



## CATALYTIC HYDROGENATION OF NITRATES ON Pd-In/TiO<sub>2</sub> CATALYSTS

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The activity, selectivity and stability of bimetallic Pd-In/TiO<sub>2</sub> catalysts in the reduction of nitrates have been studied. Supported palladium catalysts promoted by indium show high activity, selectivity towards nitrogen in this process. For the systems with higher amount of indium (5%Pd-8%In/TiO<sub>2</sub>) the formation of intermetallic compounds of Pd<sub>x</sub>In<sub>y</sub> type on the surface has been observed. For those systems, the selectivity towards nitrogen is lower than for 5%Pd-2%In/TiO<sub>2</sub> and 5%Pd-5%In/TiO<sub>2</sub>. Pd-In systems are characterized by high stability in the studied reaction.

### INTRODUCTION

Pollution of natural water with nitrate is a serious problem in environmental protection. An increasing necessity to protect health and environment caused that World Health Organization had set limits of nitrates in drinking water (50 mgNO<sub>3</sub><sup>-</sup>/L).<sup>1</sup> In recent years catalytic reduction of nitrates has been an alternative way to biological and physicochemical treatments due to the possibility to conduct the reduction of nitrates to atoxic nitrogen in gentle conditions. In the last decade, a lot of bimetallic systems were investigated in catalytic reduction of nitrates,<sup>2-10</sup> but the systems based on palladium promoted by an addition of second metals such as Cu, Ag, Fe have shown the best properties in this reaction.

The mechanism of the nitrate reduction over bimetallic systems proposed in literature assumes that this reaction occurs according to a bifunctional mechanism involving a direct redox mechanism on the metallic promoter, followed by a classic catalytic reaction on a noble metal.<sup>11-16</sup> In this mechanism, the existence of intermetallic compounds and their role in the creation of

catalytic properties of bimetallic systems have not been considered. However, the presence of intermetallic compounds in supported bimetallic systems can lead to the occurrence of a new type of active centers on the surface (Pd<sub>x</sub>In<sub>y</sub>). The existence of this form on the surface could cause the reduction of nitrates ions into NH<sub>4</sub><sup>+</sup> ions instead of nitrogen. It could be an alternative path of the reaction and could complete the hypothetical reaction scheme for catalytic hydrogenation of nitrates on Pd-M/support catalysts (Fig. 1).

Taking chemical properties of various supports into consideration, the kind of support could influence the creation of intermetallic compounds. The existence of intermetallic compounds on the surface of bimetallic palladium catalysts were detected in the case of Pd-In/Al<sub>2</sub>O<sub>3</sub> systems.<sup>17</sup> These bimetallic catalysts were characterized by high activity in the reduction of nitrates, however, together with the higher amount of indium in these systems, selectivity towards to nitrogen decreased. This work presents the studies of activity and selectivity of the palladium catalysts promoted with indium and supported on titanium oxide.

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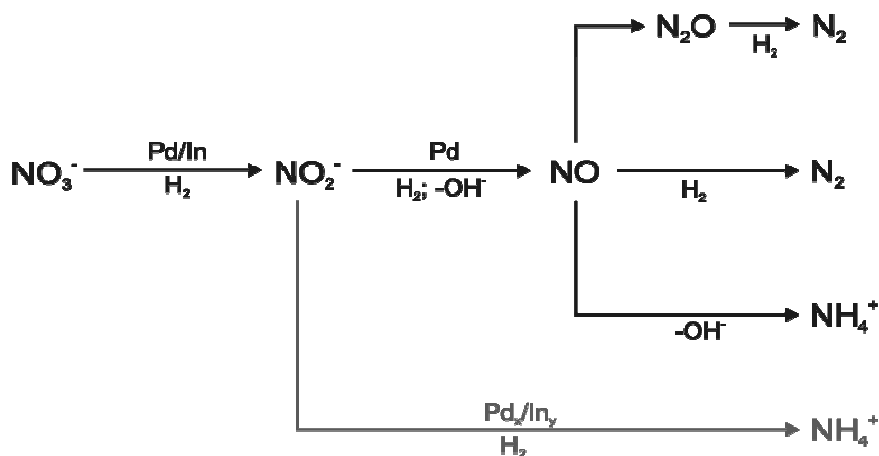


Fig. 1 – The hypothetical reaction scheme for catalytic hydrogenation of nitrates on Pd-M/support catalysts.

## RESULT AND DISCUSSION

The study of Pd-In/TiO<sub>2</sub> catalysts in the reduction of nitrates showed a high conversion of nitrates even for large amounts of indium (5%Pd-8%In/TiO<sub>2</sub>) (Fig.2a). What is more, the catalysts Pd-In supported on TiO<sub>2</sub> are characterized by good selectivity towards nitrogen (Fig.2b). With the rise in the amount of indium in those systems (to the 5w.t-%), the selectivity towards nitrogen also increases.

The catalysts Pd-In supported on TiO<sub>2</sub> are also characterized by high stability. The stability of the

chosen bimetallic system (5%Pd-2%In/TiO<sub>2</sub>) in the catalytic hydrogenation of nitrates in an aqueous phase was shown in Fig.3. The stability of catalysts was estimated on the basis of activity changes during twelve 60-minute-long measurement cycles. The process of reduction was conducted for the steady amount of catalyst ( $m_{\text{cat}} = 1.0 \text{ g}$ ) without its removal from the reaction mixture in the subsequent cycles. After each 60-minute-long measurement cycle, a new portion of nitrates (100 ppm) was introduced to the reaction mixture.

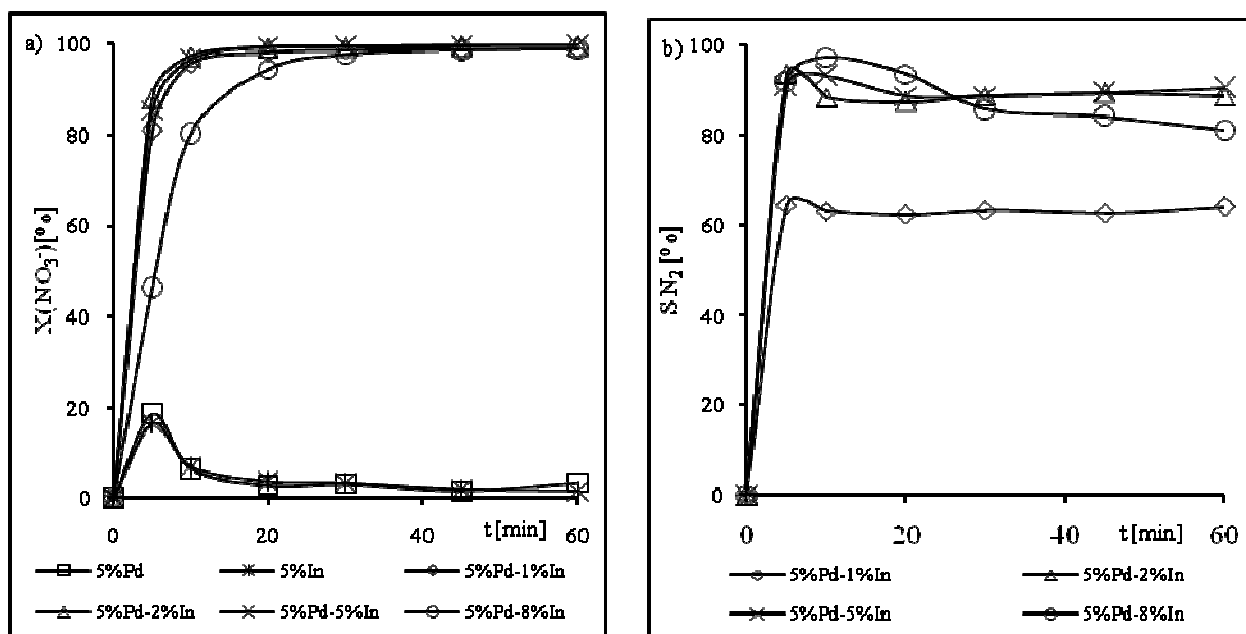


Fig. 2 – a) Conversion of nitrates (X) and b) selectivities to nitrogen (S N<sub>2</sub>) in the presence of Pd-In/TiO<sub>2</sub> catalysts during nitrate removal.

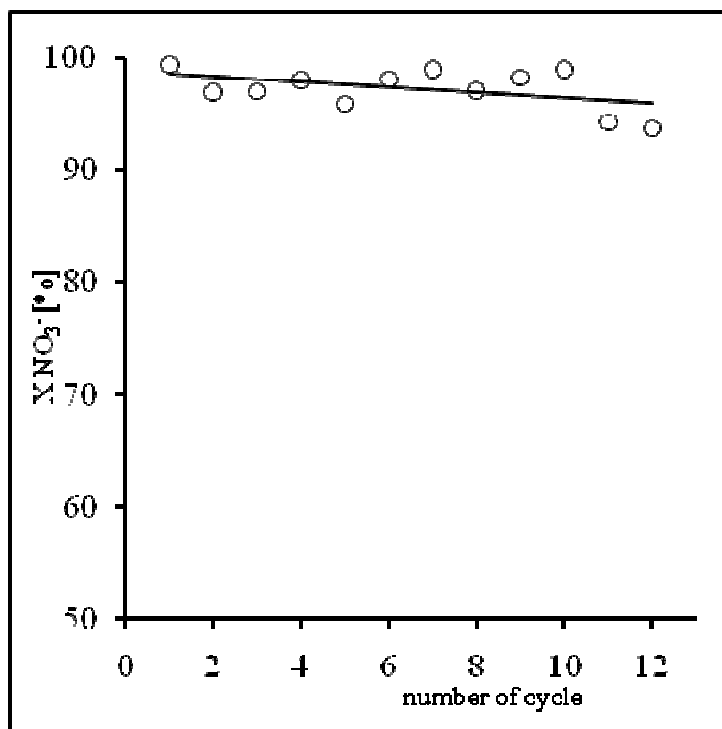


Fig. 3 – The stability of 5%Pd-2%In/TiO<sub>2</sub> catalyst in the reduction of nitrates at 293K.

In order to get to know the interaction between Pd and In on the surface of TiO<sub>2</sub>, XRD studies and temperature-programmed reduction (TPR) were performed. The XRD studies (Fig.4) indicate the presence of the crystalline phase of palladium for all bimetallic catalysts. However, the crystalline phase of indium was not observed. Only in the case of catalysts with a high amount of indium (5-8wt.%In), the crystalline phase of  $_{0.52}\text{In}_{0.48}\text{Pd}$  was noticed. Simultaneously, 5%Pd-8%In/TiO<sub>2</sub> catalyst is characterized by higher selectivity to ammonia than for 5%Pd-2%In/TiO<sub>2</sub> and 5%Pd-5%In/TiO<sub>2</sub> (Fig. 5). Those results are in a good agreement with those obtained for the Pd-In catalysts supported on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, for which an increase in the intermetallic phase was proportional to the concentration of ammonia in the final product.

TPR of the monometallic indium catalyst (5wt-%In/TiO<sub>2</sub>) shows (Fig. 6) a broad peak with a maximum rate of reduction at the temperature of 260°C. For the monometallic palladium catalyst (5wt.-%Pd/TiO<sub>2</sub>) and bimetallic 5%Pd-1%In/TiO<sub>2</sub> system, one negative peak connected with the composition of  $\beta$ -PdH was only observed. This peak decreases and moves towards lower

temperatures together with the increase in the amount of indium. This behaviour indicates the decrease in the formation of  $\beta$ -PdH phase. For the bimetallic catalyst 5%Pd-2%In/TiO<sub>2</sub>, additional broad reduction peak can be seen in the temperature range 100-400°C. However, in the case of 5%Pd-5%In/TiO<sub>2</sub>, three maxima on the TPR spectrum at temperatures 200°C, 250°C and 320°C can be seen. This is probably connected with the reduction of palladium oxide strongly bounded with the surface of the support (max. 320°C) and with the reduction of indium oxide (max. 250°C). The peak whose maximum is present at the temperature of 200°C is likely to be related with the reduction of Pd<sub>x</sub>In<sub>y</sub>O<sub>2</sub>, the occurrence of which proves intermetallic interactions in the system. For the catalysts 5%Pd-8%In/TiO<sub>2</sub>, the dominating reduction effect takes place at the temperature of 250°C. This temperature refers to the reduction of indium oxide. That may be related to the surface segregation of indium, which can cause the decrease in the activity of 5%Pd-8%In/TiO<sub>2</sub> catalyst in the studied reaction.

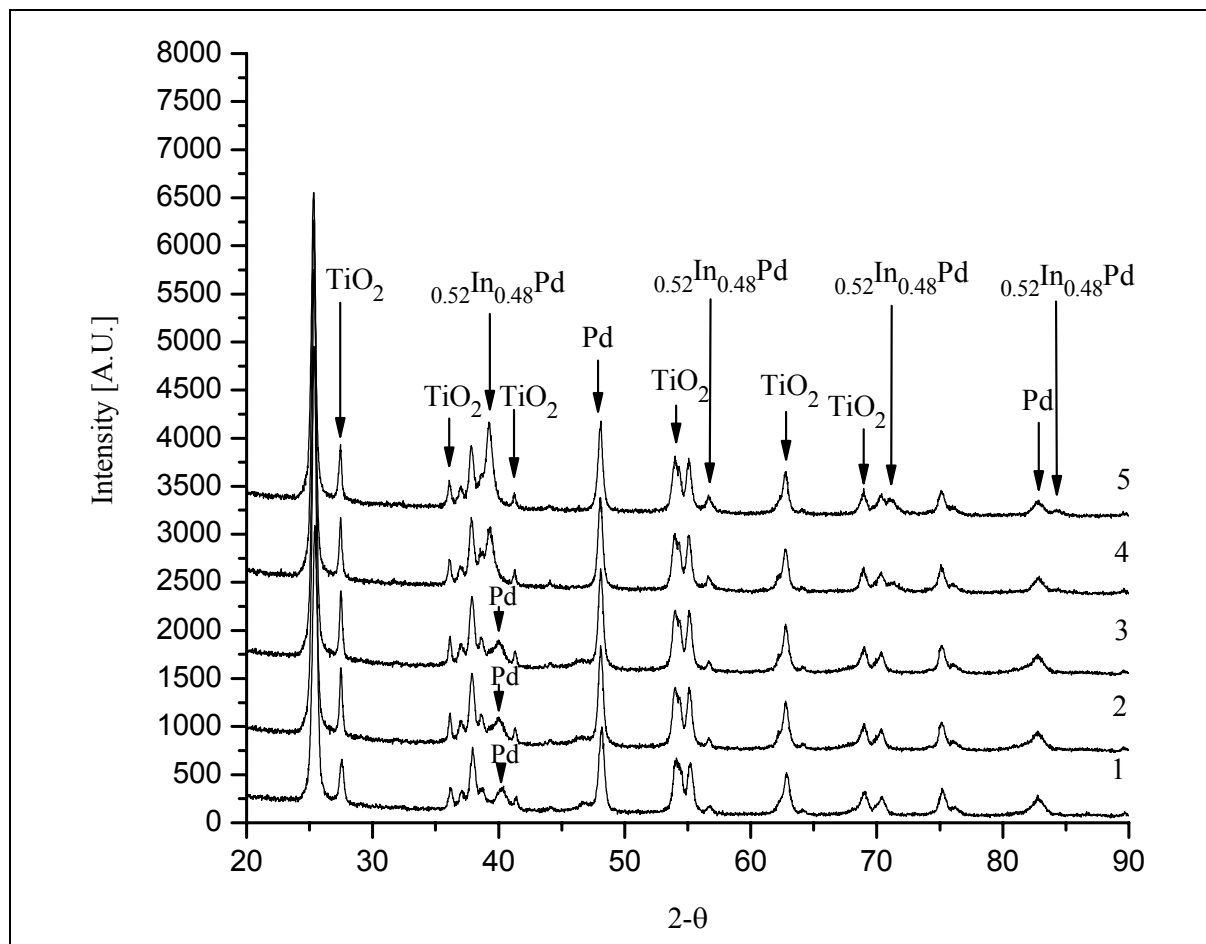


Fig. 4 – Diffractograms of Pd-In/TiO<sub>2</sub> catalysts (1 - 5%Pd; 2 - 5%Pd-1%In; 3 - 5%Pd-2%In; 4 - 5%Pd-5%In; 5 - 5%Pd-8%In). Crystalline phases were identified by references to the ASTM data file.

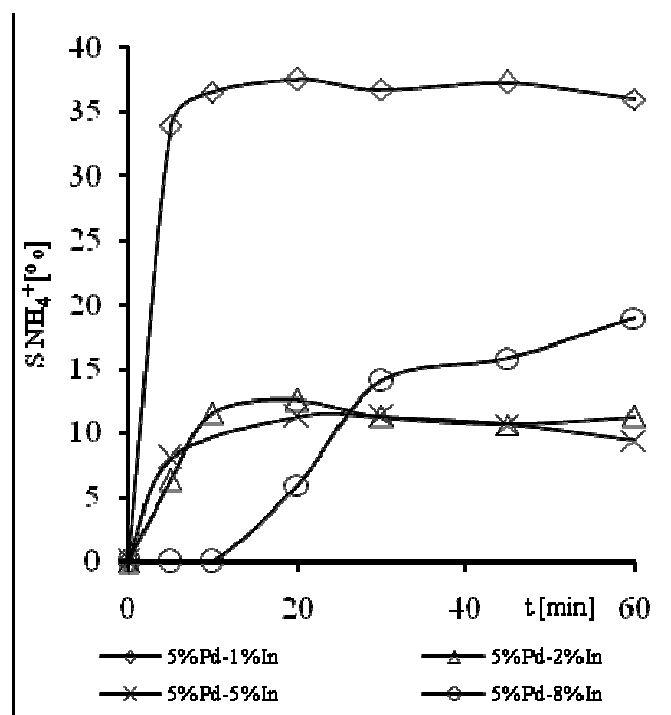


Fig. 5 – Selectivities to ammonia (S NH<sub>4</sub><sup>+</sup>) in the presence of Pd-In/TiO<sub>2</sub> catalysts during nitrate removal.

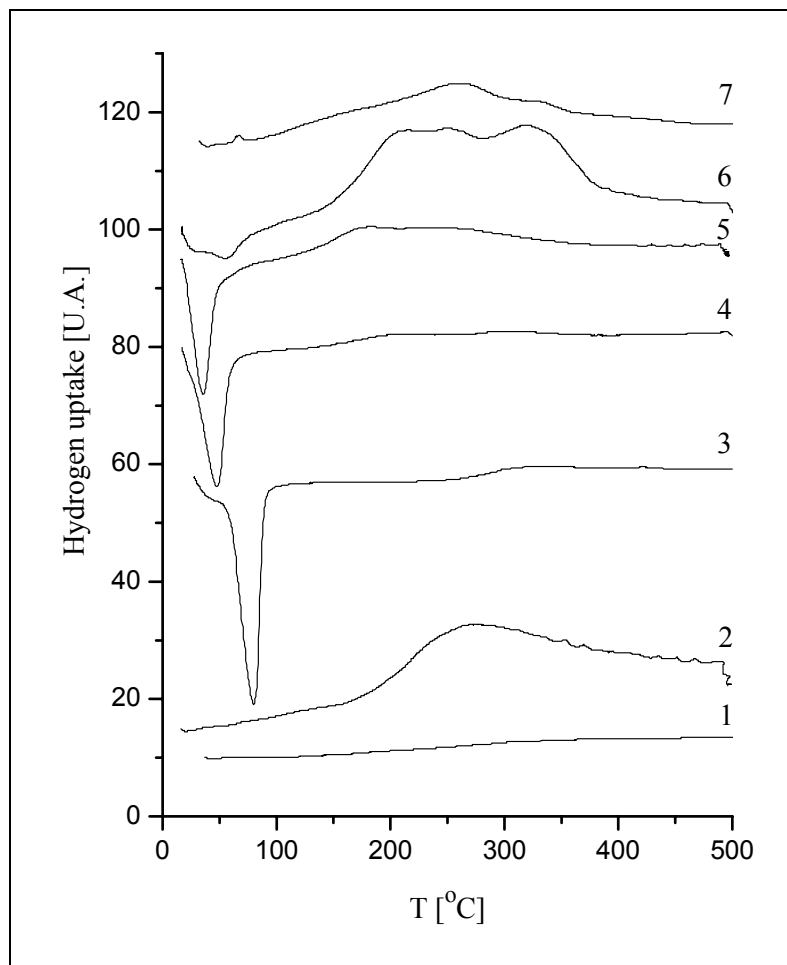


Fig. 6 – Temperature-programmed reduction of Pd-In/TiO<sub>2</sub> (1 – TiO<sub>2</sub>; 2 – 5%In/TiO<sub>2</sub>; 3 – 5%Pd/TiO<sub>2</sub>; 4 – 5%Pd-1%In/TiO<sub>2</sub>; 5 – 5%Pd-2%In/TiO<sub>2</sub>; 6 – 5%Pd-5%In/TiO<sub>2</sub>; 7 – 5%Pd-8%In/TiO<sub>2</sub>) catalysts after their oxidation in oxygen atmosphere at 500°C for 2h.

## EXPERIMENTAL

### Catalysts preparation

Bimetallic Pd-In/TiO<sub>2</sub> catalysts containing 5 wt.-% Pd and 1.0-8.0 wt.-% In were obtained through coimpregnation of support (TiO<sub>2</sub>, P-25 Degussa) with water solution of Pd(NO<sub>3</sub>)<sub>2</sub> (the MLS-1200 Mega Microwave Digestion System (Milestone) was used for complete digestion of metallic Pd in HNO<sub>3</sub> (POCh Gliwice)) and In(NO<sub>3</sub>)<sub>3</sub> (99.9%, Aldrich). The catalysts were dried in air at 110°C for 6h, activated in the oxidizing atmosphere (773K, 4h) and reduced in hydrogen atmosphere (573K, 2h) directly before the measurements.

### Catalytic measurements

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 (50mmol/dm<sup>3</sup>) to pH 5.5 in the reaction medium. The reaction was conducted at 293K. The mixture was stirred at 300 rpm, and hydrogen was bubbled through at 0.2 dm<sup>3</sup>/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 (CNaNO<sub>3</sub>=1.6mmol/dm<sup>3</sup>). 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 (Merc Hitachi) coupled with a variable wavelength UV detector LaChrom L-7400 (Merc Hitachi). The analytical wavelength was 210 nm. In our investigation, Merck C<sub>18</sub> LiChrospher RP-18 (5- $\mu$ m) column (250 mm x 4.0 mm i.d.) was used. The water of octyloamine phosphorate (5mmol/dm<sup>3</sup>, pH 6.3) was used as a mobile phase. The flow rate of octyloamine phosphorate was 1.0 cm<sup>3</sup>/min. For the samples, concentrations of NH<sub>4</sub><sup>+</sup> ions were analyzed spectrophotometrically with the use of ammonia-test (2.6-193 mg NH<sub>4</sub><sup>+</sup>/dm<sup>3</sup>, Merck).

### Powder X-ray diffraction

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer. The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40KV and 30 mA. Divergent optics were used in a Bragg-Brentano (flat-plate sample) geometry, with fixed divergence (1/20) and antiscatter (10) slits. Incident and receiving 0.04 rad Soller slits were used to limit axial divergence, and a nickel filter on the receiving side

was used to eliminate CuK $\alpha$  radiation. Data were collected in the range 20 - 90° 2 $\theta$  with step 0.0167° and exposition per one step of 20 s. A PANalytical X'Celerator detector based on Real Time Multiple Strip technology capable of measuring the intensities simultaneously in the 2 $\theta$  range of 2.1220 was used. Crystalline phases were identified by referring to ICDD PDF-2 (ver. 2004) data base.

#### Temperature-programmed reduction (TPR) measurements

The catalysts samples (0.2g), prior to TPR measurements were calcined at 500°C for 2h in oxygen and then flushed with helium at the same temperature for 0.5h. 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 (10vol.% of H<sub>2</sub>) and a linear temperature growth of 10°C/min. The flow rate of gases was 30cm<sup>3</sup>/min.

#### CONCLUSIONS

From the conducted research, we can conclude that Pd-In/TiO<sub>2</sub> catalysts are characterized by high activity. The conversion of nitrates for all studied bimetallic systems practically reaches 100%. However, those systems varied in selectivity. In the systems with high amount of indium, for which the formation of intermetallic compounds (Pd<sub>x</sub>In<sub>y</sub>) on the surface has been observed, the selectivity toward nitrogen was lower than for those systems for which the formation of intermetallic compounds has not been noticed.

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