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HYDROGENOLYSIS AT Sn/GROUP VIII SURFACE ALLOYS

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Catalysis at Experimentally Designed Surfaces: n-Butane Hydrogenolysis at Sn/Group VIII Surface Alloys

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Abstract

Bimetallic $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/M(111) [M=Ni, Pt] surface alloys have been prepared in an ultrahigh vacuum system and used in model moderate pressure (1-200 Torr) catalytic reactions. Hydrogenolysis of n-butane ($H_2/n\text{-C}_4 = 20$) has been used to characterize the effects of ordered bimetallic ensembles relative to those available at the respective (111) surfaces. The effect of alloying Sn into the Ni(111) surface produced an overall lowering of the catalytic reactivity nearly equal to the number of Ni surface sites lost upon producing the $\sqrt{3}\times\sqrt{3}R30^\circ$ surface alloy. In addition, the overall rate of hydrogenolysis of n-butane at the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy was also found to have decreased (although not in proportion to the loss of total Pt atoms). Catalytic deactivation due to carbon buildup was observed to decrease significantly at both of the ordered $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/M(111) surface alloys under reaction conditions.

1.0 Introduction

Bimetallic Sn/Pt group catalysts are commonly used in the processing of petrochemicals [1]. However, the catalytic effect created by alloying Sn with the Group VIII metal is not fully understood. Sinfelt has postulated [1] that ensemble formation during the alloying process leads to enhanced selectivity for hydrocarbon isomerization in preference to the undesired hydrogenolysis reactions in petrochemical reformation. However, a detailed molecular description of the chemical reactions based on the specific bimetallic ensemble formation has not been elucidated. In this study the formation of contiguous metal atom ensembles on the (111) faces of Pt and Ni through thermal annealing of ultrathin Sn deposits will be reviewed in the context of their chemical reactivity for n-butane hydrogenolysis.

2.0 Experimental

The experiment was carried out on a UHV/Microreactor instrument equipped with AES, XPS, LEED, TDMS and inert gas LEISS characterization capabilities that has been described in detail before [2-4]. Surface preparations, reagents, and characterization of the specific $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/M(111) surface alloys are described elsewhere [4,5]. For batch catalytic reactions the surface alloys were prepared on both sides of the initial single crystal templates. The hydrogenolysis and isomerization activation energies were determined for the single crystals and the

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Sn/Group VIII surface alloys at a total pressure of 210 Torr and a H₂/n-C₄ ratio of 20. Activity results for the reactions are based on the initial number of sites for the Ni(111) surface (1.88×10^{15} atoms/cm²), and the Pt(111) surface (1.505×10^{15} atoms/cm²). Activity results for the surface alloys are in relation to the respective single crystals from which they are derived.

3.0 Results and Discussion

Vapor deposition of Sn on the (111) surfaces of Pt, Pd and Ni with subsequent annealing to 1000K produces a sharp $\sqrt{3} \times \sqrt{3}R30^\circ$ LEED pattern as schematically depicted in figure 1 along with the idealized real space representation of the surface alloy [4-6]. The suggested real space surface alloy structure is based upon inert gas LEISS, LEED, and AES measurements for each individual case. Furthermore, for both of the $\sqrt{3} \times \sqrt{3}R30^\circ$ Sn/M(111) surface alloys, the Sn adatoms have been explicitly determined, by alkaline LEISS, to be nearly coplanar with the metal substrate adatoms (+0.2 Å Sn outward buckling for Pt and +0.4 Å for Ni [5,6]). These surfaces provide unique, well defined templates with exact surface arrangements of metal atoms upon which explicit chemical reactions can be conducted.

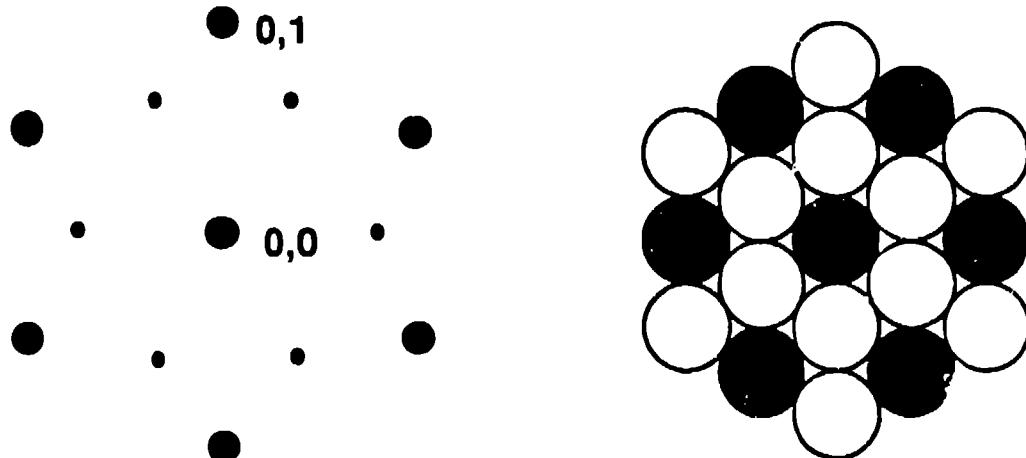


Figure 1 - LEED Pattern of $\sqrt{3} \times \sqrt{3}R30^\circ$ Sn/M(111) (M=Ni, Pt) (left) Surface Alloys and Real Space Model (right)

As an example, the hydrogenolysis of n-butane over the $\sqrt{3} \times \sqrt{3}R30^\circ$ Sn/M(111) [M=Ni, Pt] surface alloys was examined. An Arrhenius plot for the n-butane hydrogenolysis reaction over the Ni(111) and the $\sqrt{3} \times \sqrt{3}R30^\circ$ Sn/Ni(111) is shown in Fig. 2. The activation energy of the reaction was calculated to be 150 kJ for both surfaces. For both the clean Ni and the $\sqrt{3} \times \sqrt{3}R30^\circ$ Sn/Ni(111) surface alloy the reaction proceeded by multiple hydrogenolysis (e.g., C₄ cleavage down to C₁ fragments) with exclusive production of methane. After reaction, the Ni(111) surface was found to be deactivated because of carbon buildup. In fact, after an initial batch reaction over Ni(111), the reactivity drops by at least three orders of magnitude if subsequent reactions are attempted without cleaning the surface. Post-reaction examination using AES also confirmed the accumulation of C (data not shown for brevity). In contrast, no apparent deactivation was observed for reactions conducted using the $\sqrt{3} \times \sqrt{3}R30^\circ$ Sn/Ni(111) surface alloy even after

several reaction runs, provided that the temperature remained below 625K. For reactions above 625K, rapid C buildup was observed on the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Ni(111) surface alloy. Note also that the Arrhenius plot exhibits a strong break in activity above this temperature.

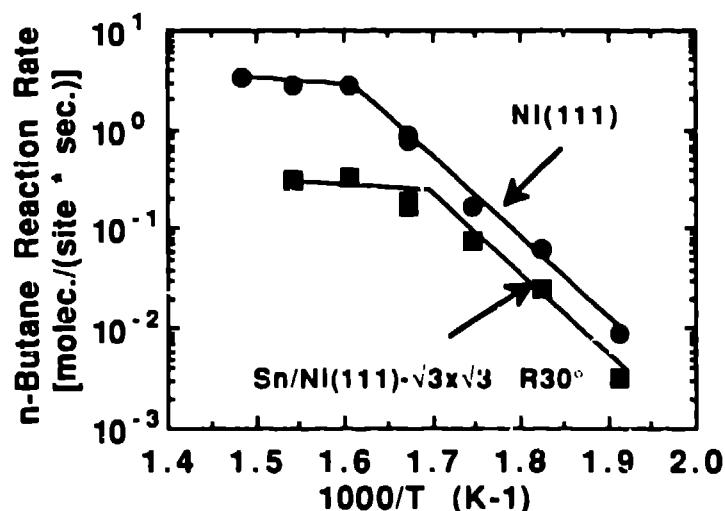


Figure 2 - Specific reaction rates for the hydrogenolysis of n-butane at Ni(111) and the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Ni(111) surface alloy

The rates of n-butane hydrogenolysis at the Pt(111) and the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy are shown in Fig. 3. The activation energy was determined to be 115 kJ/mole for both the Pt(111) and the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy.

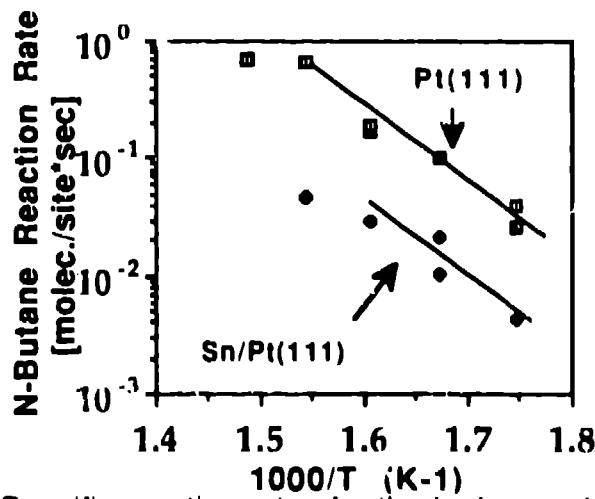


Figure 3 - Specific reaction rates for the hydrogenolysis of n-butane at Pt(111) and the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy

It is quite evident that the presence of Sn in the surface alloy lowers the activity towards hydrogenolysis by approximately an order of magnitude. The Pt(111) surface exhibits multiple hydrogenolysis over the temperature range of this investigation. Hydrogenolysis of n-butane at 573K produced a selectivity (mole %)

of 55 CH₄, 28 C₂H₆, and 16 C₃H₈; however, only a small amount of isobutane was observed above the background impurity level (isobutane < 1 mole %). The $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy produced only methane and isobutane (no C₂ or C₃ fragments). At 573K, the temperature at which maximum isobutane production is attained, the mole percentages were determined to be 75 methane and 25 isobutane.

The selectivity and activation energy observed for n-butane hydrogenolysis at the Ni(111) surface are comparable to those previously seen for Ni films and for Ni supported on alumina [7,8]. In fact, the Ni films results produced an activation energy of 140 kJ/mole and a selectivity of greater than 90% for CH₄ above 500K [7]. At the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Ni(111) surface alloy the n-butane hydrogenolysis activity was diminished by approximately the number of displaced surface Ni atoms. Evidently the adsorption and reaction site requirements of the n-butane (and further reaction intermediates) were not sterically hindered by the inclusion of Sn atoms in the surface plane, even though a 0.4Å outward buckling exists for this surface alloy [6]. Carbon buildup was significantly lower at the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Ni(111) surface alloy as examined post-reaction by AES. Previous catalysis studies using Ni alloy surfaces have also demonstrated this [9,10].

The activity for n-butane hydrogenolysis at Pt(111) is quite comparable to that of a supported Pt/SiO₂ catalyst [11], and the selectivity is near that reported by Anderson for Pt thin films [8,12]. However, previous single crystal results have shown higher levels of isomerization than seen here [13]. Although our results match those seen on thin films and supported catalysts, the slight isobutane impurity can not be excluded as an inhibitor of this reaction. Hydrogenolysis of n-butane at the $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy produces a dramatic lowering in overall activity and an increase in the isomerization activity. The $\sqrt{3}\times\sqrt{3}R30^\circ$ -Sn/Pt(111) surface alloy, however, shows an increased isomerization activity but at lower rates than can be accounted for by loss of surface Pt atoms. This suggests that the electronic effects of Sn in the surface plane are clearly perturbing the surface reaction chemistry. Very carefully controlled surface science experiments using thermal desorption mass spectroscopy and surface vibrational probes have recently shed light on these perturbations [14].

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