The enhanced catalytic activity of Cu/SAPO-34 by ion exchange method for selective catalytic reduction of nitric oxide

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Abstract

The Cu/SAPO-34 catalysts were prepared via the ion exchange process for achieving improved catalytic activity. Effects of various parameters including copper ions sources, copper ions loadings and ion exchange temperature on catalyst performance of the Cu/SAPO-34 catalysts were investigated. The results showed that the Cu/SAPO-34 catalysts roughly maintained similar cubic-like morphology and crystalline structure with the SAPO-34 catalyst, and achieved enhanced catalytic activity. Among various copper ion sources, the Cu/SAPO-34 catalyst using Cu(CH$_3$COO)$_2$ as copper ion source demonstrated high nitric oxide conversion rate. Increasing the copper ion loadings, the nitric oxide conversion rate of the Cu/SAPO-34 catalysts achieved significant improvement. However, when the copper ion loadings exceeded 0.01 mol, the nitric oxide conversion rate began to decline. The catalytic activity of the Cu/SAPO-34 also closely depended on ion exchange temperature. The nitric oxide conversion rate of the Cu/SAPO-34 catalyst showed a trend of first increasing and then decreasing with the improvement of ion exchange temperature, and the recommended ion exchange temperature was 60 °C. Hydrothermal aging treatment further confirmed the good stability of the Cu/SAPO-34 catalyst. Moreover, kinetic investigation was carried out, which was in agreement with the SCR results.

1. Introduction

Nitrogen oxides (NO$_x$) emissions from fossil-fuel power plants and automobiles are responsible for environmental issues such as photochemical smog, ozone depletion, and acid rain [1–7]. Fortunately, there is a growing concern for our environment protection, and many promising technologies such as selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), three-way catalysis, and pulsed corona discharge are adopted to solve those issues [8]. Especially, SCR with NH$_3$ as the reducer (NH$_3$-SCR) has been recognized as the most effective way of reducing NOx emission. NH$_3$-SCR technology is a process in which NH$_3$ reacts selectively with NOx over catalyst surface to produce harmless N$_2$ and H$_2$O at a certain temperature (generally about 150 °C–500 °C). Furthermore, as the core of this technology, various SCR catalysts have been widely explored in the past few decades [9]. Among them, zeolite-based SCR catalysts have attracted a great deal of attention for their merits of high nitric oxide conversion rate in relatively wide temperature windows and low cost [10]. Early efforts are always focused on zeolite secony mobil-5 (ZSM-5), Beta zeolite, etc. Recently, the silicoaluminophosphate-34 (SAPO-34) catalyst has been widely concerned for high catalytic activity in the denitration process [11–13]. However, the SAPO-34 catalyst is very sensitive to a humid environment, and is prone to hydrolysis, resulting in serious structural deterioration because of the irreversible hydrolysis of bridge hydroxyl group [14].
To solve this problem, many researchers adopted the method of incorporating Cu$^{2+}$ into the SAPO-34 catalysts to improve the SCR activity [15]. Wang et al fabricated the Cu/SAPO-34 catalysts by using ion-exchange process and found that Cu$^{2+}$ species existing as isolated ions were active sites of SCR reaction [16]. Petitto and Delahay investigated the relationship between the Si content and the catalytic activity of the Cu/SAPO-34 catalysts. Their results demonstrated the low Si content was beneficial to achieve high nitric oxide conversions [17]. Xue et al prepared the Cu/SAPO-34 catalysts by loading various Cu$^{2+}$ concentrations via ion exchange process, and showed that excessive Cu$^{2+}$ loading would inhibited the nitric oxide conversion [18]. Niu et al studied the influences of calcination temperatures, Cu$^{2+}$ sources, and co-template concentrations on catalytic performance of the Cu/SAPO-34 catalysts, and found that the Cu/SAPO-34 catalyst with ca. 3.44% Cu$^{2+}$ loading at the calcination temperatures of 750 °C possessed high nitric oxide conversion [19]. Liu et al presented their work on the Cu/SAPO-34 catalysts obtained via ion exchange process. They reported that incorporated Cu$^{2+}$ into SAPO-34 improved the activity at high temperatures, which suppressed the competitive oxidation of NH$_3$ [20].

These previous researches indicated the catalytic performance of the Cu/SAPO-34 catalysts were markedly influenced by several important parameters such as ion exchange conditions. However, they were not comprehensively considered by the researchers. Inspired by the works of these early pioneers, here, we prepared the Cu/SAPO-34 catalysts by the ion-exchange method, systemically investigated the influences of various parameters such as copper ions sources, copper ions loadings and ion exchange temperature on catalyst activity of Cu/SAPO-34 catalysts, and characterized the morphology, structure, and chemical composition of Cu/SAPO-34 catalysts by SEM, XRD, XPS and N$_2$ adsorption techniques.

2. Experimental

2.1. Catalysts fabrication

The SAPO-34 catalyst was firstly prepared via the hydrothermal route. H$_3$PO$_4$ (26.12 g) was dissolved in deionized water (120 g) with stirring, and then pseudo-boehmite (15.99 g) was slowly added under continuous agitation for 12 h. Subsequently, silica sol (15.99 g) and triethylamine (40.40 g) were added in the above gel under continuous stirring, respectively. The resultant mixture was sealed in a 100-ml Teflon-lined autoclave and crystallized in a drying oven for 72 h at 200 °C. Afterwards, the obtained products were centrifuged and washed with deionized water, then dried at 100 °C overnight, followed by calcinating at 550 °C for 6 h.

The Cu/SAPO-34 catalysts obtained by adjusting copper sources, copper loadings and exchange temperatures were fabricated via the exchange method. Initially, 10 g of SAPO-34 powder was mixed with 200 ml of NH$_4$NO$_3$ (0.1 M) at 80 °C for 2 h, and then, it was washed with deionized water and dried at 110 °C for 5 h. Secondly, mixing various copper sources (CuSO$_4$, Cu(NO$_3$)$_2$, CuCl$_2$, and Cu(COOH)$_2$) at different exchange temperature (40, 60, or 90 °C) for 3 h. Finally, these products were dried by deionized water, dried at 110 °C for 12 h, followed by calcinating at 550 °C for 5 h.

2.2. Characterization

The crystal structure of catalysts was identified using an x-ray diffractometer (XRD, D/Max-2400). The morphologies of catalysts were examined by scanning electron microscope (SEM, Philips XL30 FEG). The chemical composition of catalysts was analyzed using x-ray photoelectron spectroscopy with an Al-Ka source (XPS, Thermo SCIENTIFIC ESCALAB 250). The specific BET surface area of catalysts was analyzed adopting N$_2$ adsorption-desorption measurements on a Quantachrome autosorb-iQ$_2$ Analyzer. NH$_3$-SCR technique generally adopted NH$_3$ as the reductant to react with nitric oxide to produce harmless N$_2$ and H$_2$O. The SCR reaction was as follows:

$$4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$$

The SCR activity of catalysts was measured in a fixed-bed reactor, and the test process could refer to our previous paper (figure 1) [21]. To investigate the hydrothermal stability of Cu/SAPO-34 samples, the catalysts were hydrothermally aged at 750 °C for 16 h in a flow of 10% H$_2$O/air. The hydrothermal aged sample was named as A-Cu/SAPO-34.

3. Results and discussion

3.1. Structure, morphology, and catalytic activity

X-ray analysis was generally used to verify the crystalline phases of nanomaterials. XRD results of the SAPO-34 and Cu/SAPO-34 catalysts were presented (figure 2). As observed, both the samples exhibited similar XRD patterns and the same characteristic diffraction peaks ($2\theta = 9.5°, 12.7°, 16.0°, 20.8°, 26.0°$, and $31.0°$) were
observed, which agreed with the standard SAPO-34 (CHA type) structure well [22, 23]. Additionally, we also found that introducing Cu precursor did not induce an evident impact on the crystal structure of the Cu/SAPO-34 catalyst, and only led to peak intensity decline.

The surface morphologies of the two catalysts were examined by SEM (figure 3). The former demonstrated cubic-like nanostructure with average sizes of about 900 nm. After copper ions were loaded, the obtained Cu/SAPO-34 catalyst maintained similar morphology with copper ions-free catalyst, but the average dimension decreased to about 700 nm. Furthermore, the crystal structure of the Cu/SAPO-34 became slightly poor due to some fragments aggregated on the surface of the Cu/SAPO-34 catalyst, which well supported the XRD analysis.

The XPS wide scan spectra in figure 4(a) approved the presence of Al, Si, Cu, P, C, N, and O in the Cu/SAPO-34, implying it consisted of the SAPO-34 structure containing copper ions. Figure 4(b) presented the high resolution spectrum of Cu 2p (the 2p orbital of Cu element), which underwent spin–orbit splitting, producing two spin–orbit peaks, namely Cu 2p3/2 and Cu 2p1/2. The binding energies of the two spin–orbit contribution were 933.3 and 953.1 eV, respectively [24]. Generally, these two peaks were used as the characteristic to determine copper ions, implying that copper ions had been successfully loaded on the SAPO-34 surface and mainly existed as the Cu2+ state [20].

Figure 5 presented the nitrogen adsorption-desorption isotherms of the two catalysts. Both of them demonstrated typical type IV curves with the hysteresis loop, and the corresponding BET surface area was
25.49 m² g⁻¹ and 31.78 m² g⁻¹, respectively, which showed a facilitation effect towards the SCR reaction after loading copper ions.

Figure 6 compared the nitric oxide conversion rate of two catalysts at a temperature range from 100 to 550 °C. We can see that the conversion rate of the SAPO-34 ranged from 83% to 84%, while after loading copper ions, the catalytic activity of the Cu/SAPO-34 achieved a great improvement at 175 °C–550 °C, and the conversion rate was almost 100%. Therefore, it can be concluded that the loading of copper ions greatly improved the catalytic activity of the SAPO-34 catalysts because of introducing more active sites for SCR reaction.

3.2. Effect of copper ions sources on catalytic activity
The loading of active copper ions in the SAPO-34 catalyst played a decisive part in the improvement of its catalytic performance, and the copper ions sources were one of the key parameters [19]. The crystalline phases of the Cu/SAPO-34 catalysts synthesized via different copper ions sources were analyzed by XRD patterns. The CHA characteristic peaks were observed in the four catalysts (figure 7). There were no significant changes in diffraction peaks with different copper ions sources.

Figure 8 showed the nitric oxide conversion rate of the Cu/SAPO-34 catalysts from four copper ions sources. The nitric oxide conversion rate of the four catalysts drastically increased with the improvement of reaction temperature and reached a steady state. Further increasing reaction temperature beyond 450 °C, the nitric oxide conversion rate began to deduce. The maximal catalytic activity and widest active window (175 °C–550 °C) were achieved when using Cu(CH₃COOH)₂ as the copper ions sources.

3.3. Effect of copper ions loadings on catalytic activity
After revealed the relationship between copper ions sources and catalytic activity, we further investigated the influence of copper ions loadings on the structure and SCR performance of the Cu/SAPO-34 catalysts. Figure 9 provided the XRD patterns of the Cu/SAPO-34 catalysts from several copper ions loadings. These Cu/SAPO-34 catalysts still demonstrated CHA structures. The slight difference was that the peak intensities declined with the increase of copper ions loadings. Figure 10 showed the nitric oxide conversion rate of the Cu/SAPO-34 catalysts from different loadings. The catalytic performance of the Cu/SAPO-34 catalysts achieved improvement as the increase in the copper ion loading up to 0.01 mol, however, further increasing the
Figure 4. XPS spectra of the Cu/SAPO-34 catalyst: (a) a wide scan spectrum (b) Cu 2p spectrum.

Figure 5. Nitrogen adsorption-desorption isotherms of two catalysts.
Figure 6. Nitric oxide conversion rate of two catalysts.

Figure 7. XRD patterns of the Cu/SAPO-34 catalysts from four copper ions sources.

Figure 8. Nitric oxide conversion rate of the Cu/SAPO-34 catalysts from four copper ions sources.
copper ion loading, the catalytic activity began to decline. The phenomena could be attributed to that high copper ions loading caused the accumulation of other copper species [19], which limited the location for Cu$^{2+}$ active sites in the SAPO-34 catalysts, not only affecting catalysis crystallinity but also decreasing the catalytic activity at high temperature [17].

3.4. Effect of ion exchange temperature on catalytic activity

The catalytic activity of the Cu/SAPO-34 also closely depended on ion exchange temperature. It was noticeable these Cu/SAPO-34 maintained CHA framework structure at different ion exchange temperature (figure 11). The diffraction peaks of the catalyst synthesized at 60 °C demonstrated high peak intensity. Figure 12 presented the conversion rate of nitric oxide of the Cu/SAPO-34 catalysts fabricated at various ion exchange temperature. Similarly, the nitric oxide conversion rate of the Cu/SAPO-34 catalyst showed a trend of first increasing and then decreasing with the improvement of ion exchange temperature. When the ion exchange temperature was set at 60 °C, high SCR activity was achieved, which agreed with the XRD result.

Additionally, the hydrothermal stability of Cu/SAPO-34 catalyst was further studied. As shown in figure 13, compared with the Cu/SAPO-34 catalyst, after hydrothermal aging treatment, the catalytic activity of the A-Cu/SAPO-34 did not significantly decline at the low-temperature range (100 °C–300 °C). Only when the reaction temperature exceeded 300 °C, the catalytic activity started to demonstrate slightly decrease, implying its good hydrothermal stability. Kinetic investigation was carried out to calculate the turnover frequency (TOF) and activation energy (Ea) of the Cu/SAPO-34 catalyst before and after hydrothermal treatment (figure 14) [25–27].
Figure 11. XRD patterns of the Cu/SAPO-34 catalysts at varied ion exchange temperature.

Figure 12. Nitric oxide conversion rate of the Cu/SAPO-34 catalysts at varied ion exchange temperature.

Figure 13. Nitric oxide conversion rate of the Cu/SAPO-34 and A-Cu/SAPO-34 catalysts.
The Ea value of the Cu/SAPO-34 catalyst obtained from the fitting lines was 41.98 kJ mol$^{-1}$. The hydrothermal treatment at 750 °C increased the Ea value to 44.23 kJ mol$^{-1}$, implying high energy barrier for the SCR reaction.

4. Conclusion

We prepared the SAPO-34 catalyst via hydrothermal synthesis and then introduced copper ions by ion exchange method. After doped with copper ions, the Cu/SAPO-34 catalyst did not demonstrate significantly change on structure and morphology. It was also easy to find that incorporating Cu$^{2+}$ into the SAPO-34 catalyst could improve its catalytic activity. When using Cu(CH$_3$COOH)$_2$ as the copper ions sources, the maximal catalytic activity and widest active window (175 °C–550 °C) were achieved. When Cu$^{2+}$ loading was more than 0.01 mol, the catalytic performance of the Cu/SAPO-34 catalyst began to decrease as a result of the accumulation of other copper species, limiting the location for Cu$^{2+}$ active sites in the SAPO-34. The nitric oxide conversion rate of the Cu/SAPO-34 catalyst increased with the improvement of ion exchange temperature, and started to decrease as the ion exchange temperature exceeded 60 °C. Hydrothermal aging treatment did not significantly decrease the catalytic activity of the Cu/SAPO-34 catalyst, further confirming its good stability. Moreover, kinetic investigation was conducted, which was consistent with the SCR results.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Kompio P G W A et al 2012 A new view on the relations between tungsten and vanadium in V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts for the selective reduction of NO with NH$_3$ J. Catal. 286 237–47
[2] Yang J C et al 2014 Experimental study on NO$_x$ reduction from staging combustion of high volatile pulverized coals. Part 1, Air staging Fuel Process. Technol. 126 266–75
[3] Huang X M et al 2015 Selective catalytic reduction of NO with NH$_3$ over V$_2$O$_5$ supported on TiO$_2$ and Al$_2$O$_3$: a comparative study J. Mol. Struct. 1098 289–97
[4] Ma Z R et al 2015 Impacts of niobia loading on active sites and surface acidity in NbO$_x$/CeO$_2$–ZrO$_2$ NH$_3$–SCR catalysts Appl. Catal. B 179 380–94
[5] Liu J et al 2019 Structure, synthesis, and catalytic properties of nanosize cerium-zirconium-based solid solutions in environmental catalysis Chinese J. Catal. 40 1438–87
[6] Liu J et al 2019 Aluminum hydroxide-mediated synthesis of mesoporous metal oxides by a mechanochemical nanocasting strategy J. Mater. Chem. A 7 22977–85
[7] Liu J et al 2018 Fe/Beta@SBA-15 core–shell catalyst: interface stable effect and propene poisoning resistance for NO abatement AIChE J. 64 3967–78
[8] Mahmoudi S et al 2010 NOx formation and selective non-catalytic reduction (SNCR) in a fluidized bed combustor of biomass Biomass Bioenergy. 34 1393–409
[9] Liu J et al 2011 Low-temperature selective catalytic reduction of NOx with NH3 over metal oxide and zeolite catalysts—a review Catal. Today 175 147–56
[10] Schwidder M et al 2008 The role of NO2 in the selective catalytic reduction of nitrogen oxides over Fe-ZSM-5 catalysts: active sites for the conversion of NO and of NO/NOx mixtures J. Catal. 259 96–103
[11] Suzuki K et al 2011 Ammonia IRMS-TPD measurements on Bronsted acidity of proton-formed SAPO-34 Phys. Chem. Chem. Phys. 13 3111–8
[12] Ishihara T et al 1994 Copper ion exchanged silicoaluminophosphate (SAPO) as a thermostable catalyst for selective reduction of NOx with hydrocarbons Stud. Surf. Sci. Catal. 84 1193–509
[13] Haw J et al 1996 Physical organic chemistry of solid acids: lessons from in situ NMR and theoretical chemistry Acc. Chem. Res. 29 259–67
[14] Mees F D P et al 2003 Improvement of the hydrothermal stability of SAPO-34 Chem. Commun. 144–5
[15] Wang J et al 2015 Improvement of low-temperature hydrothermal stability of Cu/SAPO-34 catalysts by Cu2+ species J. Catal. 322 84–90
[16] Wang L et al 2012 Location and nature of Cu species in Cu/SAPO-34 for selective catalytic reduction of NO with NH3 J. Catal. 289 21–9
[17] Petitto C et al 2015 Selective catalytic reduction of NOx by NH3 on Cu-SAPO-34 catalysts: influence of silicium content on the activity of calcined and hydrotreated samples Chem. Eng. J. 266 404–10
[18] Xue J et al 2013 Characterization of copper species over Cu/SAPO-34 in selective catalytic reduction of NOx with ammonia: relationships between active Cu sites and de-NOx performance at low temperature J. Catal. 297 56–64
[19] Niu C et al 2016 High hydrothermal stability of Cu–SAPO-34 catalysts for the NH3–SCR of NOx Chem. Eng. J. 294 254–63
[20] Liu X et al 2017 Evolution of copper species on Cu/SAPO-34 SCR catalysts upon hydrothermal aging Catal. Today 281 596–604
[21] Tao P et al 2017 Effects of V2O5 and WO3 loadings on the catalytic performance of V2O5-WO3/TiO2 catalyst for SCR of NO with NH3 Global NEST J. 19 168–6
[22] Sjovall H et al 2009 Detailed kinetic modeling of NH3 and H2O adsorption, and NH3 oxidation over Cu-ZSM-5 J. Phys. Chem. C 113 1393–405
[23] Wijayanti K et al 2015 Impact of sulfur oxide on NH3–SCR over Cu–SAPO-34 Appl. Catal. B 166–167 568–79
[24] Pauly N et al 2014 Determination of the Cu2p primary excitation spectra for Cu, Cu2O and CuO Surf. Sci. 620 17–22
[25] Liu J et al 2020 Deep understanding of strong metal interface confinement: a journey of Pd/FeOx catalysts ACS Catal. 10 8930–9
[26] Liu J et al 2018 Fe/Beta@SBA-15 core–shell catalyst: interface stable effect and propene poisoning resistance for NO abatement AIChE J. 63 3967–78
[27] Cao Y et al 2018 The influence of low-temperature hydration methods on the stability of Cu–SAPO-34 SCR catalyst Chem. Eng. J. 354 85–92