PHYSICAL PROPERTIES OF A CATALYST
INTERMETALLIC COMPOUND InPd

Seminar 1a

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Abstract:

First of all I am going to introduce you to catlysts. Then I will intend few words for presenting palladium element from catalytic point of view. I will present you mechanism of active site isolation principle and how such compounds can be tailored for specific reactions. Discussion will continue with InPd crystal sample and its structure. With brief insight I will describe physical properties of investigated InPd compound with measured data interpretation. In the conclusion there will be comparison of investigated sample with already known GaPd system.
1. Introduction

Nowadays catalysts play an important role in everyday life. For example, palladium-based catalysts are important for selective hydrogenation of alkynes (in organic chemistry, an alkyne is an unsaturated hydrocarbon containing at least one carbon—carbon triple bond between two carbon atoms) [wikipedia]. In industry, they are responsible for purifying feedstock of acetylene which is used for polymerization of ethylene to polyethylene. For such specific purposes, it is desired to have catalysts with high selectivity and long-term stability. Because commercially used catalysts are not perfect in the sense that they do not completely specialize for desired reaction, it is important to search for new catalytic materials with superior selectivity and of course better long-term stability [6]. Compounds with such properties that show superior stability and selectivity over commercially used catalyst Pd/Al₂O₃ was found to be palladium-based gallium intermetallic compound. More specific GaPd and Ga₃Pd₅ ratios that crystallize in a FeSi structure type and in a Ir₃Ge₇ structure type, where active site isolation is realized. We get active site isolation by separating Pd atoms with incorporating another type atoms in Pd lattice in mentioned case that is with Ga atoms where this principle is ideally realized because of stoichiometric ratio 1:1. By incorporating different kinds of secondary atoms, we can directly manipulate physical properties of catalyst and tailor it for specific chemical reactions. Example for that kind of compound is InPd that also crystallizes in CsCl structure type and for that reason it is a good candidate for selective hydrogenation of alkynes. There were already made theoretical studies on decomposition of methanol to CO and H₂ on the InPd surface by density functional theory and just recently also experimental studies. In this seminar, I will present measured physical properties of intermetallic compound with stoichiometric ratio In₅₂Pd₁₇.₈ and compare these results with already known GaPd properties.
2. Catalysts

Catalyst is a material which alters the velocity of a chemical reaction. Those materials stay the same through a reaction and do not enter or get consumed by reaction in any way. Catalyst assists a chemical reaction by lowering activation energy that reactants must overcome to realise chemical reaction. Such materials that accelerate chemical reactions are called catalysts. On the other hand materials that decrease the rate of a chemical reaction are called inhibitors, which I will not talk about.[1]

![Figure 1. A schematic representation of activation energy in chemical reaction with catalyst and lowering of activation energy without catalyst. Graph shows endothermic reaction.[2]](image)

Catalysts are classified by three main types: heterogeneous catalysis, homogeneous catalysis and enzyme catalysis. In all those cases catalysts play exactly the same role of accelerating the rate of chemical reactions. Those types of catalysts differ by phase that they are into.

Heterogeneous catalysts are separated in phase compared with reactants. Catalyst is usually in solid phase (metal or non metal) and it assist reaction by temporary bonding atoms to its surface (active site principle), which allows their internal bonds to break more rapidly. Such catalysts are mostly used in industry.

Homogeneous catalyst are those that are in the same phase that other reactants. Reaction is realized in solution that is in homogeneous system.

Final type of catalysts are biological catalysts. Those are enzymes, always protein in nature that speed up biological reactions. Enzymes operate similar as heterogeneous catalysts where reaction is accelerated by active site.

There are three main mechanisms how reaction occurs. First mechanism, both molecules A and B attach to catalytic surface and get bind, new molecule is released from surface. Second mechanism, molecule A attaches to catalytic surface, when molecule B passes by, it is attracted to A, so B bind to A and new molecule get detached. Third mechanism, one of the molecule attaches to catalytic surface (let say it is molecule A), then other molecule B flies with some velocity to molecule A and crashes with it. With enough kinetic energy, reaction is realized and new molecule get realised of catalytic surface.[3]

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[1]: Reference for catalysts and inhibitors
[2]: Reference for figure 1
[3]: Reference for catalytic mechanisms
Figure 2. A schematic representation of catalytic process. (1) molecule is temporarily bound to catalytic surface. (2) one hydrogen attached to molecule. (3) second hydrogen attached and molecule detaches from catalyst surface.[4]

3. Palladium

Elementary palladium is a noble metal with unique catalytic properties. It has the ability to dissociate and dissolve hydrogen. Pure palladium can absorb in volume approximately 935 times more hydrogen than its own volume, which means that we can store one liter of hydrogen in one milliliter of palladium measured at room temperature and atmospheric pressure. From a catalytic point of view, catalysis is carried out on the surface of catalyst, where only adsorption on the surface is relevant. In this case, chemisorption is based on the interaction of the d-band of the Pd metal with the π-bonding system of the unsaturated hydrocarbons. Hydrocarbons form π-bonds with the surface of Pd metal, conduction-band electrons in the Pd metal attract hydrocarbon molecule. Properties of pure palladium can change under reaction conditions due to the accumulation of deposits, which can even penetrate the surface to some depth. Newly formed surface Pd-X (X = C, H) in fact becomes a catalyst, which is responsible for changes in selectivity. In case of X = C selectivity increases and on the other hand where X = H selectivity decreases. Thickness of the modified surface PdC is only two to three atomic layers and is responsible for selective hydrogenation of alkynes. This change occurs because carbon atoms incorporate themselves between palladium atoms and by this increase in selectivity from the surface, which allows less possibilities of absorption configurations.[5,6]

4. Active site isolation principle

As mentioned above, selectivity is connected with active sites on catalytic surface. Selectivity can be increased by three ways, by increasing Pd-Pd distances and reducing Pd-Pd coordination number (geometrical effect), by altering electronic structure (electronic effect) or by reducing number of Pd atoms on the surface (kinetic effect).

In case of InPd compound the largest effect is geometrical, because In atoms incorporate between Pd atoms which increases distances of active sites. For example, acetylene can bind to Pd atoms via two ways, with π bond or with double σ bonds. For hydrogenation of acetylene to ethylene, the former molecule must bind to surface with π bond, otherwise if acetylene binds to surface with double σ bond we get ethane. In other words, there is no selectivity (we do not know which reaction will occur). Actually In atoms increase distances between active sites, leaving a reduced number of possible configurations that is only selectively reaction will occur.
Figure 3. A Scheme represents one molecule of acetilene temporary bonding on catalyst surface. Left we can see that molecule is bind by weak $\pi$ bond on one positionaly isolated Pd atom. On the right, molecule is bind by two $\sigma$ bonds to two Pd atoms.

In principle X atom or molecule can be anything as long as Pd atoms are separated between each other by some distance. In case of Pd-C this concept is realized to some extent. I say to some extend because such surface is not well reproducible and can not be made by controlled process. It is prefered to have orderd crystalline structure with well defined atomic distances. If well defined crystal can be made it can also be tailored to suit desired reaction. Porosity does not increase catalyst surface significantly, to increase surface it is needed to have crystal powder or even better nano particles. Intermatalic compounds are good candidates to meet such conditions. Even more, elements of intermetallic compounds are mostly bound together by double bond, which is favourable because it assures long term stability and activity of catalytic material in reaction enviroment. Strong covalent bond between Pd and X atoms drastically alters electronic states, which are directly connected with active site properties of Pd atoms. Altered electronic states are not linearly proportional to properties of constitutional elements, so it is impossible to guess catalytic properties of intermetallic compound. To understand those properties it is essential to know surface and bulk electronic properties of a crystal.

Prototype of such compound is Pd-Ga intermetallic system. There were tested two concentrations of Pd and Ga atoms (GaPd and Ga7Pd3, figure 4). In case of stoichiometric ratio 1:1 (FeSi structure type) active site principle is ideally realized because there is no other Pd atom in the first coordination sphere. Second concentration, stoichiometric ratio 7:3 (Ir3Ge7 structure type) is also good structure although there is one Pd atom in the first coordination sphere. Both mentioned intermetallic compounds showed higher selectivity and good stability over commercially used Pd/Al2O3. Long term stability is shown as a consequence of inability to absorb hydrogen, which would cause decrease in selectivity and mechanical instability.[5,6]

Figure 4. Representation of structure of Pd based intermetallic system with different concentrations. a) Pd-In system with stoichiometric ratio 1:1, b) Pd-Ga system stoichiometric ratio 7:3 (Ir3Ge7 structure type) and c) Pd-Ga system stoichiometric ratio 1:1 (FeSi structure type).[6]
5. InPd structure

Good candidate for selective hydrogenation of alkynes is also intermetallic compound InPd, because it crystallizes in FeSi structure type, where isolated active site principle is realized. Precisely for that reason intermetallic InPd crystal sample was grown by the Czochralski method.

Czochralski method is commonly used for growing single crystals. It was discovered in 1916 by Polish scientist Jan Czochralski. Process is as follows, first components in powder form are melted down. Then a crystal seed is attached to rotating rod and lowered into melted solution just that it touches the liquid state. Melted solution has to contain same elements and mass ratios that the end crystal is make of. Rod is rotating and slowly rising. Because there is temperature gradient present above liquid phase the solution that is pulled out crystalizes in the same specific composition that is in equilibrium with solution phase.

With electron probe microanalyzer (EPMA) the composition of InPd crystal was found to be In$_{52.2}$Pd$_{47.8}$. Apart from a slightly off-stoichiometric In-rich composition, unit cell remained body centered cube CsCl type (B2), with space group (no. 221), lattice parameter $a = 0.325$ nm and with two atoms in unit cell. According to binary phase diagram, intermetallic compound InPd is able to retain bcc structure type in region between 45 to 61.5 atomic percent of palladium. It is known that bcc phases of type AB (A = Pd, Fe, Ni, Co; B = In, Ga, Al) retain structural order type CsCl even for larger stoichiometric deviations. This is possible by incorporating large number of structural defect in a lattice. In case of InPd sample with In rich sample defects manifests as vacancy in lattice. In other words some Pd atoms are missing in Pd sublattice. It was determined that structural Pd vacancy concentration was 5.8 at.%. At high temperatures defects get thermally activated and the Pd vacancy concentration increases with rising temperature. If there is large number of constitutional defects present it can alter catalytic performance. In off-stoichiometric lattice diffusion can move atoms to vacancy sites causing chemical disorder. Active site isolation principle would be ideally realized only in stoichiometric ratio 1:1 and without constitutional defects.

The degree of crystallinity and structural order was determined with X - ray powder diffraction spectrum. XRD was measured by diffractometer equipped with a curved Ge(111) primary
monochromator to produce Mo Kα1 radiation (\(\lambda = 0.07093\) nm). Spectrum of X ray powder diffractogram is composed of sharp lines, typical for materials with good crystalline structure.

XRD does not give us presence of small concentration of constitutional defect. To see static disorder NMR was performed. Presence of defects was determined from NMR spectrum of quadrupolar nuclei. For such measurement it is essential that nuclei have spin larger than 1/2, in case InPd this is satisfied because \(^{115}\)In nuclei have spin 9/2. The nuclear electric quadrupole moment interacts with the electric field gradient (EFG) tensor produced by the neighboring electric charges (ionic and electronic) at the position of the resonant nucleus. Electric field gradient falls with dependence \(1/r^3\), \(r\) being the distance. For that precise reason electric quadrupole moment is sensitive only to field of neighboring atoms. If there is no defects present resonant nuclei does not feel electric gradient and the electric field contribution of neighboring atoms is zero. All three diagonal elements of electric field gradient tensor are equal, that makes tensor become a scalar and electric quadrupole interaction vanishes. As a result of ideal cubic symmetry we get one or more sharp lines in NMR spectrum. Defects manifested as missing atoms in unit cell canceling cubic symmetry and causing presence of electric field gradient at resonant nuclei sites, consequently electrical quadrupolar interaction stays different from zero. In NMR spectrum those defects represent inhomogeneous broadening around sharp line. NMR spectrum of \(^{115}\)In was performed at temperature 80 °K in magnetic field with density \(B_0 = 4.7\) T parallel to one of unit cell axis. From graph it can be seen one central transition between two energy levels \((1/2 \leftrightarrow -1/2)\) at Larmor frequency as sharp line and quite wide broadening in range of 10 MHz, which represent satellite transitions \((\pm 1/2 \leftrightarrow \pm 3/2, \pm 3/2 \leftrightarrow \pm 5/2, \pm 5/2 \leftrightarrow \pm 7/2\) and \(\pm 7/2 \leftrightarrow \pm 9/2)\) pointing out presence of EFG tensor at resonant nuclei. Width of spectrum shows that there are different combinations of defects in unit cells.[6]

![NMR Spectrum of InPd](image)

Figure 5. Graph shows NMR spectrum of \(^{115}\)In at temperature 80 °K in magnetic field 4.7 T. Sharp line in the middle represents central transition between two spin states. Broadening around central transition represents satellite transition between energies of spin states. Overall spectrum shows good crystal structure with some random defects.[6]

6. Hydrogen absorption

It is essential that catalytic material does not absorb hydrogen, otherwise it will cause deactivation of catalyst. Pure palladium is able to absorb large quantities of hydrogen, so according to palladium being one of constitutional elements it is important to measure hydrogen absorption properties of InPd intermetallic compound. Hydrogen absorption measurement was performed with thermography. This is measurement of mass deviation at rising temperature. According to theory hydrogen gets desorbed from material with rising temperature and studied material should get lighter. In other words due to
temperature increase hydrogen terminal energy $k_B T$ also increases and it can desorbed from material.

Sample was exposed to hydrogen gas for 16 hours at pressure 5 bars and temperature 300K. Data from thermography measurement were collected as temperature dependent distribution of hydrogen desorption in temperature range between room temperature and 300°C. There were no mass deviation detected in whole range, which means that InPd sample did not absorb any hydrogen in the first place. This measurement shows that InPd is fulfilling criterion for good catalytic material for hydrogenation.[6]

7. Specific heat

Temperature dependent specific heat reveals electronic density of states – DOS, which is closely connected with absorption properties of catalytic material. Specific heat of nonmagnetic metals has two contributions, one from electrons and second from phonons. At room temperature phonon contribution overrules electronic. But at temperatures near absolute zero both contributions became comparable and even distinguishable. At low temperature ($T < 10$ K) specific heat is approximated as follows:

$$C_v = \gamma T + \alpha T^3$$  \hspace{1cm} (1)

there are two coefficients, $\gamma$ belongs to electronic and $\alpha$ to lattice specific heat. Electronic specific heat is linearly dependent from temperature and its coefficient is:

$$\gamma = \left(\frac{\pi^2}{3}\right) k_B^2 g(\varepsilon_F)$$  \hspace{1cm} (2)

g($\varepsilon_F$) being electronic density of states at Fermi energy and $k_B$ Boltzmann constant. Second coefficient comes from lattice or phonon contribution and is well approximated with Debye model, where phonons are described with Bose – Einstein distribution. Coefficient can be written as:

$$\alpha = \left(\frac{12}{5}\right) \pi^4 R \left(\frac{1}{\theta_D^3}\right)$$  \hspace{1cm} (3)

where $R$ is universal gas constant and $\theta_D$ is Debye temperature. Coefficients $\gamma$ and $\alpha$ can be read out of low temperature graph of specific heat divided by temperature to square temperature. Coefficient $\alpha$ manifests as inclination value of linearly interpolated graph at temperatures lower than approximately 5 K and coefficient $\gamma$ is value of intersection between previously mentioned interpolation and $C_v/T$ axis.
Figure 6. Graph shows measured low temperature specific heat to temperature, where \( \alpha \) and \( \gamma \) can be determined. Measurements were performed in the presence of magnetic field \( B_0 \) with intensity of 0 T and 9 T. As it can be seen from the graph, no deviations were found at different magnetic field intensities.[6]

Graphically acquired \( \gamma \) and \( \alpha \) enable us to calculate electronic density of states at Fermi energy \( \varepsilon_F \) and Debye temperature \( \theta_D \). For intermetallic compound InPd, Debye temperature is 243 K and electronic density of states at Fermi energy is 0.39 states/(eV·atom).

We can also determine the theoretical value of electronic specific heat coefficient of free electron \( \gamma_F \) as follows:

\[
\gamma_F = 0.136 \left( \frac{A}{d} \right)^2 \left( \frac{e}{a} \right)^{\frac{1}{3}} \frac{m_J}{\text{mol·K}^2}
\]

(4)

Where \( A \) is mol mass in grams, \( d \) is density and \( e/a \) is the number of valence electron per atom. Quantities used in this equation were: \( A = 110.8 \text{ g}, \) \( d \approx 10.45 \text{ g/cm}^3 \) and \( e/a = 0.81 \). Equation (4) yields result \( \gamma_F = 0.60 \text{ mJ/mol·K}^2 \). It is possible to calculate thermal effective mass by a relationship:

\[
\frac{\gamma}{\gamma_F} = \frac{m^*}{m} = m_{th}^*
\]

(5)

which is \( m_{th}^* = 1.525 \). This number suits metals and free electron compounds respectively. For example, \( m_{th}^* \) of some other metals is Li: 2.3, Na: 1.3, K:1.2. The reason why the \( m^* \) in simple metals is larger than \( m \) is that the band lower than the conduction band is the core electron band, which is really not coupled to anything. Therefore, all the other bands that will couple to the Fermi electron band are those lie at energies above the conduction band minimum. The energy term will then have a negative sign, and that makes the effective mass larger than \( m \).[11]

Increase of mass is assigned to structure of electronic level and interactions between electron – phonon and electron – electron.[6,8]

8. Thermal conductivity

In a material thermal energy is transported via electrons and phonons. To define such ability thermal conductivity \( \kappa \) is introduced:

\[
\kappa = \frac{p \cdot d}{S \cdot \Delta T}
\]

(6)
where \( P \) is power, \( d \) is thickness, \( S \) is surface perpendicular to heat flow and \( \Delta T \) is temperature difference between two sites of material. Since free electrons transfer large portion of heat, electrical conductors are usually also better heat conductors compared to insulators. Intermetallic compound InPd as name suggest and as it was seen out of specific heat measurement is free electron material, so good heat conductivity is expected. Easiest way to measure thermal conductivity is to establish constant heat flow and then measure temperature difference. Faster way is continuous measurement where it is not needed to wait for constant heat flow to establish, but rather used low frequency square heat pulses. Temperature difference is than determined by a nonlinear least-squares fitting routine by followed formula:

\[
\Delta T_{\text{model}} = \Delta T_\infty \times \left\{ 1 - \frac{\tau_1 \times \exp\left(-\frac{L}{\tau_1}\right) - \tau_2 \times \exp\left(-\frac{L}{\tau_2}\right)}{\tau_1 - \tau_2} \right\}
\]

(7)

where \( \Delta T_\infty \) represents asymptotic temperature drop in sample in case of heater being on for really long time. \( \tau_1, \tau_2 \) are short and long time constant on sample. Equation is valid for pulses that supply heat to sample.

Values of thermal conductivity of InPd sample is in range of metals, which shows us that studied compound is indeed free electron material. At 20 K amounts to 6 W/K·m and at 300 K is 36 W/K·m.[6,9] To compare with some other pure metals at 225K we see that values are, Aluminium: 250 W/K·m, Cooper: 398 W/K·m, Iron: 72 W/K·m, Stainless steel: 19 W/K·m. Palladium at 300K: 72 W/K·m. In case of GaPd the values 300K is 50 W/K·m.

9. Seebeck coefficient

In some materials electric current is observed in presence of temperature gradient. Property of material to generate electric current exposed to temperature gradient is called Seebeck coefficient defined as:

\[
S = -\frac{\Delta V}{\Delta T}
\]

(8)

where \( S \) is Seebeck coefficient and \( \Delta V \) is the thermoelectric voltage. More generally it is defined in differential equation:

\[
J = -\sigma \nabla V - \sigma S \nabla T
\]

(9)

where \( J \) is the current density, \( \sigma \) is the electrical conductivity, \( \nabla V \) is the voltage gradient, and \( \nabla T \) is the temperature gradient. At \( J = 0 \) equation (9) becomes equation (8).
Since electrons travel opposite to electric field direction it is possible to get information about charge carrier type out of temperature dependent Seebeck coefficient graph. It turns out that in investigated InPd sample major charge carriers are holes. It means that sample is a metal. Seebeck coefficient can be positive (holes are charge carriers), or negative (electrons are charge carriers).[6,10]

![Seebeck coefficient graph](image)

Figure 8. Seebeck coefficient to temperature. Since it is positive it suggests that major charge carriers are holes.[6]

### 10. Electrical resistivity

Electrical resistivity is defined as:

$$\rho = \frac{U \cdot S}{l \cdot I} \quad (10)$$

where $U$ is voltage, $S$ is surface perpendicular to current flow, $l$ is length of measured sample and $I$ is current. Electrical resistivity is temperature dependent. For small temperature changes resistivity can be approximated by:

$$R(T) = R_0 [1 + \alpha(T - T_0)] \quad (11)$$

where $\alpha$ is the empirical temperature coefficient of resistance, $T_0$ is a fixed reference temperature, and $R_0$ is the resistance at temperature $T_0$. From previous measurement it can be expected that intermetallic compound InPd should be good electrical conductor. From measured data it was found that InPd compound is indeed good and magnetically unaffected electrical conductor. At low temperatures electric resistance is constant to about 30 K, which points to non-stoichiometric ratio of constitutional elements. At temperatures higher than 30 K electric resistivity increases linearly with temperature. Positive sign of temperature coefficient shows dominant mechanism of electron–phonon inelastic scattering.

![Temperature dependent electrical resistance](image)

Figure 9. Temperature dependent electrical resistance.[6]
11. Conclusion

Investigated intermetallic compound InPd that crystallized in CsCl structure type obeys active site isolation principle even if its stoichiometric ratio is not 1:1. It turns out that intermetallic compound can retain such structure for greater stoichiometric deviations. Since In$_{52.2}$Pd$_{47.8}$ does not ideally follow active site isolation principle it is expected that its catalytic properties are going to be worse compared to intermetallic compound GaPd where active site isolation is perfectly obeyed since it crystallizes with stoichiometric ratio 1:1 and is considered as prototypic catalytic intermetallic compound. From comparison of physical properties of InPd and GaPd sistem same deviation can be noticed. Electronic density states at Fermi energy of GaPd compound are for a factor 1.53 larger compared to InPd. Defects in InPd lattice that were confirmed by NMR spectrum are also seen as electrical resistivity increase and partially in thermal conductivity. Only major difference between those two compounds was found to be in Seebeck coefficient where in case of InPd dominant charge carriers are holes while in GaPd compound are electrons. In other words that means that InPd is hole-type condustor and GaPd is electron-type conductor.

12. References


