JOURNAL OF CATALYSIS 8, 105–112 (1967)

Ammonia Synthesis Catalyzed by Uranium Nitride

I. The Reaction Mechanism

N. SEGAL AND F. SEBBA

From the Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

Received July 13, 1966; revised February 7, 1967

Uranium nitride has been shown to be an interesting catalyst for synthesis of ammonia at pressures of 30 atm and at temperatures between 375° and 550°C. The apparent activation energy is about 18 kcal. It was found that pretreatment at 525°C and then freezing the equilibrium by cooling below the working temperature and subsequently raising the mixture to the synthesis temperature produced a marked increase in activity, which is transient, the catalyst slowly reverting to its steady activity.

INTRODUCTION

It has long been known that uranium (nitride) is a catalyst for the ammonia synthesis (*1–4*). That this should be so is surprising, for in the light of the current theories of the ammonia synthesis it would not be expected that an actinide metal or its bulk nitride would be an ammonia catalyst. However, the active catalyst is the nonstoichiometric uranium sesquinitride phase, which has a wide range of nitrogen composition, and therefore it is possible that the nitrogen content of the catalyst will vary during the reaction depending on the temperature and the nitrogen partial pressure. The possibility also arises that the nitrogen from the catalyst itself may influence the reaction. Because reliable data on the uranium–nitrogen system have only recently become available, it has not been possible hitherto to investigate these problems thoroughly. In fact, over 30 years ago, although in somewhat different terms, it was suggested by Frankenburger (*4*) that the system should be further studied.

U_2N_3 was first identified as having a body-centered cubic structure of the rare earth type-C, (Mn_2O_3) (*5*). This is the structure usually found for U_2N_3 and is the one with which this work has been concerned. It may be regarded as being derived from the fluorite structure of UN_2 by the ordered removal of nitrogen, with a slight distortion of the uranium sublattice. Conversely, these nitrogen vacancies in U_2N_3 may be filled by additional nitrogen atoms, and this has led to the concept of a homogeneous solid phase existing between U_2N_3 and UN_2 (*5*). Nitrides of composition $UN_{1.5+x}$ can be readily reduced with hydrogen as far as $UN_{1.5}$, after which reaction occurs only very slowly and only at elevated temperatures (*6*). This is contrary to the work of Francis and Hodge (*7*), who report no reaction between $UN_{1.75}$ and hydrogen. U_2N_3 can be pyrophoric depending on the method of preparation, and it takes up oxygen at the surface on exposure to air for some time at room temperature (*8*).

EXPERIMENTAL

Catalyst Preparation and Analysis

The uranium sesquinitride catalyst was prepared by treating small slugs of uranium metal with purified hydrogen at 225°C until all the uranium had reacted; the temperature was then increased to 850°C and the gas stream changed to purified nitrogen. When not in use the catalyst, which was used in powdered form, was stored in the dark under trichlorethylene, which was shown, by chemical and X-ray analyses, to be inert to uranium nitride.

Spectrographic analysis showed that the major impurities (other than oxygen) were iron (300 ppm on the basis of uranium in U_3O_8), carbon (100 ppm), and copper (50 ppm).

The method of Kriege (*4*) was used to determine the total uranium in the catalyst. About 200 mg of sample was weighed out in a platinum boat and ignited in a slow stream of oxygen at 800°C for 1 hr, the product being removed and weighed as U_3O_8.

The analysis of nitrogen was less satisfactory, a number of methods being attempted. Both the Kjeldahl method of Lathouse *et al.* (*10*) and an inert gas fusion method using a Leco-Nitrox 6 analyzer yielded erratic results. A recently developed, modified Kjeldahl procedure (*14*), where the sample is digested by treatment with surfuric acid and copper selenate under controlled reflux conditions, was finally adopted. This procedure gave reproducible results, but according to Milner *et al.* (*11*) the values are likely to be low by as much as 2.5%.

As there was no method available for its direct determination, oxygen was estimated by difference. It must be emphasized that, while the uranium analyses are considered to be accurate, the figures for nitrogen are probably somewhat low and those for oxygen consequently high. It is thus not justifiable to assign precise formulas to the samples.

X-Ray diffraction analyses were carried out on both a Phillips and a General Electric X-ray diffractometer using a copper target tube with a nickel filter.

Surface areas were determined by the continuous flow method, using nitrogen as adsorbate at −195°C and helium as carrier gas.

Apparatus

The catalytic reaction was studied at a total pressure of 30 atm in the range 338–547°C. The synthesis gas was usually the stoichiometric mixture flowing at a rate of 4.15 liter (STP)/hr.

The high-pressure system was the same as that employed by King and Sebba (*12*) in their investigation of ammonia synthesis over vanadium nitride catalysts. A known mixture of hydrogen and nitrogen was purified by passing it through consecutive beds of palladized asbestos heated to 300°C, self-indicating silica gel, potassium hydroxide pellets, and finally Anhydrone magnesium perchlorate. The mixture was then flowed through the catalyst bed at definite space velocity, pressure, and temperature, and the effluent gases analyzed. The nitrogen and hydrogen were determined by a method based on the difference in their thermal conductivities, using thermistor elements in a simple Wheatstone bridge circuit. The ammonia was analyzed continuously by an automatic coulometric titration procedure (*13*).

A simple vacuum system consisting of a single-stage rotary pump, a three-stage mercury diffusion pump, a McLeod gauge, and two cold traps, was connected to the high-pressure apparatus. This was used to ensure that no gases, other than the synthesis mixture, were in contact with the catalyst.

RESULTS AND DISCUSSION

One of the most interesting outcomes of this work has been the observation of an unusual transient behavior shown by the catalyst. Detailed consideration is given to this phenomenon in the following paper, but it must be noted here that this behavior has its origin in the fact that under some conditions the first few subsurface layers of the catalyst are able to take up additional nitrogen and that under different conditions this "extra" nitrogen is able to participate in the synthesis reaction. This further nitridation is favored by higher nitrogen pressure (according to a Henry's law relation $P_{N_2}{}^{\frac{1}{2}}$) and also by higher temperatures (since at the relatively low temperatures used the further nitridation of uranium sesquinitride is unable to reach true equilibrium).

As a result of these effects the approach to steady state in the rate of formation of ammonia under a particular set of experimental conditions was critically dependent on the immediately previous history of the catalyst. Nevertheless, the catalyst behaved consistently and reproducibly with the exception that there was a slight decrease in activity with time. Since purification of the synthesis gases was not complete, traces of oxygen and/or water vapor were probably present. Uranium nitride is thermodynamically unstable with respect to the oxide at the temperatures used, so that the catalyst was slowly and continuously being poisoned during the course of a run, with progressive decline in activity.

TABLE 1

ACTIVATION ENERGIES FOR TWO CATALYSTS

Catalyst	Temperature range (°C)	Apparent activation energy[a] (kcal/mole)
N1	338–547°	18.1
	348–547°	18.6
	347–525°	19.3
N2	375–525°	16.3
	439–500°	17.0
	375–425°	17.4

[a] Estimated error in activation energy values: 3%.

Two catalyst samples were extensively studied, catalyst N1 for 8 months, and catalyst N2 for 6 months. Values of the apparent activation energy (as calculated from log rate in mg ammonia/hr versus $1/T$) were obtained at roughly 2-month intervals for both catalysts. The results are shown in Table 1, and representative Arrhenius plots for catalyst N2 are given in Fig. 1.

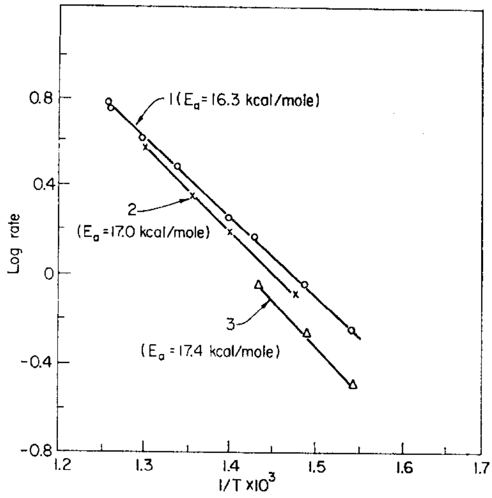

FIG. 1. Arrhenius plot for catalyst N2.

In Table 2 the results of the various chemical and physical analyses of the catalysts are given. Before N1 was removed for analysis it was kept in the synthesis gases at 375°C for about 2 weeks; it was then cooled to room temperature, a portion

TABLE 2

ANALYSES OF CATALYSTS[a]

	Catalyst N1			Catalyst N2	
	Before use	After use			
		(a)	(b)	Before use	After use
U(%)	91.00	89.80	89.71	91.02	90.84
N(%)	8.70	8.20	8.32	8.73	7.83
Impurities (%)	0.05	0.05	0.05	0.05	0.05
O(%)	0.25	1.95	1.92	0.20	1.28
Surface area (m^2/g)	1.37	—	3.92	1.29	4.07
Lattice constant	10.670	10.658	10.652	10.668	10.692
(A)	($UN_{1.60}$)	($UN_{1.65}$)	($UN_{1.68}$)	($UN_{1.60}$)	($UN_{1.50}$)
		5.472	5.470	—	5.486
		(UO_{2+x})	(UO_{2+x})	—	(UO_{2+x})
Weight (g)	3.5	—	—	3.9	—

[a] Pure $UN_{1.5}$ contains 91.8% U and 8.2% N. The impurities were estimated from the spectrographic analyses. The nitride phase had the Mn_2O_3 structure, and the oxide the fluorite structure. The oxide phase was identified as UO_{2+x}, where x is very small, probably less than 0.03 (*14*). The (approximate) nitrogen-to-uranium ratios given in parentheses after the lattice parameters were obtained by comparing the value of the latter with recent data (*15*) showing the variation of lattice constant with nitrogen content.

taken for analyses (sample a), and the procedure repeated for a temperature of 525°C (sample b). After use catalyst N2 was reduced in a stream of pure hydrogen at 525°C for 1 week before being analyzed.

Table 1 shows that there was a steady increase in the activation energy of both catalysts with time. Also, N1 has a somewhat higher value than N2. It has already been noted that there is a slow decline in activity of each catalyst during the course of its use and that this is a result of the slow continuous oxidation of the catalyst.

It seems reasonable to relate the increasing activation energy to the increasing degree of oxidation. The higher activation energy over N1 can be accounted for on the same basis, since this catalyst was found to contain a greater fraction of uranium dioxide. The higher contamination of N1 was probably the result of an inadvertent fault in the gas purification system shown after N1 was introduced into the reactor.

The mechanism by which oxygen poisoning increases the activation energy is uncertain. The presence of the oxide would increase the nonuniformity of the surface in the electronic, structural, and chemical senses. Although hydrogen would probably adsorb on uranium dioxide, it is doubtful that nitrogen would do so, or at least not in the same way as on uranium sesquinitride. The oxygen in UO_2 is far more strongly bonded than the nitrogen in $UN_{1.5+x}$, and this must affect the electronic configuration of the uranium atoms involved—thus the U–O interaction is strongly ionic (*16*) and the U–N interaction only weakly so (*17*).

The increase in surface area as a result of the catalytic reaction can probably be explained as follows: The catalyst was initially a relatively coarse powder. As already mentioned, the composition of the catalyst, in the first few subsurface layers, varies according to the experimental conditions. This will result in the breaking up of the powder aggregates, in the same way as the repeated hydriding and dehydriding of uranium metal yields an extremely fine powder (*18*). Moreover, the changes in surface area appeared to take place in the very early stages of use. For instance, when catalyst N2 was "fresh" the steady state rate of ammonia formation at 375°C was 0.50 mg/hr. About 1 week later the rate was 0.585 mg/hr, and after another 10 days it was 0.583 mg/hr. In other words, after the reaction had been carried out for only a short time the rate increased (corresponding to an increase in surface area), after which it remained essentially constant (the surface area remaining the same). The slight decrease in rate with time after the initial increase can be attributed, as before, to the slow formation of uranium dioxide. An increase in surface area has been noted by Haber for uranium catalysts (*1*), but the reason suggested, that this was the effect of the high pressure (about 200 atm), does not appear satisfactory, since the catalyst bed must have been at a substantially uniform pressure throughout.

From the relationship

$$k_S/k_D = K^{1/\nu_r}$$

where k_S and k_D are rate constants for synthesis and decomposition, respectively; K, is the equilibrium constant for synthesis; and ν_r, the stoichiometric number of the rate-determining step, i.e., the number of times that step must occur for the completion of the overall reaction, it is possible to relate the activation energy for the synthesis to that for the decomposition, for which there are more data available. Assuming $\nu_r = 1$, for which there now seems strong evidence in the case of iron (*19*) and which is found to be the case here (see below), it is found that the equivalent values of the activation energy for ammonia decomposition over uranium sesquinitride lie between 40 and 44 kcal/mole. These values compare closely with the values on iron and other catalysts [see Bond (*20*)]. Temkin and Kiperman (*21*) have stated that the activation energy is almost independent of the nature of the catalyst, which "proves" that the reaction mechanism is identical on various catalysts. However, it must be noted that the activation energy for the decomposition over vanadium nitride is about 56 kcal/mole (*12*).

In the present work there is strong evidence that the release of nitrogen from the

U_2N_3 catalyst causes a marked acceleration in the rate of formation of ammonia. This can be illustrated in a number of different ways, but as this is discussed more fully in the following paper (*13a*) it will be sufficient to note the effect of slowly increasing the hydrogen content of the synthesis mixture at a temperature of 375°C (Fig. 2).

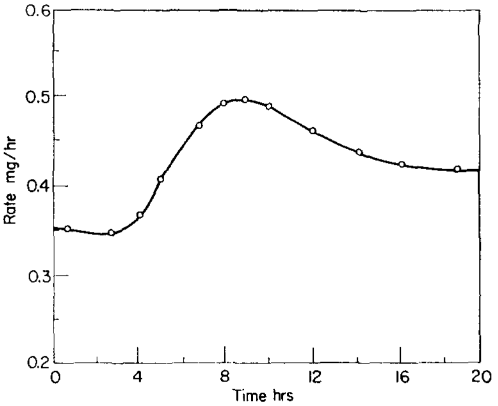

FIG. 2. Effect of increasing H_2 content on rate of ammonia synthesis.

As the percentage of hydrogen rises, the rate passes through a maximum, corresponding to the participation in the synthesis reaction of nitrogen from the catalyst in addition to that from the gas phase. There can thus be no doubt that the rate-determining step over uranium sesquinitride is the adsorption of nitrogen into an active state, for if this were not the case this additional supply of nitrogen would not affect the rate.

Figure 1 shows that the kinetics are continuous throughout the temperature range studied. Further kinetic data were obtained, at 375°C and a total pressure of 30 atm, by varying the space velocity and measuring the steady state yield of ammonia in each case (Fig. 3). An equation derivable from the stoichiometric number concept of Horiuti (*22*), assuming that $\nu_r = 1$ and that the rate of ammonia decomposition is first order with respect to the actual partial pressure of ammonia, is found to fit the data closely. The equation can be written

$$-\log\{1-(x/x_e)^2\} = (2k/V) + \text{constant} \qquad (1)$$

where k is the rate constant for synthesis; x, x_e, are actual and equilibrium partial pressures of ammonia; and V is space velocity. The data are plotted in Fig. 4. It is noteworthy that for the special case where x_e is low and the value of α in the Temkin-Pyzhev equation (*23*) is 0.5, this latter equation reduces to an expression of exactly the same form as Eq. (1) above (*24*).

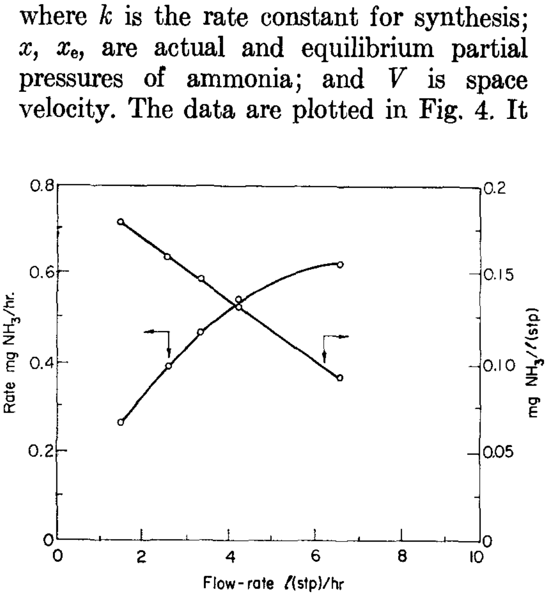

FIG. 3. Normal synthesis rate as function of gas flow rate.

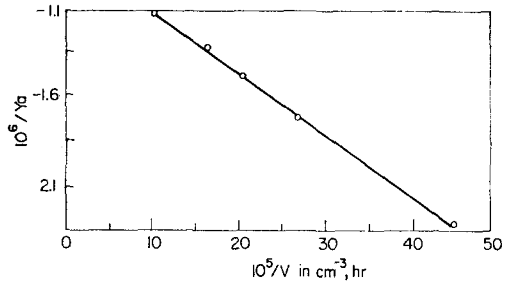

FIG. 4. Verification of rate equation (1).

It has been stated that those metals which are good ammonia catalysts are unable to form nitrides with elementary nitrogen, at least at the temperatures and pressures used in the catalytic synthesis (*20*, *25*). This being so, bulk uranium metal should not be suitable as an ammonia catalyst since under synthesis conditions it readily forms a nitride in the composition range U_2N_3–UN_2; thus according to Haber and Greenwood it is the uranium nitride, not the uranium metal, that is the active catalyst (*2*). Furthermore, the exact composition of the catalyst is a function of the experimental conditions.

Even allowing for the fact that Frankenburg (*25*) was primarily concerned with "stable" bulk nitrides, it would appear that his contention that such materials cannot be ammonia catalysts has been too rigidly defined and interpreted. He apparently excluded the possibility that the nitrogen in the bulk nitride may not all be held with the same bond strength. This weakness in his argument has been clearly demonstrated by King and Sebba (12) for the case of a vanadium nitride catalyst.

In the case of uranium sesquinitride as an ammonia catalyst it is probable that for the nitrides U_2N_3–UN_2 there is present more than one type of bonding in the bulk (*15,26*). There are probably two "main" types, one being considerably stronger than the other. The more weakly held nitrogen species is readily accommodated or expelled by the solid according to the experimental conditions.

It is thus likely that on a uranium sesquinitride catalyst which is still capable of taking up nitrogen, nitrogen chemisorbed from the gas phase may either penetrate below the surface and be accommodated in a nitrogen vacancy or else react with hydrogen (assuming that none would desorb in the presence of hydrogen and an "unsaturated" solid). The situation is well illustrated by a number of data (Fig. 5).

Curve A was obtained after reducing the catalyst at 525°C in pure hydrogen for 2 days (it was subsequently shown by X-ray diffraction that the catalyst would still have been in the U_2N_3 state), cooling to 100°C, and then heating to 375°C in a normal synthesis mixture (the curve is drawn only for the last part of the cycle). After the ammonia conversion had reached a steady value at 375°C, the temperature was dropped to 100°C and then increased again to 375°C (curve B), the gas mixture being the same throughout.

The presumed explanation for the difference in behavior is as follows: For the first curve the catalyst, after reduction with hydrogen, has initially a great affinity for nitrogen and consequently nearly all the chemisorbed nitrogen tends to penetrate below the surface. But with increasing nitrogen content in the surface layers the heat of incorporation decreases until a point is reached where the heat of further nitridation approaches the enthalpy of reaction between chemisorbed nitrogen and hydrogen, at which stage the rate of synthesis of ammonia increases. The rate increases only slowly since at first the two enthalpies are of the same order, so that there is competition for the adsorbed nitrogen either to react with hydrogen or to be incorporated. Once steady state is reached all the available nitrogen vacancies that can be filled under the prevailing conditions must be occupied, and so the second curve shows the far more rapid rate of increase of ammonia formation when all (or most) of the chemisorbed nitrogen is available for hydrogenation.

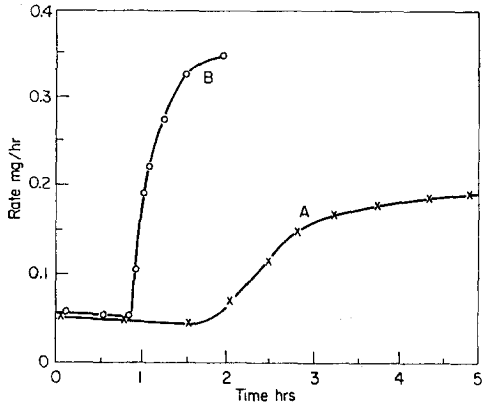

FIG. 5. Effect of pretreatment on rate of synthesis at 375°C; A, after reduction at 525°C; B, after previous steady state at 375°C.

The variation in ammonia rate with composition of the synthesis mixture at 375°C and a total pressure of 30 atm (Fig. 6), which has a broad peak extending over a wide range of gas composition, can probably be best explained as follows: In the relatively low range of nitrogen pressures the tendency is for the adsorbed nitrogen to react with hydrogen rather than to penetrate below the surface and so the rate rises rapidly. But as the nitrogen pressure is increased the incorporation process is able to commence since the subsurface layers are unsaturated with respect to the concentration that would be in "equilibrium" with the nitrogen pressure in the gas phase. Hence the additional amounts of chemisorbed nitrogen tend to penetrate below the surface, while the amount that reacts with hydrogen remains much the same. At still higher nitrogen pressures the incorporation process is even more favored and, of course, there is less hydrogen available for reaction, with the result that at the very high nitrogen (low hydrogen) gas compositions the rate begins to decrease steadily until it reaches zero at 100% nitrogen. These arguments are well supported by the behavior mentioned previously (Fig. 2).

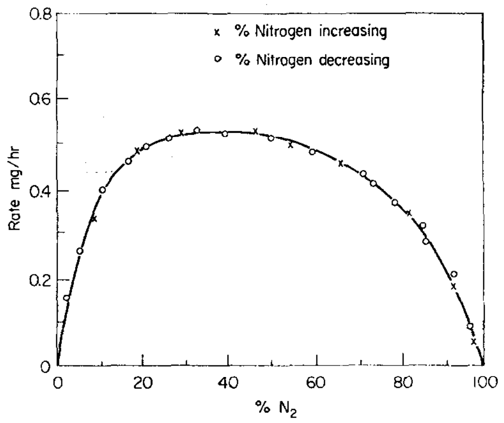

FIG. 6. Normal synthesis rate as function of gas composition.

It seems possible that the relatively weakly held nitrogen from the subsurface layers of the catalyst may participate in the synthesis even under steady conditions. This nitrogen species does react under certain circumstances, and it may be that these atoms are sufficiently mobile to migrate continuously to the surface and to react there with hydrogen. There might then be some type of dynamic exchange process between those adsorbed nitrogen atoms which are not immediately hydrogenated and the loosely bonded nitrogen atoms below the surface.

An analogy might then be drawn between the present uranium nitride–nitrogen system and the various metal oxide–oxygen systems which have been extensively studied in chemisorption and catalytic processes. The possible correspondence between the nitride–nitrogen and oxide–oxygen systems has been noted before (*20, 28*), as has the structural similarity between U_2N_3–UN_2 and various rare earths oxides (*26*). The work of Winter (*29*) is of significance since he has shown that lattice oxygen lying close to the surface of the catalyst, in addition to a species chemisorbed from the gas phase, can take part in catalytic reactions involving oxygen-containing gases. Of particular note is that in the interaction of oxygen with the Mn_2O_3–MnO_2 system oxygen exchange occurs between gas and solid (*30*).

On a weight for weight basis, a promoted iron catalyst is at least 150 times as active as uranium nitride, but then the surface area of uranium nitride is very much less than that of the iron catalyst. It is also possibly partially poisoned by oxygen. Could the surface area be markedly increased and the oxygen poisoning eliminated, uranium nitride might become a possible rival to the iron catalyst.

ACKNOWLEDGMENT

Thanks are expressed to the Atomic Energy Board of South Africa for financial support for this work.

REFERENCES

1. HABER, F., *Z. Elektrochem.* **16,** 244 (1910).
2. HABER, F., AND GREENWOOD, F. C., *Z. Elektrochem.* **21,** 241 (1915).
3. KRÖGER, C., *Z. Elektrochem.* **38,** 670 (1933).
4. FRANKENBURGER, W., *Z. Elektrochem.* **38,** 818 (1933).
5. RUNDLE, R. E., BAENZIGER, N. C., WILSON, A. S., AND MCDONALD, R. A., *J. Am. Chem. Soc.* **70,** 99 (1948).
6. RUNDLE, R. E., *et al.*, AECD 2247, Atomic Energy Commission, U. S. (declassified May 1962).
7. FRANCIS, K., AND HODGE, N., AERE-R3710, Atomic Energy Research Establishment, Harwell, U. K. (1961).
8. DELL, R. M., AND ALLBUTT, M., AERE-R4253, Atomic Energy Research Establishment, Harwell, U. K. (1962).
9. KRIEGE, O. H., LA-2307, Los Alamos Scientific Laboratory, New Mexico (1959).

10. Lathouse, J., Huber, F., and Chase, D. L., *Anal. Chem.* **31,** 1606 (1959).

11. Milner, G. W. C., Jones, G., Crossley, D., and Phillips, G., AERE-R4713, Atomic Energy Research Establishment, Harwell, U. K. (1964).

12. King, D. A., and Sebba, F., *J. Catalysis* **4,** 253 (1965).

13. Segal, N. S., and Wodley-Smith, R., *Anal. Chem.* **38,** 828 (1966).

13a. Segal, N., and Sebba, F., *J. Catalysis* **8,** 113 (1967) (following paper).

14. *Natl. Bur. Std. Circ.* **539,** Vol. 2, p. 33 (1953).

15. Trzebiatowski, W., and Troc, R., *Bull. Acad. Polon. Sci.* **12,** 681 (1964).

16. Riviere, J. C., AERE-R4631, Atomic Energy Research Establishment, Harwell, U. K. (1964).

17. Riviere, J. C., private communication, 1964.

18. Bugl, J., and Barrer, A. A., paper presented at Intern. Symp. on Compounds of Interest in Nucl. Reactor Technology, 1964.

19. Tanaka, K., Yamamoto, O., and Matsuyama, A., paper presented at Third Intern. Congr. Catalysis, Amsterdam, 1964.

20. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.

21. Temkin, M. I., and Kiperman, S., *J. Phys. Chem. U.S.S.R.* **21,** 927 (1947); *Chem. Abstr.* **42,** 2501 g.

22. Horiuti, J., *J. Res. Inst. Catalysis Hokkaido Univ.* **1,** 8 (1948).

23. Temkin, M. I., and Pyzhev, V., *Acta Physico-Chim. U.S.S.R.* **12,** 327 (1940); as quoted in ref. (*24*).

24. Bokhoven, C., van Heerden, C., Westrik, R., and Zwietering, P., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 3, p. 318. Reinhold, New York, 1955.

25. Frankenburg, W. G., *in* "Catalysis" (P. H. Emmett, ed.), p. 193. Reinhold, New York, 1955.

26. Segal, N. S., Ph.D. thesis, University of the Witwatersrand, Johannesburg, South Africa, 1965.

27. Tamaru, K., *Bull. Chem. Soc. Japan* **37,** 771, 1087 (1964); paper presented at Third Intern. Congr. Catalysis, Amsterdam, 1964.

28. Sachtler, W. M. H., and van Reijen, L. L., *J. Res. Inst. Catalysis Hokkaido Univ.* **10,** 87 (1962).

29. Winter, E. R. S., *Advan. Catalysis* **10,** 196 (1958).

30. Morita, N., *Bull. Chem. Soc. Japan* **15,** 1 (1940).