

## RESEARCH NOTE

# The Effect of Hydrogen Treatment of Active Carbon on Ru Catalysts for Ammonia Synthesis

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Alkali metals or their oxides (hydroxides), alkaline earth metal oxides, and lanthanide oxides have been found to greatly promote the activity of Ru catalysts in ammonia synthesis (1–7). This promotion effect has been suggested to relate with electron transfer from the above materials, whatever used for the support, the promoter, or in combination, to the Ru atoms (6, 7). The wavenumber in IR spectrum of the adsorbed  $\text{N}\equiv\text{N}$  species decreases with changing the support from  $\text{Al}_2\text{O}_3$  to  $\text{MgO}$ .  $\text{MgO}$  is regarded to donate its electrons more easily to Ru atoms due to its low electronegativity. The IR bands further decreases if promoters such as alkali metal hydroxides are added (8). Ru/active-carbon (A.C.) catalyst without any promoters shows no activity since the A.C. withdraws electrons from Ru. However, in this work we have focused our attention on A.C. supported Ru catalysts because of its high surface area and common use in the industry as catalyst support.

A.C. has been studied as a support for Ru catalysts with alkali “metal” promoters such as Na, K, and Cs, and Cs–Ru/A.C. was found to be the most active at 588 K under atmospheric pressure of  $\text{N}_2 + 3\text{H}_2$  (1). However, since the promoter alkali “metals” were too sensitive to oxygen-containing compounds ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and etc.), it was deactivated and could not be recovered by the subsequent hydrogen treatment.

In order to prepare a practical ruthenium catalyst supported on active carbon, alkali metal nitrates and alkaline earth metal nitrates were applied (2). Alkaline earth metal nitrates ( $\text{Ba}(\text{NO}_3)_2$ ) was found to be as effective as alkali metal nitrates ( $\text{Rb}^+$ ,  $\text{Cs}^+$ ) and the working states have been expressed as  $\text{BaO-Ru/A.C.}$  or  $\text{CsOH-Ru/A.C.}$  However, the activity itself was not so high. This was probably due to the electron-withdrawing from the Ru atoms by such functional groups as  $=\text{S}$ ,  $=\text{NH}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$  in the A.C.

Similar works have been reported on high surface area graphite (HSAG), which was first developed in the UK (9) and the first commercial ammonia plant using Ru catalyst in the world was said to run on a kind of Ru/HSAG catalyst since 1992 in Canada (10–12). The catalyst used has been reported to be very efficient and stable (13). Other research groups such as Rama Rao *et al.* have tried to prepare Ru catalysts supported on carbon-covered alumina (CCA). The activity of this catalyst for ammonia synthesis was found to be substantially improved, since CCA offers the purity of carbon and reduces the acidity of alumina (14). More recently, Kowalczyk *et al.* have achieved a very active Ru catalyst supported on A.C. which was treated for 2 h at 2173 K in an atmosphere of helium at a reduced pressure of 400 Pa (15, 16).

Various kinds of thermal treatment of A.C. at extremely high temperature under an inert gas atmosphere changed the porous property of A.C., usually a sharp decrease in the total volume of pores, especially the loss of micropores. To some extent it led to graphitization. This structure modification was commonly considered to account for the high activity of the catalysts.

However, the authors have found that the removal of impurities in the A.C. plays a much greater and more significant role in the catalytic behavior of the catalysts. In this work, we have succeeded in eliminating such electronegative impurities as S, N, O, and Cl by the treatment of commercial A.C. with hydrogen at high temperatures. Three kinds of nitrate salts,  $\text{CsNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ , and  $\text{Ce}(\text{NO}_3)_3$ , were used as the promoters for Ru/A.C., based on the results of our recent works (17, 18). We are trying to show that the hydrogen treatment of A.C. is independent of the promoters action in improving the activity.

Granular commercial active carbons (#76 made of wood from Wako Chemicals, #75 of pitch from Kureha Chemicals, and #80 of coal from Kanto Chemicals) were first ground into about 8–12 mesh size. Two grams each were treated

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in a quartz reactor by increasing the temperature up to 1073 K or 1188 K at a rate of 5 K min<sup>-1</sup> under hydrogen flow (30 ml min<sup>-1</sup>). Treatment of the A.C. was continued at the final temperature for 12 h or more (*step 1*).

Twenty-nine thousandths grams of Ru<sub>3</sub>(CO)<sub>12</sub> (Tanaka Precious Metal Co.) was subsequently dissolved in 30 ml of THF (special grade from Wako Chemicals) and 0.669 g of the treated A.C. was subsequently added to this solution. The THF solvent was evaporated in a rotary-evaporator at about 300 K after the impregnation process of 12 h (*step 2*).

The Ru<sub>3</sub>(CO)<sub>12</sub> catalyst was transferred into a reactor and slowly heated from room temperature to 573 K at 2.3 K min<sup>-1</sup> under vacuum. The temperature was decreased immediately after it reached 573 K (*step 3*).

Finally, the promoter (CsNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, or Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, all special grade from Wako Chemicals) was dissolved in an appropriate amount of distilled water and the above Ru/A.C. catalyst was immersed in the solution. After 6 h, the water was then evaporated by using a water bath at 373 K, followed by drying in air at 393 K (*step 4*).

All catalysts were pre-reduced at 473 K with hydrogen (50 ml min<sup>-1</sup>) for 5 h and then reduced at the corresponding reduction temperatures (588, 673, 733, 773, 823, and 873 K) for another 3 h with synthesis gas (*step 5*).

The ammonia synthesis reaction was carried out in a stainless steel reactor under a flow system at atmospheric pressure (17, 18). The activity was measured after the catalyst was stabilized at the reaction temperature (usually 588 K, unless stated otherwise) for 90 min in a flow of 3H<sub>2</sub> + N<sub>2</sub> (60 ml min<sup>-1</sup>). The ammonia yield was calculated by detecting the conductivity decrease of the protons in the sulfuric acid solution (0.00216 N, 200 ml at 298 K) with respect to the time, where the vent gas from the reactor was passed through the sulfuric acid solution. The detection error of this method is not greater than 5%.

In this work, we found that both the hydrogen treatment temperature of the active carbon (*step 1*) and the reduction temperature of the catalyst (*step 5*) greatly influenced the activity of Ru-BaO/A.C. Hydrogen treatment of A.C. at such high temperatures as 1123 K (*step 1*) was found to eliminate or reduce the surface acidic impurities which withdraw electrons from the Ru. Impregnated and decomposed Ru<sub>3</sub>(CO)<sub>12</sub> on such active carbon could be the active centers. However, Ru catalysts supported on A.C. without a promoter showed almost no activity for ammonia synthesis at 588 K. The effect of the hydrogen treatment of A.C. (*step 1*) became remarkable only when a promoter such as Ba(NO<sub>3</sub>)<sub>2</sub> was added (*steps 4, 5*). Moreover, the efficiency was also affected by the reduction temperature of the catalyst (*step 5*). This situation is shown in Fig. 1. Here the rates of ammonia synthesis at 588 K of various Ru-BaO/A.C. are plotted as a function of the reduction temperature (*step 5*). The A.C. used for preparing these samples was treated differently (*step 1*) as cited in the figure caption. The sample

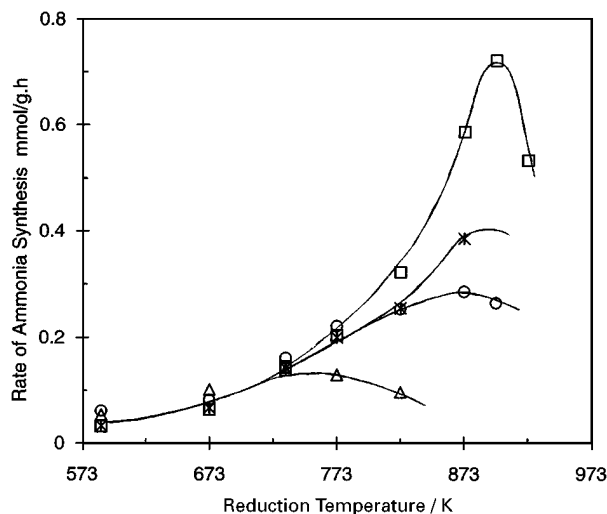


FIG. 1. Ammonia activity of 1 wt% Ru-15BaO/A.C. as a function of the reduction temperature. Ru precursor: Ru<sub>3</sub>(CO)<sub>12</sub>. Four kinds of A.C. (#76) were used: (Δ) nontreated A.C.; (○) A.C. treated at 1073 K for 14 h; (\*) A.C. further treatment of (○) at 1188 K for 20 h; and (□) A.C. further treatment of (\*) at 1188 K for another 18 h.

with A.C. which had been treated at such high temperatures as 1188 K was highly promoted by the addition of Ba(NO<sub>3</sub>)<sub>2</sub>. Those which had been treated for a longer time at 1188 K were promoted further.

When hydrogen reacts with the acidic functional groups or impurities in A.C., the reactant volume should decrease since the products (H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S, etc.) are condensed in the liquid nitrogen trap attached to the circulation system. Figure 2 shows the time course of the hydrogen pressure in the closed circulation system in which the reactor temperature increased from 298 to 1123 K. Thermal gravimetry analysis (TG) of the A.C. in hydrogen flow (300 ml min<sup>-1</sup>) at a ramping rate of 5 K min<sup>-1</sup> was also carried out on SII 320U (Seiko Corporation) and the data is shown in Fig. 3.

In Fig. 2, 1.013 g of A.C. (#76) was preheated at 773 K for 3 h under vacuum to ensure the removal of most of the adsorbed water and gases. Few of the functional groups or impurities in A.C. is believed to be decomposed during this treatment, since no effect on the catalytic activity can be observed (2). As shown in Fig. 2, 4.19 mmol of hydrogen was introduced into the reactor after it cooled down to 298 K. The temperature of the reactor was raised again at a rate of 5 K min<sup>-1</sup> up to 1123 K and then maintained at 1123 K for 12 h.

From Fig. 2, we can see the initial increase of the hydrogen pressure due to the desorption of some adsorbed hydrogen when the temperature increased (thermal expansion of the gas in the reactor was excluded). A great consumption of the hydrogen was observed between 678 and 1038 K and was thought to reduce the surface halogen and parts of the sulfur, because these impurities can be very easily removed

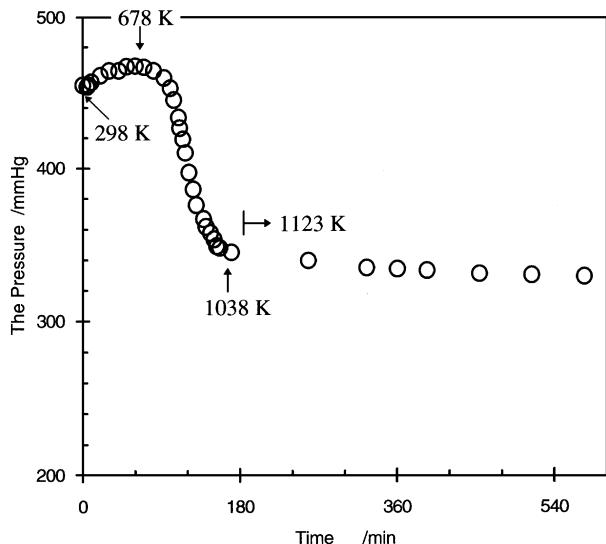
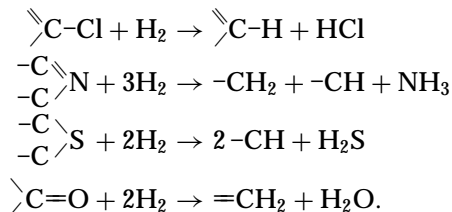


FIG. 2. The pressure changes of hydrogen in the reactor (total volume of ca 171 ml) during the treatment of A.C. (#76) as a function of the treatment time. A liquid nitrogen trap was used behind the reactor during the treatment.

by their reaction with hydrogen. The following reactions are considered to occur during the treatment:



Since the hydrogen consumed between 678 and 1038 K corresponds to about  $1.0 \text{ mmol g}_{\text{A.C.}}^{-1}$ , the weight loss was estimated to be 3.6 wt%. The slow decline in hydrogen pressure after the temperature reached 1123 K indicates the further reduction of bulk sulfur, and the removal of functional

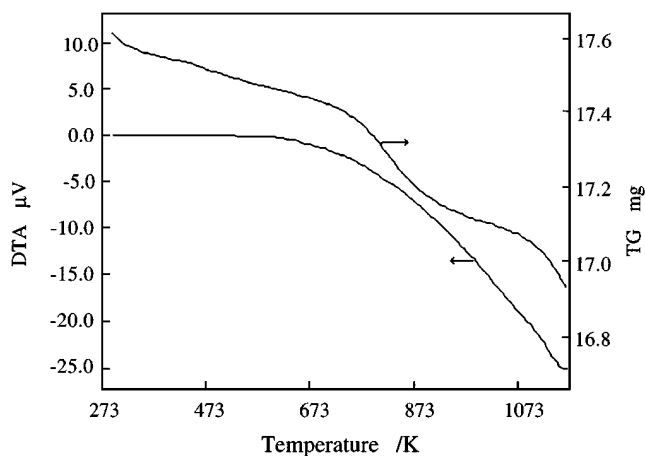


FIG. 3. A TG-DTA analysis of A.C. (#76) in hydrogen.

groups such as  $\text{-COOH}$ ,  $\text{=C=O}$ ,  $\text{-C-N}$ , since these groups are, chemically, strongly bound with carbon.

Although the heating rates ( $5 \text{ K min}^{-1}$ ) are the same, the TG results (Fig. 3) are slightly different from the hydrogen consumption (Fig. 2). The first slow weight loss up to 678 K in TG may be due to the desorption of water which has been eliminated before the loss of hydrogen as shown in Fig. 2. A clear weight loss between 678 and 1038 K was also observed in TG (in Fig. 3), in accordance with the data shown in Fig. 2. No remarkable thermal change could be detected during the entire hydrogen treatment of A.C. The weight loss caused by the hydrogen treatment between 678 and 1038 K was about 1.8 wt%, which is rather small compared with the value calculated above. Further more, it was noted in Fig. 3 that another heavy weight loss started from 1108 K. Because the TG reflects only the mass changes of the A.C. during the hydrogen treatment, not concerning with the reduction process, the second weight loss may suggest that some of the reduced impurities by hydrogen at 678–1038 K still remains on the A.C. and begins to evaporate at above 1108 K. This accounts for the discrepancy in the weight loss between the calculated (3.6 wt%) based on the hydrogen consumption and the observed (1.8 wt%) by TG. It is therefore understood clearly in Fig. 1 that the prolonged treatment of the A.C., resulting in the increase of the activity, is mainly an evaporation of impurities rather than a deep reduction of the A.C.

Elemental analysis was carried out for the three commercial A.C.s used including #76, and the results are shown in Table 1. We can see that the content of carbon increased dramatically and those of hydrogen and nitrogen decreased when the reduction treatment was prolonged. Due to the loss of hydrogen in the A.C., which may indicate the change of a C-C single bond to a C=C double bond, the actual hydrogen consumption should be more than that, as shown in Fig. 2. Both sulfur and halogen could not be detected after hydrogen treatment of A.C. (#76) at 1123 K for 12 h.

In order to confirm whether this proper hydrogen treatment is effective on any kind of A.C. in preparing Ru catalysts for ammonia synthesis, three kinds of commercial A.C.s (#75, #76, and #80) from different manufacturers were used to examine their activity. The composition analysis is listed in Table 1. The original contents of carbon, sulfur, and halogen differ from each other. The surface area (BET) data are only a little different.

The activities for ammonia synthesis of the Ru catalysts supported on these A.C. are shown as a function of the reduction temperature (step 5) of the catalyst in Fig. 4. It is interesting to note that, for the catalysts using nontreated A.C. as the support, the optimum activities varied greatly due to the different content of sulfur and halogen. However, all of the catalysts performed much the same activity pattern after the A.C. was treated with hydrogen at 1123 K for more than 24 h. It is considered that the ruthenium particle

TABLE 1  
Elemental Analysis (wt%) of Active Carbons; Effect of Hydrogen Treatment

Source <sup>a</sup>	Red. conditions	S. area <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	H	C	N	Halogen	S(SO <sub>4</sub> <sup>2-</sup> )	Others (ash and O)
#76	Untreated	934	1.11	88.77	0.21	3.58	0.57	5.76
	Up to 1123 K in 4 h	—	0.34	94.47	—	n.d.	0.13	5.06
	At 1123 K for 12 h	1078	0.17	95.49	0.16	n.d.	n.d.	4.18
#80	No treatment	1084	1.17	92.42	—	2.84	0.46	3.11
	At 1123 K for 48 h	914	1.08	93.29	—	n.d.	n.d.	5.63
#75	No treatment	1007	1.00	92.51	—	n.d.	n.d.	6.49
	At 1123 K for 48 h	978	0.69	96.67	—	n.d.	n.d.	2.64

<sup>a</sup> #76 Wako Chemicals (wood), #75 Kureha Chemicals (pitch), #80 Kanto Chemicals (coal).

<sup>b</sup> BET surface area.

forming process (*steps 2 and 3*) and the promoter activation process (*steps 4 and 5*) are in the same condition, almost free from the initial source, for the three A.C.s which have been purified.

We used different precursors of the Ru compounds in preparing the catalysts and the obtained data is shown in Figs. 1 and 4. The Ru(acac)<sub>3</sub> sample exhibited better results than Ru<sub>3</sub>(CO)<sub>12</sub>, which has been confirmed by the conventional H<sub>2</sub> chemisorption and TEM pictures that the dispersion of catalysts prepared from Ru(acac)<sub>3</sub> is higher than that prepared from Ru<sub>3</sub>(CO)<sub>12</sub>. However, the effects of hydrogen treatment of the A.C. was not dependent on these sources. Discussions of the role of the Ru sources on the Ru particle size and the ammonia synthesis will be discussed elsewhere (19).

Figure 5 showed the activities of CsOH, Ce<sub>2</sub>O<sub>3</sub>, and BaO promoted Ru catalysts supported on treated and

nontreated A.C. The hydrogen treatment of A.C. at 1123 K for 12 h (*step 1*) had almost no effect on the pore size distribution and the surface area of the various A.C.s, as shown in Table 1. However, we found that it at least doubled the maximum activities of the Ru catalysts for the synthesis of ammonia, no matter which promoter was used. When we compared the kind of promoter with regard to the hydrogen treated A.C.s, however, great differences could be observed. CsNO<sub>3</sub> became ineffective when the reduction temperature (*step 5*) became higher than 723 K. On the other hand, Ce(NO<sub>3</sub>)<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> showed remarkable efficiency for ammonia synthesis when the catalysts were reduced with hydrogen (*step 5*) at temperatures ranging from 773 to 873 K. This different promotion effect is only dependent on the properties of the promoters and the interaction between promoter and Ru metals. Due to the low melting point, CsOH evaporates

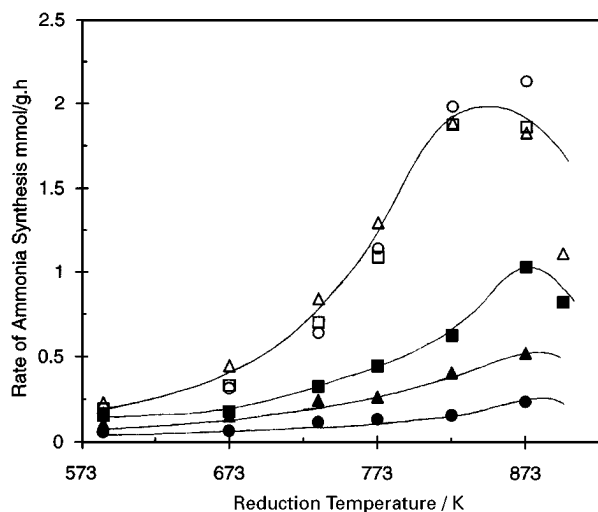


FIG. 4. Ammonia activity of 2 wt% Ru-5BaO/A.C. as a function of the reduction temperature. Ru precursor: Ru(acac)<sub>3</sub>. Solid marks represent nontreated A.C.; Open marks represent A.C. treated at 1123 K for 48 h; Triangles stand for A.C. #76, circles for #80, and squares for #75.

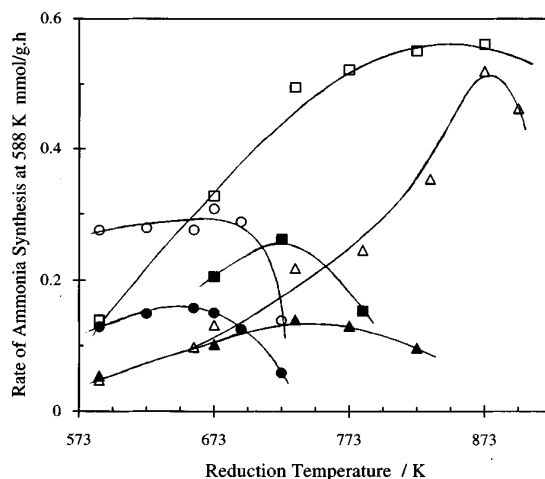


FIG. 5. Ammonia activity of Ru catalysts as a function of the reduction temperature. Solid marks represent nontreated A.C.; Open ones represent A.C. treated at 1123 K for 12 h. Ru precursor: Ru<sub>3</sub>(CO)<sub>12</sub>. Circles stand for 2 wt% Ru-10CsOH/A.C., triangles for 2 wt% Ru-10BaO/A.C., and squares for 2 wt% Ru-5Ce<sub>2</sub>O<sub>3</sub>/A.C.

when the reduction temperature is higher than 698 K while  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ce}(\text{NO}_3)_3$  could not be completely decomposed at low reduction temperatures (20).

Conclusively, hydrogen treatment of commercial A.C. at high temperatures (*step 1*) ranging from 1073 to 1188 K successfully removed the impurities from A.C. with little change in the pore site and its distribution, thus leading to the design of effective Ru catalysts, of which the activity for ammonia synthesis was found to be doubled ( $\text{CsOH}$  promoted) or tripled ( $\text{BaO}$  and  $\text{Ce}_2\text{O}_3$  promoted). Furthermore, the activity increases further with prolonging the hydrogen treatment. As supports, various kinds of commercial A.C. led to low and quite scattered activities in ammonia synthesis because of the difference in impurity contents. However, the activities became remarkably high and their efficiencies became independent of the source when A.C. was treated with hydrogen.

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