

RKCL3260

THE EFFECT OF SURFACE ION-INDUCED DEFECTS ON CO ADSORPTION ON POLYCRYSTALLINE Ni

S.N. Trukhan and V.P. Ivanov

Boriskov Institute of Catalysis, Novosibirsk 630090, Russia

Received July 30, 1997

Accepted July 20, 1998

Abstract

CO adsorption on polycrystalline nickel was investigated by dynamic secondary ion mass-spectroscopy at 10^{-5} - 10^{-3} Pa and 300 - 500 K. An increase of secondary ion currents $\text{NiCO}^+ / \text{Ni}^+$ ratio was found in the range from 300 to 350 K, while at $T > 350$ K it decreased sharply. These data were explained by a kinetic model, in which adsorption and desorption of tightly bound CO goes through weakly bound CO formed due to ion-induced defects.

Keywords: Ion-induced adsorption, Ni, CO, defects

INTRODUCTION

CO adsorption on rough metal surfaces is known to differ from that on smooth ones. Previously, we found new CO_{ads} state induced by ion-induced defects with binding energy lower than on a smooth surface [1]. The formation of a weakly bound state was also observed during the CO adsorption on stepped faces of Ni(221), (331), (551) [2].

These facts differ from the CO adsorption on Pt foil, where defects result in the formation of a more tightly bound CO state [3].

The surface defects on Ni also affect the adsorption kinetics. In fact, the sticking probability of CO on the surface subjected to ion bombardment decreases from 0.9 [4,5] to 0.65 [1] in comparison with the CO sticking probability for low index faces. It is unusual that CO first adsorbs on the surface defects despite lower binding energy on defective sites [6,7].

In the present work we continue the investigation of the influence of ion-induced defects on the CO adsorption kinetics on polycrystalline nickel in the temperature range of 300 - 500 K.

EXPERIMENTAL

A description of the apparatus used in this work and sample preparation was reported elsewhere [1]. Here it is necessary only to note that now during experiments we could resistively heat the sample up to 1300 K. The temperature was measured with a W-Re thermocouple and stabilized within $\pm 3^\circ\text{C}$.

RESULTS AND DISCUSSION

The temperature dependence of the peak intensities ratio - $F(T) = I(\text{NiCO}^+) / I(\text{Ni}^+)$ is shown in Fig. 1. The following procedure was used for obtaining each value shown on the diagram. The sample was annealed in vacuum at 1050 K for 5 min. Then CO was introduced into the chamber during

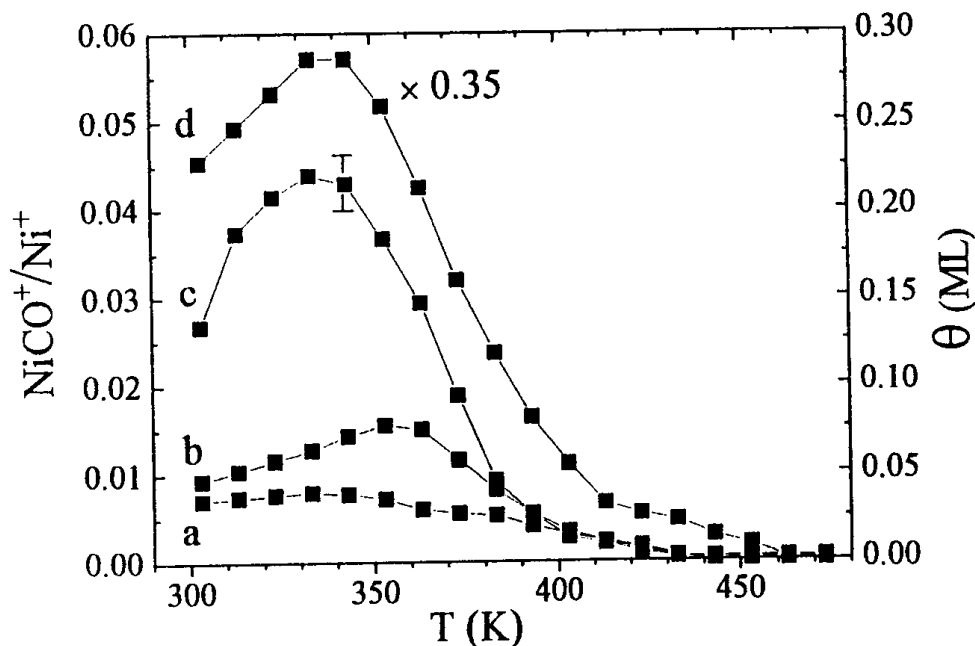
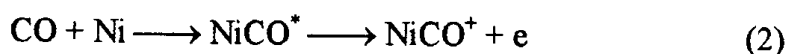


Fig. 1. Dependences of $F = I(\text{NiCO}^+) / I(\text{Ni}^+)$ and CO coverage on temperature during nickel bombardment with Ar^+ (4 keV, 45° , 0.02 A/m^2) ions at different CO pressures: (a) 4×10^{-6} ; (b) 10^{-5} ; (c) 2×10^{-5} ; (d) 2×10^{-4} Pa

the sample cooling up to a certain pressure at approximately 470 K, and the sample was further cooled to the desired temperature. As this temperature was reached, the ion gun was turned on and the signal registration was performed. F values shown in Fig. 1 within 10 % accuracy correspond to stationary values, which are set after a 100 - 500 s bombardment (doze $\sim 10^{20} \text{ m}^{-2}$).

One may see from Fig. 1 that there is a sharp increase of the ratio F in the range of 300 - 350 K.

The modeling of the secondary ion emission by the classical dynamics method shows that the NiCO^+ ion formation is caused by the reaction of a CO molecule with an emitted Ni^+ ion or Ni atom in a near surface layer [8]:



The equilibrium constants of the specified reactions will be written in the following way:

$$k_1 = \frac{[\text{NiCO}^+]}{[\text{Ni}^+]\cdot[\text{CO}]} \sim \frac{I(\text{NiCO}^+)}{I(\text{Ni}^+)\cdot\theta}, k_2 = \frac{[\text{NiCO}^+]}{[\text{Ni}]\cdot[\text{CO}]} \sim \frac{I(\text{NiCO}^+)}{I(\text{Ni}^+)\cdot\theta} \quad (3)$$

It follows from (3) that

$$F = \frac{I(\text{NiCO}^+)}{I(\text{Ni}^+)} \sim (k_1 + ak_2)\theta \quad (4)$$

i.e., ion current of NiCO^+ divided by Ni^+ is proportional to the CO coverage.

In fact, the proportionality of F to the CO coverage was revealed in a number of studies [9]. Since the temperature dependence of constants k_1 and k_2 is $k_0 \exp(-\Delta G/RT)$, the F value should also depend on the sample temperature. The investigation of the adsorbed CO layer on polycrystalline nickel by the static SIMS shows that the F value increases with the temperature rise from 295 to 365 K, while the CO coverage apparently decreases [10]. This fact also provides evidence for the "chemical" approach to the mechanism of the NiCO^+ ion formation.

Based on these assumptions, we suppose that F is proportional to the CO coverage. It was found that at $P_{\text{CO}} > 10^{-4} \text{ Pa}$ and $T = 300 - 350 \text{ K}$ the F value remains nearly constant and equal to 0.20 ± 0.03 . At such conditions the coverage should be close to saturated and therefore, $\theta = (5.0 \pm 0.6) \times F$.

Comparing the F values (Fig. 1) with the ones received by static SIMS for maximum CO coverages [10], one can see that our data have much more abrupt temperature dependence. It allows to neglect the temperature dependence of constants in eq. 4 in our case and consider that the raise of F in the range of 300 - 350 K is caused by the increase of CO coverage only.

It is not possible to explain such coverage rise by simple CO adsorption with a sticking probability about 1. Moreover, as the simulation shows, there is one more abnormality in the coverage dependence on temperature shown in Fig. 1. It is associated with a sharp coverage reduction at temperatures about 30 - 40 K lower than the calculations predict.

We tried to describe the F dependences within the framework of a kinetic scheme which includes adsorption in the tightly bound state CO_t through a weakly bound state CO_w as well as directly from gas phase CO_g :

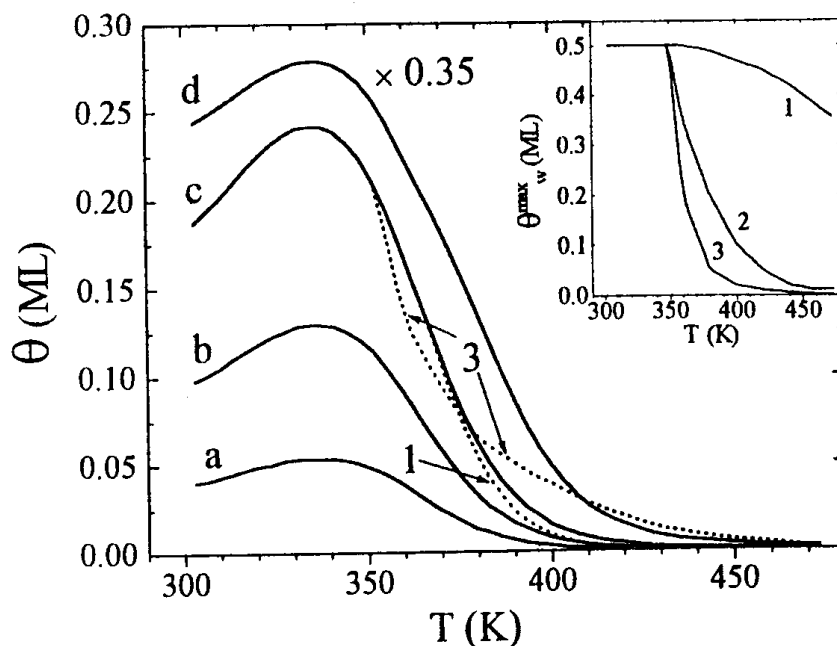
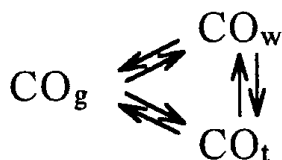


Fig. 2. Solid lines are calculated dependences of the CO coverage on T of nickel surface bombarded with argon ions at different CO pressures: (a) 4×10^{-6} ; (b) 10^{-5} ; (c) 2×10^{-5} ; (d) 2×10^{-4} (d) Pa. Dependences of $\theta_w^{\max}(T)$ presented on insert and labeled by number 2. See the text for values of kinetic parameters S_t , S_w , E_w^{dif} , D_w^0 , D_t^0 . Dashed lines are θ_{CO} dependences on T at $P_{\text{CO}} = 2 \times 10^{-5}$ Pa for $\theta_w^{\max}(T)$ 1 and 3

In the scheme we also took into account thermal and ion-stimulated desorption diffusive exchange between the adsorbed states and reduction of the concentration of defects during the temperature increase (see application).

As the calculations show, it is possible to describe the experimental data in the whole temperature range, if one accepts fit parameters equal to the following values only: CO sticking probability in the tightly and weakly bound states $S_t = 0.05 \pm 0.05$ and $S_w = 0.55 \pm 0.05$, pre-exponential factors for the CO diffusion from the tightly bound to the weakly bound state and back $D_t^0 = 10^{-(6 \pm 1)} \text{ m}^2/\text{s}$, $D_w^0 = 10^{-(9 \pm 1)} \text{ m}^2/\text{s}$, activation energy for diffusion from weakly bound to tightly bound state $E_w^{\text{diff}} = 67 \pm 5 \text{ kJ/mol}$ (diffusion energy for back hop - $E_t^{\text{diff}} = 96 \pm 5 \text{ kJ/mol}$ (see application)). Calculated curves $\theta(T)$ for the given values are shown in Fig. 2. The values of the given parameters actually mean that a direct adsorption $\text{CO}_g \rightarrow \text{CO}_t$ is practically impossible and the filling of the tightly bound state occurs only by the diffusive exchange with the weakly bound state.

The calculations also show that the desorption of the tightly bound state through the weakly bound one: $\text{CO}_t \rightarrow \text{CO}_w \rightarrow \text{CO}_g$ plays a basic role in the sharp fall of the CO coverage in the 350 - 400 K temperature range. This desorption pathway of the tightly bound state is a result of bombardment which leads to a continuous creation of surface defects.

Our values of the activation energy for the CO diffusion are higher and the values of the diffusion pre-exponential factor D_w^0 are lower than the ones known from literature: $E_a = (15 - 30) \text{ kJ/mol}$, $D^0 = (10^{-10} - 10^{-5}) \text{ m}^2/\text{s}$ [11]. The reason of the given discrepancy may be the fact that the group - CO molecule and ion-induced defect - is something average between a CO molecule adsorbed on a smooth surface and some molecular compound - Ni_nCO with $n > 1$. In such a case one of the stages of CO diffusion from a defective to a smooth site is the Ni_nCO decay. The activation energy of this process may be quite comparable with the value of $E_w^{\text{des}} = 105 \text{ kJ/mol}$ (see application). According to the Kassel model of monomolecular reactions, the pre-exponential coefficient for the decay rate of polyatomic molecule and hence D_w^0 may be a few orders of magnitude lower than the normal value obtained from the transition state theory (see for ex. [12]).

The simulation results have one more peculiarity. It consists in the necessity to accept S_t to be by about an order of magnitude lower than that for smooth Ni faces in order to describe experimental dependencies $F(T)$. However, the total sticking coefficient remains rather high, and it is equal to $\theta_t^{\text{max}} S_t + \theta_w^{\text{max}} S_w = 0.25$. The following explanation of this disagreement seems to be the most probable. It is known that CO adsorption on low index faces goes through a highly mobile physisorbed state - CO_p [4,5,13]. The defects on the surface can act as centers for the primary CO_p condensation in the CO_w state, resulting in a sharp reduction of the direct CO adsorption rate on smooth surface faces, *i.e.* to a S_t fall.

There are several reasons for S_w being less than unity. First, this may be a specific peculiarity of the surface defectiveness. So, for small Ni clusters with an obviously high surface defectiveness, $S \cong 0.5$ [14]. Second, the argon ion beam can influence the adsorption. This influence, in particular, may consist in the transfer of a part of the primary ion beam kinetic energy to CO_p molecules through collision cascades. The increase in the kinetic energy of CO_g and, as a consequence, CO_p at an initial adsorption stage results in the decrease of S from 0.9 to 0.5 [4,5].

APPLICATION

The rate of coverage change of the tightly bound state can be written as:

$$\begin{aligned} \frac{d\theta_w}{dt} = & \frac{f_{ad}S_w}{N} (\theta_w^{\max} - \theta_w) - \theta_w k_w^{\text{des}} - \frac{f_{ion}}{(A/A_0)} \sigma_w \theta_w \\ & - \theta_w (\theta_t^{\max} - \theta_t) k_w^{\text{dif}} + \theta_t (\theta_w^{\max} - \theta_w) k_t^{\text{dif}} \end{aligned}$$

The first term in the equation describes adsorption, the second - thermal desorption, the third - ion-stimulated desorption, the fourth and the fifth - diffusive exchange between states.

The equation for $d\theta_t/dt$ looks similarly.

Designations and explanations:

f_{ad} , f_{ion} are the fluxes of CO molecules and Ar^+ ions respectively. The values of f_{ad} , f_{ion} were calculated from the CO pressure and Ar^+ current density: $f_{ad} = P (2 \pi m_{\text{CO}} k_B T)^{-1/2}$, $f_{ion} = J / e$, where m_{CO} is the CO molecular mass and e is the electron charge.

A_0 , A are the initial sample surface area and the one increased during the ion bombardment. During the bombardment the surface area increases due to the macroroughnesses development according to the law $A = A_0 (1 + \alpha t^{1/2})$ [1]. As the estimations show, in the temperature range of 300 - 350 K and the current density specified above $\alpha = 0.02 \text{ s}^{-1/2}$, $A / A_0 = 1.5$ after the 500 s bombardment. At $T \geq 380 \text{ K}$ such an increase does not occur. This is most likely related to the roughness annealing. The data of other authors confirm the fact of the sharp increase in the annealing rate of the defects at such temperatures. An appreciable reduction in the concentration of steps was found on the Ni(110) surface bombarded by Ne^+ (10 keV, $j = 0.006 \text{ A/m}^2$) ions at $T > 350 \text{ K}$ [15].

N is the number of adsorbed centers normalized by the surface area. This value was accepted to equal the maximum CO coverage of a polycrystalline nickel film - $7 \times 10^{18} \text{ m}^{-2}$ [16].

θ_w^{\max} , θ_t^{\max} are the fractions of surface where CO forms the weakly bound or the tightly bound state, respectively. It is assumed that $\theta_w^{\max} + \theta_t^{\max} = 1$. Thermodesorption studies show that the fraction of the weakly bound state on Ni(221), (331), (551) faces varies from 0.3 to 0.6 [2]. It was shown that the concentration of steps on the Ni(110) during the surface bombardment by Ne^+ (10 keV, $j = 0.006 \text{ A/m}^2$) ions remains constant in the temperature range of 300 - 350 K [15]. In the present calculations the fractions of the defective and smooth surface sites at 300-350 K were set equal to 0.5. At $T > 350 \text{ K}$ the amount of defects will decrease due to annealing [15]. At $\theta_w^{\max}(T)$ functions indicated in the insert to Fig. 2, the calculated dependencies of the CO coverage on temperature are shown in Fig. 2. One can see that the reduction of defective surface area at $T > 350 \text{ K}$ almost by two orders of magnitude has only a small influence on $\theta(T)$.

σ is the cross-section of the ion-stimulated desorption. The values of σ_t and σ_w were assumed to equal $8 \times 10^{-19} \text{ m}^2$ and $18 \times 10^{-19} \text{ m}^2$, respectively [1].

k^{des} , k^{dif} are the rate constants for the desorption and diffusion calculated as $k^{\text{des}} = \nu^{\text{des}} \exp(-E^{\text{des}}/RT)$, $k^{\text{dif}} = (4D^0/a^2) \exp(-E^{\text{dif}}/RT)$, where D^0 is the pre-exponential factor for the diffusion, a^2 is the area of the adsorption site ($a^2 = 1/N$), E is the activation energy, R is the gas constant. The values of $\nu^{\text{des}}_t = 10^{15} \text{ s}^{-1}$ and $E^{\text{des}}_t = 134 \text{ kJ/mol}$ were accepted for the activation energy and pre-exponential factor for the desorption of the tightly bound state [17,18]. For the weakly bound state, the pre-exponential factor ν^{des}_w was also 10^{15} s^{-1} and $E^{\text{des}}_w = 105 \text{ kJ/mol}$, according to its desorption temperature [19]. The activation energy for CO diffusion from the tightly bound to the weakly bound state depends on the back hop energy according to the obvious formula

$$E^{\text{dif}}_t = (E^{\text{des}}_t - E^{\text{des}}_w) + E^{\text{dif}}_w$$

Derivatives $d\theta_{w,t}/dt$ are zero under stationary conditions and we come to a system of two equations, from which θ_w and θ_t can be found.

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