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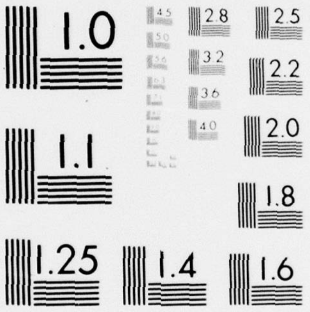

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CHEMICAL REACTIONS ON SOLID SURFACES USING MOLECULAR BEAM TECHNIQUES

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Thermal energy molecular beams have been used to study chemical interactions with metal surfaces. Chemisorption of simple molecules such as H_2, O_2, CH_4, C_2H_x and CO was investigated on single and polycrystalline surfaces of Pt, Ni, Co, and Ag. Kinetic parameters and reaction mechanisms were determined for model catalytic reactions including CO and C_2H_x oxidation and methanation from H_2/CO mixtures.

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ABSTRACT

Thermal energy molecular beams have been used to study chemical interactions with metal surfaces. Chemisorption of simple molecules such as H_2, O_2, CH_4, C_2H_x and CO was investigated on single and polycrystalline surfaces of Pt, Ni, Co, and Ag. Kinetic parameters and reaction mechanisms were determined for model catalytic reactions including CO and C_2H_x oxidation and methanation from H_2/CO mixtures.

1. INTRODUCTION

This final report summarizes the work performed under ONR Contract No. N00014-72-C-0247 during the period commencing 1 January 1972 and ending 31 March 1977.

Modulated molecular beams have been used to study the adsorption and reaction of chemical species on single crystal metal surfaces. In particular, chemisorption of the simple gases O_2, H_2, CO, CH_4, C_2H_2, C_2H_4 and C_2H_6 has been investigated on Pt(111) and Ag(111) surfaces. The kinetics of the oxidation of these gases was also studied by the molecular beam technique. Reactions of H_2 with CO for form hydrocarbon products have also been studied on Ni, Co, and Fe as well as Pt. Surface conditions leading to extraordinarily high activity for the formation of the product CH_4 were found for Ni and Co. Activity enhancements of greater than 10x and 100x, respectively, could be achieved over the clean surface condition by incorporating oxygen into the lattice by exposure to O_2. These highly active surfaces are stable in H_2/CO mixtures below 675°K.

2. EXPERIMENTAL RESULTS

Molecular beams are widely recognized as the most appropriate technique for studies of chemical interactions on an atomic level. Much of our understanding of the chemical interactions of atoms, molecules, ions and excited species has been achieved by this experimental method. However, relatively little use has been made of beams to study interactions on surfaces. Recent work has demonstrated, however, that beams are extremely useful for these heterogeneous studies as well.

From a physical point of view, molecular beams offer the advantage of allowing the investigator to characterize the initial conditions of the beam species. The incident momentum (angle of incidence), energy, and chemical composition of the beam are readily controlled. Also, the internal energy of the beam species, including rotational, vibrational and electronically excited states can be selected. While we do not currently utilize internal state selection, by simply specifying the incident angle and temperature of a single reactant species on an "ideal" clean, single crystal surface, many of the ambiguities of typical reaction cell studies are eliminated. First, with beams we can be certain that the products we observe are the result of a single encounter of the beam species with the surface. Modulation of the beam eliminates the contribution of ambient vacuum species or multiple collisions of the beam with other surfaces when phase sensitive detection is employed. Second, after reacting at the surface, line-of-sight mass spectrometry eliminates any subsequent reactions that might change the compositions of the desorbed products. This is of primary importance in catalysis since very reactive chemical radicals can sometimes be generated by surface reactions. Moreover, these initial chemical products are often the intermediates in a series of reactions that occur when multiple surface and gas-phase collisions are allowed. The importance of these subsequent reactions is quickly appreciated if we consider that in a flowing reaction cell, perhaps 10^{15} surface and gas-phase collisions can occur before the chemical composition of the products is determined.

2.1 C_2H_4 OXIDATION ON Ag(111)

The catalytic oxidation of ethylene (C_2H_4) is an important commercial process, ethylene oxide being the thirteenth largest volume organic chemical produced in the U.S. Since Ag is thought to be the catalyst for this process, we undertook a study of the interaction of C_2H_4 with O_2 on Ag(111). The reactivity on Ag(111) was found to be low and below the level of detectability using the conventional molecular beam (M.B.) geometry. Using a modified isotropic source geometry for increased signal the product CO_2 was detected. No C_2H_4O was detected, however. It was possible with the M.B. configuration to observe the fragmentation of C_2H_4 to C_2H_3 (10%) and C_2H_2 (5%) on Ag(111). The details of this work were presented as Technical Report No. 1 and also published ("Studies of the Catalytic Reaction of C_2H_4 and O_2 on Ag(111) Surfaces" by Joe N. Smith, Jr., R. L. Palmer, and D. A. Vroom, J. Vac. Sci. Technol. 10(2), 373 (1973).

Some investigations of the oxidation of C_2H_2 and CO on Ag(111) were made, but the reactivity was found to be much greater and more amenable to study by M.B. on Pt(111).

2.2 CO OXIDATION ON Pt(111)

Pt(111) has a high activity for the oxidation of CO due to its ability to dissociatively chemisorb O_2 without forming an unreactive oxide. The "sticking" coefficient for O_2 on Pt(111) was measured to be about 10^{-3} by titration with CO. The reaction product CO_2 was observed to desorb in a very peaked distribution about the surface normal ($\sim \cos^6\theta$) indicating an activation barrier to adsorption of $\sim$ 7 kcal/mole. The high mobility of CO on the Pt(111) surface was dramatically demonstrated and indicated primarily a Langmuir-Hinshelwood (L-H) reaction mechanism with the adsorbed CO capable of sampling a large surface area before reacting with a chemisorbed oxygen atom. At temperatures below $\sim 250^{\circ}$C the O_2/CO balance becomes very critical since CO blocks the chemisorption of O_2, whereas the oxygen saturated surface still readily chemisorbs CO. Thus, the Pt(111) surface remains catalytically active only for $O_2/CO \geq \frac{S_{CO}}{S_{O_2}}$ (i.e., $\sim 10^2$) as the temperature is lowered and/or the total pressure is increased. This figure, of course, would vary for other crystal faces and on rough surfaces because the sticking coefficient of oxygen, S_{O_2}, is strongly affected by these parameters.

Further details of this work are given in Technical Report No. 2. The results were also published ["Molecular Beam Study of CO Oxidation on a (111) Platinum Surface," R. L. Palmer and Joe N. Smith, Jr., J. Chem. Phys. <u>60</u>, 1453 (1974)]

2.3 C_2 HYDROCARBON OXIDATION ON Pt(111)

Further insights into oxidation catalysis on Pt(111) were made in a study of the oxidation of the C_2 hydrocarbons (C_2H_2, C_2H_4, C_2H_6). It was found that, aside from the initial sticking probabilities, the oxidation of these three species was identical. This result is consistent with other studies which indicate that the C_2 hydrocarbons chemisorb as an acetylenic species at elevated temperatures. The sticking coefficients for C_2H_2, C_2H_4, and C_2H_6 were ~ 1.0, ~ 0.5, and $< 10^{-3}$, respectively. While the chemisorption of C_2H_2 and C_2H_4 were rapid, C_2H_6 chemisorption was quite slow and apparently activated, although the magnitude of its activation barrier was not determined.

The surface temperature dependences of the three oxidation products, CO, CO_2 and H_2O, were measured and found to have a common slope in excess oxygen of 16 kcal/mole. This result indicates a rate limiting step common to all three products. Since the surface mobility of oxygen is the only process common to all three products it was concluded that the activation barrier to the diffusion of atomic oxygen is 16 kcal/mole on the Pt(111) surface.

The details of these experiments were written up and circulated as Technical Report No. 3. This work was also published in the open literature ["Molecular Beam Study of Oxygen and C_2 Hydrocarbon Chemisorption and Reactions on Pt(111)," Robert L. Palmer, J. Vac. Sci. and Technol. 12(6), 1403 (1976)].

2.4 H_2/CO METHANATION STUDIES

Molecular beams were used to study the important catalytic methanation reaction. After an unsuccessful effort to study the reaction in the 10^{-7}-10^{-5} torr regime, the apparatus was modified for studies in the 1 torr range. Studies were made on the transition metals in group VIII, but were most extensive on Ni, Co and Fe. Marz grade (99.999%) foil was used in this study at higher pressures, rather than single crystal films. One interesting result of this study was the discovery of greatly enhanced catalytic activity with oxygen treated Ni and Co foils. Enhancements of greater than 10x and 100x, respectively, were seen in the methanation rates on incompletely reduced surfaces. Apparently "doping" of the surface with small amounts of oxygen (1-3%) has a large affect on the catalytic activities of Ni and especially Co. On the other hand, Fe foils showed a decrease in activity after exposure to oxygen. Other workers have also reported increased catalytic activities due to surface oxygen in Rh (Ref. 1), and Pt (Ref. 2). This is an important parameter that has been overlooked in earlier studies on these surfaces, including possibly our own work on Pt(111) which may have been influenced by the presence of small amounts of oxygen.

The mechanism for CH_4 formation on the oxygen activated Ni and Co surfaces was found to involve a surface carbide intermediate, in agreement with the studies by Wise, et al. (Ref. 3) and Ponec (Ref. 4). These results are contrary to the long held belief that the direct dissociation of CO on these surfaces is inconsequential and the important intermediate is either HCO or CHOH. Of course, these intermediates cannot be ruled out for conditions which differ greatly from those which show rapid CO dissociation.

The methanation work has been written up and distributed as Technical Report No. 4. It has also been submitted to Journal of Catalysis and will appear there soon.

3. SUMMARY

The molecular beam technique has been shown to be of use in the study of a wide variety of surface chemical reactions. On smooth, single crystal surfaces the angular dependences of the incident reactions and the desorbed products gives information about the energetics of the interaction with the surface. We have observed the H_2, CO_2 and C_2H_6 chemisorption is activated on Pt(111), as evidenced by the sharply peaked desorption behavior of these gases. With molecular beams we have also obtained reliable kinetic data that helps to further clarify the catalytic processes involved in the model reactions studied.

By controlling the surface conditions, very large increases in catalytic activity have been achieved. Although surface morphology (e.g., roughness) is important, the activities of smooth, clean, single crystal surfaces can be quite high. The catalytic methanation activities of Ni and Co are also greatly enhanced by small amounts of surface oxygen. This parameter may also account for discrepancies in the reported behavior of Pt surfaces, for example.

4. PUBLICATIONS AND PRESENTATIONS

4.1 PAPERS PUBLISHED

1. "Studies of the Catalytic Reaction of C_2H_4 and O_2 on Ag(111) Surfaces," Joe N. Smith, Jr., R. L. Palmer, and D. A. Vroom, J. Vac. Sci. and Technol. 10(2), 373 (1973). (Technical Report No. 1)

2. "Molecular Beams Study of CO Oxidation on a Platinum Surface," R. L. Palmer and Joe N. Smith, Jr., J. Chem. Phys. 60, 1453 (1974). (Technical Report No. 2)

3. "Molecular-Beam Study of Oxygen and C_2 Hydrocarbon Chemisorption and Reactions on Pt(111)," Robert L. Palmer, J. Vac. Sci. and Technol. 12(6), 1403 (1975). (Technical Report No. 3)

4. "Mass-Spectrometric Measurements of Enhanced Methanation Activity Over Cobalt and Nickel Foils," R. L. Palmer and D. A. Vroom, to be published in Journal of Catalysis. (Technial Report No. 4)

4.2 TALKS PRESENTED

1. "Studies of the Catalytic Reaction of C_2H_4 and O_2 on Ag(111) Surfaces," Joe N. Smith, Jr., R. L. Palmer, and D. A. Vroom, American Vacuum Society Meeting, Chicago, Ill., Oct. 1972.

2. "Molecular Beam Studies of Oxidation on (111) Pt Surfaces," R. L. Palmer and Joe N. Smith, Jr., Third North American Meeting of the Catalysis Society, San Francisco, Feb. 1974.

3. "Molecular Beam Studies of Catalytic Oxidation on Pt Surfaces," R. L. Palmer and Joe N. Smith, Jr., Third North American Meeting of the Catalysis Society, San Francisco, Feb. 1974.

4. "Oxidation of the C_2 Hydrocarbons on Pt(111) Films," R. L. Palmer, California Catalysis Society, Anaheim, November 1974.

5. "Studies of H_2/CO Reactions Using a Fast Flow Catalytic Reactor," R. L. Palmer, California Catalysis Society, Berkeley, March 1976.

6. "Studies of CO and Hydrogen Reactions on Cobalt and Nickel Surfaces at Low to Intermediate Pressures," R. L. Palmer, Gordon Research Conference on Catalysis, New London, June 1976.

7. "Molecular Beam Studies of Model Catalytic Chemical Reactions," R. L. Palmer, American Chemical Society, New Orleans, March 1977.

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