Effect of methanation of active carbon support on the barium-promoted ruthenium catalyst for ammonia synthesis

Hai Sheng Zeng, Takashi Hihara, Koji Inazu and Ken-ichi Aika *

Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
E-mail: kenaika@chemenv.titech.ac.jp

Received 16 April 2001; accepted 11 July 2001

The effect of the induced methanation of hydrogen-treated active carbon (HTAC) support on the structural change and then catalytic activity over Ba-promoted Ru/HTAC catalysts ($Ba(NO_3)_2$ and $RuCl_3$ were precursors) for ammonia synthesis was investigated. It was found that a moderate degree of the methanation of HTAC support increased the catalyst surface area and pore volume significantly rather than destroyed the porous structure. But the methanation of carbon support might accelerate the growth of Ru particles, which finally led to the low activity. We suggested that both the dechlorination temperature (refer to the reductive dechlorination of $RuCl_3$ to form Ru on HTAC) and the hydrogenolysis temperature (refer to the hydrogenolysis of $Ba(NO_3)_2$ on Ru/HTAC) have binary effects on the catalytic activity, respectively. On the one hand, the dechlorinating effect and the hydrogenolysis effect increased with the increase of H_2 treatment temperature. On the other hand, simultaneously the methanation degree of the support increased too in above both processes. The performance of the catalyst was the combined result of the interaction of the amount of residual chlorine, Ru particle size, and the active promoter component. A respective control of the methanation degree during the catalyst preparation and activation processes was suggested to be necessary for the practical use of the promoted Ru/C catalyst.

KEY WORDS: ammonia synthesis; ruthenium; methanation of carbon support; dechlorination; hydrogenolysis; porosity

1. Introduction

As the second-generation catalyst for ammonia synthesis, a kind of Ru catalyst has been industrially used [1]. It was reported that Ru catalysts were susceptible to the promoter and support [1]. In our previous work [2], we presented the application of low-cost $RuCl_3$ as precursor to prepare a Ru catalyst with hydrogen-treated active carbon (HTAC) as a support, which is considered to be one of the prospective practical catalysts. Since the presence of chlorine derived from $RuCl_3$ could significantly spoil the catalytic activity of the Ru catalyst, H_2 treatment was necessary to eliminate chlorine and form metallic Ru. $RuCl_3$ itself is easily reducible with H_2 treatment, but the complete removal of chlorine from the catalyst system is difficult [3]. Therefore, compared to other activation methods when chlorine-free Ru compounds are used as precursors, the H_2 treatment condition used to activate the $RuCl_3$-derived catalyst was very critical in order to eliminate the chlorine as much as possible [2]. However, Ru is a good catalyst for methanation of the carbon support [4–6]. Thus, the critical H_2 treatment might destroy the fine structure of the carbon support and consequently lower the catalytic activity of the Ru/C catalyst [7–10]. So far there seems to be no clear opinion about the role of induced methanation on the catalytic activity, in spite of the importance of carbon support for this Ru/C catalyst.

We suppose there are three key factors that affect the catalytic activity for the HTAC-supported, Ba-promoted Ru catalyst for ammonia synthesis prepared with $Ba(NO_3)_2$ and $RuCl_3$ as precursors. The three factors, which are functions of the H_2 treatment temperature, are considered to be: the amount of residual chlorine, the structure of HTAC and Ru cluster, the state of the Ba promoter and its interaction with the Ru particle. Since these three factors will change simultaneously when the H_2 treatment temperature is changed, it is not easy to study one factor independently. According to the activity results [2], it was found that the optimal dechlorination temperature for removing chlorine from $RuCl_3$/HTAC to prepare Ru/HTAC was 450 °C (for 24 h), and the optimal hydrogenolysis temperature for decomposing $Ba(NO_3)_2$ on the Ru/HTAC catalyst to activate the catalyst was 550 °C (for 3 h). These are related to the first and the third factor and were discussed earlier [2]. In addition, we also found that the methanation of HTAC occurred when the H_2 treatment temperature was higher than 475 °C for both the dechlorination process and the hydrogenolysis process. Namely, the deep dechlorination process was not ever increasingly favorable but possibly the induced methanation might have led to lowering the catalytic activity. However, the deep hydrogenolysis process seemed to be quite effective even though the methanation of the HTAC support greatly occurred. Therefore, it is interesting to know how the induced methanation affected the catalyst. In this work, the structural change, *i.e.*, the porosity change, of these H_2-treated samples is investigated with N_2 physisorption. Based on the porosity investigation, the relations of the structural factor with other active species-concerned factors will be

* To whom correspondence should be addressed.

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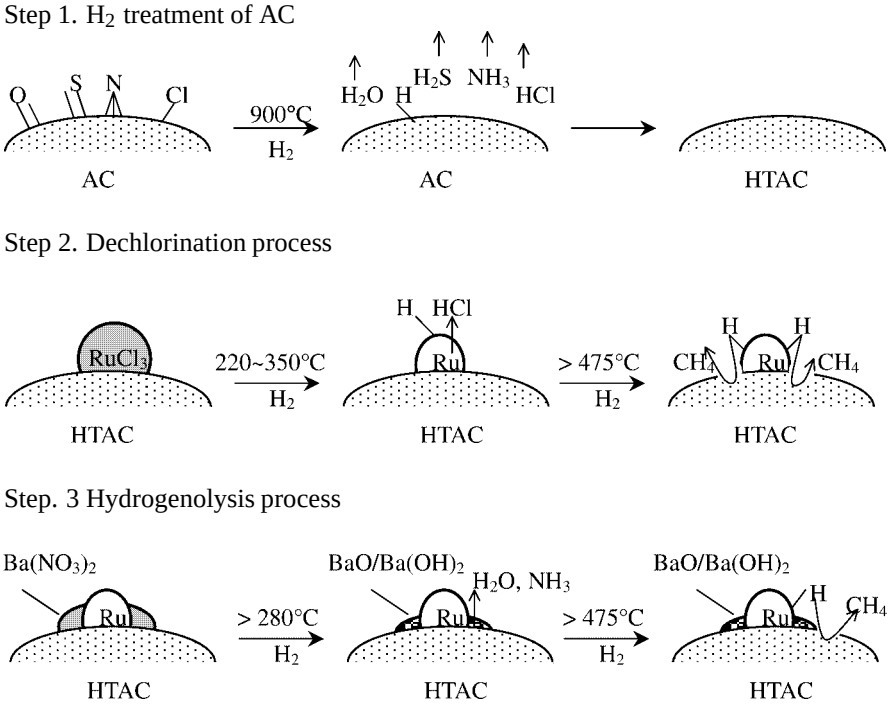

Figure 1. A supposed diagrammatic representation of catalyst preparation and catalyst activation processes concerning the hydrogen treatment.

discussed in order to distinguish its respective role on the catalytic activity. Helpful information is supplied for the treatment and even the practical operation of the Ru/C catalyst.

2. Experimental

2.1. Catalyst preparation, catalyst activation, and ammonia synthesis

The catalyst preparation and activation processes that are involved in H_2 treatment are illustrated in figure 1. Firstly, temperature-programmed treatment of raw active carbon (AC) (100 g, bead-shaped, average diameter around 0.7 mm, Kureha Chemical Industries) was carried out at 900 °C for 90 h with H_2 (20 ml/min) to remove the possible electron-withdrawing impurities, such as =S, =NH, –COOH, –CHO, halogen, *etc.* that can be poisonous for Ru catalysts [11–13] (step 1). The hydrogen-treated active carbon is indicated as "HTAC" hereafter. Analytical results are summarized in table 1. It was found that the high-temperature H_2 treatment greatly improved the support purity without distinct textural change [2].

Subsequently, HTAC was impregnated with $RuCl_3$ (Ru : HTAC = 5 : 100 wt/wt) in acetone solution. After drying, the obtained $5RuCl_3$/HTAC was dechlorinated by H_2 reduction to form metallic Ru (5Ru/HTAC) at a temperature ranging from 350 to 600 °C for 24 h (step 2). TG-MS results in our previous work [2] revealed that the chlorine started to be removed easily at the low temperature of 220 °C and seemed to be finished around 350 °C. But the methanation of the HTAC support was also observed when the dechlorination temperature was increased above 475 °C.

Table 1
Comparison between active carbon (AC) and hydrogen-treated active carbon (HTAC).

	Density[a] (g/ml)	Surface area[b] (m^2/g)	Component (wt%)			
			C	H	Cl	Others
AC	0.55 ± 0.05[c] 0.85 ± 0.05[d]	990	96.59	0.83	0.01	2.57
HTAC		796	99.21	0.45	n.d.[e]	0.34

[a] Data from supplier.
[b] BET specific surface area.
[c] Bulk density.
[d] Particle density.
[e] n.d. = not detected.

Then, 5Ru/HTAC was impregnated with $Ba(NO_3)_2$ (promoter precursor) in water solution (Ba/Ru = 1 : 1 in mol). The dried sample is a catalyst indicated as "$1Ba(NO_3)_2$–5Ru/HTAC".

Finally, ammonia synthesis was performed in a computer-controlled flow system at 315 °C with synthesis gas $N_2 + 3H_2$ (60 ml/min, 1 atm) after the $1Ba(NO_3)_2$–5Ru/HTAC catalyst (0.200 g) was hydrogenized for 3 h with H_2 (50 ml/min, 1 atm) in a temperature ranging from 315 to 575 °C in order to activate the catalyst (step 3). The catalytic activity of the catalysts for ammonia synthesis was thus measured as a function of hydrogenolysis temperature.

TG-MS data [2] showed that the decomposition of $Ba(NO_3)_2$ started at about 280 °C. As similar to the dechlorination process, the methanation of the HTAC support

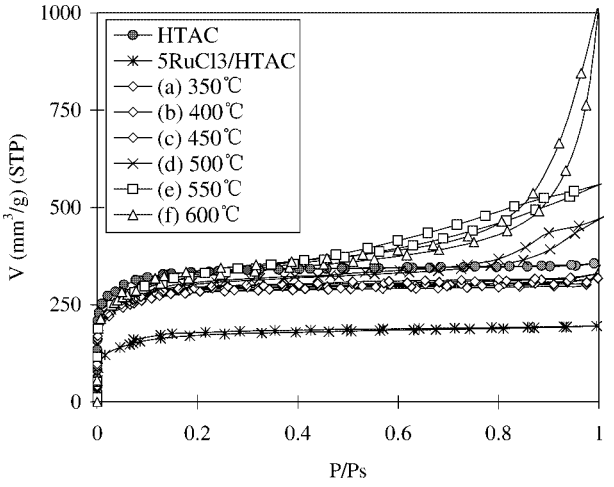

Figure 2. N_2 adsorption and desorption isotherms of samples HTAC, $5RuCl_3$/HTAC, and 5Ru/HTAC which were prepared with a dechlorination temperature ranging from (a) 350 to (d) 600 °C, respectively.

occurred when the hydrogenolysis temperature was above about 475 °C.

2.2. Characterization of catalyst

Static N_2 physisorption at −196 °C on the samples (about 20 mg) was measured automatically by using a BELSORP 28SA instrument. The specific surface area was calculated by using the BET equation from the adsorption isotherm. The pore size distribution and pore volume distribution were calculated with the conventional Dollimore–Heal (DH) method [14,15] from the desorption isotherms.

XRD patterns were obtained with a standard diffractometer with the scanning rate of degrees 2θ at 2.000°/min. No instrumental broadening corrections or experimental error were taken into account here.

3. Results

3.1. N_2 adsorption and desorption isotherms

N_2 physisorption was tested in order to investigate the porosity change of catalysts during the preparation and activation processes (figure 2). With the increase of dechlorination temperature above 450 up to 600 °C, the total adsorption volume of N_2 ($P/P_s = 1$) on 5Ru/HTAC samples gradually increased, whereas it was similar for 5Ru/HTAC samples having a dechlorination temperature within the range of 350–450 °C. For the $5RuCl_3$/HTAC sample, the total N_2 adsorption volume was the lowest. If paying attention to the desorption isotherm of each sample, we can observe the hysteresis loops on 5Ru/HTAC samples which were dechlorinated above 450 up to 600 °C. These isotherms were also changed from the Langmuir type I to Langmuir type IV. In a sense, the increase of N_2 adsorption capacity with the change of isotherm type represents the transformation of the Ru/HTAC samples from microporous to mesoporous, and even to macroporous [16]. Since Ru catalyzed the methanation of the HTAC support when the dechlorination temperature was above 475 °C, it can be supposed that the methanation of the HTAC support was the cause for the porosity change. Actually, due to the same cause, the similar phenomenon was observed on the $1Ba(NO_3)_2$–5Ru/HTAC catalyst after hydrogenolysis was done at the high temperature of 575 °C.

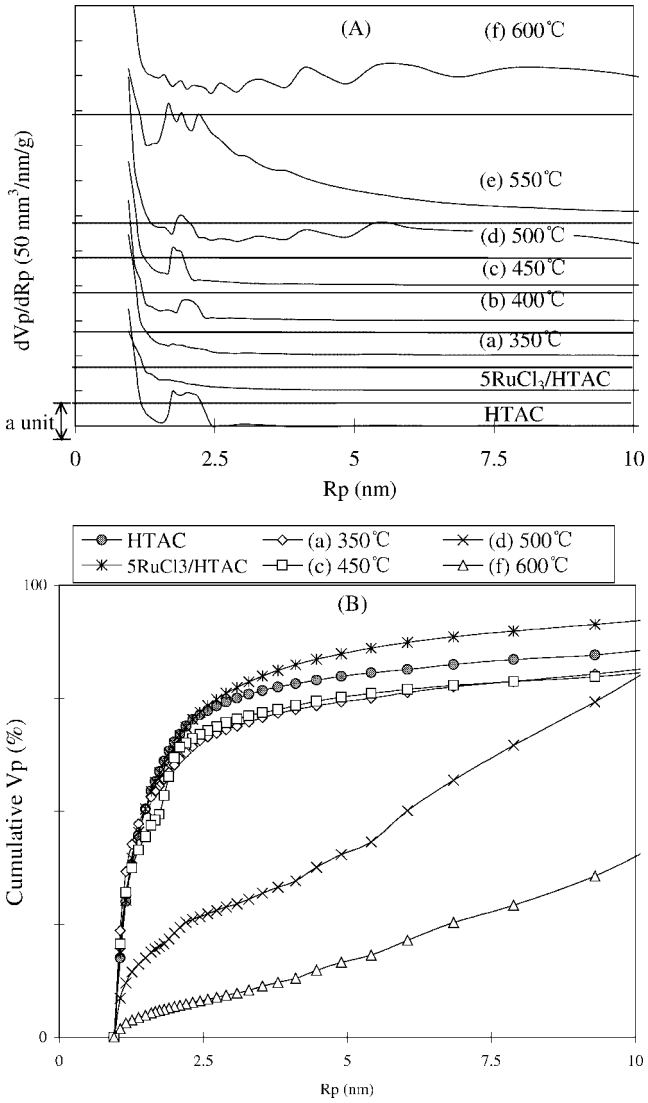

Figure 3. (A) Pore size distribution and (B) pore volume distribution of samples HTAC, $5RuCl_3$/HTAC, and 5Ru/HTAC which were prepared with a dechlorination temperature ranging from (a) 350 to (d) 600 °C, respectively.

3.2. Pore size distribution

Figure 3(A) shows the pore size distribution of 5Ru/HTAC samples. For the HTAC sample, a peak between 1.5 and 2.5 nm is found and no apparent peak exists above this radius on the pore size distribution curve. It means that HTAC was mainly composed of pores of radii ranging between 1.5 and 2.5 nm. After the impregnation of $RuCl_3$ (*i.e.*, for the $5RuCl_3$/HTAC sample), this peak disappeared. With the increase of dechlorination temperature from 350 to

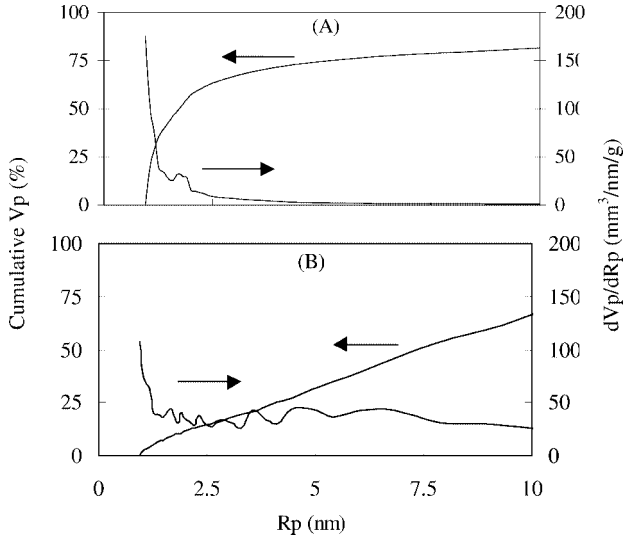

Figure 4. Pore size distribution and pore volume distribution of catalysts $1Ba(NO_3)_2$–5Ru/HTAC: (A) before hydrogenolysis, (B) after hydrogenolysis at 575 °C.

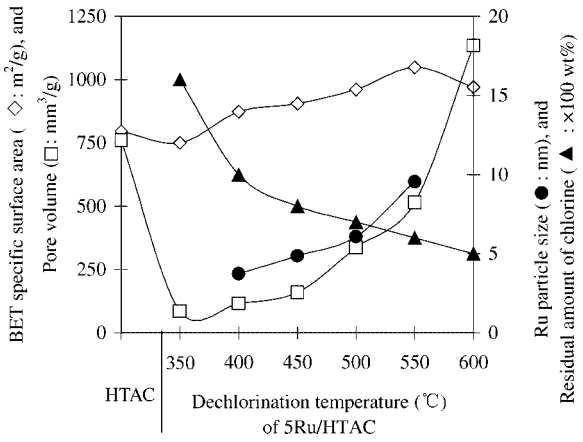

Figure 5. BET specific surface area (◇), pore volume (□), Ru particle size (●) (from [2]), and residual amount of chlorine (▲) (from [2]) of samples HTAC, and 5Ru/HTAC which were prepared with a dechlorination temperature ranging from 350 to 600 °C, respectively.

450 °C, a narrow peak between 1.6 and 2.1 nm subsequently reappeared. Then, with the further increase of dechlorination temperature to 500, 550, and up to 600 °C, it can be clearly observed that the pore size of the 5Ru/HTAC samples distributed broadly and remarkably not only between 2 and 10 nm, but also above 10 nm.

We suppose that the disappearance of the pores of radii of 1.5–2.5 nm over sample $5RuCl_3$/HTAC was due to the pore filling or blocking of pore openings by the impregnated bulky $RuCl_3$ clusters, which might also be adsorbed on the inner wall of larger pores. The increase of dechlorination temperature (350–450 °C) might remove the bulky chlorine ions leaving small-sized Ru particles and make some once covered pore openings re-exposed. Because of the above mentioned factors, the total pore volumes of these samples must be smaller than that of HTAC (see figure 5), as also being represented in figure 2 that the total N_2 adsorption

Table 2
Pore volume distribution of samples at different procedures.

Sample	Cumulative pore volume (%)	
	R_p < 2.5 nm	R_p < 10 nm
HTAC	71	86
$5RuCl_3$/HTAC	72	93
5Ru/HTAC (dechlorinated at)		
350 °C	66	82
450 °C	67	81
500 °C	27	84
600 °C	8	44
$1Ba(NO_3)_2$–5Ru/HTAC[a]		
Before hydrogenolysis	63	82
After hydrogenolysis[b]	14	71

[a] Prepared with dechlorination temperature of 450 °C.
[b] Hydrogenolysis temperature was 575 °C.

volumes were lower. For 5Ru/HTAC samples that were dechlorinated above 450 °C (500–600 °C), the methanation might break the wall of adjacent micropores around the Ru metal and combine the micropores into mesopores, and even macropores.

3.3. Pore volume distribution

Combined with pore size distribution, the pore volume distribution supplies more information about the pore structure (figure 3(B)). HTAC support, $5RuCl_3$/HTAC sample, and 5Ru/HTAC samples that were treated under 450 °C were not much different from each other. The pore volume percentages of pore radii below 2.5 nm and below 10 nm are shown in table 2. Whereas for samples 5Ru/HTAC dechlorinated at 500 and 600 °C, the percentage pore volume of radius below 2.5 nm significantly decreased to 27 and 8%, respectively (figure 3(B) and table 2). This clearly indicates that the increase of dechlorination temperature enlarged micropores and hence increased average pore radius due to the methanation of support. This result coincided with the pore size distribution result.

In order to depict how the methanation of the HTAC support impacted on the catalyst structure during the hydrogenolysis process, determinations of the pore size distribution and the pore volume distribution were also done (figure 4, table 2). Before the hydrogenolysis, catalyst $1Ba(NO_3)_2$–5Ru/HTAC showed almost the same results as those of sample 5Ru/HTAC that was dechlorinated at the same temperature of 450 °C. After being hydrogenized at 575 °C, it showed similar results to those of sample 5Ru/HTAC that was dechlorinated at a similar temperature of 600 °C. Therefore, it can be supposed that both in the dechlorination process and in the hydrogenolysis process, the induced methanation of HTAC support had an almost similar effect on the structural change of the catalyst.

3.4. Pore volume and specific surface area

From the above discussion, the change of pore volume (figure 5) with the H_2 treatment temperature can be reason-

ably understood. After the impregnation of $RuCl_3$ on HTAC, due to the pore blocking or pore filling, the pore volume sharply decreased from the 760 of HTAC to about 90 mm^3/g. Then with the increase of dechlorination temperature from 350 to 450 °C, the pore volume gradually increased since the re-dispersion of the Ru cluster might expose some once covered pores. Above 500 to 600 °C, due to the methanation of the support, a lot of new micropores might be produced around the Ru particle, the walls between the adjacent pores might be broken, thus as a result, the pore volume significantly increased.

Compared to the HTAC sample, for sample 5Ru/HTAC dechlorinated at 350 °C, the specific surface area slightly decreased to 750 m^2/g (figure 5). With further increase of dechlorination temperature, the specific surface areas gradually increased with a final decrease at 600 °C. Methanation of carbon occurred around the vicinity of Ru metal particles, where dissociated active hydrogen was supplied (figure 1). The moderate degree of methanation may make wide pores well developed and keep the surface area high. On the other hand, the serious degree of methanation may enlarge pores possibly but to decrease total surface area.

It is very interesting to have observed that the above structural changes of active carbon support resulted from the methanation catalyzed by Ru metal are similar to the phenomena that occurred during the preparation of active carbon when increasing the "burn-off" degree of carbon [17,18], where the "burn-off" is used to partially gasify the raw material (for example, coal) by oxygen to get a modified carbon textural structure. At low degree of burn-off, the carbon has a highly microporous character, whereas at high degree of burn-off, some of the micropores are converted into meso- and macro-pores [17,18]. Our findings are supposed to agree with these phenomena.

3.5. Ru particle size

For 5Ru/HTAC samples, with the increase of dechlorination temperature from 400 to 500 °C, the average Ru particle size increased gradually from 3.74 to 6.08 nm (figure 5). When the dechlorination temperature was increased up to 550 °C, Ru particle size remarkably increased to 9.55 nm. It can be judged that the sintering of Ru particles might occur when methanation occurred. For the factors resulting in the increase of Ru particle size or the sintering of Ru particles, besides the applied high temperature, the methanation of the HTAC support is probably another important factor. The increase of Ru particle size might be accelerated by the methanation of carbon between Ru particles, which finally lead to the agglomeration of Ru particles.

XRD patterns of sample 5Ru/HTAC are shown as a function of dechlorination temperature in figure 6. With the elevated dechlorination temperature, the width of Ru reflection peaks gradually reduced, which represents the increase of Ru particle size. However, it can be seen that a broad peak ranging from 42 to 45°, the background peak of the HTAC support [2], disappeared with the increase of temperature.

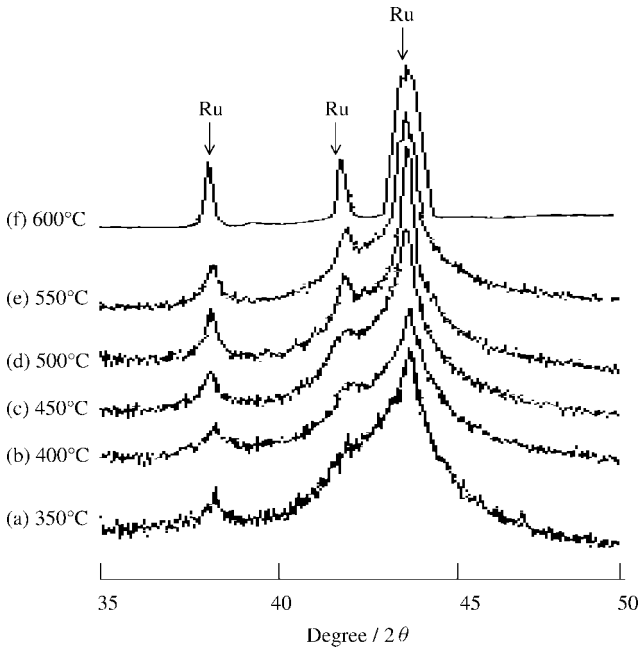

Figure 6. XRD patterns of 5Ru/HTAC samples which were prepared with a dechlorination temperature ranging from (a) 350 to (f) 600 °C, respectively.

As a result, the once hidden two Ru shoulder peaks gradually separated. Micro-grain carbon surrounding the Ru particles might have been gasified by methanation.

4. Discussion

4.1. Effect of dechlorination temperature on the catalytic activity: relation between the amount of residual chlorine and the methanation degree of carbon support

Several characterization results of the 5Ru/HTAC samples are summarized as a function of dechlorination temperature in figure 5. Since the main aim of the dechlorination process used is to eliminate the negative-effected chlorine as much as possible from the Ru catalyst. Therefore, firstly the amount of residual chlorine on the catalyst is an important factor. Compared to the 4.49 wt% of chlorine (theoretic value) on the $5RuCl_3$/HTAC sample, the amount of residual chlorine on the 5Ru/HTAC sample dechlorinated at 350 °C decreased to 0.16 wt%, which equals about 4% of the original amount of chlorine. Namely, about 96% of chlorine had easily been eliminated from $5RuCl_3$/HTAC under such a low temperature of 350 °C. When the dechlorination was done at 450 °C, the residual chlorine further decreased to 0.08 wt%. Then, even for dechlorination temperature up to 600 °C, the residual amount of chlorine decreased slightly and there was still 0.05 wt% of residual chlorine. It verifies that a very small amount of residual chlorine could not be eliminated completely [3].

The activity test results (figure 7) clearly show that the optimal dechlorination temperature was 450 °C (for 24 h). Deep dechlorination degree improved the TOF from the 2.14×10^{-3} of 400 °C up to the 4.38×10^{-3} of 550 °C.

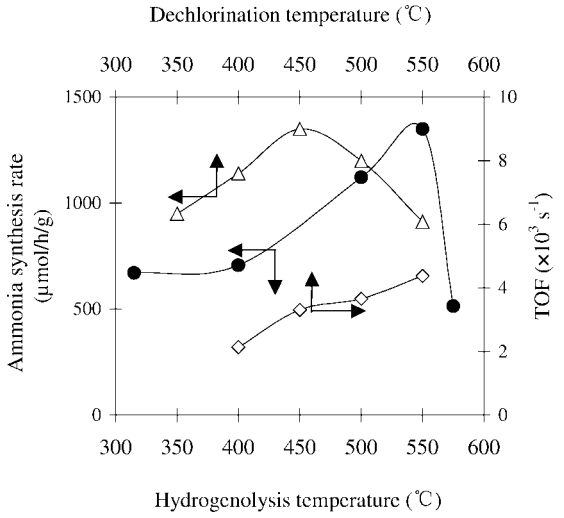

Figure 7. Ammonia synthesis rate as a function of hydrogenolysis temperature over a catalyst $1Ba(NO_3)_2$–5Ru/HTAC prepared with a dechlorination at 450 °C for 24 h (which is taken as one example (•)), as well as a function of dechlorination temperature over catalysts $1Ba(NO_3)_2$–5Ru/HTAC (all activities correspond to the hydrogenolysis temperature of 550 °C (△)) with the corresponding TOF (◊). Reaction conditions: 315 °C, 1 atm, $N_2 + 3H_2$, SV = 18000 h^{-1}. Note: TOF is obtained by applying $NH_3/Ru_{surface}$ and assuming Ru particle sphere-shaped with concentration of surface atoms of 1.63×10^{19} m^{-2} and density of 12.45 g/cm^3.

However, the apparent catalytic activity decreased when dechlorination temperature was above 450 °C.

From the above porosity investigation, it has been understood that the induced methanation of the HTAC support did not destroy the porosity but increased the surface area and pore volume. The increase of porosity could not be the primary factor to decrease the catalytic activity of the catalyst. However, the methanation of the carbon support could be the main factor to accelerate the growth of Ru particles. The growth of Ru particles decreased the Ru dispersion, thus the exposed surface area of active metal. The decrease of catalytic activity above 450 °C of dechlorination temperature must be related to the increase of Ru particle size. Therefore, during the dechlorination process, with the increase of dechlorination temperature, both the positive effect resulting from the decrease of the amount of residual chlorine and the negative effect resulting from the increase of Ru particle size were simultaneously increased. The dechlorination temperature had binary effects on the catalytic activity. As a combined result, an optimal dechlorination condition at 450 °C (for 24 h) was observed.

4.2. Effect of hydrogenolysis temperature on the catalytic activity: relation between the hydrogenolysis of promoter and the methanation degree of carbon support

During the hydrogenolysis process, promoter precursor $Ba(NO_3)_2$ was hydrogenized to form an active component of $BaO/Ba(OH)_2$ on Ru/HTAC for ammonia synthesis [19,20]. In this study, it was found that the optimal hydrogenolysis temperature (figure 7) was 550 °C, higher than the methanation temperature of 475 °C. Similar to the dechlorination temperature, the hydrogenolysis temperature also might have a binary effect on the catalytic activity.

The decomposition of $Ba(NO_3)_2$ started and finished at a low temperature (figure 1). However, the increase of hydrogenolysis temperature to 550 °C led to the further increase of catalytic activity. It is considered that the formation of the active component of $BaO/Ba(OH)_2$ is important for getting high catalytic activity, since the promoter is very important for the Ru catalyst [1]. In our recent work we have found that the BaO component of the decomposed mixture of $BaO/Ba(OH)_2$ is more active for ammonia synthesis possibly, and a high hydrogenolysis temperature seems to be beneficial for getting this active component [21]. Therefore, in a temperature range, the catalytic activity increased with the increase of hydrogenolysis temperature.

On the other side, the hydrogenolysis temperature higher than 475 °C would cause the methanation of the HTAC support. As discussed before, the induced methanation of the carbon support in the hydrogenolysis process did not destroy the porosity of the catalyst, in contrast, the surface area and pore volume increased as similar to the dechlorination process. Therefore, the porosity change in the hydrogenolysis process should not be the primary factor, but the growth of Ru particles accelerated by the methanation of the carbon support was the main factor to decrease the catalytic activity.

Namely, hydrogenolysis temperature should also have a binary effect on the catalytic activity. The increase of amount of active promoter component BaO played a positive effect and the increase of Ru particle size played a negative effect. Both the positive effect and the negative effect would increase simultaneously with the increase of hydrogenolysis temperature. As a combined result, the optimal hydrogenolysis temperature was observed at 550 °C (for 3 h) in this study. When the hydrogenolysis temperature was much higher (for instance, 575 °C), then the activity began to decrease.

For the phenomenon that the obtained optimal hydrogenolysis temperature was 550 °C (for 3 h), much higher than the starting temperature of methanation of 475 °C, another factor might be that the hydrogenolysis time was only 3 h in this study which was too short to lead to a serious methanation of HTAC support. In addition, it is widely accepted that the promoter locating at the surrounding of Ru particles could prevent the methanation of HTAC catalyzed by Ru and the agglomeration of Ru particles [2,8]. Thus, for a short hydrogenolysis time, the optimal hydrogenolysis temperature could be higher than the methanation temperature. This finding is very important for understanding the activation process in practical use. Methanation of this kind of catalyst is thought to be no serious problem under the practical ammonia synthesis plant operated below 400 °C.

5. Conclusions

The induced methanation of HTAC support catalyzed by metallic Ru, which occurred above 475 °C during both

the dechlorination process and the hydrogenolysis process, played an important role on the preparation and activation of Ba-promoted Ru/HTAC catalyst for ammonia synthesis using $Ba(NO_3)_2$ and $RuCl_3$ as precursors. The N_2 physisorption revealed that a moderate methanation degree could increase some surface area and pore volume by eliminating the pore blocking and developing the pore channel, rather than seriously destroy the porous structure of the catalyst. But we suggested that the methanation of the carbon support might accelerate the growth of Ru particles even at a moderate H_2 treatment temperature, which finally led to the decrease of activity.

The increase of H_2 treatment temperature could bring a positive effect on catalytic activity by decreasing the amount of residual chlorine during the dechlorination process and by creating a more active component and active site for ammonia synthesis during the hydrogenolysis process, respectively. However, with the increase of positive effects, the negative effects resulting from the methanation of the support would simultaneously increase too. The activity test results showed that the optimal temperatures were 450 °C (for 24 h) for the reductive dechlorination process and 550 °C (for 3 h) for the hydrogenolysis process. The performance of the catalyst might be a combined result of the interaction of the amount of residual chlorine, Ru particle size, and the active promoter component. Thus, a respective control of the methanation degree during the catalyst preparation and activation processes was thought very important for the practical use of the promoted Ru/C catalyst.

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