

Interaction between Cesium Chloride Molecules and Metal Atoms under Coadsorption on a Single Graphite Layer on Iridium

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Abstract

Using the method of continuous flow to investigate the kinetics of reaction between atoms and molecules, the efficiency of substitution reactions (K, Na, Li)+ CsCl is shown to decrease. The efficiency is found to strongly depend on temperature tending to saturation with decreasing temperature. This fact is in accordance with Bonzel's concept.

1. Introduction

The study of the interaction between particles of different nature during coadsorption on solid surfaces is one of the main problems of Chemistry and Surface Physics.

The dissociation of molecules during a coadsorption with alkali metal atoms has been investigated in [1]. The increase of the dissociating CO molecule fraction was observed during the adsorption of CO on Ni (100)+ Na, K, Cs [1]. When correlating the linear sizes of the Auger peaks C and O on pure and alkaline-promoted surfaces of Ni (100), the alkali adatoms were found to cause decomposition of CO on the Ni (100) surface. The fraction of the dissociating CO molecules is a linear function of the alkaline atom concentration, within the limits of the internal coatings. For ceration similar coating of alkaline metal atoms, the probability of dissociation increases with the binding energy, not for all of the adsorbed CO molecules but only a part of them; i.e. there are CO molecules in the same states as at a low concentration of alkaline atoms ($< 1.10^{14} \text{ cm}^{-2}$). The amount of the CO molecules that dissociates in the presence of Na, K and Cs is 1: 1.45: 2.2. This ratio is comparable to the ratio relating the adatom effective charges on the surface ($q_{Na} : q_K : q_{Cs} = 1 : 1.4 : 1.9$) calculated in [2].

To explain the available experimental data on the coadsorption of alkaline metal atoms and gas molecules on metals, a model for the surface atom-gas complex has been proposed by Bonzel [3]. This model based on the transition of electrons from the surface top to CO molecule, has been introduced to explain the increase in adsorption energy in Fe + K catalists [4, 5]. Bonzel has applied this model using Pt (111) + K + CO. The donor-acceptor adsorption binding of CO with metal, including the transition of electron from the 5σ orbital of the molecule to the conduction band of the metal, and the inverse transition of the charge from a high level to the vacant 2π orbital of CO, splitting into bonding and nonbonding orbitals due to the interaction with metal, is assumed in the model [6]. Bonzel supposed that on migration of the CO to the alkaline atom, an additional charge passes to the CO molecule in the 2π -orbital region. This fact agrees with the observed increase of φ , a decrease in valence frequency and increase of adsorption energy.

Bonzel argues the reason for the charges transfer as follows. The potassium adsorbed on the Pt (111) surface decreases the work function. However, the φ values measured are average for every coating θ by potassium and give no information about the local change of the work function near the K adatoms. Experiments on the adsorption of Xe atoms on a pure metal partially coated by alkaline atoms [8] offer the following main results: the work function of free of alkali is similar to that of the pure metallic surface; regions with a reduced value of the work function are restricted in area by sizes of the alkaline atom cross section. This conclusion agrees well with a small length of scanning in metals [9]. Due to a local change of the work function on alkali absorption, one can also expect a strong local effect of alkali on the gas chemisorption.

Substitution reactions $K + RbCl \rightleftharpoons KCl + Rb$ [10] and $Na + CsCl \rightleftharpoons NaCl + Cs$ [11] were investigated with a Pt (8% W) alloy saturated by carbon, and the samples were placed in surface ionization differential detectors for separate recording of the alkaline metal atoms and alkaline-haloid salt molecules in the mixed flows of these particles [12]. The steady-state flow method provided a constant concentration of particles on the surface. The reaction product (CS) was decreasing alloy temperature, the probability of reaction increases as the Cs^+ ion current increases. The low-temperature part of Cs^+ ion current practically corresponds to a total substitution of Cs atoms in CsCl molecules by Na. It is our opinion that the obtained probability of the substitution reaction (somewhat less than 100%) can be explained by one of the following reasons:

- a) the existence exchange reaction $Cs + NaCl \rightleftharpoons CsCl + Na$;
- b) the concentration of Cl atoms in CsCl flow;
- c) the decrease in work function of alloy due to Na coating.

The conclusion, useful for detection of molecular flows, as expressed in [10, 11], consists in the fact that by the substitution reaction, atom flows with high ionization potentials can be recorded. The authors called a surface ionization of particles formed as a result of reaction "the chemical surface ionization".

The regularities obtained in [11] are difficult to interpret due to the lack of sufficiently passive and stable surface of the carbon-saturated Pt (8% W) alloy.

According to Bonzel, a local interaction between the adsorbed atoms and molecules

should essentially depend on the ionization potential atoms [3]. To study this problem, we compared the results of interaction of CsCl molecules with simultaneously adsorbed atoms of one of the alkaline elements K ($V = 4.34$ eV), Na ($V = 5.14$ eV) or Li ($V = 5.4$ eV). These elements are used as the promoters in heterogeneous catalytic dissociation reactions.

Investigation of the coadsorption of CsCl molecules with Z (K, Na, Li) atoms on the surface of single layer graphite on Ir (Ir-C) has been reported in [14-16].

The method of continuous flows of particles was used and the kinetics of reaction between Z (K, Na, Li) atoms and CsCl molecules with different T, ν_z and ν_{CsCl} was experimentally investigated via the following two characteristics:

1) The reaction efficiency [14]

$$\eta(T) = \frac{\nu_{CsCl} - \nu'_{CsCl}}{\nu_{CsCl}} = \frac{\nu'_{Cs^+}(T)}{\nu_{CsCl}} \quad (1)$$

where ν'_{CsCl} is the inverse molecule flow desorbed from the emitter and uninvolved in the reaction. The difference $\nu_{CsCl} - \nu'_{CsCl}(T)$ is equal to the amount of Cs atoms separated during reaction as the CsCl molecules are not reflected from the Ir-C surface [17]. These atoms are desorbed as Cs^+ ions by surface ionization on Ir-C temperatures higher than the threshold temperatures for the light ionization of Cs on Ir-C according (1), $0 \leq \eta \leq 1$.

2) The utilization factor of the Z atoms in reaction [16]

$$\chi(T) = \frac{\nu'_{Cs^+}(T)}{\nu_z} \quad (2)$$

Which connects directly the amount of the Cs^+ ions with the flow of ν_z atoms, and thus determines the sensitivity of its detection by chemical ionization. If the valence of the Z atoms is n, then for limited substitution, $nCsCl + Z \rightleftharpoons nCs$, $0 \leq \chi \leq n$.

It should be noted that the main point of works [10-13] is the study of $\eta(T, \nu_z, \nu_{CsCl})$ which can be determined according to (1) and (2), $\eta(T)$ and (T) are related by similar relationship

$$\chi(T) = \frac{\eta(T)\nu'_{CsCl}}{\nu_z} \quad (3)$$

The method of steady-state flow provides that the concentration of particles on the surface is constant and is highly sensitive at the transformation of evaporated particles into ions through light surface ionization [13]. In this case every particle evaporated from the surface becomes the ion and this is inaccessible to other forms of ionization. At evaporation of the Cs atoms from the graphite single layer on Ir (111), light surface ionization takes place.

The atoms emerge from the surface passive relative to dissociation of CsCl molecules and do not enter into chemical reaction with reagents and weakly affect the composition of the reaction products [14-18]. In papers the well-studied slightly defect Ir (111)-C surface passive relative to dissociation of CsCl molecules was used [19, 20].

When papers [14-16] are considered, we come to the following conclusion concerning the dependence on Vz .

The typical relationship $\log \eta = f(T)$ for continuous flow of CsCl molecules and other flows of Na (the low background Cs⁺ currents are taken into account) are presented in Fig. 1 [14]. As seen in Fig. 1, the η value strongly depend on T. With decreasing T, the η value increases and tends to saturation at low temperatures. The saturation is attributed to full use of one of the reagents in reaction. Thus for curves 1-5 at T = 740 K, $\chi \approx 1$ indicates the exchange reaction $\text{Na} + \text{CsCl} \rightarrow \text{NaCl} + \text{Cs}$ with a full use of Na atoms on the surface. In [14-16] $\eta_{\text{max}} = 0,8$ and $\eta_{\text{max}} = 1$ for $\text{Na} + \text{CsCl} \rightarrow \text{NaCl} + \text{Cs}$ and $\text{K} + \text{CsCl} \rightarrow \text{KCl} + \text{Cs}$ systems, respectively (Fig. 2).

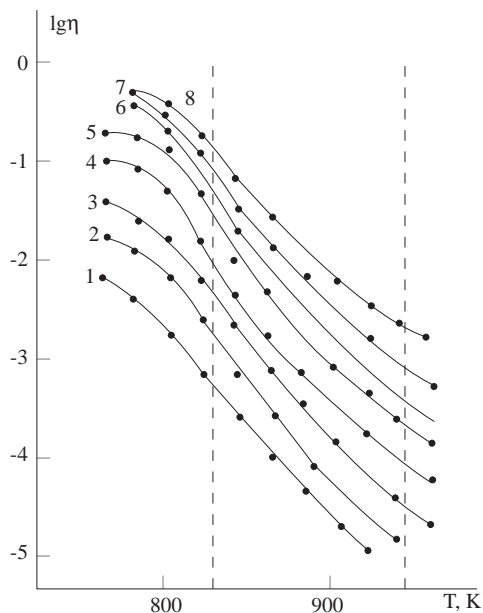


Figure 1. The dependences $\log \eta = f(\nu)$ for the continuous flow of CsCl $\nu_{\text{CsCl}} = 3.3 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and different flows of Na ν_{Na} ($\text{cm}^{-2} \text{ s}^{-1}$): 1 - $2.9 \cdot 10^{10}$; 2 - $7.9 \cdot 10^{11}$; 3 - $1.8 \cdot 10^{11}$; 4 - $4.2 \cdot 10^{11}$; 5 - $8.8 \cdot 10^{11}$; 6 - $1.9 \cdot 10^{12}$; 7 - $4.1 \cdot 10^{12}$; 8 - $8.6 \cdot 10^{12}$.

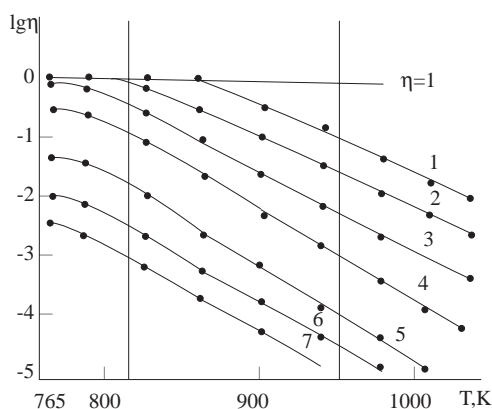


Figure 2. The dependences $\log \eta = f(\nu)$ for the continuous flow of CsCl $\nu_{\text{CsCl}} = 3.2 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and different flows of K ν_{K} ($\text{cm}^{-2} \text{ s}^{-1}$): 1 - $2.1 \cdot 10^{13}$; 2 - 10^{12} ; 3 - $2.6 \cdot 10^{12}$; 4 - $7.5 \cdot 10^{11}$; 5 - $1.4 \cdot 10^{11}$; 6 - $3.7 \cdot 10^{10}$; 7 - $1.3 \cdot 10^{10}$.

In accordance with Bonzel's concepts, one expect that for same adsorbent the η value will decrease in K, Na, Li series.

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To clarify if η for reaction $\text{Li} + \text{CsCl} \rightarrow \text{LiCl} + \text{Cs}$ can be equal to 1 on an Ir-C surface, a special investigation was carried out. The flow of ν_{Li} was highly increased (so that $\nu_{Li} \gg \nu_{CsCl}$). Consequently, it was found that at low temperature ($T = 800 \text{ K}$) the η value is independent of T (the region II in Fig. 3).

The obtained results are shown in Fig. 4. It is seen that η is practically independent of ν_{Li} , over an order of magnitude flow range and with increasing ν_{Li} the value of is no more than $\eta_{\max} = 0.4$.

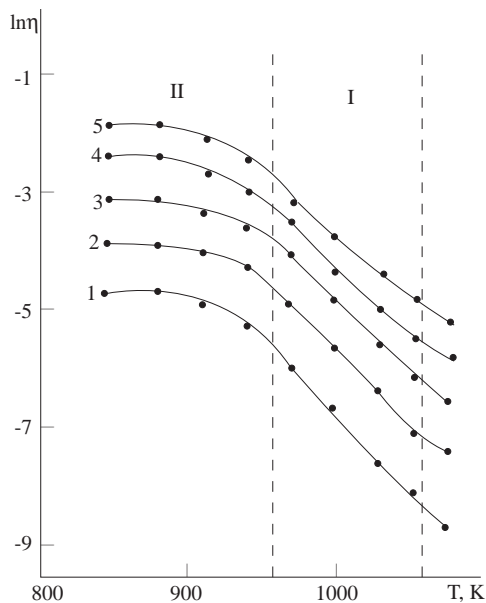


Figure 3. The dependences $\log \eta = f(\nu)$ for the continuous flow of CsCl $\nu_{\text{CsCl}} = 1.6 \cdot 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ and different flows of Li ν_{Li} ($\text{cm}^{-2} \text{ s}^{-1}$); 1 – $2.1 \cdot 10^{11}$; 2 – $3.1 \cdot 10^{11}$; 3 – $7.5 \cdot 10^{11}$; 4 – $2.1 \cdot 10^{12}$; 5 – $4.3 \cdot 10^{12}$;

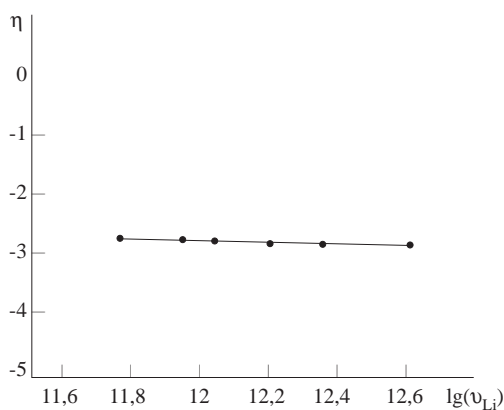


Figure 4. The dependences $\eta = f(\log \nu_{Li})$ $\nu_{\text{CsCl}} = 3.3 \cdot 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$, $T = 800 \text{ K}$ $\nu_{\text{Li}} = 5.8 \cdot 10^{11} \div 4 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$.

2. Conclusion

Using the method of continuous flows and investigating the kinetics of reactions between atoms and molecules, it has been shown that the efficiency of substitution reaction (K , Na , L) + CsCl decrease under specific conditions.

The efficiency is found to be strongly temperature dependent, tending to saturation with decreasing temperature.

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