Selective Hydrogenation of Acetylene on Nanocrystalline α-Al_2O_3 supported Pd Catalysts: Influences of Preparation Method and Support Crystallite Size

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Introduction

Most of polymer-grade ethylene is produced by thermal cracking of hydrocarbons in the presence of steam or by recovery from refinery cracked gas. Maximum acetylene contaminant allowable in the ethylene feed is about 5 ppm [1]. Hydrogenation of acetylene in the presence of ethylene requires high selectivity to ethylene in order to prevent ethylene loss [2].

Pd/α-Al_2O_3 catalyst is commonly used for selective acetylene hydrogenation. Several attempts have been made to improve the selectivity of Pd/α-Al_2O_3 catalysts [3,4]. In this work, the effect of support crystallite size on the catalytic properties of Pd/α-Al_2O_3 catalysts in selective acetylene hydrogenation has been studied. Nanocrystalline α-Al_2O_3 was prepared via solvothermal, sol-gel, and precipitation methods.

Materials and Methods

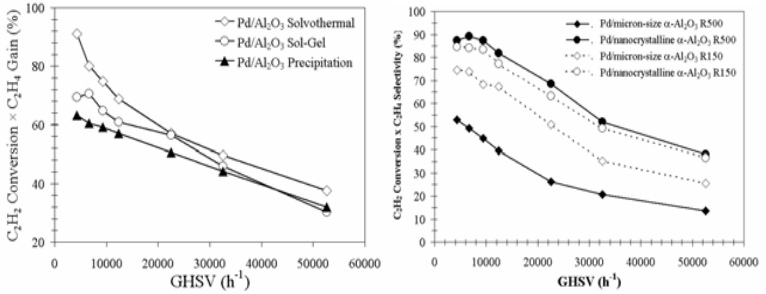
For the solvothermal method, aluminum isopropoxide (AIP, 25g) and toluene were used as the starting material. Aluminium nitrate, ethanol, and urea solution were used for the sol-gel method. For the precipitation method, ammonium aluminium sulfate and ammonium hydrogen carbonate in aqueous solution were used. The micron-sized α-Al_2O_3 was the commercially available α-Al_2O_3 from Sigma-Aldrich. Various analytical techniques such as N_2 physisorption, X-ray diffraction, CO pulse chemisorption, H_2 temperature program reduction, temperature program desorption, infrared spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy were employed in order to investigate the physicochemical properties of Al_2O_3 supports and corresponding Pd/Al_2O_3 catalysts.

Results and Discussion

The obtained results suggest that the interaction between Pd metal and α-Al_2O_3 support was affected by the crystallite size of α-Al_2O_3. Reduction at 500°C could result in stronger metal-support interaction between Pd metal and α-Al_2O_3 for the nanocrystalline α-Al_2O_3 supported catalysts and as a consequence, ethylene selectivity was enhanced due to the lower adsorption strength of ethylene as can be found in other catalyst systems such as Pd/TiO_2 [5]. The absence of strong metal-support interaction in the case of Pd/micron-sized α-Al_2O_3 was probably due to sintering of Pd^0 metal during high temperature reduction.

The effect of nanocrystalline porosity of α-Al_2O_3 obtained from various preparation methods on the catalytic properties of Pd/α-Al_2O_3 was also investigated. It was found that the sol-gel method yielded smallest crystallite size of α-Al_2O_3 with little pore volume and surface area. Mesopore structure with average pore size 15-27 nm were obtained via solvothermal and precipitation methods. Suitable properties of the solvothermal-derived α-Al_2O_3 such as high surface area and narrow pore size distribution were found to result in the best catalyst performance of Pd/α-Al_2O_3 catalysts among the various catalysts studied. The α-Al_2O_3 solvothermal not only provided the highest Pd dispersion and smallest Pd particle size but it also facilitated H_2 reduction at low temperature and desorption of ethylene and CO.

Figure 1 Catalyst performances in the selective hydrogenation of acetylene



Significance Pd catalysts supported on the solvothermal-derived nanocrystalline α-Al_2O_3 exhibited superior performances in the selective acetylene hydrogenation than those supported on commercial micron-sized α-Al_2O_3 and α-Al_2O_3 prepared via sol-gel and precipitation method. Reduction at 500°C also led to improvement of ethylene yield for the Pd/nanocrystalline α-Al_2O_3 but not for the Pd/micron-α-Al_2O_3.

References

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