Article

An Investigation into the Bulk and Surface Phase Transformations of Bimetallic Pd-In/ Al_2O_3 Catalyst during Reductive and Oxidative Treatments In Situ

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Abstract: A series of oxidative treatments of PdIn-supported intermetallic nanoparticles at different temperatures were performed. The bulk and surface structure of catalyst during phase transformation was investigated by bulk- and surface-sensitive techniques (in situ XAFS, DRIFTS of adsorbed CO). It was found that comparison of palladium and indium fractions in bulk and on the surface suggests the formation of a «core-shell» structure. According to obtained results, the core consists of In-depleted intermetallic compound or inhomogeneous bimetallic phase with the inner core of metallic Pd, when a mixture of indium oxide, metallic palladium and small part of PdIn is present on the surface.

Keywords: intermetallic compounds; PdIn catalysts; in situ XAFS spectroscopy; DRIFTS of adsorbed CO

1. Introduction

It is deliberate maximization of the number of active centers that is the major tool to improve the efficiency of supported catalysts [1]. In order to obtain a catalyst with active metal atoms atomically dispersed among atoms of a less active metal one may rely on the concept of intermetallic compounds (IMCs) [2]. The strictly ordered structure where atoms of one metal are regularly isolated from each other by atoms of the second metal is the key feature of such compounds. Potential applications of intermetallic nanoparticles in various fields of catalysis have recently been discussed in numerous papers [3–9].

The specific interaction between the two elements leads to an alteration of catalytic properties of the active metal resulting in an increased selectivity [10]. More specifically, when atoms of a very catalytically active metal get diluted with atoms of a less active component in a regularly structured IMC, the selectivity and activity could be balanced by designing appropriate atomic configurations. Many combinations of active-less active metal pairs forming IMCs have been tested as highly efficient catalysts, in particular Pt-Fe for the oxygen reduction reaction (ORR) [11–13], Pt-Zn for the organics electrooxidation in fuel cells [14,15], Pt-Co,In,Sn for the alkane dehydrogenation [16–18], Pd-Ga,In for the CO_2 hydrogenation to methanol [19,20], Pd-Ga,Zn,Zr for the methanol steam reforming [21,22], and many others.

In addition, the structure of intermetallic compounds is more stable as compared to disordered alloys and substitutional solid solutions [23]. Despite the enhanced bulk stability, the surface of intermetallic compounds is labile and very sensitive to a reactive exposure, such as air [24]. It has been shown earlier that sub-surface layers of some

palladium-based IMCs, such as PdGa, Pd₃Ga₇, Pd₂Ga, PdZn, and PdIn, get enriched with the more oxophilic element upon partial oxidation. Since these intermetallic compounds in the form of nanoparticles are highly efficient catalysts towards methanol steam reforming and acetylenic bond hydrogenation, it is extremely important to elucidate bulk and surface stability of such systems under reactive conditions. Unfortunately, information about their structural stability is scarce and sometimes contradictory.

Bimetallic PdIn catalysts are highly promising systems for a wide range of catalytic processes, such as methanol synthesis from CO₂ and H₂ [25], methanol steam reforming [26], ethane dehydrogenation [27], selective hydrogenation of triple $\text{C}\equiv\text{C}$ bonds [28], ethanol oxidation [29], nitrate hydrogenation [30], hydrodechlorination of 4-chlorophenol [31], etc. There are several IMCs that are known to form in the Pd-In system, including Pd₃In, Pd₂In, PdIn, Pd₂In₃, and PdIn₃ [32]. Among them, the 1:1 PdIn nanosystem is best studied so far although IMCs of other stoichiometries are also of potential interest for catalysis [33]. According to our previous reports, Pd-In/Al₂O₃ samples showed excellent alkene selectivity towards selective acetylene [34] and diphenylacetylene (DPA) hydrogenation [33]. Their superior catalytic properties are explained in terms of the formation of IMC with single-atom Pd surface sites isolated from each other by rather inert In atoms. However, our previous results indicated that an exposure of PdIn to synthetic air lead to a deterioration of the initial structure [35]. Furthermore, it was mentioned in [36] that PdIn nanoparticles underwent decomposition with the formation of a core-shell structure during the oxidative dehydrogenation of 1-butene, but the actual phase composition remained unknown.

This work is aimed at revealing conditions of deterioration of the bulk and surface structure of PdIn supported intermetallic nanoparticles by XAFS and DRIFTS techniques in situ, which provide information on fractions of palladium and indium in each phase after the oxidative treatments. The data provided by bulk- and surface-sensitive probes would help us to determine the extent of stability of Pd single-atom surface sites and exact conditions of their transformations. The oxidative treatments are presently limited to a maximum temperature of 250 °C in order to avoid progressive sintering and thus clearly differentiate between surface segregation and particle growth effects.

2. Results and Discussion

2.1. TEM Characterization

TEM micrographs of the bimetallic PdIn/Al₂O₃ catalyst under study in the as synthesized and treated forms are presented in Figure 1. The freshly reduced catalyst (Figure 1a) contains nearly spherical nanoparticles with a relatively narrow and symmetrical size distribution covering the range of 2–6.5 nm (Figure 1b). The morphology of the supported nanoparticles is essentially preserved after the oxidative treatment (Figure 1c,d). The nearly spherical shape of the nanoparticles is still evident although the mean particle diameter decreases slightly from 5.1 nm to 4.2 nm, which may be due to a partial loss of indium (see below for more details). It is apparent that no significant sintering occurs under the conditions applied.

2.2. EXAFS and XANES Spectroscopy In Situ

2.2.1. Palladium Extended X-ray Absorption Fine Structure

EXAFS Fourier transforms for Pd and In K-edges of Pd-In/Al₂O₃ catalyst after different reductive and oxidative treatments are presented in Figure 2. Pd K spectrum of initial sample reveals an intense peak at ~ 2.3 Å in the R- δ scale, which corresponds to the «palladium-metal» distance (Figure 2a, curve 1). According to the fit results, this peak can be attributed either to the first coordination sphere of monometallic palladium (2.75 Å) or to distance between Pd and In in the first coordination sphere of an intermetallic Pd-In compound (2.76–2.81 Å). Apparently, the initial sample contains both monometallic palladium and bimetallic Pd-In phases. Both Pd-Pd and Pd-In coordination bonds can contribute to the shell: these distances are too close to each other [25,27] while Pd and In

are characterized by very similar atomic numbers Z to be unambiguously distinguished by Pd K-edge EXAFS.

The reduction of the catalyst in situ leads to a small shift in the Pd-M distance from 2.74 Å to 2.76 Å indicating the preferred formation of the bimetallic phase. Consecutive oxidative treatments of Pd-In/ Al_2O_3 sample at 25 °C, 100 °C and 250 °C gave no drastic changes in Pd K EXAFS data. The only change observed is a slight reverse shift of Pd-M distance from 2.76 Å to 2.73 Å, accompanied by an increase in the coordination numbers from 5.6 to 7.9 (Figure 2a, Table 1). Therefore, during the oxidative treatment an intermetallic compound partially decomposes with the formation of the monometallic Pd phase. It should be noted that no formation of palladium oxide in noticeable amounts is observed.

Figure 1. Representative TEM micrographs (a,c) and nanoparticle size distributions (b,d) within the Pd-In/ Al_2O_3 catalyst before (a,b) and after (c,d) the in situ oxidative treatment.

Figure 2. Fourier transforms of Pd (a) and In (b) K-edge EXAFS spectra measured in situ after specific treatments: (1) initial sample (2) reduction at 500 °C for 1 h (3) oxidation at 25 °C for 30 min (4) oxidation at 100 °C for 30 min (5) oxidation at 250 °C for 30 min.

Table 1. Alteration of coordination numbers during the in situ treatments of PdIn/Al₂O₃ catalyst.

X-ray Absorption Edge	Scattering Pathway	Initial Sample	H ₂ /He, 500 °C, 1 h	O ₂ /N ₂ , 25 °C, 30 min	O ₂ /N ₂ , 100 °C, 30 min	O ₂ /N ₂ , 250 °C, 30 min
Pd K	In	7.4	6.3	5.6	7.9	7.9
	O	5.4	-	2.8	3.8	4.6
In K	Pd	3.9	4.7	3.0	4.4	1.4
	In	-	2.4	2.1	1.0	1.4

2.2.2. Indium Extended X-ray Absorption Fine Structure

Unlike Pd K-edge spectra, the shapes of the EXAFS spectra of In K edge are significantly different from each other depending on the catalyst treatment (Figure 2b). The In K spectrum of initial sample has an intense peak at ~1.7 Å in the R-δ scale. According to simultaneous modeling on Pd and In K-edges, this peak can be ascribed to the In-O distance (2.13–2.14 Å) in the first coordination sphere of In₂O₃. Although the most of indium is in the oxidized state, the presence of a small peak at 2.74 Å corresponds to the In-Pd coordination sphere of bimetallic phase. The reduction of PdIn/Al₂O₃ sample at 500 °C for 1 h in a 5% H₂/He flow in situ results in the complete reduction of indium and formation of bimetallic PdIn phase, as evidenced by the elimination of the In-O distance and appearance of new peaks corresponding to In-Pd and In-In coordination spheres (Table 1). It has been shown previously that in this case the formation of an intermetallic compound with a cubic structure and molar In:Pd ratio close to 1 is most likely [25,27]. According to the fit, the

In-Pd and In-In interatomic distances are 2.75 Å and 3.20 Å, respectively. These values are smaller than the ones from PdIn reference data (ICSD № 59473, In-Pd distance is 2.81 Å and In-In is 3.24 Å), which could be due to the small size of supported nanoparticles.

An oxidative treatment of the sample under ambient conditions leads to a significant increase in the intensity of the peak related to the first coordination sphere of In_2O_3 . Therefore, the intermetallic structure gets partly decomposed upon contact with oxygen at room temperature. A further increase in the oxidation temperature from 25 °C to 100 °C and 250 °C is accompanied by progressive severe PdIn destruction as evidenced by the increase in the In-O coordination numbers with simultaneous decrease of contribution from In-Pd scattering pathway. The formation of indium oxide suggests that the dominant fraction of indium from the bulk segregates on the surface of the particles. A rough estimate of palladium and indium amounts in the resultant phases can be assessed using the linear combination fit of XANES spectra.

2.2.3. XANES Linear Combination Fit

It is possible to estimate the fraction of PdIn phase during the oxidative treatment with XANES data fit with a linear combination of reference spectra. Pd K and In K-edge XANES spectra of the catalyst after the reduction in situ were taken as references for the intermetallic PdIn compound. XANES linear fit of Pd K spectra was processed using Pd foil as the reference, because no noticeable amounts of PdO was found during measurements. In addition, no In^0 was also detected in the In K XAS, therefore In K-edge XANES analysis was carried using only In_2O_3 and InPd. According to obtained results (Table 2), the initial sample contains approximately 48 at.% of palladium and 35 at.% of In in the bimetallic compound, which differs from stoichiometry of PdIn. The same situation is observed for the catalyst after the oxidative treatment at different temperatures. This may indicate that a certain fraction of PdIn intermetallic compound undergoes indium segregation to the catalyst surface and subsurface layers during oxidation giving rise to the formation of In-depleted bimetallic phase, as mentioned in [36]. Considering the trend of indium segregation, the formation of disordered phase with an irregular distribution of indium is also possible. This data confirms the high sensitivity of intermetallic compound to oxygen, which is manifested itself in the oxidation of as much as 40 at.% of the total amount of indium at room temperature. In addition, the presence of metallic palladium without noticeable traces of oxide may indicate the formation of a core-shell structure with metallic palladium forming the core. The possibility of the formation of such structures as a result of the chemical and subsequent structural evolution of the intermetallic compound is shown in [37]. The partial coverage of monometallic Pd nanoparticles by In_2O_3 can be another explanation of the observed effect.

Table 2. Estimates of the Pd and In fractions in different phases from the linear combination fit of XANES spectra.

Step	Pd K XANES Linear Fit		In K XANES Linear Fit	
	Pd in PdIn, at. %	Pd in Monometallic Pd, at. %	In in PdIn, at. %	In in In_2O_3 , at. %
initial sample	48	52	35	65
reduced 500 °C	100 ¹	-	100 ¹	-
oxidized 25 °C	79	21	60	40
oxidized 100 °C	74	26	50	50
oxidized 250 °C	55	45	34	66

¹ XANES spectra of sample reduced in situ were used as a reference for the PdIn intermetallic compound.

2.3. DRIFT Spectroscopy of Adsorbed CO

Figure 3 shows the carbonyl region (2200–1800 cm^{-1}) of the DRIFT-CO spectra for the bimetallic Pd-In/ Al_2O_3 catalyst after specific reductive and oxidative treatments. DRIFT spectrum of adsorbed CO for the initial sample (curve 1) reveals two broad absorption bands in the range of 2200–1800 cm^{-1} . The most intense peak with centered at $\sim 2087 \text{ cm}^{-1}$

is assigned to linearly bonded CO on palladium atoms, whereas a broad asymmetric band with a lower intensity at 2000–1800 cm^{-1} belongs to bridge- and hollow-bonded CO forms. The appearance of this band indicates the presence of contacting palladium assemblies, which are characteristic of bulk metallic palladium.

IR spectrum of freshly reduced bimetallic Pd-In/ Al_2O_3 catalyst exhibits a single intense band centered at 2066 cm^{-1} attributable to CO adsorbed linearly on Pd atoms (Figure 3, curve 2) in the structure of the intermetallic PdIn compound. As it has been shown before [35], the absence of additional bands in 2000–1800 cm^{-1} confirms the formation of surface structure with isolated palladium sites. The shift of the absorption band towards low wavenumbers relative to spectrum of metallic Pd [38] also confirms the presence of a close contact between palladium and indium atoms.

Upon the oxidation treatment under ambient conditions, the peak broadens and shifts towards higher frequencies by $\sim 10 \text{ cm}^{-1}$. The simultaneous appearance of a broad band at 1957 cm^{-1} indicates the formation of bridge-bonded CO species, which means the partial destruction of the PdIn bimetallic phase with the simultaneous formation of monometallic palladium nanoparticles on the surface of the catalyst. An increase in temperature of the oxidative treatment to 100 °C and 250 °C leads to narrowing of the peak of linearly adsorbed CO with its further shift to $\sim 2090 \text{ cm}^{-1}$. It should be noted that no bands corresponding to CO adsorbed on PdO are observed under these conditions.

Figure 3. DRIFT spectra of adsorbed CO for PdIn/ Al_2O_3 after treatments in situ: (1) initial sample; (2) reduction at 500 °C for 1 h; (3) oxidation at 25 °C for 30 min; (4) oxidation at 100 °C for 30 min; (5) oxidation at 250 °C for 30 min. Blue solid line corresponds to metallic Pd, red dotted line to bimetallic phase.

The fraction of remaining intermetallic compound on the surface of the catalyst after the oxidative treatments can be roughly estimated by deconvolving the peaks of linearly adsorbed CO (Table 3). According to the peak deconvolution procedure, a half of bimetallic compound on the catalyst surface is converted into monometallic Pd in the initial sample. The oxidative treatment under mild conditions after the in situ reduction leads to a deterioration of ~30% from the PdIn IMC. A further oxidation causes decomposition of up to ~62% of the total amount of the surface bimetallic phase. It should be noted that the position of the band related to the bimetallic component shifts from 2064–2066 cm^{-1} to 2076 cm^{-1} with increasing oxidation temperature. Reasons for this shift are not completely clear for the moment, but it can be due to changes in the local environment of atoms in the surface or subsurface region. A similar shift of the band position corresponding to linear CO was observed for Pd-Ag/ Al_2O_3 catalysts with different Ag: Pd molar ratios [39]. It has been shown for the Pd_xAg_y system that an increase in the fraction of Pd in the composition of particles leads to a shift of the absorption band towards larger wavenumbers.

Table 3. Estimates of Pd fractions in the forms of PdIn and in monometallic palladium from FTIR data (according to the deconvolution of peaks of linearly adsorbed CO).

Step	Pd in PdIn, at. %	Pd in Monometallic Pd, at. %
initial sample	49	51
reduced 500 °C	100	-
oxidized 25 °C	71	29
oxidized 100 °C	51	49
oxidized 250 °C	38	62

3. Materials and Methods

3.1. Catalyst Preparation

The bimetallic Pd-In/ Al_2O_3 sample used in the study was prepared via the incipient wetness impregnation of Al_2O_3 («Sasol», $S_{\text{BET}} = 56 \text{ m}^2/\text{g}$) by a mixed equimolar solution of $\text{Pd}(\text{NO}_3)_2$ and $\text{In}(\text{NO}_3)_3$ with subsequent drying in air at room temperature and reduction in 5% H_2 /Ar flow at 550 °C for 3 h.

3.2. Transmission Electron Microscopy

The morphology of the catalyst before and after the oxidative treatment was studied using a Hitachi HT7700 transmission electron microscope (Hitachi Ltd., Tokyo, Japan). Before the measurements, the sample was deposited onto a 3 mm carbon-coated copper grids from an isopropanol suspension. TEM images were acquired at an accelerating voltage of 100 kV in the bright-field mode.

3.3. In Situ XAFS-Spectroscopy

Pd and In K-edge XAFS spectra of the Pd-In/ Al_2O_3 sample were measured in situ at the «Structural Materials Science» beamline of the Kurchatov synchrotron radiation source (NRC «Kurchatov Institute», Moscow, Russia) [40]. The catalyst loading (120 mg) was carefully ground in a mortar to obtain a fine powder that was then pressed into a pellet. The latter was fixed in a sample holder and placed into the in situ chamber for measurements [41]. The spectra recording was carried out in the transmission mode by means of two ion chambers filled with Ar. A Si (220) channel-cut monochromator with a nominal energy resolution of $\Delta E/E \sim 2 \cdot 10^{-4}$ was used for the energy scanning. Pd and In foils were used for the sake of photon energy scale calibration. XAFS spectrum of In_2O_3 was obtained as a reference for the deconvolution of the experimental XANES into a linear combination of reference spectra. The high-temperature in situ chamber was flushed with helium before the measurements. The spectra were obtained after the following steps: (1) initial sample under ambient conditions; (2) reduction in a 5% H_2 /He flow (200 mL/min, 500 °C, 1 h, spectrum was recorded after cooling in H_2 /He to 25 °C); (3) oxidation at 25 °C for 30 min in an O_2 / N_2 flow; (4) oxidation at 100 °C for 30 min; (5) oxidation at

250 °C for 30 min. Heating and cooling during the oxidation steps were carried out in the inert atmosphere. Processing of obtained spectra was carried out with the Athena and Artemis codes [42,43] of the IFEFFIT software package (Naval Research Laboratory, Washington, DC, USA). XAFS analysis was carried out using the. Normalized EXAFS oscillations were k^2 -weighted and analyzed over a $2.5\div 12.0\text{ \AA}^{-1}$ k -range for the Pd K-edge and in $2.5\div 11.0\text{ \AA}^{-1}$ for the In K-edge spectra. Fourier transforms were fitted in a $2.0\text{--}3.0\text{ \AA}$ R -range for reduced sample and in $1.2\text{--}3.0\text{ \AA}$ for the catalyst after the oxidative treatments. Amplitude reduction factor (S_0^2) was defined for Pd (0.76) and In (0.80) from reference foils and kept constant in the fits.

3.4. DRIFT Spectroscopy of Adsorbed CO

Measurements of DRIFT spectra of adsorbed CO in situ were performed with a Tensor 27 spectrometer (Bruker, Billerica, MA, USA) equipped with a high-temperature cell (Harrick Scientific Products, Inc., Pleasantville, NY, USA) and a LN₂-cooled MCT detector. The loading of powdered catalyst («initial sample», 20 mg) was placed into the cell and purged by an Ar flow for 10 min at 50 °C with subsequent recording of background spectrum. DRIFT spectra of adsorbed CO (250 scans, resolution 4 cm^{-1}) were recorded during 10 min at 50 °C under a 0.5% CO/He flow ($30\text{ cm}^3/\text{min}$). As the next step, the catalyst was reduced at 500 °C for 1 h in a 5% H₂/Ar flow ($30\text{ cm}^3/\text{min}$) and cooled down from 500 °C to 150 °C in the reductive atmosphere with cooling to 50 °C under an Ar flow. Recording of background and spectra of adsorbed CO was carried according to the procedure described before. The next steps were subsequent oxidation at 25 °C, 100 °C, and 250 °C for 30 min under an O₂/N₂ flow ($30\text{ mL}/\text{min}$) followed by registration of background spectrum and spectra of adsorbed CO at 50 °C after each step of the oxidative treatment. Spectra deconvolution, baseline correction and curve fitting were performed with the OriginPro software (OriginLab Corporation, Northampton, MA, USA) [44]. FTIR-CO spectra were deconvolved between 2100 cm^{-1} and 2000 cm^{-1} using two Gaussian curves.

4. Conclusions

According to XAFS and DRIFTS results, an oxidation treatment of the catalyst under ambient conditions in situ leads to a partial decomposition of the intermetallic compound, which becomes more pronounced with increasing temperature. The evaluations of the fractions of the remaining intermetallic compound made by bulk and surface-sensitive techniques differ markedly, since the catalyst surface is more sensitive to treatments than its bulk. A comparison of palladium and indium fractions in different phases determined by XAFS and DRIFTS techniques suggest the formation of a «core-shell» structure during the oxidative treatment similar to the results described in [36]. The core of such a structure is enriched with In-depleted intermetallic compound; the formation of an inhomogeneous bimetallic phase with the inner core of metallic palladium is also possible (Figure 4). An oxidative treatment at 250 °C leads to the oxidation of ~66 at.% out of the total In amount in the sample. The surface of the oxidized catalyst consists of a mixture of nanoparticles of indium oxide, metallic palladium and small amount of residual PdIn.

The above results should be taken into account in the design of novel catalysts for specific applications as well as in the rational selection of post-synthesis treatment strategies of catalysts prior to catalytic tests. The findings for the PdIn catalyst described herein could prove relevant for other catalytic systems. We plan to continue our efforts towards establishing correlations between fine details of the surface composition and structure of bimetallic nanocatalysts and their catalytic properties. Deliberate methods for the synthesis of IMC nanoparticles corresponding to stoichiometries other than 1:1 in the Pd-In system as well as studies on their structural response to treatments in reactive atmospheres under controlled conditions will be emphasized in the future.

Figure 4. Tentative models of supported PdIn nanoparticles after the reductive and oxidative treatments.

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