

The influence of interaction between palladium and indium on the activity of Pd–In/Al₂O₃ catalysts in reduction of nitrates and nitrites

I. Witońska, S. Karski^{*}, J. Rogowski, N. Krawczyk

Institute of General and Ecological Chemistry, Technical University of Lodz, ul. Żeromskiego 116, 90-924 Lodz, Poland

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Abstract

The influence of indium addition on the catalytic properties of palladium catalysts supported on Al₂O₃ in the reaction of nitrates reduction to nitrogen was studied. It was found that indium did not show any activity by itself, but acted as a “promoter” for the catalytic activity of monometallic Pd/Al₂O₃ catalysts. The X-ray diffraction (XRD) and Time-of-flight secondary ion mass spectrometry (ToF-SIMS) studies proved the existence of intermetallic interactions between Pd and In, which probably modified activity and selectivity of bimetallic catalysts in this reaction. The ToF-SIMS technique showed the presence of intermetallic compounds in all the studied bimetallic systems, which could not be proved by XRD measurements in the case of the systems with a small amount of indium.

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1. Introduction

Supported palladium catalysts have been widely used in chemical and petrochemical industry as well as in the environment protection. One of the general problems taking place during catalytic processes in industry is the inevitable deactivation of the catalysts.

In order to minimize the problem of deactivation of catalysts and improvement of their selectivity, the modification of catalysts was made through the introduction of various metallic promoters. Monometallic catalysts are more often replaced by multicomponents systems.

Bimetallic palladium systems (Pd–M) are a large and important group of heterogeneous catalysts which have been used in many reactions of reduction and oxidation. One of the examples of promoting Pd by an addition of a second metal deals with the Lindlar catalyst PdPb/CaCO₃ for the selective hydrogenation of alkynes [1]. In those reactions high selectivity was also observed upon alloying Pd with Sn [2,3], Ag [4], Fe [5], Co [6] and Cu [7,8]. The bimetallic Pt–Pd system on acidic supports shows higher activity in hydrodearomatization than the monometallic

Pd and Pt catalysts [9]. The addition of Mo [10], Cu [11] or Cr [12] to Pd catalysts increases activity and selectivity to N₂ in the reaction between NO and CO, which is important for three way catalysts used in cars. It was shown that the addition of Bi and Tl to Pd/SiO₂ increased the selective hydrodechlorination of CCl₂FCHF₂ to CH₂FCF₂Cl and CH₂FCHF₂ [13]. The hydrogenation of nitrates to N₂ in contaminated drinking water is promoted by the addition of Cu [14–16], Ag [17–19] and Sn [20,21] to Pd catalysts. The industrial catalyst for hydrogenation of nitrobenzene is a trimetallic catalyst PtPdFe/C [22].

A lot of interesting information about the effect of co-metals on the performance of Pd in bimetallic catalysts is presented in the paper of Coq and Figueras [23]. The catalytic properties of Pd are discussed in the frame of electronic and geometric effects. This review is restricted to Pd–M catalysts operating in a reductive atmosphere.

In the past few years various bimetallic palladium based catalysts have been used in commercial oxidation processes. One of the well-known catalysts in the oxidative esterification reaction is Pd–Te catalyst [24]. Palladium catalysts promoted with bismuth and thallium are characterized by high selectivity in the reaction of oxidation of glucose to gluconic acid and lactose to lactobionic acid [25–28]. In recent years Pd–Pb catalysts have been used in the direct production of methyl methacrylate from methacrolein, methanol and oxygen [29]. A great interest has

^{*} Corresponding author. Tel.: +48 42 631 30 94.
E-mail address: karski@p.lodz.pl (S. Karski).

also been paid to the Pd–Bi systems for the direct production of benzylacetate [30].

The examples listed above prove a great theoretical as well as practical importance of Pd-based catalysts. Even though various promoters have been used for different reduction and oxidation reactions, their precise role is still not known. Most of the interpretations on the role of promoters are rather hypothetical. This is probably due to the lack of information about the exact surface structure.

Supported Pd–In catalysts were not widely investigated in the chemical processes, but there is some information in literature about their activity and selectivity in the reduction of nitrates [31–34]. However, the reason for the promoting effect of indium in bimetallic Pd–In/support systems is still not explained.

In this paper, we would like to present an influence of indium addition on the activity and selectivity of palladium catalysts in the reduction of nitrates to nitrogen in water. The catalysts were characterized by X-ray diffraction (XRD), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), temperature-programmed desorption of H₂ (TPDH₂) and temperature-programmed reduction (TPR).

2. Experimental

2.1. Catalyst preparation

Bimetallic Pd–In/Al₂O₃ catalysts containing 5 wt.% Pd and 0.5, 1, 2 and 5 wt.% In were obtained through coimpregnation of support (Al₂O₃, Fluka 506 C, 143 m²/g) with water solution of In(NO₃)₃ (99.9%, Aldrich) and Pd(NO₃)₂ (the MLS-1200 Mega Microwave Digestion System (Milestone) was used for complete digestion of metallic Pd in HNO₃ (POCh Gliwice)). The water was evaporated at an increased temperature under vacuum. The catalysts were dried in air at 110 °C for 6 h, calcined at 500 °C for 4 h in air atmosphere and then reduced in hydrogen atmosphere for 2 h at 300 °C, directly before the measurements.

2.2. Catalytic measurements

2.2.1. Reduction of nitrates and nitrites

The hydrogenation of nitrate or nitrite solutions was performed in a thermostated glass reactor equipped with a stirrer, a hydrogen supply system, a burette and a pH electrode. The ammonia formed during the reduction was neutralized by the addition of aqueous solution of HCl (50 mmol/dm³) to pH 5.5 in the reaction medium. The reaction was conducted at 20 °C. The mixture was stirred at 300 rpm, and hydrogen was bubbled through at 0.2 dm³/min. No rise in temperature due to the heat of the reaction was observed in any of the runs since the reactor was operated with low concentration of nitrate (1.6 mmol/dm³) or nitrite (2.1 mmol/dm³). No pressure control was required as the total operating pressure in the system was equal to atmospheric pressure. Because three phases were present in the reactor, the system used is treated as a slurry reactor.

Samples of the reaction medium were taken every 5, 10, 20, 30, 45 and 60 min, filtered and analyzed using a liquid chromatograph LaChrom (Merck Hitachi) coupled with a variable

wavelength UV detector LaChrom L-7400 (Merck Hitachi). The analytical wavelength was 210 nm. In our investigation, Merck C₁₈ LiChrospher RP-18 (5-μm) column (250 mm × 4.0 mm i.d.) was used. The water solution of octyloamine phosphorate (5 mmol/dm³, pH 6.3) was used as a mobile phase. The flow rate of octyloamine phosphorate was 1.0 cm³/min. For the samples, concentrations of NH₄⁺ ions were analyzed spectrophotometrically with the use of ammonia-test (2.6–193 mg NH₄⁺/dm³, Merck).

2.2.2. Powder X-ray diffraction

Powder X-ray diffraction patterns were obtained with a Simens D5000 diffractometer using Cu Kα radiation (λ = 154.18 pm). Crystalline phases were identified by references to the ASTM data files.

2.2.3. Temperature-programmed reduction and temperature programmed desorption of H₂ (TPDH₂) measurements

TPR and TPD measurements were carried out in a flow apparatus described in Ref. [35].

The catalyst samples (0.1 g), prior to the TPR measurements were calcined at 500 °C for 2 h in oxygen and then flushed with helium at the same temperature for 0.5 h. After cooling to room temperature in helium atmosphere, temperature programmed reduction measurements were carried out. TPR runs were performed in the temperature range 25–500 °C, using a mixture of hydrogen-argon (10 vol.% of H₂) and a linear temperature growth of 10 °C/min. The flow rate of gases was 30 cm³/min.

For TPDH₂ measurements samples of catalysts weighing 0.5 g were used. Before sorption measurements, samples of mono- and bimetallic catalysts were reduced with hydrogen at 300 °C for about 1 h and then flushed with argon at the same temperature and for the same amount of time. After cooling to room temperature and sorption of hydrogen (0.5 h), TPD measurements were carried out. Argon was used as a carrier gas. The flow rate of gas was 40 cm³/min. Catalyst samples were heated at the rate of 20 °C/min.

2.2.4. Time of flight secondary mass spectrometry

Secondary ions mass spectra and images were recorded with a ToF-SIMS IV mass spectrometer manufactured by ION-TOF GmbH, Muenster, Germany. The instrument is equipped with liquid metal ⁶⁹Ga⁺ primary ion gun and a high mass resolution time of flight mass analyzer. Two different working modes of primary Ga⁺ gun were used during the measurements. A high current bunched mode characterized by high mass resolution was applied for spectra acquisition. Images were recorded in a burst alignment mode which provide high lateral resolution. Secondary ion mass spectra were recorded from an approximately 100 μm × 100 μm area of the sample surface. During the measurement the analyzed area was irradiated with the pulses of 25 keV ions at 10 kHz repetition rate and average ion current 2.5 pA. The analysis time was 50 s giving an ion dose below static limit of 1 × 10¹³ ions/cm². Secondary ions emitted from the bombarded surface are mass separated and counted in the time of flight (ToF) analyzer. For each catalyst mass spectra were recorded from at least three places at the sample surface.

A low energy electron flood gun was used for charge compensation. Prior to the image acquisition secondary ion mass spectra of the sample surface were recorded and then appropriate ion peaks were chosen for the imaging. Images of the surface show emission intensities of the corresponding secondary ions from a selected number of surface points obtained by rastering the primary ion beam over the analyzed area.

The catalyst samples for ToF-SIMS analysis were prepared by pressing pellets.

3. Results and discussion

Catalytic results are expressed as conversion (X , %) and selectivity (S , %). Those parameters were defined as

$$X (\%) = [1 - (C/C_0)] \times 100$$

$$S (\%) = [C_A/(C_0 - C)] \times 100$$

where C_0 was a molar concentration of nitrates or nitrites at the beginning of the reduction process, C a molar concentration of nitrates or nitrites after time t , and C_A a molar concentration of products (nitrites or ammonia) after time t . The selectivity to N_2 was defined as $S_{N_2} (\%) = 100 - S_{NO_2^-} - S_{NH_4^+}$.

Fig. 1 shows the conversion degree of nitrate and selectivities towards NO_2^- , NH_4^+ and N_2 for chosen monometallic systems containing 5%Pd/ Al_2O_3 and 5%In/ Al_2O_3 as well as for palladium catalysts supported on alumina and modified with indium.

The presented picture shows that the conversion of palladium catalysts modified with indium is considerably higher than in the case of monometallic systems. It is noteworthy that activity was enhanced by the addition of only 0.5 wt.% In (In/Pd=9.3 at.%) and the maximum activity was observed at 2 wt.% In (In/Pd=37.1 at.%). However, the addition of greater amounts of indium (for 5 wt.% In, the metal promoter proportion in bimetallic phase reached 92.7 at.%) caused the decrease in activity of bimetallic Pd–In/ Al_2O_3 systems in the reaction of nitrate reduction in water. The same phenomenon was observed for the supported palladium systems promoted with copper and silver [19,36,37]. Those publications showed that for both types of palladium-based catalysts the activity for nitrate reduction appears to go through a maximum for a promoter content between 33 and 50 at.%, depending on the catalyst. The presented results obtained for the Pd–In/ Al_2O_3 catalysts in the reduction of nitrates are in good agreement with the results proclaimed in literature.

For the catalyst 5%Pd–5%In/ Al_2O_3 , which is characterized by the lowest activity, the highest concentrations of nitrites in the reaction mixture were observed. The relatively high concentration of NO_2^- ions is noticed even at the end of the reaction (Fig. 1). It is worth emphasizing that we did not observe the formation of ammonia, which is a by-product of the reduction of nitrates. However, the NH_4^+ ions were detected in the reaction mixture for bimetallic catalysts containing smaller amounts of indium (0.5–2 wt.%).

Taking into consideration the formation of undesirable products (nitrites and ammonia) and high activity in the nitrate

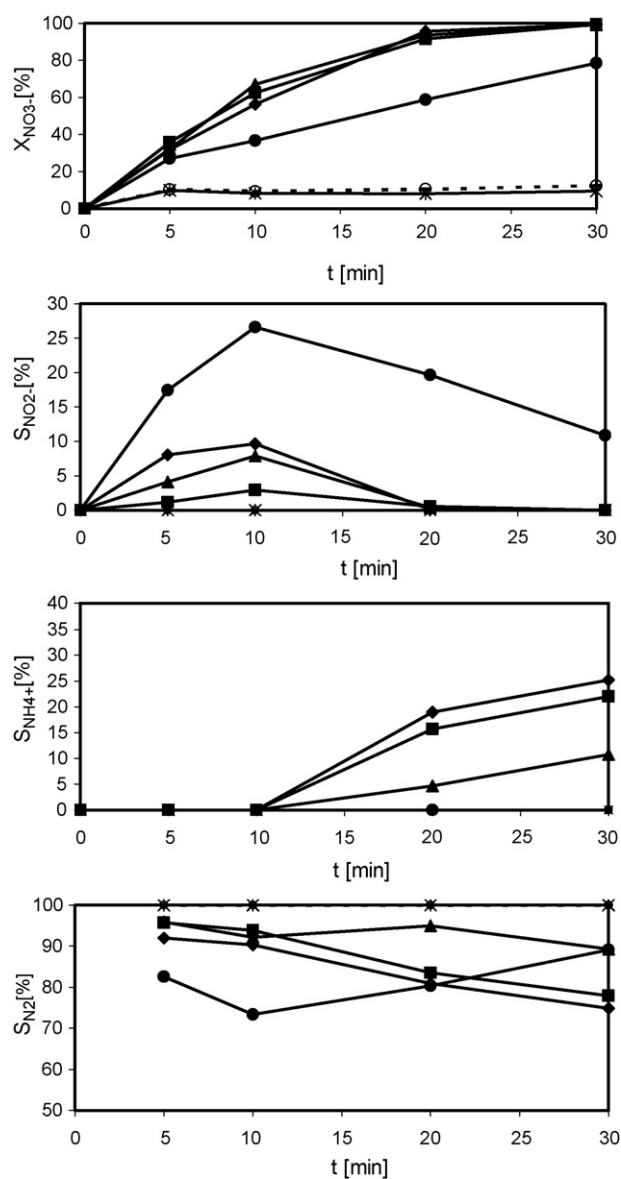


Fig. 1. Conversion of nitrates (X) and selectivities to nitrites ($S_{NO_2^-}$), ammonia ($S_{NH_4^+}$) and nitrogen (S_{N_2}) in the presence of catalysts: 5%Pd/ Al_2O_3 (○); 5%In/ Al_2O_3 (✱); 5%Pd–0.5%In/ Al_2O_3 (◆); 5%Pd–1%In/ Al_2O_3 (■); 5%Pd–2%In/ Al_2O_3 (▲); 5%Pd–5%In/ Al_2O_3 (●) as a function of time.

reduction, the system containing 5%Pd–2%In/ Al_2O_3 seems to be an optimal catalyst for this process. This catalyst is characterized by a conversion degree (about 95%) after a relatively short time of reaction (20 min) and good selectivity towards N_2 (about 95%).

The behaviour of bimetallic Pd–In/ Al_2O_3 catalysts in the reduction of nitrites is quite similar to the one in the reduction of nitrates. In the case of this reaction, the catalyst 5%Pd–5%In/ Al_2O_3 also shows the lowest conversion degree (Fig. 2). The different behaviour of bimetallic Pd–In/ Al_2O_3 catalysts with a higher amount of indium (5 wt.% In) in comparison with catalysts containing 0.5–2 wt.% In could be connected with various surface structures of those catalysts.

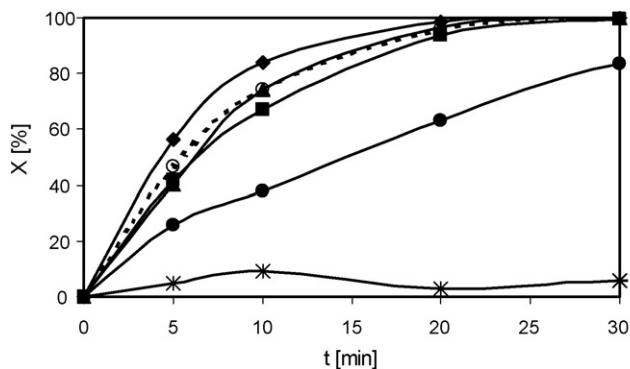


Fig. 2. Conversion of nitrites (X) in the presence of catalysts: 5%Pd/Al₂O₃ (○); 5%In/Al₂O₃ (✱); 5%Pd–0.5%In/Al₂O₃ (◆); 5%Pd–1%In/Al₂O₃ (■); 5%Pd–2%In/Al₂O₃ (▲); 5%Pd–5%In/Al₂O₃ (●) as a function of time.

In order to investigate the surface structure of palladium catalysts promoted with indium the XRD study was used. In Fig. 3 the X-ray diffractograms related to the monometallic system (5%Pd/Al₂O₃) and to the bimetallic

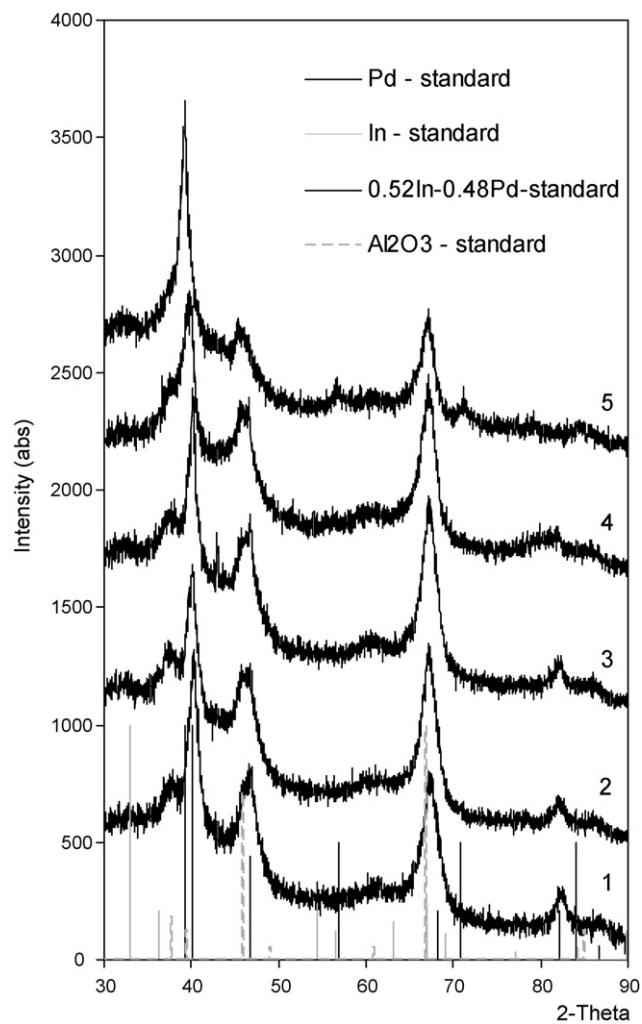


Fig. 3. Diffractograms of: (1) 5%Pd/Al₂O₃; (2) 5%Pd–0.5%In/Al₂O₃; (3) 5%Pd–1%In/Al₂O₃; (4) 5%Pd–2%In/Al₂O₃; (5) 5%Pd–5%In/Al₂O₃ catalysts. Crystalline phases were identified by references to the ASTM data file.

Table 1

Metal particle size of the Pd–In/Al₂O₃ catalysts calculated according to the Scherrer equation

Pd content (%)	In content (%)	Crystallites size (nm)
5	0	6.6
5	0.5	6.9
5	1	7.2
5	2	7.2
5	5	6.5

lic systems (5%Pd–0.5%In/Al₂O₃, 5%Pd–1%In/Al₂O₃, 5%Pd–2%In/Al₂O₃, 5%Pd–5%In/Al₂O₃) are reported.

From the obtained diffractograms we can see the presence of metallic palladium phase in all supported bimetallic systems. On the other hand, the presence of metallic indium was not observed in Pd–In/Al₂O₃ catalysts. However, in the case of the diffractogram obtained for 5%Pd–5%In/Al₂O₃ catalyst, which is characterized by the lowest activity in nitrates reduction, the new maxima were observed. The positions of the new maxima indicated the appearance of a new intermetallic phase In_{0.52}–Pd_{0.48} in this bimetallic system.

According to the Scherrer equation, the metal particle size of monometallic and bimetallic catalysts was calculated (Table 1). The dispersion of the metallic phase was quite good. The metallic particle size in monometallic 5%Pd/Al₂O₃ catalyst was 6.6 nm and after the introduction of In (0.5–5 wt.%) it almost remains the same. Therefore, the unique changes in the conversion practically resulted from the strong metals interactions on the surface rather than from the changes in the metal particle size.

To get a better understanding of the nature of the interactions between palladium and indium on the surface of alumina, the samples of chosen bimetallic catalysts were characterized by ToF-SIMS. This technique made it possible to observe the changes of catalyst surface which are invisible for XRD.

Fig. 4 shows a secondary ion image of palladium catalyst supported on alumina and modified with indium after oxidation in air atmosphere for 4 h at 500 °C and reduction in hydrogen atmosphere for 2 h at 300 °C. The brightness of particular places in the images corresponds to the intensity of secondary ions emission.

The obtained images of bimetallic catalysts show that increased concentrations of In and Pd were observed on the same areas, which demonstrated strong interactions between those metals on the surface of alumina. ToF-SIMS peak intensity ratios PdIn⁺/Pd⁺ (Table 2) were taken as the measure of surface concentration of PdIn phase. On the basis of the obtained results it was found that the participation of PdIn phase on the surface rises together with the increase in percentage content of indium in bimetallic catalysts (Fig. 5). The measured ToF-SIMS peak intensities of ions In⁺ and Pd⁺ emitted from the studied surfaces of bimetallic catalysts stay in good agreement with our expectations. Moreover, the ToF-SIMS study of 5%Pd–5%In/Al₂O₃ catalyst reveals the high surface concentration of indium in comparison with palladium, which could also be the reason for decrease in activity of this system in nitrates reduction. The increased surface concentration of indium can also be the rea-

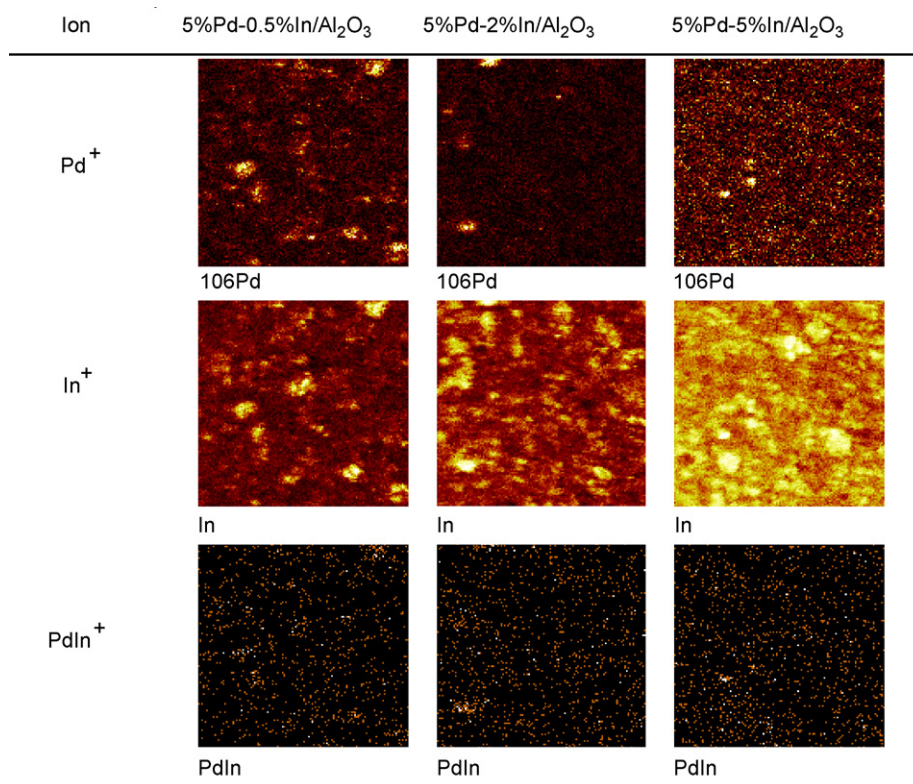


Fig. 4. Positive secondary ions ToF-SIMS images of the Pd–In/Al₂O₃ catalysts surfaces after a single oxidation–reduction cycle; the analyzed area of the surface 500 μm × 500 μm; burst alignment working mode of primary Ga⁺ gun; spatial resolution of images was set to 128 × 128 pixels.

son for the observed high nitrites concentration in the reaction mixture (Fig. 1).

The samples of bimetallic catalysts were also characterized by temperature programmed desorption of H₂ and temperature programmed reduction. Fig. 6 shows the results of temperature-programmed desorption of hydrogen (TPD_{H₂}) for the monometallic system 5%Pd/Al₂O₃ and for bimetallic systems 5%Pd–0.5%In/Al₂O₃, 5%Pd–1%In/Al₂O₃ and 5%Pd–5%In/Al₂O₃ in the temperature range 25–500 °C.

A wide desorption peak can be observed for catalyst 5%Pd/Al₂O₃ at the temperature ranging from 25 to 315 °C and the peak with the maximum rate of desorption at the temperature of about 450 °C. The presence of these peaks in the thermogram indicates that several adsorption states exist, which is the result of occurrence of different adsorption centres with specific bond strength of hydrogen. The high temperature (about 450 °C) of the maximum rate of hydrogen desorption indicates that strongly bound hydrogen exists on the surface of 5%Pd/Al₂O₃ catalyst. The hydrogen which is too strongly bound

on the surface of palladium can be the reason for low activity of monometallic palladium catalyst in the reduction of nitrates (Fig. 1).

The introduction of even a small amount of indium contributes to the decrease in the size of desorption peaks, which means that the amount of strongly sorbed hydrogen on Pd–In/Al₂O₃ systems decreases in comparison with monometallic systems, which can have an influence on the activity.

Fig. 7 presents TPR spectra obtained for 5%Pd/Al₂O₃, 5%In/Al₂O₃ and for bimetallic systems 5%Pd–1%In/Al₂O₃, 5%Pd–2%In/Al₂O₃, 5%Pd–5%In/Al₂O₃ after calcination in O₂ at 500 °C for 2 h.

In the case of catalysts 5%Pd/Al₂O₃ and 5%Pd–1%In/Al₂O₃ instead of hydrogen adsorption peaks only desorption peaks were observed. It leads to a conclusion that the total reduction of all oxide forms took place at room temperature. Moreover, Pd has the ability to form hydride phases under normal conditions. The desorption peaks observed for 5%Pd/Al₂O₃ and for bimetallic systems with a small amount of indium in the TPR

Table 2
ToF-SIMS peak intensity for the analyzed samples of Pd–In/Al₂O₃ catalysts

Catalysts	Peaks intensity (the number of counts)			Relative intensity of peaks	
	In ⁺	¹⁰⁶ Pd ⁺	PdIn ⁺	PdIn ⁺ /Pd ⁺	In ⁺ /Pd ⁺
5%Pd–0.5%In/Al ₂ O ₃	83,309	15,430	326	0.021	5.399
5%Pd–2%In/Al ₂ O ₃	183,940	8,185	386	0.047	22.473
5%Pd–5%In/Al ₂ O ₃	441,403	7,316	453	0.062	60.334

The analyzed area of the surface 500 μm × 500 μm; burst alignment working mode of primary Ga⁺ gun; spatial resolution of images was set to 128 × 128 pixels.

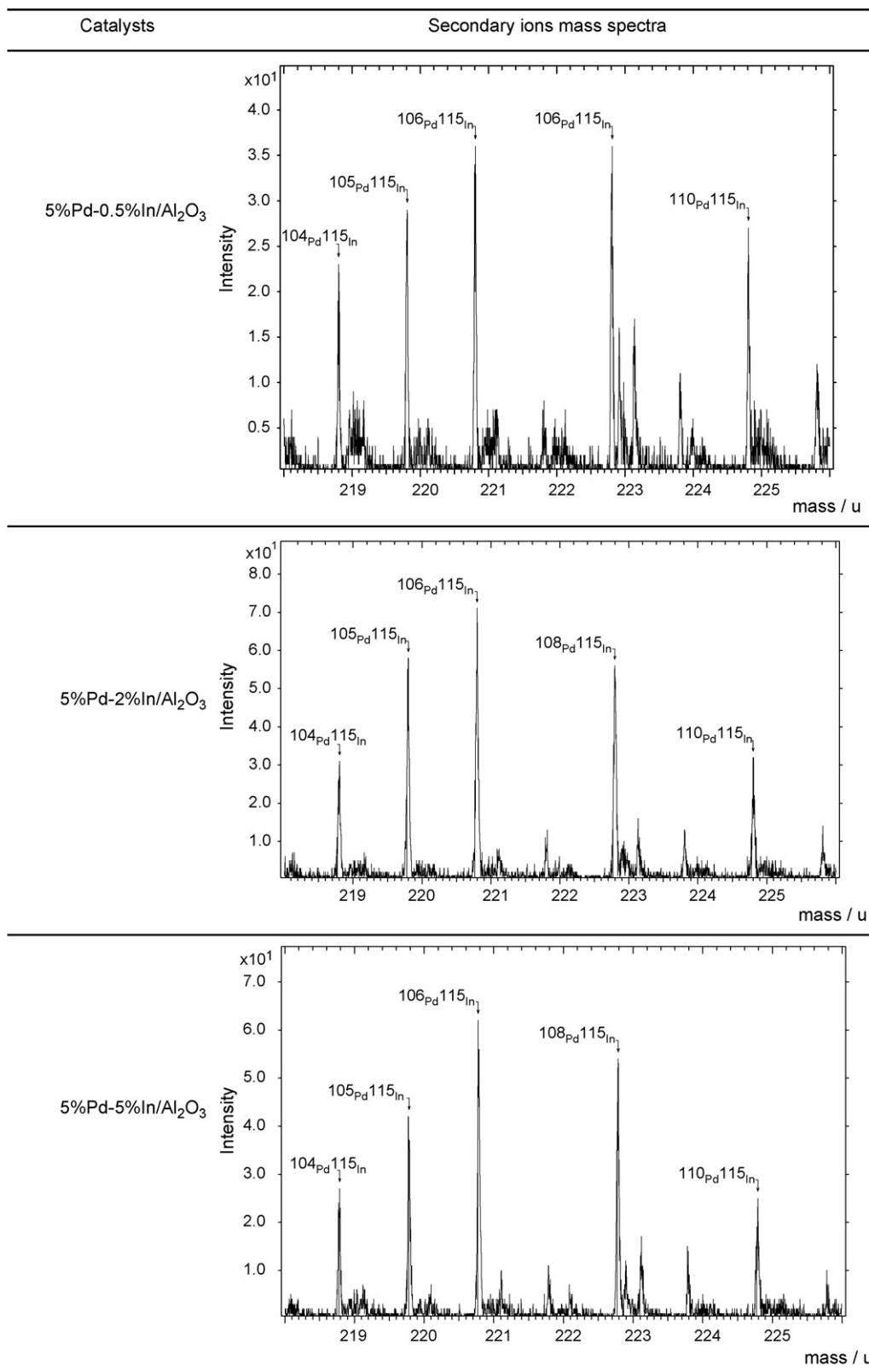


Fig. 5. The ToF-SIMS (+) spectra of Pd–In/Al₂O₃ catalysts after oxidation at 500 °C in air atmosphere reduction at 300 °C.

process at a temperature around 80 °C probably correspond to β -PdH decomposition.

An addition of greater amounts of indium (2–5 wt.% In) results in the disappearance of the desorption peak suggesting

that the β -PdH formation was inhibited. For those bimetallic catalysts the adsorption peaks connected probably with the reduction of mixed palladium–indium oxides were observed. The appearance of the reduction peak at the temperature about

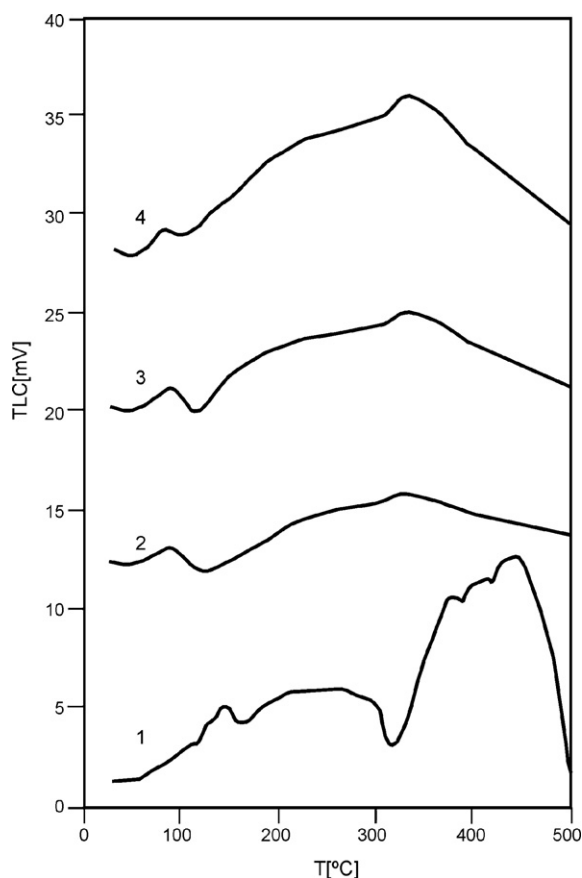


Fig. 6. Temperature-programmed desorption of H_2 from the surfaces of the systems: (1) 5%Pd/ Al_2O_3 ; (2) 5%Pd–0.5%In/ Al_2O_3 ; (3) 5%Pd–1%In/ Al_2O_3 ; (4) 5%Pd–5%In/ Al_2O_3 after adsorption of H_2 at room temperature. Adsorption of H_2 was conducted in a continuous method (0.5 h, flow rate of H_2 40 cm^3/min , rate of heating 20 $^\circ C/min$). In all measurements the same amount of catalyst 0.5 g was used.

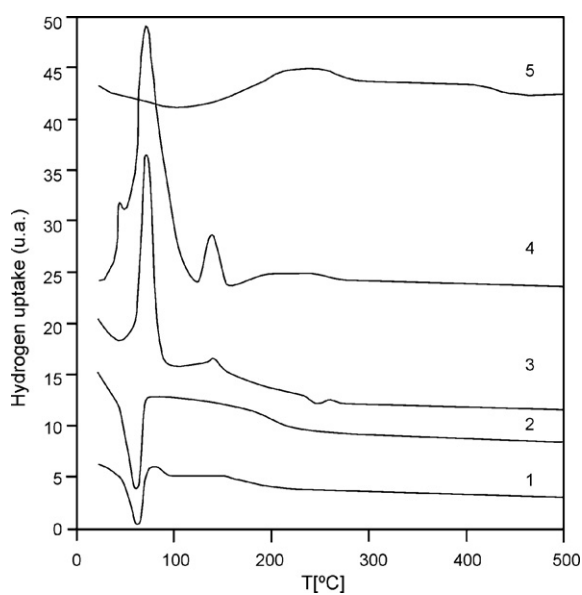


Fig. 7. TPR of (1) 5%Pd/ Al_2O_3 ; (2) 5%Pd–1%In/ Al_2O_3 ; (3) 5%Pd–2%In/ Al_2O_3 ; (4) 5%Pd–5%In/ Al_2O_3 ; (5) 5%In/ Al_2O_3 catalysts after their oxidation in oxygen atmosphere at 500 $^\circ C$ for 2 h.

150 $^\circ C$ for the 5%Pd–2%In/ Al_2O_3 and 5%Pd–5%In/ Al_2O_3 catalysts might indicate the formation of a certain mixed oxide form strongly bonded with the support. The existence of this form could lead to the formation of intermetallic compounds in reduction atmosphere. For those systems the formation of $In_{0.52}Pd_{0.48}$ phase was indicated by XRD measurements and confirmed by ToF-SIMS study.

4. Conclusions

Bimetallic 5%Pd–0.5%In/ Al_2O_3 , 5%Pd–1%In/ Al_2O_3 and 5%Pd–2%In/ Al_2O_3 catalysts are characterized by high activity in the reduction of nitrates and nitrites. System containing a higher amount of indium (5%Pd–5%In/ Al_2O_3) show poorer activity in the studied reactions. The ToF-SIMS measurements showed the presence of intermetallic compounds in all studied bimetallic catalysts. This technique is a very sensitive method for the examination of the surface structure. On the basis of the ToF-SIMS results an increase in the surface concentration of intermetallic compounds with an increase in indium content in bimetallic systems were observed. As a measure of the concentration of those compounds, the ratio of $PdIn^+$ ion emission intensity to Pd^+ was assumed. For the catalyst with composition 5%Pd–5%In/ Al_2O_3 , the intermetallic phase $In_{0.52}Pd_{0.48}$ was also detected by XRD. This method enables the detection of only relatively high concentrations of intermetallic compounds in the bimetallic catalysts. Because of this, the lowest activity of 5%Pd–5%In/ Al_2O_3 in the reduction of nitrates and nitrites may be connected with an appropriately large amount of this compound on the surface.

On the other hand, the ToF-SIMS study reveals the increased concentration of indium in comparison with palladium on the surface of bimetallic systems. This fact could also have an influence on the observed changes in activities.

Summing up, on the basis of our investigations we can say that there are two effects which can influence activity of Pd–In/ Al_2O_3 catalysts in the reduction of nitrates and nitrites: the formation of intermetallic phase and/or the increase in indium surface concentrations in those bimetallic systems.

References

- [1] H. Lindlar, *Helv. Chem. Acta* 35 (1952) 446.
- [2] H.R. Aduriz, P. Bondariuk, B. Coq, F. Figueras, *J. Catal.* 129 (1991) 47.
- [3] S.H. Choi, J.S. Lee, *J. Catal.* 193 (2000) 176.
- [4] E.A. Sales, M.J. Mendes, F. Bozon-Verduraz, *J. Catal.* 195 (2000) 96.
- [5] R. Bachir, P. Marécot, B. Didillon, J. Barbier, *Appl. Catal. A* 164 (1997) 313.
- [6] F.B. Noronha, M. Schlam, R. Fréty, G. Bergeret, B. Morawek, *J. Catal.* 186 (1999) 20.
- [7] L. Gucci, Z. Schay, Gy. Stefler, L.F. Liotta, G. Deganello, A.M. Venezia, *J. Catal.* 182 (1999) 456.
- [8] L.V. Nosova, V.I. Zaiikovskii, Yu.A. Rondin, *React. Kinet. Catal. Lett.* 53 (1994) 131.
- [9] T. Fujikawa, K. Tsuji, H. Mizuguchi, H. Godo, K. Idei, K. Usui, *Catal. Lett.* 63 (1999) 27.
- [10] M. Schlam, M.A.S. Baldanza, M.A. Vannice, *J. Catal.* 185 (1999) 138.
- [11] M. Fernández-García, M. Martinem-Arias, C. Belver, J.A. Anderson, J.C. Conesa, J. Soria, *J. Catal.* 190 (2000) 378.

- [12] A. El Hamdaoui, G. Bergeret, J. Massardier, M. Primet, A. Renouprez, J. Catal. 148 (1994) 47.
- [13] R. Ohnishi, W.L. Wang, M. Ichikawa, Appl. Catal. A 113 (1994) 29.
- [14] J. Batista, A. Pintar, M. Ceh, Catal. Lett. 43 (1997) 79.
- [15] F. Deganello, L.F. Liotta, A. Macaluso, A.M. Venezia, G. Deganello, Appl. Catal. B 24 (2000) 256.
- [16] A.C.A. De Vooy, R.A. Van Santen, J.A.R. van Seen, J. Mol. Catal. A 154 (2000) 203.
- [17] S. Karski, Chem. Environ. Res. 15 (1/2) (2006) 123.
- [18] I. Witońska, S. Karski, J. Gołuchowska, React. Kinet. Catal. Lett. 90 (1) (2007) 107.
- [19] F. Gauthard, F. Epron, J. Barbier, J. Catal. 220 (2003) 182.
- [20] A. Garron, K. Lázár, F. Epron, Appl. Catal. B 59 (2005) 57.
- [21] A. Garron, F. Epron, Water Res. 39 (2005) 3073.
- [22] A.M. Strätz, in: J.R. Kosak (Ed.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1984, p. 335.
- [23] B. Coq, F. Figueras, J. Mol. Catal. A 173 (2001) 117.
- [24] Mitsubishi Chemical Industries, US Patent 3,922,300 (1975).
- [25] S. Karski, I. Witońska, J. Mol. Catal. A 191 (2003) 87.
- [26] S. Karski, I. Witońska, Kinet. Catal. 45 (2) (2004) 256.
- [27] S. Karski, I. Witońska, J. Mol. Catal. A 245 (2006) 225.
- [28] S. Karski, J. Mol. Catal. A 253 (2006) 147.
- [29] S. Yamamatsu, Shokubai 43 (7) (2001) 549.
- [30] T. Miyake, A. Hattori, M. Hanaya, S. Tokumaru, H. Hamaji, T. Okada, Top. Catal. 13 (2000) 243.
- [31] L. Lemaingnen, C. Tong, V. Begon, R. Burch, D. Chadwick, Catal. Today 75 (2002) 43.
- [32] S. Ambonguilat, H. Gallard, A. Garron, F. Epron, J.P. Croué, Water Res. 40 (2006) 675.
- [33] U. Prüsse, M. Hähnlein, J. Daum, K.D. Vorlop, Catal. Today 55 (2000) 79.
- [34] U. Prüsse, K.D. Vorlop, J. Mol. Catal. A 173 (2001) 313.
- [35] T. Paryjczak, J. Rynkowski, S. Karski, J. Chromatogr. 188 (1980) 254.
- [36] S. Hörold, T. Tacke, K.D. Vorlop, Environ. Technol. 14 (1993) 931.
- [37] F. Epron, F. Gauthard, C. Pinèda, J. Barbier, J. Catal. 198 (2001) 309.