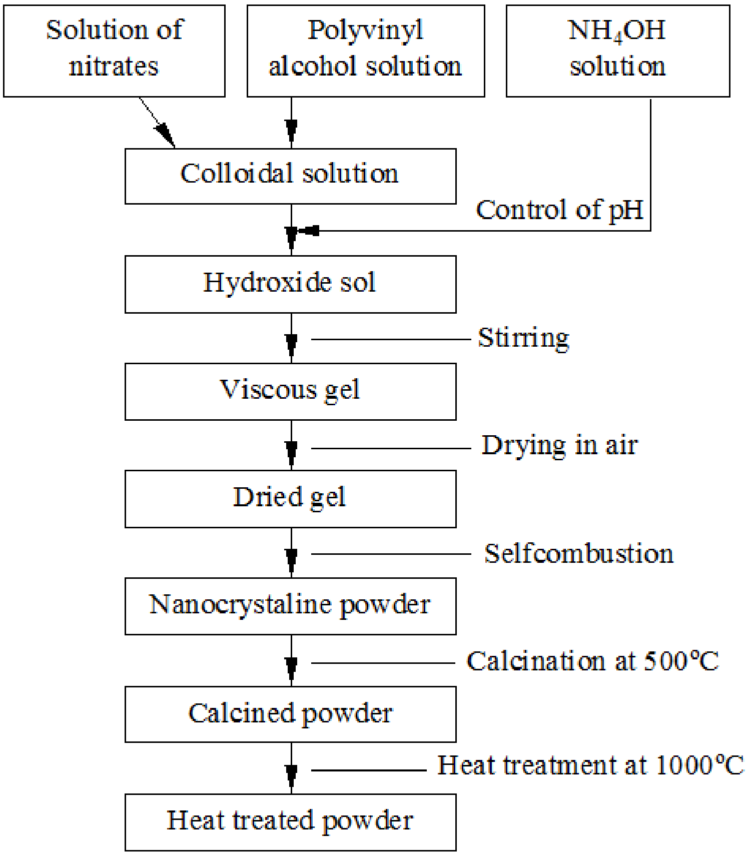
Synthetic report of scientific activity

Regarding project implementation during 5.10.2011 – 5.10.2016

Contract No. **295/2011**

Project „NEW NANOSTRUCTURED SEMICONDUCTING OXIDE MATERIALS FOR CATALYTIC COMBUSTION OF SOME GASES IN REDUCED CONCENTRATIONS"

The perovskite and ferrite – type oxides are promising catalysts in the flameless combustion of volatile organic compounds (VOCs). The purpose of this project was to comparatively evaluate catalytic activity of some perovskites and ferrites in combustion reactions of acetone, benzene, propane and Pb free gasoline in air. These oxides are considered as potential substitutes for noble metal catalysts, which are expensive. Perovskite and ferrite catalysts combine low cost, thermo-chemical stability at high operating temperature and satisfactory catalytic activity.



The preparation procedure by self- combustion

The performance of a catalyst depends on its physical-chemical properties which are strongly affected by the synthesis technique of the catalyst. In the present project the self-combustion method was used to prepare nanocrystalline powders of various perovskites and ferrites. Metal nitrates, ammonium hydroxide and polyvinyl alcohol were used as starting materials. The preparing method included the following steps: (1) dissolution of metal nitrates in deionized water; (2) polyvinyl alcohol (10% concentration) addition to nitrate solution to make a colloidal solution; (3) NH_4OH (10% concentration) addition to increase pH to about 8; a sol of metal hydroxides in polyvinyl alcohol and ammonium nitrate were obtained; (4) stirring at 80^0C for 10 minutes to turn the sol of metal hydroxides into viscous gel; (5) drying the gel at 100^0C for 12 hours; (6) self-combustion; the dried gel was locally ignited by an electrically heated wire and an exothermic reaction takes place. Once initiated, the combustion wave spontaneously auto propagated (less than 30 seconds) through the dried gel and results a loose powder. During the combustion reaction, the temperature is of about 1000^0C and the nucleation of very fine crystallites takes place; (7) calcination at 550^0C for 15 min of the burnt powder to eliminate any residual organic compound; (8) heat treatment in air of the calcined powders, to achieve a complete crystallization of ferrites. The preparation procedure by self-combustion is schematically presented in Figure. The main feature of self-combustion method is the intimate mixing of ions, so that nanocrystals can occur at relatively low temperatures. Using the present procedure, fine, homogeneous and pure ceramic powders can be obtained at a lower temperature than that of the conventional ceramic method.

XRD analyses (PANALYTICAL X' PERT PRO MPD powder diffractometer and CuKα radiation) were performed on all fresh samples to assess the presence and purity on the expected phases and to gather information about the degree of crystallization. The spectra were scanned between 20 and 80^0 (2θ) at a rate of 2^0/min. The average crystallite size was evaluated using the Scherrer equation $D = 0.9\lambda/\beta\cos\theta$, where λ is the radiation wavelength (0.15405 nm) of CuKα, β is the half width of the peak and θ is the Bragg diffraction peak angle.

A scanning electron microscope (JEOL-200 CX) was used to visualize the surface morphology. The elemental composition of the surface particles was examined with Energy Dispersive X-ray Spectrometer (Genesis, EDX).

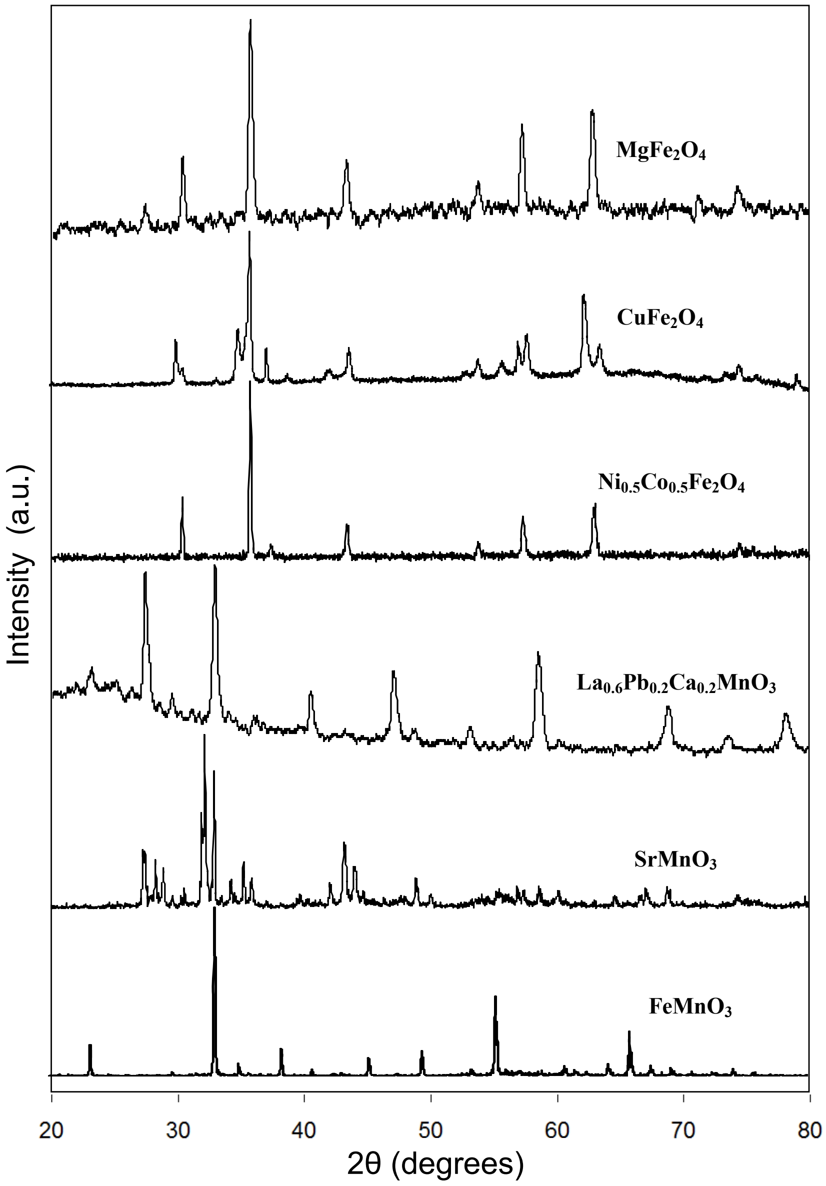
A Quantachrome automated gas adsorption system (Quantachrome Instruments) was used to obtain N_2 adsorption isotherms at 77 K. Samples were degassed at 200 ^{0}C under vacuum (10^{-3} Pa) for 3 h prior to adsorption/desorption experiments. The BET specific surface area (S_{BET}) was determined using the standard Brunauer-Emmett-Teller method on the basis on the adsorption data.

Catalyst activity tests were conducted in laboratory with a flow type set-up (flow rate of 100 cm^3/min,gas concentration in air of 1 – 2 ‰ and the gas hourly space velocity, GHSV, of 5100 h^{-1}). The catalyst powder (0.3-0.5 g) was sandwiched between two layers of quartz wool in a quartz tubular micro-reactor (ϕ = 7 mm) placed in an electrical furnace. The increase of the temperature was made in steps of 50 ºC, from 0 ^{0}C to 500 ^{0}C. At every predetermined temperature, because of catalytic combustion, the exit gas concentration will be smaller than the inlet gas concentration. The catalytic activity of the heat-treated materials under study was evaluated in terms of the conversion degree of the gases over these materials as:

$$Conv = \frac{c_{in} - c_{out}}{c_{in}} x100\% ,$$

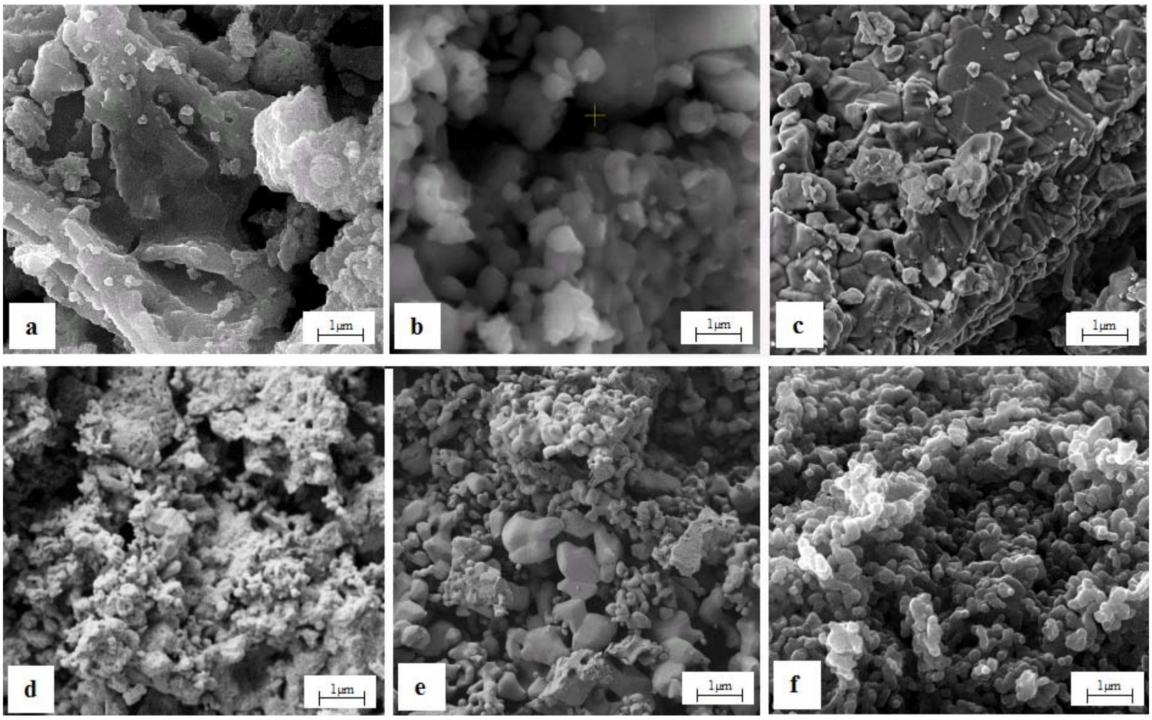
where c_{in} and c_{out} are the inlet and outlet gas concentration, respectively, measured by a photo-ionization detector (PID-TECH) for VOCs. Data were collected when the flameless catalytic combustion had reached a steady state, after about 20 minutes at each temperature. Similar results were obtained when the experiments were repeated decreasing the temperature, suggesting the time stability of the ferrite and perovskite catalysts and the absence of the deactivation.

In Figure are shown XRD patterns of six oxide compounds prepared by self-combustion and heat treated. Diffractograms show well-defined peaks indicating a good crystalline quality of the powders. The broadening of the peaks indicates the generation of crystallites in the nano-size range. Phase identification was performed using PDF standard cards. Results revealed that all samples were monophase, without any second phase.



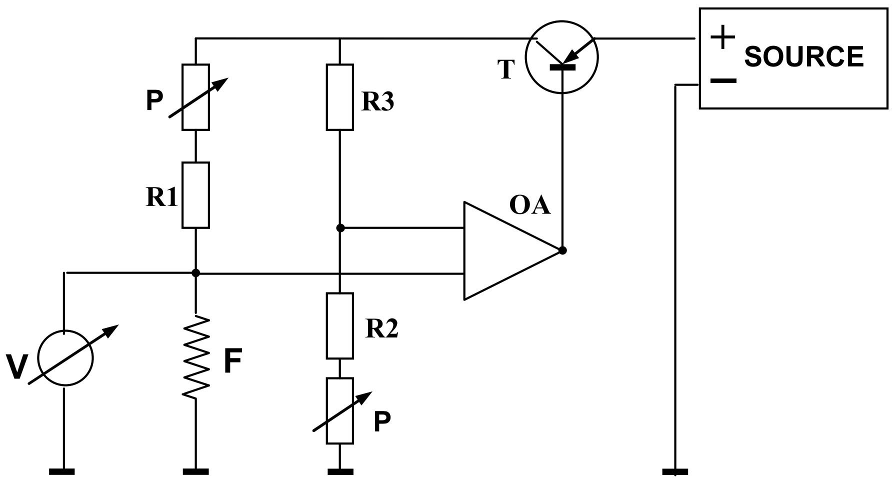
Powder X-ray diffraction patterns of some samples

The surface morphology of the six powders can be observed in the SEM images given in the following Figure. These micrographs reveal that in these materials, the nanometric particles (< 100 nm) are clustered into mini- or macro- agglomerates with irregular shapes and sizes. Larger agglomerates are dispersed among small agglomerates. The images also reveal the presence of inter-agglomerate pores.



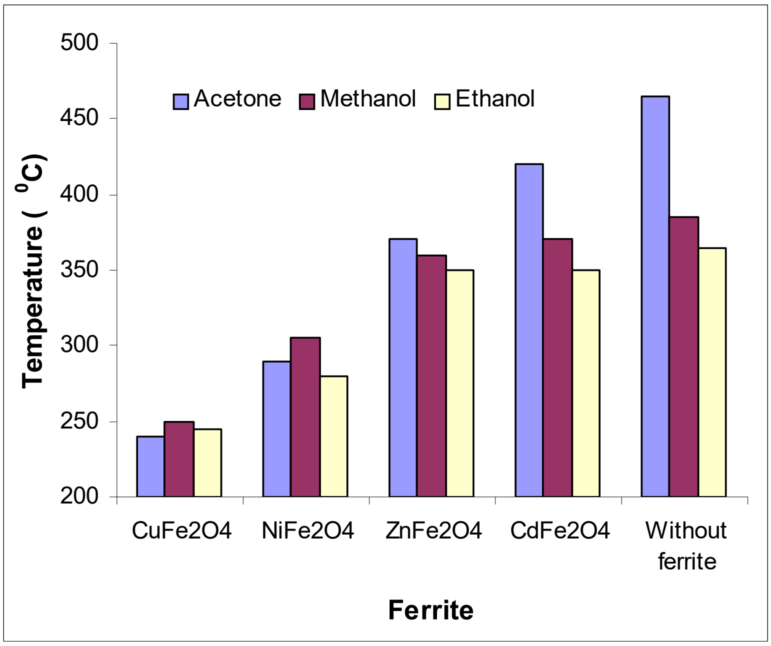
SEM images of: a) $MgFe_2O_4$; b) $CuFe_2O_4$; c) $Ni_{0.5}Co_{0.5}Fe_2O_4$;
d) $SrMnO_3$; e) $FeMnO_3$; f) $La_{0.6}Pb_{0.2}Ca_{0.2}MnO$

The catalytic activity of some ferrites was appreciated based on the establishing the minimum temperature at which the catalytic combustion reaction of acetone/air, ethanol/air and methanol/air mixtures appears at atmospheric pressure. The experiments were carried out with a set-up (Figure) which mainly consists of a Wheatstone bridge. In a branch of the bridge is connected a tungsten filament, electrically isolated and covered with a thin layer of ferrite powder (about 2 mg). Tungsten does not have catalytic properties in the investigate temperature range, 20 – 500^{0}C. In the presence of gas/air mixture, the filament is heated to a certain temperature and the bridge is equilibred. When the combustion reaction of the gas over ferrite catalyst starts, an increase of the filament temperature occurs and this increasing is automatically counterbalanced by a decrease in the filament voltage.



Set-up for analysis of catalytic activity

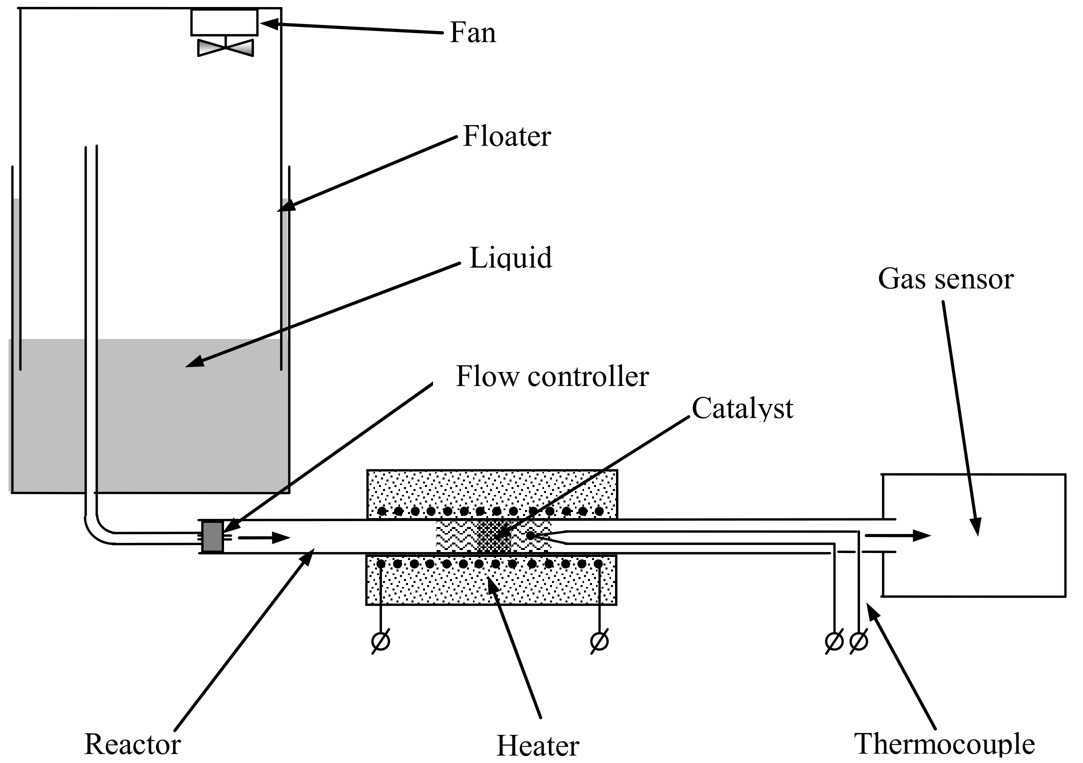
The temperature at which appears a decrease in the filament voltage is the minimum temperature for the start of the catalytic combustion reaction of the gas over the ferrite surface.



Minimum temperature of gas catalytic combustion over some ferrite catalysts

Some obtained results are given in Figure.

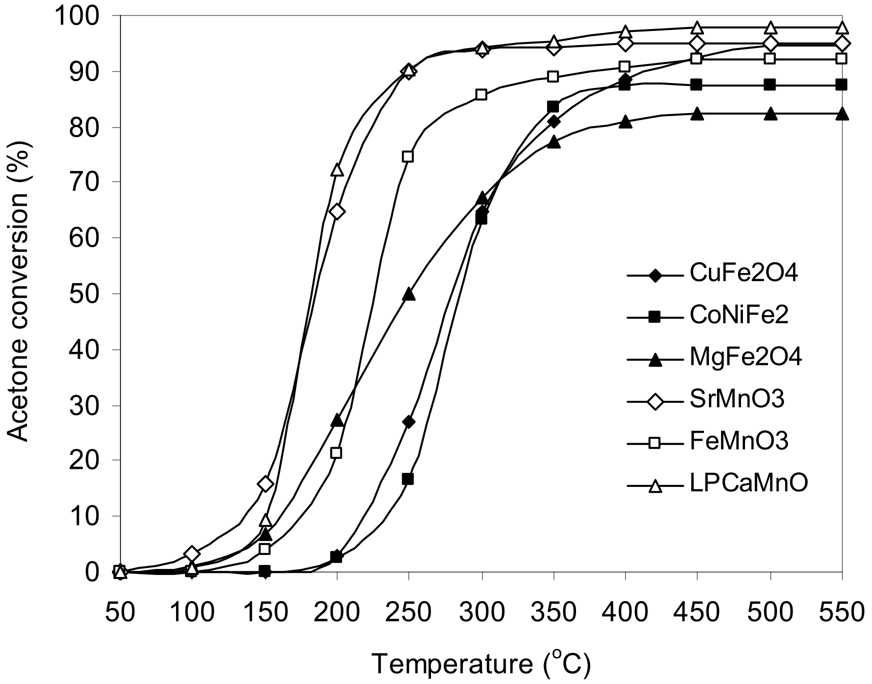
The catalytic combustion reaction of acetone, benzene, propane and Pb free gasoline in air over ferrite or perovskite catalysts as a function of reaction temperature was carried out with a flow type set-up (Figure) which consists of a reservoir for 1 - 2‰ test gas-air mixture, a dispenser with a constant flow rate of 100 cm^3/min, a tubular micro-reactor and gas detector ‘Gray Wolf Sense” with a photo-ionization detector (PID-TECH) for VOCs. The micro-reactor is a quartz tube with an internal diameter of 7 mm. The tubular reactor was loaded with 0.3 – 0.5 g of powdered catalyst. The catalyst powder was sandwiched between two layers of quartz wool in the isothermal



Set-up to determine the gas conversion degree at various temperatures middle part of the micro-reactor. A thermocouple was placed in the proximity of the catalyst to measure the temperature of the gas. The micro-reactor is placed in an electrical tube furnace which assures an uniform and adjustable temperature between 50 and 550^{0}C on the catalyst zone. The gas mixture (air + test gas) in rezervoir flows through the heated catalyst. The increase of the temperature was made stepwise. At every predetermined temperature, as a result of catalytic combustion, the gas concentration at the exit of reactor, measured by PID, will be smaller than the inlet gas concentration. The degree of conversion of gases over catalysts at a certain temperature was calculated as:

$$Conv = \frac{c_{in} - c_{out}}{c_{in}} x100\% ,$$

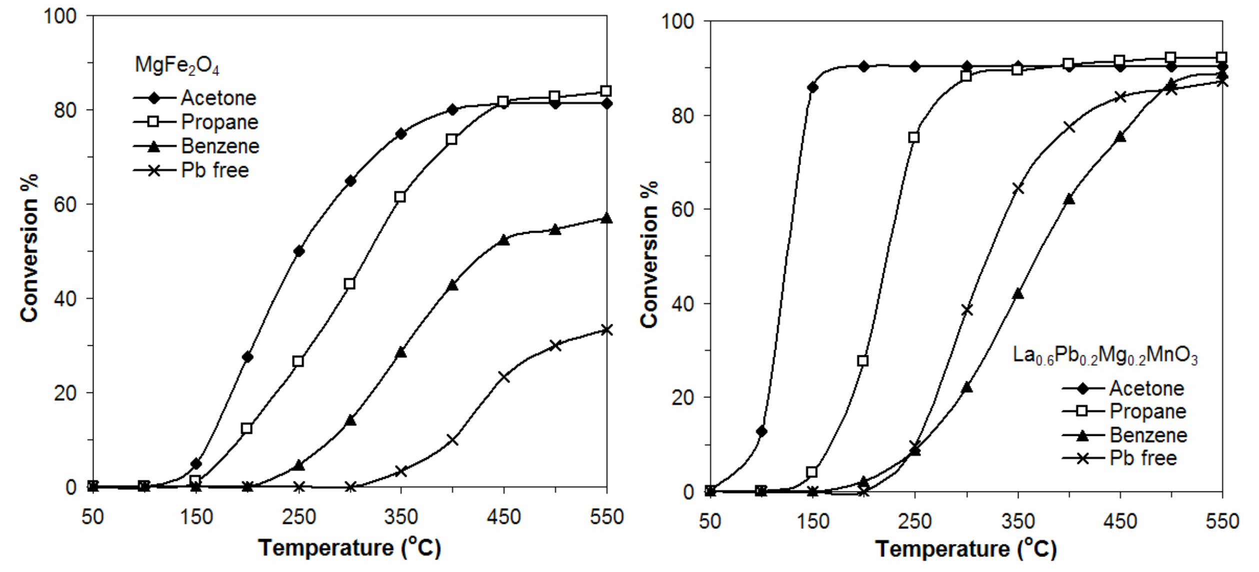
where c_{in} and c_{out} are the inlet and outlet gas concentration, respectively.



Conversion versus temperature in the catalytic combustion of acetone over $MgFe_2O_4$, $CuFe_2O_4$, $Ni_{0.5}Co_{0.5}Fe_2O_4$, $SrMnO_3$, $FeMnO_3$ and $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ catalysts

The catalyst activity of the prepared nanopowders was tested in the combustion reaction of acetone, benzene, propane and Pb free gasoline. The results are given in following two Figures, where the measured values of conversion degree of gases are plotted as a function of the reaction temperature. Each datum is the average of three steady state measurements. Typical S-shaped curves were obtained, describing the variation of the conversion degree with increase of the reaction temperature. At decreasing temperature, the conversion levels were almost identical with those obtained at increasing temperature and S-shape curves superposed. These results show a good stability of the catalysts during the catalytic tests and the absence of any deactivation of the catalysts in all the experimental conditions tested.

The comparison of the obtained results revealed that the catalytic activities of the perovskite catalysts differ substantially from those of the ferrite catalysts. It is obvious in Figures that the S-curves involving perovskite catalysts are shifted to lower temperatures relative to those of ferrite catalysts. This means that the perovskite catalysts are more active in the gas oxidation at low temperature than the ferrite catalysts. Also, it should be noted that the combustion reaction of VOCs gases over perovskite catalysts starts at much lower temperatures (with about 100 ^{0}C) than over ferrite catalysts and the conversion degree sharply increases with increasing temperature. The difference in the catalytic activity of the two catalyst systems cannot be explained by their different specific areas. For example, the specific surface area of $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ perovskite was 12.6 m^2/g and that of $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrite was 26.5 m^2/g, but their catalytic activities differ significantly The perovskite catalysts were able to convert 95 – 97 % acetone at low temperature, of 300 ^{0}C, whereas the conversion over ferrites was of about 65 % only. Higher activities of perovskites compared to those of ferrites allow one to speculate that their crystalline structure and structural defects (oxygen vacancies) may account for obtained results in the VOC combustion over the two material types (perovskites and ferrites).



Conversion of acetone, propane, benzene and Pb free gasoline vs. temperature over $La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$ perovskite and $MgFe_2O_4$ spinel catalysts

The temperature T_{50} (the temperature necessary for 50% gas conversion) is usually chosen as the main indicator of catalytic activity of a given catalyst. At T_{50} temperature the catalytic activity for the total oxidation of gases is sufficiently high and the interactions between catalyst surface and reactants are intense. The lower this parameter is, the higher the activity of the catalyst is. In the two figures can be observed that the T_{50} values for VOC conversion over perovskites are lower in comparison with those obtained over ferrite catalysts. Therefore, the catalytic activity of the perovskites is higher.

The better catalyst performance of the perovskites compared to the ferrite catalysts under the same reaction conditions may be explained by the large increase in the oxygen vacancies in the surface regions generated by the presence of ions with variable valence. Although the mechanism of complete gas oxidation over metal oxide compounds is not precisely known, the interaction of surface active oxygen species with reactants ("suprafacial mechanism") is a widely accepted explanation for the VOC full oxidation over mixed oxide catalysts for $T \leq 400\ ^0C$. According to this accepted opinion, the oxygen vacancies play an important role in the catalytic activity of the oxide catalysts, these being responsible for the adsorption/desorption properties of the gas phase. More oxygen vacancies will involve a larger density of adsorbed oxygen species (O^-, O^{2-}, O_2^-), weakly anchored on the catalyst surface, which favor the VOCs oxidation. The larger the number of oxygen adsorbed, the more active would be the catalyst for gas oxidation. The surface oxygen species involved in the catalytic oxidation of VOCs may come from the gaseous molecular oxygen or from the lattice oxygen. The involvement of the lattice oxygen cannot be excluded, although its mobility is smaller than that of surface adsorbed oxygen. The formation of the defective structures in the perovskite structure using partial substitutions by ions of lower valence will facilitate the mobility of the lattice oxygen (via oxygen vacancy mechanism) and the material will be more active for oxidation reactions.

Perovskite-type mixed oxides may be promising catalysts for catalytic combustion of acetone and propane at low temperatures (bellow 300^0C).