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Effect of calcination temperatures on ammonia selective catalytic oxidation by Cu/SSZ-13 catalysts

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Abstract. The Cu/SSZ-13 catalysts prepared by the impregnation method were applied to ammonia selective catalytic oxidation (NH₃-SCO). The effect of the calcination temperature on the catalytic performance was investigated. The structural and physico-chemical properties of the catalysts were investigated by XRD, N₂ adsorption-desorption isotherms, XPS, NH₃-TPD and H₂-TPR. It is found that the increase of calcination temperature favors the ammonia conversion at low temperatures. Meanwhile, overhigh calcination temperature (>500 °C) would lead to the decrease of catalytic activity. The Cu/SSZ-13-500 catalyst shows the highest catalytic performance and exhibits more than 70% NH₃ conversion at 200 °C. The NH₃-TPD and H₂-TPR results confirmed that Cu/SSZ-13-500 owned more Lewis acid sites and CuO species, which were beneficial for ammonia adsorption and activation.

1. Introduction

As one of the atmospheric pollutants, ammonia (NH₃) mainly comes from agricultural, industrial and mobile sources. For example, slipping ammonia caused by incomplete reaction of the NH₃-SCR system can be discharged directly into the atmosphere, which is harmful to human health and environment [1]. Therefore, it is necessary to reduce ammonia slipping from the steam. Ammonia selective catalytic oxidation (NH₃-SCO) is a promising technology to convert slipping ammonia into harmless nitrogen. However, one of the major problems in NH₃-SCO technology is to develop catalysts combined high low-temperature catalytic activity with N₂ selectivity. The Cu/CHA catalysts have been reported to be effective for NH₃-SCO reaction [2]. However, the effect of calcination temperatures on its catalytic performance has not been studied yet.

In this work, Cu/SSZ-13 catalysts calcinated at various temperatures were prepared by the conventional impregnation method. The results show that calcination temperature has great effect on the acidic and redox properties of Cu/SSZ-13 catalysts and thus affect the catalytic performance at low temperatures.



2. Experimental section

2.1. Catalysts preparation

Cu/SSZ-13 catalysts were prepared by the impregnation method and calcinated at various temperatures (400, 450, 500 and 550 °C). The loading content of Cu were 10 wt.% (the weight percent of copper oxide to H/SSZ-13). The samples were denoted as Cu/SSZ-13-X, where X represents corresponding calcination temperature.

2.2. Physical and chemical characterization

N₂ adsorption-desorption isotherms were obtained by Belsorp Max II analyzer (MicrotracBEL, Japan). The specific surface area and pore volume are calculated by BET method.

X-ray diffraction (XRD) patterns were tested by D/Max-2200 diffractometer (Bruker, Germany). The scanning range was from 5 to 50° and the scanning speed was 5°·min⁻¹.

X-ray photoelectron spectrum (XPS) tests were conducted by Escalab 250Xi instrument (Thermo Fisher Scientific, USA).

Temperature programmed desorption of ammonia (NH₃-TPD) experiments were performed in a fixed bed reactor equipped with MultiGas TM 2030 HS FTIR analyzer (MKS, USA). Before test, the samples (0.1 g) were pretreated at 300 °C with N₂ flow and cooled down to 100 °C. 500 ppm NH₃ was injected into reactor until adsorption saturation. Then the samples were purged under N₂ atmosphere to sweep the physically adsorbed ammonia. Finally, the desorption results were obtained from 100 to 750 °C and the heating rate was 10°·min⁻¹.

Temperature programmed reduction with H₂ (H₂-TPR) experiments were measured in AutoChem II 2920 instrument (Micromeritics, USA). The samples (0.1 g) were pretreated at 300 °C in Ar atmosphere and cooled down to 50 °C. Then the samples were reduced by 5 vol.% H₂/Ar from 50 to 600 °C and the heating rate was 10°·min⁻¹.

2.3. Catalytic performance tests

The catalytic performance was evaluated at atmospheric pressure in a laboratory-scale fixed bed reactor and measured from 150 to 400 °C. The total flow rate was 500 mL·min⁻¹ and the weight hourly space velocity (WHSV) was 600, 000 mL·g⁻¹·h⁻¹.

3. Results and discussion

3.1. NH₃-SCO catalytic performance

NH₃-SCO catalytic performances of Cu/SSZ-13-X catalysts are shown in Fig.1 and Fig.2. All the samples showed nearly 80% NH₃ conversion and over 90% N₂ selectivity from 250 to 400 °C at high space velocity, indicating that the catalysts had good catalytic performance. In particular, Cu/SSZ-13-500 catalyst exhibited the best activity from 150 to 250 °C and had the widest temperature window. The generated by-products at low temperature are mostly N₂O, while those at high temperature are mostly NO_x.

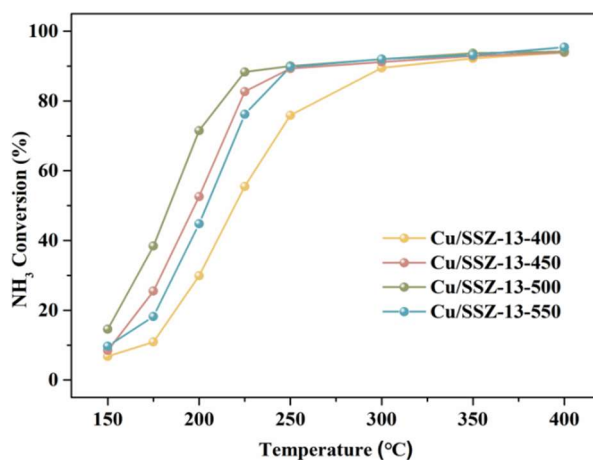


Figure 1. The NH_3 conversion of Cu/SSZ-13-X catalysts with different calcination temperatures.

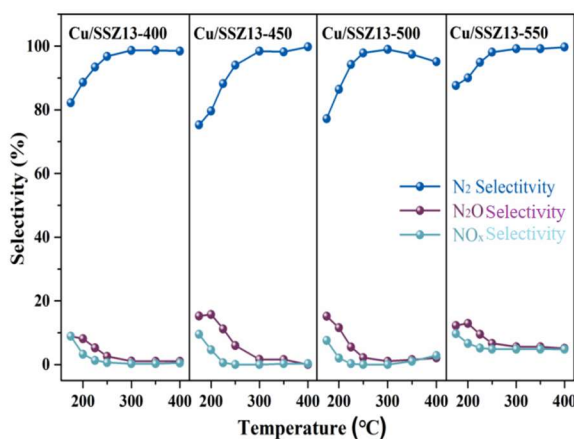


Figure 2. The selectivity of Cu/SSZ-13-X catalysts with different calcination temperatures.

3.2. BET and XRD results

Table 1 shows the BET results of Cu/SSZ-13-X catalysts. As seen from Table 1, the introduction of copper lead to the decrease of specific surface area (S_{BET}) and pore volume (V_{pore}) of H/SSZ-13 support. This phenomenon may be due to the blocking of pore structure of H/SSZ-13 caused by copper species. Fig. 3 shows the XRD patterns of H/SSZ-13 and Cu/SSZ-13-X catalysts. It is clearly seen that Cu/SSZ-13-X catalysts still maintain the typical structure of chabazite (CHA). Besides, the obvious characteristic peak ascribed to CuO were detected in 35.3° and 38.5° among all samples. The average sizes of CuO (D_{CuO}) were calculated by Scherrer equation and showed in Table 1. It can be inferred that Cu/SSZ-13-500 had the smallest particles of CuO species.

Table 1. The physical properties of H/SSZ-13 and Cu/SSZ-13-X catalysts with different calcination temperatures.

Samples	$S_{\text{BET}}(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{pore}}(\text{cm}^3 \cdot \text{g}^{-1})$	$D_{\text{BJH}}(\text{nm})$	$D_{\text{CuO}}(\text{nm})$
H/SSZ-13	697.6	0.35	2.03	-
Cu/SSZ-13-400	533.4	0.32	2.37	24.7
Cu/SSZ-13-450	589.1	0.28	1.87	23.3
Cu/SSZ-13-500	609.4	0.28	1.86	18.4
Cu/SSZ-13-550	621.0	0.29	1.86	23.6

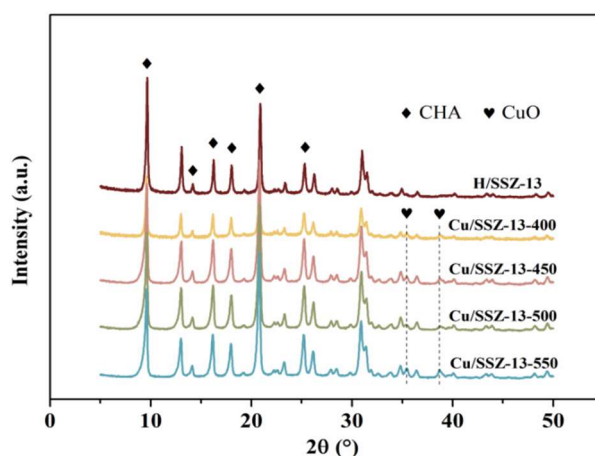


Figure 3. The XRD profiles of Cu/SSZ-13-X catalysts with different calcination temperatures.

3.3. XPS results

XPS analysis is a method to determine the content and valence of copper species on the catalyst surface. As shown in Fig. 4, the Cu 2p_{3/2} peaks at around 935.8 eV and the satellite peaks (940.0 ~ 950.0 eV) were ascribed to Cu(II), while the peaks at around 933.3 eV were assigned to Cu(I) and Cu⁰ [3]. The ratios of Cu(II)/Cu(I)+Cu⁰ were calculated and summarized in Table 2 to further study the contents of different copper species on the catalyst surface. As shown in Table 2, Cu/SSZ-13-500 contained the most contents of Cu(II), followed by Cu/SSZ-13-450 and Cu/SSZ-13-550, at last Cu/SSZ-13-400.

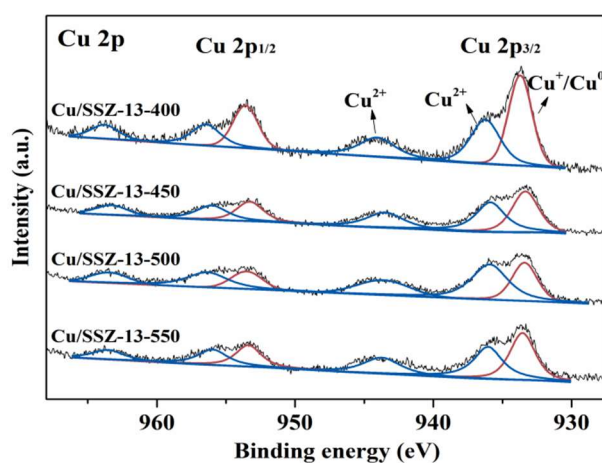


Figure 4. The XPS profiles of Cu/SSZ-13-X catalysts with different calcination temperatures.

Table 2. The amount ratio of surface Cu(II) and Cu(I)+Cu⁰, NH₃ desorption amounts and H₂ consumption of Cu/SSZ-13-X catalysts with different calcination temperatures.

Samples	$\frac{\text{Cu(II)}}{\text{Cu(I)} + \text{Cu}^0}$	NH ₃ desorption amounts ($\mu\text{mol} \cdot \text{m}^{-2}$)			H ₂ consumption ($\text{mmol} \cdot \text{g}^{-1}$)		
		I	II	III	CuO	Cu(I)	Total
H/SSZ-13	-	0.23	-	1.00	-	-	-
Cu/SSZ-13-400	0.71	0.41	0.50	0.67	0.39	0.53	0.92
Cu/SSZ-13-450	0.94	0.41	0.62	0.79	0.39	0.51	0.90
Cu/SSZ-13-500	1.54	0.09	0.75	0.81	0.54	0.42	0.96
Cu/SSZ-13-550	0.91	0.59	0.69	0.82	0.38	0.41	0.79

3.4. NH_3 -TPD results

As seen in Fig. 5, the NH_3 -TPD curves of Cu/SSZ-13-X catalysts mainly contain three different NH_3 desorption peaks, which are marked as peak I, II and III. Among them, the desorption peak I can be attributed to the physically absorbed ammonia (weak acid sites). The desorption peak II can be ascribed to the ammonia absorbed on the Lewis acid site generated by copper species (middle acid sites). However, the desorption peak III is assigned to the ammonia absorbed on Brønsted acid sites related to the framework (strong acid sites) [4-5]. Table 2 shows the ammonia desorption amounts of different acid sites. It is well known that the Lewis acid sites were found to be more active in the NH_3 -SCO reaction at low temperatures. Cu/SSZ-13-500 exhibited the highest amount of middle acid sites ($0.75 \text{ } \mu\text{mol} \cdot \text{m}^{-2}$), indicating its best ammonia adsorption capacity.

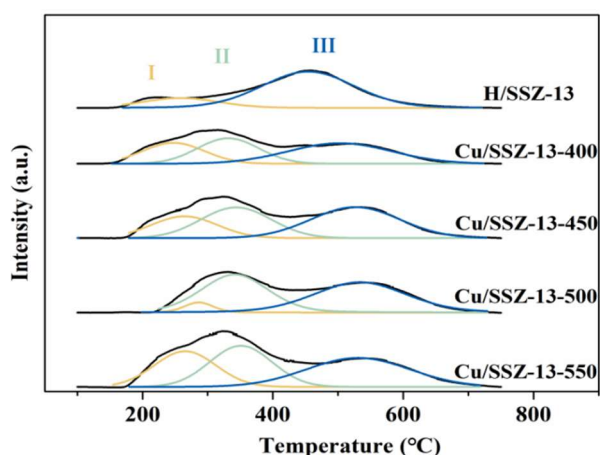


Figure 5. The NH_3 -TPD profiles of Cu/SSZ-13-X catalysts with different calcination temperatures.

3.5. H_2 -TPR results

Fig. 6 shows the H_2 -TPR profiles of Cu/SSZ-13-X catalysts. It can be easily seen that there are two obvious reduction peaks obtained among all samples. The peak α can be ascribed to the reduction of surface CuO to Cu^0 and the peak β can be assigned to the reduction of Cu(I) to Cu^0 [6]. Besides, the area of each reduction peak reflects the contents of each copper species. As seen from Table 2, the surface CuO of Cu/SSZ-13-500 (0.54 mmol/g) is much higher than that of other samples. Many studies confirmed that CuO species is the most active component among Cu-based catalysts in NH_3 -SCO reaction [7]. According to the results of NH_3 -SCO catalytic performance, high CuO ratio is the key factor for best activity of Cu/SSZ-13-500.

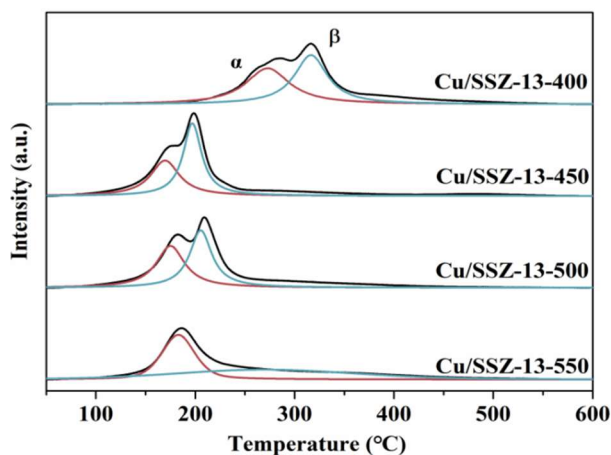


Figure 6. The H_2 -TPR profiles of Cu/SSZ-13-X catalysts with different calcination temperatures.

4. Conclusion

Cu/SSZ-13 catalysts with different calcination temperatures were synthesized by impregnation method and used for NH₃-SCO reaction. They exhibited good NH₃ conversion and N₂ selectivity in a wide temperature window. The relationship of their structure and different performance at low temperatures was explored. The calcination temperature has great influence on the properties of copper species and acid sites. Both the acidic and redox properties in the Cu/SSZ-13-X catalysts determined their NH₃-SCO performance. The higher CuO ratio and more Lewis acid sites enabled Cu/SSZ-13-500 catalyst exhibited the better NH₃-SCO performance.

Acknowledgments

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