

Activity and deactivation of Au/TiO₂ catalyst in CO oxidation

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Received 20 October 2003; received in revised form 20 October 2003; accepted 12 December 2003

Abstract

The activity, long-term stability and the reasons for deactivation of a nanosize gold-supported Au/TiO₂ in CO oxidation were investigated. Characterization of the catalyst sample was made by XPS, FTIR, TEM, BET, “depletive” oxidation and TPD instrumental methods. In spite of the experimentally proved very high activity at temperatures below 213 K, the catalyst exhibited a gradual decrease in initial activity. Two main reasons for the catalyst deactivation were found: (i) capability to adsorb CO and accumulate it as carbonates, this deactivation is reversible and after heating the catalyst surface is restored by CO₂ evolution; (ii) agglomeration of Au particles, which causes irreversible, however weak deactivation.

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Keywords: Gold supported oxide catalyst; Au/TiO₂; CO oxidation; Long-term stability; Deactivation

1. Introduction

Neutralization of gas emissions containing CO and toxic organic compounds by catalytic combustion is a widely used method based on complete oxidation over suitable catalyst systems in the presence of oxygen or ozone [1–5]. Nanosize gold containing catalysts belong to the most active oxide catalysts for CO oxidation, which are active below 0 °C. Highly dispersed (2–4 nm) gold, deposited by the so-called deposition–precipitation method [6–8] on reducible semiconductor metal oxides as well as on hydroxides of alkali earth metals exhibit a high activity towards CO oxidation at low temperatures. The above method ensures optimum size, shape and deposition of the gold clusters on the oxide support by controlling the pH value, the initial concentration of the HAuCl₄ solution and the calcination temperatures of the samples [9,10]. Preliminary heating [11,12] of gold catalysts is not less important for their high activity, as well.

The activities of the gold containing catalysts were studied with respect to both ozone decomposition [13,14] and complete oxidation of benzene for Au/V₂O₅/TiO₂ and

Au/V₂O₅/ZrO₂ catalysts with oxygen or ozone [15–17]. A significant drop of the reaction temperature was observed as compared to cases with oxygen as oxidizing agent.

Regardless of the experimentally established very high activity of these catalysts, they show a gradual decrease in initial activity with time [18,19]. This instability is one of the reasons for which gold catalysts have not yet found practical application.

The main purpose of the present work was to investigate the catalytic behaviour and the reasons for deactivation of a gold containing TiO₂ catalyst prepared by the deposition–precipitation method. Oxidation of CO was used as a test reaction, oxygen from the air being the oxidizing agent.

2. Experimental

2.1. Sample preparation

The sample was prepared in a “Contralab” laboratory reactor (Conraves AG, Switzerland) under complete control of all parameters: temperature, pH, stirrer speed, and reactant feed flow rates. All chemicals used were “analytical grade”. The anatase was prepared by hydrolysis of TiCl₄ with ammonia at pH 9 and a low temperature. A

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deposition–precipitation technique was used to prepare the gold, containing catalyst. This method took place by precipitation of aqueous solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and Na_2CO_3 at constant pH and temperature upon titania, preliminary suspended in water by ultrasound. The resulting precipitate was aged for 1 h at 60°C , then filtered and washed carefully until complete elimination of Cl^- anions. The sample was dried under vacuum at $T = 80^\circ\text{C}$ and calcined in air at 400°C for 2 h. The sample contained 3 wt.% of gold.

2.2. Sample characterization

The specific surface area of the catalyst was determined by the BET method using low-temperature nitrogen adsorption on a “Flow Sorb II-2300” device. The value obtained was $86\text{ m}^2/\text{g}$.

Transmission electron microscopy (TEM) characterization of the catalyst was performed in a Hitachi-H-600-2 electron microscope. The sample was dispersed in bidistilled water by ultrasound. After that the drops were transferred to a carbon-coated bronze mesh and dried. The average size of the gold particles on anatase was 3.6 nm.

The IR spectra were recorded on a Nicolet Avatar 360 spectrometer at a spectral resolution of 2 cm^{-1} accumulating 64–128 scans. For the adsorption experiments, self-supporting pellets were prepared from the sample powders and treated directly in the purpose-made IR cell. The latter was connected to a vacuum-adsorption apparatus with a residual pressure below 10^{-4} Pa . The cell allowed the IR measurements to be performed both at ambient temperature and at 100 K. Carbon monoxide (>99.997) was supplied by Merck. Prior to the adsorption measurements, the samples were activated by heating for 1 h in oxygen at 573 K and 1 h evacuation at the same temperature (oxidized samples) within the cell system. To obtain “reduced” samples, the pellets were treated in hydrogen (27 Pa) for 1 h at 573 K and then evacuated at the same temperature for 1 h.

The XPS studies were performed in a VG Escalab II electron spectrometer using $\text{Al K}\alpha$ radiation with an energy of 1486.6 eV. The residual gas pressure in the analysis chamber was 10^{-7} Pa . The binding energies (BE) were determined utilizing the C1s line (from an adventitious carbon) as a reference with an energy of 285.0 eV. The accuracy of the measured BE was $\pm 0.2\text{ eV}$.

Temperature programmed desorption of the catalyst investigated was performed in an argon (99.999%) flow with a gas flow rate of 4.4 l/h and a pressure of 0.101 MPa. The investigation proceeded at temperatures ranging from 293 to 573 K with a heating rate of 10 K/min. The mass of the catalyst samples was 0.25 g, the catalyst volume -0.15 cm^3 , the catalyst grain size 0.3–0.5 mm and the volume rate was $30,000\text{ h}^{-1}$ (calculated on the total catalyst bed volume). The CO and CO_2 concentrations were determined with an accuracy of $\pm 0.1\text{ ppm}$ using a Maihak gas analyser. The same analyser measured the oxygen with an accuracy of $\pm 100\text{ ppm}$.

2.3. Catalyst activity measurements

The catalytic activity of the sample was studied in an isothermal plug flow reactor permitting work under steady-state conditions without temperature gradients. The size of the catalyst particles (0.3–0.5 mm) was chosen, taking into account the reactor diameter (6.0 mm) and the volume rate ($30,000\text{ h}^{-1}$) in order to reduce the effect of diffusion. The gas flow rate was 4.4 l/h, the catalyst bed volume 0.15 cm^3 and the catalyst mass -0.25 g .

The catalytic oxidation of CO was performed at temperatures between 213 and 393 K, the oxidizing agent used being oxygen from the air (gas mixture: O_2 20%; and N_2 80%). The preliminary treatment of the catalyst included heating in air flow at 393 K for 1 h.

The amount of CO was dosed by an Ismatex MS2/6 (Switzerland) pump. The initial concentrations of carbon monoxide ranged from 0.06 to 0.24 vol.%. The carrier gas was air (mixture of 20% O_2 , 80% N_2).

The experiment on the so-called depletive oxidation [20] was carried out in a gradientless reactor. A carbon monoxide flow (0.4 vol.%) in argon (99.999%) was passed through the catalyst bed at 298 K, which ensured absence of oxidizing agent from the gas phase. The oxidation was controlled on the basis of the CO_2 concentration at the outlet of the reactor.

3. Results and discussion

3.1. Catalytic activity

Fig. 1 presents the temperature dependence of the catalytic activity of the Au/TiO₂ catalyst.

The apparent activation energy of 25 kJ/mol in the pseudo-kinetic region was calculated using a first order kinetics equation. Varying the inlet concentration of CO, the temperature dependence of the conversion of the reaction under consideration with catalyst Au/TiO₂ was obtained. The reaction order $n = 0.85$ was estimate with respect to CO. In order to determine the reaction order toward

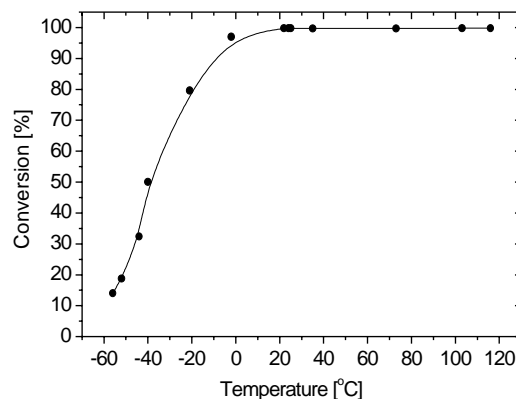


Fig. 1. Conversion-temperature dependence of CO oxidation on Au/TiO₂ catalyst: $C_{\text{CO}} = 1800\text{ ppm}$, $E_{\text{app.}} = 25\text{ kJ/mol}$.

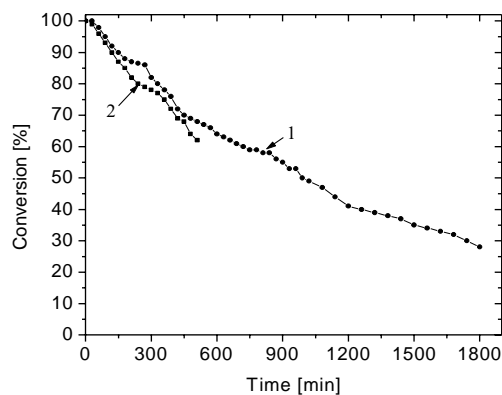


Fig. 2. Activity changes in CO oxidation at room temperature (298 K): 1, fresh sample; 2, Au/TiO₂ after heat-treatment at 300°C (TPD).

oxygen with the same catalyst, the inlet concentration of oxygen was varied. At high oxygen concentrations (above 10 vol.%), the reaction order was 0.07, i.e. the reaction rate was almost independent of the amount of introduced oxygen. At low concentrations (below 10 vol.%), the effect of the introduced oxygen amount increased, i.e. the reaction order rate became 0.2 at 2% O₂.

3.2. Deactivation

Despite the high activity of the investigated Au/TiO₂ catalyst, it displayed a gradual activity decrease with time (Fig. 2, curve 1).

Some changes in chemical composition and structure of the surface layer or the bulk of the catalyst were assumed to occur during CO oxidation. The change may be due to phase transitions such as formation of carbonates and/or blocking of the active sites of CO oxidation.

Low-temperature CO adsorption on a preliminary oxidized sample of Au/TiO₂ leads to the appearance of a series of bands with maxima at 2202, 2180, 2149, 2123 and 2107 cm⁻¹ (Fig. 3, spectra a).

With the decrease in the coverage, the intensities of all bands also decrease. More detailed analysis shows that the

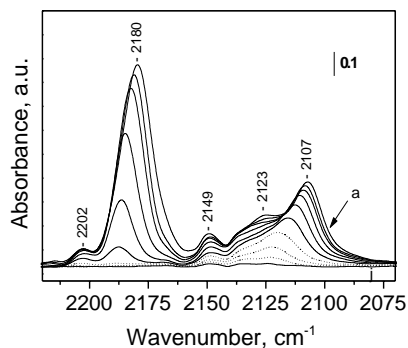


Fig. 3. FTIR spectra of CO (270 Pa equilibrium pressure) adsorbed at 85 K on oxidized sample (a) and after evacuation at 100 K (b, c) and during a gradual increase of temperature (d–j).

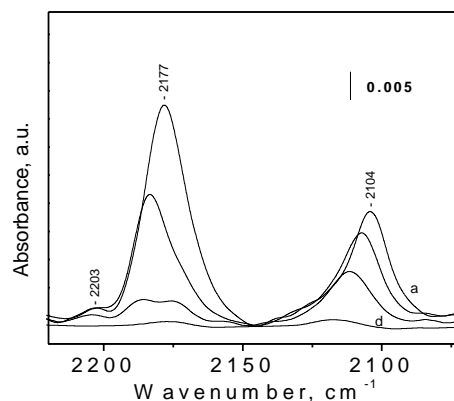


Fig. 4. FTIR spectra of CO (270 Pa equilibrium pressure) adsorbed at 85 K on reduced sample (a) and after evacuation at 100 K (b) and during a gradual increase of temperature (c and d).

bands at 2202 and 2180 cm⁻¹ are disappearing faster than the remaining bands (Fig. 3, spectra b–g), which indicates weaker bonds of the surface species. According to the literature [21], these bands can be assigned to two different types of Ti⁴⁺–CO carbonyl complexes. Due to the absence of d-electrons in the outer electronic layer, Ti⁴⁺ ions can interact with the adsorbed CO molecules by σ and/or electrostatic connection. The carbonyls formed are instable and can be observed mainly at low temperatures. A basic problem is the true interpretation of the oxidation state of gold sites, which have adsorbed CO. It has been established that Au⁺–CO and Au⁰–CO complexes also appear at 2150–2100 cm⁻¹ [21]. That because we investigated low-temperature CO adsorption on a reduced Au/TiO₂ sample (Fig. 4). In this case, together with the characteristic band of Ti⁴⁺–CO carbonyl complexes, there is a band with a maximum at 2104 cm⁻¹, which can be assigned to Au⁰–CO carbonyls. The decrease in the coverage affects the intensity of the band at 2104 cm⁻¹, which is accompanied by blue shift (Fig. 4, spectra a–d).

Comparison of the two sample spectra shows that (i) the band at 2107 cm⁻¹, observed after CO adsorption on an oxidized sample has a behavior similar to that of the band at 2104 cm⁻¹, which permits its attribution to Au⁰–CO carbonyl complexes and (ii) the bands at 2149 and 2123 cm⁻¹, which were not observed after CO adsorption on a reduced sample, should be due to Au⁺–CO carbonyl complexes. These two bands are unsynchronized in their changes and hence, they are due to two different Au⁺ sites.

At the same time in the region of 1700–1200 cm⁻¹ there is formation of three bands having their maxima at 1578, 1317 and 1224 cm⁻¹ (spectra are not shown), due to the appearance of a thin surface layer of carbonates and/or carbonate-like species on the support. In the CO oxidation reaction the intensities of these three bands increase significantly [22]. The formation of the above layer reveals that a large part of the adsorbed amount of CO is accumulated as a carbonate phase.

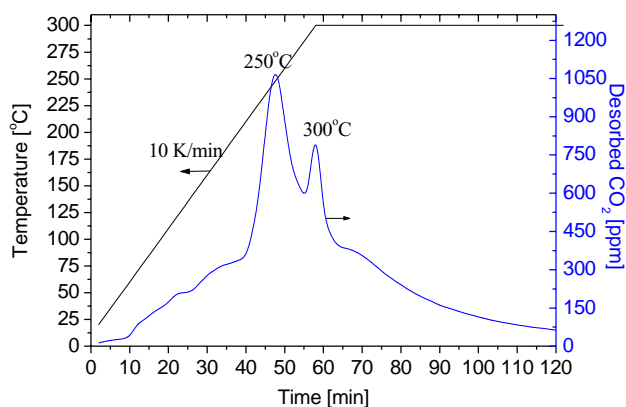


Fig. 5. TPD treatment of Au/TiO₂ catalyst. Carrier gas: argon, maximum temperature of 573 K; heating rate of 10 K/min.

Adsorption of CO on the catalyst surface was observed and discussed in a series of works [23–26] on the basis of FTIR spectra and MS study. Other authors [18] registered the existence of a carbonate phase formed by the metal of the support as a thin surface layer. Hence, the catalyst deactivation may be due to the formation and stabilization of the carbonate layer on the oxide surface, this leading to a change in chemical composition of the catalyst. The formation of such a layer can also explain the experimentally observed adsorption of part of the introduced CO amount during the study of the catalysts activity, the difference in carbon balance attaining up to 10–15%.

In order to investigate the possibility of formation of such a carbonate layer, the catalyst was subjected to TPD in an inert gas (argon) flow during heating up to 573 K with a heating rate of 10 K/min. The results obtained within 120 min are presented in Fig. 5. It was found that during desorption in an argon flow up to 573 K the catalysts evolved CO₂, producing two peaks: at 523 and 573 K. After reaching 573 K, the temperature was maintained constant for 1 h until the concentration of evolved CO₂ was of order of that observed at room temperature. The total amount of CO₂ evolved during the TPD experiment was calculated to be 4.58 mg, which corresponds to the formation of a monolayer of chemisorbed CO on the BET specific surface area. The two peaks of CO₂ observed during TPD may be due to evolution of adsorbed CO₂ produced during the reaction at a lower temperature and to evolution of decomposed surface carbonates at higher temperature.

From the foregoing it may be concluded that the change in activity and long-term stability of the catalyst under consideration is probably due to its tendency to adsorb CO, accumulate it as carbonates during the experiment and to stabilize this carbonate layer. The deactivation in this case is reversible (Fig. 2, curve 2) and after heating the catalyst surface is liberated by evolution of carbon dioxide.

An additional experiment was performed in order to elucidate whether this deactivation is a result of adsorption of reaction product CO₂ instead of reagent CO. A CO₂ flow

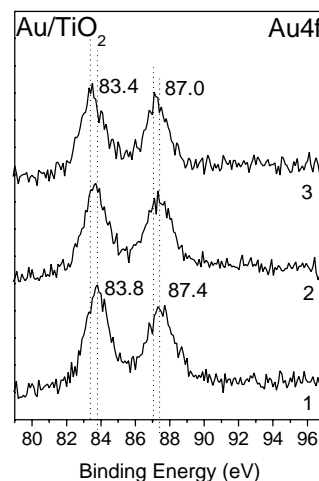


Fig. 6. XPS spectra of the Au/TiO₂ catalyst: 1, fresh sample; 2, sample after 30 h work; 3, sample after TPD.

was passed through the catalyst layer at low temperature (233 K) for 3 h. The data obtained confirmed that no CO₂ adsorption took place.

After temperature-induced decomposition and removal of the formed carbonate species followed by cooling to room temperature ($T = 298$ K) and admittance of the CO and air mixture, the activity of the Au/TiO₂ catalyst was almost completely restored. As shown in Fig. 2 (curve 2), the resulting conversion at room temperature was approximately the same. In order to establish the additional structural changes of the catalyst surface due to temperature increase during the catalytic test, XPS spectra of a fresh and a used sample were recorded.

Usually the BE of core electrons for small metal clusters deposited on the support are shifted to higher values in comparison with BE for the large bulk metals. The XPS spectra of the two used Au/TiO₂ samples (Fig. 6) show a shift (of about 0.4 eV) toward lower binding energies in comparison with the fresh one. This shift can be assigned to the changes in electronic structure with increasing size of the gold clusters deposited on the support, which indicates agglomeration of the particles when the catalyst is working. At the same time, a decrease in amount (by about 20%) of the gold nanoparticles per unit catalyst surface is observed, probably caused of agglomeration. As a result of this sticking and size increase of the nanosized gold, the catalyst changes its surface properties, which decreases its activity. This agglomeration process leads to irreversible although weaker deactivation.

It could be said that the second reason for the activity decrease of gold catalyst is associated with the agglomeration of the Au particles. The increase in size of the Au clusters and the disappearance of the fine structure and the high dispersion, which determine the high activity of gold catalysts, were also observed by Goodman et al. [12,19] who associated the agglomeration with the oxidation of the metal oxide support by the oxygen treatment.

In order to make an approximate evaluation of the reactivity of surface oxygen of the catalyst Au/TiO₂, we performed the so-called “depletive” oxidation [20]. It consists in investigation of the temperature dependence of the interaction rate of CO with the surface oxygen of the catalyst in the absence of an oxidizing agent from the gas phase. For that purpose, CO (inlet concentration 0.4 vol.%) in an argon flow was passed through the catalyst layer at 300 K. A 99% conversion gradually decreasing to 22% for 1 h was registered. Subsequent introduction of air was accompanied by restoration of the catalyst activity in 30 min up to the initial conversion value (about 99%). Additional introduction of a CO and Ar mixture led to a quicker activity decrease, i.e. from 99 to 31% conversion for about 30 min. The results are given in Fig. 7.

The conclusion to be made on the basis of the foregoing is that in the absence of an oxidizing agent, CO causes partial reduction of the catalyst surface, being oxidized itself by the lattice oxygen of the corresponding oxide and different peroxy species formed during the calcinations pretreatment [27]. When the surface oxygen is “exhausted”, the activity decreases. The introduction of air in which there is an excess of oxygen with respect to the introduced CO amount, restores the initial activity and saturates the deficient in oxygen catalyst surface. This restoration is not instantly and needs some time. Repetition of the same procedure leads to a faster deactivation, which reveals the incomplete restoration of the initial structure of the support.

3.3. Reaction mechanism and mechanism of deactivation

Low-temperature catalytic oxidation on a gold-supported catalyst occurs on the Au particle-TiO₂ boundary. The oxygen atoms from the oxide support are affected by the gold particles being in contact with them and their bonding to the metal ion is stretched tight. It is this “tension” zone that represents an attractive and competitive stronger site of CO oxidation.

As a result of the present investigation, the following model of the reaction mechanism and mechanism of deactivation can be proposed:

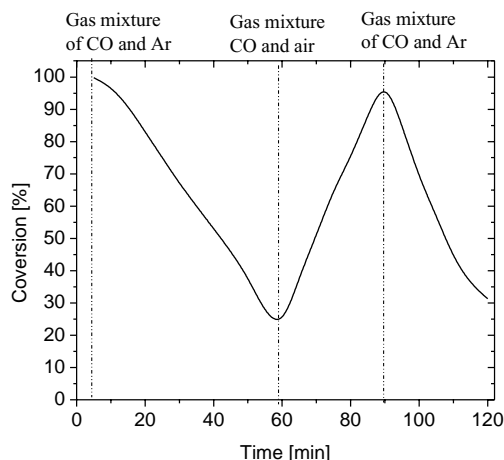
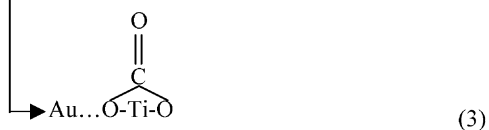
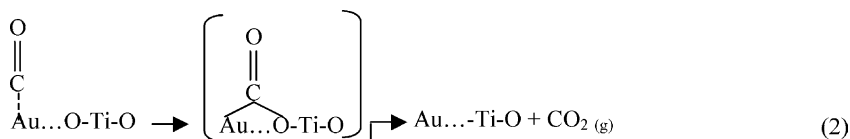
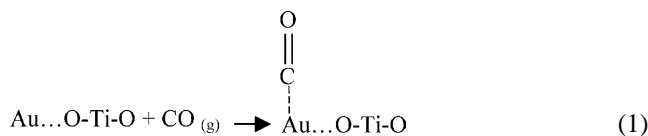
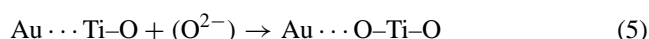
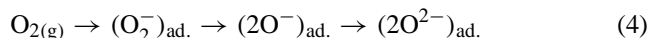


Fig. 7. Results from so-called ‘depletive’ oxidation on a fresh sample of Au/TiO₂ catalyst at room temperature (298 K).



The first step (1) of the proposed oxidation mechanism includes CO adsorption on the gold particle. During the second step (2), CO adsorbed on a gold particle as surface carbonyl, transform into an intermediate complex, which decomposes following two alternative parallel pathways. If the intermediate complex decomposes evolving the reaction product and liberating the active site, the second step can take place. The other possibility (3) for the intermediate complex is the change into surface carbonates deposited on the oxide support. This carbonatisation process leads to deactivation of the catalyst. We think that reaction (3) has a much lower rate as compared to reaction (2). As a result of reaction (3), the amount of lattice oxygen of the metal-support border gradually decreases because of covering of the support surface area with carbonates.

The oxygen coming from the gas phase is adsorbed on the oxygen vacancies of the metal oxide surface, passing through several oxidation forms and filling up the stores of surface oxygen (4). During the last step (5), the missing oxygen on the active site is restored and can again take part in the oxidation process.

Formation of carbonates takes place only on the gold-support border, but as a result of carbonate ion migration, they cover all the surface of the catalyst. When the

surface is completely covered, the access of new oxygen is prevented, as well. Due to the accumulation of a carbonate layer, the gold particles are separated from the support and the formation of the active complex is prevented and the catalyst deactivated.

4. Conclusion

On the basis of the present study it may be concluded that gold containing TiO₂ catalyst is highly active in the catalytic oxidation of carbon monoxide. The deactivation of the investigated gold containing oxide catalyst is due, on the one hand, to its readiness to adsorb CO as surface carbonates and to stabilize them as a carbonate layer. This deactivation is reversible and the catalyst liberates its surface by CO₂ evolution after heating. The other reason for the observed decrease in activity of the gold catalyst is the disturbance of the finely disperse structure of the nanosized gold on the surface caused by the catalyst use itself, by treatment with oxygen and by heat-treatment. The resulting agglomeration causes irreversible although weak deactivation.

Acknowledgements

Authors gratefully acknowledge the financial support (project X-1005) by the National Science Fund at the Ministry of Education and Science, Bulgaria.

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