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An efficient route for the preparation of activated carbon supported ruthenium catalysts with high performance for ammonia synthesis

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ABSTRACT

An impregnation–precipitation method was developed for the preparation of activated carbon supported ruthenium-based catalysts for ammonia synthesis. The ammonia concentration in the outlet of reactor for the Ba–Ru–K/AC catalysts prepared via impregnation–precipitation method is as high as 20.4 vol% at 648 K, pressure of 10 MPa and with a space velocity of 10,000 h^{-1}, which is much higher than that of catalysts obtained via other preparation methods. The high performance of the catalyst is attributed to the efficient removal of chlorine ions and high dispersion of Ru nanoparticles, which is confirmed by element analysis, X-ray photoelectron spectroscopy, CO-chemsorption, and transmission electron microscopy. The present study provides a new concept for the preparation of carbon supported ruthenium based catalyst, which can be easily applied to industry and suitable for scale up production.

1. Introduction

The synthesis of ammonia from hydrogen and nitrogen is an important process in chemical industry. The annual production of ammonia is around 180 million tons. The present iron based catalysts require relatively high temperature and pressure in order to achieve certain productivity, and are energy unfavorable. Although the invention of the $Fe_{1-x}O$-based catalyst improves the catalytic performance at relatively lower pressure and temperature [1,2], it is difficult to further reduce the temperature and pressure for fused iron catalysts. Consequently, many researchers proposed several alternative catalysts, such as ruthenium catalyst which has been studied intensively since 1970s and are considered as the second generation catalysts for ammonia synthesis [3–7].

In the last several decades, a considerable body of papers studied on the types of supports [5–8], promoters [9–11], and precursors of ruthenium compounds have been published [12–16]. Among all supports, carbon materials including activated carbon and graphitic carbon supported ruthenium catalysts have the highest activities. It is generally accepted that the alkali and alkali earth metal such as Ba, K, and Cs is the most active promoters for ammonia synthesis [17,18]. Ru compounds which can be used as precursors include K_2RuO_4, $RuCl_3{\cdot}3H_2O$, $Ru_3(CO)_{12}$, $Ru(NO)(NO_3)_3$ and $Ru(NH_3)_5Cl_3$ [12–16]. Among all precursors, $RuCl_3$ is the most commonly used one because of its low-cost and stable chemical properties. However, it is generally accepted that chlorine ion is a severe poison for ruthenium catalysts [19–23]. Tennison claimed that the presence of one chlorine atom on the surface influences up to 6 surrounding Ru atoms [24]. Kowalczyk et al. [25] found that the chlorine-free Ru/C catalyst is more than twice as active as the Ru/C catalysts prepared with $RuCl_3$ as precursor for ammonia decomposition. Therefore, when $RuCl_3$ is used as Ru precursor, the removal of Cl^- is critical to obtain high performance for ammonia synthesis catalysts. Usually, the most widely used method for removal of Cl^- is hydrogen reduction method (HRM) [23–26]. It has been reported that content of chlorine ions decreases when the temperature of reduction is increased. However, chlorine still remains even after a reduction at 973 K [26,27]. Generally, the hydrogen reduction method involves usage of H_2 and high temperature, which usually results in the sintering of Ru metal particles. Especially for the activated carbon supported ruthenium catalysts, the increasing of reduction temperature will also cause the methanation of carbon supports, which is detrimental for the stability of catalysts.

Recently, Lin et al. [28] reported a hydrazine liquid reduction method (LRM) which involves reduction of $RuCl_3$ by hydrazine in KOH solution under mild conditions for alumina supported Ru catalysts. The activity of the catalyst prepared by liquid reduction method is higher than that of hydrogen-reduced catalysts. But the LRM process involves hazardous chemicals (N_2H_4), which is not highly acceptable in view of environment protection. Another method for the removal of Cl^- such as hot-water washing method has been proposed in the silica-supported ruthenium catalyst [29].

In the present paper, the composition of catalysts was fixed on di-promoted Ba–Ru–K/AC catalysts based on our previous research results and literatures [17,18]. Special attention was paid to the preparation methods for the ruthenium based ammonia synthesis

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catalysts by using cheap and stable $RuCl_3$ compound as precursor. An impregnation–precipitation method (IPM) has been developed and compared with hydrogen reduction method (HRM).

2. Experimental

2.1. Catalyst preparation

Activated carbon was provided by Hainan Yeqiu Industrial Co. Ltd., and $Ba(NO_3)_2$, KNO_3 and $RuCl_3$ were obtained from Sinopharm Chemical Reagent Co. Ltd., and Sino-Platinum Metals (SPM) Co. Ltd., respectively. All the chemicals were used as received without any further purification. The particle size of the activated carbon used in this study is in the range of 1.0–1.4 mm. Prior to the preparation of catalysts, the activated carbon (marked with AC0) was treated at 1123 K for 12 h in hydrogen flow (marked with AC1) and washed with 30% HNO_3 at 363 K for 5 h (marked with AC2). The residues on the above activated carbons (AC2) were further washed by distilled water either 3 times (marked with AC3) or washed more than 10 times (marked with AC4). The above activated carbons were finally dried at 393 K overnight before being used as catalyst support.

2.1.1. Preparation of catalyst via impregnation–precipitation method (IPM)

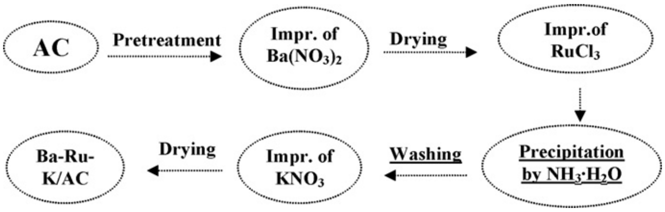
The above pretreated activated carbon (AC4) was first impregnated with $Ba(NO_3)_2$ solution at room temperature, dried at 110 °C for 8 h. Subsequently, the above sample was impregnated with aqueous ruthenium trichloride solution for 12 h at room temperature. Then the wet sample was precipitated by diluted ammonia solution (or KOH, $NaHCO_3$, Na_2CO_3, $CO(NH_2)_2$, and H_2O) at certain temperature for various time. After deposition, the solid was washed by deionized water several times at desired temperature until no Cl^- can be detected by $AgNO_3$ solution, and dried at 110 °C for 8 h. KNO_3 was impregnated via the same procedure with impregnation of $Ba(NO_3)_2$. The nominal Ba, Ru and K loading of the catalysts was 2.6, 2.6 and 9.1 wt% respectively. An overview of preparation process for this method is presented in Scheme 1.

2.1.2. Preparation of catalysts via H_2 reduction method (HRM)

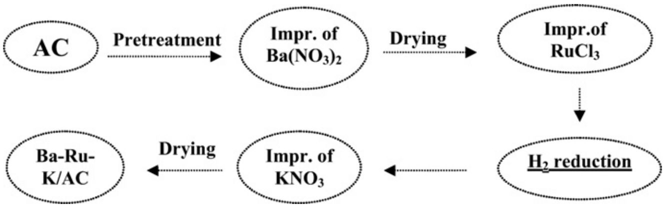
The preparation of the catalysts by H_2 reduction method is similar to that of the impregnation–precipitation method, except for that the sample was reduced under pure H_2 with a flow rate of 60 mL/min at 723 K for 12 h after the impregnation of $RuCl_3$ without using the precipitation and washing steps. An overview of preparation process for this method is presented in Scheme 2.

2.2. Test of activity

Ammonia synthesis reaction over the sample was carried out in a fixed-bed reactor with an inside diameter of 14 mm at the temperature of 648–673 K, space velocity of 10,000 h^{-1} and pressure of 10 MPa. The catalyst bed was diluted with quartz (1.0–2.0 mm) loaded in the isothermal zone of the reactor, and both the ends of the catalyst bed were also filled with the quartz to prevent the synthesis gas from channeling. The catalysts were activated by the mixture of N_2 and H_2 (H_2:N_2 = 3:1) at a pressure of 5.0 MPa and with a space velocity of 30,000 h^{-1} at 673, 698, 723, and 748 K for 4, 8, 8, and 4 h, respectively. After the activation, the temperature was decreased to 673 K and initial activity was measured. Then the temperature was increased to 748 K for 16 h with space velocity of 30,000 h^{-1}, and pressure of 5 MPa to test the stability of the catalysts. After the thermal resistance test, the final activities were measured. The concentration of ammonia in the exit gas of the reactor under given conditions was measured by a method of sulfuric acid neutralization. All the activity data used in present paper were measured after thermal resistance tests at the above mentioned conditions. The synthesis gas was derived from the decomposition of ammonia with deep removal of H_2O, CO, CO_2 and residual NH_3 over Pd, 13X, and 5A molecular sieves.



Scheme 1. The scheme for impregnation–precipitation method (IPM).



Scheme 2. The scheme for H_2 reduction method (HRM).

2.3. Characterizations

The method proposed by Boehm et al. [30] was used for the chemical titration of AC surface groups. According to Boehm method, $NaHCO_3$ (pKa = 6.37) neutralizes carboxylic groups, Na_2CO_3 (pKa = 10.25) neutralizes carboxylic and lactonic groups, NaOH (pKa = 15.27) neutralizes carboxylic, lactonic and phenolic structures. The activated carbon samples were added to the excess standard base solutions (0.01 mol/L NaOH, 0.02 mol/L Na_2CO_3, 0.02 mol/L $NaHCO_3$). The acidic surface functional groups of the carbon surface were determined by back-titration with HCl solution after the system reached the equilibrium state.

Determination of the pH values of activated carbon: The measurements were carried out according to GB/T 12496.20-90. 2.5 g of activated carbons were weighted, and added to a flask filled with 50 mL of boiling water. The above mixture was boiling for 5 min. After that, the activated carbon was filtrated and 5 mL of the liquid part was used for the measurement of pH value. The pH value was measured by Sartorius pH meter with pH/ATC electrode.

The elemental content of Ba and Ru in the solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES on SpectroCiros CCD). All the solutions were collected and diluted to 1 L. The chloride content in the catalysts was determined by energy dispersive spectrum.

Nitrogen sorption isotherms were determined at 77 K by a Micromeretics ASAP 2020 instrument in static measurement mode. Before the measurement, the samples were degassed at 523 K for 10 h.

Transmission electron microscopy (TEM) was performed on a TECNAI G2 F30 S-TWIN FEI Tecnai electron microscope with a field emission gun as the source of electrons operated at 300 kV. Samples were mounted on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

CO-chemisorptions were carried out on a Micromeritics AutoChem 2910 instrument. The catalyst was reduced in a H_2 flow at 723 K for 4.0 h. The sample was subsequently purged with helium for 1.5 h to remove H_2 adsorbed on the surface of the catalyst, then been cooled down to room temperature in helium. CO-chemisorption was measured by the pulse method by introducing 5% CO + 95% He flowing over the sample.

X-ray photoelectron spectroscopy was done on a Kratos AXIS Ultra DLD analytical instrument. A monochromatic Al Kα radiation (1486.6 eV) with analyzer pass energy of 80 eV was operated at 3 mA and 15 kV. The pressure in the XPS sample analysis chamber was less than 8×10^{-8} Torr.

3. Results and discussions

3.1. Optimization of AC support

The commercial activated carbons differ from porosity, chemical surface properties, and impurities, such as P, S, N, O and Cl, which have significant effects on the performance of ammonia synthesis catalyst. It has been reported that pretreatment of activated carbon by hydrogen can reduce the content of impurities [19,20], and then almost identical performance can be achieved for catalysts supported on different activated carbons.

The data of the surface functional groups and pH values for activated carbon treated with different methods are given in Table 1. It can be seen that the amount of basic groups increases from 0.03 to 0.50 mmol/g and the surface pH value increases from 9.1 to 10.2 and the surface functional groups such as –COOH, –OH, and –COR are completely removed after the activated carbon was pretreated by H_2. It is well documented that the surface functional groups are very important for the dispersion of ruthenium, while the basic groups are not suitable for the anchoring of noble metal ions. Prado-Burguete et al. [31] found that the oxygen surface groups of the carbon support play a major role in the final metal dispersion. To make the chemical properties of the activated carbon surface uniform, treatment of nitric acid is necessary as reported in many references [32–35]. Han et al. [36] reported that when the activated carbon was treated with appropriate amounts of HNO_3, the quantity of mesopores and surface hydroxyl groups can be increased and higher hydrophilic property can be achieved as well which leads to higher dispersion of ruthenium and enhanced activity of the catalyst prepared by impregnation of $RuCl_3$ aqueous solution. As can be seen in Table 1 and Fig. 1, most of the surface functional groups are recovered after nitric acid treatment and the amount of oxygen surface groups increases significantly.

The dispersion of the ruthenium nanoparticles for the catalysts supported on the above activated carbons with various pretreatments is also given in Table 1. It shows that the dispersion of ruthenium supported on the as-received activated carbon and AC1 with H_2 pretreatment is about 17.1 and 16.6%, respectively, which is quite similar. This means pretreatment of support by H_2 cannot improve the dispersion of Ru metal particles. However, after the activated carbon was pretreated by nitric acid, the dispersion of Ru and catalytic activity were improved significantly.

The surface functional groups such as carboxyl, lactones, and phenols decompose upon heating under helium atmosphere releasing CO and CO_2 at different temperatures. Thus He-TPD was employed for the determination of the surface functional groups of activated carbon. It has been widely accepted that each type of oxygen-containing functional groups decomposes to a defined product, e.g., a CO_2 peak results from carboxylic acids at low temperatures, or lactones at higher temperatures; carboxylic anhydrides originate both a CO and a CO_2 peak; phenols, ethers, and carbonyls (and quinones) originate a CO peak [37,38]. The profiles of He-TPD show that the amount of CO_2 decreases after H_2 pretreatment, and increases dramatically after nitric acid treatment (Fig. 1(a)), indicating that the materials contain relatively more carboxyl and phenolic hydroxyl groups after treatment by nitric acid.

Table 1
Effect of the pretreatment on concentration of surface functional groups (mmol/g) and pH values for activated carbons and dispersion of Ru and activities of ammonia synthesis for Ba–Ru–K/AC catalysts.

Samples	Notes	A-COOH +A-COR +A-OH	A-COOH	A-COR	A-OH	Basic Group	pH	S.A.	P.V.	Ru Particle size (nm)	Ru Dispersion (%)	NH_3 (vol%)[a]	
												648 K	673 K
AC0	Untreated	0.16	0	0.10	0.06	0.03	9.1	1238	0.65	7.9	17.1	9.3	18.0
AC1	Treated by H_2	None	None	None	None	0.50	10.2	1156	0.59	8.1	16.6	8.6	17.7
AC2	Treated by H_2 and nitric acid	1.02	0.86	0.19	None	None	3.8	1156	0.59	4.7	28.6	17.5	22.7
AC3	AC treated by H_2 and nitric acid (washing 3 times)	1.02	0.86	0.16	None	None	4.0	1156	0.59	3.6	37.8	18.4	22.8
AC4	Treated by H_2 and nitric acid (washing 10 times)	1.02	0.76	0.29	None	None	4.3	1281	0.63	3.7	35.6	20.4	23.1

[a] The activities were measured at 10 MPa, 10,000 h^{-1}.

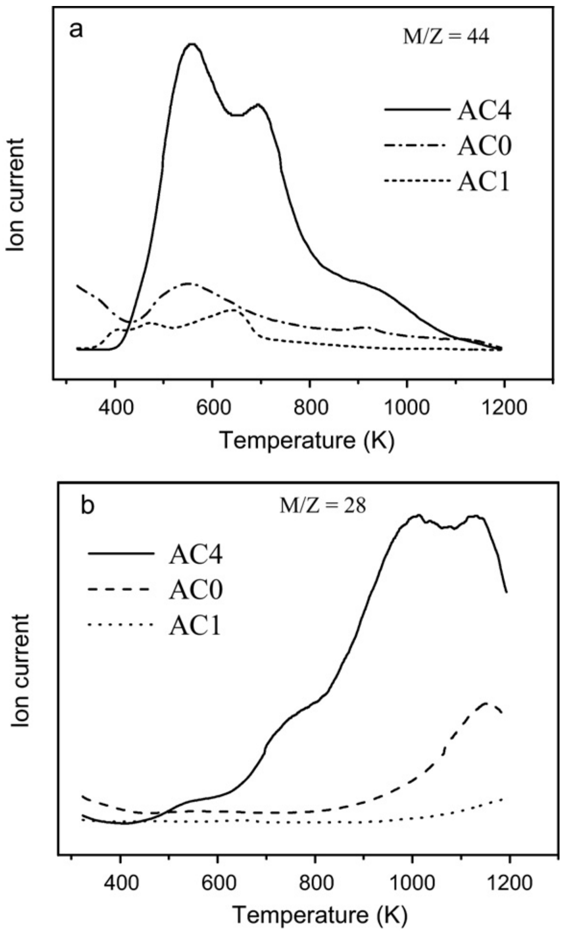


Fig. 1. He–TPD–MS profiles of the raw activated carbon (AC0), the raw AC after treated via H_2 at 1173 K for 3 h (AC1), and AC1 treated by concentrated nitric acid solution (AC4). (a) The desorption spectra of the CO_2 ($m/e = 44$); (b) The desorption spectra of the CO ($m/e = 28$).

The trend of CO curve is similar to that of CO_2 according to Fig. 1(b). These results further confirm the results obtained by chemical titration that most of the functional groups can be generated and recovered by nitric acid treatment. Therefore, the AC supports used in present investigation are pretreated via H_2 at 1173 K and nitric acid with concentration of 30% to obtain an optimized performance of the catalysts.

3.2. *Optimization of the impregnation–precipitation method*

Impregnation is a widely used method for preparing supported catalyst and it is able to prepare supported noble metal catalysts with low metal loading and high dispersion. Although $RuCl_3$ is relatively cheap and stable compares with other Ru precursors such as K_2RuO_4, $Ru_3(CO)_{12}$ and acceptable for the large scale production, the Cl^- in $RuCl_3$ is a severe poison for ammonia synthesis. Therefore, the removal of Cl^- is crucial to obtain catalysts with high performance when $RuCl_3$ is employed as a precursor. According to the calculation result as follows:

$$RuCl_3 + 3OH^- = Ru(OH)_3 + 3Cl^- \quad (1)$$

$$K_{sp}(Ru(OH)_3) = [Ru^{3+}] \times [OH^-]^3 = 1 \times 10^{-36} (298\,K) \quad (2)$$

Ru ions can be precipitated in the form of hydroxide facilely because the $K_{sp}(Ru(OH)_3)$ is so low. For example, when pH value of the solution is 7.0, the concentration of Ru^{3+} in aqueous solution is 10^{-15} mol/L. The chloride ions in $RuCl_3$ can be replaced completely by OH^-, and removed by the washing solution in form of Cl^-. If this process can be realized during the catalyst preparation, the shortcomings of the reduction by H_2 can be completely avoided, and the preparation process can be simplified significantly with thermal treatment and H_2-reduction steps removed. Consequently, we adopted IPM to remove the Cl^- in the $RuCl_3$ and immobilize the Ru precursor. The types of precipitators and washing process were investigated in detail.

Table 2
Effect of different precipitators on the Ru dispersion and catalytic performances for Ba–Ru–K/AC catalysts.

Precipitants	Ru dispersion (%)	Ru grain size (nm)	NH_3 (vol%)[a]	
			648 K	673 K
$NH_3{\cdot}H_2O$	35.6	3.7	20.4	23.1
KOH	23.7	5.7	16.3	22.5
$NaHCO_3$	22.5	6.2	16.0	22.5
Na_2CO_3	10.7	12.5	14.1	20.3
$CO(NH_2)_2$	6.2	21.7	14.2	20.1
Deionized water	5.3	25.5	11.7	19.6

[a] The activities were measured at 10 MPa, 10,000 h^{-1}.

3.2.1. *Precipitators*

Obviously, the alkaline solutions (such as KOH, Na_2CO_3, $NaHCO_3$, $NH_3{\cdot}H_2O$, CO $(NH_2)_2$) can be used as the precipitators. The effect of different precipitators on the particle size of the Ru and catalytic activity are listed in Table 2. With the selected precipitators, the catalyst precipitated by ammonia hydroxide has the highest Ru dispersions and the highest activities. The catalyst been prepared without any precipitators only H_2O was used for same procedures has the lowest activity among all the catalysts prepared, which indicates that the precipitation process is necessary to improve the performance of the Ru/AC catalysts. The activities of the catalysts prepared by using strong alkalis such as KOH, $NaHCO_3$, and Na_2CO_3 are not as high as the catalysts prepared with ammonia hydroxide. It should be noted that $CO(NH_2)_2$ may be a better precipitating agent as it releases NH_3 sluggishly if the precipitation is undertaken under proper conditions. Considering the method suitable for scale up production, the ammonia solution is cheaper and easier to be operated, we did not choose $CO(NH_2)_2$ as precipitator in the present work. In the following experiments, the ammonia hydroxide was used as precipitator and studied in detail for the investigation of IPM.

In order to prove the effect of base used as a precipitating agent for the deposition of Ru precursor, in removing the chloride moiety, the comparison experiment was conducted in a separate experiment. During this experiment, AC4 was further treated with the same ammonia solution used in the above preparation process, followed by washing with distilled water several times. This support was used for preparation of Ba–Ru–K/AC catalyst with Ru deposition by impregnation (without base precipitation). It is found that the activity of catalysts prepared via this method is similar to that of the untreated one and much lower than that of catalysts prepared via IPM method. This result indicates that the liquid phase pretreatment of AC support has no positive effect on the activity of the catalysts. Further confirms that the role of ammonia solution is precipitation of Ru^{3+} and thus resulting in effective removal of Cl^- as will be discussed the following sections.

3.2.2. *Concentration of the precipitated solutions*

The effect of the concentration of ammonia hydroxide solutions during precipitation on the catalytic activity is summarized in Fig. 2. Apparently, the activity of the catalyst increases with the concentration of the ammonia and decreases with further increasing of ammonia concentration. We suggest that small $Ru(OH)_3$ clusters can be easily formed in diluted ammonia solution, and thus results

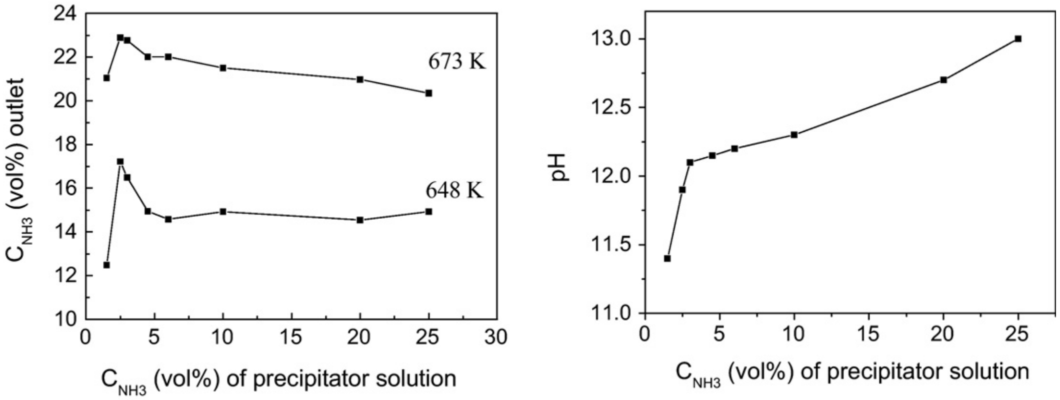


Fig. 2. (Left) Effect of precipitator concentration on the catalyst activity (10 MPa, 10,000 h^{-1}); (right): pH values of the precipitator solution vary with the ammonia concentration.

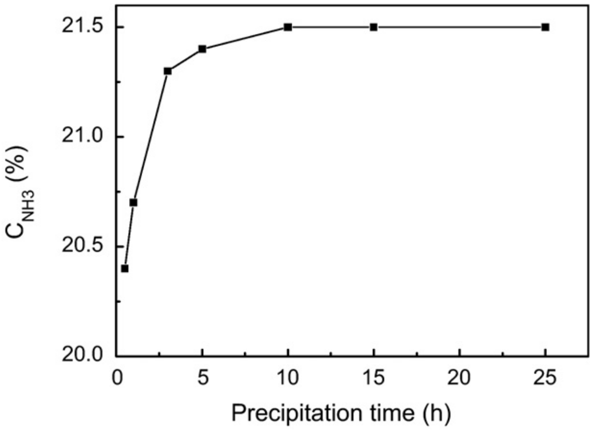


Fig. 3. Effect of precipitation time on activity of the catalysts.

in catalysts with high Ru dispersion and high activity. With higher concentration of ammonia and pH value, the rates of $Ru(OH)_3$ clusters formation may be too fast which may cause the conglomeration of ruthenium clusters.

3.2.3. Precipitation time

Fig. 3 illustrates the effect of precipitation time on the activities of the catalyst. It is found that the catalytic activity increases slightly with the precipitation time and is stabilized when precipitation time reaches 5 h. This indicates that ruthenium ions can be completely precipitated after 5 h. Practically, in order to guarantee the completed precipitation, the precipitation time of 8 h is adopted for the preparation of the optimized catalyst.

3.2.4. Effect of the washing process

The washing process is necessary to remove the Cl^- carried by $RuCl_3$ precursor. The variation of activities and contents of Cl^- in the catalysts with washing temperatures are shown in Table 3. It can be seen that less of chloride ions are left on catalyst at higher washing temperature. This trend is similar to that of catalytic performance. Optimal activity was achieved when the catalyst was washed at 363 K. The volume of the washing water needed for removing the remaining Cl^- is not only associated with the washing temperature, but also with washing time. With the identical washing time, the lower of the washing temperature, more water are necessary. When the temperature was increased to 363 K, twice washing are enough to remove Cl^- in the catalyst. Under the conditions studied, the optimum washing procedure is three times of washing at 363 K with about 90 mL of water.

Table 3
Effect of washing temperature on the Cl^- content remained in the catalysts and activity for Ba–Ru–K/AC catalysts.

Experiments entries	Washing temperature (K)	Cl (wt) %	NH_3 (vol%)[a]	
			648 K	673 K
1	303	0.35	15.4	20.8
2	323	0.26	17.2	21.8
3	343	0.16	19.2	22.7
4	363	0.10	20.2	22.8

[a] The activities were measured at 10 MPa, 10,000 h^{-1}.

Table 4
ICP analysis results for the washing solutions after ammonia precipitation during preparation.

Experiment No.	C_{Ru} (ppm)[a]	C_{Ba} (ppm)[a]	Loss of Ru (%)[b]	Loss of Ba (%)[b]
1	5.6	31.5	4.7	26.2
2	5.1	29.9	4.2	24.9
3	5.4	33.3	4.5	27.7
Average	5.4	31.6	4.5	26.3

[a] All the water used for washing was collected and diluted to 1 L for ICP analysis.
[b] Calculated by C_{Ru} (ppm) or C_{Ba} (ppm) in solutions and total Ru^{3+} and Ba^{2+} ions loaded on catalysts.

Due to the present method involving a washing procedure, the leaching of components is a very important issue for its successful application in industry. Because of the strong absorption ability and acid–base resistance character of activated carbon, it is difficult to totally dissolve the catalysts in acid solution which makes the direct analysis of actual Ru loadings in Ru/AC catalysts inaccurate by ICP or other techniques especially for the catalysts with such low Ru loadings (the target loading of Ru is 2.6 wt%). We tried to dissolve the catalyst in several mixtures of acids, but the analysis results are not repeatable. Therefore, the loss of catalyst components was studied by analyzing the solution collected during washing process. Firstly, all the water used during the experiments were collected and diluted to 1 L, and then it was analyzed by ICP method. The data are given in Table 4. To minimize the experimental deviation, the experiments were repeated 3 times. It can be seen that ca. 5 ppm of Ru ions and 32 ppm of Ba ions were detected in the diluted washing solution. The average loss of ruthenium and barium is about 4.5 and 26.0%, respectively. This means that the precipitation of $Ba(NO_3)_2$ is not completely and part of Ba^{2+} is dissolved in the washing solution. Because the K_{sp} of $Ba(OH)_2$ is 5.0×10^{-3} in comparison with the K_{sp} of $Ru(OH)_3$ of 1.0×10^{-36}, it is reasonable that the loss of Ba^{2+} is higher than that of Ru^{3+}. According to our previous optimized catalyst components and preparation conditions [18], Ba has to be impregnated before Ru to get highly active ammonia synthesis cat-

Table 5
Catalytic performance and remained content of Cl^- of Ba–Ru–K/AC catalysts prepared via different methods.

Catalysts	Chlorine removal methods	Cl (wt%)	NH_3 (vol%)[a]	
			648 K	673 K
10	HRM	0.29	17.8	21.5
11	IPM	0.10	20.4	23.1
12	Untreated	4.57	15.4	21.1
13	LRM	0.22	18.5	22.9

[a] The activities were measured at 10 MPa, 10,000 h^{-1}.

alyst. Therefore, the leaching of Ba is unavoidable. The optimized barium loading can be adjusted accordingly during the preparation of the catalysts. This is not a problem for production considering the solution can be recycled during the production of commercialized catalysts.

3.3. Comparison of Ba–Ru–K/AC catalysts prepared via different methods

3.3.1. Performances of Ba–Ru–K/AC catalysts prepared via different methods

The catalytic performances and Cl^- contents for the Ba–Ru–K/AC catalysts prepared via different methods are summarized in Table 5. It can be seen that Cl^- content for untreated catalyst is 4.57 wt%, and the outlet ammonia concentration of this catalyst is 15.4% at 648 K, 10 MPa, and with space velocity of 10,000 h^{-1}. The chlorine content is relatively low for the catalysts prepared via other methods. Among them, the content of Cl^- for the catalyst prepared via the IPM is the lowest one, with only 0.10% Cl^- remained. The NH_3 concentration for the catalysts prepared by IPM reaches 20.4% at 648 K, which is the highest among all catalysts and under similar conditions, the NH_3 concentrations for the catalysts prepared via HRM and LRM are 18.5 and 17.8%. The NH_3 concentrations for the catalysts prepared by HRM and IPM are similar which is 23% at 673 K. Because the activities of the optimized Ba–Ru–K/AC catalyst prepared via IPM at high temperature are approaching to the equilibrium limits (for example, equilibrium concentration of ammonia is 25.4% at 673 K and 10 MPa, 31.2% at 623 K and 10 MPa). Our target is to develop the catalysts with high performance at low temperature and pressure which favor both the energy efficiency and productivity. In this point of view, the catalyst prepared by IPM method is competitive for industrialized application.

3.3.2. Characterizations of Ba–Ru–K/AC catalysts prepared via different methods

It is known that the ruthenium nanoparticles supported on activated carbon are difficult to be observed by transmission electron microscope due to the influence of activated carbon, especially for the catalysts with high loading of promoters [39]. To avoid the disturbance of the promoters on the dispersion of Ru, the Ru/AC catalysts without promoters were prepared by HRM and IPM for the

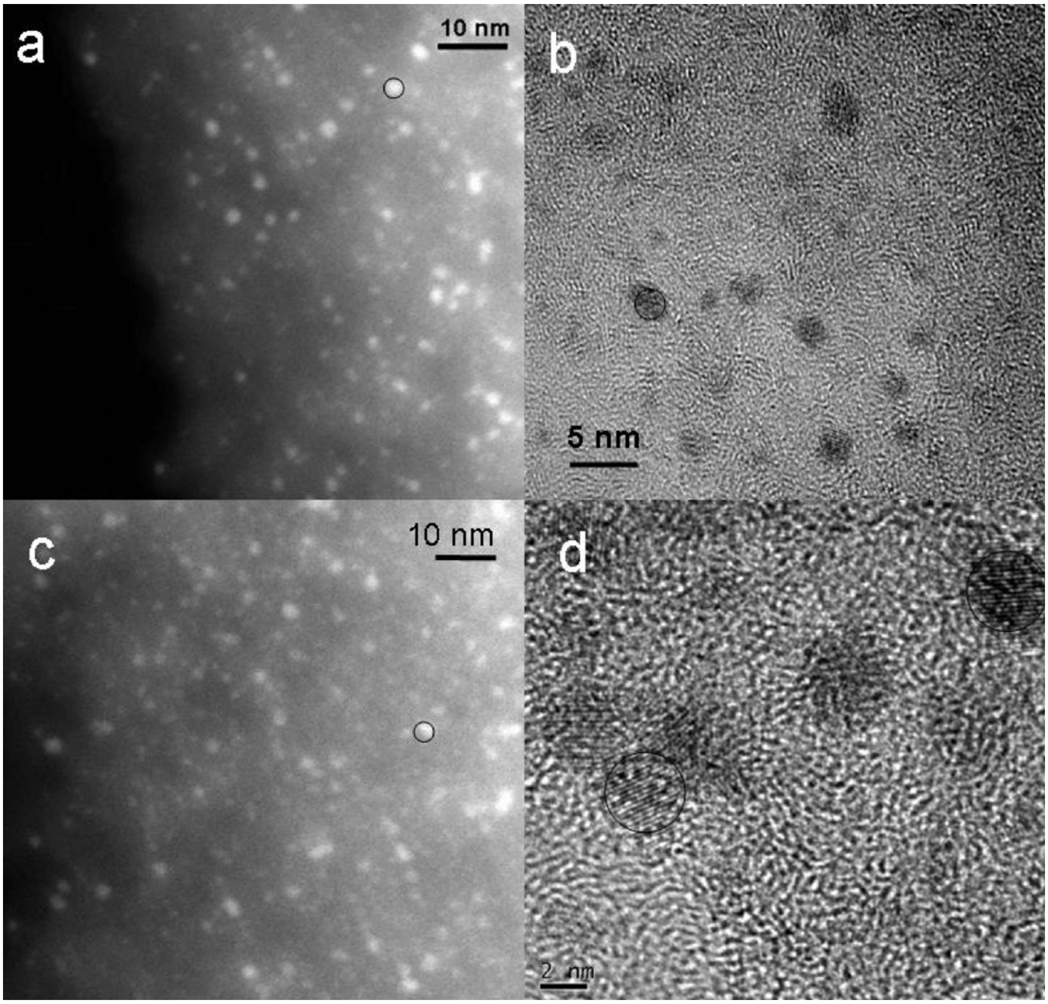


Fig. 4. STEM (a) and (c) and HRTEM (b) and (d) images for Ru/AC catalysts prepared via H_2 reduction (a) and (b) and precipitation methods (c) and (d). The bright dot in the STEM images and black dot in TEM is Ru as confirmed via EDS.

Table 6
Dispersion of Ru nanoparticles for Ru/AC, Ba–Ru/AC and Ba–Ru–K/AC catalysts prepared via different methods determined by CO-chemsorption method.

No.	Catalysts	Preparation methods	Dispersion (%)	Ru particle size (nm)	Ru surface area (mL/sample)	Ru surface area (mL/metal)
3	Ru/AC	HRM	47.0	2.9	4.5	171.5
5	Ru/AC	IPM	64.0	2.1	6.1	233.7
7	Ba–Ru/AC	HRM	35.5	3.8	3.4	129.8
9	Ba–Ru/AC	IPM	53.0	2.5	5.0	193.6
10	Ba–Ru–K/AC	HRM	14.3	9.4	1.4	52.3
11	Ba–Ru–K/AC	IPM	35.6	3.7	2.9	111.1

TEM characterization. The HRTEM and STEM images of Ru/AC prepared by IPM and HRM methods are illustrated in Fig. 4. The white dots distribute on STEM images and black dots on TEM images are ruthenium particles which are confirmed by EDS analysis (results are given in Fig. 5). It can be seen that the Ru particle sizes are in the range of 2–3 nm and are highly dispersed on the activated carbon [40]. Consequently, the dispersion of Ru particles was characterized by CO-chemsorption for the various promoted catalysts, as shown in Table 6. Dispersion of Ru particles for the catalysts prepared via IPM is higher than that of the catalysts prepared via HRM for all Ru/AC, Ba–Ru/AC, and Ba–Ru–K/AC catalysts. It can be seen that the dispersion of Ru decreases with addition of Ba and K promoters. This is due to that part of the Ru particle is covered by promoters which cannot be contacted with CO probe molecule. These results are inconsistent with the TEM observations. We suggest that the difference of Ru dispersions determined by CO-chemsorption and TEM characterizations is caused by the existence of Cl^-. Because Cl^- ions remain on the catalyst usually bond tightly with Ru atoms, which will affect the CO-chemisorption and consequent determination of dispersion of Ru atoms as reported in literature [41,42].

In order to study the effect of precipitation on the state of ruthenium ions, the above catalysts were characterized by XPS spectroscopy. Specific attention was paid to comparison of the Cl/Ru ratio for Ru/AC catalysts prepared via impregnation and impregnation–precipitation method. Fig. 6 shows the XPS spectra of Ru 3d and 3p region for the as-prepared and reduced Ru/AC catalysts prepared by impregnation and precipitation methods. Since the C 1s peak covers the Ru $3d_{3/2}$ signal and partially overlaps with the Ru $3d_{5/2}$ peak, a quantitative estimation of the oxidation states is difficult from those spectra. Hence the Ru $3p_{3/2}$ region was measured for the analysis. Due to low Ru loading, the signal of 3p is quite weak although the accumulated time is prolonged. Therefore, the Ru $3p_{3/2}$ signal are only used to calculate the total area, which is not deconvoluted. The Ru $3d_{3/2}$ peak is overlapped with the C-1s peak at 285 eV derived from carbonaceous impurities (CH_x) originally present on the catalyst surface or slowly accumulated in the spectrometer. Consequently, only the peak at 281 eV which is assigned to Ru $3d_{5/2}$ is used in the following discussion. The analysis results are summarized in Table 7. The Ru 3d spectrum from the pure $RuCl_3$ (sample 1) is also given for comparison. The main peak of Ru 3d spectrum for the as-prepared catalysts prepared via different methods is at 281.3 eV. This peak shifts to 280.7 eV for reduced catalysts. The components at lower binding energy are assigned to Ru(0) and anhydrous RuO_2 species, whereas the component at 281.3 eV matches the character of $RuCl_3$ for the sample 2 prepared by impregnation method, which is shifted by 0.3 eV compared to pure $RuCl_3$. And the similar position for the sample 4 prepared by precipitation method could be assigned to hydrous RuO_2 (also written as RuO*x*H*y*), which is reported to have a higher BE than its anhydrous form [43]. The presence of RuO_3 was excluded in favor of the hydrous amorphous $RuO_2{\cdot}xH_2O$, since the former is thermodynamically unstable under the reduction temperatures employed here [44]. As reported in reference [45], for the Ru/MgO and $Ru–Cs^+$/MgO samples, the E (Ru $3d_{5/2}$) values are 279.5 and 279.0 eV, respectively, which are 0.7 and 1.2 eV lower than the value of E (Ru $3d_{5/2}$) observed for the bulk Ru metal (280.2 eV). The negative shift of the Ru 3d core level spectrum with respect to that of bulk Ru metal has been considered as the transfer of electron density from the basic support to supported Ru metal particles. But this phenomenon is not observed for activated carbon supported ruthenium catalysts.

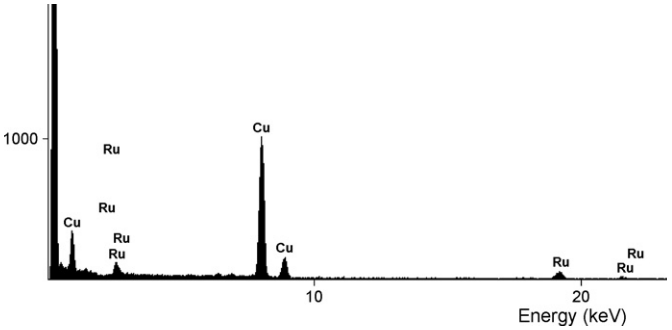


Fig. 5. EDS data for the bight region in the STEM images in Fig. 4(a).

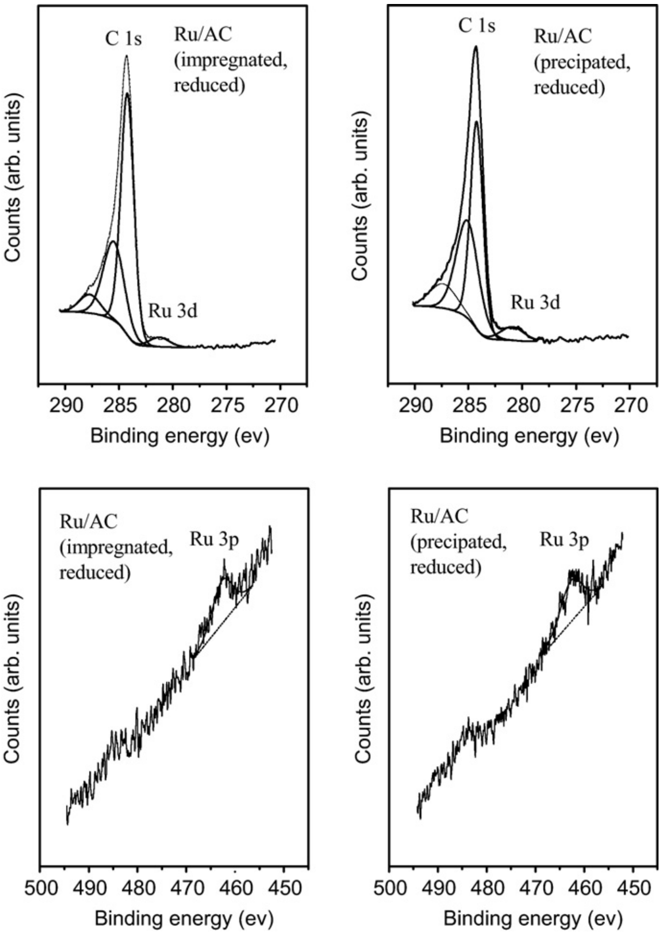


Fig. 6. XPS spectra (Ru 3d, and Ru 3p) for Ru/AC catalysts prepared via different methods.

Table 7
XPS data analysis results for the Ru/AC catalysts prepared with different methods.

No.	Samples	Preparation methods	Ru Position (eV)		Species	Area (%)			Cl/Ru	
			3d	3p		Ru 3d	Ru 3p	Cl	3d	3p
1	$RuCl_3 \cdot H_2O$		281.6	463.1	$RuCl_3$	0.18	0.16	0.27	1.5	1.7
2	As prepared Ru/AC	HRM	281.3	463.0	$RuCl_3$	0.02	0.02	0.06	4.2	4.2
3	Reduced Ru/AC	HRM	280.7	461.9	RuO_2/Ru	0.02	0.02	0.08	4.0	4.0
4	As prepared Ru/AC	IPM	281.4	462.9	$Ru(OH)_3$	0.04	0.03	0.05	1.3	2.0
5	Reduced Ru/AC	IPM	280.9	462.7	RuO_2/Ru	0.04	0.04	0.06	1.6	1.4

The area ratio of Ru and Cl elements calculated by XPS spectra are given in Table 7. It can be seen that the Cl/Ru ratio for samples 2 and 3 prepared by impregnation methods has similar value, which is about 4.0. While the Cl/Ru ratios for samples 4 and 5 decrease significantly. It is found that the content of Cl after reduction of the catalysts by H_2 does not decrease although the valence of Ru changes from 3+ to 0. It could be that the reduction product of HCl is reabsorbed on the surface of activated carbon due to the strong adsorb ability of the support. This further confirms that the precipitation and washing process is more effective than direct impregnation method for removal of Cl^-.

All the characterizations regarding to the main difference between the catalysts prepared via HRM and IPM is the content of Cl^- remained on the catalysts. Although according to the TEM results, the dispersion of the ruthenium is similar for the catalysts prepared by above two methods, the dispersion of Ru determined by CO-chemsorption is lower for the catalysts prepared by HRM (14.3%) than that of the catalysts prepared by IPM (35.6%). If we draw a pattern for the relationship between the activity and Cl^- content (which is given in Fig. 7), it can be seen that the activity increase lineally with decreasing of residual Cl^- content, especially at very low residual Cl^- content range. It also can be seen that the slop of the line is very large. That strongly suggests that small amount of Cl^- has large effects on the performances of the catalysts.

It should be pointed out that the composition and preparation of catalysts were also optimized for the catalysts prepared via HRM. Therefore, the activity at 673 K is similar with that of the catalysts prepared via IPM (23.1% compares to 22.9%). This activity is near the thermodynamic equilibrium of the system. Both of them have high Ru dispersions and low Ru loadings (2.6 wt%), and the particle size is in the optimized range of 2 and 3 nm (from TEM observation given in Fig. 4, which is taken to optimized one for the generation of active B5 sites). The differences of the activity at 648 K or the improvement of the activity from 18.5% (HRM) to 20.4% (IPM) are due to the efficient removal of Cl^-. This improvement makes big sense for a more efficient, cheap, and energy saving catalysts that can be used in industry.

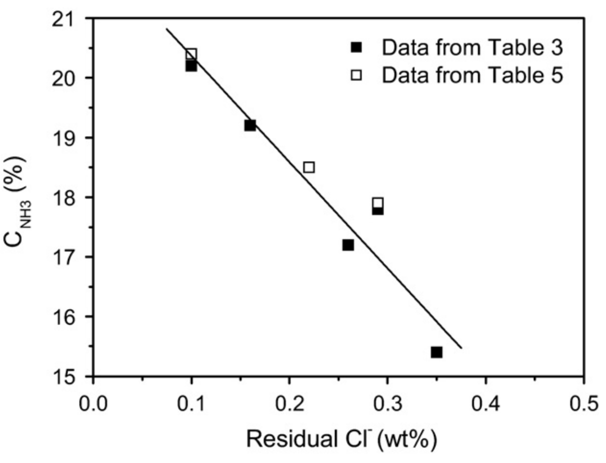


Fig. 7. The relationship of catalysts activity at 10 MPa, 10,000 h^{-1}, and 648 K with Cl^- contents. The data are obtained from Tables 3 and 5.

4. Conclusions

In summary, the present investigation gives an optimized impregnation–precipitation method for the activated carbon supported ruthenium catalyst. It is found that pretreatment by nitric acid combined with H_2 is necessary to improve activity of the Ba–Ru–K/AC ammonia synthesis catalyst. Introducing a precipitation and washing step after the impregnation of $RuCl_3$ precursor is effective to remove of Cl^- and thus obtain a high performance catalyst. The H_2 reduction step during preparation can be left out and low cost $RuCl_3$ precursors can be used without worry about the poison of Cl^- in present impregnation–precipitation method (IPM), which can be easily performed and suitable for scale-up production.

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References

[1] H.Z. Liu, X.N. Li, Z.N. Hu, Appl. Catal. A: Gen. 142 (1996) 209–222.
[2] N. Pernicone, F. Ferrero, I. Rossetti, L. Forni, P. Canton, P. Riello, G. Fagherazzi, M. Signoretto, F. Pinna, Appl. Catal. A: Gen. 251 (2003) 121–129.
[3] Z. You, I. Balint, K. Aika, T. Baba, J. Catal. 251 (2007) 321–331.
[4] H. Bielawa, O. Hinrichsen, A. Birkner, M. Muhler, Angew. Chem. Int. Ed. 40 (2001) 1061–1063.
[5] C.H. Liang, Z.L. Li, J.S. Qiu, C. Li, J. Catal. 211 (2002) 278–282.
[6] T.W. Hansen, J.B. Wagner, P.L. Hansen, S. Dahl, H. Topsoe, C.J.H. Jacobsen, Science 294 (2001) 1508–1510.
[7] E. Truszkiewicz, W. Raróg-Pilecka, K. Schmidt-Szałowski, S. Jodzis, E. Wilczkowska, D. Łomot, Z. Kaszkur, Z. Karpinski, Z. Kowalczyk, J. Catal. 265 (2009) 181–190.
[8] L. Forni, D. Molinari, I. Rossetti, N. Pernicone, Appl. Catal. A: Gen. 185 (1999) 269–275.
[9] I. Rossetti, N. Pernicone, L. Forni, Appl. Catal. A: Gen. 208 (2001) 271–278.
[10] I. Rossetti, N. Pernicone, L. Forni, Catal. Today 102 (2005) 219–224.
[11] I. Rossetti, F. Mangiarini, L. Forni, Appl. Catal. A: Gen. 323 (2007) 219–225.
[12] I. Rossetti, L. Forni, Appl. Catal. A: Gen. 282 (2005) 315–320.
[13] T.W. Hansen, P.L. Hansen, S. Dahl, C.J.H. Jacobsen, Catal. Lett. 84 (2002) 7–12.
[14] Y. Zheng, Z.H. Li, H.Y. Yu, R. Wang, K.M. Wei, J. Mol. Catal. A: Chem. 301 (2009) 79–83.
[15] P. Seetharamulu, K.H.P. Reddy, A.H. Padmasri, K.S.R. Rao, B.D. Raju, Catal. Today 141 (2009) 94–98.
[16] J. Ni, R. Wang, J.X. Lin, K.M. Wei, Chin. J. Catal. 30 (2009) 185–190.
[17] M. Guraya, S. Sprengera, W. Rarog-Pilecka, D. Szmigiel, Z. Kowalczyk, M. Muhler, Appl. Surf. Sci. 238 (2004) 77–81.
[18] X.N. Wang, H. Zhu, W.Q. Xia, H.Z. Liu, Chin. J. Catal. 21 (2000) 276–278.
[19] J.A. Mieth, J.A. Schwarz, J. Catal. 118 (1989) 203–217.
[20] T. Narita, H. Miura, M. Ohira, Appl. Catal. A: Gen. 32 (1987) 185–190.
[21] J. Kubota, K. Aika, J. Phys. Chem. 98 (1994) 11293–11300.
[22] W. Arabczyk, U. Narkiewicz, D. Moszynski, Appl. Catal. A: Gen. 134 (1996) 331–338.
[23] S. Murata, K. Aika, Appl. Catal. A: Gen. 82 (1992) 1–12.

[24] S.R. Tennison, in: J.R. Jennings (Ed.), Catalytic Ammonia Synthesis: Fundamentals and Practice, Plenum Press, New York, 1991, 303.
[25] Z. Kowalczyk, M. Krukowski, W.R. Pilecka, Appl. Catal. A: Gen. 248 (2003) 67–73.
[26] Z. You, K. Inazu, K. Aika, T. Baba, J. Catal. 251 (2007) 321–331.
[27] H.B. Chen, J.D. Lin, Y. Cai, Appl. Surf. Sci. 180 (2001) 328–335.
[28] B.Y. Lin, R. Wang, J.X. Lin, S.W. Du, X.J. Yu, K.M. Wei, Catal. Commun. 8 (2007) 1838–1842.
[29] X. Wu, B.C. Gerstein, T.S. King, J. Catal. 135 (1992) 68–80.
[30] H.P. Boehm, E. Diehl, W. Neck, R. Sappok, Angew. Chem. Int. Ed. 3 (1964), 669-377.
[31] C. Prado-Burgute, A. Linares-Solano, F. Rodriguez-Reinoso, C.S. Martinez De Lecea, J. Catal. 128 (1991) 397–404.
[32] A.E. Aksoylu, M. Madalena, A. Freitas, M.F.R. Pereira, J.L. Figueiredo, Carbon 39 (2001) 175–185.
[33] A.E. Aksoylu, M. Madalena, A. Freitas, J.L. Figueiredo, Appl. Catal. 192 (2000) 29–42.
[34] X.J. Yu, B.Y. Lin, B.B. Gong, J.X. Lin, R. Wang, K.M. Wei, Catal. Lett. 124 (2008) 168–173.
[35] F. Rodríguez-reinoso, Carbon 36 (1998) 159–175.
[36] W.F. Han, H.Z. Liu, H. Zhu, Catal. Commun. 8 (2007) 351–354.
[37] H.P. Boehm, Carbon 40 (2002) 145–149.
[38] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Carbon 37 (1999) 1379–1389.
[39] C.J.H. Jacobsen, S. Dahl, P.L. Hansen, E. Tornqvist, L. Jensen, H. Topsoe, D.V. Prip, P.B. Moenshaug, I. Chorkendorff, J. Mol. Catal. A: Chem. 163 (2000) 19–26.
[40] J. Okal, M. Zawadzki, L. Kepinski, L. Krajczyk, W. Tylus, Appl. Catal. A: Gen. 319 (2007) 202–209.
[41] M. Kantcheva, S. Sayan, Catal. Lett. 60 (1999) 27–38.
[42] J.A. Mieth, J.A. Schwarz, J. Catal. 118 (1989) 218–226.
[43] R. Chetty, W. Xia, S. Kundu, M. Bron, T. Reinecke, W. Schuhmann, M. Muhler, Langmuir 25 (2009) 3853–3860.
[44] D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, Langmuir 15 (1999) 774–779.
[45] Y.V. Larichev, B.L. Moroz, V.I. Zaikovskii, S.M. Yunusov, E.S. Kalyuzhnaya, V.B. Shur, V.I. Bukhtiyarov, J. Phys. Chem. C 111 (2007) 9427–9436.