Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Ethane and propane dehydrogenation over PtIr/Mg(Al)O

Jason Wu, Shaama Mallikarjun Sharada, Chris Ho, Andreas W. Hauser,
Martin Head-Gordon, Alexis T. Bell *

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720-1462, United States

A B S T R A C T

Increased demand for light alkenes has motivated research on the catalytic dehydrogenation of the light alkanes and on understanding the role of catalyst composition on the activity, selectivity, and stability of Pt-based catalysts used for this purpose. The present study examines the structure and performance of Pt–Ir catalysts for ethane and propane dehydrogenation, and compares them with the performance of Pt and Pt–Sn catalysts. Nanoparticles of Pt, PtSn, and PtIr were prepared in a colloidal suspension and then dispersed onto calcined hydrotalcite (Mg(Al)O). After characterization to confirm formation of a bimetallic alloy, it was observed that at high conversions, $Pt_3Ir/Mg(Al)O$ exhibited lower initial activity than $Pt_3Sn/Mg(Al)O$ but greater stability to coke deposition. Intrinsic rate measurements at low feed residence time revealed the following trend in activity: $Pt_3Sn > Pt_3Ir > Pt$. DFT calculations carried out on tetrahedral clusters (Pt_4, Pt_3Ir, Pt_3Sn) reveals that this trend in activity can be replicated and Ir is capable of alkane activation, a trait unique to this bimetallic system.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Ethylene and propylene are used extensively as building blocks to produce a wide array of products, including plastics, rubbers, fuel blending agents, and chemical intermediates [1–3]. The conventional methods for producing light alkenes include steam cracking and fluid catalytic cracking of naphtha or gas oil. A typical product distribution from high-severity naphtha cracking yields 35% selectivity to ethylene and 15% selectivity to propylene, with substantial quantities of methane and coke as byproducts [4]. The low selectivity towards light alkenes and the drive to find more economical feedstocks compared to petroleum, has motivated the petrochemical industry to consider catalytic dehydrogenation of light alkanes as an attractive alternative. With the recent boom in natural gas production, especially in the United States, ethane and propane have become readily available and, hence, attractive the starting materials for the production of ethylene and propylene. The hydrogen produced as the principal byproduct of light alkane thermal dehydrogenation is also desirable, since it can be used as a fuel to provide the energy needed for the endothermic dehydrogenation process and for heteroatom removal from petroleum.

The most active catalyst for alkane dehydrogenation is platinum, but in its pure form, it suffers from low olefin selectivity and rapid coke deposition, leading to catalyst deactivation [3,5]. The addition of promoters, such as Sn, In, or Ga [6–12], has been found to be effective in increasing alkene selectivity and suppressing coke formation [6,8,13–17]. Both geometric and electronic effects of the promoters have been proposed to elucidate their roles in modifying the catalyst for the reaction [18–21]. Catalyst stability can be further enhanced by using a metal oxide support free of acid sites that can promote side reactions and additional coking [17,22–24]. Calcined hydrotalcite, or Mg(Al)O, has been shown to be an ideal support for this reaction. Moreover, the Al cations present at the surface of this support surface stabilize the dispersed metal nanoparticles against sintering [25].

While primary attention has been given to Sn as the promoting element, a recent computational study has found Ir to be an effective promoter for propane dehydrogenation, and shows that Pt–Ir bimetallic particles should exhibit higher activity and greater stability than pure Pt [26]. Previous experimental studies of bimetallic Pt–Ir catalysts as reforming catalysts have shown that such catalysts are more active and less prone to coke formation compared to pure Pt [27–31]. In contrast to other promoting elements, Ir is unique in that it is capable of alkane activation [29,32–34]. It is also noted that promotion of Ir together with Sn has been shown to significantly improve propane dehydrogenation activity while suppressing hydrogenolysis and other side reactions [35,36]. Therefore, Pt–Ir catalysts represent an interesting system in which both metals are capable alkane activation, but in the absence of a promoter, suffer from low selectivity and stability.

The aim of the present work was to investigate the catalytic properties of Pt–Ir catalysts for ethane and propane dehydrogenation, and to compare their performance with Pt and Pt–Sn catalysts. Pt–Ir nanoparticles were prepared in colloidal suspension and then supported on calcined hydrotalcite (Mg(Al)O) using procedures described in Ref. [6]. This catalyst preparation procedure was employed in order to produce nanoparticles of nearly uniform particle size and composition. Density functional theory calculations of the energies and Gibbs free energies of ethane dehydrogenation were carried out using a Pt_3X ($X = Sn, Ir$) cluster to develop an understanding of the roles of Sn and Ir in enhancing catalyst activity for alkane dehydrogenation.

2. Experimental

2.1. Synthesis of platinum, platinum–iridium, and platinum–tin nanoparticles

Platinum nanoparticles were synthesized by reduction of a platinum acetylacetonate ($Pt(acac)_2$, 97%, Aldrich) dissolved in octyl ether (OE, 99%, Aldrich) by 1,2-hexadecanediol (HDD, 90%, Aldrich) in the presence of oleylamine (OAm, 70%, Aldrich) and oleic acid (OA, 99%, Aldrich) [37]. In a typical procedure, all of the components were added to a 25 mL three-necked flask and the resulting solution was heated to 563 K at a rate of 2 K/min and maintained at this temperature for 30 min before cooling down to room temperature. To produce Pt–Ir or Pt–Sn bimetallic particles, iridium acetylacetonate ($Ir(acac)_3$, 97%, Aldrich) or tin acetylacetonate ($Sn(acac)_2$, 99.9%, Aldrich), respectively, was added together with $Pt(acac)_2$ at the start of the synthesis in the appropriate ratio. Further details of the synthesis can be found in Table S1 of the Supporting information. All the experiments were conducted under Ar using a standard Schlenk line. After the solution had cooled to room temperature, a large amount of anhydrous ethanol was added in order to aid the separation of the Pt nanoparticles, which was achieved by centrifugation at 3000 rpm for 5 min. The solid material produced in this manner was dispersed in anhydrous toluene to form a stable colloidal suspension. Details concerning the preparation of all samples are listed in Table S1.

2.2. Synthesis of Pt/Mg(Al)O, PtIr/Mg(Al)O, PtSn/Mg(Al)O

Synthetic hydrotalcite ($Mg_6Al_2(CO_3)_3(OH)_6 \cdot 4H_2O$, 100%, Aldrich) was calcined in air at 823 K for 5 h at a rate of 5 K/min. In a typical procedure, an appropriate volume (5 mL) of the toluene suspension of Pt or Pt-X ($X = Ir, Sn$) particles dispersed in toluene was added to a suspension of 0.2 g Mg(Al)O in 10 mL anhydrous toluene. The mixture was stirred overnight before the resulting product was precipitated by adding three times the volume anhydrous ethanol and separated by centrifugation. The solid material was heated at 723 K for 1 h in air to remove the surface capping agents and then reduced in an atmosphere of H_2 in Ar (10 vol.%) at 873 K for 1 h.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 Discover GADDS Powder XRD equipped with a Cu Kα source (wavelength of 1.5418 Å). XRD scans were recorded digitally with a step size of 0.02 and evaluated with profile fitting methods. Transmission electron microscopy (TEM) was carried out at the Electron Microscopy Laboratory of the University of California, Berkeley using a FEI Tecnai 12 transmission electron microscope. The samples were prepared by adding ethanol (2 mL) to the colloid (1 mL), and the mixture was centrifuged to separate the particles. The black precipitate was re-suspended in 2 mL of toluene, and

0.1 mL of this solution was further diluted with 2 mL of toluene; 10 μL of the suspension was dropped onto a lacey carbon copper grid. For the supported catalysts, 10 mg of the catalyst was ground in 5 mL of ethanol and 20 μL of the suspension was dropped onto a lacey carbon copper grid.

The Pt, Ir, and Sn contents of the bulk catalysts were determined by inductively coupled plasma—optical emission spectrometry (ICP-OES) by Galbraith Laboratories, Knoxville, TN. Elemental maps were recorded with a custom-modified FEI Titan electron microscope equipped with a Bruker Nano EDS detector at the National Center for Electron Microscopy. Maps were recorded at 200 kV at a beam current of 0.5 nA in the STEM mode after selecting a region of the sample by using the HAADF image. All elemental maps used a pixel dwell time of 150 ms with averaging of at least 100 frames with drift compensation. Bruker ESPRIT software package was used to quantify the maps by fitting and subtracting the Bremsstrahlung background using regions without peaks. After this step, the Pt Lα emission peak at 9.439 keV and the Ir Lα peak at 9.175 keV were integrated and converted to atomic compositions by using Cliff–Lorimer factors.

2.4. Catalyst testing

Ethane and propane dehydrogenation was carried out in a fixed-bed, quartz reactor (7 mm internal diameter). In a standard procedure, the catalyst materials were pressed, crushed, and sieved into small pellets (250–500 μm in diameter). Prior to testing, the pelletized catalyst was heated at 723 K overnight in air to remove possible moisture from the support. The catalyst was heated to 873 K (15 K/min) in 1 atm 20% H_2 in He using a three-zone furnace and then maintained at 873 K for 1 h to fully reduce it. A feed containing alkane, hydrogen, and helium was used to determine the activity, selectivity, and stability of all Pt/Mg(Al)O and PtX/Mg(Al)O ($X = Ir, Sn$) samples for ethane and propane dehydrogenation. The partial pressure of the alkane and the H_2/alkane ratio were fixed at 0.202 bar and 1, respectively. The reaction products were analyzed on-line by a gas chromatography–mass spectrometer (GC–MS, Varian, Model 320). A flame ionization detector (FID) was used to quantify the concentrations of all organic compounds eluting from the capillary column. Rates were normalized per gram Pt in the catalyst.

2.5. DFT calculations

The theoretical examination of ethane dehydrogenation on Pt and its alloys was conducted along the lines of a previous computational study [21]. Tetrahedral arrangements of pure platinum, Pt_4, and alloys, Pt_3X ($X = Ir, Sn$) were chosen to represent the catalyst [21]. The minimum energy configurations for the Pt_4, Pt_3Ir and Pt_3Sn correspond to a spin triplet, quartet and singlet, respectively.

All calculations were performed using the Q-Chem software package [38], with the ωB97X functional [39], and the triple-zeta valence basis set of Weigend and Ahlrichs [40], from which the f-functions were removed for performance reasons. The Stuttgart/Köln effective core potential [41,42] was used for all metals. The transition states for the rate-limiting step, the first C–H bond breaking, were calculated using the freezing string method [43,44].

Vibrational frequency calculations were performed on all structures, in order to verify the nature of stationary points as well as to calculate thermodynamic corrections. Vibrational analysis showed several low vibrational frequencies, corresponding to hindered or rocking modes of ethane relative to the metal cluster. The most commonly employed approximation of a rigid rotor-harmonic oscillator (RRHO) can yield erroneous thermodynamic corrections for low-lying frequencies. Therefore, the quasi-harmonic interpo-