

Structural and Catalytic Investigation of Active Site Isolated Pd-Ga and Pd-Sn Intermetallic Compounds

J. Osswald,¹ R. Giedigkeit,² M. Armbrüster,² R.E. Jentoft,¹ F. Girgsdies,¹ U. Wild,¹
Y. Grin,² R. Schlögl,² and T. Ressler¹

¹Anorganische Chemie, Fritz-Haber-Institut der MPG, Berlin

²Chemische Metallkunde, MPI für Chemische Physik fester Stoffe, Dresden

Introduction

Acetylene hydrogenation to ethylene ($C_2H_2 + H_2 \rightarrow C_2H_4$) is a common method for removing traces of acetylene to purify the ethylene feed for the production of polyethylene. Typical hydrogenation catalysts like Pd dispersed on metal oxides are commonly used for acetylene hydrogenation in the ethylene feed. However, these catalysts show a limited selectivity (total hydrogenation to ethane and formation of C_4 hydrocarbons) and stability (sintering and catalyst poisoning) ^[1;2]. The limited selectivity in the acetylene hydrogenation of typical Pd catalysts can be attributed to the presence of ensembles of active sites on the catalyst surface ^[3-5] and the formation of Pd hydrides under reaction conditions ^[6-8]. In this work Pd intermetallic compounds are described that permit tailoring of the isolation of the active site, which results in a superior selectivity and stability under ethylene hydrogenation conditions.

Pd based intermetallic compounds PdGa, Pd₃Ga₇ and PdSn₂

Binary Pd-Ga and Pd-Sn intermetallic compounds were prepared by melting approximate amounts of the elements in a glassy carbon crucible under Ar atmosphere in a high frequency induction furnace. The samples were powdered in a ball mill. In the crystallographic structures of PdGa, Pd₃Ga₇, and PdSn₂ all Pd atoms are surrounded by a coordination sphere of 7 or 8 Ga atoms, or 8 Sn atoms, respectively.

Methods

Thermal stability of the intermetallic compounds in inert and reactive gas atmosphere was determined by in situ X-ray diffraction (XRD), in situ X-ray absorption spectroscopy (EXAFS) and thermal analysis (TG/DSC). Nitrogen adsorption (BET), CO chemisorption, IR absorption spectroscopy, scanning electron microscopy (SEM), X-

ray photoelectron spectroscopy (XPS) and Ion scattering spectroscopy (ISS) were employed to investigate the surface properties of the intermetallic compounds. Catalysis studies were carried out in a plug flow reactor (C_2H_2 / H_2 ratio 1:2) with gas phase analysis using mass spectrometry (MS) and gas chromatography (MicroGC).

Results

In situ XRD and EXAFS measurements in helium, hydrogen, or acetylene and hydrogen feed up to 350 °C resulted in a high thermal and structural stability of the intermetallic compounds. No formation of Pd hydride phases could be detected. TG/DSC in hydrogen as well as XPS and ISS show the presence of an oxide layer on the surface of the intermetallic compounds. IR studies of adsorbed CO shows only a low signal at 2051 cm^{-1} for a single bonded CO molecule on an isolated Pd atom. The intermetallic compounds exhibited high activities in acetylene hydrogenation to ethylene in the temperature range from 100 °C to 300 °C and with increasing selectivity with increasing temperature. Compared to a conventional Pd/Al₂O₃ catalyst (5 wt%, BET surface area: 114 m²/g, CO chemisorption on the active metal: 5.3 m²/g) the intermetallic compounds show a higher selectivity to ethylene with respect to the conversion of acetylene.

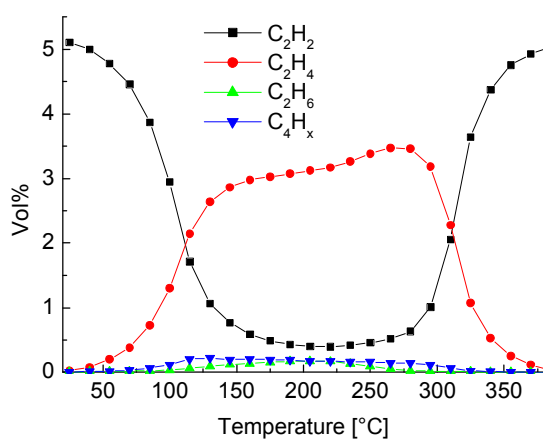


Figure 1: Acetylene hydrogenation (5% C₂H₂ +10% H₂) of PdGa

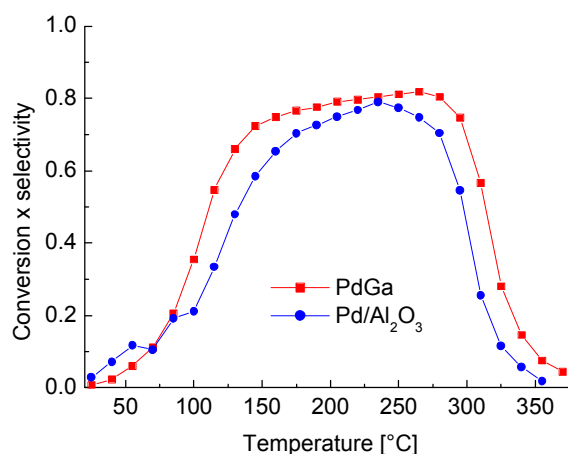


Figure 2: Conversion times selectivity of PdGa (30 mg) and Pd/Al₂O₃ (1 mg, 5% wt Pd)



MAX-PLANCK-GESELLSCHAFT

XXXVIII. Jahrestreffen Deutscher Katalytiker

16.03. – 18.03.2005, Weimar



Literature:

- [1.] G. Ertl, H. Knoerzinger, J. Weitkamp, *Handbook of heterogeneous catalysis*, VCH, **1997**.
- [2.] A. Molnar, A. Sarkany, M. Varga, *Journal of Molecular Catalysis A* **2001**, 173 185-221.
- [3.] E. W. Shin, C. H. Choi, K. S. Chang, Y. H. Na, S. H. Moon, *Catalysis Today* **1998**, 44 137-143.
- [4.] S. Leviness, V. Nair, A. H. Weiss, Z. Schay, L. Guzzi, *Journal of Molecular Catalysis* **1984**, 25 131-140.
- [5.] V. Ponec, *Advances in Catalysis* **1983**, 32 149-214.
- [6.] Palczewska, *Hydrogen Effects in Catalysis*, (Eds.: Z. Paal, P.G. Denon) Marcel Decker, **1988**, pp. 372-397.
- [7.] G. C. Bond, P. B. Wells, *Journal of Catalysis* **1966**, 5 65-&.
- [8.] A. M. Doyle, S. K. Shaikhutdinov, S. D. Jackson, H. J. Freund, *Angewandte Chemie-Int. Edt.* **2003**, 42 5240-5243.