

Atomic-Scale Site Isolation in a Model AuPd Catalyst

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Introduction

In heterogeneous catalysis, while specific reaction ensembles are frequently discussed [1], to date direct atomic control of specific sites has not yet been reported. Here we present scanning tunneling microscopic (STM) images of a Pd monomer-pair catalytic site on a AuPd(100) bulk alloy surface that is highly selective for vinyl acetate synthesis from ethylene and acetic acid [2]. We also demonstrate that our sample preparation method has a direct effect on the surface Pd distribution, which is far from random with a marked preference for the local $c(2 \times 2)$ configuration, i.e., a monomer-pair configuration. Moreover, we show that using the unique thermodynamic properties of AuPd mixtures, it is possible to control the distribution of Pd atoms globally, and thus isolate preferred catalytic sites potentially for optimum catalytic selectivity [3].

Materials and Methods

The experiments were performed in ultrahigh vacuum (UHV) at room temperature, using an Omicron VT-STM. The AuPd(100) bulk alloy single crystal was purchased from Matek, and the ordered surface was obtained through sputter-anneal cycles. The sample was equilibrated at 820 K (as measured by an IR pyrometer) before imaging. The STM images were processed to enhance chemical contrast between Au and Pd atoms. The geometric configuration of each Pd atom was determined and totaled as occurrence, which was then compared to the calculated probability of the corresponding configuration, assuming a complete random distribution. This comparative process was done for the AuPd(100) surface studied here, as well as for a previously imaged Au₃Pd(100) surface [4].

Results and Discussion

STM images of AuPd(100) showing chemical contrast between Au and Pd atoms (Fig. 1) indicate Pd arrangements that deviate significantly from a random distribution (Fig. 2B). In contrast the previously imaged Au₃Pd(100) surface (Fig. 2A) shows a more random distribution of Pd sites. For the AuPd(1 : 1) alloy, the preferred configurations are all related to the $c(2 \times 2)$ structure with respect to the surface lattice, i.e. similar to the monomer-pair catalytic site. The different distributions of the two surfaces can be understood by their respective thermodynamic properties [5] and the surface preparation methods. The local $c(2 \times 2)$ Pd arrangement of AuPd(100) is due to its equilibration temperature above the critical temperature, where short-range order (SRO) is dominant and long-range order is absent. The SRO is the key property that allows control of isolated Pd sites over this surface.

Significance

Our findings demonstrate that known thermodynamic properties of solid mixtures can be utilized to control surface site isolation globally, on the atomic scale. This method differs from previous examples of site isolation in that it does not rely exclusively on

randomness. The use of SRO—an inter-atomic property—allows for direct control over the degree of randomness. We believe that this method will impact catalysis (e. g. design of novel model catalysts) as well as other technological areas involving a “bottom up” approach to custom surfaces, e.g. self-assembly, or molecular electronics.

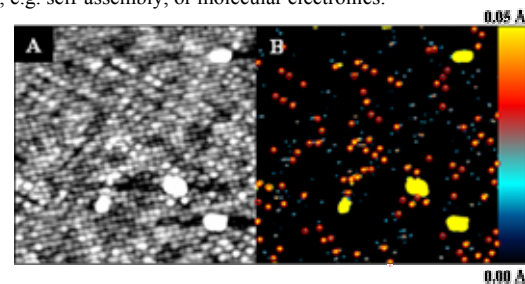


Figure 1. (A) STM image of AuPd(100) showing chemical contrast. (B) Same image processed to differentiate Pd (yellow) from the Au surface atoms (masked in black).

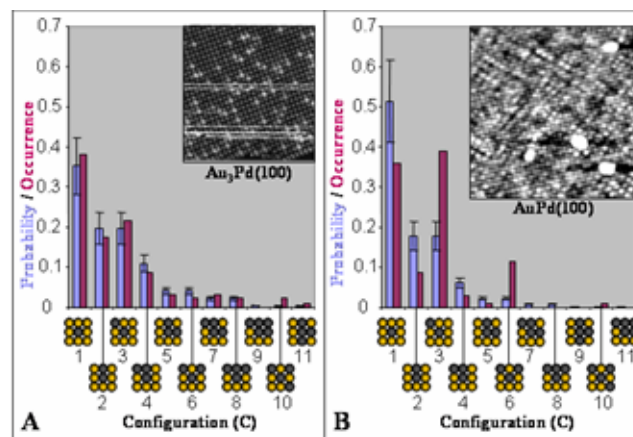


Figure 2. Comparison of Pd distributions between (A) Au₃Pd(100) and (B) AuPd(100). The distribution in (A) is clearly more random than that in (B). Preferred Pd arrangements in (B) are C = 3 and 6. The image in (B) is the same image shown in Fig. 1.

References

- 1 Bell, A. T., *Science* 299, 1688 (2003).
- 2 Chen, M. S. *et al.*, *Science* 310, 291 (2005).
- 3 Callahan, J. L., and R. K. Grasselli, *AIChE J.* 9, 755 (1963).
- 4 Aschoff, M. *et al.*, *Surf. Sci.* 415, L1051 (1998).
- 5 Okamoto, H., and T. B. Massalski, *Bull. Alloy Phase Diagrams* 6 (1985).