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Calorimetric Measurement of the Interaction of Propylene, Acetylene, and Methane with Dysprosium Films at Room Temperature

Rare earth metals and their intermetallics have found applications in heterogeneous catalysis (*1*), including cracking, hydrogenation, and other reactions of hydrocarbons (*2, 3*), yet little has been published on chemisorption of hydrocarbons by rare earths. To our knowledge, the only reported research work has been a UPS and Auger electron spectrocopic study of the adsorption of C_2H_4 and C_2H_2 on the Gd(0001) surface in a range of temperatures (*4*) and a brief summary on the interaction of hydrocarbons with Dy from this laboratory (*5*). In the present communication we report on exploratory calorimetric experiments with the adsorption of initial doses of C_3H_6, C_2H_2, and CH_4 admitted to polycrystalline dysprosium films at room temperature. The obtained data are interpreted in terms of thermochemical cycles utilizing data of our previous thermochemical and XPS measurements of the interaction of hydrogen (*6, 7*), carbon monoxide (*8–10*), and oxygen (*9–11*) with films of rare earths.

EXPERIMENTAL

The experiments were performed in a glass calorimeter for work with metal films, connected to a volumetric adsorption apparatus (*12, 13*). For the present study the apparatus was supplemented by an analytical ion gauge AIG 50 (Centronic, Croydon, UK) employing a miniature quadrupole-type gauge head for determination of partial pressure in the mass range 2 to 50 amu. The gauge was located close to the calorimeter cell and could be separated by a magnetically operated glass cut-off filled with a Ga–In–Sn eutectic. It was used in a static regime without pumping during the experiment. The calorimetric was the same instrument as that used in the above-mentioned previous measurements. It is suitable only for fast adsorption processes in which the gas pressure above the film falls under 10^{-4} to 10^{-5} Torr (1 Torr = 1.33×10^{-2} Pa) in a few tens of seconds at most. Heat produced at a lower rate cannot be determined exactly, if at all, on account of dissipation of a considerable portion of the heat to the gas phase (*13*).

The films of dysprosium were evaporated from an outgassed specimen of the metal onto the inner wall of the calorimeter glass cell thermostated to 285 K. The evaporation took 15–20 min at a background pressure of the order of 10^{-9} Torr. The films weighed about 3 mg and their average thickness calculated from the density of metallic dysprosium amounted to approximately 50 nm. However, a high internal porosity and a strong inhomogeneity of the thickness along the film area should be expected. The specimen of dysprosium of a claimed purity of 99.99% was prepared in the Institute of Metallurgy of the Academy of Sciences of the USSR. The following Matheson gases were used: propylene, CP; methane, research purity; acetylene, purified grade.

The measurements were performed at 295 K. The heat produced by the particular doses of gas (typically about 1×10^{-7} mole) was evaluated by a procedure outlined earlier (*12*) with an accuracy of several percent.

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RESULTS

Propylene. A fresh dysprosium film weighing 3.2 mg chemisorbed three successively admitted doses of propylene fast and with heats of 155, 153, and 144 kcal/mole (1 kcal = 4.184 kJ), respectively. The amount chemisorbed in this way was equivalent to 10.8 μmole of propylene per 100 mg of film. The next doses were adsorbed at a sharply falling rate with a heat decreasing to approximately 25 kcal/mole. The residual gas mass spectrum above the film (taken several tens of minutes after the propylene was admitted) showed the presence of a small amount of methane which was very slowly disappearing.

Methane. In order to find out whether dysprosium is reactive enough to chemisorb methane at room temperature and low pressure, a fresh film weighing 2.7 mg was exposed to methane doses. Production of heat started immediately upon the admission of methane, but it was protracted up to approximately 10 min in the first dose and rapidly decelerated up to full stop in the next three doses. Residual gas remained above the film from the very beginning and increased with successive admissions of methane. The mass spectrum showed peaks of methane, in addition to small peaks of carbon monoxide and water. The total sorption capacity of the film was approximately 2.4 μmole of methane per 100 mg of film. This represents about 20% of the capacity for the rapidly chemisorbed portion of the admitted propylene and about 7% of the capacity for rapid chemisorption of carbon monoxide (*8*).

An exact value of the heat produced could not be determined because of slow sorption of a major fraction of each dose, while the calorimeter used was designed for fast processes only. A rough estimate, however, showed that the total heat effect of the first dose exceeded 65 kcal/mole. The heat estimated for two subsequent doses appeared to be higher than some 45 kcal/mole.

Acetylene. When the uptake of methane reached 2.4 μmole per 100 mg of film and no further methane could be chemisorbed, the calorimeter was evacuated and three doses of acetylene were successively admitted. They were adsorbed fast with heats of 100, 104, and 96 kcal/mole, respectively. Residual pressure above the film was negligible after the first dose and was but slightly higher after the subsequent doses. The mass spectrum showed peaks of methane, carbon monoxide, and water. The capacity of the film for chemisorption of acetylene was by at least several tens percent higher compared to that of propylene.

DISCUSSION

The experimental evidence outlined suggests that the first portions of propylene, acetylene, and methane admitted to a sufficiently clean dysprosium film completely disintegrate into C and H atoms. Each C and H atom is bonded to x and y atoms of dysprosium, respectively. This suggestion, which we briefly mentioned earlier (*5*), is based on the following arguments.

Propylene. The proposed overall process may be written as

$$C_3H_6 \rightarrow 3\ C\text{–}Dy_x + 6\ H\text{–}Dy_y. \quad (1)$$

Heat of atomization of propylene at 298 K is 820.44 kcal/mole (*14*). The bonding energy of H and C atoms to dysprosium can be estimated from the heats of interaction of H_2 (*6*), CO (*8*), and O_2 (*11*) with dysprosium films, amounting to 48.9, 86.7, and 228.8 kcal/mole, respectively. By combining these heats with dissociation energy of 104.2, 257.3, and 119.1 kcal/mole for the H_2, CO, and O_2 molecule, respectively, we obtain for bonding energy of H, C, and O atoms to dysprosium 76.6, 170.0, and 174.0 kcal/mole, respectively. Hence, the heat effect of process (1) should be $[(3 \times 170.0) + (6 \times 76.6) - 820.4] = 149.2$ kcal/mole. This compares reasonably well with the actually measured heats of propylene adsorption in the low-uptake region and shows that total disintegration of propylene is a predominant process in the beginning. The following decrease in the heat signals a lower degree of propylene dissociation. The C_mH_n species formed cannot be identified merely from heat values. Methane found in the residual gas indicates that the decomposition of propylene proceeds stepwise and that C_1 and C_2 intermediates are likely formed.

Bonding of the H and C atoms to dysprosium is assumed to be the same as that which we have suggested for chemisorption of H_2 (*6*) and CO (*8–10*), respectively: H atoms arising on the surface move rapidly into the film bulk, forming a nonideal solution which readily transforms into a hydrogen-deficient dihydride. By contrast, C atoms do not penetrate deep under the surface at room temperature, but remain close to it and cause its gradual geometric and/or electronic blocking. XPS spectra of the C(1*s*) binding energy after exposure of dysprosium film to CO (*9, 10*) indicated that at low uptake of CO, carbidic carbon formed, while at an increasing consumption of CO, atomic and probably graphitic (*10*) types of carbon gradually appeared. To clarify the nature of carbon species formed from propylene, surface-sensitive spectroscopies should be applied.

The suggested surface-blocking effect of the formed carbon species is corroborated by the observed termination of fast and strong interaction at an uptake of 10.8 μmole of C_6H_6 per 100 mg of film. Namely, this is roughly one-third of the 25–30 μmole found with CO (*8*) whose molecule provides a single C atom. Approximately the same efficiency in the surface blocking by carbon species originating from the two gases is thereby implied.

Methane. Heat of atomization of methane is 397.2 kcal/mole (*14*). A complete decomposition of methane by dysprosium according to the scheme

$$CH_4 \rightarrow C\text{–}Dy_x + 4\ H\text{–}Dy_y \qquad (2)$$

should produce a heat of $[170.0 + (4 \times 76.6) - 397.2] = 79.2$ kcal/mole, if the above-derived energies for the formed bonds are used. As already mentioned, a rough estimate showed that the heat effect of the first dose exceeded 65 kcal/mole. Thus the value of 79.2 kcal/mole required by Eq. (2) seems to be quite possible with the initially chemisorbed amount of methane. The falling heat in the subsequent adsorption suggests that the degree of dissociation of methane progressively decreases with the increasing uptake.

The falling heat, its protracted production pointing to a considerable energy of activation, and the low uptake attained indicate that only the most active sites on the film surface are capable of dissociatively chemisorbing methane under the given conditions. This is in line with the general views of the chemisorption of methane by metals (*15, 16*).

Acetylene. The high and rapidly produced heat and the negligible residual pressure above the film in the low-uptake region indicate that acetylene is readily and practically completely decomposed:

$$C_2H_2 \rightarrow 2\ C\text{–}Dy_x + 2\ H\text{–}Dy_y. \qquad (3)$$

From recommended Laidler parameters (*14*), a heat of 391.7 kcal/mole is estimated to result from the atomization of acetylene at room temperature. Using the above-estimated energies for the C–Dy_x and H–Dy_y bonding, we obtain for process (3) a heat of $[(2 \times 170.0) + (2 \times 76.6) - 391.7] = 101.5$ kcal/mole. This is in good accord with the heats actually found for the first three doses.

The higher chemisorption capacity of dysprosium film towards C_2H_2 compared with C_3H_6 is consistent with the concept of surface blocking by the formed carbon species.

The small amounts of methane and CO detected by the analytical ion gauge in the higher uptake region might be due to the reactions $4\ C_2H_2 \rightarrow 2\ CH_4 + 6\ C$ and $C_2H_2 + 2\ O_{ads} \rightarrow 2\ CO + 2\ H$, occurring in the ion gauge used itself. The available evidence is not sufficient to prove this.

The exploratory thermochemical data obtained suggest that propylene, acetylene, and also, to a very limited extent, methane undergo predominantly complete decomposition when admitted at room temperature to a sufficiently clean dysprosium film. The H atoms formed readily penetrate deep into the film structure, while C atoms remain close to the surface and gradually block its chemisorption activity. The hydrocarbon disintegration is probably connected with the very high bonding energy of H and C atoms to dysprosium. With the increasing uptake, the degree of dissociation of the hydrocarbon molecules decreases. Methane can be chemisorbed only by the most active surface sites.

As we mentioned earlier (*5*), this interpretation is in line with a study in the C_2H_4–Pd(100) system (*17*) which suggested that the strengths of the H-to-metal and C-to-metal interactions play a crucial role in the decomposition pathway of ethylene on the given surface. An important support for our conclusions, based on thermochemical evidence, has been provided by a thorough UPS and Auger electron spectroscopic study of the interaction of ethylene and acetylene with the Gd(0001) surface (*4*). Yet a difference concerns the views on the fate of the H atoms formed. Our suggestion that at room temperature H atoms penetrate into the film structure while C atoms remain close to the surface is based on our previous calorimetric and XPS experiments with chemisorption of hydrogen and carbon monoxide by thin films of dysprosium.

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