



Highly selective Pd/Al₂O₃ catalyst for hydrogenation of methylacetylene and propadiene in propylene stream prepared by γ -radiation

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ABSTRACT

Pd/Al₂O₃ catalyst was successfully prepared by γ -radiation induced reduction and showed much higher selectivity in the hydrogenation of methylacetylene and propadiene in propylene stream than catalysts prepared by chemical reduction and calcination method. Characterizations by TEM, XPS, and in situ FTIR proved that the irradiation process was beneficial in achieving uniform distribution of Pd particles on the surface of Al₂O₃ by strengthened Pd–support interaction. The irradiation process was also responsible for the dominant Pd(1 1 1) plane and the strong adsorption to target reactant of Pd sites, which we think are the reasons for the high selectivity of the catalyst.

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1. Introduction

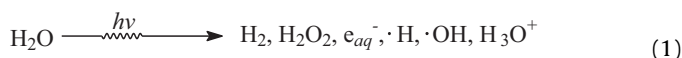
Propylene, known for the raw material of polypropylene (PP), is one of the most important basic chemicals. Propylene is mainly produced by cracking process in ethylene plants. Hydrocarbon feed, including naphtha, liquefied petroleum gas (LPG) and ethane, is broken down to produce cracked gas, which including lighter alkenes, such as ethylene and propylene. In a subsequent process, C₂, C₃, C₄ and other fractions are separated. The C₃ cut contains 1–7 mol% methylacetylene and propadiene (MAPD), which are poisonous to catalyst for propylene polymerization and would severely reduce the quality of polypropylene. To obtain high purity propylene for polymerization, Pd/Al₂O₃ catalyst is commonly used in industrial process for converting MAPD selectively to propylene.

The selectivity of Pd catalyst is crucial for the hydrogenation of MAPD. Pd/Al₂O₃ catalyst used in industry is often prepared by a two-step method. Pd precursor is impregnated on Al₂O₃ support, then the support is calcined at a high temperature (300–500 °C) to form PdO on Al₂O₃. The calcination step turns Pd precursor to PdO and strengthens the interaction between Pd particles and support, thus the catalyst can maintain stable performance during regeneration cycles. However, this step also brings negative effects. (1) Calcination at high temperatures will cause the sintering effect of Pd particles, which would reduce the performance of the catalyst

[1]. (2) The calcination step is energy-consuming and gas waste produced is hazard for environment. (3) The catalyst in the form of PdO has to be pre-reduced to Pd(0) before it can be used for hydrogenation process, which takes extra time and increases operation cost.

To overcome these problems, many new methods use room temperature reduction or activation as a substitute of the calcination step. Nonthermal plasma was used to activate Pd catalysts to improve the selectivity in acetylene hydrogenation [2–4]. UV radiation was employed to reduce Pd precursor to Pd(0) with controllable Pd shell thickness [5]. Chemical reduction methods were also used to prepare Pd catalysts. The reducing agents include alkali metal borohydrides, aldehyde, hydrazine, etc. [6–8]. However, these methods are hardly applicable for the mass production of industrial catalysts due to weak penetration of plasma and UV light, the high expense of chemicals, or the complex preparation procedures.

Recently, the use of ionizing radiation to prepare supported catalyst arose many attentions [9–14]. Ionizing radiation consists of subatomic particles or electromagnetic waves that are energetic enough to detach electrons from atoms or molecules, ionizing them [11]. γ -Rays and electron beam are the most common forms of ionizing radiation used in industry. The irradiation of aqueous solution produces ions, radicals and molecules by the radiolysis of water:



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