Selective hydrogenation of acetylene over alumina supported Pd and Pd-Mg catalysts

Ying Ji, Chunkai Shi, Amir Karimloo, Jessica Elizalde and Ben Jang*
Department of Chemistry, Texas A&M U.-Commerce
Commerce, TX 75429-3011
*ben_jang@tamu-commerce.edu

Introduction

Selective hydrogenation of acetylene in the presence of ethylene is an important industrial process for polyethylene industry since acetylene poisons the ethylene polymerization catalyst. Supported Pd catalysts are widely used to selectively convert acetylene to ethylene in the presence of ethylene [1]. Continuous publications in this subject area demonstrate that further development of Pd-based catalysts with improved selectivity and activity for acetylene hydrogenation under ethylene rich conditions is of industrial interest [1-4]. It has been reported that Pd-based catalysts with various promoters, such as Cu, Ag, Au, Pb, etc., can significantly enhance the selectivity while decreasing the activity of acetylene conversion [1]. Potassium or sodium as a promoter, on the other hand, showed increased activity for acetylene conversion while not compromising the selectivity toward ethylene [2,3]. The result was rationalized by the selective adsorption of triple carbon-carbon bond via the alkali metal cation-π interaction [4]. Since alkaline earth metals would potentially have similar effects as alkali metals, this investigation focuses on the effect of magnesium as a promoter for the selective hydrogenation of acetylene in the presence of ethylene. The results below demonstrate that magnesium is an effective promoter of alumina support Pd catalysts for selective hydrogenation of acetylene to ethylene.

Experimental

1/8" alumina pellets (from Alfa Aesar) were crushed and sieved to 20-40 mesh sizes. These particles are then dried at 200°C for 12 hours followed by cooling down to room temperature in a desiccator. The resulted particles are impregnated with calculated mixed solution of palladium nitrate and magnesium nitrate (Alfa), based on the incipient wetness technique. The obtained materials after drying at 120°C for 12 hours are designated as $1\%Pd/Al_2O_3$ and $1\%Pd\_x\%Mg//Al_2O_3$ (x = 0.5, 1.0 and 2.0).

Reduction of catalysts was carried in UHP hydrogen at 400°C for 2 hours. The reaction study was performed using a feed composition of 1.14% C_2H_2, 4.76% H_2 and balanced C_2H_4 with a space velocity of 84,000 h^{-1}. The reaction temperature is set from 25°C to 85 °C and linearly increased with a heating rate of 0.2 °C/min. The product compositions were analyzed every 10 minutes. The acetylene conversion, selectivity to ethylene and ethylene yield are defined as:

% C_2H_4 selectivity = (1- produced C_2H_6/converted C_2H_2) ×100
% C_2H_2 conversion = (decreased C_2H_2/ C_2H_2 in feed) ×100
% C_2H_4 yield = % C_2H_2 conversion x % C_2H_4 selectivity

Results and Discussion

As shown in Figure 1a, the addition of magnesium increases the acetylene conversion activity. The enhancement increases with the loading of magnesium, especially from 25° to 45°C. The effect of magnesium on the selectivity to ethylene, on the other hand, changes with Mg loading. The addition of 0.5% or 2.0% Mg decreases the selectivity, but 1.0% loading increases the selectivity. The overall effect, as shown in Figure 1b, indicates that 0.5% Mg increases the yield of acetylene to ethylene while 1.0% and 2.0% leadings shift the maximum yield temperature to lower temperatures with slightly lower overall yields. The result demonstrates that Mg is a potential promoter to modify the activity and selectivity of alumina support Pd catalysts for selective hydrogenation of acetylene to ethylene in the presence of ethylene.

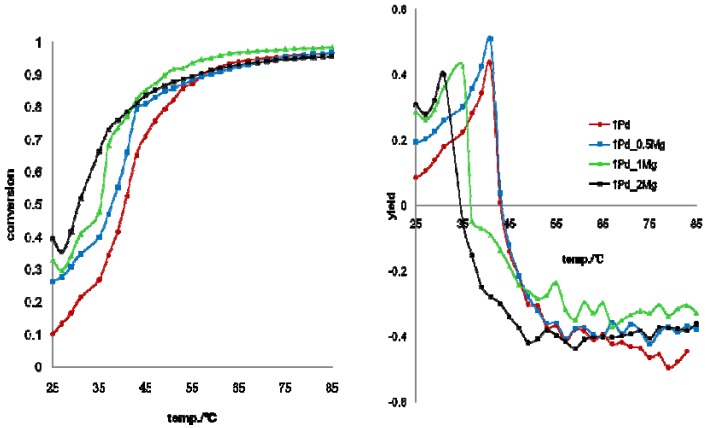

Figure 1. (a) acetylene conversion activity and (b) ethylene yield as function of temperature.

Significance

This is, to our knowledge, the first report of using magnesium as a promoter of supported Pd catalysts for selective hydrogenation of acetylene. Magnesium nitrate is reducible at lower temperatures than potassium or sodium precursor. It has the potential to combine the benefits of different types of promoters known to industry, including Ag, Pb, K etc., into one. Other specific unique properties, including the reduction phenomena, metal particle formation, composition and distribution, etc., of supported Pd-Mg catalysts will be discussed in the full presentation.

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