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Novel Pt/Mg(In)(Al)O catalysts for ethane and propane dehydrogenation

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ABSTRACT

Catalysts for the dehydrogenation of light alkanes were prepared by dispersing Pt on the surface of a calcined hydrotalcite-like support containing indium, Mg(In)(Al)O. Upon reduction in H_2 at temperatures above 673 K, bimetallic particles of PtIn are observed by TEM, which have an average diameter of 1 nm. Analysis of Pt L_{III}-edge extended X-ray absorption fine structure (EXAFS) data shows that the In content of the bimetallic particles increases with increasing bulk In/Pt ratio and reduction temperature. Pt L_{III}-edge X-ray absorption near edge structure (XANES) indicates that an increasing donation of electronic charge from In to Pt occurs with increasing In content in the PtIn particles. The activity and selectivity of the Pt/Mg(In)(Al)O catalysts for ethane and propane dehydrogenation reactions are strongly dependent on the bulk In/Pt ratio. For both reactants, maximum activity was achieved for a bulk In/Pt ratio of 0.48, and at this In/Pt ratio, the selectivity to alkene was nearly 100%. Coke deposition was observed after catalyst use for either ethane or propane dehydrogenation, and it was observed that the alloying of Pt with In greatly reduced the amount of coke deposited. Characterization of the deposit by Raman spectroscopy indicates that the coke is present as highly disordered graphite particles <30 nm in diameter. While the amount of coke deposited during ethane and propane dehydrogenation are comparable, the effects on activity are dependent on reactant composition. Coke deposition had no effect on ethane dehydrogenation activity, but caused a loss in propane dehydrogenation activity. This difference is attributed to the greater ease with which coke produced on the surface of PtIn nanoparticles migrates to the support during ethane dehydrogenation versus propane dehydrogenation.

1. Introduction

Ethylene, propylene, and butene are used extensively to produce rubber, plastics and many other products. The conventional source of these light alkenes is steam cracking of alkanes, naphtha, or gas oil. This process is typically carried out at 1123 K and is not selective. For example, steam cracking of naphtha produces ethene yields of 30% and propene yields of 20%, with substantial quantities of methane and coke as byproducts. Catalytic dehydrogenation of alkanes provides an alternative for producing light alkenes as well as hydrogen, a product required for many refinery operations, most notably heteroatom removal. While thermal dehydrogenation, like steam cracking, is an endothermic process, it occurs at lower temperatures, 973–1073 K, but can also produce methane and coke as byproducts.

Platinum is the most effective transition metal for promoting alkane dehydrogenation; however, in order to achieve high alkene selectivity, it must be promoted with an element, such as Sn, Zn, Ge, Ga, or In, which interacts with the Pt to form a bimetallic alloy [1–9]. Bimetallic nanoparticles of Pt and the alloying element have also been found to produce less coke [10–14], a product that can contribute to deactivation of the catalyst. Catalyst stability is further enhanced by using a metal oxide support free of acid sites that can promote carbon deposition through polymerization of the product alkene [14–19]. Recent work has shown that calcined hydrotalcite-like materials, referred to as Mg(Al)O, are ideal for this purpose [11,20,21]. Moreover, the Al cations present at the support surface help stabilize the dispersed metal particles against sintering [22].

Of the promoting elements listed earlier, the greatest attention has been given to Sn [13,14,23–29]. This element can be introduced by coimpregnation of Pt and Sn precursors into a metal oxide support or by first forming a supported Pt catalyst and then impregnating it with a solution containing the Sn precursor. The properties of the catalyst have been found to depend on the composition of the Pt and Sn precursors and the catalyst preparation procedure [14]. By contrast, the performance of PtIn catalysts is less dependent on the composition of the Pt and In precursors and the procedure used for catalyst preparation [30]. PtIn catalysts have also been found to be more homogenous in composition than PtSn particles [31] and to be stable for dehydrogenation of C_4 and C_5 alkanes [3]. Consequently, PtIn catalysts could potentially be effective catalysts for dehydrogenation of light alkanes in general.

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We have recently reported a novel approach for producing PtGa bimetallic nanoparticles exhibiting high activity and selectivity for ethane and propane dehydrogenation, as well as reduced carbon deposition [32]. These catalysts were prepared by dispersing Pt nanoparticles onto a calcined hydrotalcite-like support containing Ga, Mg(Ga)(Al)O. Upon H_2 reduction of Pt/Mg(Ga)(Al)O at 873 K, a part of the Ga^{3+} cations at the surface of the support were reduced and the resulting Ga atoms formed PtGa bimetallic particles by alloying with the supported Pt particles. Since In can be introduced into the support in a manner similar to Ga, we undertook an investigation of the properties of Pt/Mg(In)(Al)O catalysts for light alkane dehydrogenation. Here we report on the preparation, characterization, and evaluation of such catalysts for ethane and propane dehydrogenation. XANES and EXAFS were used to track the alloy composition of the catalyst as a function of the bulk In/Pt ratio and examine the effect of reduction temperature on alloy formation. Information about metal particle size before and after catalyst use was obtained by STEM, whereas Raman spectroscopy was used to identify type of coke deposited following ethane or propane dehydrogenation.

2. Experimental

2.1. Catalyst preparation

Mg(In)(Al)O was synthesized using the following procedure. A mass of 58.31 g of $Mg(NO_3)_2\ 6H_2O$ (Alfa Aesar, 98–102%), appropriate amounts (depending on the desired In loading) of $Al(NO_3)_3{\cdot}9H_2O$ (Alfa Aesar, 98–102%) and $In(NO_3)_3{\cdot}{\times}H_2O$ (Alfa Aesar, 99.9%) were dissolved in 250 ml deionized water, and 1.2 g of Na_2CO_3 (EMD Chemicals Inc, 99.5%) and 11 g of NaOH (Fisher Scientific, 98.3%) were dissolved in 250 ml deionized water. These two solutions were then mixed dropwise with stirring, at about 333 K in about 20 min, and aged at room temperature for 18 h. The resulting suspension was filtered, and the solid product dried in air overnight at 383 K. The hydrotalcites-like material obtained in this manner was heated in air to 973 K at 2 K/min and maintained at this temperature for 10 h to obtain the calcined support, Mg(In)(Al)O. Mg(Al)O was prepared in a similar manner.

The same amount of Pt was dispersed onto 1 g of the calcined support by incipient wetness impregnation, using a solution containing 21 mg of Pt(acetylacetonate)$_2$ (Sigma Aldrich, 99.99%) dissolved in 1.5 ml toluene. The resulting mixture was stirred until powdery, then left at room temperature in air for 2 h, and finally dried overnight at 383 K in an oven. After drying, the catalyst was reduced at 723 K for 2 h (5 K/min temperature ramp) in 10% H_2/Ar (60 cm^3/min). In this manner, a series of Pt/Mg(In)(Al)O catalysts were prepared with different bulk In/Pt ratio.

2.2. Catalyst characterization

The content of Pt, Mg, Al and In were determined by Galbraith Laboratories (Knoxville, TN) using inductively coupled plasma optical emission spectroscopy. The BET surface area of Pt/Mg(Al)(In)O was determined by the multi-point method using an Autosorb-1 instrument (Quantachrome Corporation). Prior to measuring the adsorption isotherm, each sample was degassed at 573 K for 22–24 h. The hydrotalcite-like material was characterized by X-ray powder diffraction before and after calcination, using a Siemens Diffractometer D 5000 with CuKα radiation ($\lambda = 1.5418$ Å) at 20 kV and 5 mA. The samples were scanned from 2θ values of 5° to 70° with a step size of 0.02° and a dwell time of 1.0 s. The dispersion of Pt on Pt/Mg(Al)(In)O was determined by H_2 chemisorption using a AutoChem II 2920 (Micromeritics Instrument Corporation). About 60 mg of Pt/Mg(In)(Al)O was loaded into a quartz cell and then reduced in flowing 10% H_2/Ar (50 cm^3/min). The temperature of the sample was raised at 5 K/min to 873 K and then maintained at this level for 2 h. The sample was then flushed in flowing Ar for 90 min and then cooled down to 313 K. The uptake of chemisorbed hydrogen was then measured by determining the uptake of H_2 from pulses using a TCD detector. The pulse size was 50 cm^3/g, and the time between pulses was 10 min.

Electron micrographs of the support, with and without Pt, were taken using an aberration-corrected FEI Titan 80/300-kV TEM/STEM located at Oak Ridge National Laboratory. Bright-field and high angle annular dark-field (HAADF) STEM images were recorded simultaneously to get full information of the microstructure. HAADF images were acquired with a 300-kV accelerating voltage with a convergence angle of 30 mrad and a large inner collection angle of 75 mrad. The contrast of the acquired HAADF images is sensitive to atomic number. To minimize electron beam radiation on the sample, all images were acquired in regions that had not been previously illuminated, shortly after the electron beam had been aligned in a neighboring region. Electron energy loss spectra were acquired for 3 s with a convergence angle of 30 mrad and collection angle of 35 mrad. The data were processed through DigitalMicrograph.

Pt L_{III}- and In K-edge XAS data were collected at the Advanced Photon Source at Argonne National Lab on beamline 10-BM with a Si(1 1 1) monochromator crystal detuned by 40%. The sample was located between two ionization chambers, and a reference foil was placed after the second ionization chamber for energy calibration. Nitrogen and argon gas was used in the ionization chambers for Pt L_{III}- and In K-edges, respectively, and all samples were investigated in transmission mode. All six samples with In/Pt ratios (In/Pt = 0, 0.33, 0.48, 0.88, 1.7, 5.6) were prepared simultaneously under three different pretreatment conditions: 723 K for 1 h in 4% H_2/He at 100 cm^3/min, 873 K for 1 h in 4% H_2/He at 100 cm^3/min, and 873 K for 1 h in 10% O_2/N_2 after pretreatment at 873 K in hydrogen. All samples were cooled to ambient temperature in He flowing at 100 cm^3/min and then transferred to the beamline for immediate EXAFS characterization.

EXAFS data were analyzed using the program Ifeffit and the graphical user interfaces Athena and Artemis [33]. The incident photon energy was calibrated to a reference Pt foil. The edge energy was set to the first inflection point on the rising part of the absorbance edge. Data were normalized using a pre-edge line fit from −150 to −50 eV below the edge and a quadratic polynomial with a k-weight of two from 150 to 749 eV above the edge energy. A spline was fit to the data $0 < k < 15$ Å^{-1} after the edge. The data for $3.5 < k < 12.1$ Å^{-1} were fit from 1.8 to 3.2 Å for catalysts treated in hydrogen at 873 K and from 1.4 to 3.2 Å for the other two pretreatments using k-weights of 1, 2, and 3. For all pretreatments, the initial Pt and In paths were taken to be 2.8 Å. The same mean square disorder, σ^2, and edge energy were used for both paths, but the path lengths were allowed to vary independently. For the samples pretreated in hydrogen at 723 K, a third oxygen path was added at a distance of 2 Å, and the bond length and coordination number were allowed to vary separately. The same structural disorder parameter and edge energy for the Pt and In paths were used in the oxygen path. Theoretical standards were constructed using known crystal structures of PtIn alloys [34], as well as Pt oxides [34].

2.3. Catalyst testing

Reactions were carried out in a quartz reactor with an inner diameter of 7 mm. Prior to testing, the catalyst (0.025 g, 0.25–0.5 mm particle size) was heated at 10 K/min to 873 K in 20% H_2 in He and then maintained at this temperature for 1 h. The catalyst bed was heated by a three-zone furnace (Applied Test System, Inc.)