



Preparations of C/SiC composites and their use as supports for Ru catalyst in ammonia synthesis

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ABSTRACT

A series of C/SiC composites was successfully synthesized via the carbothermal reduction of carbonaceous silicon xerogel, which was prepared from the sol gel method by using tetraethoxysilane TEOS and saccharose as the raw materials. The obtained samples were characterized by X ray powder diffraction XRD and N₂ physical adsorption. The specific surface areas of the as prepared C/SiC composites varied from 329 to 849 m²/g. The average pore diameters and the total pore volumes were in the range of 4.5–7.6 nm and 0.53–1.12 cm³/g, respectively. The as prepared C/SiC composites were proved to be effective supports for Ru catalysts for ammonia synthesis. At 435 °C, 10.0 MPa and a N₂/H₂ (1/3) flow rate of 10 000 h⁻¹, the optimum activity of 15.9% ammonia in the effluent was reached when C/SiC-5 (C/TEOS molar ratio = 5) was used as the catalyst support.

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1. Introduction

Ru-based catalysts are considered to be the second-generation catalysts for ammonia synthesis since they exhibit remarkably high activity compared to the conventional Fe-based catalysts under similar conditions [1–3]. Usually the highly active Ru-based catalysts are supported on activated carbon or graphitized activated carbon. A significant drawback of using activated carbon as support is that activated carbon is prone to methanation under high pressure and high temperature. To avoid the loss of carbon, the reaction temperature should be strictly controlled under 430 °C. Another limitation of the current Ru–C catalysts is their poor mechanical properties. The susceptibility to pulverization of the catalysts under high pressure and high space velocity would result in the deactivation of the catalysts.

To enhance the stability of the carbon-type supports, a number of treatments have already been taken. Kowalczyk et al. [4,5] found that the activity of the Ru–C catalysts was remarkably improved when the activated carbon supports had been treated at 1900 °C under an inert atmosphere of helium. Although the high-temperature treatment on the carbon-supports could effectively

decrease the methanation reaction, it could also modify the structure of activated carbon, resulting in the decrease in pore volume, the loss of micropores and the appearance of graphitization and layered structure. Forni et al.'s [6] studies on the effect of carbon pretreatment on the activity for ammonia synthesis showed that the catalytic activity sharply decreased due to the change of the porous property and the purity of the activated carbon when the treatment temperature was above 1900 °C. Zhong and Aika [7–9] showed that the impurities in activated carbon could influence the catalytic behavior of the catalysts. The elimination of the electron-withdrawing components such as S, O, and Cl by treating activated carbon with hydrogen at high temperature could increase the catalytic activity as well. Many new carbon materials such as "Sibunit" carbon, fullerene, carbon molecular sieve and carbon nanotube have also been used as supports for the Ru-based catalysts [10,11]. However the problem of the methanation on these carbon-based supports has not yet been solved. Non-carbon-based supports, such as Al₂O₃, MgO, TiO₂, SiO₂, Nb₂O₅, ZrO₂, rare-earth oxides and their mixtures have also been studied as the supports for Ru catalysts. These oxides-based Ru catalysts have not been industrialized because their catalytic activity is inferior to that of the activated carbon-based catalysts, probably due to the interaction between the supports and the active components. In view of the high thermodynamic stability of Al₂O₃ and the excellent electron-donating ability of carbon, carbon-coated Al₂O₃ has recently been developed and used as support for the Ru catalysts. These carbon-coated Al₂O₃ supported Ru catalysts exhibit superior catalytic activity under normal temperature and pressure [12]. However, they are still not industrialized at present.

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SiC is a kind of covalent material [13] with a tetrahedral structural unit similar to diamond. It is known to possess unique properties such as high thermal conductivity, chemical stability, excellent mechanical strength and resistance toward oxidation [14–16]. The specific surface area of modified SiC can reach $140 \text{ m}^2/\text{g}$ [17] and therefore could be a promising catalyst support. In our other studies, the purified SiC, which was synthesized from our previous studies, was used as support for Ru catalysts in ammonia synthesis, and the latest results showed that Ru/SiC catalyst exhibited fairly high activity for ammonia synthesis (with the outlet concentration of ammonia up to 11.8%). The high specific surface area of active carbon and the prominent mechanical strength and chemical inertness of SiC reminded us that the introduction of C into SiC is expected not only to increase the specific surface areas of SiC but also to modify its microstructure. Such a modification could help to disperse the noble metal (Ru) on the support as well as to enhance the mechanical strength of the support and improve the resistance of the support to methanation in the reaction conditions, and therefore it is anticipated that it would promote both the catalytic activity and the stability of the catalyst. In this paper, we report the preparations of the C/SiC composites as support for Ru catalysts and their application in the ammonia synthesis. The effect of the amount of promoter (K) in the ammonia synthesis activity was also studied.

2. Experimental

2.1. Preparations of C/SiC composites

In a mixture of 20 ml ethanol (AR grade) and 30 ml distilled water, 25 g saccharose (SA, AR grade) and 10 ml 3.5 wt % oxalic acid (AR grade) were dissolved under magnetic stirring. Oxalic acid was used to promote the hydrolysis of TEOS [18]. Next, 67, 50, 40 or 33 ml tetraethoxysilane (TEOS, AR grade, $\rho = 0.93$) was added to the solution at the molar ratio of C/TEOS is 3, 4, 5 and 6, respectively. The mixture was stirred magnetically at 50°C until the gel formed.

The gel was dried at 120°C for 24 h to form xerogel. The obtained xerogel was placed in an alumina tube and then placed at the center of a tube furnace. The xerogel was heated from room temperature to 1000°C at a rate of $4^\circ\text{C}/\text{min}$, and then to 1500°C at a rate of $2^\circ\text{C}/\text{min}$ in a $30 \text{ cm}^3/\text{min}$ argon flow. The temperature was kept at 1500°C for 12 h to facilitate the carbothermal reduction. After cooling to room temperatures, the samples were immersed in hydrofluoric acid solution (HF, 40%) for 12 h to remove the residual SiO_2 . The C/SiC composites prepared from the precursors with C/TEOS molar ratio of 3, 4, 5 and 6 were denoted as C/SiC-3, C/SiC-4, C/SiC-5 and C/SiC-6, respectively. The contents of SiC of the corresponding production were estimated by the thermogravimetric analysis (TGA).

2.2. Characterizations of C/SiC composites and their supported Ru catalysis

The X-ray diffraction (XRD) technique using Cu-K α radiation in a Bruker-D8 Advance diffractometer with 40 mA, 40 kV was used to identify the compounds. (Ni-filtered, $\lambda = 0.15406 \text{ nm}$, scanning rate $2^\circ/\text{min}$). Thermal analyses were carried out at the heating rate of $10^\circ\text{C}/\text{min}$ in air on a Perkin Elmer TGA 7 analyzer to calculate the content of SiC of the as-prepared C/SiC composites. Low-temperature nitrogen adsorption was carried out in a NOVA win4200 Brunauer–Emmett–Teller (BET) apparatus to measure the surface area and pore structure of the prepared C/SiC composites. The linear range of the adsorption isotherms spanning a range of P/P_0 of 0.05 to 0.35 was used to calculate the specific surface area of the samples. The Barrett–Joyner–Halenda (BJH) pore-size dis-

tribution was calculated based on the desorption isotherm. The chemisorption study was carried out using an AutoChem 2910 instrument (Micromeritics). The catalyst (ca. 150 mg) was reduced in a H_2 stream at 450°C for 2 h. The sample was subsequently flushed with a helium stream for 1.5 h to remove H_2 adsorbed on the surface of the catalyst, and it was finally cooled in a helium stream to 25°C . CO chemisorption was measured by the pulse method by introducing 5% CO + 95% He flowing over the sample maintained at 25°C . Ru dispersion, the specific metal surface area and the Ru particle size were calculated from the cumulative volume of CO adsorbed during pulse chemisorption [19].

2.3. Preparations of Ru–C/SiC catalysts and the activity measurements

The Ru catalyst was prepared using a several-step impregnation method. The various C/SiC composites were impregnated with RuCl_3 in aqueous solution at room temperature. Ru/C/SiC was obtained by reducing $\text{RuCl}_3/\text{C/SiC}$ in flowing hydrogen at 450°C for 5 h. Then Ba and K as promoters were added to the Ru/SiC by the several-step impregnation method with the aqueous solution of $\text{Ba}(\text{NO}_3)_2$ and KNO_3 , respectively. The content of Ru, K and Ba were set at 4, 4 and 12–28 wt%, respectively (the weight were counted as metal in relation to the mass of C/SiC composites).

Measurement of the catalytic activity in ammonia synthesis was performed in a stainless steel reactor. The catalyst (2 ml) with particle size (12–16 meshes) was first activated by a gas flow of $\text{H}_2 + \text{N}_2$ (3:1, v/v) at 500°C for 2 h before the measurement. The catalytic reaction was carried out at 480°C and 10.0 MPa by flowing a gas mixture ($\text{H}_2:\text{N}_2$ at 3:1 v/v) at a flow velocity of $10\,000 \text{ h}^{-1}$ through the activated catalyst and the concentration of NH_3 in the effluent was determined by a chemical titration method [20]. The catalytic activity was expressed as NH_3 vol. %.

3. Results and discussion

3.1. The formation of C/SiC precursors

The formation of the gel comprises the processes of hydrolyzation and polycondensation of TEOS to form a three-dimensional Si–O–Si network. The faster the network grows, the shorter the gelation time is. The amount of SA plays an important role in the hydrolysis and condensation of TEOS. Fig. 1 shows the variation in the gelation time as a function of different C/TEOS molar ratios in the precursors. It clearly shows that for C/TEOS molar ratio in the range of 3.0–4.5, the time of gelation remains almost constant at 12–13 h. That is to say, the amount of SA does not have signifi-

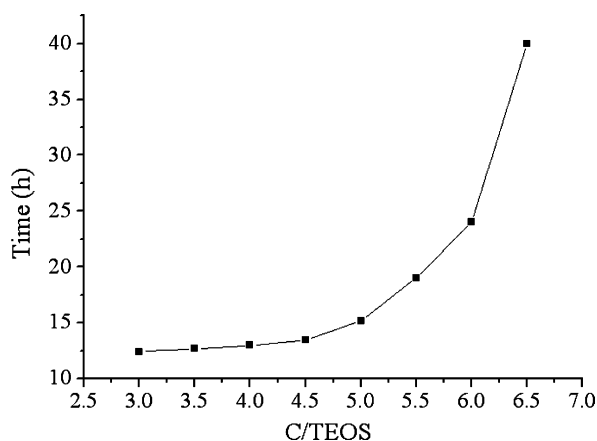


Fig. 1. The change of gelation time of TEOS as a function of the ratio of C/TEOS.

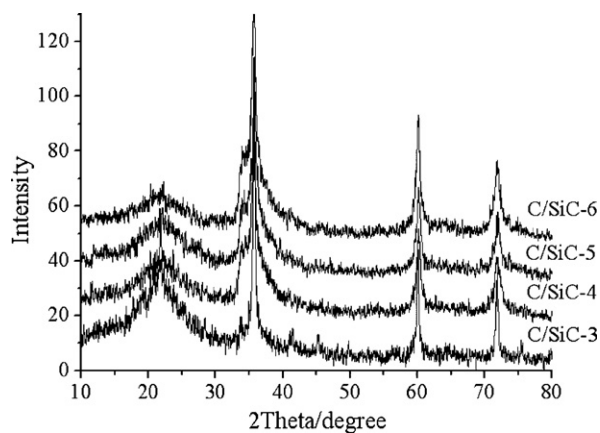


Fig. 2. XRD patterns of C/SiC composites (before HF treatment) prepared from precursors with different C/TEOS molar ratio.

cant impact on the gelation time in this C/TEOS molar ratio range. However, the required gelation time significantly increases when the molar ratio of C/TEOS is higher than 5.0. It takes about 40 h to obtain the gel when the molar ratio of C/TEOS is 6.5. This means that an excess of SA somewhat retards the hydrolysis and condensation reactions.

3.2. Characterizations of C/SiC composites and their supported Ru catalysis

3.2.1. XRD and TG analysis

XRD patterns of C/SiC composites (before HF treatment) prepared from precursors with different C/TEOS molar ratio are shown in Fig. 2. All samples show sharp and intense diffraction peaks at $2\theta = 35.6^\circ$, 60.2° and 72.1° , which are characteristic of β -SiC [21]. In addition, with an increase in the C/TEOS molar ratio in the precursors, a decrease in the intensity of SiO_2 phase is observed in the as-prepared C/SiC composite (before HF treatment). This indicates that an increasing amount of carbon in the precursors might be helpful for the transition of SiO_2 to SiC.

Fig. 3 shows the theoretical values and the experimental values of the SiC weight contents of the C/SiC composites prepared from the corresponding precursors with different C/TEOS molar ratios. The ideal reaction formula of formation of SiC from silica and carbon can be written as follows [22]:

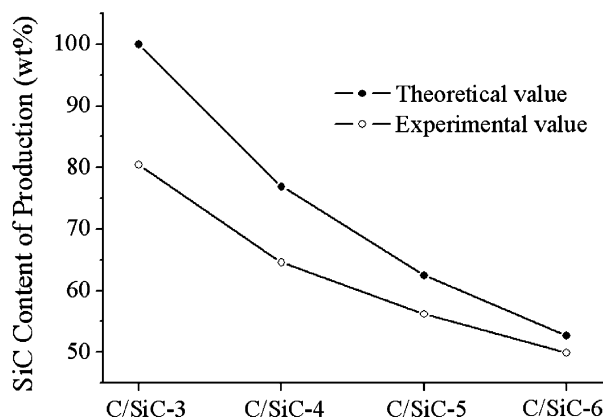
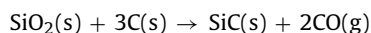


Fig. 3. The theoretical values and the experimental values of the SiC weight contents of the C/SiC composites.

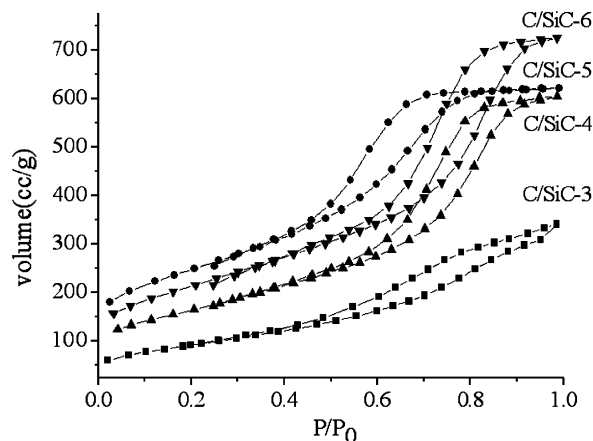


Fig. 4. The nitrogen adsorption-desorption isotherms of the different C/SiC composites.

The theoretical values of Fig. 3 were derived from the above reaction formula. The experimental values of SiC weight contents of C/SiC-3, C/SiC-4, C/SiC-5 and C/SiC-6 are 80.5, 64.6, 56.2 and 50.2 wt%, respectively. The discrepancy between the theoretical values and the experimental ones may be due to the reaction of a small amount of unreacted amorphous SiO_2 with HF. With an increase in the C/TEOS molar ratio in the precursors, the content of SiC of the as-prepared C/SiC composite reaches the theoretical value, which further confirms that the transition of SiO_2 to SiC is improved with the increasing amount of carbon source in the precursors.

3.2.2. BET-BJH analysis

Fig. 4 shows the nitrogen adsorption-desorption isotherms of the samples. All samples display the type IV adsorption curve with hysteresis loops in the P/P_0 range of 0.5–0.9 and indicate that the as-prepared samples are mesoporous materials. The BET surface areas of the C/SiC composites are shown in the Table 1. It is obvious that the specific surface areas of the C/SiC composites sharply increase with an increase in the carbon amount. The pore size distributions of the corresponding samples calculated from the BJH method shows that the average pore sizes of C/SiC-3, C/SiC-4, C/SiC-5 and C/SiC-6 are around 7.6, 7.5, 7, 4.5 nm respectively (Fig. 5) and the total pore volumes are shown in the Table 1. The average pore-size of the C/SiC composites has a tendency to shift to a lower diameter with the increase in the carbon amount. The total pore volume of the C/SiC composites displays a different tendency, which

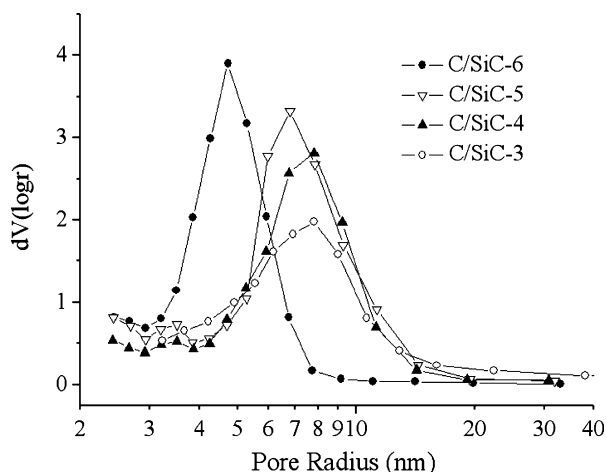


Fig. 5. The pore-size distribution of the different C/SiC composites.

Table 1
Relevant parameters of Ru catalysts supported on different C/SiC composites.

Samples	Surface area of C/SiC (m ² /g)	Pore volume (cm ³ /g)	Ru dispersion (%)		Ru surface area (m ² /g metal)		Ru size (nm)		Activity (vol. %) ^a
			Be ^b	Af ^c	Be	Af	Be	Af	
C/SiC-3	329	0.53	23.48	21.85	85.76	79.81	5.64	6.06	10.91
C/SiC-4	577	0.93	25.56	23.93	93.34	87.42	5.31	5.53	11.50
C/SiC-5	740	1.12	27.47	25.91	100.3	94.65	4.82	5.11	12.40
C/SiC-6	849	0.96	27.98	26.24	102.2	95.84	4.73	5.05	11.61
SiC	118	0.38	4.03	3.56	17.95	15.80	27.81	31.60	9.88
Al ₂ O ₃	258	0.35	11.43	9.75	50.90	35.65	9.81	13.25	3.23

^a Reaction conditions: Ru = 4 wt%, Ba = 4 wt%, K = 12 wt%, 450 °C, SV = 10 000 h⁻¹, N₂:H₂ (V/V) = 1:3.

^b Be = the catalyst before ammonia synthesis reaction.

^c Af = the catalyst after ammonia synthesis reaction.

first increases and then decreases with the increment in the carbon amount, and C/SiC-5 shows the maximum pore volume. A drop in the total pore volume of the C/SiC-6 may be due to the excess of carbon partially blocking the small pores.

3.3. Catalytic activity for ammonia synthesis

3.3.1. Activity for ammonia synthesis over Ru catalysts supported on different C/SiC composites

The as-prepared different C/SiC composites supported Ru catalysts were prepared and their activity for ammonia synthesis was investigated. Relevant parameters of the supports and the result of the activity measurements are listed in Table 1. The catalytic activity of pure SiC-supported and γ -Al₂O₃-supported Ru catalysts for ammonia synthesis has been compared with that of a C/SiC-supported Ru catalyst under similar conditions. It is obvious that the C/SiC-supported Ru catalyst exhibits the highest activity for ammonia synthesis (Table 1). This is because the active component (Ru particles) has high specific surface area (85–100 m²/g metal) and small particle size (ca. 5 nm) and is highly dispersive on the C/SiC composites. The dispersion and the particle size of Ru only changed slightly after the ammonia synthesis, indicating that the C/SiC-supported Ru catalysts are stable. In contrast, the active component (Ru) on pure SiC or γ -Al₂O₃ is not as effective as that on C/SiC since the Ru particles are larger. Moreover, the Ru particle size on pure SiC and γ -Al₂O₃ increased after the ammonia synthesis reaction, indicating poor catalytic stability.

Among the C/SiC-supported Ru catalysts, the C/SiC-5 composite supported Ru catalyst possesses the highest activity. The ammonia concentration in the effluent reaches 12.4% at 450 °C in a 3:1 mixture of H₂ and N₂ when Ru, Ba, and K loadings were 4, 4, and 12 wt%, respectively. The comparison of the catalytic activity of C/SiC-3, C/SiC-4 and C/SiC-5 reveals that the activity of the Ru catalysts increases with the specific surface areas of the supports. A high surface area and a well-developed porosity are essential for achieving large metal dispersions (see Table 1), usually resulting in high catalytic activity. At first glance it is a little weird to find that the C/SiC-6 supported Ru catalyst shows lower activity than the C/SiC-5 supported Ru catalyst although the former possesses the highest specific areas among this series of supports. However, this phenomenon can be well explained by their different pore structures. Although higher specific area of the support would favor the dispersion of the Ru catalyst and a higher dispersion of the catalyst on the support would certainly lead to a higher catalytic activity, for an already well dispersed catalyst, the catalytic activity is not governed by the specific surface area of the support. In this regard, the pore structure of the support would play an important effect. Since C/SiC-6 has a lower total pore volume compared to C/SiC-5, the former supported Ru catalysis displays a lower activity on ammonia synthesis.

3.3.2. The effect of the temperature on the catalytic activity

The C/SiC-5 Ru catalyst with K–Ba double-promoter were prepared to study the effect of the temperature on the catalytic activity in ammonia synthesis. Fig. 6 shows the activity of the catalyst in the temperature region of 410–485 °C under a N₂/H₂ (1/3) flow of 10 000 h⁻¹ at 10.0 MPa when Ru, Ba, and K loadings were 4, 4, and 12 wt%, respectively. It is found that the C/SiC-5 supported Ru catalyst exhibits a certain catalytic activity at 10.0 MPa and 410 °C. The catalytic activity expressed as the ammonia concentration in the effluent increases with the reaction temperature and it reaches a maximum value of 13.5% at 435 °C. A drop in the catalytic activity is observed when the reaction temperature is higher than 435 °C. It is evident that when the reaction pressure is fixed at 10.0 MPa to make the C/SiC-5 supported Ru catalyst more efficient, the optimal temperature should be 435 °C. In the meantime, the catalytic activity of the traditional Fe-based catalyst (ICI-74-1) reached the maximum activity of 14.1% ammonia in the effluent at 450 °C under similar synthesis conditions. Although the catalytic activity of ICI-74-1 catalyst is comparable to the present C/SiC-supported Ru catalysts, the C/SiC-supported Ru catalysts can perform at lower temperatures, which is beneficial to the reduction of the energy consumption.

3.3.3. The effect of the potassium concentration on the catalytic activity

Several studies have shown that the activity of Ru catalyst is highly dependent on the properties of both the supports and the promoters [23,24]. Alkali metals, alkali-earth metals and rare-earth elements are common promoters for Ru catalysts. The strong promoting effect of alkali metals can be attributed to their strong electron donation to ruthenium metal, thus accelerating the dis-

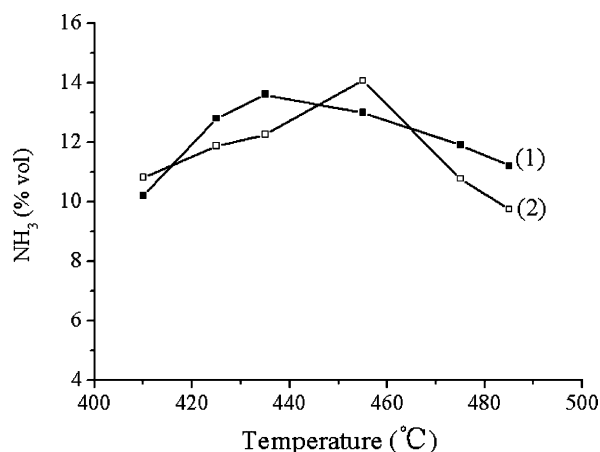


Fig. 6. NH₃ concentration in the effluent as a function of reaction temperature (1) C/SiC-5 supported Ru catalyst and (2) the traditional Fe-based catalyst (ICI-74-1).

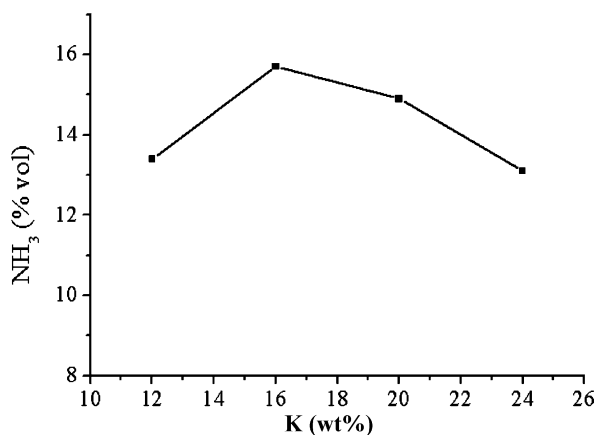


Fig. 7. The effect of the K concentration on the ammonia synthesis activity.

sociation of N₂ at the active site of ruthenium [25]. Fig. 7 shows the effect of the amount of the promoter (K) on the catalytic activity at 435 °C, 10.0 MPa and a N₂/H₂ (1/3) flow of 10 000 h⁻¹ when Ru and Ba loadings were 4 and 4 wt%, respectively. It clearly shows that the activity for ammonia synthesis could be improved by the addition of potassium. The optimum activity of 15.9% ammonia in the effluent can be reached when the amount of potassium is 16.0 wt%. The catalytic activity decreases with the increase in the potassium promoter when the potassium content is above 16.0 wt%. The drop in the activity with an increase in the potassium content is probably due to the fact that too much potassium species might block the pores of the support and that thus the effective contact between the reaction gas and the surface active sites is suppressed. The catalytic activity of the C/SiC-supported Ru catalysts with proper promoter (K, Ba) components loadings exceeded that of the ICI-74-1 catalysts, indicating that the C/SiC composites can be used as a promising supports for Ru catalysts in ammonia synthesis.

3.3.4. The thermal stability of C/SiC-5 supported Ru catalyst

The catalytic activity over C/SiC-5 supported Ru catalyst treated at 1.0 MPa and 500 °C in a H₂ + N₂ mixture for 20 h was investigated. It is found that under similar reaction conditions, an activity of 15.7% ammonia in the effluent over the treated catalyst can be obtained, which is almost similar to that over the untreated catalyst. This indicates that the C/SiC-5 supported Ru catalyst are quite stable at 500 °C and the as-prepared C/SiC composites are effective supports for Ru catalysts in ammonia synthesis.

4. Conclusions

A series of mesoporous C/SiC composites with high specific surface areas and large total pore volumes was prepared. As effective supports, they were used in the preparation of C/SiC supported Ru catalysts for ammonia synthesis. When C/SiC-5 was used as the catalyst support, and the Ru, Ba, and K loadings were 4, 4, and 16 wt%, respectively, the optimum activity of 15.9% ammonia in the effluent can be reached at 435 °C, 10.0 MPa and a flow rate of 10 000 h⁻¹. Furthermore, the test of the resistance to deactivation also shows that the C/SiC-5 supported Ru catalyst has a prominent thermodynamic stability. Our results indicate that C/SiC composites would be an effective new type of support for Ru catalysts in ammonia synthesis.

Acknowledgments

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