

Investigation of CO Oxidation by NO with Application of Semiconductor Gas Sensors

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Abstract

Catalytic activity of platinum supported on SnO₂ in the reaction of CO oxidation by NO was examined. Catalysts were tested in gas mixture containing 1 vol.% of NO and 1 vol.% of CO in helium; activation procedure consisted of treatment of the catalysts with CO at 500°C. Improvement of catalytic activity after activation process was observed. The mechanisms of the oxidation and activation process with application of semiconductor resistive sensors made of Pt/SnO₂ were investigated.

Keywords: CO oxidation by NO, semiconductor gas sensors, Pt/SnO₂

Introduction

Semiconductor gas sensors such as resistive sensors are devices commonly used in environmental monitoring. Principles of operation of this type of sensor are based on changes of sensing layer resistance in the presence of detected gas. The material frequently used in sensing layer construction is doped tin dioxide [1-3], a system apply also as catalyst of carbon oxide oxidation [4-6], methane oxidation [7] or NO_x reduction [8]. Since the surface of the sensor is built of catalysts and the detection process consistent with typical catalytic process stages, the analysis of detection signal of the sensor can be use for investigating the mechanism of catalytic reaction.

The emission of nitrogen oxide, especially from mobile sources, is one of the major problems of air pollution [9]. The high emission is caused by the exhausts of diesel engines or lean-burn gasoline engine systems [10], which is convenient because of low fuel consumption. In the case of lean-burn systems conventional exhaust gas converter – three-way catalyst (TWC) – does not remove NO_x efficiently enough. That is why reduction of nitrogen oxides

is an important challenge. Combining the processes with simultaneously removing another toxic component of air, such as carbon monoxide, causes significant interest of the reaction of CO oxidation by NO [11, 12].

In the mid-1970s the application of doped tin dioxide in the CO oxidation by NO_x was investigated. Interaction between NO and SnO₂ surface was studied by Solymosi and Kiss [13, 14] or Niwa et al. [15]. Fuller and Warwick [16] examined the reduction of nitrogen oxide over that system by carbon oxide.

Loading of noble metal on metal oxide surface improves catalytic activity in many oxidation reactions, therefore application of Pt/SnO₂ catalyst in the oxidation of CO by NO seemed to be an interesting issue and investigation of the mechanism of this reaction is the aim of this paper. Since this catalyst is also typical material for resistive sensor construction, a Pt/SnO₂ sensor was applied in the investigation.

Experimental Procedures

SnO₂ (Aldrich, S_{BET} = 5.16m²/g) and Al₂O₃ (Fluka, S_{BET} = 120.5 m²/g) were used as supports. Platinum (1 and 10 wt.%) was deposited on the supports by wet impregna-

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tion with aqueous solution of H_2PtCl_6 . The samples were dried at $200^\circ C$ for 2h and calcined in air at $600^\circ C$ (Pt/SnO₂) or $400^\circ C$ (Pt/Al₂O₃) for 4h.

The catalytic activity measurements were carried out using Temperature Programmed Surface Reaction method (TPSR) in the range of $25-600^\circ C$, with a linear increase and decrease of temperature. Gas mixtures contained: 1 vol.% NO in helium; 1 vol.% CO in helium; 0.5-2 vol.% CO + 1 vol.% NO in helium, flow rate was $40\text{ cm}^3/\text{min}$, Fuji IR Gas Analyzer as a CO₂ detector was used.

Resistive sensor were prepared by pressing the catalysts and electrodes under pressure $35\text{ T}/\text{cm}^2$ by hydraulic press [17]. A scheme of sensors construction is shown in Fig. 1.

The detection measurements were carried out in the range of temperature $150-450^\circ C$. Sensors were exposed to alternating gaseous atmosphere consisting of helium and: 1 vol.% NO in helium, 1 vol.% CO in helium, and 0.5-2 vol.% CO + 1 vol.% NO in helium. Gas flow rate was from $40\text{ cm}^3/\text{min}$.

Results and Discussion

Catalytic activity of tin dioxide and systems containing 1 wt.% and 10 wt.% of platinum loaded on tin dioxide were examined. The results of catalytic tests are depicted in Fig. 2. The highest CO conversion of examined systems is 28% reached at $500^\circ C$ for catalyst 1% Pt/SnO₂. In the case of 10% Pt/SnO₂ and SnO₂ the CO conversion at this temperature is 21% and 11%, respectively. In the case of all catalyst CO oxidation starts at $200^\circ C$.

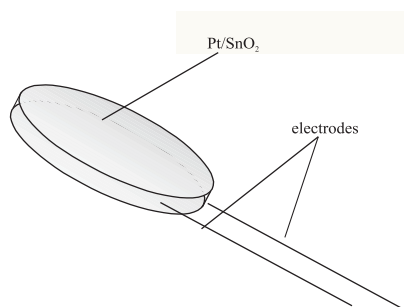


Fig. 1. A scheme of resistive sensor construction.

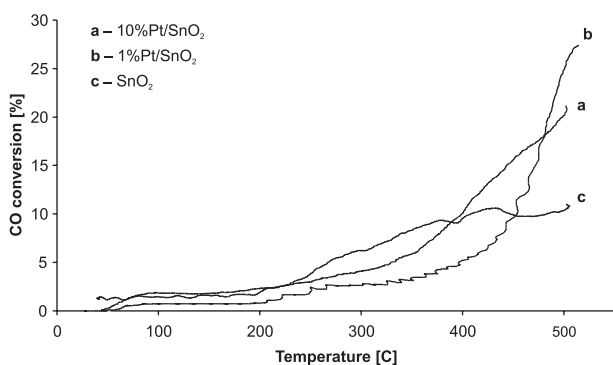


Fig. 2. The CO conversion versus temperature for: a) 10%Pt/SnO₂, b) 1%Pt/SnO₂ and c) SnO₂.

Catalytic activity of platinum supported on aluminum oxide, commonly used catalyst of NO and CO reaction, was examined for comparison. The CO conversion starts at $110^\circ C$ and reaches 98% at $460^\circ C$, which is illustrated in Fig. 3.

In order to improve catalytic activity, Pt/SnO₂ was heated at $500^\circ C$ for an hour in gas mixture containing 5 vol.% of carbon oxide in helium. The treatment caused significant increase of 1% Pt/SnO₂ systems activity: CO conversion starts at $70^\circ C$, at temperature $600^\circ C$ conversion reaches 89%, when CO conversion over non-activated catalyst at this temperature was 28% (Fig. 3)

In order to explain the mechanism of described activation and CO-NO reaction, detection measurements with activated and nonactivated resistive sensor made of 1%Pt/SnO₂ were carried out. Interaction between CO and SnO₂ can be analyzed based on changes of sensing layer resistance in the presence of a reduction agent – carbon monoxide. The detection signal of nonactivated 1% Pt/SnO₂ sensor during programmed changes of CO concentration (0.25-1 vol.% of CO in helium) is depicted in Fig. 4. Resistance of the sensor in pure helium holds at a stable level, when 0.25 vol.% of carbon monoxide appears in gas mixture resistance significantly decreases. Further increasing CO concentration cause relatively smaller changes of sensor resistance.

In the case of resistive sensors made of n-type semiconductor oxides, such as SnO₂, a drop in resistance is caused by

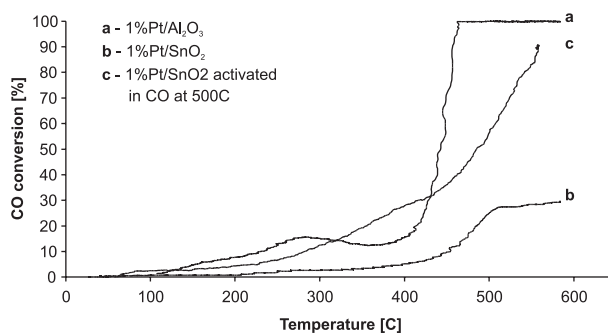


Fig. 3. CO conversion versus temperature for: a) 1%Pt/Al₂O₃, b) 1%Pt/SnO₂ before activation and c) 1%Pt/SnO₂ after activation in CO at $500^\circ C$.

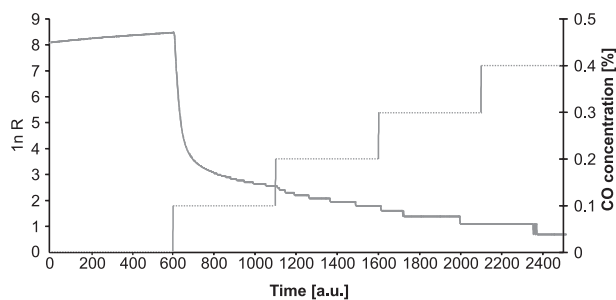
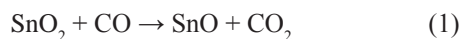


Fig. 4. The detection signal of nonactivated 1% Pt/SnO₂ sensor during programmed changes of CO concentration (0.25-1 vol.% of CO in helium) versus time, $250^\circ C$.

decreasing the concentration of conductivity bond electrons. Based on obtained results, interaction between catalyst and CO (under oxygen deficiency conditions) can be interpreted as reaction of chemisorbed carbon oxide molecule and SnO₂ lattice oxygen, which consequently leads to reduction of Sn⁺⁴ to Sn⁺², forming of double ionized oxygen vacancies (V^{**}_O) and releasing electrons, resulting in an increase of sensor conductivity, according to reactions 1 and 2.



The changes of resistance of the sensor exposed to gaseous atmosphere consisted of 1 vol.% of NO and 0.25-1 vol.% of CO are minor in comparison with previous results (Fig. 5). Adding 0.25 vol.% of CO to mixture of 1 vol.% of NO in helium causes a twice smaller increase of resistance than adding the same amount of CO to pure helium. It is probably a consequence of forming chemisorbed NO_(ads) on tin dioxide surface. The presence of NO_(ads) protects the SnO₂ surface from the reaction of CO and lattice oxygen.

In the previous paragraph we assumed the occurrence of NO forms on the SnO₂ surface. In order to determine the form of NO, detection measurements with dosage of 0.5-1% of NO in helium to helium atmosphere were carried out; the results are illustrated in Fig. 6. When 0.5 vol.% of NO appears, a large decrease and next in-

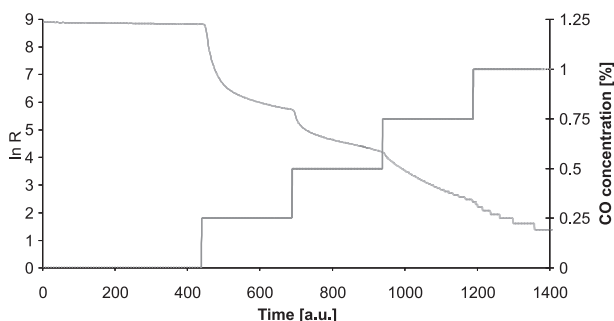


Fig. 5. The detection signal of nonactivated 1% Pt/SnO₂ sensor during programmed changes of CO concentration (0.25-1 vol.% of CO) in mixture of 1 vol.% of NO in helium versus time, 250°C.

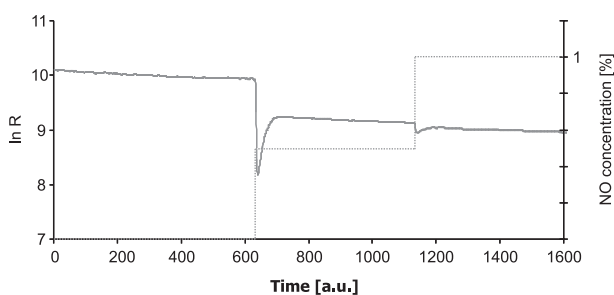
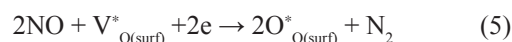
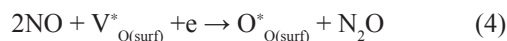
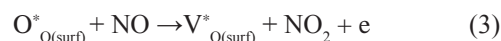


Fig. 6. The detection signal of nonactivated 1% Pt/SnO₂ sensor during programmed changes of NO concentration (0.5-1 vol.% of NO) in helium versus time, 250°C.

crease of resistance is observed; however, resistance does not increase up to the initial level.

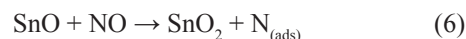
We assume that the drop of resistance is caused by tin dioxide surface reduction according to equation 3, whereas growth of the resistance is a consequence of processes described by equations 4 and 5.



The results of analogue measurements for 1%Pt/SnO₂ sensor activated by CO at 500°C, depicted in Fig. 7, show a small decrease followed by three times larger increase of sensor resistance. Observed considerable increase of detection signal can be a consequence of the reaction of NO and oxygen species formed on SnO₂ surface during the former activation process.

Briefly summarizing, the oxidation of CO by NO over activated Pt/SnO₂ system can be described as:

1. The reaction of nitrogen oxide with previously reduced SnO surface leading to oxidizing SnO to SnO₂ and production of N₂ (equation 6).



2. The adsorption of CO on platinum surface, spill-over of adsorbed CO on SnO₂ surface and reduction of formerly oxidized SnO₂ to SnO.

Stages 1 and 2 follow each other; the scheme of proposed mechanism of the reaction is presented in Fig. 8.

We postulate probable mechanism of CO oxidation by NO consisting of two main stages. Occurring more than one reaction stage can be confirmed by oscillations of the sensor signal occurring under specific conditions. Oscillatory behavior of kinetic origin in the case of NO decomposition was recently describe in literature by Turek [18]. The results of our experiments with the sensor exposed to gaseous atmosphere consisted of 1 vol.% of NO and 0.25-1 vol.% of CO at 150°C, depicted in

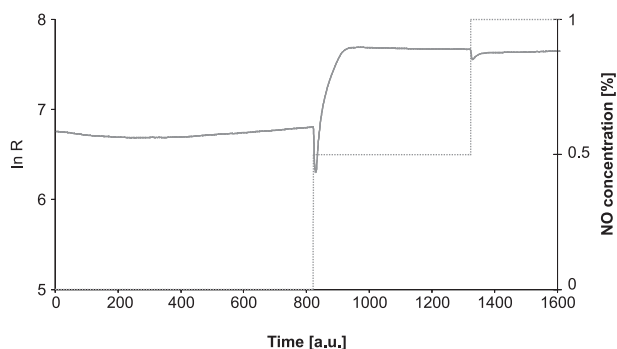


Fig. 7. The detection signal of activated 1% Pt/SnO₂ sensor during programmed changes of NO concentration (0.5-1 vol.% of NO) in helium versus time, 250°C.

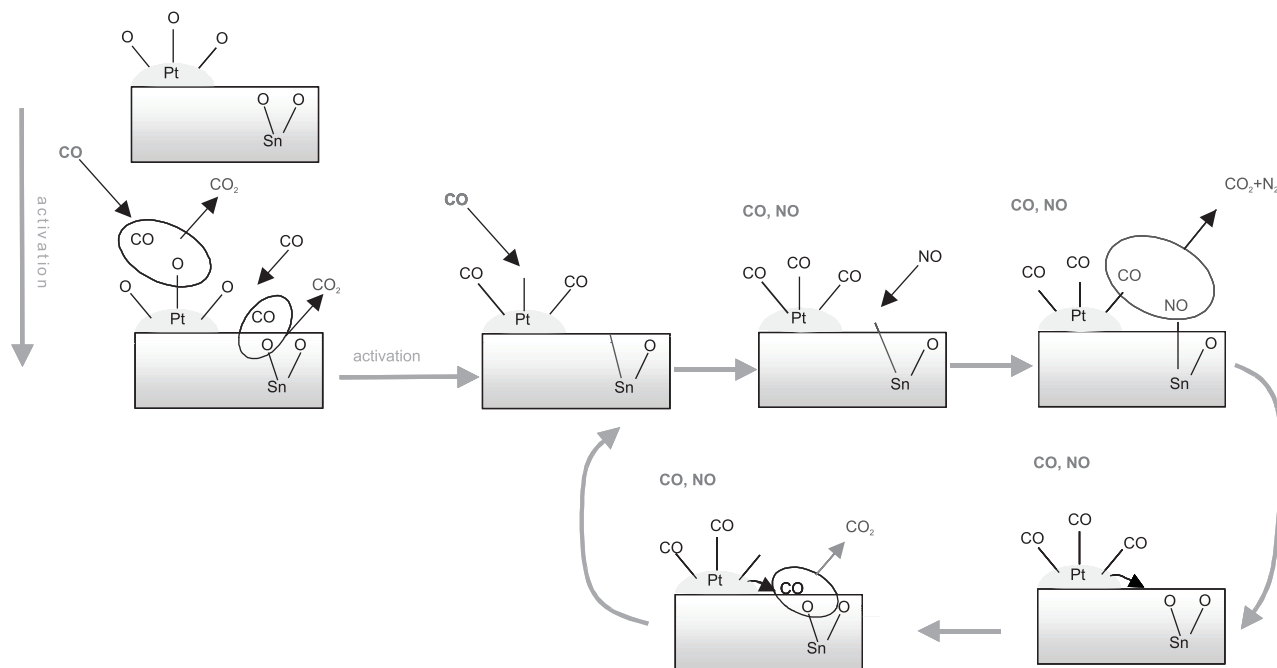


Fig. 8. Proposed mechanism of CO oxidation with NO over Pt/SnO₂ catalyst.

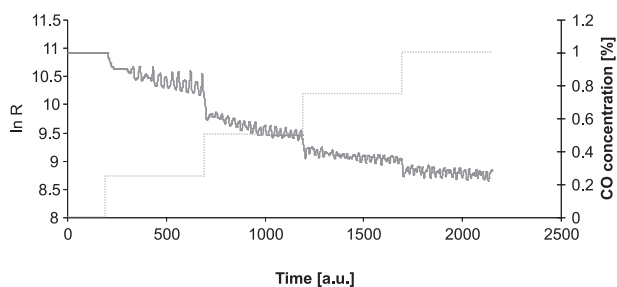


Fig. 9. The detection signal of 1% Pt/SnO₂ sensor during programmed changes of CO concentration (0.25-1 vol.% of CO) in mixture of 1 vol.% of NO in helium versus time, 150°C

Fig. 9 reveal oscillatory character of the detection signal. Moreover, amplitude of oscillations depends on CO concentration. The observed phenomenon is caused by the difference in the rate of particular reaction stages. The difference does not occur at considerably higher temperature, e.g. at 250°C, which was presented in Fig. 5 and discussed above.

Conclusion

Taking into the consideration our results we can state that:

- activation of 1% Pt/SnO₂ catalyst improves catalytic activity of the system in the oxidation of CO by NO, conversion at 600°C raise from 28% for non-activated catalyst to 89% for activated catalyst,
- mechanism of the observed activation is based on reduction of SnO₂ surface by CO,

- the proposed mechanism of the investigated CO–NO reaction consists of two main stages whose rates depend on reaction temperature,
- analysis of the resistive sensors detection signal can be an efficient tool in the examination of the reaction of carbon oxide oxidation by nitrogen oxide.

Acknowledgments

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