

Propane Dehydrogenation to Propylene on Ni and Ni-Sn Catalysts

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Introduction

Propylene is used in the production of many high-volume chemicals, such as polypropylene and other polymers, propylene oxide, propionaldehyde, acrolein, acrylonitrile and acetone. Since the demand for propylene is projected to increase steadily, it is highly desirable to develop efficient technologies for the direct conversion of propane to propylene. Current commercial technologies for non-oxidative propane dehydrogenation to propylene ($C_3H_8 = C_3H_6 + H_2$) over CrO_x or Pt-Sn catalysts have disadvantages due to catalyst coking and sintering of the active metals. The need for continuous catalyst regeneration complicates the process and increases energy consumption. In addition, high reaction temperatures of 800-980 K further increase energy consumption.

Ni is cheaper than Pt and less hazardous than Cr. However, pure Ni catalyzes only propane decomposition with C-C bond breaking. In this work, reaction testing of Ni, Ni-Sn and Sn catalysts demonstrates that Ni-Sn is highly selective in catalyzing propane dehydrogenation to propylene. The reasons why the reaction products change dramatically after Sn addition to Ni were identified by studying differences in propylene adsorption at the molecular level on Ni and Ni-Sn single-crystal surfaces with temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS) and density functional theory (DFT) calculations.

Materials and Methods

Ni/SiO₂, Ni-Sn/SiO₂ (1:1 atomic Ni to Sn surface ratio) and Sn/SiO₂ catalysts were prepared using an incipient wetness impregnation method. Ni particles in both Ni and Ni-Sn catalysts had an average size of 20 nm based on H₂ TPD and transmission electron microscopy (TEM) measurements. The catalysts were tested in a fixed-bed flow reactor with 20% C₃H₈/Ar. Propylene adsorption and surface reactions were studied using well-defined single-crystal surfaces of Ni(110) and c(2×2)-Sn/Ni(110) (1:1 atomic Ni to Sn surface ratio, the same as in the Ni-Sn/SiO₂ catalyst). Propylene TPD experiments were performed in a three-level, stainless-steel ultrahigh vacuum (UHV) chamber, with the sample in the line of sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer. The IRAS experiments were performed in a separate UHV chamber using a Bruker Vertex 70 instrument with a grazing incidence of 75° from the surface normal and a liquid nitrogen cooled mercury-cadmium-telluride detector. Gradient-corrected periodic DFT calculations with the DMol³ code were performed for determining geometries, adsorption energies and vibrational frequencies for propylene on Ni(110) and c(2×2)-Sn/Ni(110) surfaces, the same single-crystal surfaces that were used in the experimental TPD and IRAS measurements.

Results and Discussion

Reaction products change significantly from mostly methane, hydrogen and surface carbon over Ni to propylene and hydrogen over Ni-Sn (Figure 1). Propylene formation over Ni-Sn starts at a moderate temperature of 630 K. Since the activity of Sn by itself is low, Sn serves as a promoter for Ni. The promoter effects are attributed to a lower adsorption energy of molecularly adsorbed propylene and suppression of propylidyne formation on Ni-Sn based on TPD and IRAS measurements as well as DFT calculations. On Ni, propylene forms a π -bonded structure with $\nu(C=C)$ at 1506 cm⁻¹, which desorbs at 170 K, and a di- σ -bonded structure with $\nu(C=C)$ at 1416 cm⁻¹, which desorbs at 245 K. The di- σ -bonded structure is asymmetric, with the methylene C being in the middle of the Ni-Ni bridge site, and the methylidyne C atom being above one of these Ni atoms. Therefore, this structure can also be characterized as a hybrid between di- σ - and π -bonded structures. Only a fraction of propylene desorbs from Ni because propylene can convert into propylidyne, which decomposes further. In contrast, propylene forms only a π -bonded structure on Ni-Sn with $\nu(C=C)$ at 1506 cm⁻¹, which desorbs at 125 K (Figure 2). The low stability of this structure enables propylene to desorb fully, resulting in high reaction selectivity in propane dehydrogenation to propylene over Ni-Sn.

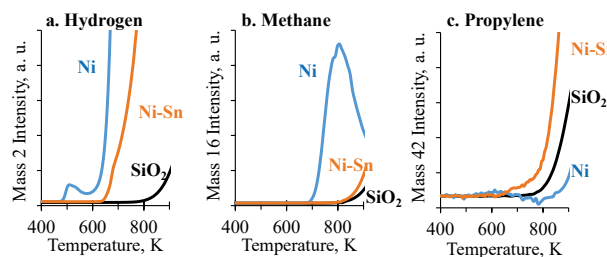


Figure 1. Mass spectra for temperature programmed reaction of propane for Ni/SiO₂ and Ni-Sn/SiO₂ catalysts and SiO₂ support. The results for Sn/SiO₂ (not shown) were similar to those for SiO₂.

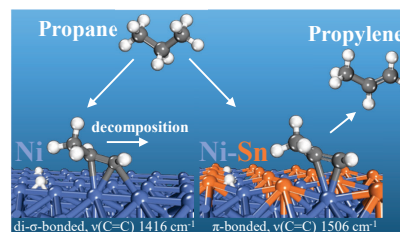


Figure 2. Experimental and computational results show that on Ni, propylene adsorbs strongly and converts into propylidyne, which decomposes further. In contrast, on Ni-Sn, propylene forms a weakly bonded structure which desorbs fully, resulting in high reaction selectivity in propane dehydrogenation to propylene over the Ni-Sn catalyst.

Significance

Ni-Sn is identified as a highly selective catalyst for the direct propane dehydrogenation to propylene. The high reaction selectivity is due to the lower stability of molecularly adsorbed propylene and suppression of propylidyne formation in the presence of Sn. These findings will be useful in the development of improved catalysts for propane dehydrogenation to propylene and multiple other hydrocarbon reactions that require selective activation of C-H bonds without breaking C-C bonds.