

Rational catalyst design by using the concept of active-site isolation for the selective hydrogenation of acetylene: the Pd-Ga intermetallic compounds

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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 ethylene feed for the production of polyethylene. Economic efficiency requires high selectivity of acetylene hydrogenation in the presence of ethylene excess preventing the hydrogenation of ethylene to ethane. Typical hydrogenation catalysts are palladium dispersed on metal oxides. Palladium shows high activity but only limited selectivity and long-term stability in acetylene hydrogenation because of the formation of ethane and oligomerisation reactions to C_4H_x and higher hydrocarbons as well as deactivation by carbon deposits ^[1; 2].

The limited selectivity of Pd catalysts in acetylene hydrogenation can be attributed to the presence of ensembles of active sites on the catalyst surface ^[3-5]. Active-site isolation leads to increased Pd-Pd distances on the catalyst surface and to weakly π -bonded acetylene on top of a Pd atom (so-called “geometric effect”) and results in a preferred semi-hydrogenation of acetylene to ethylene and reduced deactivation by suppressing hydrocarbon decomposition. Additional to the “geometric effect”, a “kinetic effect” caused by the absence of hydride formation which reduces hydrogen supply for the hydrogenation reaction and an “electronic effect” influences the adsorption and desorption properties of acetylene and ethylene on modified Pd surfaces were discussed. Well-defined intermetallic compounds of palladium with gallium were selected to verify the concept of active-site isolation for selective acetylene hydrogenation. PdGa ^[6] and Pd₃Ga₇ ^[7] are potential catalysts for hydrogenation reactions because of the presence of isolated Pd atoms in their structure.

Thermal and structural investigation of PdGa and Pd₃Ga₇ were performed by TG/DSC, in situ XRD and in situ EXAFS in inert and reactive gas atmosphere. These compounds showed a high structural stability from 295 K up to 650 K in helium, oxygen and hydrogen as well as in acetylene feed indicative of maintaining the isolation of the active sites under

hydrogenation conditions. No indication of hydrogen incorporation (hydride formation) was found. The catalytic performance of Pd-Ga intermetallic compounds was tested by acetylene hydrogenation in the presence of ethylene. Commercial Pd/Al₂O₃ (5 wt%) and an unsupported silver-rich Pd alloy Pd₂₀Ag₈₀ were used as references. Acetylene hydrogenation on PdGa and Pd₃Ga₇ showed considerable high selectivity and long-term stability [8]. Palladium supported on alumina showed a strong deactivation behaviour and very low selectivity. The Pd-Ag alloy Pd₂₀Ag₈₀ showed less deactivation compared to Pd/Al₂O₃ but resulted in a significantly lower selectivity compared to PdGa and Pd₃Ga₇.

Intermetallic compounds of Pd with Ga show superior catalytic properties like selectivity and long-term stability in acetylene hydrogenation and are promising candidates for industrial applications. These intermetallic compounds with constant composition and ordered structures seem to validate the concept of active-site isolation, which thus can be used for rational design of novel heterogeneous catalysts.

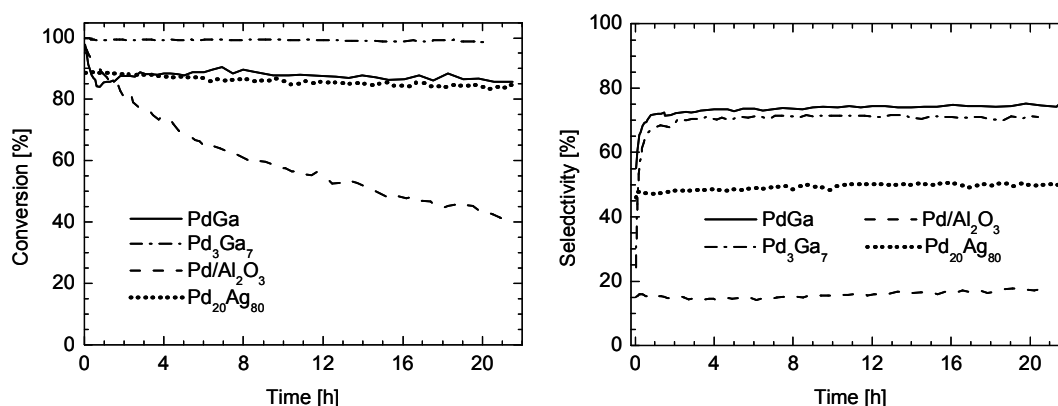


Figure 1: Acetylene conversion (left) of PdGa (40 mg), Pd₃Ga₇ (100 mg), Pd/Al₂O₃ (0.15 mg) and Pd₂₀Ag₈₀ (200 mg) in 0.5% C₂H₂ + 5% H₂ + 50% C₂H₄ isothermal at 473 K and corresponding selectivity (right).

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