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Exoelectron Emission Accompanying Catalytic Reactions in Adsorbed Layers

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Emission of negative charges (electrons and ions) has been observed during catalytic decomposition of methanol and formic acid and hydrogen oxidation in adsorbed layers on Al_2O_3, NaCl, and NiO catalysts. Thermal emission curves characterize the energy spectrum of surface trapping levels of electrons participating in the catalysis.

I. INTRODUCTION

Detailed investigation of exoelectron emission started with the papers published by Kramer in 1950–1960 (*1*, *2*). Since exoemission characterizes weakly bonded electrons trapped on solid surfaces, certain workers (*3*, *4*), even at very early stages of the study, suggested a possible relationship between this phenomenon and adsorption/catalysis. Later it was found that the adsorption of active gases and vapors (*5*) as well as their desorption (*6*) cause emission of negative charges. All these phenomena together with other forms of low-temperature emission are generally referred to as "exoemission." Recently, some papers have appeared pointing to a direct relation between emission and catalysis. Sato and Seo (*7*) investigated ethylene oxidation on a silver catalyst, using a gas-flow G-M counter to detect exoelectrons, and ethylene as the quenching gas. Emission intensity was found to be proportional to the generation rate of ethylene oxide. Such experiments, however, are misleading because catalytic reactions involving oxygen and water (as reaction product) may affect the count characteristics of the detector. More trustworthy results have been obtained by Hoenig and Tamjidi who studied the catalytic oxidation of CO, H_2, and NH_3 on platinum (*8*). The temperature range of 775 to 800°C in which they carried out their reactions was, however, characteristic of neither catalysis nor exoelectron emission. The phenomenon they described is thermoelectron emission from platinum wire, the work function of which changed in the presence of adsorbed substances, but not exoemission which takes place in the pre-Richardsonian region ($T \leq 500°C$) (*2*). The high currents (of about 10^{-9} A) reported by Hoenig and Tamjidi (*8*) are also not typical of exoemission where measured currents lie within 10^{-17} to 10^{-19} A.

The present paper reports an investigation of thermostimulated exoemission accompanying certain heterogeneous catalytic reactions in adsorbed layers at 100 to 400°C. Simultaneously, thermodesorption measurements were made. Decompositions of methanol on Al_2O_3 and NaCl, formic acid on NaCl, and hydrogen oxidation on NiO were the reactions studied.

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II. EXPERIMENTAL

Exoemission was recorded by means of a secondary electron multiplier at 10^{-5} Torr under continuous evacuation (*9*). The catalytic reactions in the adsorbed layer were studied side by side with thermodesorption in a system where the vacuum was created in the same manner as in that for exoemission measurements. Since it is difficult to detect active reactants (alcohol vapors, formic acid vapors, etc.) by means of an ionization manometer or by mass-spectrometer sensors due to possible side reactions on filaments, pressure was measured in the course of the reactions by a McLeod manometer in a closed vessel with condensation analysis of liberated vapor. Thermodesorption measurements were coordinated with emission measurements. The apparatus and experimental procedure for thermodesorption investigations are described in detail elsewhere (*10*).

Powder samples of Al_2O_3, NaCl, and NiO and single crystals of NaCl were used as catalysts. Al_2O_3 was obtained by dissolving "pure"-grade aluminum powder in KOH followed by precipitating with carbonic acid and heating at 500°C. X-ray structure analysis showed the γ-Al_2O_3 structure. The specific surface area measured by low-temperature krypton adsorption was $S = 215$ m^2/g. Commercial NaCl samples, "chemically pure"-grade powder samples, and single crystals grown from melt by the Kyropoulos method were used. NiO was prepared by prolonged heating of commercial "analysis-pure" nickel nitrate in air at 600°C. The catalysts were used in the exoemission and thermodesorption measurements in the following quantities: Al_2O_3—20 mg, NaCl powder—200 mg, and NiO—50 mg. The single crystals were $14 \times 8 \times 0.7$ mm^3 in size. The vacuum vessels and measurement conditions (components of the residual gas in the system, linear heating rate, quantities of catalysts, and adsorption procedure) were identical in the thermostimulated emission and thermodesorption experiments.

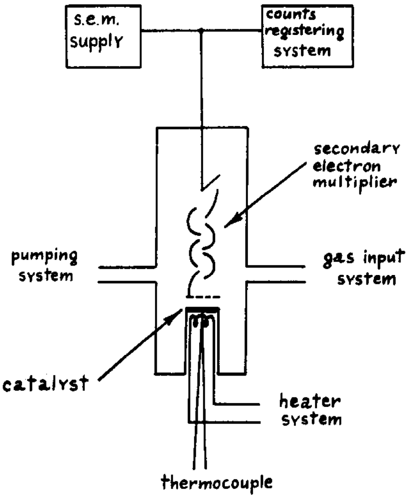

Fig. 1. Scheme of the apparatus for exoemission measurements.

The experimental system for the investigation of exoemission is schematically shown in Fig. 1. In Fig. 2, curves 1 relate to the "background noise" in exoemission and gas evolution in thermodesorption for linear heating of the holder without a sample. The experimental procedure was as follows.

The test samples were placed in the form of a thin (0.3 mm) layer on a metal holder and heated in vacuum (T = 400°C, $P = 10^{-5}$ Torr, t = 2 hr). Upon subsequent linear heating, exoemission and gas liberation from the sample did not exceed the background level. Immediately after heating, the reagents were subjected to adsorption. Adsorption of methanol vapor was carried out directly in the vessel for exoemission (thermodesorption) measurements on Al_2O_3 and NaCl catalysts at 20°C and P = 4 Torr for 30 min. Since formic acid vapor affects the multiplier sensitivity, its adsorption was carried out by dripping HCOOH droplets on the NaCl single crystal.

To investigate hydrogen oxidation on NiO, the sample was activated in oxygen (P = 4 Torr, T = 400°C) after heat treat-

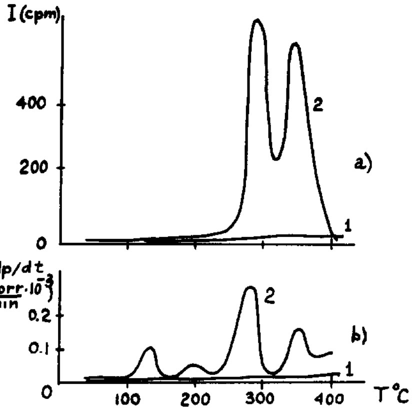

FIG. 2. (a) Curve 1, thermostimulated emission (TSE) background from holder without a sample. Curve 2, TSE accompanying catalytic decomposition of methanol in an adsorbed layer on NaCl (powder, sample 1). (b) Curve 1, thermodesorption rate from holder without a sample. Curve 2, from NaCl powder containing adsorbed methanol.

ment. Hydrogen adsorption was effected ($P = 4$ Torr, $T = 150°\text{C}$) upon cooling and further evacuation.

After adsorption the samples were further evacuated at 20°C to about 10^{-5} Torr and heated at a constant rate of about 15°C/min, concurrently recording emission and pressure of evolving gases. In thermodesorption experiments the gases evolved in a specific temperature range were collected in a liquid nitrogen-cooled trap and subjected to condensation analysis. Condensation analysis of gases released upon heating of the holder in the absence of a catalyst revealed no gases condensable at liquid nitrogen temperature (sample temperature $T = 350°\text{C}$, $P = 6 \times 10^{-4}$ Torr).

III. RESULTS

The experimental results are plotted in Figs. 2–6 (a and b). Curves in the upper section (a) are thermostimulated emission (TSE) curves. It is seen that after adsorption of the reactants (alcohol vapor, formic acid, or successively $O_2 + H_2$) pronounced surges of TSE current appear in certain temperature ranges. By magnetic discrimination experiments (*11*) it was found that besides electrons negative ions are also emitted. The results characterizing ion emission are marked by black dots in Figs. 3 and 6a: Emitted ions contribute up to 50% of the total exoemission current in TSE glow curves.

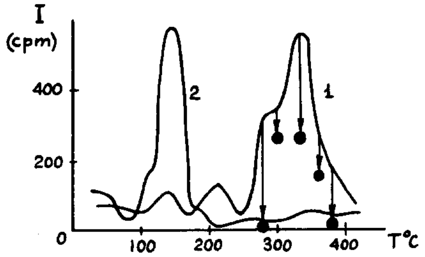

FIG. 3. TSE accompanying catalytic decomposition in an adsorbed layer on NaCl (powder, sample 2) of methanol (curve 1, dehydrated sample, black dots in magnetic field; curve 2, hydrated sample).

Exoelectron emission, like catalysis, is a structure-sensitive phenomenon. For this reason, the number and ratios between emission peak intensities (and desorption

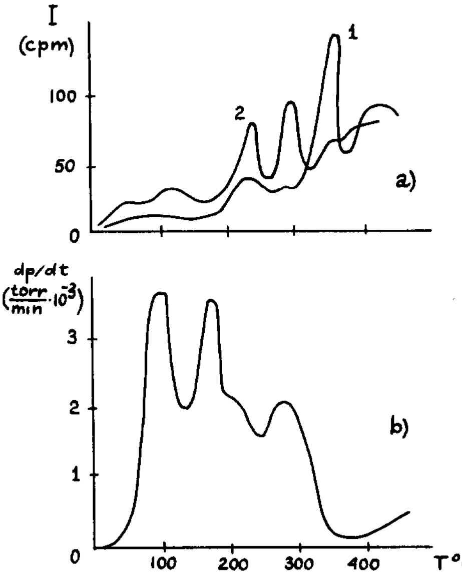

FIG. 4. (a) TSE accompanying catalytic decomposition of methanol in an adsorbed layer on $\gamma\text{-Al}_2\text{O}_3$ when the reaction was carried out for the first time (curve 1) and for the second time (curve 2) with the same sample. (b) Desorption rate from $\gamma\text{-Al}_2\text{O}_3$ containing adsorbed methanol.

rates) are strongly influenced by catalyst preparation conditions. Particularly important are the conditions of heat treatment in vacuum determining catalyst dehydration. Reproducibility of the results in thermostimulated exoemission is demonstrated, for example, by comparing curve 1 in Fig. 3 and curve 2 in Fig. 2a obtained for two batches of NaCl powder samples.

Reactions in adsorbed layers are known to have specific features: Both the catalysis initiation temperature and reaction direction are variables (*12*). The results of the thermodesorption investigations of gas release in thermostimulated emission are plotted in Figs. 2, 4, 5 and 6. Thermodesorption rate curves were obtained by differentiating $p = f(T, t)$, where T is temperature and t is time. It was found that methanol decomposition on Al_2O_3 and NaCl powder proceeds via dehydration yielding dimethyl ether and water: The gases not condensable at liquid nitrogen temperature amounted to 5 to 10% by volume.

Figures 2 and 3 show the results of exoemission and thermodesorption investigations of methanol decomposition on NaCl powder. It is seen there that the maximum desorption rates correspond to emission peaks at 280 to 290 and 330 to 350°C and less intensive peaks at 140 to 150 and 200 to 220°C (Fig. 2a and curve 1, Fig. 3) (Fig. 2b). The condensation analysis of gases evolved in the investigated temperature range (20–400°C) showed that alcohol decomposes via dehydration to 75%. Figure 4 illustrates results for methanol decomposition on Al_2O_3. Here, the emission peaks at 220 to 230 and 290°C correspond to the maximum (inflexion points) on the thermodesorption rate curve. In the course of heating (20–350°C) methyl alcohol was dehydrated to about 30%. Absence of thermodesorption peaks at 300 to 400°C, where pronounced emission peaks are observed, was probably due to readsorption of the products owing to the high adsorption capacity of porous γ-Al_2O_3 with its well-developed surface.

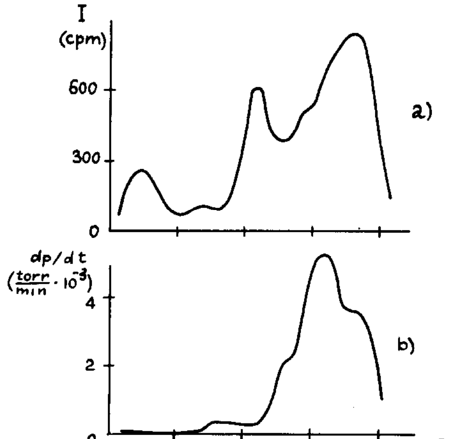

FIG. 5. (a) TSE; (b) thermodesorption rate in formic acid decomposition on NaCl single crystal.

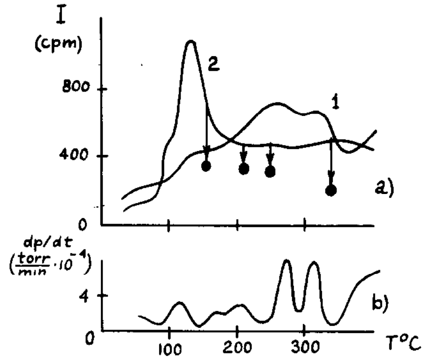

FIG. 6. (a) TSE accompanying hydrogen oxidation in an adsorbed layer on NiO for the first (curve 1) and second (curve 2) reaction with the same sample (black dots, in magnetic field). (b) Thermodesorption rate in hydrogen oxidation in an adsorbed layer on NiO.

The catalytic decomposition products were detected essentially at $T > 200°C$, and the weaker low-temperature emission peaks were due, in our opinion, to recombination in the adsorbed layer ("precatalytic state"). Intense desorption rate peaks at $T \leq 200°C$ (Fig. 4b) are chiefly due to desorption of unreacted alcohol.

If a catalyst is subjected to repeated treatment with reactant (P = 4–10 Torr) the shape of the TSE curves changes: The low temperature maxima become more intense (Fig. 4a, curve 2; Fig. 6a, curve 2). This means that an active surface is formed during catalytic reaction, i.e., the number of sites having lower negative charge emission activation energies increases. We believe that these sites contain hydroxyl groups (or water molecules) formed on the dehydrated surface due to the interaction of the catalyst with water [product of alcohol decomposition (Fig. 4a) or hydrogen oxidation (Fig. 6a)]. Indeed, when studying methanol decomposition on NaCl we did observe the water-promotion effect. Figure 3 shows the results of TSE in the decomposition of methanol adsorbed on a dehydrated (curve 1) and hydrated (curve 2) surface. It therefore follows that in the presence of water the intense TSE peak shifts toward lower temperatures, and the processes in the adsorbed layer involving emission of negative charges take place at $T \approx 150°C$. Water promotion effects, in particular, in alcohol decomposition, have been known for a long time in catalytic research (*13*).

In formic acid decomposition on NaCl single crystal, the broad structured TSE maximum at 210 to 360°C corresponds to the broad desorption rate maximum in the same temperature range (Fig. 5a and b). Analysis of the products showed that the reaction proceeds largely via dehydrogenation (40% conversion of the total amount of HCOOH in the adsorbed layer) and 20% via dehydration.

IV. DISCUSSION

The mechanism of negative charge emission in catalytic reactions is not clear at present and cannot be explained by the existing physical models of exoemission. To explain emission during oxidation of CO, NH_3, and H_2 on platinum, Hoenig and Tamjidi (*8*) have based their arguments on certain speculative ideas derived by analogy from some of the published data concerning exoemission and catalysis. On the basis of the results of Delshar (*5*) who observed intense exoemission during chemisorption of oxygen on nickel, they regard adsorption of reactants as the stage of heterogeneous catalysis reactions responsible for the emission of negative charges.

The experimental procedure which we used to study catalysis in the adsorbed layer avoids the adsorption stage as being the cause of electron emission. In our earlier work (*6*, *14*) we have found that the thermostimulated exoemission centers act as the thermodesorption centers as well and desorption is accompanied by emission of negative charges as electrons and ions. Consistency between the temperatures of TSE in catalytic reactions and the desorption rate maxima of reaction product is also evident from Figs. 2, 5, and 6.

On the basis of an analysis of a vast amount of her own and other published data, one of us (*15*) suggested a physicochemical mechanism for thermostimulated emission comprising the following main stages: heating → phase conversions in adsorbed surface compounds (hydrate for example) → breaking of bonds resulting in the formation of a mobile layer of active particles (ions, radicals) → recombination of active particles in the adsorbed layer → desorption → formation of strains → deformation in the near-surface layer → emission of negative charges (positive charging of the surface).

This mechanism is based on the experimental fact that exoemission does not occur on most solid surfaces devoid of adsorbed layers (*16*). Supposedly, the active particle recombination energy is released near lattice defects, the active sites, energetically separated from the bulk, where this energy is not dissipated through phonons but is imparted to trapped electrons. Trapping levels may be formed either by lattice defects (of the color-center type) or by ions of adsorbed substances (such as O^-, OH^-, CH_3O^-, etc.).

By analogy between the above physicochemical surface processes underlying exoemission, as already discussed (*15*), and general concepts in catalysis (*17, 21*), we believe that this mechanism is also valid for adsorption–desorption and catalysis processes. Formation of catalytically active strains due to desorption has been considered by Peri (*18*) and a mobile adsorbed layer model—migrating or "hopping" molecules, the precursors of desorption—has been suggested by de Boer (*19*).

From the foregoing it may be concluded that the negative charge emission that we observed during catalysis in the adsorbed layer is due to elementary interactions of active particles on the catalyst surface followed by desorption and relaxation of strains.

The mechanism of catalytic decomposition in the adsorbed layer accompanied by emission of negative charges can be represented as follows:

$$CH_3OH_g \rightarrow CH_3OH_{ads} + Q_{ads}$$

$$CH_3OH_{ads} \rightarrow CH_3{}^{\cdot}{}_{ads} + OH^{\cdot}{}_{ads}$$

$$CH_3OH_{ads} \rightarrow CH_3O^{\cdot}{}_{ads} + H^{\cdot}{}_{ads}$$

$$CH_3O^{\cdot}{}_{ads} + CH_3{}^{\cdot}{}_{ads} \rightarrow CH_3OCH_{3ads} + Q_{recom} \rightarrow CH_3OCH_{3g}$$

$$H^{\cdot}{}_{ads} + OH^{\cdot}{}_{ads} \rightarrow H_2O_{ads} + Q_{recom} \rightarrow H_2O_g.$$

The dissociative adsorption processes yielding active radicals are known to be an intermediate stage in several heterogeneous catalysis reactions, such as alcohol decomposition. In the work of Vasserberg *et al.* (*17*) where dehydration reactions of certain alcohols in the adsorbed state was studied, it has been shown that the intermediate surface forms are radical-like. For example, they possess such typical properties of free radicals as their ability to catalyze the *para-ortho* hydrogen conversion reaction which takes place under the action of unpaired electrons, and to initiate polymerization reactions.

Dissociative adsorption is also possible producing ion-radical forms which carry certain negative and positive charge:

$$CH_3OH_{ads} \rightarrow CH_3{}^{+}{}_{ads} + OH^{-}{}_{ads}$$

$$CH_3OH_{ads} \rightarrow CH_3O^{-}{}_{ads} + H^{+}{}_{ads}$$

It may be mentioned here that the formation of $C_2H_4O^-$-type radicals in heterogeneously catalyzed hydrocarbon oxidation was proved by the EPR method (*20*).

We believe that the emission of negative charges may be caused by the following recombination processes:

$$CH_3O^{-}{}_{ads} + CH_3{}^{\cdot}{}_{ads} + Q_{recom} \rightarrow CH_3OCH_{3g} + e\uparrow$$

$$OH^{-}{}_{ads} + H^{\cdot}{}_{ads} + Q_{recom} \rightarrow H_2O_g + e\uparrow$$

$$OH^{-}{}_{ads} + H^{\cdot}{}_{ads} + Q_{recom} \rightarrow H_2O^{-}{}_g$$

$$e_{loc} + Q_{recom} \rightarrow e\uparrow, \text{ etc.}$$

A similar oxidation mechanism, however, without any regard for electron transitions, was suggested by Khasin and Boreskov (*21*). It has since been found by the EPR method that oxygen is adsorbed on oxide surfaces in the form of ion-radicals, such as O_2^- and O^-. In considering oxidation mechanisms, it is assumed that the electron liberated during the reaction passes over to the catalyst. Our investigation has shown that these weakly bonded electrons can be emitted from the surface. It was verified experimentally (Figs. 3 and 6) that ions are emitted side by side with electrons. In accordance with our mechanism, the energy necessary for negative charge emission is supplied by the recombination heat (*15*).

In some studies devoted to catalysis it is suggested that the products of dissociative water adsorption, especially protons owing to their high mobility, can act as energy carriers in surface migration and recombination processes. This probably explains the promoting effect of water on exoemission (see Fig. 3) and many catalytic conversions. It is known, for instance, that surface diffusion of water sometimes has a specific influence on chemisorption and catalysis (*13*).

Thus, it has been established in the present work that heterogeneous catalytic reactions taking place in the adsorbed layer with participation of water (protons) are accompanied by emission of negative charges (electrons and ions). The TSE curves enable one to obtain through a single experiment qualitative information about the spectrum of surface electron trapping levels generated by the defects, the active sites of catalysis. Owing to the high sensitivity of the method, using exoemission it is possible to study catalytic effects on single crystals. Hoenig and Tamjidi (*8*) consider that exoelectron emission can be used as a measure for the rate of usual catalytic reactions. However, we failed to detect exoemission in alcohol dehydrogenation on zinc oxide. Likewise Sato and Seo (*7*) could observe exoemission in the catalytic oxidation of ethylene on silver only when the reaction proceeded via ethylene oxide formation. According to our data, intensive spontaneous exoemission accompanying catalysis in the temperature range of usual catalytic reactions ($T \leq 500°\mathrm{C}$) occurs only when water is one of the reaction products.

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