JOURNAL OF CATALYSIS **28**, 174–178 (1973)

NOTES

Catalytic Activity and Alloy Composition of Clean Surfaces of Copper–Nickel

Many studies have been carried out on copper–nickel alloys in seeking the fundamental basis of catalysis by metals and alloys in connection with the electronic structure of alloy catalysts. One of the most important problems to study in this field has been to clarify the correlation between the catalytic activity and surface composition of copper–nickel alloys. From the viewpoint of "clean surface approach," evaporated films have been currently used as alloy catalysts. A doubt, however, has arisen as to whether or not alloy film catalysts have a homogeneous composition.

Sachtler and his coworkers (*1*, *2*) presented an evidence by means of work-function measurement that the evaporated films of copper–nickel alloys separate into two phases with annealing *in vacuo* at not very high temperatures ($\simeq$200°C). Similar results on the thin films of copper–nickel alloys by means of X-ray diffraction have been reported by Campbell and Emmett (*3*). However, there have been pronounced discrepancies of the catalytic activity patterns in the experimental results even in use of similar film catalysts of copper–nickel alloys. These discrepancies might be attributed to the some differences in alloy composition, structure, and impurities of the uppermost surface layers which could be greatly influenced by the preparation method of alloy catalyst films.

It is the purpose of the present communication to reveal the correlation between catalytic activity and the alloy composition of the clean surface of copper–nickel alloy plates. In the present study, catalytic activity in the hydrogen–deuterium exchange reaction was observed on clean surfaces of copper–nickel alloys which were prepared by argon ion-beam bombardment in an ultrahigh vacuum apparatus ($\sim 10^{-10}$ Torr), and the alloy composition of the clean surface was determined by means of Auger electron spectroscopy (*4*, *5*).

Using the specimen of 0.6 mm in thickness and 2 cm^2 total geometric surface area, surfaces were cleaned by the argon ion-beam bombardment (*6*) after heating at 800°C for 8 hr *in vacuo*. The reaction chamber was capable of evacuating to the pressure of 1×10^{-9} Torr or less by two sputter ion pumps, and reactant gases stored in a grease-free system were admitted to the reaction chamber through cold traps and metal valves.

The catalytic activity of pure nickel prepared with the argon ion-beam bombardment ($P_{\mathrm{Ar}} = 10^{-4}$ Torr, 5 μA/cm^2, 500 eV) was increased gradually with the increase of sputtered surface layers and came to equilibrium after the sputtering out about 80 monolayers. The surface impurities in the Auger spectra were not detectable after the sputtering of several tens of monolayers by the bombardment. These findings suggest that the enhancement of catalytic activity could be attributed to the removing of surface impurities with the bombardment.

The catalytic activity and activation energy of pure nickel to the hydrogen–deuterium exchange reaction is compared to those by several workers (Table 1). The

TABLE 1

Catalytic Activity of Nickel to the Reaction of Hydrogen-Deuterium Exchange[a]

	Form of catalyst	Surface treatment	Rate constant, k_m (molecules/cm^2 · sec)	Activation energy (kcal/mole)
This work	Plate	Argon ion-beam bombardment	3.2×10^{16}	2.7
Shooter and Farnsworth (*7*)	Plate	Argon ion glow discharge	3.6×10^{16}[b]	—
Shooter and Farnsworth (*7*)	Evaporated film		0.39×10^{16}[b]	2.4
Eley and Shooter (*8*)	Wire	High temperature flashing	0.46×10^{16}[b]	2.4
Eley and Norton (*9*)	Wire	Oxidation–Reduction, flashing	$4.4–6.7 \times 10^{16}$[b]	2.4

[a] The total pressure of the reactant gases is 0.23 Torr. ($P_{H_2} = P_{D_2}$) and the reaction temperature is 273°K.

[b] The k_m values at total reactant pressure of 0.23 Torr and temperature of 273°K were calculated according to the activation energy (2.4 kcal/mole) and pressure dependency ($k_m \propto P^{0.4}$) (*9*).

catalytic activity of copper–nickel alloys cleaned by the same bombardment was observed against their surface compositions that were determined by Auger spectroscopy as shown in Fig. 1. The activity was observed to be greatest in pure nickel and then to decrease exponentially as copper content in alloys increases. It is obvious that the catalytic activity of pure nickel was almost unchanged after annealing at 300°C for 20 min, while even those of copper–nickel alloys were decreased considerably after the annealing.

It has been reported in the previous studies (*4, 5, 10*) that the surface composition of copper–nickel alloys by means of Auger spectroscopy was changed considerably by the surface treatments. In the case of 80% nickel alloy, for example, nickel became dense after the ion bombardment, while copper became dense after the oxidation–reduction or the annealing treatment. Tarng and Wehner (*11*) and Quinto *et al.* (*12*) have also reported in their Auger spectroscopy studies that copper atoms were removed preferentially by the sputtering.

In the present paper, it should be emphasized that the catalytic activity of clean surfaces of copper–nickel alloys could be closely related to the surface composition

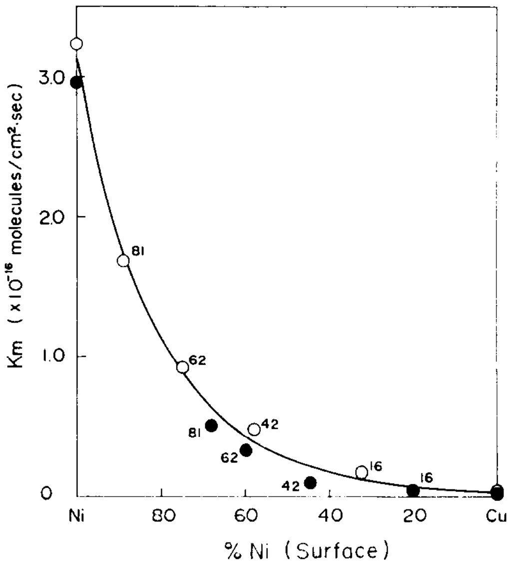

Fig. 1. The catalytic activity of copper–nickel alloys as a function of surface composition of nickel determined by Auger spectroscopy. Pressure of reactant gases, $P_{H_2} = P_{D_2} = 0.115$ Torr; reaction temperature, 273°K. The numerical value with each point indicates the composition of nickel in the bulk alloy. ○: After removing about 100 surface monolayers by the argon ion-beam bombardment. ●: After the vacuum annealing (10 min, 300°C) subsequent to the argon ion-beam bombardment.

of nickel which was determined precisely by Auger spectroscopy. However, the present evidence is not yet conclusive as to whether only the surface content of nickel is connected with the catalytic activity or the electronic factor is connected with it.

ACKNOWLEDGMENTS

The authors are greatly indebted to Dr. K. Nakayama, Mr. M. Ono, and Mr. H. Shimizu of the Electrotechnical Laboratory, Tokyo for their interest and valuable discussions throughout this work.

REFERENCES

1. SACHTLER, W. M. H., AND DORGELO, G. J. H., *J. Catal.* **4**, 654 (1965).
2. SACHTLER, W. M. H., AND JONGPIER, R., *J. Catal.* **4**, 665 (1965).
3. CAMPBELL, J. S., AND EMMETT, P. H., *J. Catal.* **7**, 252 (1967).
4. TAKASU, Y., YAMASHINA, T., SHIMIZU, H., ONO, M., AND NAKAYAMA, K., *Shokubai* **13**, 170P (1971).
5. NAKAYAMA, K., ONO, M., AND SHIMIZU, H., *J. Vac. Sci. Technol.* **9**, 749 (1972).
6. ONO, M., *J. Vac. Soc. Jap.* **14**, 94 (1971).
7. SHOOTER, D., AND FARNSWORTH, H. E., *J. Phys. Chem. Solids* **21**, 219 (1961).
8. ELEY, D. D., AND SHOOTER, D., *J. Catal.* **2**, 259 (1963).
9. ELEY, D. D., AND NORTON, P. R., *Discuss. Faraday Soc.* **41**, 135 (1966).
10. ONO, M., TAKASU, Y., NAKAYAMA, K., AND YAMASHINA, T., *Surface Sci.* **26**, 313 (1971).
11. TARNG, M. L., AND WEHNER, G. K., *J. Appl. Phys.* **42**, 2449 (1971).
12. QUINTO, D. T., SUNDARUM, V. S., AND ROBERTSON, W. D., *Surface Sci.* **28**, 504 (1971).

YOSHIO TAKASU
TOSHIRO YAMASHINA

Department of Nuclear Engineering,
Hokkaido University,
Sapporo, Japan 060
Received June 26, 1972

Determination of Proton Acidity of Solid Catalysts by Chromatographic Adsorption of Sterically Hindered Amines

To be useful, an acidity measurement of a solid catalyst should fulfill two requirements: (1) it should be simple to carry out; and (2) it should determine the seat of catalytic activity. Adsorption measurements of basic reagents such as ammonia (*1*, *2*), *n*-butylamine (*3*), or quinoline (*4*) appear to fulfill the first requirement but do not fulfill the second. For example, on a unit surface basis pure alumina chemisorbs more ammonia than silica–alumina (*1*), yet alumina is inactive for cumene cracking* under conditions that silica–alumina is highly active (*5*). On the other hand, though infrared measurements of chemisorbed pyridine provide proton acidity values that correlate with catalytic activity (*7*), this type of measurement is not simple. It would be much easier to determine surface acidity by measuring chemisorption of a basic reagent that is specific for proton acidity—if such a reagent exists.

Thirty years ago, Brown, Schlesinger, and Cardon (*8*) began a series of studies of the acid-base reactions of substituted boranes with a variety of substituted amines. These studies revealed that the stability of the resulting "salts" was strongly dependent on the size and number of alkyl groups attached to the acid and

---

* Presumably, the inactivity of alumina results from its lack of proton acidity—infrared measurements show that pyridine chemisorbed on alumina is entirely in a coordinated state (*6*).