Effect of hydrogen treatment of active carbon as a support for promoted ruthenium catalysts for ammonia synthesis

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Hydrogen treatment of active carbon (A.C.) at temperatures ranging from 1073 to 1188 K for 12 h is an effective method for eliminating surface impurities, leading to the preparation of useful ruthenium catalysts; for example, 2 mass% Ru–BaO/A.C. (Ba/Ru = 5) yields 2 mmol NH_3 h^{-1} g^{-1} at 588 K under 1 atmosphere.

Many researchers have pursued various alternatives in making pure carbon materials which are used as support material for ruthenium catalysts in the synthesis of ammonia. HSAG (high surface area graphite) was first developed in the UK[1] and the first commercial ammonia plant to use ruthenium catalysts has operated using a type of Ru/HSAG catalyst since 1992 in Canada. The catalyst used has been reported to be very efficient and stable.[2] Ruthenium catalysts supported on carbon-covered alumina (CCA) was found to be substantially improved for the synthesis of ammonia since CCA offers the purity of carbon and eliminates the acidity of alumina.[3,4] More recently, a very active Ru catalyst supported on A.C. which is treated for 2 h at 2173 K in an atmosphere of helium (400 Pa) has been reported.[5,6] The authors suggest that the high activity is due to differences in the support (A.C.) which may have similar properties to HSAG.

In this work, we have successfully eliminated the impurities such as S, N, O and Cl by treating commercial A.C. with hydrogen at moderate temperatures (1073–1188 K). We have used $Ba(NO_3)_2$ and $CsNO_3$ as the promoters because these were found to be the most effective on Ru/A.C. while $Ce(NO_3)_3$ was also used based on the results of our most recent work.[7,8]

Three kinds of granular active carbons (8–12 mesh size, 2 g) were treated in a quartz reactor by increasing the temperature to 1073 or 1188 K at a rate of 5 K min^{-1} under a flow of hydrogen (30 ml min^{-1}) and kept at the final temperature for 12 h or more. The Ru/A.C. catalysts were prepared by impregnating A.C. with $[Ru_3(CO)_{12}]$ or $[Ru(acac)_3]$ in THF and finally heated from room temp. to 573 K in 2 h *in vacuo*.[7,8]

All the catalysts (usually 0.2 g) were pre-reduced at 473 K with hydrogen (50 ml min^{-1}) for 5 h, then reduced at the corresponding reduction temperatures for 3 h. The ammonia synthesis reaction was performed in a stainless-steel reactor (id = 6.5 mm) under a flow system under atmospheric pressure at 588 K.[7,8] The flow rates of H_2 and N_2 were set at 45 and 15 ml min^{-1}, respectively.

Elemental analysis was also carried out for these three commercially available A.C. samples and the results are shown in Table 1. We can see that the content of the carbon increases dramatically and hydrogen and nitrogen decrease when the reduction treatment is prolonged. The surface areas (BET) and the XRD patterns are only slightly different. Neither sulfur nor halogen can be detected after hydrogen treatment of A.C. (no. 76) at 1123 K for 12 h.

In this work we found that two hydrogen treatment procedures, namely, the treatment of the active carbon and the treatment of the catalyst, influenced the activity of $Ru–Ba^{2+}$/A.C. Hydrogen treatment of A.C. at high temperatures such as 1123 K enabled the elimination or reduction of the surface acidic impurities which withdraws electrons from Ru. Impregnated and decomposed $[Ru_3(CO)_{12}]$ on such active carbon proved effective in the preparation of an efficient catalyst for ammonia synthesis. However, ruthenium catalysts supported on A.C. without the promoter showed almost no activity for the synthesis reaction at 588 K. The effects of hydrogen treatment of A.C. were found to be remarkable only when a promoter such as $Ba(NO_3)_2$ was added. Moreover, the activity was also affected by the reduction temperature of the catalyst, as is shown in Fig. 1. The A.C. used for preparing these samples has been treated differently as is cited in the figure caption. The sample with A.C. which had been treated at such high temperatures as 1188 K was highly promoted by the addition of $Ba(NO_3)_2$. Those samples which had been treated for a longer time at 1188 K showed a more remarkable promotion as can be seen in Fig. 1.

The ammonia activity for the ruthenium catalysts supported on various kinds of A.C. has been shown to be a function of the reduction temperature of the catalyst as indicated in Fig. 2. We have noted here that for the catalysts with non-treated A.C. as the support, the activities varied remarkably owing to the difference in the sulfur and halogen content. However, it is most interesting to note that the catalysts performed much the same after the A.C. was treated with hydrogen at 1123 K for > 24 h. This clearly indicates that the catalytic behavior of the Ru

Table 1 Elemental analysis (mass%) of active carbons; effect of hydrogen treatment

Source[a]	Reduction conditions	Surface area[b]/ m^2 g^{-1}	H	C	N	Halogen	$S(SO_4^{2-})$	Others (ash and O)
#76	No treatment	934	1.11	88.77	0.21	3.58	0.57	5.76
	Up to 1123 K for 4 h	—	0.34	94.47	—	n.d.[c]	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

[a] #76 from Wako Chemicals (wood), #75 from Kureha Chemicals (pitch), #80 from Kanto Chemicals (coal). [b] BET surface area. [c] n.d. = Not detected.

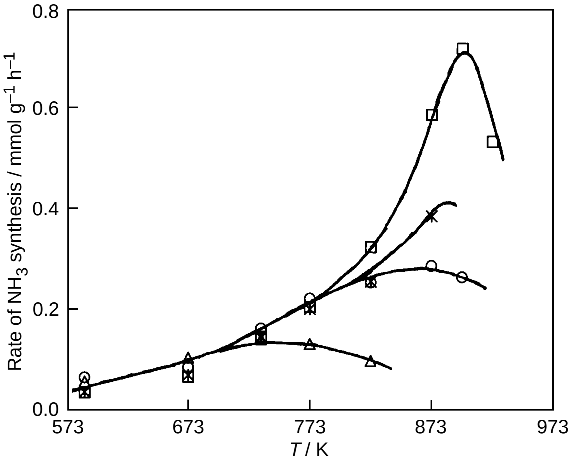

Fig. 1 Ammonia activity of 1 mass% Ru–15Ba^{2+}/A.C. as a function of reduction temperature (T). Ru precursor $[Ru_3(CO)_{12}]$. Four kinds of A.C. (#76) were used: (△) non-treated A.C.; (○) A.C. treated at 1073 K for 14 h; (*) A.C. (○) further treated at 1188 K for 20 h; and (□) A.C. (*) further treated at 1188 K for 18 h.

catalysts is mainly dependent on the purity of the A.C., while not influenced by the original source or the porosity of the A.C.

The elimination of the impurity species, usually with high electronegativity, reduces the capability of A.C. to withdraw electrons from the Ru atoms and the promoter, and simultaneously enhances the electron donation of the promoter to ruthenium.

Hydrogen treatment at temperatures ranging from 1073 to 1188 K for > 12 h was found to be the significant and decisive factor in removing impurities such as sulfur and halogen left on commercial A.C. during the activation process and/or when adding the binder while the surface area and the porous structure of the A.C. was not affected. This moderate reduction treatment of A.C. (support) doubles or even triples the activities for Cs^+-, Ba^{2+}- or Ce^{3+}-promoted Ru catalysts for ammonia synthesis. Furthermore, the activity increases with prolonged hydrogen treatment. As supports, the different kinds of A.C. exhibited low and quite varied activity for ammonia synthesis owing to differences in impurity content. However, any A.C. treated with hydrogen was found to show equally high activity. Our studies which have been based on detailed and repeated research work have demonstrated that the removal of such impurities such as sulfur and halogens as well as the elimination of the acidic functional groups in A.C. by hydrogen treatment led to higher activity of the ruthenium catalysts, thus paving the way for the preparation of an efficient and effective catalyst for ammonia synthesis.

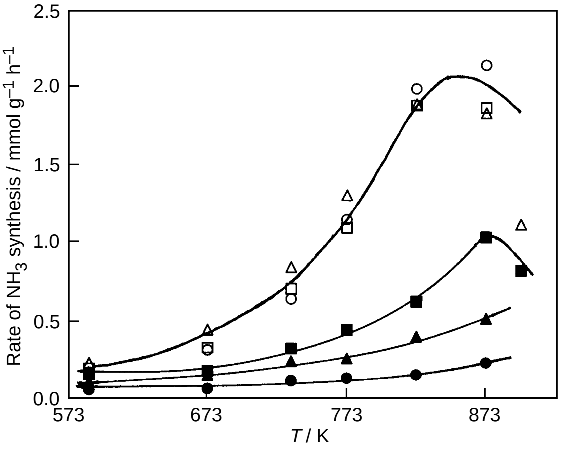

Fig. 2 Ammonia activity of 2 mass% Ru–5Ba^{2+}/A.C. as a function of reduction temperature. Ru precursor $[Ru(acac)_3]$. Solid symbols represent non-treated A.C.; open symbols represent A.C. treated at 1123 K for 48 h; triangles, A.C. #76; circles, #80; squares #75.

Footnote

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