April, 1990] © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 63, 1221—1225 (1990)* 1221

Promoter Effect of Alkali Metal Oxides and Alkali Earth Metal Oxides on Active Carbon-Supported Ruthenium Catalyst for Ammonia Synthesis

Ken-ichi AIKA,* Toshikazu KAWAHARA, Shuzo MURATA, and Takaharu ONISHI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

(Received November 25, 1989)

Promoter effects of alkali metal nitrates and alkali earth metal nitrates on Ru/A.C. (active carbon) were studied in order to prepare an effective catalyst for ammonia synthesis. Of alkali metal nitrates, $RbNO_3$ was more effective than $CsNO_3$ and KNO_3. Alkali earth metal (Mg, Ca, Sr, Ba) nitrates were also found to be effective promoters on Ru/A.C. catalysts. Of them heavier alkali earth metal elements were more effective (Ba>Sr>Ca>Mg). $Ba(NO_3)_2$ was as effective as $CsNO_3$, which was not expected from the stand point of electronegativity. The transformation of promoter precursors to active compounds (nitrates to oxides or hydroxides) and the interaction of promoters and ruthenium were discussed. Precursor of ruthenium salt was also studied. $RuCl_3 \cdot 3H_2O$ and $[Ru(NH_3)_6]Cl_3$ gave higher activities than $Ru_3(CO)_{12}$. It was discussed that $RuCl_3$ gave finer Ru particles than $Ru_3(CO)_{12}$ on active carbon. The turn over frequency (TOF) of Ru-Rb^+/A.C. was lower than those of Ru-Cs^+/Al_2O_3 and of Ru-Cs^+/MgO.

Various supported Ru catalysts have been studied for ammonia synthesis.[1] Although Ru/A.C. (active carbon) is not active for this reaction, it becomes a quite effective catalyst when alkali metals are added.[2] In this case, heavier alkali metal elements are more effective promoters (Cs>K>Na). It has been discussed that the A.C. withdraws electrons from the Ru surface which has been neutralized by addition of alkali metals. The electron-rich surface is inferred to be active for the dissociation of dinitrogen, the rate-determining step of ammonia synthesis.

Although alkali metals are good electron donors, they are quite sensitive to oxygen-containing compounds such as water and dioxygen. In the presence of water, alkali metals are turned into oxides or hydroxides which still have some promoting effects.[3,4] Thus, precursors which could give stable alkali metal oxides or hydroxides were studied on Ru/Al_2O_3 or Ru/MgO. $CsNO_3$ was found to be an effective precursor which was decomposed to Cs_2O and/or CsOH.[3,4] Precursors of alkali metal oxides and alkali earth metal oxides have also been studied on Ru/A.C. as patent works.[5-7] However, no academic data have been disclosed so far. The purpose of this work is to study the effect of alkali metal oxides and alkali earth metal oxides or their hydroxides on Ru/A.C. and also to study on precursors of Ru compounds. Although different active carbons had different characteristics from one another depending on precursors or preparation conditions, coconut active carbon was used here for comparison with results of our former study on Ru-K/A.C. (coconut active carbon).[2]

Experimental

Coconut active carbon (A.C.) (from Dai-ichi Tanso Ltd.), sieved to 8—10 mesh, washed, and dried, was impregnated with $RuCl_3 \cdot 3H_2O$ in aqueous solution at room temperature. More than 2 h was necessary to complete the adsorption of $RuCl_3$, which was examined by the change in solution color. Then, promoter nitrates (mostly from Kanto Chemical Co.) were added to the solution and allowed to stand for more than 4 h for the impregnation. The catalyst was dried in a drying oven (383 K). A standard catalyst contains 1 g of 2 wt% Ru/A.C. and promoter compounds with a mole ratio of 10/1 against Ru. The ratio of promoter to Ru was changed from 7 to 25 (mol/mol) in the case of $RbNO_3$. RbOH and Rb_2CO_3 were also studied as precursors.

$Ru_3(CO)_{12}$ and $[Ru(NH_3)_6]Cl_3$ were examined as Ru precursors instead of $RuCl_3 \cdot 3H_2O$. The active carbon was impregnated with $Ru_3(CO)_{12}$ in THF (tetrahydrofuran) solution for 4 h. The sample was dried in a rotary evaporator at 303 K. Subsequently, the sample was evacuated in a glass tube at 623 K for 2 h, then dipped into $RbNO_3$ aqueous solution for more than 4 h and dried at 383 K. $[Ru(NH_3)_6]Cl_3$ was brought on A.C. similarly to $RuCl_3 \cdot 3H_2O$. Some samples of active carbon were refluxed in an HNO_3 solution (4, 8, or 12 M) at about the boiling temperature for 1 h. The evolved NO_x was treated with H_2O_2 solution.

Dried catalyst such as $RuCl_3 \cdot 3H_2O$-$RbNO_3$/A.C. which should give 1 g of (Ru+A.C.) was taken in a glass reactor and evacuated for 1 h. The sample was heated gradually up to 673 K for 3 h under circulated hydrogen and kept at 673 K for 8 h in a closed circulation system. The ammonia synthesis rate was measured at 673 K with 80 kPa (600 Torr) of N_2+3H_2 gas with a liquid nitrogen trap.[2-4] The flow rate was estimated to be ca. 3.6 L (STP) h^{-1}. The activity was measured for more than 7 h to confirm the steady activity. The weight of catalyst used to represent the activity ($\mu mol\, h^{-1} g^{-1}$) means the weight sum of reduced Ru and A.C. without the promoter.

Since adsorbed hydrogen might spill over to active carbon, hydrogen adsorption is not suitable for surface characterizaion. The samples were characterized by a TEM (Hitachi, 200 kV) by Mr. R. Ohki of our University. The diameter of Ru particles was measured by sampling about

100 particles from TEM pictures. The average value was calculated by $(\sum n_i d_i^2/\sum n_i)^{0.5}$, where n_i is the number of particles having a diameter of d_i. Hydrogen consumption was measured during the reduction of $RuCl_3 \cdot 3H_2O$–$RbNO_3$/A.C. (Rb/Ru=10 mol/mol) catalyst which gave one gram of 2 wt% Ru (0.198 mmol)/A.C. The reduction of $RuCl_3$ and hydrogenation of $RbNO_3$ ($RuCl_3 + 10RbNO_3 + 41.5 H_2 \rightarrow Ru + 5Rb_2O + 3HCl + 10NH_3 + 25H_2O$) needs 184 ml (STP) of H_2, while about 200 ml of H_2 was consumed.

Results

Effect of Reduction Temperature. The rate of ammonia synthesis was measured over Ru/A.C. catalysts promoted with various nitrates and the effect of reduction temperature was studied. The Ru precursor was $RuCl_3 \cdot 3H_2O$. The activity decreases when the reduction temperature is increased as shown in Figs. 1 and 2. Two reasons are suggested: 1) a sintering of Ru; 2) a migration of promoter oxides from Ru metal surface to active carbon or an evaporation of promoter oxides from the catalyst. $RuCl_3$ is reduced around 393 K, while the nitrate is considered to be decomposed over the reduced Ru surface by hydrogen above 573 K.[3] Activity decrease at high temperature is more extensive for the catalyst with alkali metal promoter (Fig. 1) than with alkali earth metal promoter (Fig. 2). Since the former metal oxide tends to vaporize more easily than the latter metal oxide at high temperature, the second reason seems to be more important.

Effectiveness of Promoter. The promoter actions of alkali metal (K, Rb, Cs) nitrates and alkali earth metal (Mg, Ca, Sr, Ba) nitrates are compared in Table 1. For the alkali earth metal elements, heavier elements were more effective (Ba>Sr>Ca>Mg). For the alkali metal elements, however, Rb was more effective than Cs (Rb>Cs>K). Furthermore, the order of effectiveness is as follows: Rb>Ba>Cs>K>Sr>Ca>Mg> none. The effectiveness of $Ba(NO_3)_2$ was an unex-

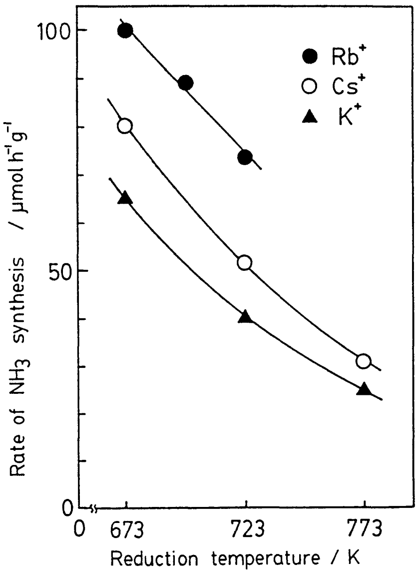

Fig. 1. Rate of ammonia synthesis on 2wt% Ru-alkali metal ion/A.C. (alkali metal/Ru=10 mol/mol) as a function of the reduction temperature. The rate was measured at 673 K under 80 kPa of N_2+3H_2.

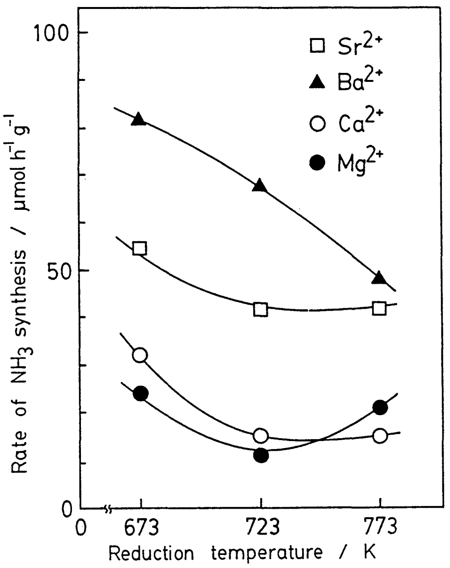

Fig. 2. Rate of ammonia synthesis on 2wt% Ru-alkali earth metal ion/A.C. (alkali earth metal/Ru=10 mol/mol) as a function of the reduction temperature. The rate as measured at 673 K under 80 kPa of N_2+3H_2.

Table 1. Promoter Effect on the Rate of Ammonia Synthesis over 2 wt% Ru/A.C.[a]

Promoter element (M)	Promoter precursor	M/Ru (mole ratio)	Activity[b] µmol h^{-1} g^{-1}	Ru particle diameter/nm
None	—	0	0	—
K	KNO_3	10	65	—
Rb	$RbNO_3$	10	100	3.7
Cs	$CsNO_3$	10	80	6.2
Mg	$Mg(NO_3)_2$	10	24	—
Ca	$Ca(NO_3)_2$	10	32	—
Sr	$Sr(NO_3)_2$	10	55	—
Br	$Ba(NO_3)_2$	10	83	4.0

a) Ru precursor is $RuCl_3 \cdot 3H_2O$, and A.C. is not treated by acid. b) Reduction temperature 673 K, reaction temperature 673 K, and N_2+3H_2=80 kPa (600 Torr).

pected result. In this case $Ba(NO_3)_2$ was more effective than $CsNO_3$ which was known to be an excellent promoter.[3,4] One reason for the less activity of Ru-Cs^+/A.C. may be due to the larger particle size (Table 1). The apparent activation energies were 14 and 17 kcal mol^{-1} for Rb and Ba promoted Ru/A.C., respectively.

Effect of Rb/Ru Ratio. Since $RbNO_3$ was found to be the best promoter in this system, the amount of $RbNO_3$ was changed and the activity was measured. The results are shown in Fig. 3. In the case of 2 wt% Ru/A.C., an Rb/Ru ratio of 20 gave the maximum activity. The activity at 623 K of the sample reduced at the same temperature is shown in the same figure. The activity at 673 K should be 2.3 times as high as that at 623 K if the apparent activation energy of Ru-Rb^+/A.C. (14 kcal mol^{-1}) is considered. However, the maximum activities at both reaction temperatures are not different so much. Thus, it is concluded that the sample reduced at 623 K is more active.

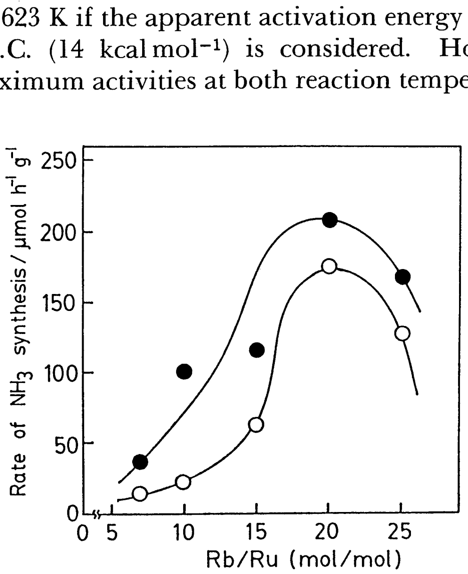

Fig. 3. Rate of ammonia synthesis under 80 kPa of N_2+3H_2 on 2 wt% Ru-Rb^+/A.C. as a function of Rb/Ru mol ratio. Closed circles: Rate was measured at 673 K on the catalyst reduced at the same temperature. Open circles: Rate was measured at 623 K on the catalyst reduced at the same temperature.

Effect of Rb Precursor. Promoter effects of RbOH and Rb_2CO_3 were examined and compared with that of $RbNO_3$ in Table 2. All the rubidium salts are effective, $RbNO_3$ giving the best result.

Effects of Active Carbon Treatment and Ru Precursor Compound. Active carbon was refluxed in HNO_3 aqueous solution at around the boiling point, dried, and used as a support. Such active carbons were impregnated with each of three kinds of Ru compounds and finally impregnated with $RbNO_3$. The activities of thus prepared catalysts (2 wt% Ru-Rb^+/A.C.) were compared with that of the standard catalyst. The results are shown in Table 3. Generally, $RuCl_3 \cdot 3H_2O$ and $[Ru(NH_3)_6]Cl_3$ precursors gave better results than $Ru_3(CO)_{12}$ precursor. $Ru_3(CO)_{12}$ is known to react with surface OH on Al_2O_3.[8] However, active carbon has less OH groups than Al_2O_3, which may be one reason why $Ru_3(CO)_{12}$ precursor gives less Ru dispersion and less activity. The particle diameter of Ru from $Ru_3(CO)_{12}$ is larger than that from $RuCl_3$ on 12 M HNO_3 active carbon (see Table 3). The 12 M HNO_3 treatment gives a somewhat

Table 2. Effect of Rb Precursor on the Rate of Ammonia Synthesis over 2 wt% Ru/A.C.[a]

Promoter precursor	Rb/Ru (mole ratio)	Activity[b] μmol h^{-1} g^{-1}	Particle diameter/nm
$RbNO_3$	10	100	3.7
$RbNO_3$	20	209	—
RbOH	10	104	—
RbOH	20	160	—
Rb_2CO_3	10	40	—
Rb_2CO_3	20	169	—

a) Ru precursor: $RuCl_3 \cdot 3H_2O$. b) Reduction temperature 673 K, reaction temperature 673 K, and N_2+3H_2=80 kPa (600 Torr).

Table 3. Effect of Ru Precursor and Active Carbon Treatment[a] on the Rate[b] of Ammonia Synthesis over 2 wt% Ru-Rb^+/A.C.[c]

HNO_3 concn/M[d] for A.C. treatment[a]	Ru precursor	Activity[b] μmol h^{-1} g^{-1}	Ru particle diameter/nm
No treatment	$[Ru(NH_3)_6]Cl_3$	112	—
4	$[Ru(NH_3)_6]Cl_3$	87	—
8	$[Ru(NH_3)_6]Cl_3$	105	—
No treatment	$RuCl_3 \cdot 3H_2O$	100	3.7
4	$RuCl_3 \cdot 3H_2O$	96	—
8	$RuCl_3 \cdot 3H_2O$	112	5.2
12	$RuCl_3 \cdot 3H_2O$	88	—
Baked A.C.[e]	$RuCl_3 \cdot 3H_2O$	105	—
No treatment	$Ru_3(CO)_{12}$	32	5.8
4	$Ru_3(CO)_{12}$	27	—
8	$Ru_3(CO)_{12}$	34	—
12	$Ru_3(CO)_{12}$	48	—

a) A.C. is refluxed in HNO_3 solution for 1 h. b) Reduction temperature 673 K, reaction temperature 673 K, and N_2+3H_2=80 kPa (600 Torr). c) Rb precursor, $RbNO_3$; Rb/Ru=10 mol/mol. d) 1 M=1 mol dm^{-3}. e) A.C. is heated at 773 K for 5 h..

Table 4. Effect of NH_3 and H_2O Treatment of Ru/A.C. on the Activity[a] of 2 wt% $Ru\text{-}Rb^+/A.C.$[b]

Treatment	Rb/Ru ratio	Activity[a] μmol $h^{-1}g^{-1}$	Ru particle diameter/nm
None	10	100	3.7
None	20	209	—
None	25	170	3.7
H_2O	10	80	—
NH_4OH	10	161	—
NH_4OH	20	184	—

a) Reduction temperature 673 K, reaction temperature 673 K, and N_2+3H_2=80 kPa (600 torr). b) Ru precursor, $RuCl_3 \cdot 3H_2O$; Rb precursor $RbNO_3$; active carbon is treated with 12 M HNO_3 solution.

better ammonia synthesis activity probably because the active carbon surface has more OH groups than the untreated one. The total number of surface oxide on active carbon has been reported to be doubly increased by a 13 M HNO_3 treatment. Hydrogen treatment of A.C. at 773 K has been suggested to remove surface sulfur impurities which could help to improve $Ru_3(CO)_{12}$ impregnation.[9] The heat-treated A.C. (773 K) had no effect on the catalyst prepared from $RuCl_3 \cdot 3H_2O$; it gave the same activity (Table 3).

Effect of NH_4OH Washing. After the active carbon which had been treated with 12 M HNO_3 solution was impregnated with $RuCl_3 \cdot 3H_2O$ and dried, the catalyst sample was washed with water (300 ml) or 0.1% NH_3 aqueous solution (300 ml). The sample was further impregnated with $RbNO_3$ (Rb/Ru=10) and dried. The activities are compared as shown in Table 4. The water treatment caused no effect, whereas the ammonia washing increased the activity if the samples with an Rb/Ru ratio of 10 are compared. However, if the samples with Rb/Ru ratios of 20 to 25 are compared, the activities are much the same. This suggests that a part of Rb^+ ions are used for the reaction with chloride ion.

Discussion

Support Effect: Comparison of Activities Between $Ru\text{-}Rb^+/A.C.$ and $Ru\text{-}Cs^+/Al_2O_3$ or $Ru\text{-}Cs^+/MgO$. The activity of 2 wt% $Ru\text{-}Rb^+/A.C.$ (Rb/Ru=20) at 588 K is estimated to be 47 μmol $h^{-1}g^{-1}$ from the activation energy. One g of reduced 2 wt% Ru/A.C. (calculational base for activity measurement) contains 198 μmol Ru. The Ru particle diameter from the TEM data (3.7 nm) gives the Ru dispersion to be 36%.[10] Thus the TOF (turn over frequency) at 588 K calculated as 47/198/0.36/3600 gives 1.8×10^{-4}, which is lower than that for $Ru\text{-}Cs^+/Al_2O_3$ (about 6×10^{-4}) and that for $Ru\text{-}Cs^+/MgO$ (about 20×10^{-4}).[3,4] The Cs/Ru ratios were 10 in the case of the latter two catalysts. The promoter is considered to cover both Ru and support surface. Since A.C. has a higher surface area (c.a. 1000 m^2g^{-1}) than Al_2O_3 and MgO, A.C. is inferred to need a more quantity of promoter to give the maximum activity. Indeed, the maximum activity was obtained when Rb^+/Ru was 20 as shown in Fig. 3. However, it is clear that the activity of $Ru\text{-}Rb^+/A.C.$ is lower than those of $Ru\text{-}Cs^+/Al_2O_3$ and $Ru\text{-}Cs^+/MgO$. The alkali metal nitrates are supposed to be decomposed by the hydrogen which is activated on Ru metal surface. After the decomposition, the alkali metal oxides or hydroxides may migrate onto the support surface. Thus, the relative affinity of promoter for Ru against that for the support should be an important factor for the effectiveness of the promoter. This is one reason why the TOFs depend on the kind of support even if the active element and the promoter are the same.

Alkali Earth Metal Compounds as Promoters. In this work, $Ba(NO_3)_2$ was found to be an effective promoter. The activity of $Ru\text{-}Ba^{2+}/A.C.$ was next to that of $Ru\text{-}Rb^+/A.C.$ and even better than that of $Ru\text{-}Cs^+/A.C.$ Similar results have been reported, although reaction conditions and amounts of promoters are not constant.[6]

The dissociation of N-N bond, the rate-determining step of ammonia synthesis, has been discussed to be promoted by the electron donation of promoters to Ru surface.[3,4] Electronegativities of support and promoter compounds are used as a rough criterion which is well correlated with the ammonia activity on Ru surface.[4] From this point of view, the alkali metal oxides are expected to be more effective promoters than alkali earth metal oxides. The values of electronegativities of promoter compounds are as follows: 1.20 (Cs_2O), 1.31 (Rb_2O), 1.31 (K_2O), 1.77 (BaO), 1.87 (SrO), 1.87 (CaO), and 2.05 (MgO). If Cs^+ works as CsOH just as on Al_2O_3,[3] the electronegativities of alkali metal hydroxides (1.73 for CsOH and 1.80 for RbOH) should be applied. These values are near to those of alkali earth metal oxides. There are no data which show chemical states of alkali metal and alkali earth metal compounds here. On Ru/A.C., however, the states of alkali metal compounds might be different from those of alkali earth metal compounds. Of course, atomic structures between Ru atom and the promoter compounds should be studied in detail in the future.

Another point is the relation among Ru, the promoter (MO), and the support. The following surface reactions are considered:

$$\text{Ru} + \text{MO} \rightleftarrows \text{Ru-OM}, \tag{1}$$

$$\text{Support} + \text{MO} \rightleftarrows \text{Support-OM}, \tag{2}$$

$$\text{Ru} + \text{Support} \rightleftarrows \text{Ru-Support}. \tag{3}$$

A.C. is considered to withdraw electrons from Ru by Reaction 3. Thus, the large amount of promoter is necessary to neutralize A.C. by Reaction 2. Finally, the activity would increase as the promoter interacts effectively by Reaction 1. According to the situation of $CsNO_3$, $Ba(NO_3)_2$ is decomposed to BaO on Ru surface, and a part of BaO may stay on Ru and another part would migrate to the support.[3] Owing to its less mobility, BaO is considered to stay longer than Cs_2O and CsOH on Ru surface. This is because Ba^{2+} is as effective as Cs^+ although its electron donating ability is smaller than that of Cs compounds. The way of transformation of promoter compounds may be different among $RbNO_3$, RbOH, and Rb_2CO_3. This should affect all Reactions 1—3, which is the reason for the different promoter effects shown in Table 2.

Conclusion

On active carbon, $RuCl_3 \cdot 3H_2O$ and $Ru(NH_3)_6Cl_3$ were found to be effective precursors of Ru catalysts. Alkali earth metal nitrates, especially $Ba(NO_3)_2$, were found to be as effective as alkali metal nitrates on Ru/A.C. The chemistry among Ru, support, and promoter was suggested to be important to synthesize better catalysts.

References

1) A. Ozaki and K. Aika, "Catalysis-Science and Technology," ed by J. R. Anderson and M. Boudart, Springer-Verlag, New York (1981), Vol. 1, p. 87.

2) K. Aika, H. Hori, and A. Ozaki, *J. Catal.*, **27**, 424 (1972).

3) K. Aika, K. Shimazaki, Y. Hattori, A. Ohya, S. Ohshima, K. Shirota, and A. Ozaki, *J. Catal.*, **92**, 296 (1985).

4) K. Aika, A. Ohya, A. Ozaki, Y. Inoue, and I. Yasumori, *J. Catal.*, **92**, 305 (1985).

5) R. M. Elofson and F. F. Gadallah, U. S. Patent 4142993 (1979); *Chem. Abst.*, **90**, 157747e (1979).

6) A. I. Foster, P. G. James, J. J. McCarroll, and S. R. Tennison, Ger. Offen. 2748972 (1978); *Chem. Abstr.*, **89**, 181912e (1978).

7) J. J. McCarroll, S. R. Tennison, and N. P. Wilkinson, U. S. Patent 4600571 (1986); *Chem. Abst.*, **102**, 115282k (1985).

8) A. Zecchina, E. Guglielminotti, A. Bossi, and M. Camia, *J. Catal.*, **74**, 225 (1982).

9) M. A. Vannice and J. J. Venter, presented at the Symposium "Advances in Catalytic Chemistry IV," Snowbird, Utah, 1989.

10) J. R. Anderson, "Structure of Metallic Catalysts," Academic Press, London (1975), p. 296.