

# Low-temperature heterogeneous catalytic oxidation of CO and VOCs

**Petya Mitkova Konova**

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,  
Acad. G. Bonchev St., Bl. 11, 1113 Sofia, Bulgaria  
E-mail: [petya\\_konova@abv.bg](mailto:petya_konova@abv.bg)

Efficient oxidation of CO and volatile organic compounds (VOCs) to nontoxic products as CO<sub>2</sub> and H<sub>2</sub>O at very low temperatures is a considerable problem, which can be solved using two approaches: (i) by oxidation with ozone as oxidizing agent stronger than oxygen, or (ii) by finding catalysts, very active at low temperature. Therefore the main goals of our work are: (i) synthesis and characterization of new types catalysts on the base of transition metal oxides supported on different porous materials and investigation of their properties in respect to ozone decomposition and oxidation of CO and VOCs with ozone; (ii) investigation of the properties of highly-active catalysts on the base of nanosized gold supported on transition metal oxides in respect to low-temperature CO oxidation with oxygen.

Three different types of catalysts are subject of our investigation. The first group includes catalysts containing alumina supported unstable oxides of nickel and cobalt in higher (+3 and +4) oxidation states, which possess strong oxidation activity. The second group is more diverse and contains catalysts on the base of silver supported microporous and mesoporous materials. The third group consists of the catalysts Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub>, which contain highly active nanosized gold.

Alumina-supported nickel and cobalt oxide systems with overstoichiometric oxygen (NiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and CoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>) were investigated in respect to heterogeneous catalytic decomposition of ozone, complete oxidation of volatile organic compounds (VOCs) and oxidation of CO in presence of different oxidizing agents (ozone or oxygen). The experiments were performed in the temperature range of -50°C to 250°C in an isothermal plug-flow reactor. The catalysts were prepared by a deposition oxidation-precipitation method and were characterized by chemical analysis, XPS, XRD, IR techniques, magnetic and adsorption measurements.

The catalysts  $\text{NiO}_x/\text{Al}_2\text{O}_3$  and  $\text{CoO}_x/\text{Al}_2\text{O}_3$  show a very high activity in both reactions of ozone decomposition and oxidation with ozone. Ozone decomposition proceeds with high conversion even at temperatures below  $0^\circ\text{C}$  and reaches 100% at room temperature. Both of the catalysts remain active with the time and do not show any deactivation. Oxidation with ozone instead of oxygen leads to a higher catalytic activity at lower temperatures by change of the oxidation reaction mechanism. The  $\text{NiO}_x/\text{Al}_2\text{O}_3$  catalyst shows a higher activity towards reaction of ozone decomposition, whereas  $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalyst has a better activity in respect to complete oxidation of VOCs and oxidation of CO.

Two main reasons for the high catalytic activity of  $\text{NiO}_x/\text{Al}_2\text{O}_3$  and  $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalysts are found: (i) the high content of active and mobile oxygen obtained during the synthesis on the catalyst surface; (ii) the catalytic active complexes of  $\text{Ni}^{4+}$  and  $\text{Co}^{4+}$ , which are formed during the reaction of ozone decomposition and are able to oxidize VOCs and CO at low temperature.

The second object of our investigation are silver supported mesoporous and microporous catalysts, because silver oxides are formed easily in ozone-containing environment and they are unstable and decompose rapidly, releasing highly active oxygen. Silver modified (5 and 2 wt%) mesoporous molecular sieves (H-MCM-41, with Si/Al ratio 20, 40 and 50), zeolite catalysts (H-Beta, with Si/Al ratio 11 and 25; H-ZSM-5, with Si/Al ratio 32) and silica were synthesized by incipient wet impregnation (Imp), in-situ (IS) and ion – exchange (LSIE and SSIE) methods. The obtained catalysts were characterized by different techniques (ICP, XRD, XRF, SEM, FTIR and nitrogen physisorption) and tested in heterogeneous catalytic decomposition of ozone and oxidation reactions with ozone at ambient temperature.

It has been observed a very high catalytic activity towards ozone decomposition for all mesoporous catalysts and for some of microporous materials, while the catalysts remain active with the time on stream. The conversion for the most active catalysts (5Ag(Imp)-H(IE)-MCM-41-50, 5Ag(Imp)- $\text{SiO}_2$ , 5Ag(SSIE)-H(IE)-Beta-11 and 5Ag(Imp)-H(IE)-ZSM-5) exceed 90% at room temperature. The activity of the catalysts enhances with increase of the amount of supported silver, with decrease of the support acidity and modifying the catalyst with some additional metals. The activity of a given catalyst can increase up to 7 times depending on the method which is used for its synthesis.

The most active catalyst in the reaction of ozone decomposition - 5Ag(Imp)-H(IE)-MCM-41-50, shows also high activity towards oxidation of CO and i-propanol with ozone. A mechanism for ozone decomposition, based on the formation of two silver phases - AgO and

$\text{Ag}_2\text{O}(\text{O}_x)$  is proposed, which includes several reaction paths, without blocking the catalyst surface.

Other possibility to achieve a high conversion at low temperature in reactions of complete oxidation is to use an ordinary oxidant such as air or oxygen together with highly active catalysts, containing nanosized gold supported on different transition metal oxides. These catalysts are extraordinary active, especially in respect to CO oxidation, but are unstable and their activity decreases with the time. That is why, the third object of our research are two gold-supported catalysts and their behaviour during the catalytic tests.

The activity, long-term stability and the reasons for deactivation of nanosize gold-supported  $\text{Au}/\text{TiO}_2$  and  $\text{Au}/\text{ZrO}_2$  catalysts in CO oxidation were investigated. The catalysts were prepared by a deposition-precipitation method and were characterized by chemical analysis, adsorption measurements, XRD, XPS, FTIR, TEM, “depletive” oxidation and TPD instrumental methods.

It was found that the nanosize gold-supported catalysts ( $\text{Au}/\text{TiO}_2$  and  $\text{Au}/\text{ZrO}_2$ ) contain gold in both - metal and oxidized form. It has been observed a very high catalytic activity towards CO oxidation for both of the gold catalysts even at temperatures below  $0^\circ\text{C}$ , as  $\text{Au}/\text{TiO}_2$  catalyst is more active and has better long-term stability than  $\text{Au}/\text{ZrO}_2$  catalyst. In spite of the experimentally proved very high activity, the two catalysts exhibited a gradual decrease in initial activity with time.

It is proposed a model of reaction mechanism of CO oxidation on  $\text{Au}/\text{TiO}_2$  and  $\text{Au}/\text{ZrO}_2$  catalysts, which includes formation of an intermediate complex. This complex consists connected both CO adsorbed on a gold particle as surface carbonyl and surface lattice oxygen from the metal-support border. During CO oxidation it was observed formation and accumulation of a monolayer of chemisorbed CO as surface carbonates. When this carbonate layer stabilizes and covers all the surface of the catalyst, the access of new oxygen is blocked and the gold particles are separated from the support, i.e. the formation of the active complex is prevented. Therefore the reason for catalysts deactivation is the capability of gold catalyst to adsorb CO and accumulate it as carbonates. This deactivation is reversible and the catalysts liberate there surface by  $\text{CO}_2$  evolution after heating. During the catalytic operation, heating and treatment, the catalysts additionally decrease there activity in result of destruction of the fine structure and the high dispersion of the gold clusters caused by agglomeration. The resulting deactivation is weak, but irreversible.