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铁铜双金属催化剂选择性催化氧化氨为氮气

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摘要: 固定铜铁的总质量不变, 采用共浸渍法制备铜铁双金属催化剂. 为了更好地了解催化剂的性质, 分别用 N_2 吸附-脱附、 H_2 -程序升温还原(H_2 -TPR)、 NH_3 -程序升温脱附(NH_3 -TPD)、X射线衍射(XRD)和X射线光电子能谱(XPS)方法对制备的催化剂进行表征. 研究发现在 100000 h^{-1} 空速下, 铜铁双金属催化剂呈现出好的活性和氮气选择性. 在低温区, 随着铜含量的增加, 活性和氮气的选择性增加, 然而在高温区氮气的选择性直接和铁的含量相关. 其中催化剂 $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$, 在 350°C 氨的转化率达到最高, 在 300°C 氮气的选择性上升到 97%. $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ 在 500°C 有很高的氮气选择性甚至可以达到 98%. 并且所有的催化剂均产生很少的 N_2O 副产物. 表征结果显示催化剂的酸量和铜物种的含量可以影响催化剂的活性, 并且高的还原能力和铁含量有助于高温氮气选择性的提高.

关键词: 铁; 铜; 分子筛; 氨氧化反应; N_2 选择性; 催化剂

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Selective Catalytic Oxidation of Ammonia to Nitrogen over Iron and Copper Bimetallic Catalysts

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Abstract: Iron and copper bimetallic catalysts with fixed total contents of copper and iron were prepared by a co-impregnation method, and then used for selective catalytic oxidation of ammonia to nitrogen. The properties of the catalysts were characterized by N_2 adsorption-desorption, H_2 temperature-programmed reduction (H_2 -TPR), NH_3 temperature-programmed desorption (NH_3 -TPD), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The iron and copper bimetallic catalysts exhibited good activity and high selectivity of N_2 at the gas hourly space velocity (GHSV) of 100000 h^{-1} . The activity and N_2 selectivity in the low temperature range increased with increasing Cu loading, whereas in the high temperature range (above 400°C) the selectivity of N_2 was directly related to the content of iron. The highest NH_3 conversion was achieved at about 350°C for $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$, and the N_2 selectivity was up to 97% at 300°C . On the other hand, the extremely high N_2 selectivity about 98% was obtained over $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ at 500°C . In addition, N_2O as the by-product and greenhouse gas was obtained in very low amounts for all the catalysts. The characterization results showed that the activity was influenced by the acid content and the amounts of copper species. Moreover, the highly reducing capacity could improve the N_2 selectivity.

Key Words: Iron; Copper; Molecular sieve; Ammonia oxidation reaction; N_2 selectivity; Catalyst

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1 Introduction

NH₃ is seen as a toxic gas with a pungent odor, and shows potential damage to public safety,¹ which is used as reactants in a lot of chemical processes such as nitric acid production and urea manufacturing. As a byproduct, it is produced in many reactions such as de-nitration process. Thus environmental problems induced by ammonia emission become more severe. Selective catalytic oxidation (SCO) of ammonia to molecular nitrogen and water is proposed as an efficient and promising method to solve problems of ammonia pollution, and it has become increasingly important in recent years.

The catalytic oxidation of ammonia can proceed three reactions:^{2,3}

Except that the reaction (1) mentioned above is promoted, reactions (2) and (3) should be prevented due to the production of toxic nitrogen oxide.

To achieve such goal, various catalysts (e.g., noble metal catalysts, transition metal catalysts) for oxidizing NH₃ have been developed. The noble metals (e.g., Pt, Pd, Rh, Ag) are active for ammonia oxidation reaction,^{4–9} but the selectivity of N₂ is low. The transition metal catalysts such as V₂O₅, Fe₂O₃, CuO, MnO₂, TiO₂ are also employed for the ammonia oxidation reaction. Among them Fe₂O₃ and CuO have attracted much attention.^{10,11} Such as high activity of ammonia oxidation at high temperatures *via* Fe-based catalysts is well studied by Yang *et al.*^{12–14} However, the activity over Fe-based catalysts is very low at low temperatures. For copper-based catalysts, they behave quite opposite to Fe-based catalysts, i.e., better activity is observed at low temperatures for copper-based catalysts.^{15–19} Thus it is necessary to prepare the catalysts with both Cu and Fe, which can improve the activity at low temperatures as well as the N₂ selectivity. In this study, copper and iron catalysts were loaded into the routine support materials (ZSM-5) with different Cu/Fe mass ratios, in order for developing a better catalyst to improve the activity and N₂ selectivity for the ammonia oxidation reaction.

2 Experimental

2.1 Preparation of catalysts

The samples were synthesized by an impregnation method using FeCl₃·4H₂O (A.R.) and Cu(NO₃)₂·3H₂O (A.R.) as the metal precursors. ZSM-5 (SiO₂/Al₂O₃ molar ratio=25) was purchased in Nankai University Catalyst Factory as the support. The total content of copper and iron was maintained at 4% (mass fraction, without cordierite). Three different catalysts with different Cu/Fe mass ratios were prepared, namely Fe_{0.25}Cu_{0.75}/ZSM-5, Fe_{0.50}Cu_{0.50}/ZSM-5, and Fe_{0.75}Cu_{0.25}/ZSM-5. After impregnation, the samples were dried in the oven. And then the sample was calcined at 300 °C for 2 h and 550 °C for 3 h. After that, the catalyst powders with certain distilled water were ball-milled to form homogeneous slurry. The slurry was coated on a honeycomb cordierite (5.2 cm³, Corning, America) with the coating amount of 160 g·L⁻¹.

Fe_{1-x}Cu_x/ZSM-5 (*x*=0.75, 0.50, 0.25) with cordierites was used to evaluate the performance of catalysts.

2.2 Characterization of catalysts

N₂ adsorption-desorption isotherms were measured at -196 °C on a QUANTACHROME SI automated surface area & pore size Analyzer. Before each measurement, the catalyst powders (without cordierite) were degassed at 300 °C for 3 h under vacuum. The specific surface area and the pore size distribution of the catalyst powders were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

H₂ temperature-programmed reduction (H₂-TPR) was carried out in a quartz tubular micro-reactor equipped with a thermal conductivity detector (TCD). Prior to the analysis, 0.10 g of sample (without cordierite) was loaded into the quartz tubular micro-reactor and then pretreated with a flow of N₂ for 1 h at 450 °C. Afterwards, the sample was cooled to room temperature in N₂. The measurement was performed from room temperature to 750 °C in a flow of 5% H₂/N₂ at a heating rate of 8 °C·min⁻¹.

NH₃ temperature-programmed desorption (NH₃-TPD) was detected by a TCD. 0.10 g of the catalyst powders (without cordierite) was first pretreated at 450 °C for 1 h. Subsequently, the sample was cooled to 60 °C. After that, ammonia was adsorbed at 60 °C for 1 h, and the excess NH₃ was purged using He, then the temperature was increased linearly to 600 °C with flowing He at a heating rate of 10 °C·min⁻¹.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max-rA diffractometer (RIGAKU Corp.) with Cu K_α radiation (40 kV, 25 mA, λ=0.15406 nm). During analysis, the sample (without cordierite) was scanned from 5° to 60°. The compound was identified by comparison with reference data from the International Centre for Diffraction Data (ICDD).

X-ray photoelectron spectra of samples were performed using an AXIS Ultra DLD (KRATOS) spectrometer with Al K_α radiation (1486.6 eV). X-ray radiation was operated at 300 W by setting the electron energy analyzer.

2.3 Performance evaluation of catalysts

The catalytic reaction for ammonia selective catalytic oxidation was carried out under atmospheric pressure in a temperature-programmed reaction fixed-bed quartz-glass reactor. The inlet and outlet gas compositions were analyzed by an on-line ANTARIS IGS Analyzer. The reactant gas composition was as follows: 2×10⁻⁸ (volume fraction) NH₃, 10% O₂, 8% CO₂, and balance N₂. The gas hourly space velocity (GHSV) was 100000 h⁻¹. Before running an experiment, the catalyst (with cordierite) was pretreated under the reaction atmosphere at 500 °C for 1 h to make the property of catalyst stable. Then the temperature was decreased to the reaction temperature. Data were collected in a steady state. The NH₃ conversion and N₂O selectivity were defined as:

$$\text{NH}_3 \text{ conversion} = ([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) / [\text{NH}_3]_{\text{in}} \times 100\%$$

$$\text{N}_2\text{O selectivity} = 2[\text{N}_2\text{O}]_{\text{out}} / ([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) \times 100\%$$

It was impossible to directly measure N₂ by Fourier transform infrared (FTIR) spectrometry. N₂ selectivity was calculated based

on the following formula:

$$\text{N}_2 \text{ selectivity} = \frac{([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}})}{([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})} \times 100\%$$

3 Results and discussion

3.1 Property of catalysts

The ammonia oxidation reaction was studied on the $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ ($x=0.25, 0.50, 0.75$) catalysts (with cordierite). Fig.1 showed the results of NH_3 conversion in ammonia oxidation reaction. We could clearly see that the activity increased by increasing temperature for all the catalysts. When the appropriate amount of copper and iron was mixed, a significant influence on catalytic activity in low temperature range was observed. We found that the activity increased by increasing the mass ratio of Cu/Fe at 225–400 °C. For $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ catalyst, the NH_3 conversion was only 84% at 500 °C. However, 90% NH_3 conversion was achieved for $\text{Fe}_{0.50}\text{Cu}_{0.50}/\text{ZSM-5}$ and $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ catalysts at about 390 and 327 °C, respectively. The results of activity suggested that copper was more active than the same amount of iron at low temperatures.

Fig.2a displayed the N_2 selectivity on $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ catalysts. All the catalysts exhibited high selectivity to N_2 , in which the N_2 selectivity increased by increasing the mass ratio of Cu/Fe at lower temperatures (<400 °C), while the selectivity of N_2 increased by decreasing the mass ratio of Cu/Fe at higher temperatures (>400 °C). For example, the N_2 selectivity approached 97% for $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ catalyst at 300 °C and decreased by increasing the temperature, even the N_2 selectivity was still 88% at 500 °C. The N_2 selectivity of $\text{Fe}_{0.50}\text{Cu}_{0.50}/\text{ZSM-5}$ behaved much better than $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ due to the increasing mass ratio of Cu/Fe below 400 °C. However, the N_2 selectivity was close, regardless of the Cu/Fe mass ratio in the temperature range from 400 to 500 °C. In details, the $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ catalyst with the highest iron loading exhibited the best selectivity of N_2 (98%) at 500 °C.

From Fig.2b, we could clearly see that the selectivity of N_2O was relatively low (<5%) for all catalysts. Moreover, Cu con-

Fig.1 NH_3 conversion over $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$, $\text{Fe}_{0.50}\text{Cu}_{0.50}/\text{ZSM-5}$, and $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ catalysts

experimental condition: 2×10^{-8} (volume fraction) NH_3 , 10% O_2 , 8% CO_2 , and balanced with N_2 . The gas hourly space velocity (GHSV) was 100000 h^{-1} .

Fig.2 N_2 selectivity (a) and N_2O selectivity (b) over $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ catalysts

experimental condition: 2×10^{-8} NH_3 , 10% O_2 , 8% CO_2 , and balanced with N_2 ; GHSV=100000 h^{-1}

tributed to the low N_2O selectivity at relative low temperatures while Fe replaced the role of Cu at high temperatures.

Fig.3 showed the NH_3 conversion over $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ sample at 350 °C. 97% NH_3 conversion was observed under the condition of 2×10^{-8} (volume fraction) NH_3 , 10% O_2 , 8% CO_2 , balanced with N_2 and GHSV=100000 h^{-1} . When 5×10^{-7} (volume fraction) SO_2 was added into the reaction, NH_3 conversion sharply decreased to 38% in 0.5 h, then slightly went down to 23% in 2 h. However, NH_3 conversion increased to 65% after turning off the

Fig.3 NH_3 conversion over $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ catalyst at 350 °C
experimental condition: 2×10^{-8} NH_3 , 5×10^{-7} (volume fraction) SO_2 (when used), 10% O_2 , 8% CO_2 , and balanced with N_2 ; GHSV=100000 h^{-1}

SO₂. Fig.4 showed the NH₃ conversion over Fe_{0.25}Cu_{0.75}/ZSM-5 sample after regeneration at 550 °C for 1 h. The NH₃ conversion was increased by increasing the temperature. The NH₃ conversion exhibited some decrease compared with the fresh catalyst below 350 °C, but the high NH₃ conversion (>93%) was still obtained from 350 to 500 °C. The results indicated that SO₂ tolerance of the catalyst was not very good, but the activity was mostly recovered after regeneration.

Fig.5 exhibited the NH₃ conversion and N₂ selectivity of Fe_{0.25}Cu_{0.75}/ZSM-5 catalyst after severely aging at 800 °C for 10 h in air with 5% H₂O. NH₃ conversion increased with increasing the temperature. In addition, 90% NH₃ conversion was observed at 390 °C and the highest NH₃ conversion (about 95%) was obtained at 450 °C. We also found that Fe_{0.25}Cu_{0.75}/ZSM-5 catalyst had 76% N₂ selectivity at 300 °C. Furthermore, the selectivity of N₂ went up to 82% at 400 °C. The lowest N₂ selectivity was still 58% at 500 °C.

3.2 Textural properties of catalysts

Table 1 listed the textural parameters of Fe_{1-x}Cu_x/ZSM-5 catalysts. The adsorption-desorption isotherm shape of Fe_{1-x}Cu_x/ZSM-5 catalysts remained unchanged compared with ZSM-5 zeolite.

Fig.4 NH₃ conversion over Fe_{0.25}Cu_{0.75}/ZSM-5 catalyst after regeneration at 550 °C for 1 h

experimental condition: 2×10^{-8} NH₃, 10% O₂, 8% CO₂, and balanced with N₂; GHSV=100000 h⁻¹

Fig.5 NH₃ conversion and N₂ selectivity of the Fe_{0.25}Cu_{0.75}/ZSM-5 catalyst after aging at 800 °C for 10 h in air with 5% H₂O

experimental condition: 2×10^{-8} NH₃, 10% O₂, 8% CO₂, and balanced with N₂; GHSV=100000 h⁻¹

Table 1 Textural parameters of Fe_{1-x}Cu_x/ZSM-5 catalysts

Sample	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Average pore diameter/nm
ZSM-5	335.1	0.19	2.30
Fe _{0.25} Cu _{0.75} /ZSM-5	298.0	0.18	2.47
Fe _{0.50} Cu _{0.50} /ZSM-5	299.9	0.18	2.50
Fe _{0.75} Cu _{0.25} /ZSM-5	297.1	0.18	2.45

All the catalysts had an obvious hysteresis loop, which was H4 type (did not show in this article). However, after the copper and iron were incorporated through impregnation in the ZSM-5 zeolite, the surface areas and pore volumes decreased compared with those of ZSM-5 zeolite. For example, the values of Fe_{0.25}Cu_{0.75}/ZSM-5 decreased from 335.1 m²·g⁻¹ and 0.19 cm³·g⁻¹ to 298.0 m²·g⁻¹ and 0.18 cm³·g⁻¹. The surface area of ZSM-5 support was obtained after thermal treatment. So the reason for the loss of surface area was more likely to be the covering of the external surface of ZSM-5 by copper and iron species and blocking of the pores of ZSM-5. After the mass ratio of Cu/Fe was decreased, the surface areas and pore volumes of the catalysts still kept unchanged compared with those of Fe_{0.25}Cu_{0.75}/ZSM-5 catalyst. Thus it could be concluded that the textural properties of catalysts made little contribution to the variation of reaction activity.

3.3 XRD measurements

Fig.6 showed the XRD patterns of Fe_{1-x}Cu_x/ZSM-5 catalysts. All the catalysts exhibited typical peaks of the ZSM-5 (PDF No. 39-0225) zeolite, indicating that the structure of ZSM-5 zeolite kept intact after impregnation. The intensities of the principle diffraction peaks of the Fe_{1-x}Cu_x/ZSM-5 catalysts decreased compared with those of the ZSM-5, because the copper and iron had higher absorption coefficient for the XRD or the lower content of zeolite.²⁰ For Fe_{1-x}Cu_x/ZSM-5 catalysts, the peaks shifted to lower angles than the peaks of ZSM-5, while the values remained the same among Fe_{1-x}Cu_x/ZSM-5 catalysts. That was to say, the addition of copper and iron could enlarge crystallite di-

Fig.6 XRD patterns of different samples with Cu K_α radiation (40 kV, 25 mA, λ=0.15406 nm)

(a) the profiles of magnified peaks around 7°-9°; (b) the profiles of magnified peaks around 32°-37° (ascribed to Fe₂O₃)

mension of the pure ZSM-5, but the crystallite dimension remained unchanged with adjusting the mass ratio of Cu/Fe. It indicated that the crystallite dimension was not the main factor which influenced the activity. For $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ catalyst, no peaks associated with iron or copper compounds were found. It may be due to the interaction between copper and iron species or the low content of copper and iron species. It was in favor of the activity that Cu^{2+} and Fe^{3+} were completely incorporated into the crystal lattice of ZSM-5 zeolite.

But peaks (at 33.2° , 35.6° , 40.9° , 49.5° , and 54.1°) ascribed to Fe_2O_3 (PDF No. 33-0664) were detected for $\text{Fe}_{0.50}\text{Cu}_{0.50}/\text{ZSM-5}$ catalyst when the iron loading was further increased. Combining with the result of activity and N_2 selectivity, it can be concluded that the Fe_2O_3 species may facilitate the improvement of selectivity of N_2 at higher temperatures, but did not contribute to the activity at low temperatures.¹²

3.4 XPS results

The XPS technique was used to understand the states of Fe and Cu species. Fig. 7a showed the results of $\text{Cu } 2p_{3/2}$ of $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$. Two peaks appeared at 933.1 and 934.8 eV, which were assigned to CuO species and Cu^{2+} in zeolite.²¹ In addition, we found that the amounts of CuO species and Cu^{2+} in zeolite increased by increasing the mass ratio of Cu/Fe, which was consistent with the activity of the catalysts. We could conclude that CuO species and Cu^{2+} in zeolite contributed to good activity at low temperatures. The selective catalytic oxidation of ammonia to nitrogen was a two-step route^{12,13} that involved the oxidation of ammonia to NO_x

at CuO sites and the selective catalytic reduction of NO_x to N_2 at Cu^{2+} sites.²² Table 2 listed the XPS results of Cu $2p_{3/2}$ and Fe $2p_{3/2}$ for the samples. From Table 2, the atomic percentage of Cu^{2+} in CuO increased by increasing the mass ratio of Cu/Fe. It suggested that CuO species was a key factor to determine the activity at low temperatures. It might be due to the fact that the reaction of ammonia oxidation to NO_x was the rate determine step.²³

Fig. 7b exhibited the spectra of Fe $2p_{3/2}$ of $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ ($x=0.75, 0.50, 0.25$) catalysts. Two peaks of Fe $2p_{3/2}$ were located at 711.1 and 713.2 eV, higher than the binding energy (710.7 eV) of Fe_2O_3 ,²⁴ which strongly suggested that the iron was present as Fe^{3+} species.²⁵ The peak at 711.1 eV was assigned to the Fe_2O_3 species and the peak at 713.2 eV was the Fe^{3+} in the zeolite. From Fig. 7b and Table 2, we could see that the peak area of Fe^{3+} in the zeolite kept unchanged, while the atomic percentage of Fe^{3+} in Fe_2O_3 was decreased by increasing the mass ratio of Cu/Fe. Combining with the activity and N_2 selectivity, we could find out that Fe_2O_3 species contributed little to the SCO activity at low temperatures, which was consistent with the result of XRD. However, Fe_2O_3 species might improve the selectivity of N_2 at high temperatures because $\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$ catalyst with the largest amounts of Fe_2O_3 species had the best N_2 selectivity.

3.5 H_2 -TPR result

To understand the redox properties of the catalysts, the temperature-programmed reduction measurement was performed. H_2 -TPR of the pure ZSM-5 was also performed, and no signal peaks of H_2 consumption were found (did not show in this article). Therefore, the peaks for the catalysts were attributed to the reduction of copper and iron species. For $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ catalysts, the peaks α_1 and α_2 were attributed to the reduction of copper species, which were assigned to the reduction of Cu^{2+} to Cu^+ and Cu^+ to Cu^0 , respectively.²⁶ Moreover, the H_2 consumption ratio of α_1/α_2 was around 1, which indicated that the copper species were mostly present in the form of Cu^{2+} . This result was consistent with the spectra of Cu $2p_{3/2}$. On the other hand, the H_2 consumptions of peaks β_1 – β_3 at higher temperatures were assigned to the reduction of iron species. The peak β_1 was due to the reduction of Fe^{3+} in molecular sieves and the peak β_2 was ascribed to the reduction of Fe_2O_3 to Fe^{2+} , the peak β_3 was attributed to the reduction of Fe^{2+} species to Fe^0 . In addition, we also found that the strength ratio of $(\beta_1+\beta_2)/\beta_3$ was about 1/2, which exhibited that the iron species were mostly present in the form of Fe^{3+} . Although $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was the metal precursor, most iron species were present as Fe^{3+} after calcination, which was also proved by XPS.

Fig. 7 XPS results of Cu $2p_{3/2}$ (a) and Fe $2p_{3/2}$ (b) in $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ ($x=0.75, 0.50, 0.25$)

Table 2 XPS results of Cu $2p_{3/2}$ and Fe $2p_{3/2}$ for the samples

Sample	$A/\%$		$A'/\%$		$m(\text{Cu})/m(\text{Fe})$
	Cu^{2+} in zeolite	Cu^{2+} in CuO	Fe^{3+} in zeolite	Fe^{3+} in Fe_2O_3	
$\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$	28.2	71.8	34.5	65.5	2.3
$\text{Fe}_{0.50}\text{Cu}_{0.50}/\text{ZSM-5}$	31.2	68.8	30.8	69.2	0.8
$\text{Fe}_{0.75}\text{Cu}_{0.25}/\text{ZSM-5}$	34.8	65.2	21.9	78.1	0.2

A : atomic percent of Cu^{2+} in zeolite or Cu^{2+} in CuO; A' : atomic percent of Fe^{3+} in zeolite or Fe^{3+} in Fe_2O_3

Table 3 showed H₂ consumption of catalysts. From Table 3, the amount of H₂ consumption for peak α_1 increased by increasing the mass ratio of Cu/Fe at the low temperatures. This result was consistent with the activity of catalysts, larger amount of Cu²⁺ species contributed to better activity at low temperatures. The amount of H₂ consumption for peak β_1 of Fe_{1-x}Cu_x/ZSM-5 ($x=0.25, 0.50, 0.75$) slightly increased from 37.5 to 48.0 $\mu\text{mol} \cdot \text{g}^{-1}$ with increasing the amount of Fe. The amount of H₂ consumption for peak β_2 of Fe_{0.25}Cu_{0.75}/ZSM-5 was 42.2 $\mu\text{mol} \cdot \text{g}^{-1}$, when increased Fe loading, the value of Fe_{0.75}Cu_{0.25}/ZSM-5 increased to 117.8 $\mu\text{mol} \cdot \text{g}^{-1}$. However, the activity did not get better with decreasing the mass ratio of Cu/Fe. It suggested that Fe₂O₃ contributed little to good activity at low temperatures.

In addition, the selectivity of N₂ was significantly influenced by the reduction ability of the catalysts. The amount of H₂ consumption for copper species at low temperatures increased with increasing the mass ratio of Cu/Fe. This result was consistent with the selectivity of the catalysts, and the amount of H₂ consumption for iron species at high temperatures increased with decreasing the mass ratio of Cu/Fe, indicating that the catalysts with larger amount of iron had excellent reduction ability at high temperatures owe to the increasing of the amount of Fe₂O₃, it may be one reason for better N₂ selectivity.

From the results of XPS and TPR, we can conclude that Cu²⁺ was a main factor to improve the activity and N₂ selectivity. Furthermore, the rate-determine step ($\text{NH}_3 + \text{O}_2 \rightarrow \text{NO}_x + \text{H}_2\text{O}$) happened at CuO sites then selective catalytic reduction of NO_x to N₂ at Cu²⁺ sites. In addition, Fe³⁺ could play an important role in increasing the N₂ selectivity above 400 °C.

Moreover, we also studied the reduction of iron species of Fe₁/ZSM-5. The H₂ consumption peaks β_1 – β_3 appeared at 448, 568, and 646 °C. From Fig. 8 we found that the reduction temperatures

Fig.8 TPR profiles of Fe_{0.25}Cu_{0.75}/ZSM-5 (a), Fe_{0.50}Cu_{0.50}/ZSM-5 (b), Fe_{0.75}Cu_{0.25}/ZSM-5 (c), and Fe₁/ZSM-5 (d)

of copper species moved to lower values with decreasing loading amount of copper, and the reduction temperatures of iron species shifted to lower values as the amount of iron decreased, the gradual shifts of reduction temperature may be due to the interaction between copper and iron species.²¹ The interaction was beneficial to improve the reduction ability of the active species, which was considered as one reason for good activity.

3.6 NH₃-TPD result

In order to understand the strength and amount of different acid sites, temperature-programmed desorption of ammonia was carried out. Fig.9 showed the NH₃-TPD profiles on ZSM-5 and Fe_{1-x}Cu_x/ZSM-5 catalysts.

Two main desorption peaks were found at about 211 and 436 °C for parent ZSM-5, corresponding to the weak and the strong acid sites, respectively. The desorption peak at the lower temperatures had been proven to generate from the physically adsorbed NH₃ or ammonium species,²⁷ probably hydrogen bonded, but not the ammonia species adsorbed on acid sites and the peak at higher temperatures was ascribed to NH₃ strongly adsorbed which could determine the property of acid sites.

The peak β for the Fe_{0.25}Cu_{0.75}/ZSM-5 at about 365 °C moved to a lower temperature than parent ZSM-5, which implied that the

Fig.9 TPD profiles of pure ZSM-5 (a), Fe_{0.25}Cu_{0.75}/ZSM-5 (b), Fe_{0.50}Cu_{0.50}/ZSM-5 (c), and Fe_{0.75}Cu_{0.25}/ZSM-5 (d)

Table 3 H₂ consumption of catalysts

Sample	Peak type	Peak temperature/°C	H ₂ consumption/($\mu\text{mol} \cdot \text{g}^{-1}$)
Fe _{0.25} Cu _{0.75} /ZSM-5	α_1	245	44.1
	α_2	300	53.3
	β_1	349	37.5
	β_2	384	42.2
	β_3	469	146.3
Fe _{0.50} Cu _{0.50} /ZSM-5	α_1	220	40.9
	α_2	300	36.2
	β_1	387	45.6
	β_2	444	44.7
	β_3	523	195.8
Fe _{0.75} Cu _{0.25} /ZSM-5	α_1	216	38.1
	α_2	296	35.8
	β_1	393	48.0
	β_2	478	117.8
	β_3	588	289.2
Fe ₁ /ZSM-5	β_1	448	88.4
	β_2	568	137.3
	β_3	646	403.5

strength of the peak β was decreased. In addition, the peak β shifted to a higher temperature with increasing the amount of iron, which may be caused by the interaction between copper and iron. It could explain that the activity turned worse at lower temperatures after increasing the iron content.

From the literature,¹² the FTIR result showed that NH_3 was adsorbed on the acid sites and the intensity of adsorbed ammonia species decreased with the temperature increasing during researching the IR spectra in flowing NH_3 and O_2 . Accordingly, we could deduce that larger number of acid sites was conducive to better activity. Moreover, from Fig.9 we also found that the area of peak β of $\text{Fe}_{1-x}\text{Cu}_x/\text{ZSM-5}$ catalysts increased with increasing the mass ratio of Cu/Fe, and $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ catalyst with the largest mass ratio of Cu/Fe in this study had the best activity, indicating that the increase of the number of acid sites was corresponded to the activity date, we could deduce that the activity of the catalysts had a close relationship with the acid amounts. In other words, the conversion of ammonia increased with increasing the acid amounts.

4 Conclusions

In summary, the iron and copper bimetallic catalysts demonstrated high activity and excellent selectivity of N_2 . The activity and N_2 selectivity in low temperature range were increased by increasing the mass ratio of Cu/Fe. In contrast, the higher N_2 selectivity was achieved with larger amount of iron at higher temperatures. $\text{Fe}_{0.25}\text{Cu}_{0.75}/\text{ZSM-5}$ had the best activity and high N_2 selectivity. The characterization results indicated that strong interaction between copper and iron species was obtained. And the Cu and Fe species were mostly presented as Cu^{2+} and Fe^{3+} , respectively. The activity increased with the increase in the amount of the Cu active species at low temperatures. Larger amount of Fe_2O_3 was a probable reason for better N_2 selectivity at high temperatures. In addition, the acid content, strength of catalysts, and the redox property of catalysts also played important roles in the ammonia oxidation reaction.

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