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Palladium–gallium intermetallic compounds for the selective hydrogenation of acetylene

Part II: Surface characterization and catalytic performance

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ABSTRACT

The structurally well-defined intermetallic compounds PdGa and Pd_3Ga_7 constitute suitable catalysts for the selective hydrogenation of acetylene. The surface properties of PdGa and Pd_3Ga_7 were characterized by X-ray photoelectron spectroscopy, ion scattering spectroscopy and CO chemisorption. Catalytic activity, selectivity and long-term stability of PdGa and Pd_3Ga_7 were investigated under different acetylene hydrogenation reaction conditions, in absence and in excess of ethylene, in temperature-programmed and isothermal long-term experiments. Chemical treatment with ammonia solution—performed to remove the gallium oxide layer introduced during the milling procedure from the surface of the intermetallic compounds—yielded a significant increase in activity. Compared to Pd/Al_2O_3 and $Pd_{20}Ag_{80}$ reference catalysts, PdGa and Pd_3Ga_7 exhibited a similar activity per surface area, but higher selectivity and stability. The superior catalytic properties are attributed to the isolation of active Pd sites in the crystallographic structure of PdGa and Pd_3Ga_7 according to the active-site isolation concept.

1. Introduction

Selective hydrogenation of acetylene ($C_2H_2 + H_2 \rightarrow C_2H_4$, $\Delta H = -172$ kJ/mol) is an important industrial process to remove traces of acetylene in the ethylene feed for the production of polyethylene. Because acetylene poisons the catalyst for the polymerization of ethylene to polyethylene, the acetylene content in the ethylene feed has to be reduced to the low ppm range [1–3]. Moreover, economic efficiency requires high selectivity of the acetylene hydrogenation in the presence of an excess of ethylene to prevent the hydrogenation of ethylene to ethane. Typical hydrogenation catalysts contain palladium dispersed on metal oxides. While palladium metal exhibits high activity, it possesses only limited selectivity and long-term stability because of the formation of ethane by total hydrogenation as well as C4 species and higher hydrocarbons by oligomerization reactions [4,5].

Modification of palladium catalysts by adding promoters or alloying with other metals has been shown to result in an increased selectivity and long-term stability in the hydrogenation of acetylene [6,7]. However, the catalytic performance of these modified Pd catalysts remains insufficient and further improvements in selectivity may decrease the costs for the production of polyethylene. In addition to unsatisfactory selectivity, the long-term stability of palladium catalysts has to be improved. Catalyst deactivation by carbonaceous deposits requires frequent exchange or regeneration of the catalyst in the hydrogenation reactor. Moreover, fresh or regenerated catalysts show high activity and local overheating ("thermal run away") of the reactor and, consequently, lead to increased ethylene consumption and loss in selectivity.

The limited selectivity of Pd catalysts in acetylene hydrogenation can be attributed to the presence of active-site ensembles on the catalyst surface [6,8,9]. Active-site isolation increases Pd–Pd distances on the catalyst surface and may lead to only weakly π-bonded acetylene on top of an isolated Pd atom. Furthermore, the sequential hydrogenation of acetylene to ethylene via vinyl and vinylidene intermediates requires a decreasing active site size [10]. Therefore, a reduction of neighboring palladium sites on the sur-

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face should yield preferred hydrogenation of acetylene to ethylene [2,11–17].

In the intermetallic compounds PdGa [18–20] and Pd_3Ga_7 [20–22] the Pd atoms are only surrounded by gallium atoms in the first coordination shell and, thus, may be promising catalysts with an improved selectivity and long-term stability in acetylene hydrogenation [23]. Furthermore, modification of the electronic structure by promoting or alloying of the Pd catalyst to tailor adsorption or desorption properties may be employed to increase the selectivity in hydrogenations [6]. In addition to the local structure around the active Pd sites compared to Pd metal or conventional Pd alloys, Pd–Ga intermetallic compounds exhibit a modified electronic structure which may further improve their catalytic performance in acetylene hydrogenation [10].

Part I of this work describes the preparation of the Pd–Ga intermetallic compounds PdGa and Pd_3Ga_7 and elucidates their thermal and structural stability under various reaction conditions [24]. Part II presents results of the surface characterization by X-ray photoelectron spectroscopy, ion scattering spectroscopy and CO chemisorption measurements. The catalytic performance of PdGa and Pd_3Ga_7 in acetylene hydrogenation was investigated and compared to Pd/Al_2O_3 and an unsupported palladium–silver alloy.

2. Experimental

2.1. Synthesis and materials

Details of the preparation of the Pd–Ga intermetallic compounds are described in Part I [24]. The alloy referred to as $Pd_{20}Ag_{80}$ in the following, was prepared by melting together 1.2047 g Ag (99.995% ChemPur) and 0.3035 g Pd (99.95% ChemPur) three times in an arc melter under argon. Subsequently, the regulus obtained was enclosed in an evacuated quartz glass ampule and annealed at 800 °C for six days. After the heat treatment, the regulus was filed and the phase purity of the obtained Pd–Ag alloy (Cu type of structure, $Fm\bar{3}m$, $a = 4.0456(6)$ Å) was confirmed by X-ray powder diffraction (STOE STADI P diffractometer, CuK_{α_1} radiation, $\lambda = 1.540598$ Å, curved Ge monochromator).

2.2. Chemical etching

To increase the active catalyst surface, chemical etching was performed using ammonia solution at various pH-values. Commercial ammonia solution (Merck, 25%, p.a.) was diluted with distilled water to the required pH-value. pH measurements were performed with a Knick pH-meter 761 Calimatic and a Mettler–Toledo Inlab 422 electrode calibrated with buffer solutions (Merck centiPUR pH 7 and 9). Usually, 30 to 50 mg PdGa or Pd_3Ga_7 were added to 75 ml of the ammonia solution and stirred for 10 min at 300 K. The solution was filtered and the powder was washed with additional 50 ml of the ammonia solution. Etched samples were dried for 120 min in a desiccator evacuated to 10 mbar and stored under Ar in a glove box.

2.3. XPS and ISS

X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) were performed with a Leybold LHS 12 MCD UHV system. The samples for the measurements were prepared from milled PdGa and Pd_3Ga_7 powder. XPS data were obtained using AlK_α radiation (1486.6 eV) and a pass energy of 48 eV resulting in a spectrometer resolution of 1.1 eV. Shirley background correction and numeric integration of the peak areas were employed for XPS data reduction. Elemental composition of the near-surface region was estimated from the peak areas obtained using the corresponding sensitivity factors [25]. The palladium content was calculated from a sum of the $Pd3d_{3/2}$ and $Pd3d_{5/2}$ peaks and the carbon content was obtained from the C1*s* peak. Because of the overlapping O1*s* and $Pd3p_{3/2}$ peaks in the XP spectra, the $Pd3p_{3/2}$ peak area was calculated from the $Pd3d_{3/2}$ and $Pd3d_{5/2}$ peak areas assuming a factor of 2.9 for the $(Pd3d_{3/2} + Pd3d_{5/2})/Pd3p_{3/2}$ ratio [25]. Subsequently, the $Pd3p_{3/2}$ peak area obtained was subtracted from the O1*s* peak area to calculate the oxygen content in the near-surface region. The determined values possess a relative error of 10%. The amounts of gallium and gallium oxide were determined by fitting the $Ga2p_{3/2}$ peak with two Gauss–Lorentz profile functions (30% Lorentzian). Due to the overlapping signals, the relative error of the concentration is in the region of 20–30%. All XPS spectra were corrected for charging effects by setting the binding energy of the C1*s* peak to 284.6 eV [26].

Ion scattering spectroscopy was performed using He ions with a kinetic energy of 2 keV and an emission current of 10 mA resulting in an ion current of 1.65 μA at the sample. For ISS measurements of PdGa the first two scans were averaged and the following scans were averaged in groups of ten. In the case of Pd_3Ga_7, the first three scans were averaged and the following scans were averaged in groups of ten. Milled samples of PdGa and Pd_3Ga_7 were measured first by XPS followed by ISS measurements and another XPS measurement to reveal the surface composition of the materials and the influence of the ion scattering thereon. The influence of a hydrogen treatment on the surface composition was determined by XPS measurements before and after reduction of milled PdGa in 200 mbar H_2 at 573 K for 30 min. After a second hydrogen treatment at 673 K for 30 min, XPS spectra were taken again followed by ISS and XPS measurements. Because of the reduced thermal stability of Pd_3Ga_7, XPS and ISS measurement were performed before and after a single hydrogen treatment at 573 K according to the procedure described above.

2.4. CO chemisorption

Carbon monoxide chemisorption measurements were carried out in an Autosorb 1C (Quantachrome Instruments). The samples (PdGa: 1.5 g, Pd_3Ga_7: 1 g, Pd/Al_2O_3: 180 mg) were pretreated in the sample cell by heating them to different reduction temperatures—673 K (Pd_3Ga_7), 773 K (PdGa) or 473 K (Pd/Al_2O_3) in helium flow (20 ml/min), followed by an isothermal hydrogen treatment for 30 min (20 ml/min of hydrogen flow) and evacuation (180 min) at the pretreatment temperature. The samples were cooled down to 300 K under vacuum and additionally evacuated for 180 min. Subsequently, the CO chemisorption measurements (CO 4.7, Westfalen Gas, Germany) were performed at 300 K.

The active Pd surface area was determined by stepwise measuring the amount of chemisorbed and physisorbed CO. An initial CO pressure of 10.7 kPa was employed, followed by nine equidistant steps up to a final pressure of 106.7 kPa. The pressure drop in the sample cell can be used to calculate the amount of CO adsorbed. Both the extrapolation method and the dual isotherm method were used to distinguish between chemisorbed and physisorbed CO and to determine the active-surface area. A stoichiometric factor of 1.5 was used to account for the presence of on-top and bridged bond CO molecules on the Pd surface [27,28]. Further details are given elsewhere [29–32].

2.5. Catalysis measurements

Catalytic investigations were performed in a plug flow reactor consisting of a quartz glass tube with a length of 300 mm, an inside diameter of 7 mm and a sintered glass frit to support the catalyst. For temperature control, a thermocouple was placed inside the catalyst bed. The reactant gases were mixed with Bronkhorst mass flow controllers to a total flow of 30 ml/min.