Cyclotrimerization of Acetylene to Benzene on Au-Pd

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Introduction

Benzene has become essential to our chemical industry and is currently utilized in the manufacturing of dyes, explosives, detergents, and pharmaceuticals. The most widely used process for the production of benzene is the reforming of naphtha, an energy intensive process. It has been recently reported that acetylene can be cyclotrimerized to form benzene on Pd-based catalysts [1,2]. In this work acetylene cyclotrimerization on Pd/Mo(110) and Au-Pd/Mo(110) has been investigated using temperature programmed desorption (TPD) and steady-state kinetic measurements at realistic reaction conditions. The surface composition of a model catalyst was monitored with Auger electron spectroscopy (AES), low energy ion scattering spectroscopy (LEISS), and X-ray photoelectron spectroscopy (XPS); the adsorption/reaction site was determined using infrared reflection absorption spectroscopy (IRAS) with CO as a probe. [3]

Materials and Methods

The apparatus for these studies consists of a vacuum chamber containing a commercial PHI 5500 surface analytical instrument and a sample preparation chamber (base pressure of 10^{-10} Torr). The sample was mounted on a retraction bellows allowing an *in vacuo* transfer of the catalyst from the surface analysis chamber to the reactor (pressure range from 10^{-10} – 1000 Torr). The surface composition was determined using X-ray photoelectron spectroscopy (XPS) with a Mg–Kα source (300 W) and a pass energy of 58.7 eV. Analysis of products was carried out online using a Varian Star 3400 CX series gas chromatograph (GC) contiguous to the reactor. A sample aliquot was injected into the GC after liquid N_2 condensation following a reaction. Research grade acetylene (99.999%) was obtained from Matheson Tri-gas and cleaned by submerging the bulb in a liquid nitrogen/pentane bath. GC was used to verify the purity of the gases.

The single crystal Mo(110) catalyst used in this study was a 10 mm diameter, 1 mm thick disk. The temperature was measured during the reaction and pretreatment using a W/5% Re-W/26% Re thermocouple spot welded to the back side of the single crystal. The Mo(110) was cleaned by annealing in $5x10^{-8}$ Torr of O_2 for 10 minutes and then flashing to 2300K *in vacuo*. Au and Pd were vapor deposited onto the Mo(110) altering the deposition time to vary the Au – Pd ratio. A typical reaction time was 3 hours at a total pressure of 10 Torr. The products were condensed in a sample loop with liquid nitrogen and injected into the GC for analysis after the reaction [4].

Results and Discussion

Surface analytical studies show that a stable surface alloy of Au and Pd on Mo(110) forms upon annealing between 700 – 1000 K. A previously published [3] surface versus bulk phase diagram was used to assess the fraction of surface Pd present in these studies. This methodology allows the synthesis of Pd/Au surfaces with specific compositions and thus subsequent kinetic measurements as a function of composition. At all composition studied an Au/Pd surface is more active than a pure Pd surface for acetylene cyclotrimerization to benzene. These studies suggest that an isolated Pd (a Pd surrounded by six Au atoms) is an active site for acetylene trimerization. Figure 1 shows that on the Au/Pd surface benzene evolution occurs at a lower temperature compared to pure Pd, consistent with weaker binding of benzene to the bimetallic surface and thus to reduced dissociation, i.e. carbon formation.[3]

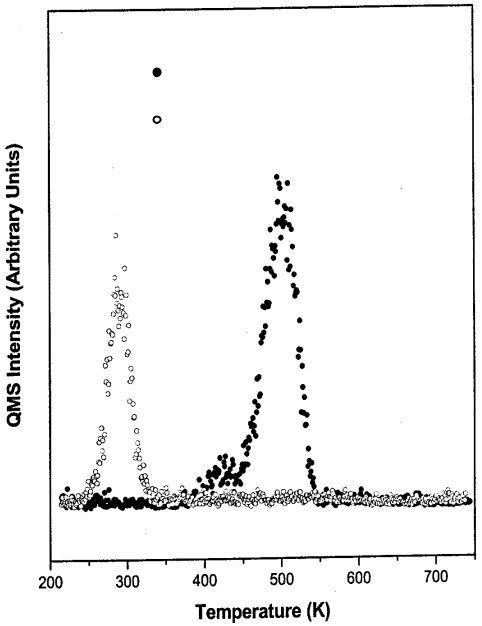

Figure 1. TPD of benzene on 10ML of Pd/Mo(110) compared with 5ML Au/5ML Pd/Mo(110)

Significance

A PdAu bimetallic catalyst was found to be more active for acetylene trimerization to benzene than is a pure Pd catalyst. This enhanced activity is attributed to the formation of isolated Pd sites, i.e. a Pd atom surrounded by Au atoms.

References

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