Hydrogen Activation by Cu–Ni Films

Rates of equilibration of H_2-D_2 on Cu–Ni alloy films, prepared as previously described (*1*), yield curved or 'broken' Arrhenius plots at several compositions (Fig. 1) as has been found elsewhere for Ni (*2*). Irrespective of mechanistic complexity it is clear that activities relative to Cu are very high (10^2–10^4-fold greater) down to 3 atom % Ni. While there is as yet insufficient evidence for the occurrence of surface phase-separation (*3*) in the Cu–Ni system (*4*), this feature ought not to be a complication for percentages of Ni less than 10, which represents the thermochemically predicted phase boundary. The results of Fig. 1 appear then to represent a clear-cut demonstration of the retention of hydrogen activating power of Ni atoms in single-phased solution in Cu even at a concentration of ~3% Ni, a conclusion suggested in the past from results with less fully characterised catalysts (*5–7*). Zhavoronkova, Boreskov, and Nekipelov (*8*) have recently reported similar results.

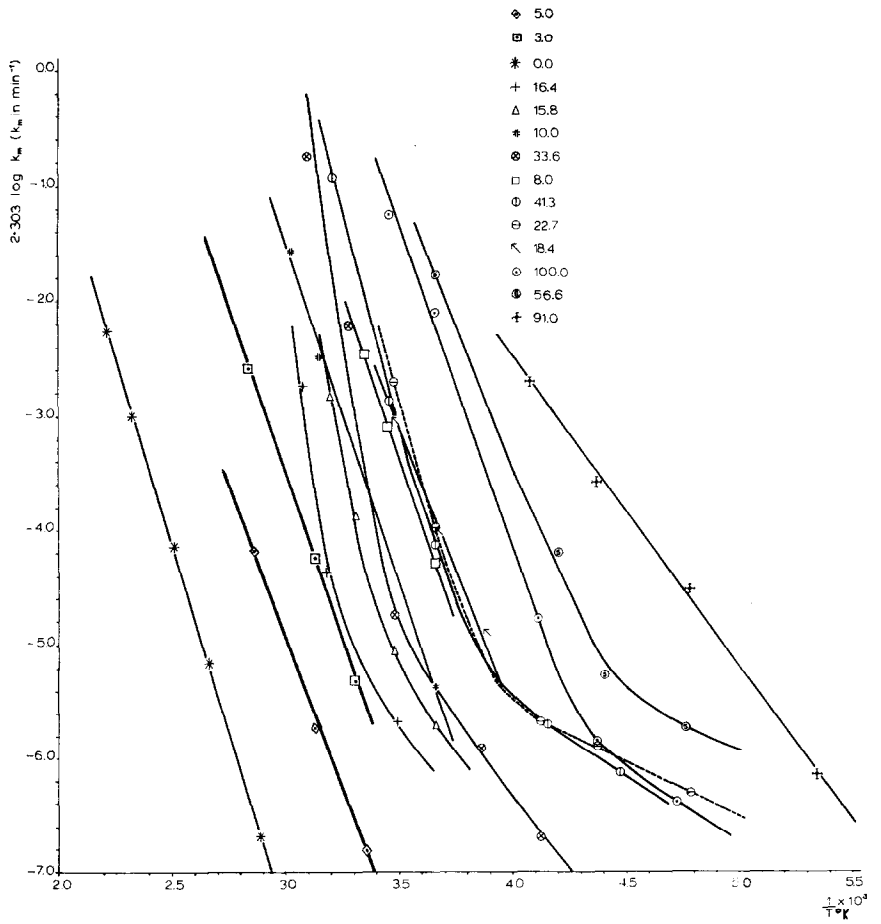

FIG. 1. Arrhenius plots for H_2–D_2 equilibration on Cu–Ni alloy films. Identifying symbols indicate composition of film in atom % Ni. Kinetic data at p = 1.0–1.3 Torr.

The seeming failure of the d-band model in describing the catalytic behavior of the Cu–Ni system, in the face of its success (*9*) in the Pd–Au series, is lessened by the evidence from electrical properties, electronic specific heat, and magnetic susceptibility that d-holes persist to the Cu-rich compositions of the Cu–Ni system (*10–11*). The configuration of Ni atoms (*10*). Briefly, the distinction in this respect between the two alloy series is thought to reside in the sensitivity to site volume of the electronic idea is that when Ni or Pd atoms have more space than in their parent lattices, the d-levels become more like the respective free–atom configurations, that is for Ni emptier and for Pd fuller. There are indications from magnetic measurements that only the Ni atom closest to a hydrogen adatom is seriously affected electronically, while adjacent Ni atoms suffer only a peripheral effect—the Ni atom concerned in the adsorption bond "becomes, in effect, no longer an active partner in the metal ensemble" (*12*). There is some indication from the selectivity for 1,3-butadiene hydrogenation that the Pd atoms retain their chemical individuality in alloy catalysis (*13*). Zhavoronkova *et al.* (*8*) have interpreted their H_2–D_2 equilibration activities on Cu–Ni catalysts on the basis that the Ni atoms are the active centers. The present results are included with those of Zhavoronkova in Fig. 2, both sets being expressed as reaction rate-constants (*2*) k_0 at a temperature of 293°K. There is reasonable agreement as to a downward trend in rates with decrease in the fraction of Ni atoms at this (and at lower) temperature. It is also consistent with the individual-atom interpretation that the activity variation is principally contained in the frequency factor (Fig. 1). We would express the caution, however, that if the Cu–Ni alloys have undergone phase separation (*3*) at their surfaces on cooling from the annealing temperature of 500°C (here) or 400°C (8), the two phases will occure together as a surface patchwork, and a pattern largely indistinguishable from that of a single-phased catalyst acting as an assembly of active Ni atoms would result. The points for low Ni (<10 atom %) alloy films are, however, free from this reservation.

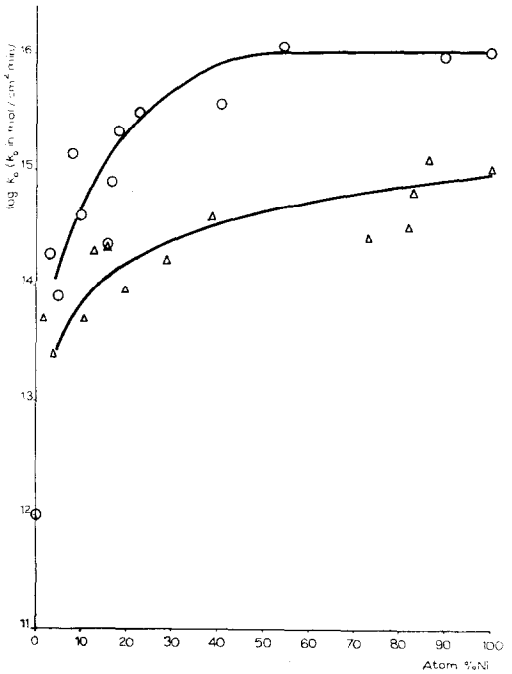

FIG. 2. Variation of activity with Ni content for H_2–D_2 equilibration at 293°K. Upper curve (circles) shows present results, and lower curve (triangles) those of Zhavoronkova *et al.* (*8*). Rate constants k_0 and k_m (Fig. 1) are as defined in (*2*). Surface area is approximated as the reactor wall area of 400 cm².

A previously reported activity pattern for olefin hydrogenation on Cu–Ni films (*14*) is consistent with the present findings and we now regard as unnecessary the supposition that atomic displacement of Ni caused by chemisorption occurs: such a process would seem to make excessive energetic demands (*15*). Preliminary indications are that activity for C–H bond breaking on Cu–Ni alloys also persists to small percentages of Ni and the same underlying reason may apply (*16*).

REFERENCES

1. BYRNE, J. J., AND CLARKE, J. K. A., *J. Catal.* **9**, 166 (1967).
2. ELEY, D. D., AND NORTON, P. R., *Discuss. Faraday Soc.* **41**, 135 (1966).

3. SACHTLER, W. M. H., AND JONGEPIER, R., *J. Catal.* **4**, 665 (1965).
4. CLARKE, J. K. A., AND BYRNE, J. J., *Discuss. Faraday Soc.* **41**, 261 (1966).
5. IPATIEFF, V. N., CORSON, B. B., AND KURBATOV, J. D., *J. Phys. Chem.* **43**, 589 (1939).
6. TAKEUCHI, T., SAKAGUCHI, M., MIYOSHI, I., AND TAKABATAKE, T., *Bull. Chem. Soc. Jap.* **35**, 1390 (1962).
7. SHALLCROSS, P. B., AND RUSSELL, W. W., *J. Amer. Chem. Soc.* **81**, 4132 (1959).
8. ZHAVORONKOVA, K. N., BORESKOV, G. K., AND NEKIPELOV, V. N., *Dokl. Akad. Nauk SSSR* **177**, 1124 (1967).
9. ELEY, D. D., *J. Res. Inst. Catal., Hokkaido Univ.* **16**, 101 (1968).
10. HUME-ROTHERY, W., "Atomic Theory for Students of Metallurgy," p. 415. Institute of Physics, London, 1960.
11. KÖSTER, W., AND SCHÜLE, W., *Z. Metallkunde* **48**, 592 (1957).
12. SELWOOD, P. W., "Adsorption and Collective Paramagnetism," p. 86. Academic Press, New York, 1962.
13. JOICE, B. J., ROONEY, J. J., WELLS, P. B., AND WILSON, G. R., *Discuss. Faraday Soc.* **41**, 223 (1966).
14. CLARKE, J. K. A., AND BYRNE, J. J., *Nature* **214**, 1109 (1967).
15. EHRLICH, G., *Discuss. Faraday Soc.* **41**, 54 (1966).
16. CLARKE, J. K. A., MCMAHON, E., AND CARR, P. F., submitted for publication.

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A Simple Micro BET System

It recently became necessary in this laboratory to determine the nitrogen BET surface areas of some well-sintered metal catalysts whose surface areas were known to be smaller than those which could be conveniently measured with the standard apparatus.

Accordingly, the system shown in Fig. 1 was devised: The adsorption cell and doser are built as a single unit comprising three Hoke 4616-M4N valves and a thermistor, installed as previously described (*1*). This particular Hoke valve was selected because of its low internal volume and excellent high vacuum properties. The portion of the system between the first two valves including the thermistor manometer comprise the doser and are enclosed in an air thermostat. The complete adsorption unit was attached to a standard high vacuum apparatus. The thermistor was calibrated with helium and nitrogen in the pressure range 10^{-1}–10^{-3} Torr using a McLeod gauge, after which the McLeod gauge was isolated from the adsorption system.

Some typical results are shown in Fig.

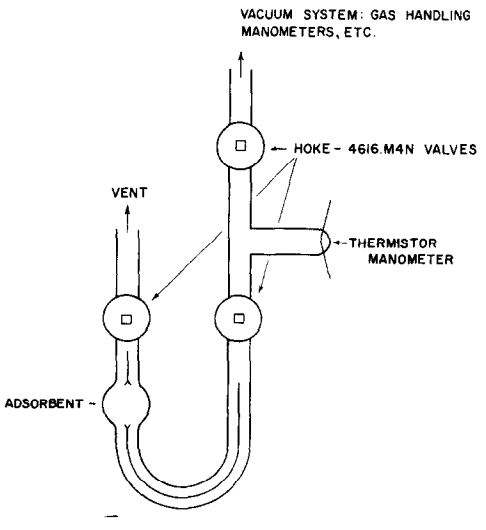

FIG. 1. The adsorption cell and doser.