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Structural and Catalytic Investigation of Active-Site Isolation in Pd-Ga 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 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, Pd_3Ga_7 and $PdSn_2$ 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 m^2/g). In the crystallographic structures of PdGa, Pd_3Ga_7, and $PdSn_2$ 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 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 and Discussion

In situ XRD and EXAFS measurements in helium, hydrogen, or acetylene and hydrogen feed up to 650 K showed a high thermal and structural stability of the intermetallic compounds. No formation of Pd hydride phases could be detected. 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 weak 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 380 to 580 K (Fig. 1). Compared to a conventional Pd/Al_2O_3 catalyst (5 wt%, BET surface area: 114 m^2/g, CO chemisorption on the active metal: 5.3 m^2/g) the intermetallic compounds show a higher selectivity to ethylene with respect to the conversion of acetylene (Fig. 2). Furthermore longtime isothermal experiments show a lower deactivation rate than the conventional Pd catalyst.

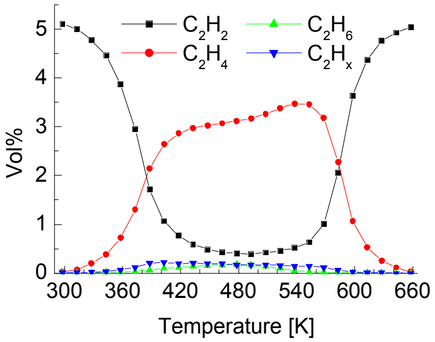

Figure 1: Acetylene hydrogenation (5% C_2H_2 +10% H_2) of PdGa

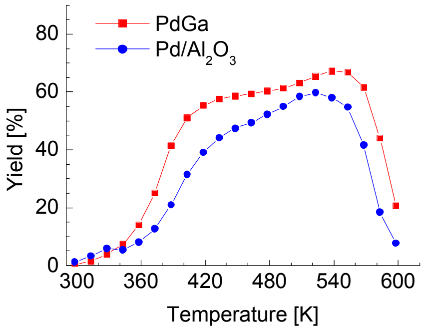

Figure 2: Ethylene yield of PdGa (30 mg) and Pd/Al_2O_3 (1 mg, 5% wt Pd)

Significance

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. New catalyst systems found thereby may exhibit superior catalytic properties such as selectivity and long-term stability, and may be promising candidates for future industrial applications.

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