

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

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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.

Materials and methods

Pd based intermetallic compounds PdGa, Pd₃Ga₇ and PdSn₂ were prepared by melting appropriate 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 (BET surface area: ~ 1 m²/g). 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.

Thermal stability of the intermetallic compounds in inert and reactive gas atmosphere was investigated by in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (EXAFS). Data obtained by XRD measurements provides structural information about the long-range order of the crystalline catalyst, whereas in situ EXAFS yields information about the short-range order of the crystalline and none crystalline phases present.

XRD measurements were conducted with CuK α radiation by using a Stoe diffractometer in Bragg Brentano geometry (secondary monochromator) and a Bühler HDK chamber. In situ EXAFS measurements performed at beamline X1 at Hasylab and beamline ID24 at ESRF (Grenoble) at Pd K-edge. XAS experiments carried out with in situ flow reactor at atmospheric pressure in transmission mode. EXAFS data were analysed with WinXAS 3.1 [9] and refined with theoretical spectra obtained with FEFF 8 [10]. 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 and discussion

In situ XRD of the Pd-Ga and Pd-Sn intermetallic compounds in hydrogen exhibited no structural changes up to 650 K. In helium and oxygen PdGa and Pd₃Ga₇ showed thermal stability while PdSn₂ started decomposing at 600 K in helium and was oxidised in the presence of oxygen. In situ EXAFS measurements of PdGa and Pd₃Ga₇ in hydrogen and acetylene hydrogenation feed showed only small change in nearest-neighbour distances and increasing Debye-Waller factors with increasing temperature. PdSn₂ exhibited a decreasing interatomic distance at 600 K in reducing atmosphere indicating the starting decomposition. Palladium hydride formation in the temperature range from 300 to 600 K could not be observed (Figure 1). In helium and in oxygen the Pd-Ga intermetallic compounds showed a high thermal stability. In contrast, the interatomic distances of PdSn₂ in helium and in oxygen decreased at 500 K, which indicates the starting decomposition of PdSn₂ to PdSn, SnO₂ and other compounds.

The intermetallic compounds exhibited high activities in acetylene hydrogenation to ethylene in the temperature range from 380 to 580 K (Figure 2). Compared to a conventional Pd/Al₂O₃ catalyst the intermetallic compounds showed a higher selectivity to ethylene with respect to the conversion of acetylene. The results presented show that structurally well-defined intermetallic compounds possess a high potential to investigate the validity of structural concepts like active site isolation in heterogeneous catalysis. Furthermore, long-time isothermal experiments show a lower deactivation rate than the conventional Pd catalyst.

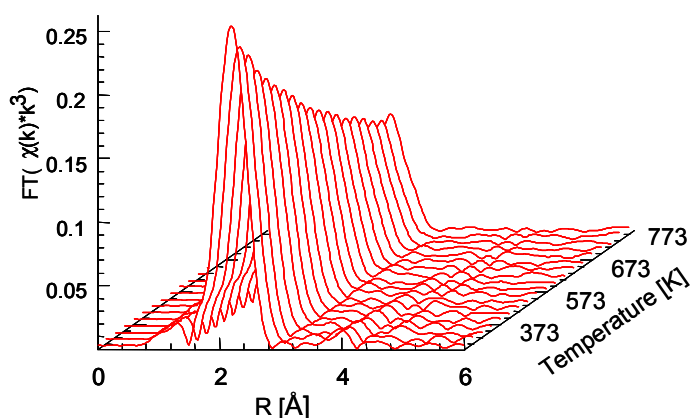


Figure 1: Radial distribution function (not phase corrected) of Pd₃Ga₇ at Pd K-edge in 50% H₂ from 300 to 773 K. The decreasing amplitude is due to the increasing Debye-Waller factor.

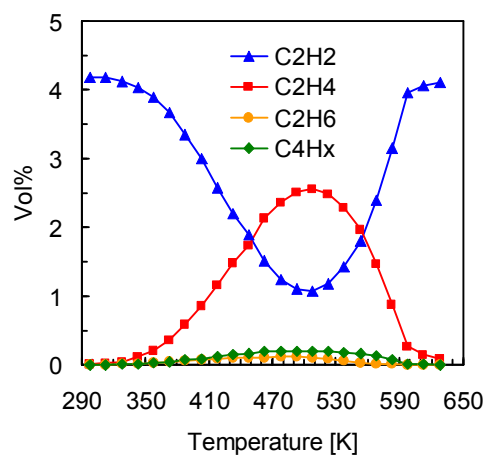


Figure 2: Acetylene hydrogenation of PdGa (C₂H₂ : H₂ = 1:2)



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