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Article

Growth of Cu/SSZ-13 on SiC for selective catalytic reduction of NO with NH₃

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ABSTRACT

Silicon carbide (SiC) was used as a support for SSZ-13 zeolite in an attempt to improve the high-temperature stability and activity of Cu/SSZ-13 in the selective catalytic reduction (SCR) of NO with NH₃. SSZ-13 was grown via a hydrothermal method using the silicon and silica contained in SiC as the source of silicon, which led to the formation of a chemically bonded SSZ-13 layer on SiC. Characterization using X-ray diffraction, scanning electron microscopy, and N₂ adsorption-desorption isotherms revealed that the alkali content strongly affected the purity of zeolite and the crystallization time affected the coverage and crystallinity of the zeolite layer. Upon ion exchange, the resulting Cu/SSZ-13@SiC catalyst exhibited enhanced activity in NH₃-SCR in the high-temperature region compared with the unsupported Cu/SSZ-13. Thus, the application temperature was extended with the use of SiC as the support.

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1. Introduction

Nitrogen oxides (NO_x) emitted from vehicles are a major contribution to air pollution because of their toxicity. Selective catalytic reduction (SCR) with NH₃ is regarded as one of the most efficient approaches to remove NO_x, transforming them into non-toxic N₂ and H₂O. This approach is widely applied as a denitration (DeNO_x) process [1–3]. Various catalysts have been developed and tested [4–6]. For example, vanadium–tungsten–titania-based catalysts have been commercially used for more than three decades [7,8]. However, these catalysts fail to

convert NO_x under lean-burn conditions with high air/fuel ratios.

Zeolites have also been widely studied for SCR with NH₃, including ZSM-5 with the MFI structure, beta zeolite, SAPO-34, and SSZ-13 with the CHA structure [9–11]. The Cu (or Fe) ion-exchanged ZSM-5 exhibited better performance than a commercial vanadia–titania catalyst [12,13]. However, their stability remains an issue because of the sintering of copper species and disruption of zeolitic crystallinity and porosity under harsh reaction conditions [14,15]. In comparison, Cu/Fe ion-exchanged beta catalysts exhibited better durability [1,16]. CHA-

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type zeolite with smaller pores and stronger acidity, especially SSZ-13 zeolite upon exchange with Cu^{2+} , has been shown with better NH_3 -SCR activity and selectivity than those of beta catalysts and ZSM-5 as well as higher hydrothermal stability [17–22]. However, these zeolite-based catalysts still undergo deactivation above 550 °C. In real applications, the temperature can reach beyond 800 °C, which frequently degrades the durability of the catalyst. Therefore, it is desirable to develop catalysts which can be applied at a wider temperature window beyond 550 °C or even higher.

Silicon carbide (SiC) is a chemically inert and mechanically stable material with a thermal conductivity that is two orders of magnitude higher than that of SiO_2 and three times higher than that of alumina [23–25]. With these interesting properties, we explore the use of SiC as the support for a zeolite-based SCR catalyst in an attempt to strengthen its anti-thermal shock and improve its high-temperature stability. Gu et al. [23] reported that a Mo-ZSM-5/porous SiC catalyst exhibited clearly improved activity in the methane dehydroaromatization reaction. In addition, Elamin and coworkers [24] reported that a SAPO-34/SiC composite with a foam structure exhibited excellent selectivity and stability in methanol dehydration to a dimethyl ether. In this study, we demonstrate that SSZ-13 can be grown directly on the surface of SiC using a hydrothermal method, as confirmed by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption results. The use of the SiC support enhances the catalytic activity of Cu/SSZ in the NH_3 -SCR reaction compared with that of unsupported Cu/SSZ-13.

2. Experimental

2.1. Chemicals

NaOH , N,N,N -trimethyl-1-ammonium adamantane (TMAdaOH), $\text{Al}(\text{OH})_3$, and fine SiO_2 powder were purchased from Sinopharm Chemical Reagent Co., Ltd., InnoCHEM, Tianjin Kemel Chemical Reagent Co., Ltd., and Shenyang Chemical Industry Co., Ltd., respectively. All the chemicals were directly used as received without further purification.

2.2. Preparation

2.2.1. Preparation of pure SSZ-13

The pure SSZ-13 was synthesized using a hydrothermal method adapted from that reported by Shishkin et al. [26]. Typically, 4 g H_2O was added to 3 g NaOH aqueous solution (1 mol/L), followed by the addition of 4 g TMAdaOH. After stirring for 30 min, 0.1 g $\text{Al}(\text{OH})_3$ and 1.2 g SiO_2 were added to the mixture. The resulting suspension was then transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and maintained at 160 °C for 2 d in a rotary oven (0.7 r/min) and subsequently cooled to room temperature. The resulting white powder was washed with ethanol and deionized water three times, sequentially, using filtration, followed by drying in air at 100 °C overnight. Finally, the powder was calcined for 5 h at 550 °C.

2.2.2. Preparation of SSZ-13@SiC

SiC samples were provided by BASF. The SSZ-13 was grown on SiC using a hydrothermal synthesis method. First, the mother liquor was prepared following the same procedure as that for the unsupported SSZ-13. Then, SiC with dimensions of 0.5 cm $\times$ 0.5 cm $\times$ 1 cm was added into the mother liquor in an autoclave with a capacity of 50 mL. After reaction at 160 °C in a rotary oven (0.7 r/min) for varying periods, the composites were collected and ultrasonically washed with deionized water in a beaker and dried in air at 100 °C overnight. SSZ-13@SiC was finally obtained following calcination for 5 h at 550 °C.

2.2.3. Preparation of Cu/SSZ-13@SiC

The SSZ-13@SiC was subjected to ion exchange using 0.5 mol/L $\text{Cu}(\text{NO}_3)_2$ aqueous solution at 80 °C for different durations, followed by calcination for 5 h at 550 °C. The resulting catalyst was named Cu(X)/SSZ-13@SiC, where X represents the Cu loading (in mass percentage). For comparison, unsupported Cu/SSZ-13 was also prepared following the same method.

2.3. Characterization

Powder XRD was performed on a Panalytical X'Pert Empyrean-100 diffractometer using a $\text{Cu } K_\alpha$ source ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. The patterns were recorded in the range of $2\theta = 5^\circ$ – 50° using a step of $0.19^\circ/\text{s}$. SEM was performed on a FEI Quanta 200 F microscope. The Cu loadings were measured using inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer 7300 DV). N_2 adsorption-desorption isotherms were measured at -196°C using a Quantachrome QUADRASORB SI system. The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation.

2.4. NH_3 -SCR activity measurements

The catalyst (0.18 g) with a size of 40–60 mesh was loaded into a fixed-bed microreactor made of quartz with an inner diameter of 6 mm. The reaction was performed under the following conditions: 500 ppm NH_3 , 500 ppm NO , 10 vol% O_2 , 5 vol% H_2O , balance N_2 , 400 mL/min total gas flow, and 80000 h^{-1} gas hourly space velocity (GHSV). The concentration of NO in the effluent was analyzed using an ECOTCH ML9841AS analyzer. The NO conversion was calculated using the following equation: $\text{NO conversion} = (\text{C}_{\text{NO,in}} - \text{C}_{\text{NO,out}}) / \text{C}_{\text{NO,in}} \times 100\%$.

3. Results and discussion

3.1. Structure of SSZ-13@SiC composites

Fig. 1 presents XRD patterns of the SiC support, pure SSZ-13, and SSZ-13@SiC. The XRD pattern for the SiC support (Fig. 1(a)) contains typical diffraction peaks for hexagonal SiC at 34.1° , 35.6° , 38.1° , and 41.4° corresponding to the (101), (006), (103), and (104) planes (PDF #49-1428), respectively. In addition, the peak at 21.6° is attributed to cubic SiO_2 (111) (PDF #27-0605), and those at 28.4° and 47.3° are indexed as the

Fig. 1. XRD patterns of SiC (a), SSZ-13 (b), and SSZ-13@SiC (c).

cubic Si (111) and (220) planes (PDF #27-1402), indicating that the SiC support contained SiO₂ and Si impurities. The XRD pattern of SSZ-13 showed a well-crystallized CHA structure without impurities. Fig. 1(c) reveals the coexistence of SSZ-13 and SiC, suggesting that the SSZ-13 layer was successfully grown in the presence of SiC. Furthermore, the structure of SiC was not damaged because all the characteristic diffraction peaks were retained. However, the SiO₂ and Si diffraction peaks initially present in the SiC support disappeared, which indicates that SiO₂ and Si were consumed as Si sources for the growth of SSZ-13.

Fig. 2(a) shows that the fresh SiC is almost black. Following hydrothermal synthesis for 5 d in the rotating oven, it became pale white (Fig. 2(d)), indicating that the SiC surface was successfully covered with a layer of SSZ-13. No obvious white powder peeled off when the SSZ-13@SiC was repeatedly rubbed on a piece of black cloth, which indicates that the SSZ-13 layer was rather strongly attached to the SiC support,

likely via chemical bonding at the interface. This bonding occurred because SiC contains SiO₂ and Si, which act as Si sources for the nucleation and crystallization of SSZ-13 during the hydrothermal synthesis. Comparison between the images in Fig. 2(b) and (e) reveals that the disordered holes of the SiC support were filled with SSZ-13, and thus, the surface became much smoother. Closer inspection of Fig. 2(f) and its inset reveals the characteristic cubic morphology of SSZ-13. However, the particles were not very homogeneous, which was likely induced by the inhomogeneity of the SiC surface (Fig. 2(c)).

3.2. Effect of synthesis conditions on the structure of SSZ-13@SiC

3.2.1. Effect of NaOH concentration

Considering that the alkalinity of the pregnant solution has an important effect on the growth of zeolite, we varied the amount of NaOH aqueous solution during hydrothermal synthesis. Fig. 3(a) shows that the resulting SSZ-13 exhibited a relatively low crystallinity for SiO₂/NaOH = 0.2. With increasing amount of NaOH, the diffraction peaks of the impurity become weaker and finally disappear for SiO₂/NaOH = 0.08. When the amount of NaOH was further increased, only the pure SSZ-13 phase was detected with a high crystallinity. This was further validated by SEM, as shown in Fig. 3(b)–(f). Many mussy and elliptical blocks were generated at low NaOH concentration (SiO₂/NaOH = 0.2), and only a few scattered small SSZ-13 cubes were observed. When the ratio of SiO₂/NaOH was decreased to 0.1, increasingly more cubes emerged, and the impurities with irregular shapes gradually disappeared (Fig. 3(e) and (f)). The size of these SSZ-13@SiC cubes varied from 2 to 7 μm.

3.2.2. Effect of crystallization time

The XRD patterns in Fig. 4(a) hardly show the characteristic diffraction of SSZ-13 on SSZ-13@SiC synthesized in only 1 d. Fig. 4(b) reveals the appearance of some sporadic cubic crystals

Fig. 2. SEM images of the SiC supports (a), surface of SiC support at different magnifications (b, c), SSZ-13@SiC composite (d), and surface of SSZ-13@SiC composites (e, f). The inset in (f) presents a magnified view of the surface of SSZ-13@SiC.

Fig. 3. Crystal phases (a) and morphologies (b–f) of SSZ-13@SiC prepared in the presence of different NaOH concentrations.

Fig. 4. Crystal phases (a) and morphologies (b–f) of SSZ-13@SiC prepared with different crystallization times. All the samples were synthesized with the SiO_2/NaOH ratio fixed at 0.08.

on the surface of SiC, and the SiC surface was still exposed on the first day. Obviously, 1 d was not sufficient to grow a full layer of SSZ-13 crystals on the surface of SiC. With the hydrothermal synthesis time extended beyond 1 d, the crystallinity improved, as reflected by the larger and more angular crystals in the SEM images. Furthermore, the SiC surface was fully covered by the SSZ-13 grains after 2 d and no SiC was exposed. The samples prepared for 2–5 d all consisted of the pure phase of

SSZ-13, and no other impurity phases were detected in the XRD patterns.

The nitrogen adsorption-desorption curves of different samples are displayed in Fig. 5(a), and their surface areas and textural properties are summarized in Table 1. Pure SSZ-13 exhibited a type-I isotherm, which is characteristic of microporous materials. Its BET surface area was $567.7 \text{ m}^2/\text{g}$, and its total pore volume and microporous pore volume were 0.31

Fig. 5. (a) N₂ adsorption-desorption isotherms of SSZ-13, SiC, and SSZ-13@SiC composites; (b) *A*_{BET} of SSZ-13@SiC as a function of synthesis time.

and 0.30 cm³/g, respectively. In comparison, the SiC support exhibited a negligible pore volume and external surface area. The surface area increased from 22.0 to 201.3 m²/g after growth of SSZ-13 on the SiC support with increasing synthesis time from 1 to 3 d. However, beyond 3 d, the specific surface area did not change much further (Fig. 5(b)). Because SiC exhibits an insignificant adsorption of N₂ and specific surface area, it can be concluded that the loading of SSZ-13 on the SiC surface increased with synthesis time. It is interesting that the growth almost stopped after the third day. Note that the BET surface area and microporous pore volume of SSZ-13@SiC were lower than those of pure SSZ-13 because the SiC itself only contributed weight but not pores. The composite obtained

for the 5 d synthesis (SSZ-13@SiC-5d) exhibited a relatively high BET surface area (196.8 m²/g) and micropore volume (0.10 cm³/g).

3.3. Characterization of Cu/SSZ-13@SiC catalyst

The Cu/SSZ-13@SiC catalyst was obtained through an ion-exchange process using the SSZ-13@SiC composites synthesized in 5 d. Fig. 6(a) shows that the Cu loading did not change the crystal phase of the SSZ-13@SiC-5d composite. No diffraction peaks related to Cu were detected, indicating well-distributed Cu species. In addition, the zeolite crystals remained cubic upon ion exchange and were homogeneous in size (Fig. 6(b) and (c)). Furthermore, Cu/SSZ-13@SiC exhibited a specific surface area of 193.0 m²/g, which was similar to that of SSZ-13@SiC-5d.

3.4. NH₃-SCR catalytic activity

Fig. 7 shows the NH₃-SCR performance of the Cu/SSZ-13 and Cu/SSZ-13@SiC catalysts with different Cu loadings. The NO conversion increased with the Cu loading on Cu/SSZ-13@SiC in the range of 0.37–1.71 wt%. The catalyst with a loading of 0.37% (denoted Cu(0.37)/SSZ-13@SiC) exhibited the lowest activity. Hardly any conversion of NO to N₂ was observed at low temperatures. The highest NO conversion was only 44% at 350 °C. Cu/SSZ-13@SiC with a Cu loading of

Table 1
Textural properties of the SiC support, SSZ-13, and SSZ-13@SiC composites.

Sample	<i>A</i> _{BET} (m ² /g)	<i>A</i> _{mic} (m ² /g)	<i>A</i> _{ext} (m ² /g)	<i>V</i> _t ^a (cm ³ /g)	<i>V</i> _{mic} ^b (cm ³ /g)
SiC	0.5	1.2	—	0	0
SSZ-13	567.7	560.1	7.6	0.31	0.30
SSZ-13@SiC-1d	22.0	11.3	10.6	0.04	0.01
SSZ-13@SiC-2d	153.9	150.4	3.5	0.09	0.08
SSZ-13@SiC-3d	201.3	193.9	7.4	0.12	0.10
SSZ-13@SiC-4d	197.4	189.5	7.9	0.12	0.10
SSZ-13@SiC-5d	196.8	188.6	8.2	0.12	0.10

^a Volume at *p/p*₀ = 0.994.

^b Obtained by the *t*-plot method.

Fig. 6. (a) XRD patterns of SSZ-13@SiC-5d and Cu/SSZ-13@SiC-5d; SEM images of SSZ-13@SiC-5d (b) and SEM image of Cu/SSZ-13@SiC-5d (c).

Fig. 7. NH_3 -SCR performance of Cu/SSZ-13@SiC with different Cu loadings compared with unsupported Cu(4.03)/SSZ-13.

1.02% (Cu(1.02)/SSZ-13@SiC) performed obviously better, and the NO conversion reached 90% around 240 °C and remained above 90% until reaching 350 °C. More interestingly, the use of Cu(1.71)/SSZ-13@SiC extended the application temperature even further because the NO conversion reached over 90% at temperatures as low as 200 °C and remained at 95% until reaching 400 °C. It dropped below 90% only around 450 °C and still retained over 70% at 500 °C. In comparison, the unsupported Cu(4.03)/SSZ-13 prepared using the same method exhibited similar catalytic performance as that reported for Cu(4.3)/SSZ-13 and Cu/SSZ-13 by Kwak et al. [27,28] with an 80% ion-exchange degree. The NO conversion over Cu(1.71)/SSZ-13@SiC was practically the same as that over Cu(4.03)/SSZ-13 below 250 °C. However, the NO conversion was much more stable at a higher temperature than that of the unsupported Cu(4.03)/SSZ-13. The latter gradually deactivated with increasing temperature, with NO conversion dropping below 90% at 400 °C, which is much lower than that of Cu(1.71)/SSZ-13@SiC. This result clearly demonstrates the effects of SiC in enhancing the activity and stabilizing Cu/SSZ-13 at high temperatures.

4. Conclusions

SSZ-13 zeolite was successfully grown on the surface of SiC, a material that exhibits good thermal conductivity, wear resistance, and chemical inertness. The Si and SiO_2 impurities in the SiC support acted as silicon sources for the growth of SSZ-13, likely leading to the formation of a chemically bonded SSZ-13 layer on SiC. The effects of different synthesis parameters on the structure and morphology of SSZ-13@SiC were investigated, and the results indicated that the use of SiC as a support for Cu/SSZ-13@SiC enhanced its activity, particularly for the catalyst Cu(1.71)/SSZ-13@SiC. The NO conversion reached above 90% close to 200 °C and was retained at this level beyond 400 °C. The use of the SiC support extended the application temperature window more broadly than that of the unsupported Cu(4.03)/SSZ-13 and enhanced the catalytic ac-

tivity of Cu/SSZ-13 in NH_3 -SCR, although the latter catalyst exhibited a much higher Cu loading.

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References

- [1] A. M. Beale, F. Gao, I. Lezcano-Gonzalez, C. H. F. Peden, J. Szanyi, *Chem. Soc. Rev.*, **2015**, 44, 7371–7405.
- [2] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B*, **1998**, 18, 1–36.
- [3] K. J. Duan, B. H. Chen, T. L. Zhu, Z. M. Liu, *Appl. Catal. B*, **2015**, 176, 618–626.
- [4] F. Gunnarsson, M. Z. Granlund, M. Englund, J. Dawody, L. J. Pettersson, H. Harelind, *Appl. Catal. B*, **2015**, 162, 583–592.
- [5] C. Thomas, *Appl. Catal. B*, **2015**, 162, 454–462.
- [6] H. Hu, S. X. Cai, H. R. Li, L. Huang, L. Y. Shi, D. S. Zhang, *ACS Catal.*, **2015**, 5, 6069–6077.
- [7] Y. Peng, W. Z. Si, X. Li, J. M. Luo, J. H. Li, J. Crittenden, J. M. Hao, *Appl. Catal. B*, **2016**, 181, 692–698.
- [8] K. A. Michalow-Mauke, Y. Lu, K. Kowalski, T. Graule, M. Nachttegaal, O. Krocher, D. Ferri, *ACS Catal.*, **2015**, 5, 5657–5672.
- [9] S. Proding, M. A. Derewinski, Y. L. Wang, N. M. Washton, E. D. Walter, J. Szanyi, F. Gao, Y. Wang, C. H. F. Peden, *Appl. Catal. B*, **2017**, 201, 461–469.
- [10] J. H. Lee, Y. J. Kim, T. Ryu, P. S. Kim, C. H. Kim, S. B. Hong, *Appl. Catal. B*, **2017**, 200, 428–438.
- [11] L. M. Yu, Q. Zhong, S. L. Zhang, *Microporous Mesoporous Mater.*, **2016**, 234, 303–309.
- [12] J. A. Sullivan, J. Cunningham, M. A. Morris, K. Keneavey, *Appl. Catal. B*, **1995**, 7, 137–151.
- [13] J. O. Petunchi, G. Sill, W. K. Hall, *Appl. Catal. B*, **1993**, 2, 303–321.
- [14] K. C. C. Kharas, H. J. Robota, D. J. Liu, *Appl. Catal. B*, **1993**, 2, 225–237.
- [15] J. Y. Yan, G. D. Lei, W. M. H. Sachtler, H. H. Kung, *J. Catal.*, **1996**, 161, 43–54.
- [16] A. Corma, V. Fornes, E. Palomares, *Appl. Catal. B*, **1997**, 11, 233–242.
- [17] Z. D. Liu, T. Wakihara, K. Oshima, D. Nishioka, Y. Hotta, S. P. Elangovan, Y. Yanaba, T. Yoshikawa, W. Chaikittisilp, T. Matsuo, T. Takewaki, T. Okubo, *Angew. Chem. Int. Ed.*, **2015**, 54, 5683–5687.
- [18] D. W. Fickel, E. D. Addio, J. A. Lauterbach, R. F. Lobo, *Appl. Catal. B*, **2011**, 102, 441–448.
- [19] J. H. Kwak, D. Tran, S. D. Burton, J. Szanyi, J. H. Lee, C. H. F. Peden, *J. Catal.*, **2012**, 287, 203–209.
- [20] B. H. Chen, R. N. Xu, R. D. Zhang, N. Liu, *Environ. Sci. Technol.*, **2014**, 48, 13909–13916.
- [21] I. Bull, W. M. Xue, P. Burk, R. S. Boorse, W. M. Jaglowski, G. S. Koermer, A. Moini, J. A. Patchett, J. Dettling, US Patent 7601662, **2009**.
- [22] J. H. Wang, H. W. Zhao, G. Haller, Y. D. Li, *Appl. Catal. B*, **2017**, 202, 346–354.
- [23] L. J. Gu, D. Ma, S. D. Yao, X. M. Liu, X. W. Han, W. J. Shen, X. H. Bao, *Chem. Eur. J.*, **2009**, 15, 13449–13455.

Graphical Abstract

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Growth of Cu/SSZ-13 on SiC for selective catalytic reduction of NO with NH₃

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This study explores growth of SSZ-13 zeolite around the SiC support. The SiC enhanced the catalytic activity of Cu/SSZ-13 for selective catalytic reduction at high temperature and widened the active temperature window.

[24] M. M. Elamin, O. Muraza, Z. Malaibari, H. Ba, J. M. Nhut, P. H. Cuong, *Chem. Eng. J.*, **2015**, 274, 113–122.

[25] Y. F. Liu, O. Ersen, C. Meny, F. Luck, C. Pham-Huu, *ChemSusChem*, **2014**, 7, 1218–1239.

[26] A. Shishkin, H. Kannisto, P. A. Carlsson, H. Harellind, M. Skoglundh,

Catal. Sci. Technol., **2014**, 4, 3917–3926.

[27] J. H. Kwak, D. Tran, S. D. Burton, J. Szanyi, J. H. Lee, C. H. F. Peden, *J. Catal.*, **2012**, 287, 203–209.

[28] J. H. Kwak, D. Tran, J. Szanyi, C. H. F. Peden, J. H. Lee, *Catal. Lett.*, **2012**, 142, 295–301.

碳化硅上生长Cu/SSZ-13分子筛及其NH₃-SCR催化性能

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摘要: 汽车尾气和柴油不完全燃烧所释放的NO_x严重污染了大气环境. 为了降低对大气的污染, 可将其催化还原成氮气. 氨气选择性催化还原(NH₃-SCR)是使用较广泛的机动车高效脱硝技术. 用于催化脱硝反应的催化剂有多种类型, 分子筛具有特殊的孔道结构和骨架结构及高比表面积, 因而已广泛用作脱硝反应催化剂. 与传统三效催化剂相比, 分子筛催化剂总体表现出更好的脱硝催化活性, 但在高温下不稳定, 容易失活, 不耐热冲击, 水热稳定性差. SiC具有耐酸碱、耐腐蚀、抗氧化、耐磨及良好的热稳定性和导电性, 因此作为催化剂载体近年来引起广泛关注. 但是其本身也存在许多缺点, 如比表面积低、表面性质不活泼、不利于金属物种分散等. 因此, 本文通过原位水热法将SSZ-13生长在SiC表面, 制备出新型催化复合材料SSZ-13@SiC. 采用X射线衍射(XRD)、扫描电子显微镜(SEM)和N₂吸附-脱附等手段研究了不同碱量和晶化时间对SSZ-13在SiC表面生长的影响, 负载Cu后获得Cu/SSZ-13@SiC作为催化剂, 研究了SiC对Cu/SSZ-13中高温下脱硝活性的影响规律. 结果表明, 碱含量会影响SSZ-13在SiC表面的结晶程度. 当SiO₂/NaOH ≥ 0.1时, SSZ-13有杂相出现, 并且结晶度都不高; 当SiO₂/NaOH < 0.1时, SiC表面会生长成纯相的SSZ-13晶粒且具有较高的结晶度. 晶化时间也会影响SSZ-13在SiC表面的覆盖程度: 反应1 d时, SiC表面会生长零星的SSZ-13晶粒; 2 d时, SSZ-13达到全面覆盖; 3 d后, SSZ-13在SiC上的生长达到饱和, 其比表面积达到最大值, 约为201.3 m²/g. 通过离子交换将不同含量Cu离子交换到分子筛表面, 其中Cu(1.71)/SSZ-13@SiC样品具有最佳的脱硝活性, 接近200 °C时, NO转化率就达到90%以上, 到高温500 °C时, NO转化率仍

能保持在70%以上. 相比于未负载的Cu/SSZ-13, Cu/SSZ-13@SiC催化剂在NH₃-SCR测试中具有更高的高温催化活性, 同时催化活性窗口明显拓宽. 上述结果说明SiC对Cu/SSZ-13的高温催化活性具有一定的提高和稳定作用.

关键词: 分子筛; SSZ-13; 碳化硅; 水热合成; 氨气选择性催化还原

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