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Article

NO_x selective catalytic reduction by ammonia over Cu-ETS-10 catalysts

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ARTICLE INFO

Article history:

Received 9 November 2013

Accepted 14 January 2014

Published 20 July 2014

Keywords:

Titanosilicate

Copper

Nitrogen oxide

Ammonia

Selective catalytic reduction

ABSTRACT

Ion exchange method was used to fabricate Cu-ETS-10 titanosilicate catalysts, which possessed high activity, N₂ selectivity and SO₂ resistance for NO_x selective catalytic reduction (SCR). N₂ sorption measurements indicated that the microporous catalysts had high surface areas of 288–380 m²/g. The Cu content and speciation were investigated by inductively coupled plasma atomic emission spectrometry, H₂ temperature-programmed reduction, and diffuse reflectance infrared Fourier transform spectroscopy. Various Cu species coexisted within the catalyst. Isolated Cu²⁺ species were the active sites for NH₃-SCR, the number of which initially increased and then decreased with increasing Cu content. The catalytic activity of Cu-ETS-10 depended on the isolated Cu²⁺ species content.

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1. Introduction

Nitrogen oxides (NO_x) are pollutants that adversely affect human health and the environment, which is an important research topic for society's current environmental ideals. Selective catalytic reduction (SCR) is a promising pathway for the efficient removal of NO_x. Zeolites are SCR materials and have received much attention in research and industry [1–6]. Cu²⁺-exchanged zeolites such as Cu-ZSM-5 [1] and Cu-Beta [7] exhibit high activities for SCR, but their poor hydrothermal durabilities limit their applications [3,8]. Cu²⁺-exchanged chabazites (Cu-CHA) exhibit high activity, selectivity and stability, and Cu-SSZ-13 and Cu-SAPO-34 [3,9] have received much attention. Such metal-containing zeolites have usually been prepared in several steps, such as hydrothermal synthesis, removal of structure-directing agents, metal ion exchange and calcination. Xiao group [10] and Moliner group [11] recently found that Cu-SSZ-13 and Cu-SAPO-34, each of them with high

activity for SCR, could be directly prepared by introducing Cu²⁺ to the synthesis precursors. This greatly simplified the Cu-zeolite synthesis process. They demonstrated the fabrication and high performance of specific Cu-zeolite catalyst orientations, using a simple synthesis process.

In 1989, the Engelhard company reported titanosilicate ETS-10 (composition of (Na,K)₂Si₅TiO₁₃·4H₂O), with a typical microporous structure [12]. The framework of ETS-10 consisted of [SiO₄] tetrahedra and [TiO₆] octahedra connected with oxygen bridges. ETS-10 included 12-member and double 7-member rings with relatively larger micropores (0.76 nm × 0.49 nm), and it possessed a high specific surface area and pore volume. The [Si₅TiO₁₃]²⁻ building blocks of ETS-10 required two positive charges to balance charge, which resulted in ETS-10 possessing a large ion exchange capacity [13]. ETS-10 has been used in adsorption [14], ion exchange [15], photocatalysis [15,16], and DeNO_x [17,18] applications. Gervasini et al. [17,18] reported the catalytic activity of Cu-ETS-10 for NO_x

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This work was supported by the National Natural Science Foundation of China (21277009) and the Funding Project for Academic Human Resources Development in Institutions of Higher Learning under the Jurisdiction of Beijing Municipality (PHR201107104).

DOI: 10.1016/S1872-2067(14)60035-8 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 7, July 2014

reduction by C_2H_4 , but for NH_3 -SCR the literatures are not seen. It is also important to understand the nature of Cu species within Cu-ETS-10. Cu-SAPO-34 and Cu-SSZ-13 [9,10,19–21] have received much attention in recent years. In contrast to these two catalysts, ETS-10 can be prepared without directing agents, so the removal of such agents during ETS-10 preparation was not necessary. The ETS-10 fabrication cost should therefore be lower than that of SAPO-34 and SSZ-13. The large ion exchange capacity of ETS-10 means that greater Cu loadings can be achieved.

Cu^{2+} species within Cu-zeolite micropores participate in charge balance, and reportedly may also be active sites for NH_3 -SCR, since the Cu^{2+} species content affects the catalytic performance [22]. Gervasini et al. [17] found that $[\text{TiO}_6]$ octahedra benefited the stabilization of isolated Cu^{2+} species in ETS-10 micropores. Therefore, Cu-ETS-10 might be expected to exhibit high activity for NH_3 -SCR.

In the current study, ion exchange method was used to fabricate Cu-ETS-10 catalysts with different Cu contents, and the NH_3 -SCR activity and selectivity for N_2 over the catalysts were measured. The physiochemical properties of the catalysts were characterized by X-ray diffraction (XRD), N_2 sorption measurements, inductively coupled plasma atomic emission spectrometry (ICP-AES), H_2 temperature-programmed reduction (H_2 -TPR), and diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO (CO-DRIFTS).

2. Experimental

2.1. Preparation of Cu-ETS-10 catalysts

ETS-10 was synthesized by a hydrothermal process [12,13,16]. Specifically, 6.6 g (165 mmol) of NaOH was dissolved in 50 mL of deionized water at 40 °C, and 7.37 g of white carbon black was added. The solution was stirred for 4 h. 1.82 mL of TiCl_4 (16.6 mmol) was added to 10 mL of water at 0 °C to form a white emulsion, which was added to the above solution. Then 4.6 g of $\text{KF} \cdot 2\text{H}_2\text{O}$ (50 mmol) was added, and the solution was stirred for 0.5 h. The resulting mixture was transferred to a polytetrafluoroethylene-lined autoclave, which was sealed and heated at 180 °C in an oven for 72 h. The product was obtained after cooling, filtering, washing, and drying.

Cations including Na^+ and K^+ existed in the pores of ETS-10 to balance the negative charge of the framework, but these could be substituted. Samples exchanged with NH_4^+ and Cu^{2+} were denoted as NH_4 -ETS-10 and Cu-ETS-10, respectively. NH_4 -ETS-10 was synthesized using a reported procedure [8]. Specifically, 20 g of ETS-10 in 1300 mL of NH_4NO_3 aqueous solution (1 mol/L) was stirred for 10 h at 85 °C. The solution was cooled, and the product collected by filtration and dried. This procedure was repeated six times to obtain NH_4 -ETS-10 with residual of 0.27% Na_2O and 0.012% K_2O . The Si/Ti molar ratio of NH_4 -ETS-10 was 4.7. For Cu-ETS-10 preparation, 10 g of NH_4 -ETS-10 in 500 mL of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution (0.1 mol/L) was stirred for 2 h at room temperature. The product Cu-ETS-10-3.9 was collected by filtration, washed, dried for 12 h at 120 °C, and calcined for 4 h in air at 500 °C. Cu-ETS-10- x

(where x is the Cu wt%) catalysts were obtained when the ion exchange process in $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution was repeated.

2.2. Catalytic reactions

The NH_3 -SCR performance was investigated using a fixed-bed quartz tube reactor, with 0.2 mL of Cu-ETS-10 (40–60 mesh) catalyst used. The total feed flow was 100 mL/min, which contained NO (0.1%), NH_3 (0.1%), O_2 (5.0%) and a balance of He with a space velocity (SV) of 30000 h^{-1} . The gas mixture in the reactor outlet included NO, NO_2 , N_2O , and N_2 determined by a gas chromatography (GC-2014C, Shimadzu) and a Bruker tensor 27 Fourier transform-infrared (FT-IR) spectrometer equipped with a 2.4 m pathlength gas cell. The NO_x conversion (X) [19] and N_2 selectivity (S_{N_2}) were calculated by:

$$X = \frac{([\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}})}{([\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}})} \times 100\%$$

$$S_{\text{N}_2} = [\text{N}_2]_{\text{out}} / ([\text{N}_2]_{\text{out}} + [\text{N}_2\text{O}]_{\text{out}} + 0.5[\text{NO}_2]_{\text{out}}) \times 100\%$$

where the 'in' and 'out' are the inlet and outlet of the reactor, respectively.

2.3. Characterization

Powder XRD patterns were recorded using a Bruker D8 Advance diffractometer, operated at 40 kV and 40 mA using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$), at $2\theta = 5^\circ$ – 45° with a step size of $0.02^\circ/\text{s}$. Specific surface areas, pore volumes, and pore size were measured on a physical adsorption instrument (Micromeritics ASAP 2020). Specific surface areas were calculated by Brunauer-Emmett-Teller (BET) method. Each sample was degassed at 250 °C under vacuum for 12 h, and N_2 was adsorbed at -196°C . Na, K, and Cu contents were determined using ICP-AES (Thermo Elemental, IRIS Intrepid ER/S). H_2 -TPR measurements were performed on a chemical adsorption apparatus (Micromeritics AutoChem II 2920) with a thermal conductivity detector (TCD). 50 mg of catalyst (40–60 mesh) was pretreated in O_2 for 30 min at 300 °C, and cooled to 40 °C in Ar. Then 10% H_2/Ar was introduced to the tube, which was then heated to 500 °C at a rate of 10 °C/min. After the baseline stabilized, signals were recorded by TCD. CO adsorption was carried out using a FT-IR spectrometer (Nicolet 6700) with a reaction chamber. Spectra were obtained from 32 scans at 4 cm^{-1} resolution. In a typical experiment, the catalyst was pretreated in 18% O_2/He for 30 min at 300 °C, to remove any adsorbed impurities. After cooling to 40 °C, the sample was purged with He for 30 min, and a background spectrum was recorded. The sample was heated to 200 °C, and 5% CO/He was introduced to the chamber, and the spectra were recorded.

3. Results and discussion

3.1. XRD and BET analyses

The XRD patterns of the as-prepared samples are shown in Fig. 1, in which all peaks could be attributed to the ETS-10 structure. There were no peaks indicating impurities or CuO

Fig. 1. XRD patterns of the Cu-ETS-10-0 (1), Cu-ETS-10-3.9 (2), Cu-ETS-10-6.6 (3), Cu-ETS-10-9.3 (4), and Cu-ETS-10-12.6 (5) catalysts.

phases. This implied that Cu species were highly dispersed on the zeolite support. The peak intensities decreased after ion exchange, perhaps associated with a partial collapse of the ETS-10 structure [13,23].

Figure 2 shows the N_2 adsorption-desorption isotherms and pore size distributions of the as-prepared Cu-ETS-10 catalysts. Table 1 summarizes the specific surface areas, pore volumes, and pore sizes of these samples. It shows that the isotherms

Fig. 2. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of the Cu-ETS-10-0 (1), Cu-ETS-10-3.9 (2), Cu-ETS-10-6.6 (3), Cu-ETS-10-9.3 (4), and Cu-ETS-10-12.6 (5) catalysts.

Table 1

Surface areas, pore volumes, and pore sizes of the Cu-ETS-10 catalysts.

Sample	Specific surface area (m^2/g)			Pore volume ^b (cm^3/g)	Pore size ^c (nm)
	BET	Micropore ^a	External ^a		
Cu-ETS-10-0	401.2	348.8	52.4	0.24	0.88
Cu-ETS-10-3.9	379.5	336.0	43.6	0.23	0.91
Cu-ETS-10-6.6	345.4	298.2	47.2	0.22	0.90
Cu-ETS-10-9.3	334.5	293.0	41.6	0.20	0.88
Cu-ETS-10-12.6	288.4	275.3	13.2	0.18	0.87

^a Determined by the t -plot approach.

^b Calculated by the single point method ($p/p_0 = 0.99$).

^c Calculated by the H-K (Saito-Foley) model.

were all of type I, indicating that all Cu-ETS-10 samples possessed microporous structure. The BET surface areas of Cu-ETS-10-3.9, Cu-ETS-10-6.6, Cu-ETS-10-9.3, and Cu-ETS-10-12.6 were 379.5, 345.4, 334.5, and 288.4 m^2/g , respectively. An increase in Cu content led to a decrease in the surface area of the Cu-ETS-10 samples, because of the partial packing of micropores and partial covering of the support surface. Similar trends were observed in the pore volumes and pore sizes. An increase in Cu content from 3.9 to 12.6 wt% decreased the pore volume from 0.23 to 0.18 cm^3/g , and decreased the pore size from 0.91 to 0.87 nm.

3.2. NH_3 -SCR activity over the Cu-ETS-10 catalyst

Figure 3 shows the NO_x conversion and selectivity of N_2 over the Cu-ETS-10 catalysts. The Cu-ETS-10-0 catalyst exhibited no activity at 150–400 °C. The NO_x conversion over the other cat-

Fig. 3. Conversion of NO_x (a) and selectivity for N_2 (b) over the Cu-ETS-10-0 (1), Cu-ETS-10-3.9 (2), Cu-ETS-10-6.6 (3), Cu-ETS-10-9.3 (4), and Cu-ETS-10-12.6 (5) catalysts. Reaction conditions: 0.1% NO , 0.1% NH_3 , 5.0% O_2 , He balance, $SV = 30000 h^{-1}$.

alysts initially increased to a maximum with increasing reaction temperature, and then decreased with further increasing temperature. The maximum conversion of NO_x over the Cu-ETS-10-3.9 catalyst was 89% at 250 °C. For the Cu-ETS-10-6.6, Cu-ETS-10-9.3, and Cu-ETS-12.6 catalysts, more than 90% of the NO_x could be removed at 216, 202, and 218 °C, respectively. The selectivity of N_2 over Cu-ETS-10-3.9 decreased with increasing reaction temperature, while those over Cu-ETS-10-6.6, Cu-ETS-10-9.3, and Cu-ETS-12.6 remained constant, because of their higher Cu contents. Under the same reaction conditions, the Cu-ETS-10-9.3 catalyst exhibited the best catalytic performance. The specific surface areas and microporous structure of the as-prepared Cu-ETS-10 samples had little effect on the catalytic performance for NO_x -SCR by NH_3 .

3.3. H_2 -TPR analysis

H_2 -TPR measurements were carried out to investigate the redox properties of the as-prepared samples. Figure 4 shows H_2 -TPR profiles of these catalysts. Four different Cu species were observed from the reduction peaks [6,24] of the Cu-ETS-10 catalysts. Reduction peak at 140–160 °C could have been due to the reduction of amorphous CuO_x . Amorphous CuO_x may have formed from Cu^{2+} agglomeration during ion exchange. Such species could be easily reduced at low temperatures, but did little to promote NO_x reduction [9]. Reduction peak at ~ 180 °C was due to the reduction of isolated Cu^{2+} to Cu^+ . Isolated Cu^{2+} species in Cu-zeolites can reportedly be reduced to Cu^+ at temperatures < 230 °C. Putluru group [6] found that isolated Cu^{2+} was reduced at ~ 180 °C in the H_2 -TPR of Cu-ZSM-5 and Cu-MOR catalysts. Isolated Cu^{2+} species in Cu-zeolite catalysts have been reported to be active sites for NH_3 -SCR [9]. The peak at 200–265 °C may have been attributed to the reduction of nano CuO crystals (nano CuO species) [6,22]. The peak at temperatures 300 °C above corresponded to the reduction of Cu^+ , and the interaction between Cu and Ti–O groups [22,25].

The areas of the reduction peaks in the H_2 -TPR profiles were used to calculate the H_2 consumption of each Cu species in

Fig. 4. H_2 -TPR profiles of the Cu-ETS-10-3.9 (1), Cu-ETS-10-6.6 (2), Cu-ETS-10-9.3 (3), and Cu-ETS-10-12.6 (4) catalysts.

Table 2

H_2 consumption of various Cu species in the Cu-ETS-10 catalysts.

Sample	H_2 consumption (mmol/g)			
	CuO_x	Cu^{2+}	nano-CuO	Cu^+ + others
Cu-ETS-10-3.9	—	0.045	0.249	0.277
Cu-ETS-10-6.6	0.038	0.185	0.439	0.288
Cu-ETS-10-9.3	0.08	0.236	0.513	0.398
Cu-ETS-10-12.6	0.241	0.225	0.614	0.407

the as-prepared Cu-ETS-10 catalysts. The results are shown in Table 2. No amorphous CuO_x species were observed in the Cu-ETS-10-3.9 catalyst, and nano CuO species were the main species, in addition to minor isolated Cu^{2+} quantities. This suggested that most Cu^{2+} dispersed on the surface of the support, during the first ion exchange. During calcination, the dispersed species became nano CuO species. The areas of the reduction peaks attributed to the reduction of amorphous CuO_x increased with increasing Cu content from 6.6% to 12.6%. This indicated an increase in the amount of amorphous CuO_x . Xue et al. [9] reported that no amorphous CuO_x existed in the Cu/SAPO-34 catalyst with Cu contents $< 2.89\%$. The peak area attributed to the reduction of isolated Cu^{2+} species in Cu-ETS-10-6.6 was higher than that in Cu-ETS-10-3.9. Thus, there were more isolated Cu^{2+} species formed in the Cu-ETS-10-6.6 catalyst during the second ion exchange, and the amount of nano CuO species also increased. Further increasing the Cu content from 6.6% to 9.3% led to more isolated Cu^{2+} species and nano CuO species. However, there were more nano CuO species and less isolated Cu^{2+} species in the Cu-ETS-10-12.6 catalyst. The amount of isolated Cu^{2+} species in the Cu-ETS-10 catalysts may have depended on the following factors. The Cu^{2+} content introduced within the micropores increased with increasing Cu content. Further increasing the Cu content resulted in destruction of the Cu-ETS-10 structure (Fig. 1), which decreased the amount of exchangeable sites. The interaction of these factors resulted in a maximum possible isolated Cu^{2+} content. In the present study, this maximum was reached in the Cu-ETS-10-9.3 catalyst.

Figure 5 shows the relationship between the amounts of isolated Cu^{2+} species and nano CuO species, NO_x conversions at

Fig. 5. NO_x conversion and the amounts of nano CuO and isolated Cu^{2+} in the Cu-ETS-10 catalysts.

200 and 400 °C, and the total Cu content of the Cu-ETS-10 catalysts. It shows that the amount of nano CuO species increased with increasing Cu content in the Cu-ETS-10 catalysts. However, the isolated Cu^{2+} content increased to a maximum, and then decreased. The Cu-ETS-10-9.3 sample possessed the highest isolated Cu^{2+} content. NO_x conversions over the Cu-ETS-10 catalysts are also shown in Fig. 5, and Cu-ETS-10-9.3 exhibited the highest activity. The isolated Cu^{2+} content and activity exhibited broad inverse-parabolic curves, as a function of Cu content. The results suggested that the activity of Cu-ETS-10 was regulated by isolated Cu^{2+} species [6,9,22,26,27]. A similar relationship between Cu species and activity was also found in Cu/SAPO-34 catalysts, and isolated Cu^{2+} species were verified as the active sites of Cu-zeolite catalysts for NH_3 -SCR [9].

3.4. CO adsorption

Figure 6 shows CO-DRIFT spectra collected after 5% CO/He was introduced to the reaction chamber for 5 min at 200 °C. The interactions between CO molecules and Cu sites in the zeolites were detected. The H_2 -TPR results indicated that isolated Cu^{2+} species could easily be reduced to Cu^+ . The band at $\sim 2155 \text{ cm}^{-1}$ was assigned to $\text{Cu}^+(\text{CO})$ (ion exchange sites) [24]. The intensity of this band for the Cu-ETS-10-9.3 sample was slightly stronger than those of the other samples, indicating it had the highest isolated Cu^{2+} species content. The band at $\sim 2145 \text{ cm}^{-1}$ red-shifted with increasing Cu content in the Cu-ETS-10 catalysts. The band at $\sim 2128 \text{ cm}^{-1}$ may have been attributed to CO adsorbed on reduced Cu^+ sites of nano CuO [24,28]. The results showed that multiple Cu species coexisted in Cu-ETS-10, and that the largest isolated Cu^{2+} content existed when the Cu content was 9.3%.

3.5. Effects of SO_2 and H_2O on the activity of Cu-ETS-10

We also investigated the influence of SO_2 and H_2O on the catalytic performance of Cu-ETS-10 for NH_3 -SCR. The results are shown in Fig. 7. It shows that when SO_2 was introduced into the feed gas, as the SO_2 content ($< 0.1\%$) and reaction time ($<$

Fig. 6. CO-DRIFTS spectra of the Cu-ETS-10-0 (1), Cu-ETS-10-3.9 (2), Cu-ETS-10-6.6 (3), Cu-ETS-10-9.3 (4), and Cu-ETS-10-12.6 (5) catalysts after the adsorption of CO at 200 °C.

Fig. 7. Effects of SO_2 and H_2O on the catalytic performance of Cu-ETS-10-9.3. Reaction conditions: NO 0.1%, NH_3 0.1%, O_2 5.0%, He balance, $\text{SV} = 30000 \text{ h}^{-1}$, 220 °C.

27 h), the NO_x conversion over Cu-ETS-10-9.3 remained at $\sim 95\%$. When 0.1% $\text{SO}_2 + 5\%$ H_2O were added into the feed gas, the NO_x conversion rapidly reduced to $\sim 20\%$. When 0.1% SO_2 was cut off, the NO_x conversion immediately recovered to $\sim 90\%$. These results indicated that separately introducing SO_2 or H_2O had a negligible influence on the catalytic performance of the Cu-ETS-10-9.3 catalyst for NH_3 -SCR. However, the simultaneous addition of SO_2 and H_2O caused a drastic decrease in NO_x conversion. This may have been associated with competitive adsorption among SO_2 , H_2O , and the reactant at the active sites [29].

4. Conclusions

0–12.6% Cu-ETS-10 catalysts with microporous structure and large specific surface areas were prepared by ion exchange method. The Cu content was regulated by the times of ion exchange. Cu species were highly dispersed on the zeolite supports. The isolated Cu^{2+} content affected the catalytic performance of Cu-ETS-10 for the NH_3 -SCR of NO_x . Under a $\text{NO}:\text{NH}_3:\text{O}_2$ molar ratio of 1:1:50 and SV of 30000 h^{-1} , the Cu-ETS-10-9.3 catalyst with the highest isolated Cu^{2+} species content exhibited superior catalytic activity: NO_x conversion was $> 90\%$ at 200–350 °C. This study on Cu-ETS-10 catalysts will benefit the design and development of SCR catalysts.

References

- [1] Liu F D, Shan W P, Shi X Y, Zhang C B, He H. *Chin J Catal* (刘福东, 单文波, 石晓燕, 张长斌, 贺泓. 催化学报), 2011, 32: 1113
- [2] Ye Q, Wang L F, Yang R T. *Appl Catal A*, 2012, 427-428: 24
- [3] Kwak J H, Tonkyn R G, Kim D H, Szanyi J, Peden C H F. *J Catal*, 2010, 275: 187
- [4] Shi X Y, Liu F D, Shan W P, He H. *Chin J Catal* (石晓燕, 刘福东, 单文波, 贺泓. 催化学报), 2012, 33: 454
- [5] Putluru S S R, Jensen A D, Riisager A, Fehrmann R. *Catal Commun*, 2012, 18: 41
- [6] Putluru S S R, Riisager A, Fehrmann R. *Appl Catal B*, 2011, 101: 183

Graphical Abstract

Chin. J. Catal., 2014, 35: 1030–1035 doi: 10.1016/S1872-2067(14)60035-8

NO_x selective catalytic reduction by ammonia over Cu-ETS-10 catalysts

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Isolated Cu²⁺ species were introduced to the titanosilicate structure by ion exchange, and the activity of the resulting Cu-ETS-10 catalysts for the NO_x selective catalytic reduction by NH₃ depended strongly on isolated Cu²⁺ content.

- [7] Corma A, Fornés V, Palomares E. *Appl Catal B*, 1997, 11: 233
- [8] Fickel D W, D'Addio E, Lauterbach J A, Lobo R F. *Appl Catal B*, 2011, 102: 441
- [9] Xue J J, Wang X Q, Qi G S, Wang J, Shen M Q, Li W. *J Catal*, 2013, 297: 56
- [10] Ren L M, Zhang Y B, Zeng S J, Zhu L F, Sun Q, Zhang H Y, Yang C G, Meng X J, Yang X G, Xiao F S. *Chin J Catal* (任利敏, 张一波, 曾尚景, 朱龙凤, 孙琦, 张海燕, 杨承广, 孟祥举, 杨向光, 肖丰收. 催化学报), 2012, 33: 92
- [11] Martínez-Franco R, Moliner M, Franch C, Kustov A, Corma A. *Appl Catal B*, 2012, 127: 273
- [12] Kuznicki S M. US Patent 4 853 202. 1989
- [13] Pavel C C, Park S H, Dreier A, Tesche B, Schmidt W. *Chem Mater* 2006, 18: 3813
- [14] Bordiga S, Pazé C, Berlier G, Scarano D, Spoto G, Zecchina A, Lamberti C. *Catal Today*, 2001, 70: 91
- [15] Ren Y H, Gu M, Hu Y C, Yue B, Jiang L, Kong Z P, He H Y. *Chin J Catal* (任远航, 辜敏, 胡怡晨, 岳斌, 江磊, 孔祖萍, 贺鹤勇. 催化学报), 2012, 33: 123
- [16] Suroli P K, Tayade R J, Jasra R V. *Ind Eng Chem Res*, 2010, 49: 3961
- [17] Gervasini A, Picciau C, Auroux A. *Microporous Mesoporous Mater*, 2000, 35-36: 457
- [18] Carniti P, Gervasini A, Auroux A. *Langmuir*, 2001, 17: 6938
- [19] Gao F, Walter E D, Washton N M, Szanyi J, Peden C H F. *ACS Catal*, 2013, 3: 2083
- [20] Yu T, Wang J, Shen M Q, Li W. *Catal Sci Technol*, 2013, 3: 3234
- [21] Wang J, Yu T, Wang X Q, Qi G S, Xue J J, Shen M Q, Li W. *Appl Catal B*, 2012, 127: 137
- [22] Jiang X Y, Ding G H, Lou L P, Chen Y X, Zheng X M. *J Mol Catal A*, 2004, 218: 187
- [23] Krisnandi Y K, Lachowski E E, Howe R F. *Chem Mater*, 2006, 18: 928
- [24] Góra-Marek K, Palomares A E, Glanowska A, Sadowska K, Datka J. *Microporous Mesoporous Mater*, 2012, 162: 175
- [25] Tounsi H, Djemal S, Petitto C, Delahay G. *Appl Catal B*, 2011, 107: 158
- [26] Pereda-Ayo B, De La Torre U, Illán-Gómez M J, Bueno-López A, González-Velasco J R. *Appl Catal B*, 2014, 147: 420
- [27] Lu G, Li X Y, Qu Z P, Zhao Q D, Zhao L, Chen G H. *Chem Eng J*, 2011, 168: 1128
- [28] Praliaud H, Mikhailenko S, Chajar Z, Primet M. *Appl Catal B*, 1998, 16: 359
- [29] Zhang Q L, Qiu C T, Xu H D, Lin T, Gong M C, Chen Y Q. *Chin J Catal* (张秋林, 邱春田, 徐海迪, 林涛, 龚茂初, 陈耀强. 催化学报), 2010, 31: 1411

Cu-ETS-10催化NH₃选择性还原NO_x性能

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摘要: 采用离子交换法制备了Cu-ETS-10钛硅分子筛催化剂, 该催化剂对于NH₃选择性催化还原(SCR) NO_x反应具有较高的催化活性、N₂选择性和抗SO₂性能。结果表明, Cu-ETS-10钛硅分子筛具有丰富的微孔结构和较高的比表面积(288–380 m²/g); 原子发射光谱、程序升温还原技术和原位红外漫反射等表征结果表明, Cu在Cu-ETS-10钛硅分子筛中具有多种存在形态, 其中Cu²⁺物种为Cu-ETS-10的活性中心, 其含量随Cu含量的增加而先增后降, 与催化活性的变化趋势一致。

关键词: 钛硅分子筛; 铜; 氮氧化物; 氨气; 选择性催化还原

收稿日期: 2013-11-09. 接受日期: 2014-01-14. 出版日期: 2014-07-20.

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基金来源: 国家自然科学基金(21277009); 北京市学术创新团队计划(PHR201107104).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).