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Summary Abstract: Interaction of NO with potassium and boron contaminated Rh surfaces

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(Received 15 September 1986; accepted 3 November 1986)

I. INTRODUCTION

Rhodium is one of the most important constituents in the automobile exhaust catalyst, and it is also effective in the transformation of synthesis gas into more valuable organic compounds. A great effort has recently been made to improve its catalytic performance by means of different additives. However, an understanding of the role of these additives requires the knowledge of their effects on the elementary steps (adsorption, dissociation, desorption, etc.) of the catalytic reactions. In the present paper we report on the influence of small amounts of boron and potassium on the interaction of NO with Rh surfaces. The effect of potassium was investigated on a Rh(111) face, while that of boron impurity on Rh foil. Boron-contaminated Rh was achieved by the segregation of boron from the bulk to the surface: the Rh foil was annealed at 750–1200 K. Potassium was deposited on a Rh(111) sample from the SAES getter source.

II. EFFECT OF BORON IMPURITY

Adsorption of NO on clean Rh foil at 300 K involves initial dissociation which is followed by the nondissociative adsorption of molecular NO. The presence of boron altered the surface behavior of Rh; the uptake of NO on boron-contaminated surface increased by about 30%–37%. The extent of dissociation (at saturation) also increased; at a higher boron impurity level (relative intensity of boron Auger signal, $R_B = B_{178}/Rh_{302}$ was 0.07) it was almost 98%. The extended dissociation of NO was exhibited by the decreased amount of NO desorbed (Fig. 1), by the less intense photoemission peak at 9.1 eV due to the 1π-5σ molecular orbital of adsorbed NO and by the enhanced intensity of the peak at 5.5–6 eV associated with adsorbed oxygen. The peak temperatures for desorption of molecularly adsorbed NO from boron-contaminated Rh were unaltered suggesting that this NO adsorbs and desorbs from Rh sites not influenced by boron impurity. However, the presence of boron greatly stabilized the adsorbed nitrogen and oxygen to the surface. This stabilizing effect was so great that the nitrogen (and oxygen) formed in the boron-promoted dissociation of NO did not desorb below 1200 K (Fig. 1).

This feature strongly suggests a direct interaction between NO and boron on the surface and the formation of very stable B–O and B–N bonds. The formation of the B–O species is supported by the appearance of a loss feature at 9.4 eV in the electron energy-loss (EEL) spectrum in the electronic range (which has been observed in the dissociation of CO_2, O_2, and H_2O on boron-contaminated Rh[1,2]) and by high-resolution Auger spectra. In the latter case two new Auger transitions appeared at 157 and 168–172 eV, which were also observed following the oxidation of boron.[3] In addition, the oxygen Auger feature was shifted from 520 to 513.7 eV. The formation of a B–N bond is indicated by EELS, by fine structure of Auger boron signal, and also by the great stabilization of N on the surface. Above 400 K a new loss appeared at 7.4 eV and a new intense Auger transition developed at 176 eV which is typical for B–N species.[4]

III. EFFECT OF POTASSIUM

Preadsorbed potassium exerted a drastic influence on the surface behavior of NO on a Rh(111) surface. The most important features were as follows: (i) potassium adatoms increased the uptake of NO; (ii) it promoted the dissociation of NO (Fig. 1); (iii) from $\theta_K = 0.17$ it induced the formation of a new, very stable adsorption state with $T_p = 700$–725 K; and (iv) the presence of NO altered the desorption behavior of potassium by greatly increasing the potassium binding energy. The desorption observed in the lower-temperature range ceased and potassium desorbed ($\theta_K > 0.17$) in two high-temperature peaks, $T_p = 870$ and 970 K.

The adsorption of NO on a K-dosed Rh(111) surface led to a much larger work function increase (max 1.2 eV at $\theta_K = 0.23$) as compared to the clean surface (0.65 eV). This indicates that in the presence of potassium an enhanced elec-

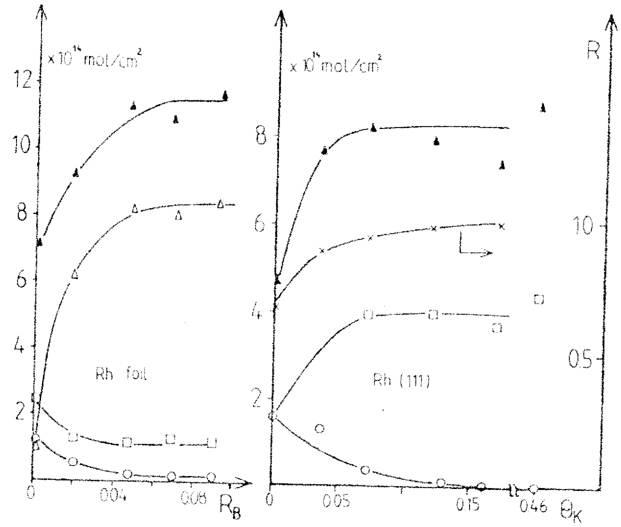

FIG. 1. Characteristic data for the effects of (a) boron and (b) potassium additives on the adsorption, dissociation, and desorption of NO. The uptake of NO at (▲) 300 K; the amount of nitrogen atoms remained adsorbed up to 1200 K (△); amounts of (□) N_2 and (○) NO desorbed. The extent of the dissociation of (×) NO.

0734-2101/87/040863-02$01.00

tron donation occurs from the K/Rh surface, very likely into the $2\pi^*$ orbital of the NO, which may lead to the formation of charged NO. We believe that this charge transfer is responsible for the enhanced dissociation of NO, as the formation of partially negatively charged NO species is accompanied by a considerable weakening of the N–O bond. Although the increased charge transfer from a K/Rh surface to the adsorbed NO strengthens the Rh–NO bond, we are of the opinion that the appearance of a new high-temperature state of NO ($T_p = 700$–725 K) is the result of the formation and decomposition of a stable surface compound between K and NO, similarly as in the case of a CO_2 + K/Rh(111) system.[5] The formation of this surface compound, very likely KNO_2 species, can cause the significant stabilization of potassium in the adsorbed layer. As the Rh(111) surface contains only adsorbed oxygen above 800 K, it is more likely that this adsorbed oxygen, and the formation of potassium oxide, are primarily responsible for the stabilization of potassium on the Rh(111) surface.

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Summary Abstract: The adsorption of simple molecules (H_2, O_2, CO) on Mn/Ru(001) surfaces

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(Received 22 September 1986; accepted 20 October 1986)

Among the 3*d* transition metals manganese has unusual physical properties and distinct chemical behavior, but its surface chemistry is still largely unexplored.[1-3] A need for a more precise understanding of its chemisorptive properties arises in view of recent discoveries of Mn based supported catalysts for the oxidative coupling of methane,[4,5] and cracking of low molecular weight paraffins.[6] So far the chemisorption studies were carried out on polycrystalline films[1,2] and bulk polycrystalline samples.[3] Although the ordered Mn overlayers grown on the oriented single-crystal surface were characterized structurally,[7,8] the adsorption properties of well-defined Mn layers are unknown. The selection of the Mn/Ru system was based on a recent report[9] on the epitaxial growth of the Mn overlayer onto Ru(001). In addition, the immiscibility of Mn and Ru facilitates the coverage determination, which is not complicated by the formation of the three-dimensional (3D) alloy.

The experiments described here were carried out under UHV conditions ($p_0 < 1 \times 10^{-10}$ Torr) using work function measurements ($\Delta\phi$), thermal desorption (TDS), ultraviolet photoemission spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED) for surface and adsorbates characterization. Mn was deposited from a shielded evaporator with a shutter and its coverages were determined by TDS and XPS.

Mn deposited onto Ru(001) at 300 K grows in 2D islands pseudomorphic with respect to the Ru(001) substrate. A complete two monolayers form first, followed by a disordered layer growth. The postdeposition anneal at 800 K leads to 3D Mn growth. Mn deposition is accompanied by a smooth work function decrease of 1.2 eV. Three desorption states are observed in TD spectra and assigned to the desorption from the first, second, and multilayer of Mn. The initial activation energy for desorption E_A of the first state is 71 kcal/mol, and multilayers desorb with zero-order kinetics and $E_A = 53.8$ kcal/mol. Despite the existence of Mn–Ru alloys[10] we found no evidence for Mn diffusion into Ru bulk.

In contrast to a clean Ru(001) surface, oxygen coadsorption on the ordered Mn monolayer leads to work function decrease with a minimum of 620 meV at oxygen exposure 4.5 L. For higher O_2 exposure we observe an increase of 300 meV and $\Delta\phi$ saturates at 12-L O_2. The $p(1\times1)$ LEED pattern disappeared rapidly before a minimum of $\Delta\phi$ was reached and no changes in the LEED were observed with increasing exposure to oxygen. Two oxygen desorption states with $E_A = 81$ and 68 kcal/mol are filled in sequentially; Mn desorbed simultaneously with strongly bound oxygen at temperature above the desorption temperature of a clean Mn layer. Changes in Mn 2*p* core levels after coadsorption of oxygen, namely, a positive binding energy shift of 1.8 eV and increased asymmetry of 2*p* levels together with a recession of the valence band from the Fermi level and a sharp peak at ~5 eV below E_F are consistent with the formation of the manganese oxide. From the measured concentration of coadsorbed Mn and O we estimate that surface stoichiometry of Mn:O is 1:1.8. Qualitatively similar behavior was observed for Mn multilayers and we conclude that oxygen is dissociatively chemisorbed, penetrates the Mn lattice, and forms the metal oxide.

Carbon monoxide coadsorption on the Mn monolayer leads to work function increase of 320 meV at saturation. The new high-temperature desorption state with estimated