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In situ surface characterization of the intermetallic compound PdGa – A highly selective hydrogenation catalyst

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ABSTRACT

The structurally well-defined intermetallic compound PdGa – a highly selective catalyst for the semi-hydrogenation of acetylene – was characterized by Fourier transform infrared spectroscopy (FTIR) *in situ* X-ray photoelectron spectroscopy and *in situ* prompt gamma activation analysis. A strong modification of the electronic states in PdGa compared to elemental Pd was revealed as well as the complete isolation of the Pd atoms on the surface of PdGa. *In situ* investigations proved the high stability of the surface, thus excluding segregation phenomena (common for alloys) or sub-surface chemistry involving C and/or H atoms (known for elemental Pd). By suppressing the sub-surface chemistry, the electronic modification as well as the site isolation lead to the high selectivity and long-term stability of PdGa in the semi-hydrogenation of acetylene.

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1. Introduction

Selective hydrogenation of alkynes is an industrially relevant and scientifically interesting reaction. For example, the semi-hydrogenation of acetylene ($C_2H_2 + H_2 \rightarrow C_2H_4$, $\Delta H = -172$ kJ/mol) is used to remove traces of acetylene from the ethylene feed to produce polyethylene (annually $> 5 \times 10^7$ t) [1]. Typical hydrogenation catalysts consist of palladium dispersed on metal oxides. Palladium metal exhibits high activity but limited selectivity. Moreover, Pd catalysts deactivate [2] under hydrogenation conditions by the formation of carbonaceous deposits resulting from polycondensation of unsaturated compounds. According to numerous surface studies [3], the presence of extended Pd sites on the catalyst surface is one of the main reasons for unselective operation. Indeed, hydrogenation of acetylene to ethylene and, consequently, to ethane requires a minimum of Pd atoms for its active site. In turn, deactivation pathways to carbon deposits via oligomerisation and formation of ethylidine require spacious active sites. The high hydrogenation activity of Pd towards ethane is attributed to the formation of β-palladium hydride and consequently, active sub-surface hydrogen [4]. The suppression of sub-surface hydrogen formation is crucial for the selective hydrogenation of acetylene.

The successful catalyst requires a modification of its structure preventing the sub-surface chemistry without elimination of the atomic hydrogen surface species. Alloying Pd with Ag is the current practical solution for acetylene hydrogenation [5]. However, random distribution of different atoms on the crystallographic sites, little electron localization between Pd and the other metal and segregation phenomena present in alloys [5] leave room for further improvement.

Recently we introduced a novel concept for the rational development of alkynes hydrogenation catalysts [6]. Exploring of the Pd–Ga intermetallic compounds allows to overcome the main drawbacks of conventional catalysts. In the utilized intermetallic compounds, Pd atoms are separated from each other and their atomic environment is fixed by the realized crystal structure which should result in single Pd sites on the surface in high abundance. In turn, covalent (directed) interaction between Pd and Ga provides *in situ* stability of the crystal structure as well as polarization of the Pd atoms to maximize the activation barrier for hydrogen atoms to enter into the bulk, thus preventing sub-surface hydrogen formation and enhancing the selectivity. The concept of using intermetallic compounds with covalent bonding rather than alloys, is a suitable way to arrive at long-term stable catalysts with

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pre-selected electronic and local structural properties. Detailed *in situ* investigations of bulk structure of PdGa and Pd_3Ga_7 by DSC/TG, XRD and EXAFS during thermal treatment under various inert or reactive gas atmospheres showed that the long- and short-range ordered crystal structures of the materials are intact up to 600 K. Both intermetallic compounds exhibit a higher selectivity and enhanced long-term stability in acetylene hydrogenation than commercial supported Pd/Al_2O_3 and an unsupported Pd–Ag alloy [6–8]. While the former studies explored the catalytic properties and the bulk stability of the compounds, we present here a careful characterization (including *in situ*) of the surface of PdGa and compare it with the bulk structure. The correlations between the surface structure and the catalytic properties are also discussed.

2. Experimental

2.1. Preparation

Details of the preparation can be found elsewhere [6–8]. Briefly, PdGa was prepared by melting the appropriate amounts of Pd (ChemPur 99.95%) and Ga (ChemPur 99.99%) under protective Ar atmosphere in a high frequency furnace and subsequent annealing of the obtained ingot in an evacuated quartz glass ampoule at 1073 K for 170 h. The phase purity was controlled by X-ray powder diffraction (Guinier camera, Huber G670, image plate, $CuK\alpha_1$ with $\lambda = 1.540562$ Å). For further investigations the material was powdered inside a glove box (Ar atmosphere, O_2 and H_2O below 1 ppm) to avoid significant contamination of the surface.

2.2. X-ray photoelectron spectroscopy (XPS)

High-pressure X-ray photoelectron spectroscopy experiments were performed at beamline U49/2-PGM1 at BESSY (Berlin, Germany). Details of the setup have been published earlier [9]. The photoelectron spectrometer system uses a differentially pumped lens system between the sample cell and the electron analyzer, allowing XPS investigations during catalytic conditions in the mbar pressure range. Dense pills of PdGa (8 mm in diameter, 0.7 mm thick) were either produced by pressing PdGa powder at room temperature in a stainless steel pressing tool (as-cast sample) or by spark plasma sintering (SPS) [10] at 873 K and 400 MPa in a tungsten carbide pressing tool. Samples were prepared in argon atmosphere inside a glove box. The as-cast PdGa pill and one of SPS-pressed pills (SPS-air sample) were exposed to air prior to the measurements, whereas a second SPS-pressed pill (SPS sample) was introduced to the XPS setup avoiding air contact by using a transfer chamber. Both SPS-pressed pills were Ar^+ sputtered prior to the measurements.

XPS investigations were performed in UHV (10^{-8} mbar) and under reaction conditions (1.0 mbar of H_2 (Westfalen Gas, 99.999%) and 0.1 mbar of C_2H_2 (solvent free, Linde, 99.6%) at 400 K). An *in situ* experiment included introduction of the gases at room temperature, equilibration for 15 min, heating the sample to the corresponding temperature with a rate of 10 K/min and equilibration for another 15 min after which the XP spectra were recorded. Gas-phase analysis was carried out using a quadrupole Balzers mass spectrometer connected by a leak valve to the experimental cell. Ion currents corresponding to acetylene ($m/e = 26$), ethylene ($m/e = 27$) and ethane ($m/e = 30$) were monitored.

To keep the information depth of the XP spectra alike, Pd3*d*, Ga3*p*, Ga3*d* and C1*s* spectra were recorded with varying wavelength of the incoming radiation, resulting in photoelectrons with similar kinetic energies. Three different kinetic energies were chosen – 780 eV, 380 eV and 150 eV – which correspond to information depths (3-times the inelastic mean free path) of ∼4 nm, 2.5 nm and 1.5 nm, respectively, for clean PdGa [11]. Surface concentrations of the elements were determined from the Pd3*d*, Ga3*p* and C1*s* peak areas.

2.3. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopic measurements were carried out using a Perkin-Elmer S 2000 spectrometer in transmission mode with a resolution of 4 cm^{-1}. PdGa powder was mixed with high surface area silica (Degussa) in a 1:10 weight ratio and subsequently pressed into thin wafers. Commercial Pd/Al_2O_3 (Sigma–Aldrich 205710, 5 wt.% Pd, BET surface: 114 m^2/g, Pd active surface area 5.6 m^2/g [7]) was used as self-supporting wafers. Prior to the measurements the samples of were treated *in situ* in a heatable section of the IR cell at 673 K for one hour in either 500 mbar of hydrogen (PdGa) or vacuum (Pd/Al_2O_3). Subsequently, the samples were cooled down to the designated temperature and FTIR spectra were collected. For each spectrum 32 scans were accumulated. To exclude any influence of SiO_2, blank measurements were performed and no bands in the region of 2100–1800 cm^{-1} were observed. Presented are difference spectra obtained by subtraction of the spectrum of the activated sample in vacuum from the spectrum in presence of the probe molecule – carbon monoxide (Messer–Griesheim, 99.997%).

2.4. Prompt gamma activation analysis (PGAA)

In situ prompt gamma activation analysis (PGAA) was performed at the cold neutron beam of the Budapest Neutron Centre, Budapest, Hungary [12]. An Al_2O_3 tube reactor (inner diameter of 2 mm) loaded with 200 mg of as-cast PdGa powder was placed into the neutron beam. The total hydrogen uptake of PdGa was studied in pure hydrogen and in a hydrogen/acetylene mixture (C_2H_2: 4 mL/min; H_2: 40 mL/min) at near room temperature and ambient pressure. Prompt gamma rays were collected by a Compton-suppressed high-purity germanium detector. The molar H/Pd ratio, i.e. the amount of hydrogen dissolved in PdGa and adsorbed on its surface, was determined from the characteristic peak areas corrected by the detector efficiency and the nuclear data of the elements [12]. Since the hydrogen spectrum contains extra contributions from gas phase hydrogen in the feed and moisture in the "viewing angle" of the detector, blank experiments were performed without PdGa in the reactor but otherwise identical conditions to subtract the extra amount of hydrogen. Experiments were also carried out with elemental Pd for comparison [13].

2.5. Scanning electron microscopy (SEM) and chemical analysis

Scanning electron microscopy was performed with a Hitachi S4800 equipped with a cold FEG (Field Emission Gun) and a Philips XL30 operating with a LaB_6 cathode. Samples were mounted on Al-holders with conducting carbon tape.

The silica (Degussa) used for preparing the FTIR wafers was chemically analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES) with a Varian Vista RL spectrometer. All values are the average of at least three replicates.

2.6. Catalysis

Details of the catalytic measurements are published elsewhere [6–8]. Measurements were carried out in a plug-flow reactor (30 mL/min) with a high excess of ethylene (0.5% acetylene, 5% hydrogen (99.999%) and 50% ethylene (99.95%) in helium (99.999%)). To introduce the small amount of acetylene, pre-mixed 5% acetylene (solvent free, 99.6%) in helium (99.996%) was used.

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