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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Selection of oxide supports to anchor desirable bimetallic structures for ethanol reforming and 1,3-butadiene hydrogenation

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ABSTRACT

Ethanol reforming and 1,3-butadiene hydrogenation reactions were studied on Pt-Ni bimetallic and monometallic catalysts supported on several supports, including γ -Al₂O₃, SiO₂, TiO₂, CeO₂, and high surface area (HSA) and low surface area (LSA) ZrO₂, to elucidate the effect of oxide supports on the bimetallic structures and catalytic activity. The catalysts were prepared by co-impregnation and were characterized by pulse CO chemisorption, transmission electron microscopy, and extended X-ray absorption fine structure. Reactions were carried out in a Fourier transform infrared batch reactor. The supports strongly affected the catalytic activity. For ethanol reforming, the activities of the Pt-Ni bimetallic catalysts were in the order TiO₂ > SiO₂ > γ -Al₂O₃ \approx LSA-ZrO₂ > CeO₂ > HSA-ZrO₂; while for 1,3-butadiene hydrogenation, the order was SiO₂ > CeO₂ > γ -Al₂O₃ > LSA-ZrO₂ > HSA-ZrO₂ \approx TiO₂. For the hydrogenation reaction, the Pt-Ni bimetallic catalysts outperformed the Pt and Ni monometallic catalysts; in contrast, for the reforming reaction, synergistic bimetallic effects were only found on SiO₂, TiO₂, and HSA-ZrO₂.

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1. Introduction

Bimetallic catalysts are used in many reactions such as hydrogenation, dehydrogenation, and reforming because their properties are often different from those of the corresponding monometallic catalysts [1–3]. Many experimental and theoretical studies have been performed to determine the activity and stability of bimetallic systems on well-defined single crystal surfaces [3–5]. The bimetallic structure strongly affects catalytic performance. For example, the Ni-terminated bimetallic

surface, with a monolayer of Ni atoms located on a Pt(111) surface, is characterized by increased interactions with adsorbates and is more active for oxygenate reforming than either of the parent metals [6–8]. In contrast, the Pt-terminated bimetallic surface, with Ni atoms located underneath the Pt(111) surface, shows a novel low-temperature hydrogenation pathway that is absent on either Pt(111) or Ni(111) [5]. These surface science results have been extended to γ -Al₂O₃ supported Pt-Ni bimetallic catalysts for hydrogenation reactions, where Pt-terminated bimetallic catalysts show higher hydro-

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genation activity than either of the monometallic catalysts [9,10].

The thermodynamically preferred configuration of the Pt-Ni bimetallic catalyst depends on the reaction environment. The Pt-terminated configuration is stable in vacuum or under a hydrogen environment; however, in the presence of adsorbed atomic oxygen, Ni atoms segregate to the surface to produce the Ni-terminated configuration [4]. The interactions between the metals and the support may also affect the configuration of the Pt-Ni bimetallic catalyst, which in turn should affect the catalytic activity for specific reactions.

Supported catalysts often exhibit different catalytic performance, depending on the nature of the support materials. For hydrogenation activity of acetone over Pt/Ni, Qi et al. [11] found that Pt-Ni/SiO₂ bimetallic catalysts exhibited significantly higher activity than Pt-Ni/ γ -Al₂O₃ and Pt-Ni/TiO₂. For reforming reactions, Menezes et al. [12] found that Pt/MgO and Pt/ZrO₂ presented better activity than Pt/Al₂O₃ and Pt/CeO₂, and correlated this effect to the strong electron-donating character of MgO and ZrO₂.

In our previous work, TiO₂ and γ -Al₂O₃ were used to study the effect of oxide supports on stabilizing desirable Pt-Ni bimetallic structures for hydrogenation and reforming reactions [13]. In the current study, ethanol reforming and 1,3-butadiene hydrogenation were used as the probe reactions to further study the effects of other oxide supports for Pt-Ni bimetallic catalysts. The oxide supports were TiO₂, γ -Al₂O₃, SiO₂, CeO₂, and ZrO₂ (both high surface area ZrO₂ (HSA-ZrO₂) and low surface area ZrO₂ (LSA-ZrO₂)). We found that the oxide supports strongly affected the catalytic activity, and that the effects were different for reforming and hydrogenation reactions. The supported catalysts were characterized using transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS) measurements to better understand the differences in activity.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnation methods. The supports, γ -Al₂O₃ (surface area: 80–120 m²/g), amorphous SiO₂ (175–225 m²/g), CeO₂ (35–45 m²/g), HSA-ZrO₂ (100–200 m²/g), LSA-ZrO₂ (20–30 m²/g), and amorphous anatase TiO₂ (180–300 m²/g), were purchased from Alfa Aesar. The X-ray diffraction (XRD) patterns of the LSA-ZrO₂ and HSA-ZrO₂ supports were reported in our previous paper [14]. The γ -Al₂O₃, SiO₂, and CeO₂ supports had standard XRD patterns. Precursor solutions were made by adding the necessary volume of deionized water to Pt(NH₃)₄(NO₃)₂ (Alfa Aesar) and Ni(NO₃)₂·6H₂O (Alfa Aesar) precursor salts. For high surface area supports (γ -Al₂O₃, SiO₂, HSA-ZrO₂, TiO₂), incipient wetness impregnation was used, while, for low surface area supports (CeO₂, LSA-ZrO₂), slurry phase impregnation was used. All the bimetallic catalysts were synthesized using co-impregnation. After impregnation, the catalysts were dried at 373 K for 10 h and then calcined at 563 K for 2 h. For the monometallic catalysts,

the metal weight loading was 1.7% Pt or 1.5% Ni. For the bimetallic catalysts, the loadings were 1.7% Pt and 1.5% Ni, corresponding to a Pt:Ni atomic ratio of 1:3.

2.2. Catalyst characterization

2.2.1. Pulse CO chemisorption

To determine the number of active sites available on the catalyst, CO uptake was measured using an AMI-200ip (Altamira Instruments, Pittsburgh, USA). Approximately 100 mg catalyst was loaded into a quartz reactor and reduced under 50% H₂/He mixture (40 mL/min) at 723 K for 1 h. After cooling in He, pulse CO chemisorption was performed at room temperature using pulses of 37 cm³/min CO in a He carrier gas. A thermal conductivity detector (TCD) was used to monitor the flow of CO out of the quartz reactor. Metal dispersion was calculated assuming a stoichiometry of M:CO = 1:1 (M = Pt, Ni).

2.2.2. TEM

TEM analysis was performed using a JEOL 2010F equipped with a Schottky field emission gun operated at 200 keV. Imaging was performed in scanning mode using a 20 nm camera length and a 0.5 nm diameter nanoprobe. Reduced catalyst samples were prepared by grinding and suspending the catalysts in ethanol, followed by dropping a small amount of this solution onto a carbon-coated copper grid. The grid was allowed to dry before loading the sample into the TEM.

2.2.3. EXAFS

To confirm the presence of Pt-Ni bimetallic bonds, EXAFS measurements of the Pt L_{III}-edge were performed on the X18B and X19A beamlines at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, USA. The catalysts were reduced under 5% H₂/He flow (40 mL/min) at 723 K for 1 h, and data were collected at room temperature. The incident and transmitted X-ray signals were collected with ionization chambers while the fluorescence signal was collected using a 12-channel germanium detector. The EXAFS spectra from the samples were calibrated to the Pt L_{III}-edge energy from a Pt reference foil collected in transmission mode. Details of the data analysis were reported in our previous work [9].

2.2.4. In-situ Fourier transform infrared (FT-IR) batch reactor

FT-IR spectroscopy was used to monitor the gas-phase concentrations of reactants and products during reaction. Spectra were recorded at a resolution of 4 cm⁻¹ using a Thermo Nicolet Nexus 470 spectrometer equipped with a mercury cadmium telluride (MCT-A) detector. The procedures for preparing samples, details of the sample holder, and the reduction conditions have been previously reported [9]. For each reaction experiment, ~25 mg of the supported catalyst was loaded into the IR cell. The catalyst was reduced by 30 Torr H₂ at 723 K. The details of the reduction were reported elsewhere [13].

For ethanol reforming, ethanol vapor and water vapor were mixed at a partial pressure ratio of 1:3, corresponding to the stoichiometry of ethanol reforming, C₂H₅OH + 3H₂O → 2CO₂ + 6H₂. To start the reaction, the reactant gas mixture was quickly

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