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Activation of Nitrogen by Alkali Metal Promoted Transition Metal
I. Ammonia Synthesis over Ruthenium Promoted by Alkali Metal

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The rate of ammonia synthesis over ruthenium was found to be remarkably promoted by addition of alkali metal, particularly when ruthenium is supported by active carbon (AC) or alumina. The synthesis rate over the 5% Ru-AC-K catalyst can be raised to about 10 times that of conventional doubly promoted iron ($Fe-Al_2O_3-K_2O$) catalyst at 250°C. Ru-AC-Cs gives even greater activity than Ru-AC-K. The catalytic activity increases with decrease in ionization potential of added alkali ($Cs > K > Na$) and with increase in the added amount of alkali metal, approaching a plateau value at around 3-4 mg-atom alkali/g-catalyst. Unsupported ruthenium is also remarkably promoted by addition of alkali metal. It is accordingly concluded that the promoter action is provided by a charge transfer from alkali metal to transition metal which brings about a higher electron density in the transition metal, a favorable state for the activation of nitrogen. The specific synthesis rates per surface ruthenium are higher over active carbon and alumina than other supports, suggesting a role of these supports as a medium of electron transfer.

INTRODUCTION

A series of studies have been made for the kinetics and mechanism of ammonia synthesis over Fe (*1*), $Fe-Al_2O_3$ (*2*) and $Fe-Al_2O_3-K_2O$ (*3*). It is accepted that the role of Al_2O_3 promoter is structural, while K_2O is believed by the authors to act as a chemical promoter changing the adsorbed main species from N to NH and accelerating the dissociation of nitrogen molecule (*1, 2*). The chemical action of K_2O has been ascribed to its electron-donating nature. Indeed, it is known that the work function of an iron surface decreases with the addition of K_2O to $Fe-Al_2O_3$, accompanying a promotion of the ammonia synthesis rate (*4, 5*). On the other hand, it is known that metallic alkali is stronger in its electron-donating nature than alkali oxide, suggesting a promising promoter for the ammonia synthesis catalyst. Based on such a consideration, the authors have found that the ammonia synthesis rates over transition metals supported by active carbon are remarkably enhanced by the addition of alkali metal (*6*). The present paper deals with ruthenium catalyst which gives the highest activity when supported on active carbon. The effect of support and the kind and amount of alkali metal will be examined to clarify the roles of catalyst components.

EXPERIMENTAL

Catalyst Preparation

Supported catalysts were prepared by impregnation of supporting material with aqueous ruthenium trichloride solution. The solution was vaporized to give dry solid. The solid was then dried at 110°C for 18 hr. Supports used were active carbon (AC), alumina, celite, glass, and silicon carbide (SiC). Two samples of active carbons, coconut carbon (8-10 #) (Dai-ichi Tanso Ltd.), AC(C), and Tsurumi Coal pellets, AC(T), were used. Elemental compositions were as follows:

	Coconut carbon AC(C)	Tsurumi coal AC(T)
C	86.4_0%	76.4_4%
N	0.0_9	0.2_0
H	0.0	0.2_1
Ash	0.8_5	6.6_4
Residual	12.6_6	16.5_1

The alumina support used was the commercial γ-Al_2O_3 produced by Sumitomo Chemical, Ltd. A 0.5% Ru–Al_2O_3 catalyst provided by Japan Engelhard, Ltd. was also used. The Ru–celite catalyst was the same as used in the previous study (7). Unsupported ruthenium was prepared by reducing $RuCl_3 \cdot 3H_2O$ powder by hydrogen at 194°C for 17 hr and treated in hydrogen at 350°C for 4 hr and 424°C for 6 hr.

Reduction of Supported Ruthenium Catalysts

After evacuation at room temperature, the catalyst was reduced by circulating hydrogen at 450 torr using a liquid nitrogen trap. The reduction temperature was raised slowly to 400°C (or 450°C in some cases) for 3–4 hr to avoid evaporation of ruthenium chloride, and kept at this temperature for 7 hr. Hydrogen consumption was completed in these hours of treatment, while, in case of Ru–AC, a slow consumption of hydrogen was observed for a long time, possibly because of the reduction of activated carbon itself. Hydrogen chloride was produced by reduction of the catalysts, except Ru–AC where 4–10 STP ml of CO_2 were evolved from 1 g of Ru–AC at 180–250°C, and no chloride ion was detected from the trapped product during the reduction of Ru–AC.

Addition and Determination of Alkali Metal

Commercial potassium (or sodium) was evaporated and transferred in vacuum from a side tube to the catalyst layer. The alkali-added catalyst was treated by circulating helium at 400°C for 4–5 hr to distribute the alkali metal over the whole catalyst layer. Cesium was prepared by heating a mixture of cesium chloride and barium azide in a side tube attached to the reactor. The catalyst was treated with water to extract alkali, and analyzed for alkali content by titration with hydrochloric acid.

Measurement of Ammonia Synthesis Rate

The apparatus for the synthesis run was a closed circulating system equipped with a reaction tube, a U tube trap (liquid nitrogen temp.), a circulation pump, a mercury manometer and a mercury gas buret. A prepared stoichiometric mixture of nitrogen and hydrogen was purified by passing through Pt–asbestos (350°C) and a liquid nitrogen trap. On introduction of the synthesis gas there was an absorption of gas without formation of ammonia for about 1 hr at 250°C. It is possible that ammonia may have been forming but was used up immediately by converting the potassium into an amide. The observed change in reactant gas composition was consistent with the formation of amide (which should be subjected to more study). After about 2 hr, the formation of ammonia was first observed from the trapped product. The rate of ammonia synthesis was obtained from the rate of volume decrease in the stationary state and constant pressure. No product other than ammonia was detected by mass spectrometry of the trapped product. The common condition for the synthesis runs is as follows: total pressure 600 torr, circulating flow rate 4.5 ± 0.2 l STP/hr.

Characterization of the Catalyst

CO chemisorption measurement was carried out to obtain the surface area of exposed ruthenium without alkali metal. The catalyst was evacuated at 200°C for 4–5 hr, followed by CO adsorption at 23°C for 1 hr in a pressure range up to $\sim$20 torr. The pressure measurement was done by an oil manometer. The surface area of support was measured by a BET method using nitrogen. X-ray analysis of Ru–AC powder was carried out using Philips apparatus.

RESULTS

Effect of Adsorbed Potassium on the Activity of Unsupported Ruthenium

Steady rate of synthesis was measured first with unpromoted ruthenium (0.385 g) and subsequently with potassium-adsorbed ruthenium at various temperatures under the standard condition ($N_2 + 3H_2 = 600$ torr, flow rate = 4.5 l STP/hr). The amount of adsorbed potassium was 4.3 wt %. The results are shown in Fig. 1 as an Arrhenius plot of the synthesis rate. It is clear that the synthesis rate remarkably increases with the addition of potassium. The temperature at which the rate of synthesis reaches 1 ml STP NH_3/hr is decreased from 421°C for the unpromoted ruthenium to 287°C for the potassium promoted ruthenium. The rate at 350°C is increased about 66 times. It is thus demonstrated that metallic potassium is an effective promoter for ruthenium. It is to be noted, however, that the apparent activation energy is increased from 23.0 to 26.4 kcal/mol.

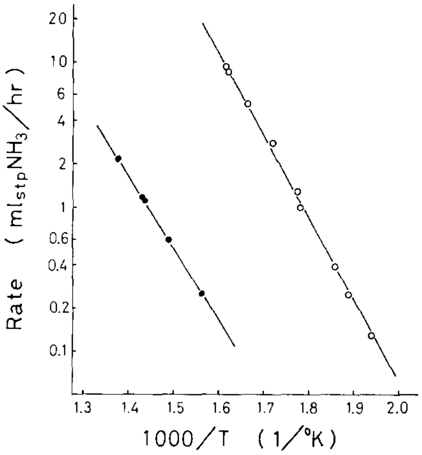

FIG. 1. Arrhenius plots of ammonia synthesis rates over ruthenium (0.385 g), with and without adsorbed potassium. Solid circle: before K addition; open circle: after K addition (4.3 wt %).

Effect of Potassium Metal on the Activities of Supported Ruthenium Catalysts

The support materials used were as follows: glass, silicon carbide, celite, alumina, and active carbon. The effect of potassium addition on the activities of supported ruthenium catalysts are exemplified in Fig. 2 (Ru-celite) and Fig. 3 ($Ru-Al_2O_3$). In both cases it is demonstrated that the activity is enhanced by the addition of potassium. The results on the other supports are shown in Table 1, together with the results on celite and alumina. All the catalysts are nonactive or have very low activity even at 400°C before the addition of potassium. But they are remarkably acti-

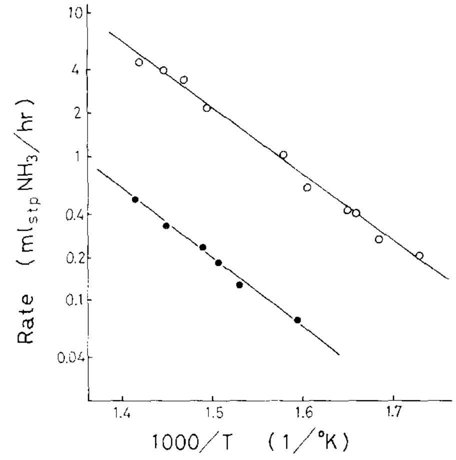

FIG. 2. Arrhenius plots of ammonia synthesis rates over 5% Ru-celite (1.5 g) with and without adsorbed potassium. Solid circle: below K addition; open circle: after K addition (5.5 wt %).

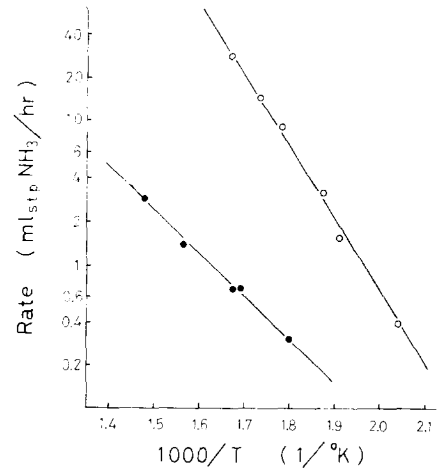

FIG. 3. Arrhenius plots of ammonia synthesis rates over 0.5% $Ru-Al_2O_3$ (4.86 g) with and without adsorbed potassium. Solid circle: before K addition; open circle: after K addition (3.5 wt %).

TABLE 1

PROPERTIES OF RUTHENIUM CATALYSTS (REACTION CONDITION: $N_2/H_2 = 1/3$, TOTAL PRESSURE 600 TORR, FLOW RATE 4.5 L STP/HR)

	Catalyst no.	1	2	3	4	5	6	7	8	9	10
	Support	None	Glass	SiC	Celite	Al_2O_3[a]	Al_2O_3[b]	AC(C)[c]	AC(C)	AC(C)	AC(T)[d]
	BET area of support (m^2/g)	—	—	—	8	355	95	1068	1068	1068	1050
	Catalyst weight before reduction (g)[e]	1.00	11.0	7.77	1.50	2.54	4.86	1.00	1.00	1.00	2.50
	Amount of ruthenium metal (mg)	385	385	183	66	60	24	23.5	23.5	44	111
	Activity before K addition										
	Rate at 400°C ($ml_{STP}NH_3/hr$)	0.60	0.06	~0	0.24	~0	2.6	0	0	0	0
	Temp. required for the rate of 1 $ml_{STP}NH_3/hr$	421°	—	—	463°	—	343°	—	—	—	—
	Activation energy (kcal/mol)	23	—	—	22.5	—	14	—	—	—	—
	K content (mg)	17	180	—	83	—	169	133	70	206	690
	Activity after K addition										
	Rate at 290°C ($ml_{STP}NH_3/hr$)	1.14	2.7	0.48	0.21	10.0	8.9	12.3	7.7	32	58
	Temp. required for the rate of 1 $ml_{STP}NH_3/hr$	287°	263°	319°	342°	218°	236°	225°	238°	207°	194°
	Activation energy (kcal/mol)	26	23	17	21	17	23	21	22	22	23
(V_g)	specific rate at 290°C ($ml_{STP}NH_3$/hr/g-catalyst)	1.14	0.25	0.062	0.14	3.94	1.83	12.3	7.7	32	23.2
(V_{Ru})	50 mg-Ru rate at 290°C ($ml_{STP}NH_3/hr$)	0.15	0.35	0.12	0.16	8.3	18.3	26.2	16.4	36.4	26.2
	CO chemisorption (ml_{STP}/g-catalyst)	0.26	—	0.07	0.13	0.87	0.15	0.50	0.50	1.00	1.37
(V_{CO})	Specific rate/CO chemisorption	4.4	—	0.9	1.1	4.5	12	25	15	32	17

[a] Sumitomo activated alumina (γ-Al_2O_3).

[b] Japan Engelhard Ltd. 0.5% Ru–Al_2O_3.

[c] Coconut active carbon.

[d] Tsurumi coal.

[e] Weight of ($RuCl_3 \cdot 3H_2O$ + Support).

vated by potassium to show detectable activities at 290°C as tabulated. If the activity is evaluated by the specific rate of synthesis per gram catalyst, V_g, the catalyst no. 10 (5% Ru–AC) ranks highest and exhibits about 2.5 times as high activity as that of conventional doubly promoted iron catalyst (*3*) at 250°C. But if the activity is evaluated by the amount of catalyst required to attain the same rate of ammonia formation at 250°C, it is estimated on the basis of the kinetic data on doubly promoted iron catalyst (*3*) that 9 times as much iron catalyst is necessary to effect the same rate as that of catalyst no. 10 (Ru–AC).

In order to compare the effect of support, the specific rate of synthesis per 50 mg of Ru, V_{Ru}, for each catalyst is indicated in Table 1. V_{Ru} is near 0.1 ml STP NH_3/hr for nos. 1–4, while near 10 ml STP NH_3/hr for nos. 5–10, about 100 times more than the former. The difference must be partly ascribed to the degree of dispersion of mounted Ru, because the surface area of the latter group of support (Al_2O_3 and AC) is much larger than the former.

CO Chemisorption on Various Ru Catalysts

Adsorption of CO on those ruthenium catalysts described above was carried out at room temperature. There was, in general, first rapid adsorption followed by slow adsorption. The amount of adsorption was taken at 1 hr after introduction of CO gas. The adsorption isotherms of CO for AC(T) and Ru–AC are shown in Fig. 4. The plots lie on straight lines. The line for AC(T) passes through the origin, suggesting a physical adsorption. Thus the amount of chemisorption can be obtained by extrapolation of the isotherm for Ru–AC to zero pressure, and shown in Table 1 as CO chemisorption. Two isotherms of CO adsorption are shown in Fig. 5 as examples. Since the amount of chemisorption of CO can be regarded a measure of exposed surface area of ruthenium, the specific activity with respect to exposed ruthenium may be relatively estimated by the rate of synthesis per CO chemisorption, V_{CO}, as shown in Table 1. The value of V_{CO} ranges from 1 (SiC) to 32 (AC). It is seen that alumina and active carbon can effect a favorable value of V_{CO} as compared with that of unsupported ruthenium (no. 1, $V_{CO} = 4.4$), and that active carbon is the best support used here.

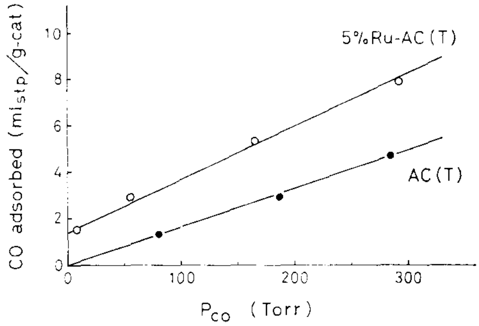

FIG. 4. Adsorption isotherms of CO for AC(T) and 5% Ru–AC(T) at 23°C.

Effect of the Kind and the Amount of Alkali Metals on the Activity of Ru–AC Catalyst

The catalytic activities of the Ru–AC catalysts were measured at 290°C changing the kind and amount of alkali metals. Figure 6 represents the relationship between activity and amount of potassium added to 2.5 and 0.5 wt % Ru–AC catalysts. It is found that no activity is detected with a catalyst of lower potassium concentration than 0.3 mg-atom/g-catalyst. The activity increases with the addition of potassium, attaining a plateau value

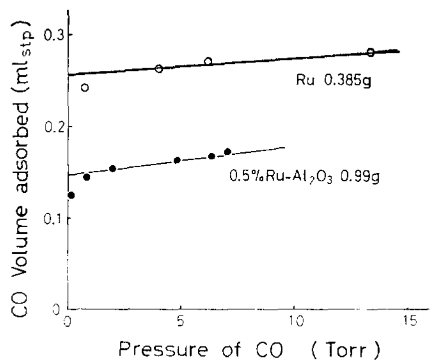

FIG. 5. Adsorption isotherms of CO for Ru metal and 0.5% Ru–Al_2O_3 at 23°C.

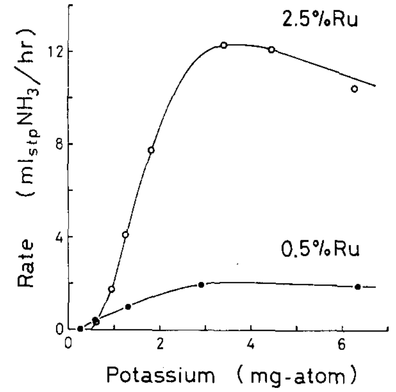

FIG. 6. Effect of potassium addition on the rates of ammonia synthesis over 2.5% Ru-AC(C) (1.0 g), and 0.5% Ru-AC(C) (1.0 g) at 290°C.

at about 3 mg-atom/g-catalyst, which is equivalent to 12 wt % of Ru-AC catalyst, and independent of ruthenium content. The activity seems proportional to ruthenium content. Figure 7 represents similar effects of the other alkali metals. The content of alkali metal at which the activity approaches a plateau value does not really depend upon the kind of alkali metal, and is located around 3–4 mg-atom/g-catalyst. These results suggest that the plateau value results from a saturation in adsorption of alkali metal on the catalyst surface, particularly on the active carbon support. The activities at 4 mg-atom/g-catalyst of alkali metals are plotted against their ionization potential in Fig. 8. It is clearly demonstrated that the activity increases with a decrease in the ionization potential of alkali metal added.

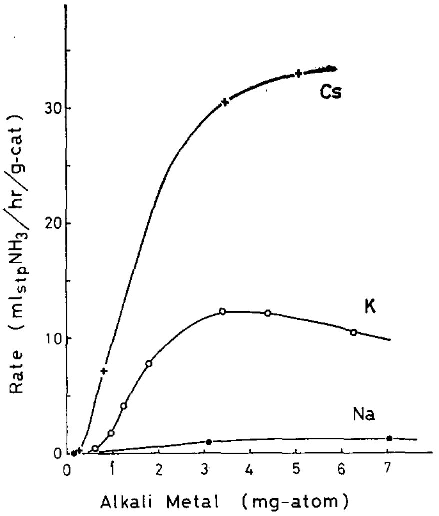

FIG. 7. Effect of alkali metal addition on the rate of ammonia synthesis over 2.5% Ru-AC(C) (1.0 g) at 290°C.

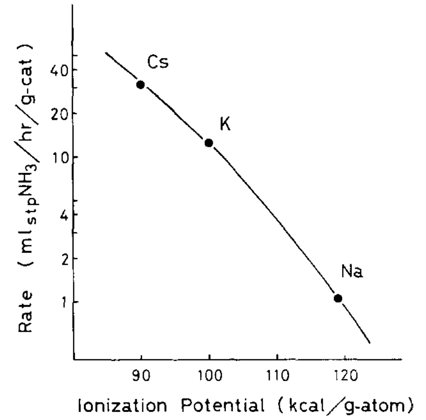

FIG. 8. Correlation between the ionization potential of alkali metal and the rate of ammonia synthesis over 2.5% Ru-AC(C) with 4 mg-atom alkali/g-catalyst.

X-ray Analysis

The active carbon is accepted to be composed of graphite-like clusters containing carbonyl groups. Graphite is known to absorb potassium, forming lamellar compounds corresponding to C_8K, $C_{16}K$, $C_{24}K$, etc., and resulting in an expansion of lattice distance from 3.34 to 5.34 Å. In this respect, X-ray analyses were made with the active carbon catalysts. AC(C) and Ru-AC(C) exhibited a broad peak at 3.74 Å which is ascribed to the graphite-like structure. However, Ru-AC(C) with adsorbed potassium gave no new peak near 5.34 Å in addition to that of 3.74 Å.

DISCUSSION

The Role of Alkali Metals

A remarkable promotion of the ammonia synthesis rate by addition of alkali metal has been found on various transition metal–AC catalysts (7): The active transition metals (Os, Ru, Fe, Co, Re, and Mo) for this new catalyst system are all known as active metals for ammonia synthesis, and the order in activity is similar to that of metal itself (*8*). This suggests that the basic pathway of ammonia formation is unchanged by the addition of potassium, and that the transition metal surface is the active site. Although the graphite–potassium complex is known to be active for the synthesis (*9*), since the active carbon with adsorbed potassium has no activity for the synthesis, the graphite–potassium complex is not responsible for the present system. The following results obtained in this study are the additional evidences for the above idea of the active surface:

(i) Unsupported ruthenium is remarkably activated by the addition of alkali metal as shown in Fig. 1.

(ii) The rate of ammonia synthesis is nearly proportional to the content of ruthenium.

It is thus concluded that alkali metal promotes the ammonia synthesis over the transition metal. The role of alkali metal in this promotion is clearly demonstrated by the result of Fig. 8. That is, the promotion is caused by an electron donation from alkali metal to transition metal. It is known that the work function of the transition metal surface decreases by adsorption of alkali metal and that an alkali metal atom gives up its electron to the transition metal (*10*). The degree of charge transfer from alkali metal to the nickel surface is admittedly of the order of $Cs > K > Na$ (*11*). A similar charge transfer should exist on the Ru surface. In this way the promotion by alkali metal is interpreted to be an electron donation to the transition metal. On the other hand, the rate-determining step of ammonia synthesis over transition metals is admittedly the dissociative adsorption of nitrogen (*1, 7, 12*). Accordingly, it follows that the chemisorption of nitrogen must be promoted by the electron donation. Although this problem should be examined by the isotopic exchange in nitrogen, it may be suggested that since nitrogen adsorption is electrophillic as shown by increase in the work function (*13*), dissociation of nitrogen is facilitated by the formation of an anionic intermediate. It is reasonable that the bond of the nitrogen molecule is weakened by the incorporation of an electron into the antibonding orbital.

The Role of Support

The role of support for the metal catalyst is conventionally considered to be the enlargement of the exposed metal surface. Since the effective site for the ammonia synthesis evidently lies on the surface of the transition metal as discussed in the preceding section, the specific activity referred to (the amount of CO chemisorption) should be unchanged by the kind of support if the role of support is conventional. The result shown in Table 1, however, clearly demonstrates that the role of support is not limited to the conventional effect. Active carbon and alumina bring about remarkably higher specific activities.

Since the role of alkali metal in the present catalyst system is the electron donation to transition metal, as concluded in the preceding section, the specificity of active carbon and alumina in the supporting action may be explained in terms of the electron donation. In this respect it should be noted that Ru metal loses its activity for the ammonia synthesis when it is supported on active carbon without potassium metal. This fact is reasonably explained by taking the electron-withdrawing nature of active carbon into account. If the activation of nitrogen requires an electron to form an anionic intermediate as discussed in the preceding section, electron withdrawal from the transition metal naturally decreases its activity for the ammonia synthesis. Thus the observed inability of the transition metal–active carbon catalyst without alkali strongly suggests that there is an electron transfer from the transition metal to active carbon. The rapid increase of activity with amount of added alkali metal as shown in Figs. 6 and 7 is reasonably understood by considering a reverse electron transfer. The amount of alkali metal required for the appearance of activity, i.e., about 0.3 mg-atom/g-catalyst may be consumed to neutralize the electron-withdrawing capacity of active carbon. In this way the role of active carbon can be reasonably understood as a medium of electron transfer from alkali to transition metal.

Another role of active carbon to be mentioned is the capacity to hold alkali metal. As suggested by the formation of the graphite–potassium complex, active carbon can strongly hold alkali metal. Alkali metal loses its metallic luster on adsorption. The observed maximum of activity on addition of potassium, as shown in Fig. 6, may be understood as a saturation of carbon with potassium metal. Excess potassium would be agglomerated.

Similar role may be expected for alumina. Flockhart *et al.* (*14*) suggested a charge transfer through alumina between two kind of adsorbates. It is possible that alumina is partly reduced to metal by reaction with alkali metal.

REFERENCES

1. AIKA, K., AND OZAKI, A., *J. Catal.* **13,** 232 (1969).

2. AIKA, K., AND OZAKI, A., *J. Catal.* **19,** 350 (1970).

3. OZAKI, A., TAYLOR, H. S., AND BOUDART, M., *Proc. Royal. Soc. Ser. A* **258,** 47 (1960).

4. KRYLOVA, E. V., KUZNETSOV, L. D., AND KONYUKHOVA, I. N., *Kinet. Katal.* **5,** 948 (1964).

5. IVANOV, M. M., RUDNITSKII, L. A., RABINA, P. D., AND KUZNETSOV, L. D., *Kinet. Katal.* **9,** 1239 (1968).

6. OZAKI, A., AIKA, K., AND HORI, H., *Bull. Chem. Soc. Jap.* **44,** 3216 (1971).

7. AIKA, K., AND OZAKI, A., *J. Catal.* **16,** 97 (1970).

8. FRANKENBURG, W. G., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. III, p. 184. Reinhold, New York, 1955.

9. SUDO, M., ICHIKAWA, M., SOMA, M., ONISHI, T., AND TAMARU, K., *J. Phys. Chem.* **73,** 1174 (1969).

10. GADZUK, J. W., *Surface Sci.* **6,** 133 (1967).

11. GERLACH, R. L., AND RHODIN, T. N., *Surface Sci.* **19,** 403 (1970).

12. AIKA, K., AND OZAKI, A., *J. Catal.* **14,** 311 (1969).

13. ENIKEEV, E. KH., AND KRYLOVA, A. V., *Kinet. Katal.* **3,** 139 (1962).

14. FLOCKHART, B. D., LEITH, I. R., AND PINK, R. C., *J. Catal.* **9,** 45 (1967).