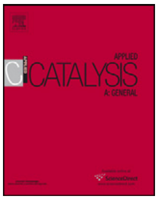
Applied Catalysis A: General 401 (2011) 12–19

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Performance of Cu-promoted Pd catalysts prepared by adding Cu using a surface redox method in acetylene hydrogenation

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ARTICLE INFO

Article history:
Received 23 February 2011
Received in revised form 18 April 2011
Accepted 25 April 2011
Available online 11 May 2011

Keywords:
Acetylene hydrogenation
Pd
Cu
Surface redox method
Ethylene selectivity

ABSTRACT

Cu-promoted Pd/Al_2O_3 catalysts were prepared by selectively depositing Cu onto the Pd surface using a surface redox (SR) method, and their performance in the selective hydrogenation of acetylene was compared with that of Ag-promoted catalysts prepared by both the SR and the conventional impregnation method. The Cu-promoted catalysts prepared by SR showed higher ethylene selectivity and activity than Ag-promoted catalysts, particularly with small amounts of added promoter. The above results were obtained because Cu added by SR was deposited preferentially onto the low-coordination sites of Pd, which were detrimental to ethylene selectivity but took a small fraction of the Pd surface that was responsible for acetylene conversion, and also because Cu had an intrinsic activity for hydrogenation. The advantages of Cu-promoted catalysts prepared using Cu as a promoter and the SR process as the promoter-addition method were conclusively demonstrated in the present study.

1. Introduction

The selective hydrogenation of acetylene is a process used to obtain pure ethylene as a feed for the polyethylene synthesis process [1,2]. Supported Pd catalysts are used in the process, but further improvement in their ethylene selectivity and in the catalyst lifetime is still needed [3]. Numerous components, including Ag, Ni, Cu, K, Au and Si, have been proposed as promoters for the Pd catalyst [4–10], and Ag is already widely used in commercial catalysts [11].

Ag is effective for promoting ethylene selectivity by electronic and geometric modifications of the Pd surface but has the drawback of lowering catalyst activity. Accordingly, it would be desirable to find promoters that could compare to Ag in promoting ethylene selectivity while maintaining the high activity of Pd.

In the present study, Cu was considered as a possible alternative to Ag because it is known to be active in the hydrogenation of unsaturated hydrocarbons, and to play the role of a selectivity promoter. For example, Wehrlia et al. demonstrated that supported Cu catalysts were active in the selective hydrogenation of unsaturated hydrocarbons such as propyne, butynes and acetylene [12–14]. Stammbach et al. also showed that Cu/SiO_2 was active in the hydrogenation of acetylene [15]. Leviness et al. used Cu as a selectivity promoter for the selective hydrogenation of acetylene [7].

The common methods for preparing bimetallic catalysts are either to co-impregnate or to sequentially add both metal components onto a catalyst support. However, the above methods encounter limitations when an alloy is to be formed between two different metals because the metal particles are usually distributed randomly on the catalyst surface, which includes the support. Recently, various methods of metal addition, such as chemical vapor deposition [16,17], electroless deposition [18–20] and surface redox reaction [21–23], have been proposed as alternatives to the impregnation method for preparing bimetallic catalysts because they allow the selective deposition of promoters onto the surface of a parent metal. Among these methods, surface redox (SR) reaction is the simplest.

In the present study, the surface of the Pd catalyst was modified with Cu, which was added using the SR method. The performance of the Cu-promoted Pd/Al_2O_3 catalysts in the selective hydrogenation of acetylene was compared with that of the Ag-promoted ones prepared by both SR and impregnation. The surface properties of the prepared catalysts were analyzed using infrared spectroscopy of the chemisorbed CO (CO-IR), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of ethylene (ethylene-TPD), and scanning-transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM–EDS).

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doi:10.1016/j.apcata.2011.04.048

2. Experimental

2.1. Catalyst preparation

1 wt% Pd/Al_2O_3 was prepared as a reference catalyst by incipient wetness impregnation using $Pd(NH_3)_4(OH)_2$ as a Pd precursor. Powdered θ-δ-alumina obtained from BASF (BET surface area, 31 m^2/g; pore volume, 0.13 cm^3/g; average pore diameter, 16.8 nm; 1 wt% Pd dispersion, 25%) was used as a support material. The prepared catalyst was dried at 383 K overnight and calcined in air at 573 K for 2 h.

Ag- and Cu-promoted Pd/Al_2O_3 catalysts were prepared by incipient wetness impregnation of Pd/Al_2O_3 with aqueous solutions of $AgNO_3$ and $Cu(NO_3)_2$, which were designated as either Pd–*x*Ag (I) or Pd–*x*Cu (I), respectively, where *x* denoted the measured atomic ratio of either Ag/Pd or Cu/Pd. An adequate concentration of each solution was used to make either the Ag/Pd or the Cu/Pd atomic ratios equal to either 0.3, 0.5 or 0.7. The nominal amount of each metal was close to the amount measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). After drying overnight at 383 K, the catalysts were calcined in air at 573 K for 2 h and subsequently reduced with a flowing H_2/N_2 gas mixture at different temperatures, which corresponded to the minimum reduction temperatures for two alloy catalysts, i.e., at 423 K for Pd–Ag and at 573 K for Pd–Cu.

In the case of catalysts prepared by SR, either Ag or Cu was deposited by reaction between Ag^+ or Cu^{2+} cations dissolved in an aqueous solution of either $Ag(NO_3)$ or $Cu(NO_3)_2$ and hydrogen atoms adsorbed onto the Pd surface. The concentrations of the cations in the solution were varied to obtain nominal atomic ratios of Ag/Pd and Cu/Pd that would equal 0.1, 0.2, 0.5 and 1.0. The catalysts prepared by SR were designated as either Pd–*x*Ag (SR) or Pd–*x*Cu (SR), where *x* denoted the measured atomic ratio of either Ag/Pd or Cu/Pd. Prior to the deposition of the promoter by SR, Pd/Al_2O_3 was reduced in H_2/N_2 at 423 K for 2 h, which was followed by cooling to room temperature in the same flow. A 5 ml aqueous solution of either Ag or Cu, prepared as described above, was injected by using a syringe into a reactor containing the pre-reduced Pd/Al_2O_3 in an air-free atmosphere, and was allowed to react with the catalyst for 1 h while the solution was stirred using a magnetic stirrer. The bubbling of hydrogen gas in the stirred solution increased the amounts of either Ag or Cu deposited on the catalyst. After being subjected to the SR process, the catalyst was washed with de-ionized water, dried overnight at 383 K and finally reduced in a mixture of H_2/N_2 gas at 423 K for Pd–Ag (SR) and 573 K for Pd–Cu (SR).

2.2. Acetylene hydrogenation

Selective hydrogenation of acetylene was performed at 333 K in a pyrex micro-reactor containing 0.03 g of catalyst. A gas mixture containing 0.95% acetylene in ethylene was used as the reactant stream. Catalysts were reduced at either 423 or 573 K in flowing H_2/N_2 prior to use in the reaction. Reaction products were analyzed with an on-line gas chromatograph (Agilent, HP 6890 with FID) using a Porapak N capillary column. The flow rate of the reactant stream was varied from 40 to 180 ml/min with an interval of 20 ml/min to change the acetylene conversion at a fixed H_2/acetylene ratio of 2. Ethylene selectivity was calculated as moles of ethylene produced per mole of acetylene converted.

2.3. Characterization

The amounts of Pd, Ag and Cu in the catalysts were analyzed by ICP-AES (Shimadzu/ICPS-1000) equipped with an optical system of double grating in Czerny-Turner mounting. The samples were first dissolved in mixed acids under microwave irradiation (Milestone/MLS 1200 MEGA), and then diluted in distilled water.

Infrared spectra were measured in a transmission mode using a Midac 2100 spectrometer equipped with an MCT detector. A 0.07 g aliquot of the sample catalyst was pressed into a self-supporting disc, placed in the IR cell with CaF_2 windows and reduced at either 423 or 573 K. The cell was evacuated at the reduction temperature for 30 min in order to remove the hydrogen that had adsorbed onto the catalyst surface, and was then cooled to room temperature. The reduced catalyst was then exposed to 14.6 Torr of CO for 5 min. The IR spectrum of CO adsorbed onto the catalyst was recorded in the 4500–500 cm^{-1} range with a 4 cm^{-1} resolution after the gaseous CO had been removed from the cell by evacuation.

The XPS was obtained using a Thermo Scientific Sigma Probe equipped with an Al Kα (1486.6 eV) anode. The electron binding energies were calibrated in reference to the C 1s peak at 284.6 eV. The reduced catalyst sample, which was protected from air oxidation by wetting the surface with iso-octane, was mounted on double-sided adhesive tape prior to fixation in an UHV chamber for the XPS analysis.

For the ethylene-TPD experiments, the catalyst sample was reduced in a micro-reactor in H_2/He at 423 or 573 K for 1.5 h. The residual hydrogen was then cleaned from the reduced metal surface by flushing with He at 423 K for 0.5 h prior to exposing the surface to ethylene. Pulses of pure ethylene (99.99%) was introduced to a reactor containing sample catalyst at room temperature until the catalyst surface was saturated with ethylene, as confirmed by monitoring ethylene signal at the reactor exit. The weakly adsorbed ethylene species were removed from the surface by flowing He, and, finally, the TPD was performed as the catalyst was heated from room temperature to 573 K at a rate of 10 K/min in a 20 ml/min flow of He. The effluent gas was analyzed using a mass spectrometer (VG Sensorlab).

STEM–EDS analysis of the catalyst was performed using an FEI Technai F20 microscope operated at 200 kV. The specimen for the STEM–EDS analysis was prepared by dropping the sample powder, which had been suspended in ethanol by ultrasonic irradiation, onto a carbon film supported on an Ni grid, followed by drying with evacuation at 363 K for 12 h. Line analysis was performed using an EDAX Apollo X SDD energy dispersive X-ray spectrometer.

3. Results

3.1. Promoter deposition

Fig. 1 shows the measured amounts of both Ag and Cu that were actually deposited onto either Pd/Al_2O_3 or Al_2O_3 by the SR method versus the nominal amounts obtained when it was assumed that Ag^+ or Cu^{2+} cations contained in the SR solution were completely deposited on the substrate. A linear relationship was observed between the two amounts when the sample catalyst was exposed to hydrogen gas that was bubbling in the SR solution, i.e., in the case of w/ H_2. In this case, all of the Ag^+ cations in the SR solution were deposited onto Pd/Al_2O_3, while Cu^{2+} cations were deposited in fractional amounts, i.e., approximately 80%. When hydrogen was not bubbled in the solution (w/o H_2), the amounts of deposited Ag or Cu decreased to different extents according to the metal. The amounts of deposited Ag increased in proportion to the nominal amounts, although the dependence was not so strong as in the case of hydrogen bubbling. However, the amounts of deposited Cu became saturated at a Cu/Pd ratio of *ca.* 0.2 even when the nominal amounts of Cu were larger than the level.

Fig. 1 also shows the results of the same SR experiments performed using Al_2O_3 as a substrate. The amounts of Ag deposited onto Al_2O_3 increased with the nominal amounts, similar to the