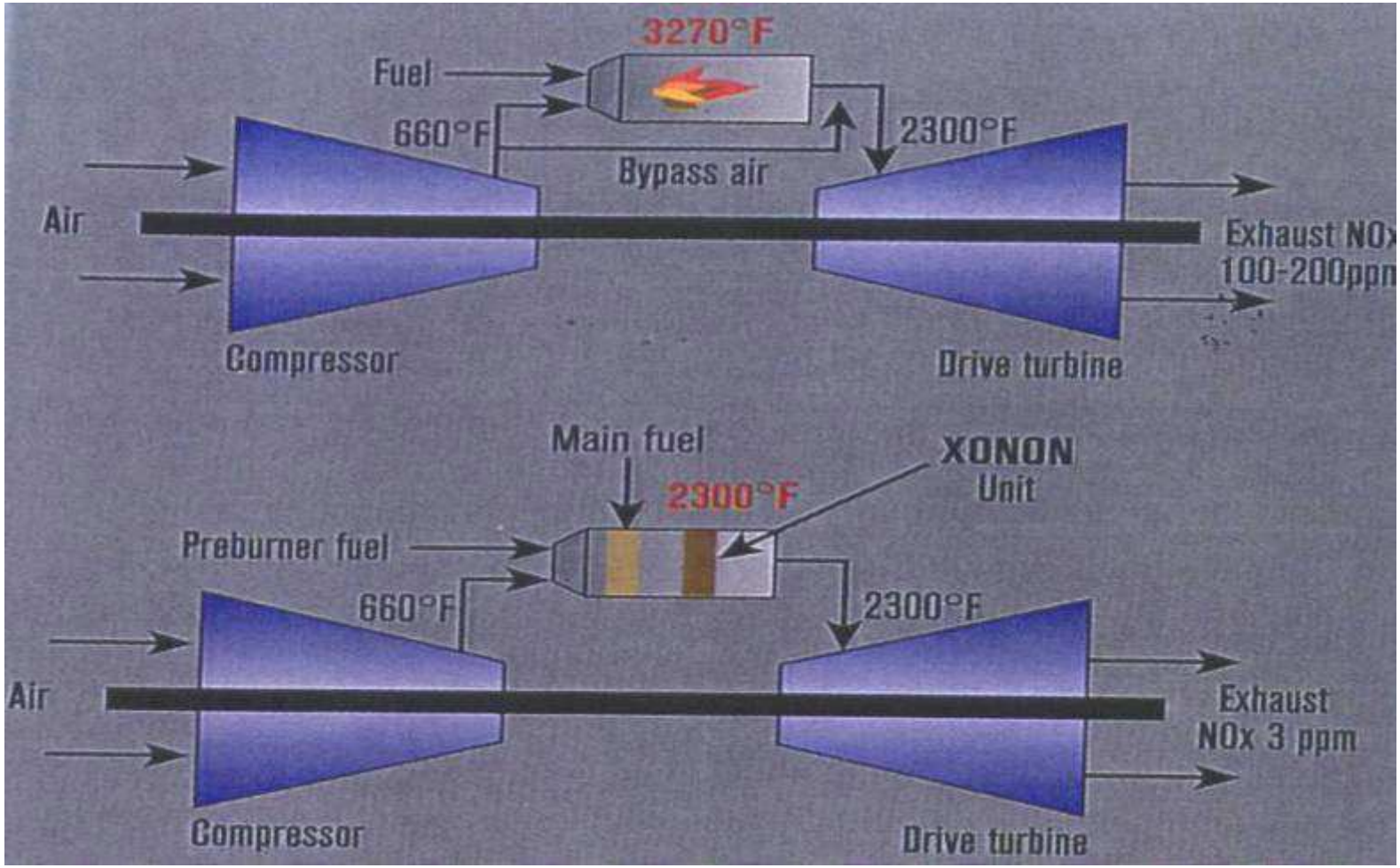
APPLICATIONS OF CATALYSTS IN GAS TURBINES

Catalytic gas turbines – catalysts allow burning of lean gas mixtures, reduce emission of NOx, unburnt fuel and decrease of heat loss due to low temperature of combustion (1200 – 1300 °C).



Gas turbine systems:
a) flame combustion,
b) catalytic combustion.

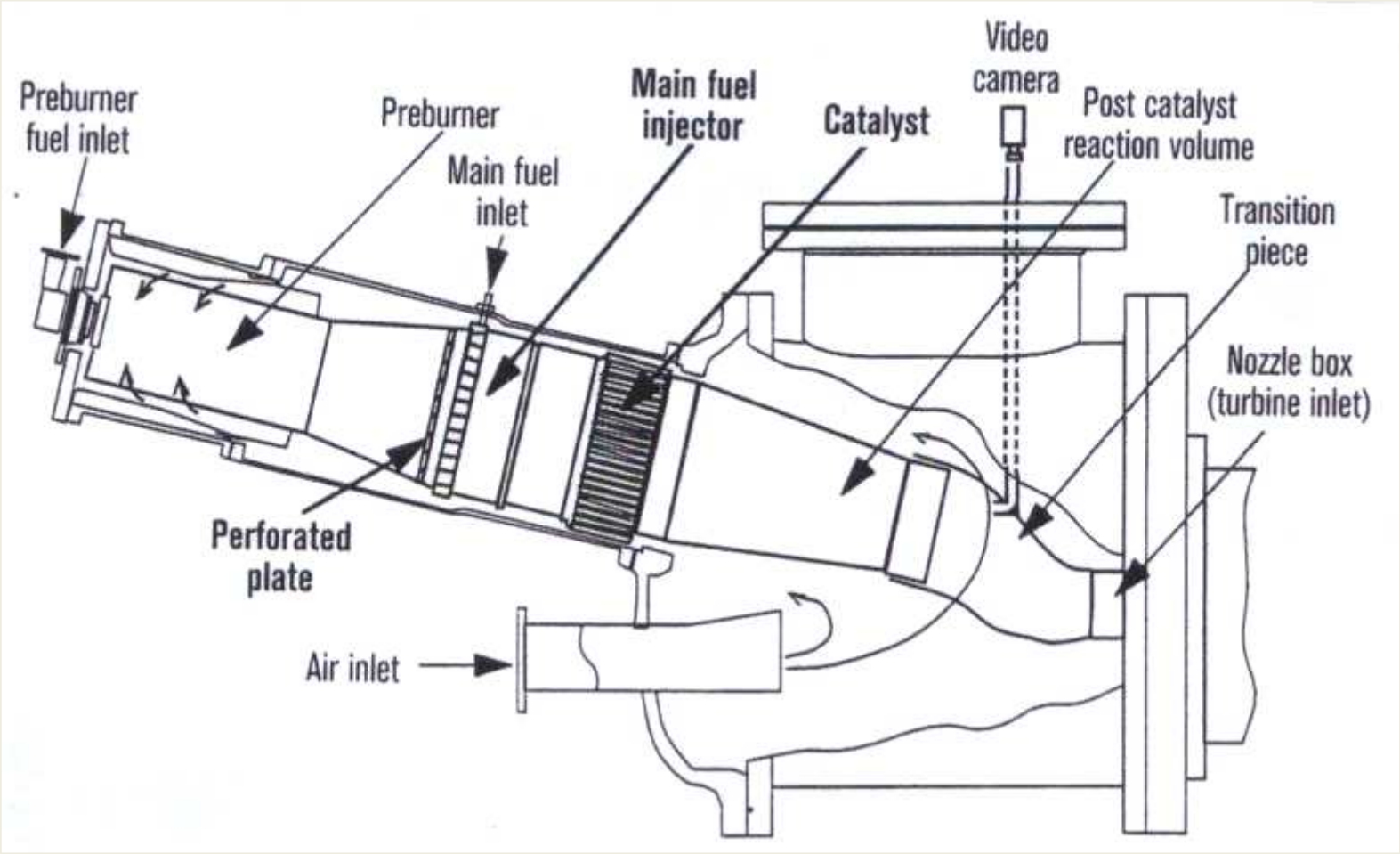
Comparison of conventional and catalytic GT



Catalytic combustion chamber GT

Catalysts

Scheme of catalytic combustion chamber of GT



APPLICATIONS OF CATALYSTS IN GAS CLEANING

Catalysts in car industry

Limited emissions of gas pollutant from SI (spark ignition) car engines:
NOx, CO, CH.

Three ways catalysts TWC (reduction and oxidation):

- reduction of NO (by CO) – over the rhodium catalyst (effective when oxygen is absent in flue gas):

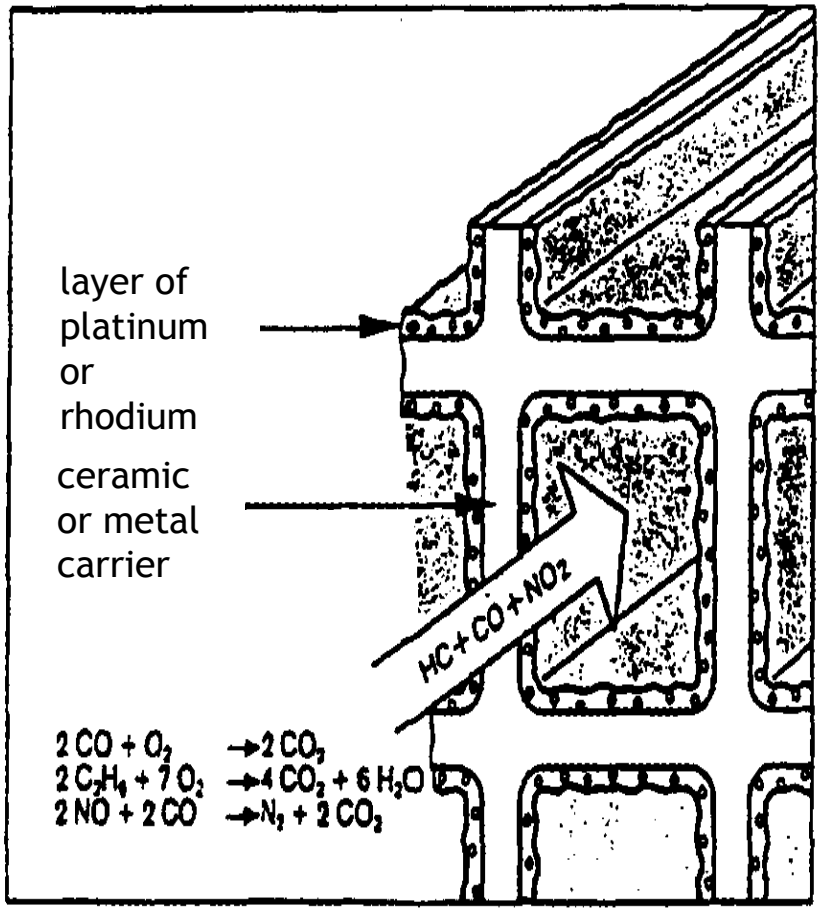
$$2NO + 2CO = N_2 + 2CO_2$$

- oxidation of CO and hydrocarbons – over the platinum catalyst (in the presence of small concentration of oxygen):

$$2CO + O_2 = 2CO_2$$

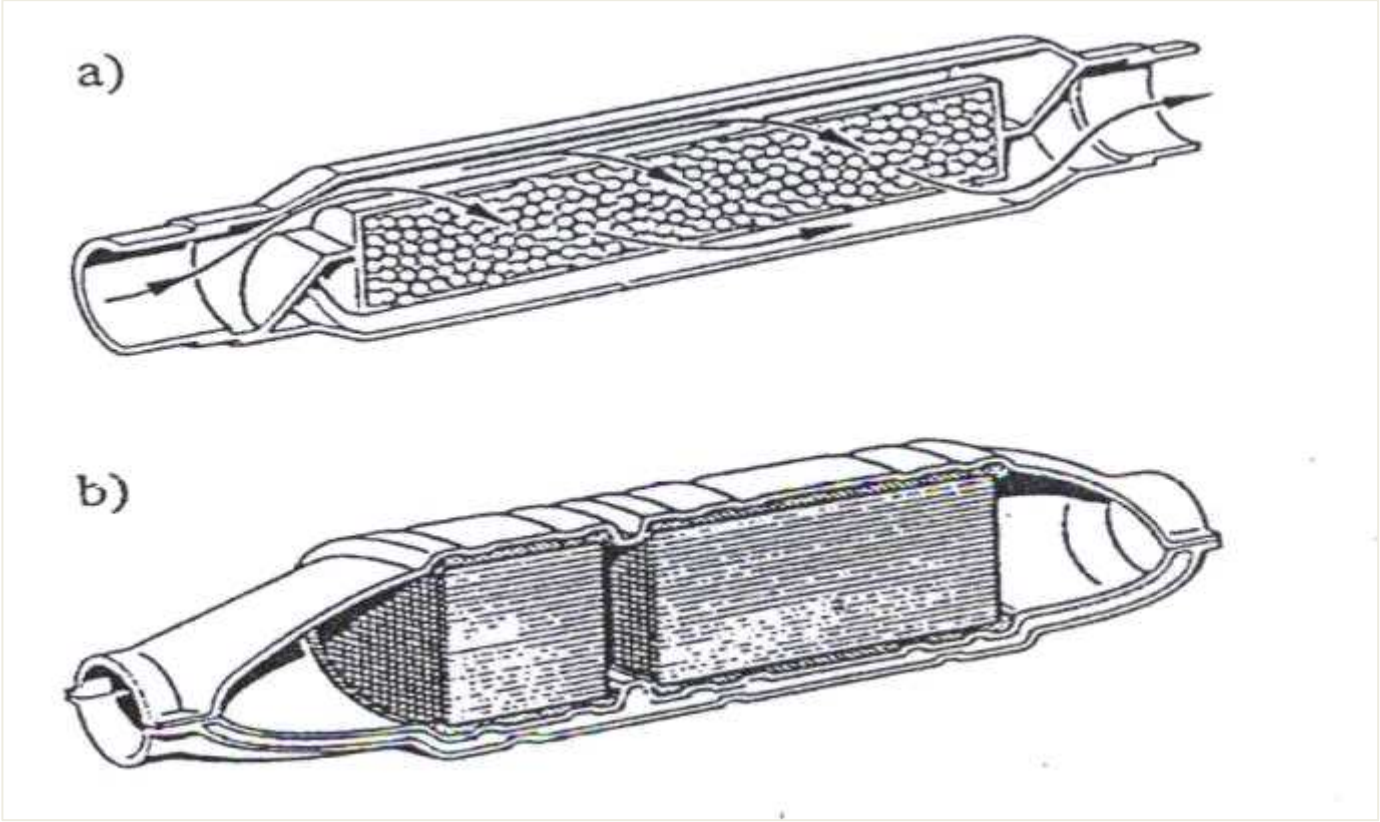
$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$

Structure and operation of the 3 way car catalyst



Carbon monoxide and hydrocarbons are oxidized in the presence of platinum by small concentration of oxygen in flue gas. The active catalytic substance (rhodium, palladium and platinum) is placed on a ceramic carrier (usually of the monolith type) or on the metallic carrier (made of sheet steel).

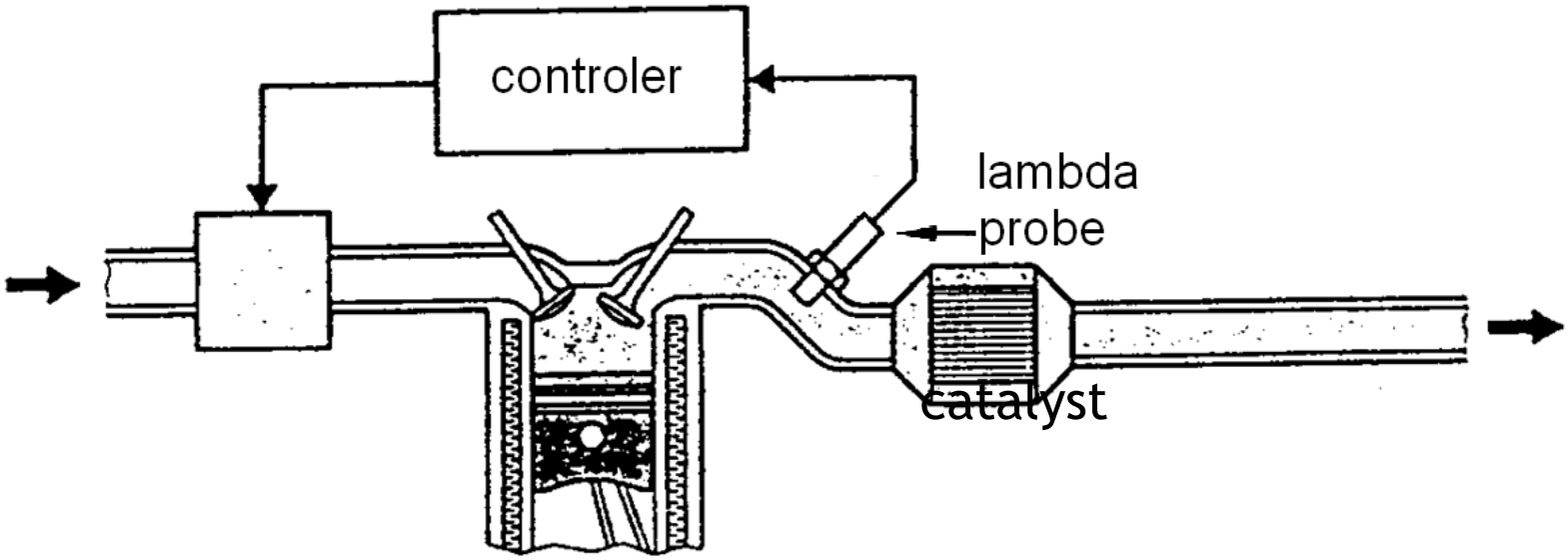
Ceramic car catalysts



Forms of catalyst carriers: a) granulates , b) monolith

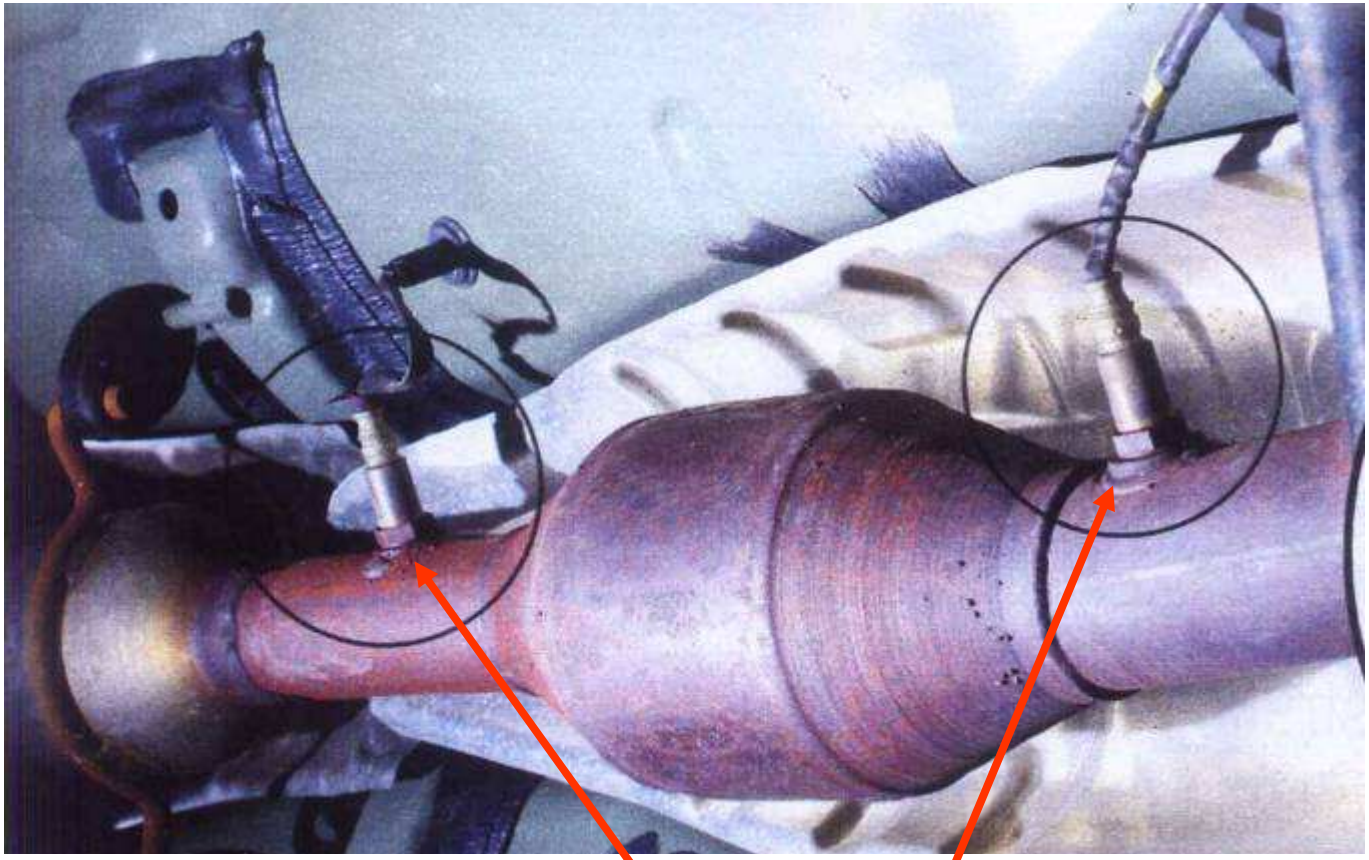
Control of oxygen content in flue gas

Near stoichiometric content of combustible mixture (λ = 0,99 ±0,5%) is possible due to computer control of air supply to the engine with the use of lambda probe.



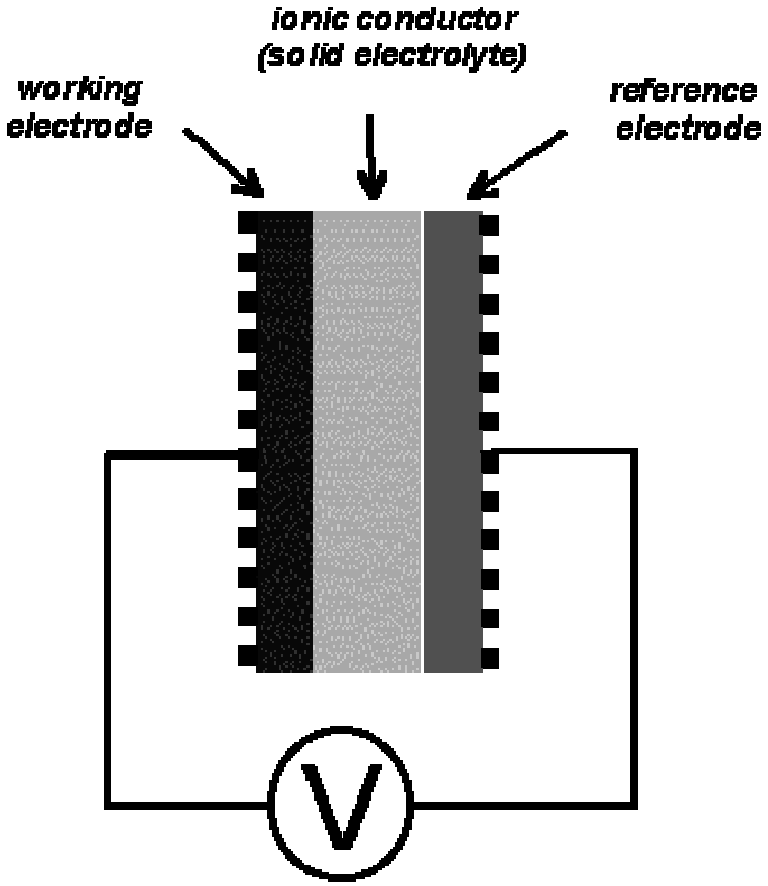
Three ways car catalyst and lambda sensor in SI engine.

Lambda probe in flue gas duct



Two lambda probes: before and after the catalyst.

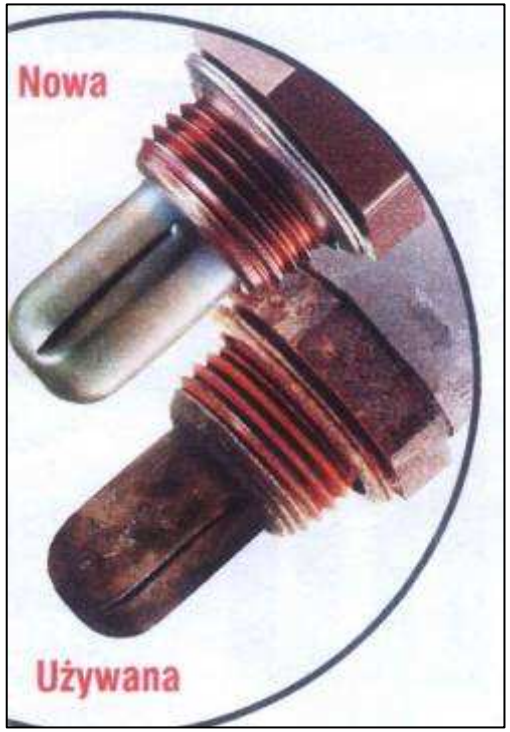
Scheme of lambda probe

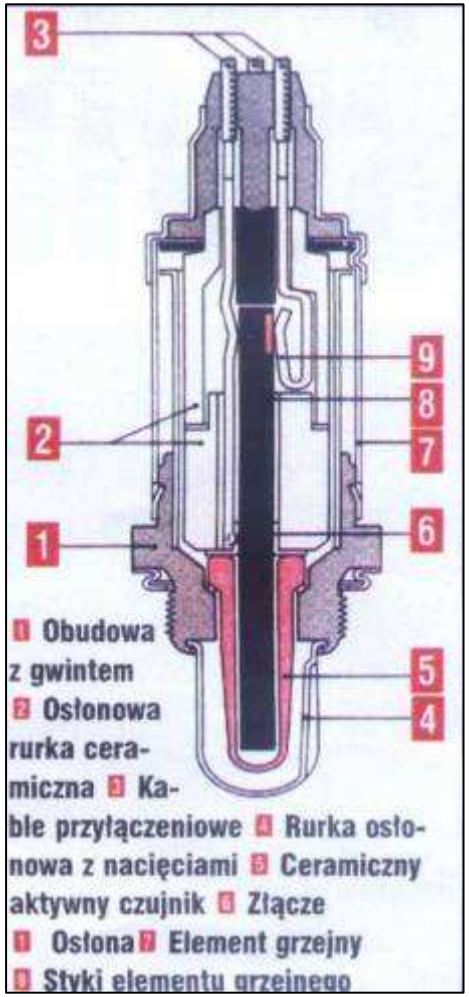


Lambda probe and its construction.

New one

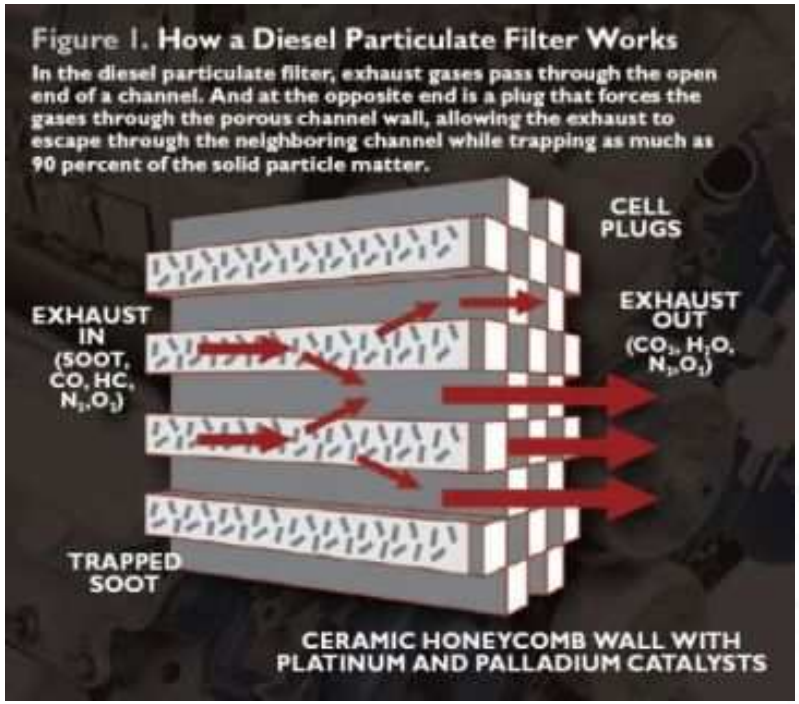
Used one





1. threaded casing
2. ceramic cover pipe
3. connection cable
4. cover with slits
5. ceramic sensor
6. connector
7. heater
8. heater contacts

Removal of soot from flue gas – VW TDI



SELECTIVE NON-CATALYTIC REDUCTION OF NO (SNCR)

Selective non-catalytic reduction of NOx – SNCR

Selective non-catalytic reduction of NO_x – reduces NO in flue gas with ammonia or urea in the presence of oxygen.

Chemical reaction of SNCR:

AMMONIA

$$NH_3 + OH = NH_2 + H_2O$$

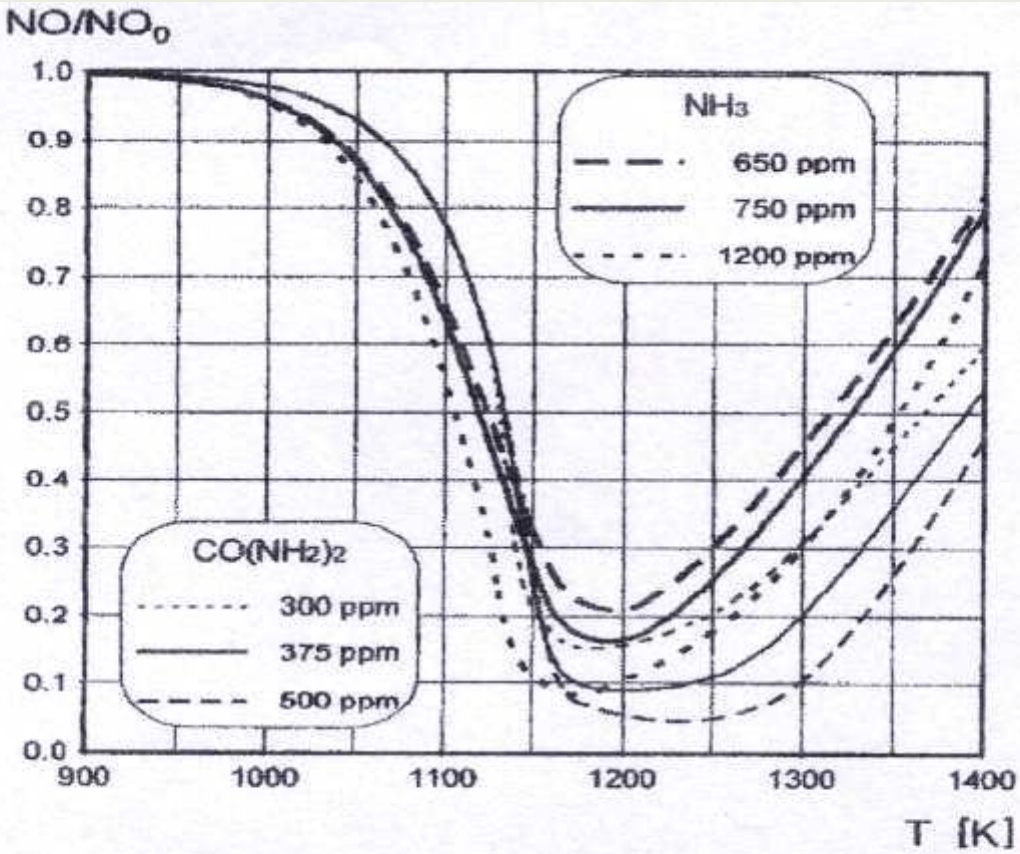
$$NH_2 + NO = N_2 + H_2O$$

UREA

$$CO(NH_2)_2 + 2NO + 1/2O_2 = 2N_2 + CO_2 + 2H_2O$$

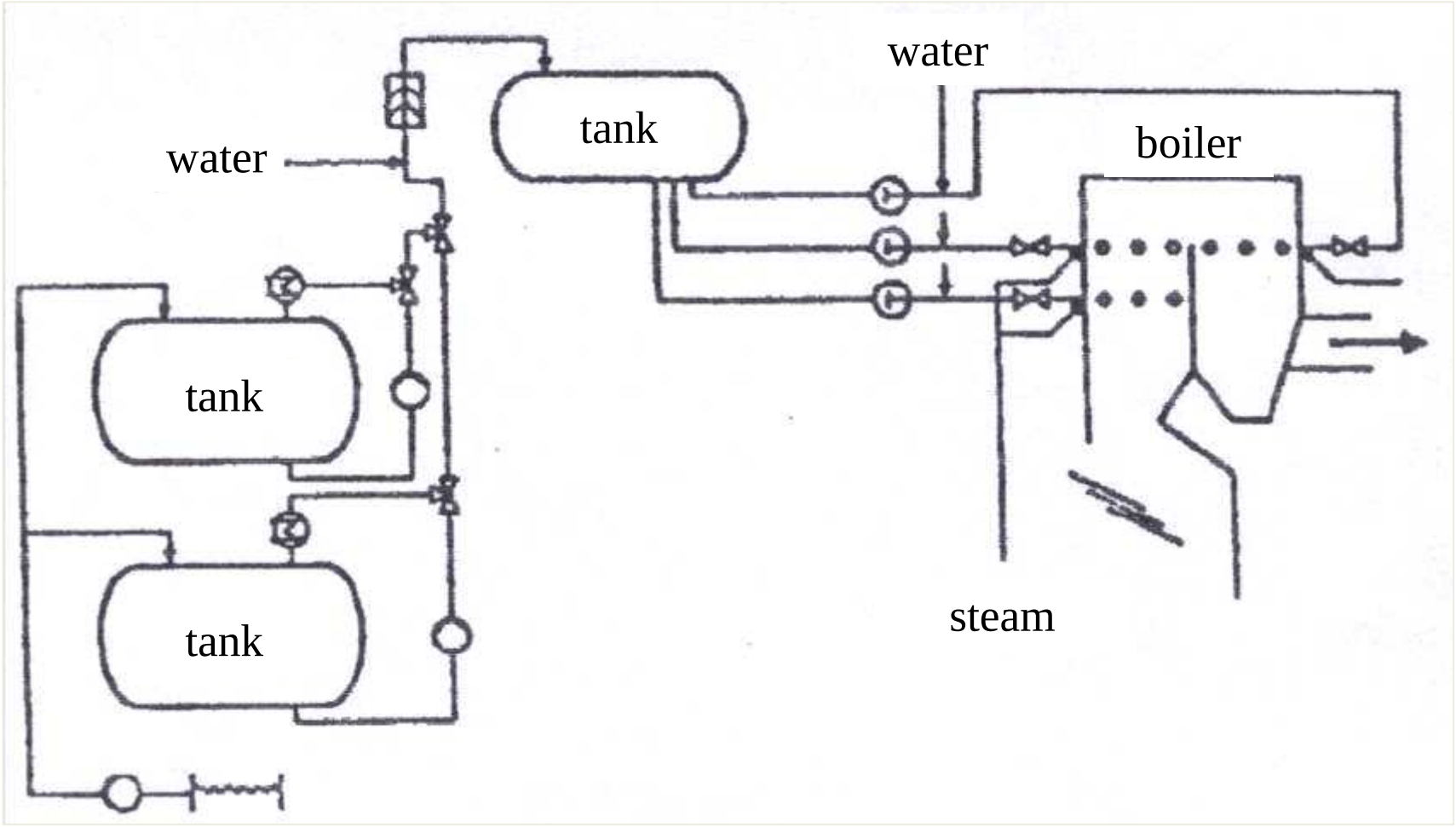
$$CO(NH_2)_2 = NH_3 + HNCO$$

Temperature „window” of selective non-catalytic reduction of NOx – SNCR



Rys. 02. Wpływ stężenia amoniaku i mocznika na redukcję NO w zależności od temperatury. Stężenie początkowe NO = 500 ppm, czas reakcji 1s, skład spalin O_2 = 6% obj., CO_2 = 8%, CO = 100 ppm reszta woda i azot, wg [14].

Scheme of the SNCR installation of NOx reduction

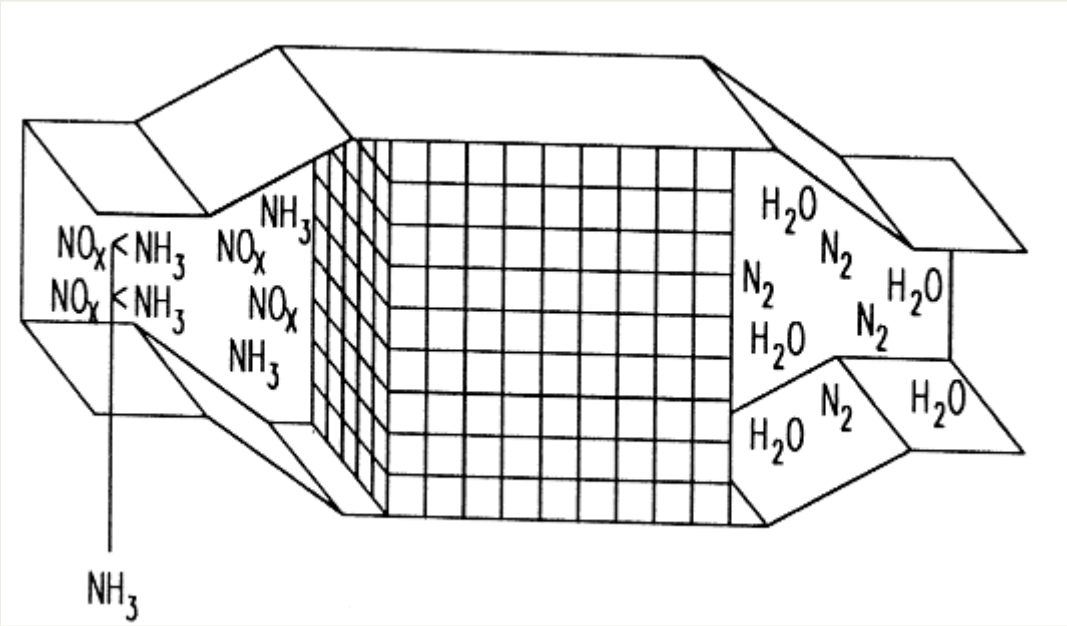


SELECTIVE CATALYTIC REDUCTION OF NO (SCR)

Scheme of the SCR installation

The active substance may be: platinum, palladium, titanium oxides, wolfram, vanadium.

Catalyst carries is ceramic monolith „honeycomb”.



Scheme of NO reduction in flue gas by SCR method.

Chemical kinetics of selective catalytic reduction SCR

The reduction process bases on chemical reactions of amine radicals with NO and NO_2. Amine radicals come from ammonia decomposition.The summary reaction assumes:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 = 3N_2 + 6H_2O$$

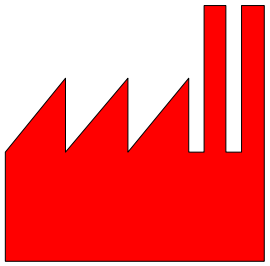
These reactions undergo in vanadium catalytic reactor in the presence of oxygen and at the temperature of flue gas in the range of 330-430 ^oC.

Applications of SCR

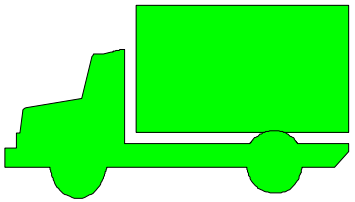
SCR has found several important applications for removal of NO from flue gas in:

- Gas turbines.
- SI engines.
- Coal-fired boilers in power plants.

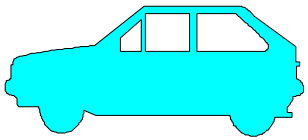
Power stations
Incineration plants
Stationary diesel engines



Trucks
Buses
Ferries
Cruise liner



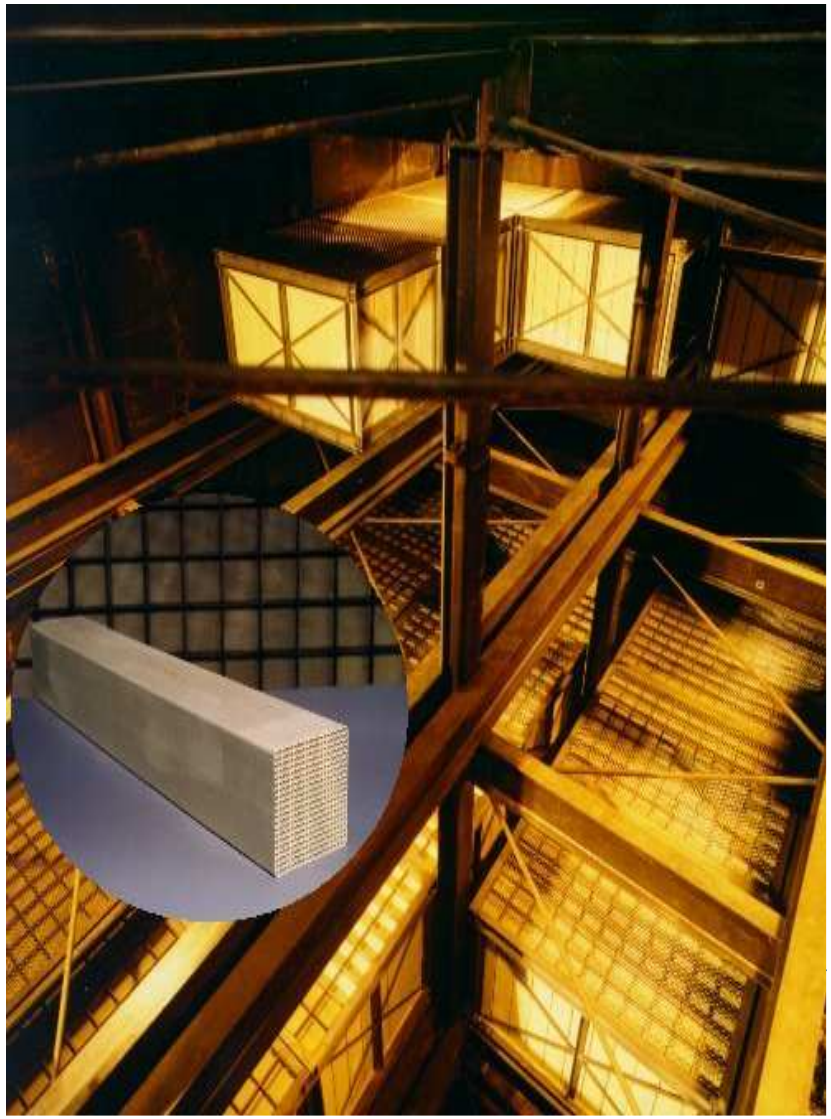
Challange:
Diesel passenger cars



Applications of SCR in power plants

•Coal-fired boilers:

Catalyst SCR reactor formation in power plant using ceramic monoliths.



NO reduction of emissions form coal -fired boilers

Pollutant	(Daily average)
Dust	20 mg/m^3
SO_2	50-100 MW: 850 mg/m^3 >100 MW: 200 mg/m^3
NO_x	50-100 MW: 400 mg/m^3 >100 MW: 200 mg/ m^3
CO	50-100 MW: 150 mg/m^3 >300 MW: 200 mg/m^3

Catalytic removal of SO2 form flue gas

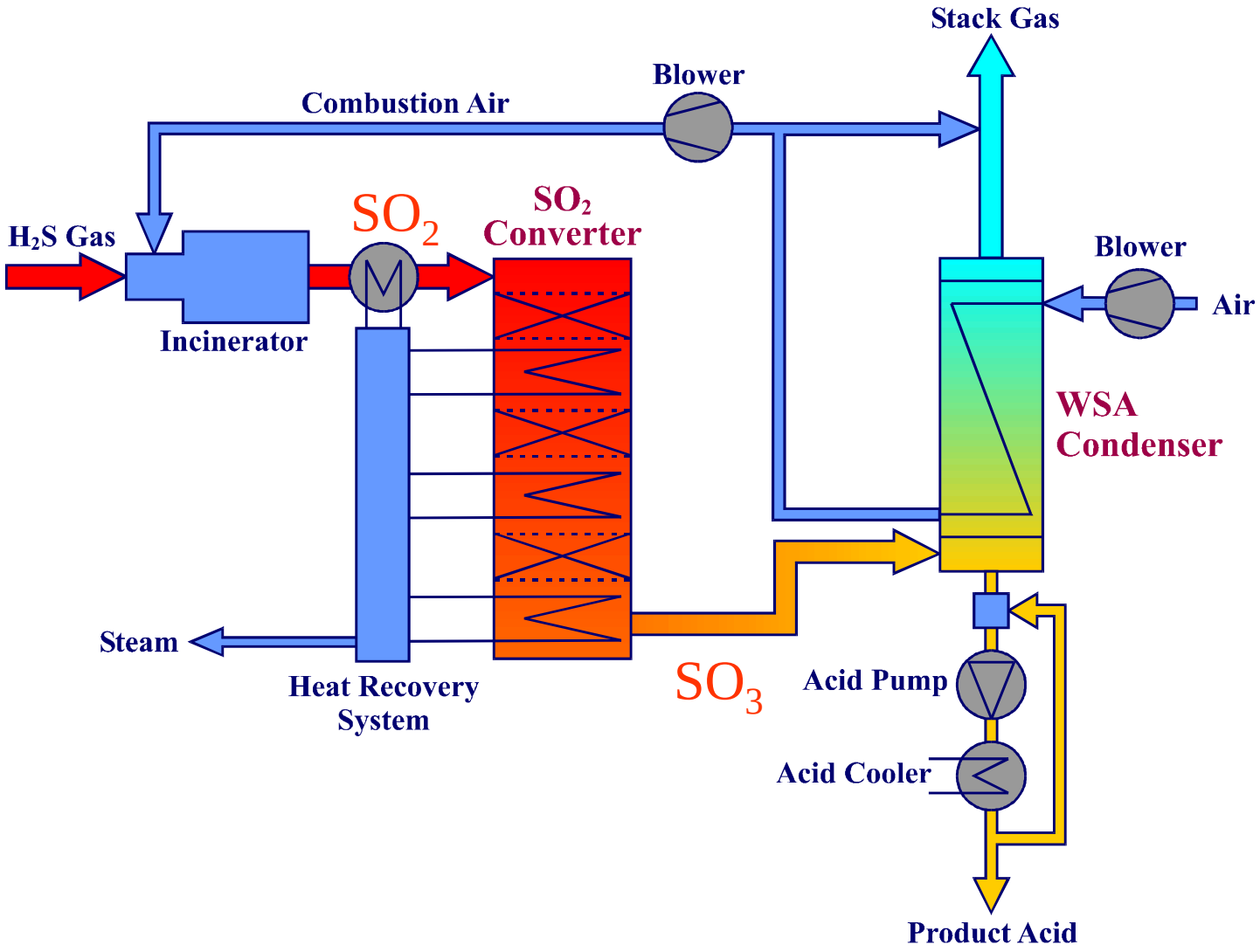
Sulfur dioxide is oxidised to sulfur trioxide (SO_3) over the vanadium catalyst in the presence of oxygen in flue gas and at the temperature range of 400 – 470 ^oC. Than the SO_3 is is absorbed by water and converted into the sulfuric acid.

The vanadium catalyst is placed on a ceramic carrier of TiO_2 or TiO_2/Al_2O_3. The oxidation reaction is:

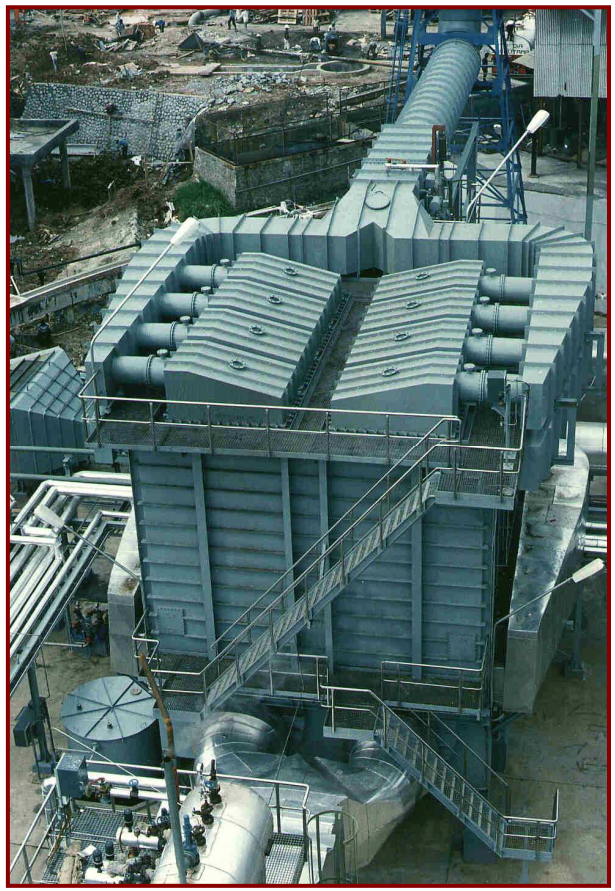
$$SO_2 + 1/2O_2 = SO_3 \text{ (catalytic)}$$

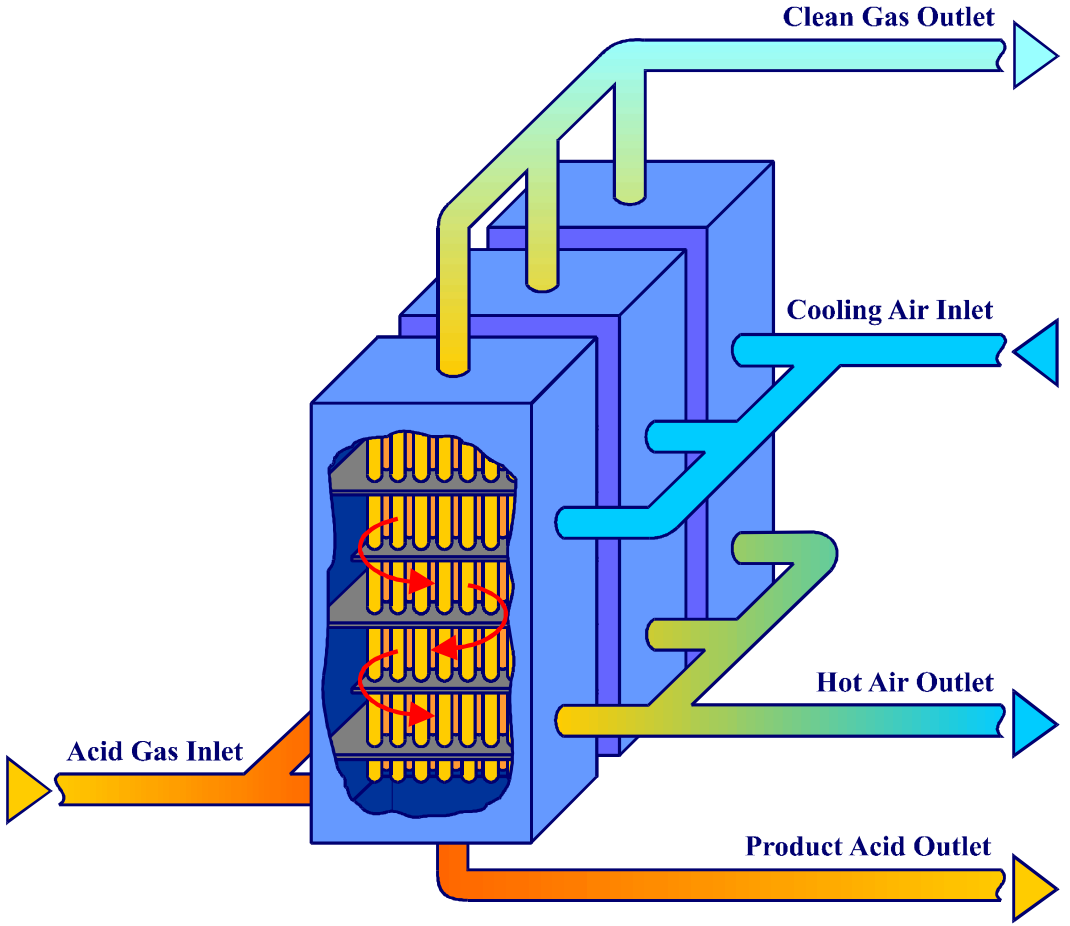
$$SO_3 + H_2O = H_2SO_4$$

WSA Process for H_2S Gas



WSA Process for H_2S Gas





Application for Power Plants SNOX™