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STUDY OF THE MAGNETIC PHASE DEPENDENCE OF THE NI-CO REACTION RA--ETC(U)
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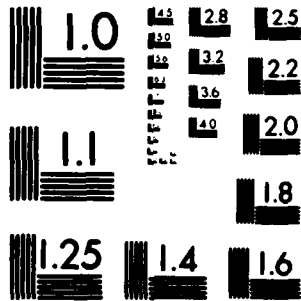
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Abstract

* Our studies of the magnetic phase dependence of chemical reactions includes both an experimental and a theoretical program. We describe below progress made during the funding period of the grant in both the experimental and theoretical programs. The experimental program focused firstly on repeating previously reported observations of a strong, oscillatory magnetic field dependence of a chemical reaction, the carbonylation of Ni to form nickel carbonyl. Using a more sensitive experimental system than that of the previous workers, we were not able to repeat their reported results. The second experimental program focused on the observation of a change in reaction rate and activation energy of the chemical reaction due to a magnetic phase transition of the reacting substrate. This phenomenon was conveniently studied using nickel copper alloys to vary the Curie temperature. Cluster calculations for the energy levels showed that the addition of a single carbon monoxide group fills the d shell and leads to a diamagnetic complex. The third experimental program addressed the observation of the Hedvall effect in a reaction where the magnetic species was purely catalytic, namely the hydrogenation of ethylene on nickel copper surfaces. The theoretical modeling was carried out with a spin polarized calculation of the energy levels of an ethylene molecule bound to a nickel cluster. This calculation shows a difference in the binding of the ethylene upon magnetization and is consistent with our observation of a Hedvall effect in the hydrogenation of ethylene.

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FINAL RESEARCH REPORT

to the

Air Force Office of Scientific Research

for research on

Study of the Magnetic Phase Dependence

of the Ni-CO Reaction Rate

AFOSR-77-3130

for the years

October 1, 1976 - September 30, 1981

Principal Investigator: M.S. Dresselhaus

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**Massachusetts Institute of Technology
Center for Materials Science and Engineering
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November 13, 1981

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Abstract

Our studies of the magnetic phase dependence of chemical reactions includes both an experimental and a theoretical program. We describe below progress made during the funding period of the grant in both the experimental and theoretical programs. The experimental program focused firstly on repeating previously reported observations of a strong, oscillatory magnetic field dependence of a chemical reaction, the carbonylation of Ni to form nickel carbonyl. Using a more sensitive experimental system than that of the previous workers, we were not able to repeat their reported results. The second experimental program focused on the observation of a change in reaction rate and activation energy of the chemical reaction due to a magnetic phase transition of the reacting substrate. This phenomenon was conveniently studied using nickel copper alloys to vary the Curie temperature. Cluster calculations for the energy levels showed that the addition of a single carbon monoxide group fills the d shell and leads to a diamagnetic complex. The third experimental program addressed the observation of the Hedvall effect in a reaction where the magnetic species was purely catalytic, namely the hydrogenation of ethylene on nickel copper surfaces. The theoretical modeling was carried out with a spin polarized calculation of the energy levels of an ethylene molecule bound to a nickel cluster. This calculation shows a difference in the binding of the ethylene upon magnetization and is consistent with our observation of a Hedvall effect in the hydrogenation of ethylene.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)

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This technical report has been reviewed and

approved for release on 10/10/1994.

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MATTHEW J. KERFER

Chief, Technical Information Division

Publications

- ✓ 1. "On the Possible Magnetic Field Dependence of the Nickel Carbonylation Rate", R.S. Mehta, M.S. Dresselhaus, G. Dresselhaus, H.J. Zeiger, Surface Science 78, L681 (1978).
- ✓ 2. "Magnetic Phase Dependence of the Nickel-CO Reaction", R.S. Mehta, M.S. Dresselhaus, G. Dresselhaus and H.J. Zeiger, Phys. Rev. Letters 43, 970 (1979).
- ✓ 3. "Magnetic Phase Dependence of the Nickel Carbonyl Reaction Rate", R.S. Mehta, M.S. Dresselhaus, G. Dresselhaus and H.J. Zeiger, Proceedings of the La Jolla Institute Workshop on Physics of Surfaces; Aspects of the Kinetics and Dynamics of Surface Reactions, 1979.
- ✓ 4. "Electronic Energy Levels of Intermediates in the Nickel Carbonylation Reaction", I.A. Howard, G.W. Pratt, K.H. Johnson and G. Dresselhaus, J. Chem. Phys. 76, 3415 (1981).
- ✓ 5. "New Morphological Transition at the Curie Temperature", M.S. Dresselhaus, Nature 292, 196 (1981).
- ✓ 6. "The Nature of the Initial Transient in the Rate of Formation of Nickel Carbonyl", by H. Mazurek, R.S. Mehta, M.S. Dresselhaus, G. Dresselhaus and H. J. Zeiger, in preparation.
- ✓ 7. "Adsorption of Ethylene on a Ferromagnetic Nickel Surface", I.A. Howard, G. Dresselhaus, K.H. Johnson and G.W. Pratt, Bull. of APS 26, 489 (1981).
8. "Electronic Structure of Ethylene-Ni₁₀ Clusters", I.A. Howard, G.W. Pratt, K.H. Johnson and G. Dresselhaus (in preparation).
- ✓ 9. "Studies of Magnetic and Electronic State Dependence of CO Reaction with Ni Surfaces", R.S. Mehta, Ph.D. Thesis, Department of Electrical Engineering and Computer Science, Jan. 1980.
- ✓ 10. "Magnetic Effects in Adsorbate Bonding to a Nickel Substrate", I.A. Howard, Ph.D. Thesis, Department of Physics, Sept. 1981.

We present below a summary of the major results of each of the papers published with support from this grant.

1. This paper discusses the previously reported observation of dramatic changes with magnetic field in the rate of $\text{Ni}(\text{CO})_4$ production. We developed an on-line detection scheme that had better sensitivity than the earlier Russian work and we did not observe any dependence of the carbonylation rate on applied magnetic field. Later measurements by other workers using different experimental techniques are in agreement with our findings.

2. This paper reports a large change in the rate of the nickel carbonylation reaction $\text{Ni} + 4(\text{CO}) \rightarrow \text{Ni}(\text{CO})_4$ at the magnetic phase transition of the nickel substrate. The activation energy is larger in the ferromagnetic state than in the paramagnetic state and the magnitude of the difference in activation energies is of similar magnitude to the exchange energy of the substrate. A series of Ni-Cu alloys was used to vary the Curie temperature in the nickel carbonylation reaction, since CO does not react with Cu.

3. This paper contains additional evidence for a Hedvall effect in the $\text{Ni}(\text{CO})_4$ reaction with regard to a change in activation energy, and is an expanded version of publication (2).

4. This paper reports the results of a calculation of the electronic structure of the various molecular complexes $\text{Ni}(\text{CO})_n$ for $n = 1, 2, 3$ and 4. It is concluded that the largest changes in the Ni electronic levels occur with the addition of a single CO group. The mono-carbonyl is calculated to be a diamagnetic species with a filled d-band. From this result we infer that this is the entity which breaks the bonds to the surface. After leaving the surface, CO groups are rapidly added to the mono-carbonyl until the $\text{Ni}(\text{CO})_4$ reaction is complete.

5. This paper was invited by the editors of Nature and comments on the relation between morphological changes observed by LEED and Hedvall effects observed in chemical reactions when a magnetic phase transition occurs.

6. This paper reports on the large pulse of $\text{Ni}(\text{CO})_4$ which is produced when the nickel carbonylation reaction is initiated. A virgin surface contains a number of extremely reactive sites which rapidly etch away, after which the steady state evolves. This manuscript is essentially complete.

7. This paper reports on a cluster calculation of ethylene on Ni. The bonding occurs to a single Ni surface atom. This calculation was undertaken to gain understanding of the Hedvall Effect that we have observed experimentally in preliminary studies of the hydrogenation of ethylene on nickel surfaces. This paper is a preliminary report on this calculation.

8. This paper is based on the Ph.D. thesis of Iris Howard and gives the results of a cluster calculation of ethylene on Ni. A spin-polarized calculation is carried out in order to model the effect of a magnetic transition on the electronic structure of ethylene on a Ni 100 surface. This paper is in preparation.

9. This is the Ph.D. thesis of R.S. Mehta which includes the work in papers 1,2,3.
10. This is the Ph.D. thesis of I.A. Howard, which includes the work in papers 4,7,8.

Invited Talks

1. G. Dresselhaus, La Jolla Institute Workshop on Physics of Surfaces; Aspects of the Kinetics and Dynamics of Surface Reactions, August, 1979.
2. G. Dresselhaus, Physics Colloquium, Boston University, October, 1979.
3. M.S. Dresselhaus, Colloquium, National Bureau of Standards, November, 1979.
4. M.S. Dresselhaus, Colloquium, Cornell University, January, 1980.
5. H.J. Zeiger, Materials Center Colloquium, M.I.T., February, 1980.

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