Efficient Low Cost Technology for VOC Abatement in Off-Gases Based on Catalytic Oxidation With Ozone.

Development of Catalytic Reactor Providing Direct Ozone Generation in Catalyst Bed for Solving of “Cold Start” Problem for Diesel Vehicles.

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Ozone induced low temperature hydrocarbons oxidation over heterogeneous catalysts of various nature.

Catalytic oxidation of Volatile Organic Compounds (VOC) is an efficient way for cleaning different types of exhausts from stationary and mobile sources. High conversion of VOC is usually achieved using oxide and noble metal catalysts at temperatures above 300-400 C.

Ozone is used as an additive to purified gas flow prior to the catalyst bed in order to clean large amounts of low VOC concentration and low temperature exhausts.

We present results of the ozone-induced oxidation of Benzene, Toluene and Propanol over bulk and supported catalysts.

Experimental

VOCs: Benzene, Toluene, Propanol

Characteristics of granulated catalysts:

- **5% MnO_2/γ-Al_2O_3 - 3.27% Mn, S_{BET}=77 m^2/g**
- **10% MnO_2/γ-Al_2O_3 - 6.95% Mn, S_{BET}=74 m^2/g**
- **3.58% Fe_20_3/γ-Al_2O_3 - S_{BET}=199 m^2/g**
- **97% CuO + 3% Al_2O_3 - S_{BET}=30 m^2/g**
- **0.5%Pd/10% MnO_2/γ-Al_2O_3 - 6.95% Mn, calcination temperature 200^{0}C**
- **γ-Al_2O_3 - S_{BET}=220 m^2/g**

Characteristics of honeycomb monolith catalysts:

- **Pt/Al_2O_3-SiO_2 (high – 0.6%, low – 0.1% Pt)**
- **Pt/Al_2O_3-SiO_2 (0.25% Pt)**
- **Pt/Al_2O_3-SiO_2 (0.3% Pt)**

Test conditions	Granulated catalysts	Monolith catalysts
Temperature	25- 70°C	25- 70°C
Space velocity	10000 h^{-1}	6000 h^{-1}
Concentration of VOC	150-600 mg/m^3	120-150 mg/m^3
Concentration of ozone	5.6 g/m^3	5.1 g/m^3
Humidity	20%	20%

Ozone-induced Catalytic Oxidation of Benzene

Catalyst 3.58% Fe_2O_3/ γ-Al_2O_3, W = 10000 h^{-1}, T = 60°C

№	concentaration, g/m^3		Conversion of Benzene, %	Ozone consumption, %
	Benzene	Ozone		
1	0.108	6.18	99.3	5.34
2	0.120	2.64	56.3	7.90
3	0.120	6.18	99.3	4.95
4	0.145	6.18	99.1	7.16
5	0.256	6.18	87.2	11.13
6	0.650	6.18	73.1	23.68

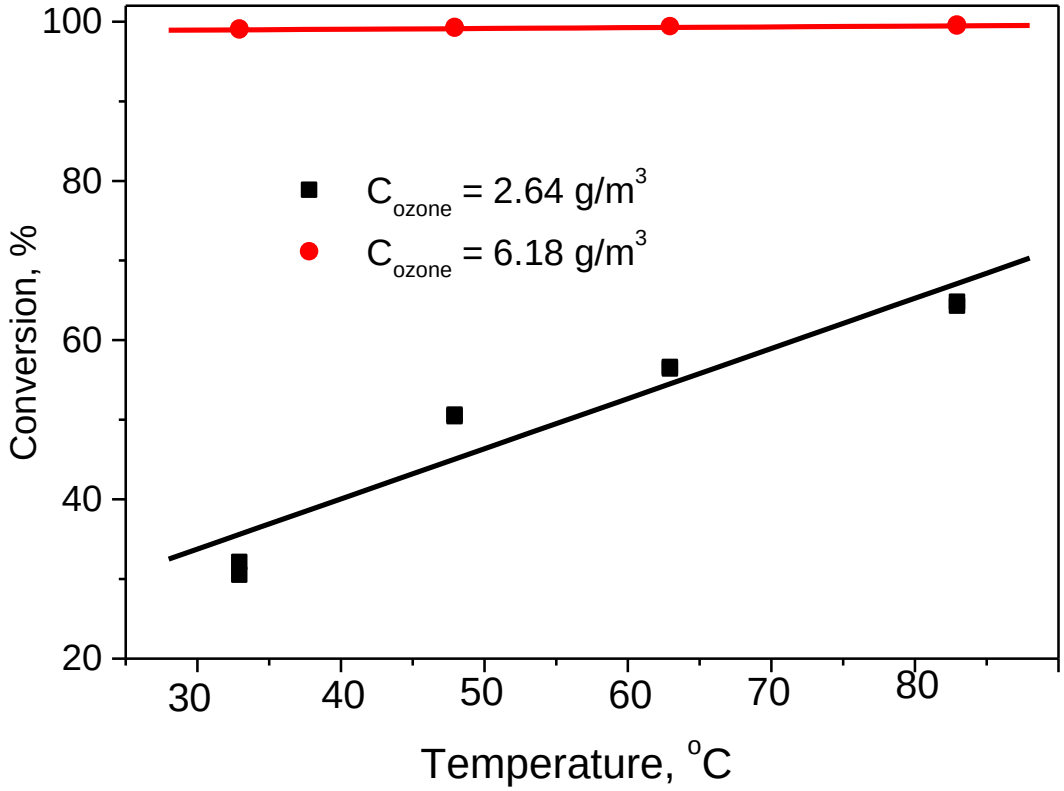
- High conversion of Benzene over the 3.58% Fe_2O_3/γ-Al_2O_3 catalyst is observed only at low concentrations of Benzene.

Catalyst γ-Al_2O_3, W = 10000 h^{-1}, C(Benzene) = 0.15 g/m^3

№	T,°C	Conversion of Benzene, %	Ozone consumption, %
1	30	10.2	0.51
2	40	11.8	0.59
3	60	12.5	0.62
4	70	15.5	0.77
5	80	18.3	0.91

- Ozone consumption efficiency is rather low, but grows with the increase of temperature.

Ozone-induced catalytic oxidation of Benzene over 3.58% Fe_2O_3/γ-Al_2O_3



W = 10000 h^{-1}, C(Benzene) = 0.12 g/m^3

Ozone-induced catalytic oxidation of Toluene and Propanol

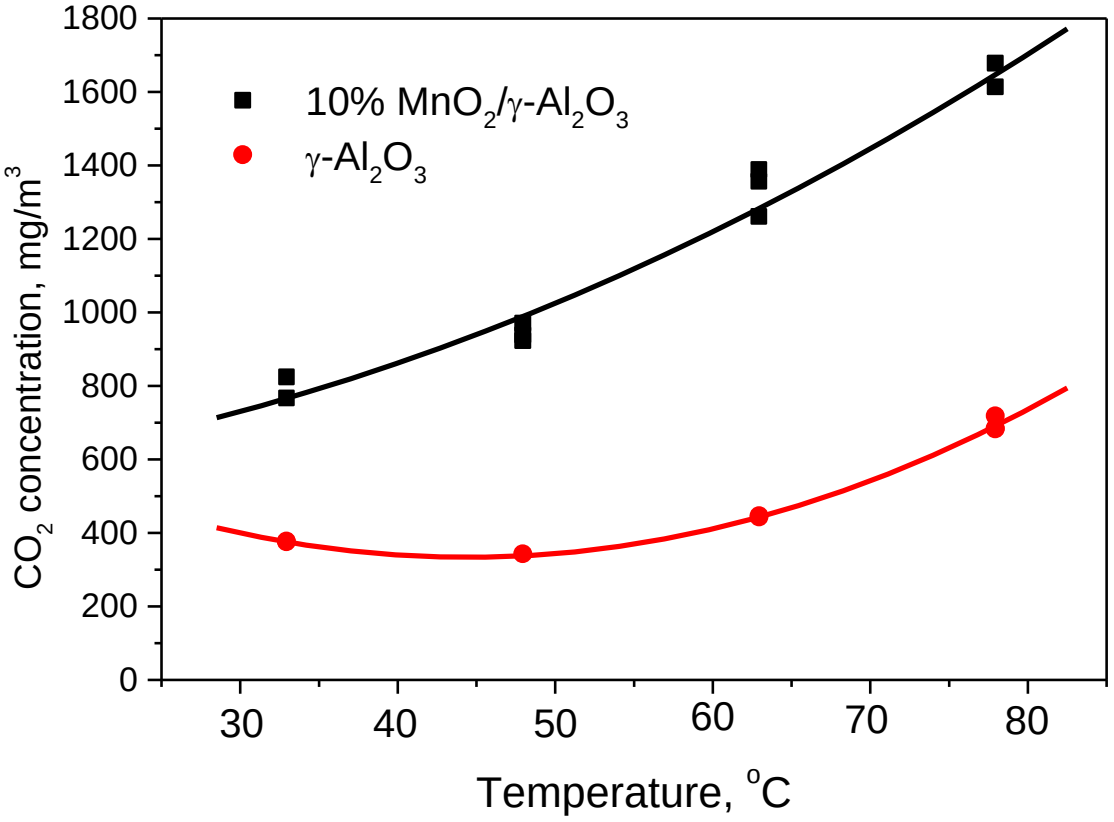
Catalyst	T, °C	Conversion, %	
		Toluene	Propanol
5% MnO_2/γ- Al_2O_3	25	97.4	69.7
	40	100.0	73.5
	60	100.0	82.4
10% MnO_2/γ-Al_2O_3	25	98.2	75.9
	40	100.0	83.1
	60	100.0	93.7
97% CuO+3% Al_2O_3	25	98.0	72.4
	40	100.0	80.5
	60	100.0	91.1
γ - Al_2O_3	25	81.0	2.1
	40	88.9	4.1
	60	95.9	5.3
Pt/Al_2O_3-SiO_2 (0.1% Pt)	25	60.7	3.1
	40	66.2	3.9
	60	74.3	6.4
Pt/Al_2O_3-SiO_2(0.25% Pt)	25	38.7	6.3
	40	50.7	7.4
	60	71.2	8.5
Pt/Al_2O_3-SiO_2 (0.3% Pt)	25	56.8	6.5
	40	58.1	9.5
	60	62.7	11.1

- Oxide catalysts are active in the oxidation of both Toluene and Propanol. Pt containing catalysts are active in the oxidation of Toluene only.

- The activity series for Toluene oxidation is the following : 10% MnO_2 $/\gamma$-Al_2O_3 > 97% CuO + 3% Al_2O_3 > 5% MnO_2/γ-Al_2O_3 > γ-Al_2O_3 > Pt/ Al_2O_3-SiO_2 (0.3% Pt)

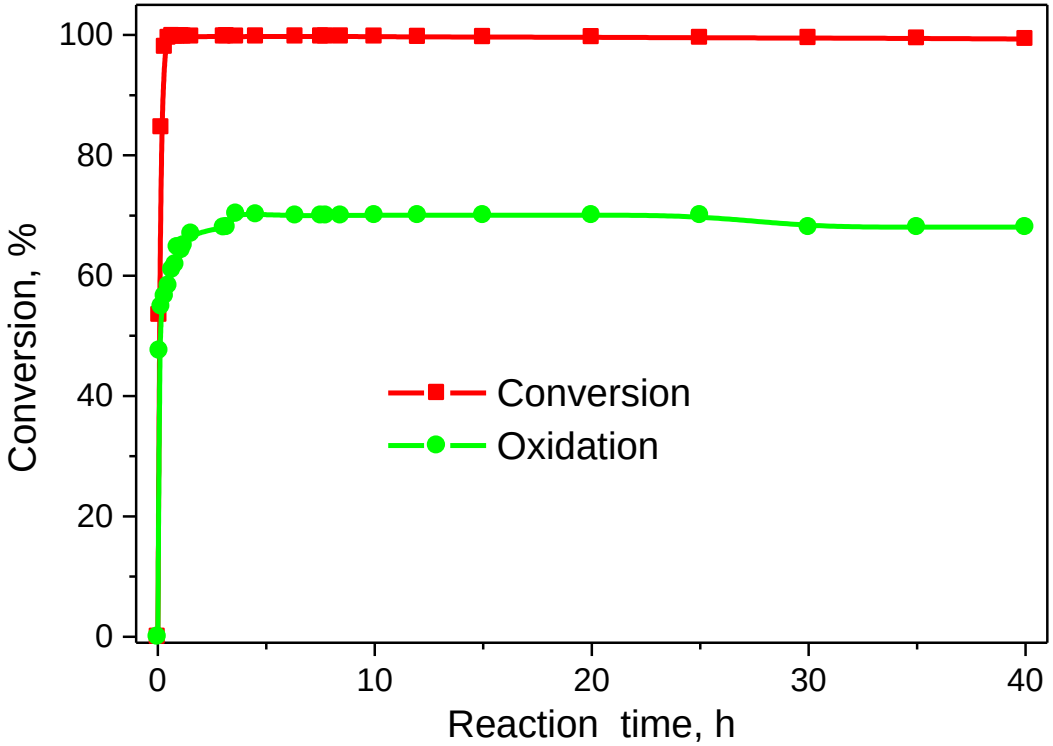
- Gas phase products of Toluene oxidation contain the traces of Benzaldehyde, Ethylbenzaldehyde, 2,4-dimethylpentane and Naphtene.

Ozone-induced catalytic oxidation of Toluene over 10% MnO_2/γ-Al_2O_3 and γ-Al_2O_3



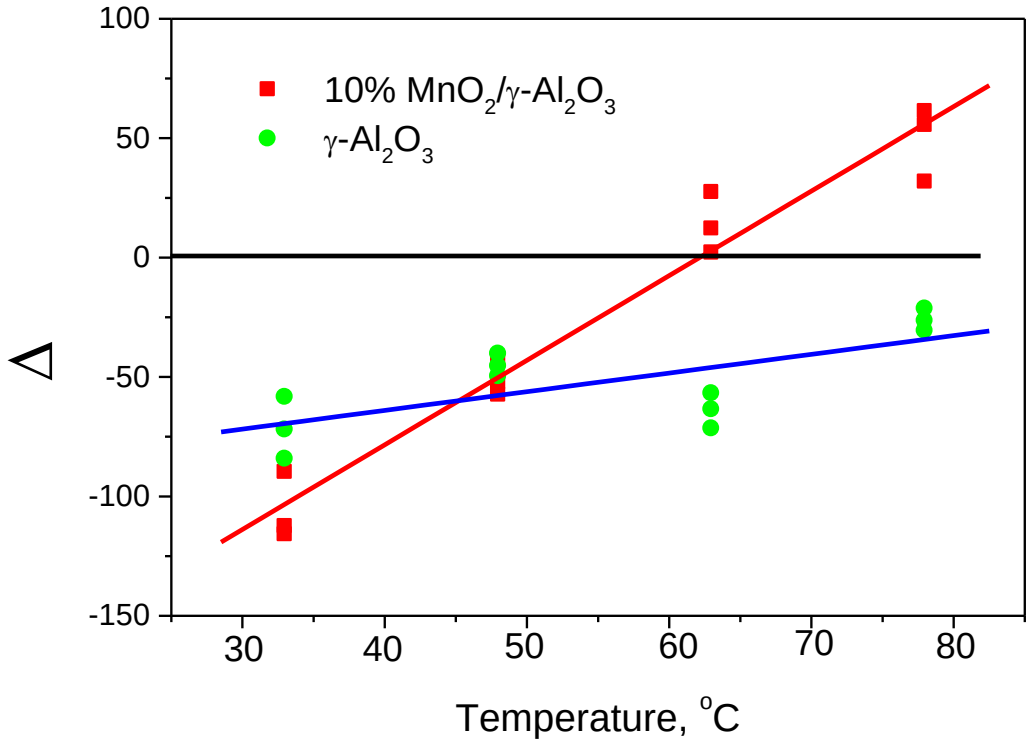
W = 10000 h^{-1}, C(Toluene) = 0.5 g/m^3, C(Ozone) = 5.1 g/m^3

Ozone-induced catalytic oxidation of Toluene over 0.5% Pd/10% MnO_2/γ-Al_2O_3



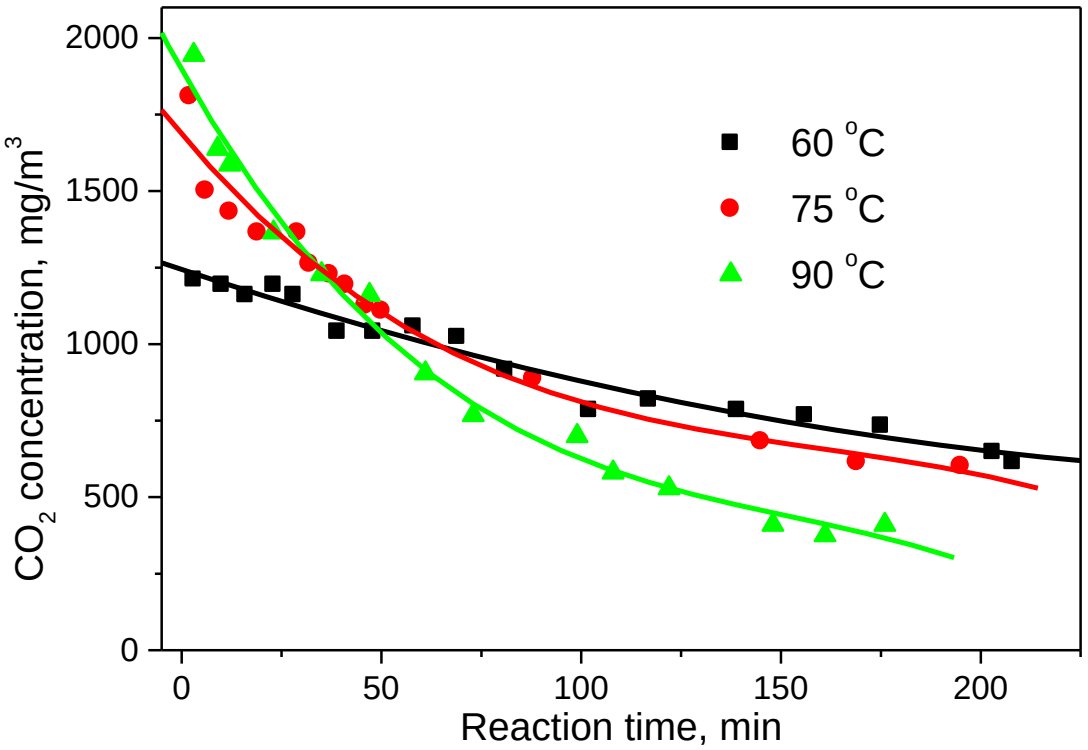
For the 0.5% Pd/10% MnO_2/γ-Al_2O_3 catalyst, conversion of Toluene prevails over its oxidation. As a consequence, accumulation of the condensed products takes place on the catalyst surface.

Accumulation partially oxidated condensed products (CP) upon ozone-induced catalytic oxidation of Toluene



- **Δ – in arbitrary units, difference /Total oxidation – formation of condensed products (CP)/**
- **There is a difference between total conversion of Toluene and its deep oxidation to CO_2 and H_2O on the catalyst 10% MnO_2/γ-Al_2O_3 и γ-Al_2O_3. Temperature increase leads to a higher extent of deep oxidation, while the total conversion was almost constant.**

Regeneration of 0.5% Pd / 10% MnO_2 / γ-Al_2O_3 by ozone



Regeneration of the 0.5% Pd/10% MnO_2//γ-Al_2O_3 catalyst, containing 7.5 wt.%. CP, by ozone for 3 hours at 60- 90 C leads to the 1.3-1.5% weight loss.

Conclusions

- Ozone-induced catalytic oxidation of Benzene, Toluene and Propanol was studied in the temperature range of 298-353 K over the catalysts: 5% MnO_2/γ-Al_2O_3, 10% MnO_2/γ-Al_2O_3, 0.5% Pd/10% MnO_2/γ-Al_2O_3, γ-Al_2O_3, 3.58% Fe_20_3/γ-Al_2O_3, 97% CuO + 3% Al_2O_3, Pt/Al_2O_3-SiO_2 (0.1% Pt), Pt/Al_2O_3-SiO_2 (0.25% Pt), Pt/Al_2O_3-SiO_2 (0.3% Pt).

- Among the volatile products of ozone-induced oxidation of Toluene were found the traces of Benzaldehyde, Ethylbenzaldehyde, 2,4–dimethylpentane and Naphtene.

- Upon oxidation of Toluene by ozone, on the surface of 10% MnO_2/γ-Al_2O_3 catalyst were found oxidative condensed products , containing benzoic acid, and also water-soluble compounds of the R-OH and R-CHO type.

- Regeneration of the 0.5% Pd/10% MnO_2/γ-Al_2O_3 catalyst by ozone was studied at 60- 90 °C .

Development of Catalytic Reactor Providing Direct Ozone Generation in Catalyst Bed for Solving of “Cold Start” Problem for Diesel Vehicles.

PROBLEM DEFINITION

- **For automobiles equipped with modern three-way catalysts, the majority of HC emissions (up to 80%) occur during the cold-start period.**

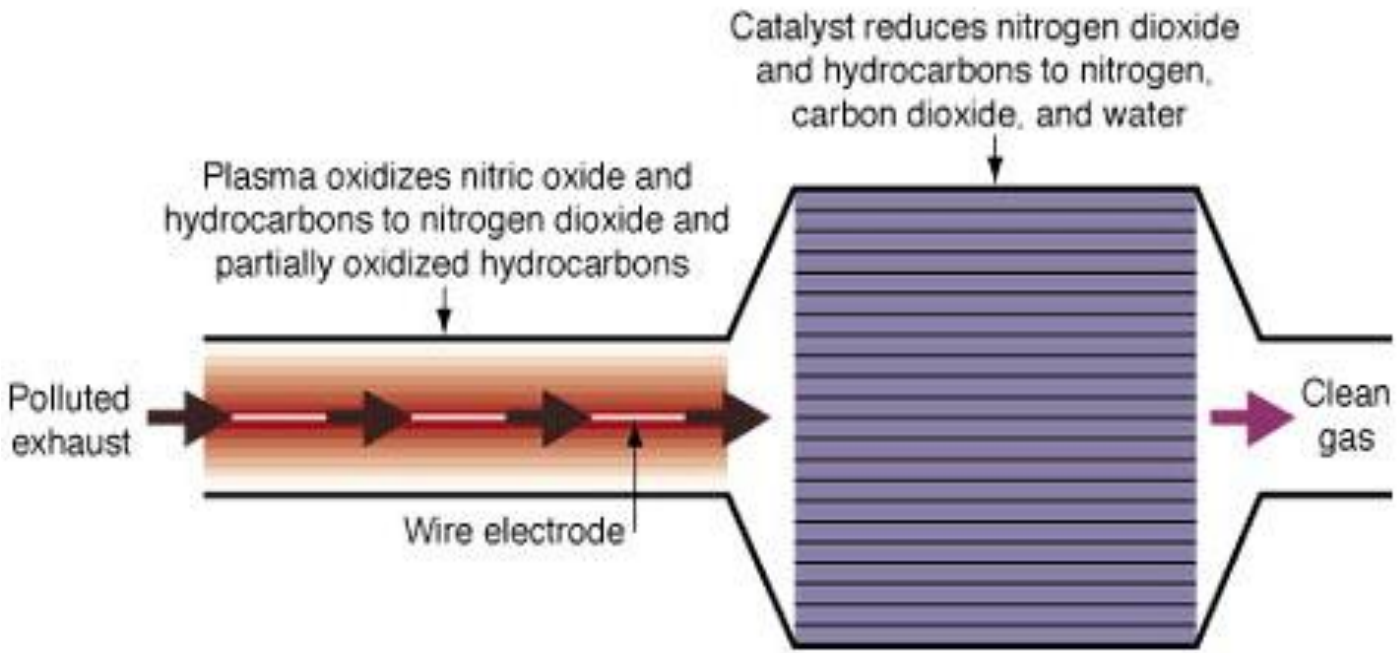
- **The cold-start period refers to the first few minutes after engine ignition before the catalyst reaches its light-off temperature (250–300^{o}C), during which any unburned HC fuel simply passes out the tailpipe to the atmosphere.**

The following approaches for solving this challenging problem are being developed:

To trap the HC emissions during the cold-start period and then release them once catalyst light-off has occurred. The HCs desorb from the HC trap and are then combusted by the catalyst. Zeolites are often suggested as a HC trap material

- To use catalytic burner for heating the catalytic monolith;
- Flash heating of the metal-made catalytic converter with electric current
- Plasma-Assisted Catalytic Reduction (PACR)
- The application of high-temperature catalyst (usually plasma coated ceramic/metal foam catalyst) close-coupled to combustion chamber
- Ozone-induced catalytic oxidation

Plasma-Assisted Catalytic Reduction (PACR)



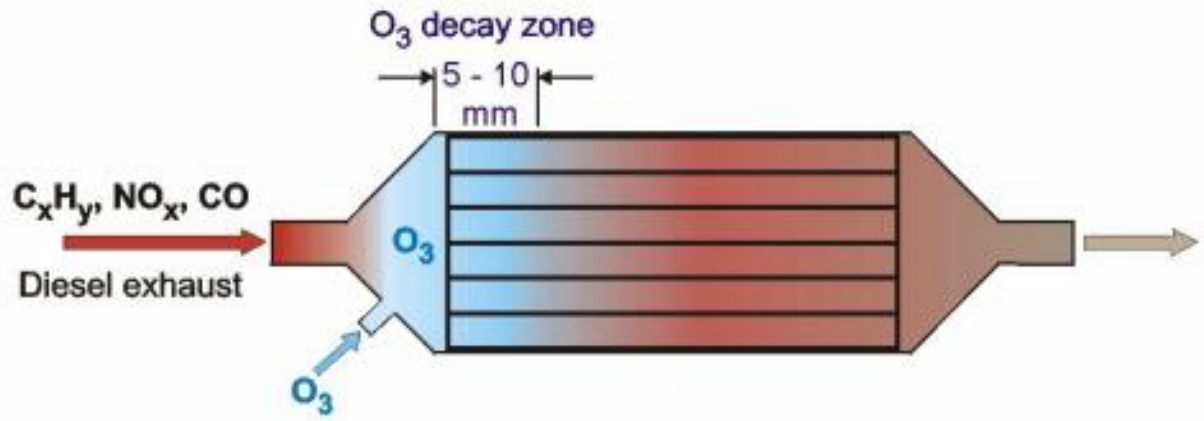
Lawrence Livermore National Laboratory

www-cms.llnl.gov/s-t/int_combustion_eng.htm

Ozone-catalytic oxidation of hydrocarbons and other VOCs attracts considerable attention during last decades because it proceeds at low temperatures as opposed to conventional thermal and thermocatalytic methods which require preliminary heating of the exhaust gases up to 400-500°C resulting in very high energy consumption for the process.

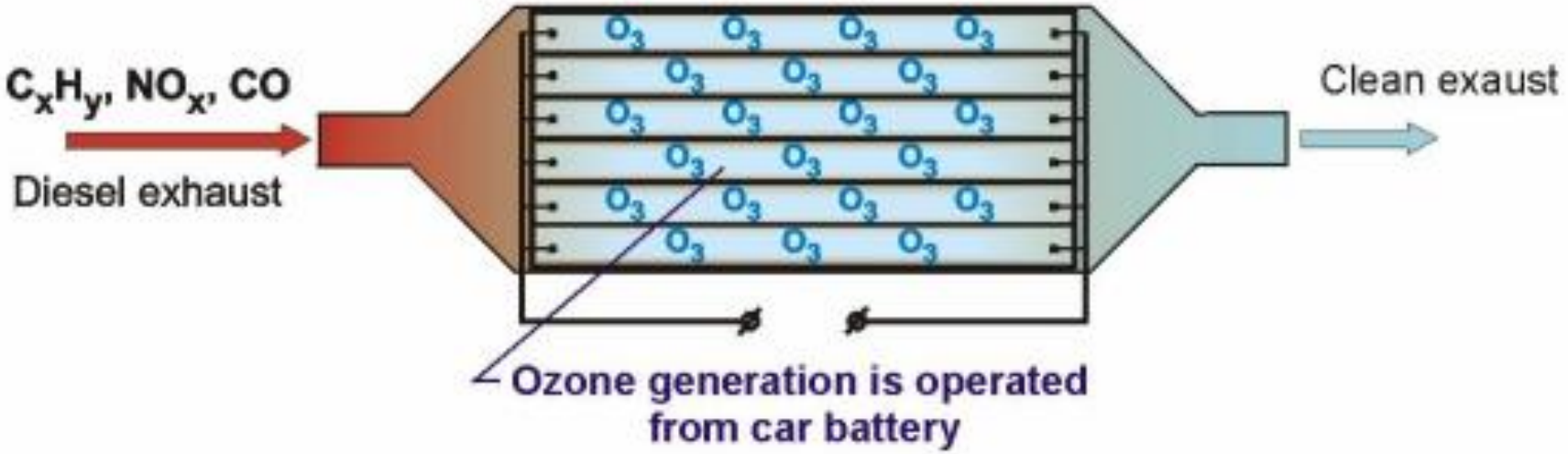
The use of ozone induced catalytic oxidation allows complete removal of pollutants at 50-60°C

Implementation of Ozone-Catalytic Method For Automotive Exhaust Purification Upon Cold Start Conditions

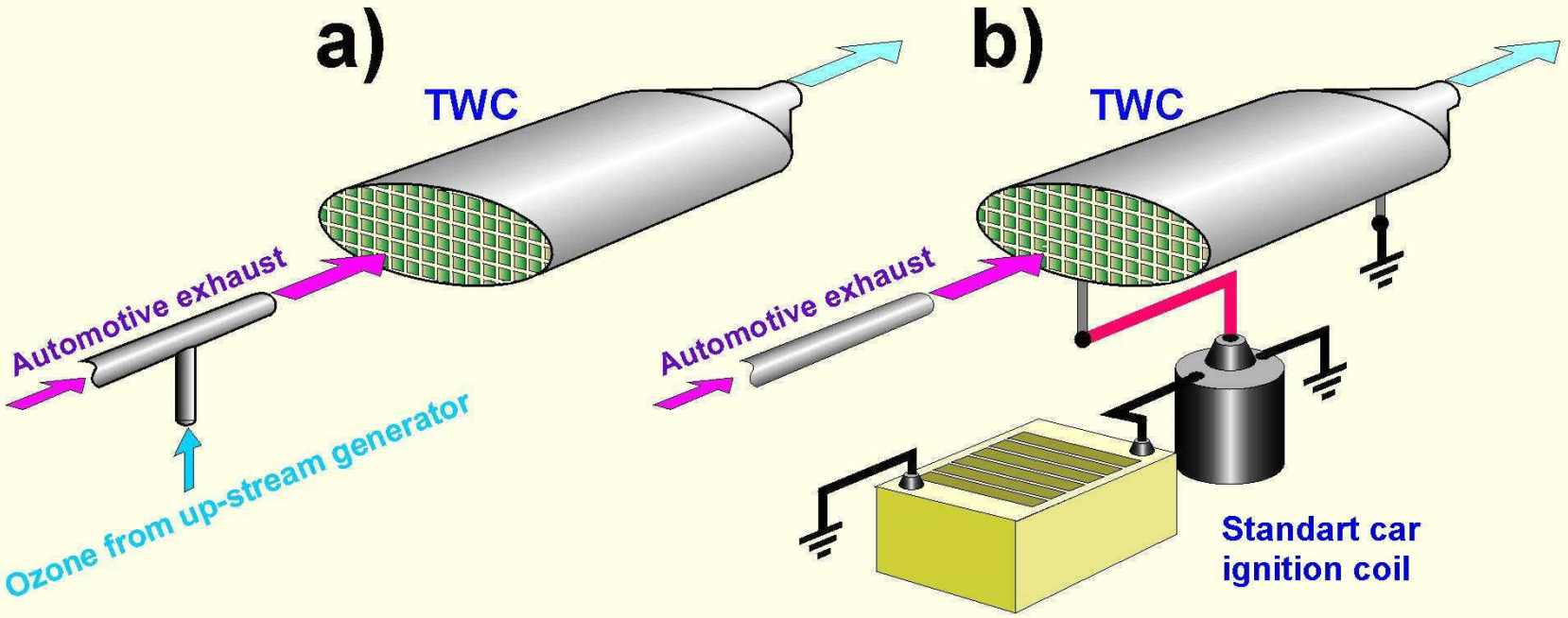


Under conventional implementation, when ozone is formed upstream the catalyst bed, the efficiency of ozone-catalytic process significantly decreases due to the parallel reaction of ozone decomposition to molecular oxygen - inactive at low temperatures

The Application of Device Developed For Automotive Exhaust Purification Upon Cold Start Conditions



Ozone-catalytic methods for diesel exhaust treatment upon cold start conditions



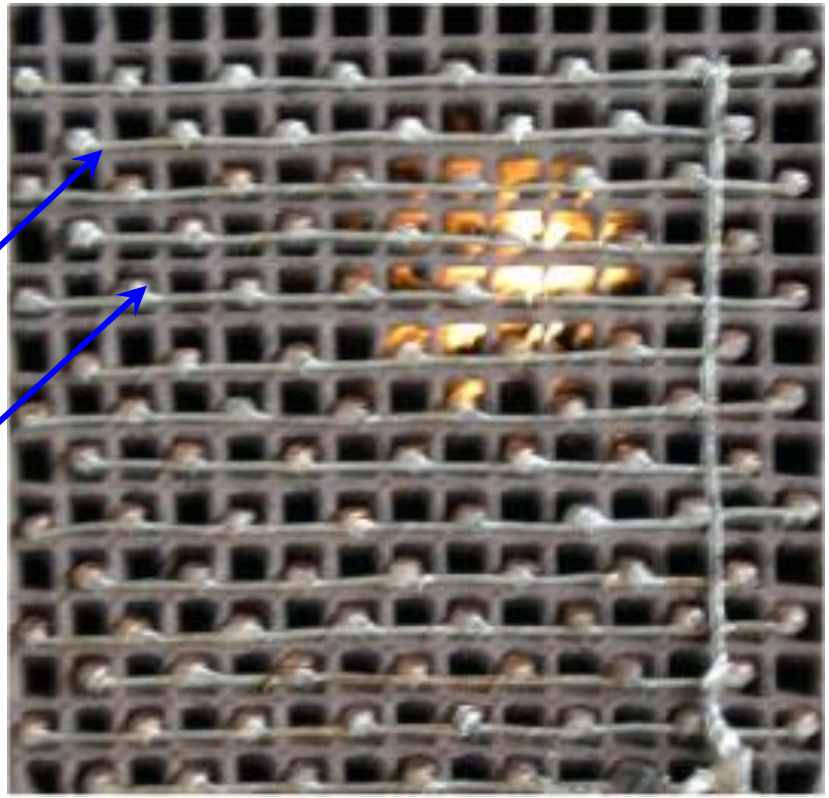
a) **Ozone injections from up-stream generator**

- Ozone decay on the first 5mm of catalytic converter
- Close to zero efficiency

b) **Direct ozone generations in the channels of TWC**

- Ozone formation along chanel catalyst

The monolithic honeycomb catalyst with electrodes inside of channels of monolith



Electrodes