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Article

Chemical deactivation of Cu-SAPO-18 deNO_x catalyst caused by basic inorganic contaminants in diesel exhaust

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ABSTRACT

Contaminants (K, Na, Ca, and Mg) were introduced into Cu-SAPO-18 via incipient wetness impregnation to investigate their effect on the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) over Cu-SAPO-18. After the introduction of contaminants into Cu-SAPO-18, the quantity of acidic sites and Cu²⁺ species in catalyst decreases owing to the replacement of H⁺ and Cu²⁺ by K⁺, Na⁺, Ca²⁺, and Mg²⁺. Furthermore, the loss of isolated Cu²⁺ induces the generation of CuO and CuAl₂O₄-like phases, which causes further loss in the Brunauer-Emmett-Teller surface area of the catalyst. Consequently, the deNO_x performance of the contaminated Cu-SAPO-18 catalysts drops. Such decline in NH₃-SCR performance becomes more pronounced by increasing the contaminant contents from 0.5 to 1.0 mmol/g_{catal}. In addition, the deactivation influence of the contaminants on Cu-SAPO-18 is presented in the order of K > Na > Ca > Mg, which is consistent with the order of reduction of acidic sites. To a certain degree, the effect of the acidic sites on the deactivation of Cu-SAPO-18 might be more significant than that of isolated Cu²⁺ and the catalyst framework. Moreover, kinetic analysis of NH₃-SCR was conducted, and the results indicate that there is no influence of contaminants on the NH₃-SCR mechanism.

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1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH₃ as the reductant has been shown to be a well-established NO_x abatement technology in diesel exhaust aftertreatment systems [1–3]. Extensive investigations have been conducted on copper-ion-exchanged zeolite catalysts as potential NH₃-SCR catalysts [4–6]. Recently, small-pore-sized Cu-chabazite (CHA) molecular sieves, e.g., Cu-SSZ-13 and Cu-SAPO-34, have received extensive attention due to their extraordinary deNO_x activities,

broad activity temperature window, and high hydrothermal stability [5,7]. In addition, both Cu-SAPO-18 and Cu-SSZ-39 molecular sieves, which possess an AEI construction similar to CHA, exhibit exceptional NO conversion and hydrothermally stable properties [8–12]. In general, the deNO_x performance and hydrothermal resistance over copper-zeolite catalyst are related to active Cu²⁺ sites and acidic sites. Meanwhile, the amount of acidic sites and Cu²⁺ substances in Cu-SAPO-18 can be tuned by altering the quantity of Si and Cu [13–15], which could facilitate the selection of more effective and hydrother-

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mally stable Cu-SAPO-18 catalysts. These realities enable Cu-SAPO-18 as a potential alternative in diesel exhaust after-treatment systems.

In practical aftertreatment applications, the resistance of SCR catalysts to thermal and chemical damage is an especially significant issue [16]. The total mileage of diesel vehicles is considerably high, and SCR catalysts are repeatedly exposed to high temperatures during the operation of the engine, which could cause the breakdown of catalyst texture and the aggregation of metal active species [17]. Furthermore, some inorganic compositions (e.g., K, Na, S, P, Ca, and Mg), which are derived from the contaminants of biodiesel, and the lubricant and fuel additives, can gradually aggregate on the catalyst surface, resulting in gradual pore blocking and the loss of active sites of SCR catalysts [16–18]. Finally, SCR catalysts will undergo a decline in catalytic activity. The influence of alkali and alkaline earth metals on SCR catalysts has attracted more interest due to their significant content in diesel derivatives [18].

Recently, the deactivation of V_2O_5/WO_3-TiO_2 , caused by K, Na, Ca, and Mg, has been investigated, concluding that the introduction of these metals brings about the decrease in acidity and redox ability of the catalyst [19–21]. There are some reports on the effect of alkali and alkaline earth metals on the structure, acidity, and active species of different Cu-based zeolites. For instance, Fehrmann et al. [22] announced that Cu-zeolite catalytic agents, which had large surface area and strong acidity, showed favorable K resistance. However, Lezcano-Gonzalez et al. [17] reported that the contamination of Cu-SSZ-13 by Ca^{2+} led to pore blocking, resulting in its deactivation. Gao et al. [23] introduced Li^+ , K^+ , Cs^+ , Mg^{2+} , and Ca^{2+} into SSZ-13, resulting in the decrease of Brønsted acidic sites (H^+). Meanwhile, the remaining H^+ content is consistent with these hydrated metal ions diameters, which is presented in the order of $Mg^{2+} > Ca^{2+} \approx Li^+ > Na^+ > K^+ > Cs^+$. Additionally, when K^+ was introduced into Cu-SAPO-34, the Cu^{2+} content and the number of acidic sites is reduced, leading to the decrease in NH_3 -SCR activity [24]. However, to our knowledge, there is no comprehensive study regarding the effect of contaminants (K, Na, Ca, and Mg) on the framework, the content of copper species, and the availability of acidic sites on Cu-SAPO-18.

Consequently, Cu-SAPO-18 catalyst, doped with diverse contaminants (K, Na, Ca, and Mg), was prepared, with the aim of elucidating the impact of these metals on the construction, availability of acidic sites and content of copper species on Cu-SAPO-18. NO conversion is discussed based on the variation in these physicochemical properties of Cu-SAPO-18. Additionally, the influence of metals on the NH_3 -SCR reaction was also investigated through kinetic examination of NH_3 -SCR.

2. Experimental

2.1. Preparation of the fresh and contaminated Cu-SAPO-18 catalysts

The Cu-SAPO-18 catalyst ($SiO_2:Al_2O_3:P_2O_5:Cu-TETA:DIPEA:H_2O = 0.6:1:0.9:0.1:1.65:45$) was directly synthesized, and the elaborate synthesis procedure was explained in other studies

[11,13]. The final Cu-SAPO-18 powder was doped with K, Na, Ca, and Mg, containing 0.5 and 1.0 mmol/ g_{catal} , by instilling the desired concentration of KNO_3 , $NaNO_3$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$ solution into the Cu-SAPO-18 catalyst. Then, the slurries were dried under air overnight at 90 °C. Next, the powders were calcined at 600 °C for 5 h. The resulting powders were labeled Cu/M-SAPO-18(x), where “M” denotes the impregnated metals (M = K, Na, Ca, and Mg) and “x” stands for the metal amount. Finally, a certain amount of Cu/M-SAPO-18(x) was coated on the cordierite, respectively. The obtained monolithic catalysts were applied to evaluate NO conversion. More details are displayed in the Supporting Information.

2.2. Catalyst characterization

N_2 adsorption-desorption was conducted on the V-Sorb 2800 P instrument to obtain the pore volume and BET specific surface area of the catalysts, and the samples were degassed at 250 °C for 5 h under vacuum before the measurement. ^{27}Al MAS nuclear magnetic resonance (NMR) spectra were obtained on an Agilent 600 DD2 spectrometer with a Larmor frequency of 156.25 MHz. The X-ray diffraction (XRD) charts were acquired from an X'Pert Pro X-ray diffractometer with $Cu-K\alpha$ radiation, at 40 mA and 40 kV. H_2 temperature-programmed reduction (H_2 -TPR) was recorded on an automatic chemisorption instrument (Auto Chem 2920II). The catalyst (50 mg) was pre-processed under Ar gas flow at 550 °C for 1.5 h and, subsequently, the catalyst was heated from ambient temperature to 1000 °C under a 10% H_2 /Ar gas mixture. As for NH_3 temperature-programmed desorption (NH_3 -TPD), the catalyst pre-treatment process was consistent with that of TPR. The NH_3 adsorption of catalyst took place at 100 °C, and the process was retained for 45 min. Ultimately, the catalyst temperature was elevated from 100 to 600 °C under Ar gas flow. The electron paramagnetic resonance (EPR) spectrum was obtained with a JEOL-FA200 apparatus. The catalyst (10 mg) placed in a tube was subjected to EPR measurements at -170 °C with a modulated frequency of 100 kHz and an amplitude of 5 G.

2.3. NH_3 -SCR performance and the dynamic measurement

The catalytic performance of monolithic Cu-SAPO-18 was carried out in a stainless-steel tubular reactor under a fixed bed. A total of 250 g/L of Cu-SAPO-18 was inserted into the constant temperature zone of the reactor. Then, a thermocouple was stuck into the uniform temperature region to detect the bed temperature. The simulated reactant gases consisted of NO, NH_3 , O_2 , and H_2O , which accounted for 0.1%, 0.11%, 5%, and 10%, respectively. Meanwhile, N_2 was used as a carrier gas to purge these reactant gases into the reactor. The H_2O was produced by an injection pump (TYD01-01) containing deionized water. The overall gas flow velocity was 1045 mL/min. After the finish of the SCR reaction inside the catalyst bed, the remaining content of NO was investigated in a waste gas emission analyzer (FGA-4100-5G). Moreover, an NH_3 trap was installed in front of the analyzer to avert errors arising from excessive NH_3 . The NO conversion was computed as

Table 1

The element composition, BET surface area, and pore volume of catalysts with and without contaminants.

Catalyst	Si:Al:P molar ratio	Cu content (wt%)	Metal content (mmol/g _{catal})	A _{BET} (m ² /g)	Pore volume (cm ³ /g)
Cu-SAPO-18	0.27:0.68:1.0	2.10	—	673	0.241
Cu/K-SAPO-18(0.5)	0.27:0.68:1.0	2.11	0.47	597	0.212
Cu/Na-SAPO-18(0.5)	0.27:0.68:1.0	2.08	0.45	587	0.206
Cu/Ca-SAPO-18(0.5)	0.27:0.68:1.0	2.08	0.44	601	0.214
Cu/Mg-SAPO-18(0.5)	0.27:0.68:1.0	2.09	0.42	612	0.218
Cu/K-SAPO-18(1.0)	0.27:0.68:1.0	2.10	0.92	403	0.143
Cu/Na-SAPO-18(1.0)	0.27:0.68:1.0	2.11	1.0	296	0.101
Cu/Ca-SAPO-18(1.0)	0.27:0.68:1.0	2.10	0.97	408	0.143
Cu/Mg-SAPO-18(1.0)	0.27:0.68:1.0	2.11	1.0	417	0.146

$$([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}) / [\text{NO}]_{\text{inlet}} \times 100\%.$$

The NH₃-SCR dynamic tests over fresh and contaminated Cu-SAPO-18 were executed in the reactor described above, using 60 g/L monolithic catalyst. The concentration of the simulated reaction gas and the corresponding overall gas flow velocity are the same as depicted above. Dynamic steady-state evaluations were conducted, ranging from 140 to 190 °C. The exhaust fumes discharged from the fixed bed were monitored by a flume emission analyzer. The calculation formula for the NH₃-SCR reaction rates is exhibited in the Supporting Information.

3. Results and discussion

3.1. Chemical composition and textural characteristics

Table 1 shows the elemental compositions of the fresh and contaminated Cu-SAPO-18 samples, and the compositions were determined by ICP-OES technology. The molar ratio of Si:Al:P in all samples is 0.27:0.68:1.0. The Cu content in fresh Cu-SAPO-18 is 2.10 wt%, and other contaminated samples present similar Cu content. Furthermore, the contents of K, Na, Ca, and Mg in Cu-SAPO-18 are analogous to the theoretical results (0.5 mmol/g_{catal} or 1.0 mmol/g_{catal}).

To determine the influence of contaminants on the Cu-SAPO-18 structure, XRD and BET tests were conducted. Fig.

1a illustrates that both fresh Cu-SAPO-18 and Cu/M-SAPO-18(0.5) catalysts exhibit the typical AEI structure [11,25] and retain similar intensities in diffraction peaks, suggesting that the loading of 0.50 mmol/g_{catal} contaminants has little effect on AEI structure or the crystallinity of Cu-SAPO-18. Moreover, there are no CuO nor K, Na, Ca, or Mg peaks observed, which indicates that they are highly dispersed on Cu-SAPO-18 or that there is a detection limitation because of their small sizes [3]. When the metal content increases to 1.0 mmol/g_{catal}, the Cu/K-, Cu/Ca-, and Cu/Mg-SAPO-18(1.0) catalysts all preserve the typical AEI framework but is accompanied by a decrease in their crystallinity. This reveals that their zeolite frameworks suffer some damage. For the Cu/Na-SAPO-18(1.0) catalyst, its crystallinity decreases noticeably (as shown in Fig. S2). Meanwhile, a rather strong tridymite diffraction peak is detected [26,27], illustrating that the introduction of excessive Na into the Cu-SAPO-18 catalyst causes partial decomposition of its structure. In addition, significant diffraction peaks of CuO species over Cu/Na-SAPO-18(1.0) catalyst at 35.5° and 38.6° are detected [13,28], causing speculation that a large amount of Na facilitates the aggregation of copper species as CuO clusters over the external surface of the Cu/Na-SAPO-18(1.0) catalyst, resulting in partial structure collapse.

As displayed in Table 1, the introduction of contaminants into Cu-SAPO-18 affects the BET surface area and pore volume

Fig. 1. XRD patterns of catalysts with and without contaminants.

of the catalyst. It is worth noting that the specific surface area and pore volume decrease for all catalysts with 0.5 mmol/g_{catal} contaminants, in contrast to the fresh catalyst, to which the partial pore blocking by copper species is ascribed [29,30]. With the increase in contaminant content to 1.0 mmol/g_{catal}, the Cu/M-SAPO-18(1.0) exhibits a greater decrease in the BET surface area and pore volume, which is due to the partial deterioration of the zeolite construction. In addition, such a decrease in the BET surface area and pore volume varies with distinct metals. For instance, the BET surface area for Cu/K-, Cu/Na-, Cu/Ca-, and Cu/Mg-SAPO-18(1.0) is reduced by 40.1%, 56.0%, 39.4%, and 38.0%, respectively, and the pore volume decreases by 40.7%, 58.1%, 40.7%, and 39.4%, respectively. This phenomenon demonstrates that the destruction on the Cu-SAPO-18 structures caused by Na is more severe than that from K, Ca, and Mg, which is in accordance with XRD results.

To further affirm the above observations, the ²⁷Al MAS NMR was measured to detect the variation in the Al coordination of Cu-SAPO-18. Fig. 2 presents the ²⁷Al NMR spectra of the fresh and contaminated catalysts. Three peaks appear for all samples at 39, 13, and –13 ppm. The three peaks are attributed to the tetrahedrally coordinated framework of Al atoms (Al^{IV}), pentahedrally coordinated Al atoms (Al^V), and octahedrally coordinated Al atoms (Al^{VI}), respectively [31,32]. The percentage ratio of the diverse Al coordination structures is summarized in Table 2. In terms of the fresh catalyst, the proportion of the framework Al^{IV} species is 61.8%. After impregnating the catalyst with 0.5 mmol/g_{catal} contaminants, the percentage of tetrahedral Al atoms in Cu/K-, Cu/Na-, Cu/Ca-, and Cu/Mg-SAPO-18(0.5) catalysts drops to 47.0%, 45.3%, 50.8%, and 55.0%, respectively. This causes the breakage of Si–O–Al bonds, leading to the transformation of framework Al^{IV} species to pentahedral and octahedral Al atoms [33]. With the increase in contaminants to 1.0 mmol/g_{catal}, the percentage of Al^{IV} species for Cu/M-SAPO-18(1.0) catalysts decreases more than that for Cu/M-SAPO-18(0.5) catalysts. It is remarkable that the loss of framework Al^{IV} species in Cu/Na-SAPO-18(1.0) is greater than that for the other Cu/M-SAPO-18(1.0) catalysts, implying a more serious destruction in the Cu/Na-SAPO-18(1.0) framework. These data are consistent with BET results.

Table 2

The percentages of the various Al coordination frameworks in the catalysts with and without contaminants based on the ²⁷Al NMR spectra results.

Catalyst	Al ^{IV} (%)	Al ^V (%)	Al ^{VI} (%)
Cu-SAPO-18	61.8	10.8	27.4
Cu/K-SAPO-18(0.5)	47.0	12.7	40.3
Cu/Na-SAPO-18(0.5)	45.3	17.5	37.2
Cu/Ca-SAPO-18(0.5)	50.8	10.9	38.3
Cu/Mg-SAPO-18(0.5)	55.0	11.1	33.9
Cu/K-SAPO-18(1.0)	42.4	18.0	39.6
Cu/Na-SAPO-18(1.0)	38.8	18.9	42.3
Cu/Ca-SAPO-18(1.0)	49.5	11.0	39.5
Cu/Mg-SAPO-18(1.0)	53.6	11.8	34.6

3.2. The combination of H₂-TPR and EPR

The H₂-TPR curves were analyzed to identify the distribution of different copper species in all samples. As seen from Fig. 3, five reduction peaks (A, B, C, E, and F) in the fresh sample are monitored. Peak A at 244 °C and peak C at 331 °C are the representative reduction peaks in the isolated Cu²⁺ substances, residing at the ellipsoidal cavity near the six-membered ring and in the center of the hexagonal prism, respectively [5,34,35]. Peak B at 289 °C corresponds to the reduction of CuO to Cu⁰ via a single-step procedure [35]. The unstable and high steady Cu⁺ substances were reduced to Cu⁰, resulting in the generation of peak E at 570 °C and peak F above 900 °C. The Cu⁺ substances are derived from two aspects, the incompletely reduced Cu²⁺ and the inherent existence in the sample [36,37]. Nevertheless, when K, Na, Ca, and Mg are introduced into Cu-SAPO-18, a new peak (D) is detected. According to the ²⁷Al-NMR results, the contaminated catalysts possess a greater extra-framework Al percentage than the fresh catalyst, and the extra-structure Al can react with isolated Cu²⁺ substances to generate CuAl₂O₄-like species [23,38,39]. Thus, the new peak (D) is assigned to the reduction of CuAl₂O₄-like species.

Based on Fig. 3a, after impregnating the fresh catalyst with 0.5 mmol/g_{catal} contaminants, the peak intensity of isolated Cu²⁺ substances in the ellipsoidal cavity (peak A) decreases

Fig. 2. ²⁷Al NMR spectra of the catalysts with and without contaminants.

Fig. 3. H_2 -TPR curves of catalysts with and without contaminants.

significantly, and the isolated Cu^{2+} substances in the hexagonal prism (peak C) are also slightly reduced. Such a decline is interpreted by the replacement of partially isolated Cu^{2+} by K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , separately. Concomitantly, the peak intensity of CuO and CuAl_2O_4 -like substances increases, owing to the fact that the replaced Cu^{2+} ions, free from the ion exchange sites, will aggregate into CuO species or react with extra-framework Al, forming CuAl_2O_4 during calcination [23,24]. This will block the micropore of the Cu-SAPO-18 catalyst. After increasing the amount of contaminants to 1.0 mmol/ g_{catal} , the fall in the peak intensity of isolated Cu^{2+} substances at low reduction temperatures is dramatic, indicating that isolated Cu^{2+} species in the ellipsoidal cavity are so unstable that they are prone to be replaced. Simultaneously, more CuO and CuAl_2O_4 species appear, arising from the transformation of many Cu^{2+} substances during calcination. Strikingly, notwithstanding the great many CuO species generated in $\text{Cu/Na-SAPO-18(1.0)}$ during calcination, the formation of CuO species would cause severe damage to its framework [39], which could be demonstrated by XRD and BET results.

In addition, EPR analysis was also measured to further investigate the coordination environment of isolated Cu^{2+} and semi-quantitatively confirm the isolated Cu^{2+} content [27,40]. As Fig. 4 shows, the Cu^{2+} substances in the fresh and contaminated hydrated Cu-SAPO-18 catalysts all show one peak, which

is an axially symmetric signal, implying that there is only one type of isolated Cu^{2+} substance in the hydrated samples. The EPR signal values of $g_{\parallel} = 2.393$ mT, $g_{\perp} = 2.06$ mT, and $A_{\parallel} = 13.11$ mT correspond to the isolated Cu^{2+} , which is octahedrally coordinated to the three oxygens of the zeolite structure and the three water molecules, residing in the ellipsoidal cavity near the six-membered ring [41,42]. However, two kinds of isolated Cu^{2+} species are observed in H_2 -TPR profiles, which might be due to the migration of isolated Cu^{2+} from one location to another during thermal treatment [5,41].

Concurrently, the amount of total isolated Cu^{2+} is semi-quantitatively determined via the double integration of the EPR spectra and the outcomes are plotted in Fig. 4c. After K, Na, Ca, and Mg impregnation, the quantity of total isolated Cu^{2+} in contaminated Cu/M-SAPO-18(x) decreases compared to the fresh catalyst, and higher contaminant content corresponds to a greater decrease in the sum of Cu^{2+} substances, revealing the H_2 -TPR outcome. Moreover, the extent of the K, Na, Ca, and Mg contaminated effect on the Cu^{2+} substances of Cu-SAPO-18 reveals a disparity. For instance, the total isolated Cu^{2+} contents in Cu/K- , Cu/Na- , Cu/Ca- , and $\text{Cu/Mg-SAPO-18(0.5)}$ are reduced by 11.3%, 20.9%, 7.7%, and 8.4%, respectively. Increasing the contaminants to 1.0 mmol/ g_{catal} , the impregnation of K, Na, Ca, and Mg decreases the sum of the total Cu^{2+} substances by 30.4%, 48.9%, 21.2%, and 24.3%, respectively. Consequent-

Fig. 4. EPR spectra (a, b) of catalysts with and without contaminants. (c) The concentration of Cu^{2+} ions of Cu-SAPO-18 determined on the basis of EPR spectra.

Fig. 5. NH_3 -TPD curves of catalysts with and without contaminants.

ly, it can be concluded that the impregnation of Cu-SAPO-18 catalyst with K and Na gives rise to greater substitution of Cu^{2+} species, especially with Na. Such a substitution will lead to the reduction in Lewis acid sites generated by isolated Cu^{2+} .

3.3. The acid site properties

The variation in acidic sites of fresh and contaminated Cu-SAPO-18 was investigated by measuring NH_3 -TPD. Fig. 5 displays the NH_3 -TPD curves. Three NH_3 desorption peaks appear, which are attributed to NH_3 molecule desorption from weak Brønsted acidic sites (peak A, Si-OH and P-OH), Lewis acidic sites (peak B), and strong Brønsted acidic sites (Si-OH-Al) and strong Lewis acidic sites related to Cu^{2+} species (peak C) [14,33,43,44]. Additionally, the K-, Na-, Ca-, and Mg-contaminated Cu-SAPO-18 catalysts also exhibit three similar desorption peaks, and the number of acidic sites is calculated from the NH_3 -TPD curves and summarized in Table 3.

As shown in Table 3, the number of overall acidic sites within Cu/M-SAPO-18(0.5) is less than that of the fresh Cu-SAPO-18 catalyst. This phenomenon is due to the Brønsted acidic sites (H^+) and Lewis acidic sites (Cu^{2+} species) being replaced by K, Na, Ca, and Mg, and the pore blocking of Cu/M-SAPO-18(0.5), which could cause partial coverage of acidic sites [17,23,45]. Moreover, Cu/K-SAPO-18(0.5) catalyst exhibits weak desorption over the entire temperature range,

suggesting that the K^+ located at ion exchange sites of Cu-SAPO-18 shows low affinity to NH_3 [23,24]. However, it seems that Na^+ could adsorb NH_3 molecules, as demonstrated by the increased number of weak and moderate acidic sites (peak A and peak B) in Cu/Na-SAPO-18(0.5) below 300 °C [23]. Meanwhile, the adsorption of NH_3 molecules onto Ca^{2+} and Mg^{2+} at moderate temperatures corresponds to the increase in the content of moderate acidic sites (peak B) of Cu/Ca- and Cu/Mg-SAPO-18(0.5) samples [17,23]. With the increase in contaminants to 1.0 mmol/g_{catal}, the overall acidic sites in Cu/M-SAPO-18(1.0) decreases strikingly, which is explained by a greater loss of H^+ and Cu^{2+} , and the covering of acidic sites, induced by local structure collapse. The impregnation of K, Na, Ca, and Mg on the raw sample took place at the expense of Brønsted acidic sites, Cu^{2+} substances, and the surface area, leading to the decrease in the overall acidic sites of Cu/M-SAPO-18(x).

Furthermore, the decrease in the overall acidic sites within Cu/M-SAPO-18(x) follows the order Cu/K- > Cu/Na- > Cu/Ca- > Cu/Mg-SAPO-18(x). This is opposite to the effective hydrated diameter of the contaminants, which is presented in the order $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$ [46]. Although two K^+ or Na^+ can substitute for two H^+ or one Cu^{2+} , and one Ca^{2+} or Mg^{2+} can replace two H^+ or one Cu^{2+} , K^+ and Na^+ with smaller hydrated diameters are more prone to enter the pores of Cu-SAPO-18 catalyst than Ca^{2+} and Mg^{2+} with larger hydrated diameters. Consequently, a larger quantity of Brønsted acidic sites and isolated Cu^{2+} is easier to exchange with K^+ and Na^+ , leading to a greater reduction in total acidic sites in Cu/K- and Cu/Na-SAPO-18(x).

Table 3

The sum of acidic sites in catalysts with and without contaminants based on the NH_3 -TPD results.

Catalyst	Acidic sites ($\mu\text{mol/g}$)			Total ($\mu\text{mol/g}$)
	Peak A	Peak B	Peak C	
Cu-SAPO-18	46	82	219	347
Cu/K-SAPO-18(0.5)	23	78	64	165
Cu/Na-SAPO-18(0.5)	64	122	68	254
Cu/Ca-SAPO-18(0.5)	42	113	155	310
Cu/Mg-SAPO-18(0.5)	43	135	165	343
Cu/K-SAPO-18(1.0)	21	43	19	83
Cu/Na-SAPO-18(1.0)	46	72	23	141
Cu/Ca-SAPO-18(1.0)	33	79	121	233
Cu/Mg-SAPO-18(1.0)	41	129	137	307

3.4. The effect of contaminants on NH_3 -SCR performance

During the de NO_x reaction, NH_3 molecules could adsorb on both isolated Cu^{2+} and Brønsted acidic sites, while the de NO_x reaction solely happens on isolated Cu^{2+} , identified as the active sites [5,33]. At low temperatures, only the NH_3 molecules adsorbed on isolated Cu^{2+} take part in the de NO_x reaction. Thus, the isolated Cu^{2+} species at low reduction temperatures affect the low-temperature NO conversion. At high temperatures, the

Fig. 6. deNO_x performance of catalysts with and without contaminants.

adsorption of NH₃ on the isolated Cu²⁺ is unstable. Therefore, the NH₃-SCR reaction occurs by supplying the NH₃ from the Brønsted acidic sites to the Cu²⁺ substances [47,48]. This indicates that the NO conversion is involved in the acidic sites and Cu²⁺ substances.

Fig. 6 depicts the NH₃-SCR performance over the fresh and contaminated Cu-SAPO-18. The fresh Cu-SAPO-18 catalyst reveals outstanding catalytic activity during the entire temperature range, and the NO conversion exceeds 90% in the temperature region of 200–525 °C because of the existence of a great many acidic sites and Cu²⁺ substances. After the doping of 0.5 mmol/g_{catal} or 1.0 mmol/g_{catal} of contaminants to Cu-SAPO-18, all contaminated catalysts suffer deactivation, and their catalytic activities decrease in the entire temperature range. The higher the contaminant content, the more pronounced the decrease in NO conversion. Such a decrease is due to the reduction in acidic sites and Cu²⁺ content, and the structural damage. Meanwhile, the decline in isolated Cu²⁺ in the ellipsoidal cavity is responsible for the decrease in the low-temperature deNO_x activity [15]. The NH₃ oxidation induced by the large quantity of CuO species leads to the decline in high-temperature NH₃-SCR activities [7]. Simultaneously, the deactivation effect of contaminants on Cu-SAPO-18 is different, which is presented by the order K > Na > Ca > Mg. For instance, the catalytic performance of Cu/Mg-SAPO-18(0.5) is approximately 87% from 275 to 450 °C. In contrast, the highest NO conversion within Cu/K-SAPO-18(0.5) is only 78% at 350–475 °C. Furthermore, comparing Cu/Ca- to Cu/Na-SAPO-18(0.5), the former exhibits slightly higher catalytic performance (around 82%) than the latter from 250 to 475 °C. For the 1.0 mmol/g_{catal} contaminants, the highest NO conversion over Cu/K-, Cu/Na-, and Cu/Ca-SAPO-18(1.0) catalysts is 24% at 525 °C, 40% at 525 °C, and 60% at 475 °C, respectively, corresponding to a decline of 76%, 60%, and 40% compared with the fresh catalyst, respectively. However, the highest catalytic activity of Cu/Mg-SAPO-18(1.0) is 85% at 425–450 °C. The deactivation in the fresh catalyst is related to the decreased level in isolated Cu²⁺ and acidic sites, and the framework damage.

Fig. 7 shows the relative number of acidic sites (according to

the NH₃-TPD results) and isolated Cu²⁺ (according to the EPR results) as a function of the actual metal content. The introduction of K, Na, and Ca into the Cu-SAPO-18 results in a reduced number of acidic sites more significant than that of isolated Cu²⁺. This shows that the K⁺, Na⁺, and Ca²⁺ ions are more apt to exchange with H⁺ than Cu²⁺. However, Mg²⁺ seems to easily substitute for the Cu²⁺ instead of H⁺, as demonstrated by the more distinct diminished level of Cu²⁺ substances in Cu/Mg-SAPO-18(x). Simultaneously, the Cu²⁺ ions, free from the Cu-SAPO-18 catalyst, can transform into the CuO species during calcination, which can cause the catalyst structural damage and decline in specific areas. Furthermore, the Cu²⁺ content of Cu/M-SAPO-18(x) follows the order: Cu/Na > Cu/K > Cu/Mg > Cu/Ca-SAPO-18(x). The decrease in the BET specific area for Cu/M-SAPO-18(x) follows the order: Cu/Na < Cu/K < Cu/Ca < Cu/Mg-SAPO-18(x). The reduction in the number of acidic sites of Cu/M-SAPO-18(x) is presented in the order: Cu/K > Cu/Na > Cu/Ca > Cu/Mg-SAPO-18(x), which corresponds to the extent of catalyst deactivation. A conclusion that can be drawn is that deNO_x activity can be jointly affected by

Fig. 7. The relative content of acidic sites (according to the NH₃-TPD results) and the relative number of isolated Cu²⁺ ions (according to the EPR results) as a function of actual metal ion content.

Fig. 8. The results of the NH_3 -SCR kinetic evaluation over catalysts with and without contaminants at low temperature.

the isolated Cu^{2+} , catalyst structure, and acidic sites. However, the acidic sites might affect the NH_3 -SCR activity more significantly than isolated Cu^{2+} and catalyst structure. Additionally, the kinetics studies were carried out at low temperature to investigate the effect of the contaminants on NH_3 -SCR mechanism. As shown in Fig. 8, all catalysts possess similar apparent activation energies, indicating that the existence of K, Na, Ca, and Mg has little influence on deNO_x mechanism over Cu-SAPO-18 [23]. Moreover, the NO conversion speeds correspond to the NH_3 -SCR activities. This suggests that a larger number of acidic sites and Cu^{2+} substances in the catalyst correspond to better catalytic activity.

4. Conclusions

Cu-SAPO-18 contaminated by K, Na, Ca, and Mg suffers deactivation in the NH_3 -SCR reaction. Such deactivation becomes more significant by increasing the contaminant content from 0.5 to 1.0 mmol/ g_{catal} . The deactivation of Cu-SAPO-18 is connected with the decline in the content of acidic sites and Cu^{2+} substances, and the framework destruction of the catalyst. When the K, Na, Ca, and Mg was introduced into Cu-SAPO-18, these metal ions, with different hydrated ion diameters, substitute for the H^+ or Cu^{2+} to different extents. This leads to different degrees of decrease in Cu^{2+} substances and acidic sites. Cu^{2+} , unable to interact with the ion exchange sites, transform into the CuO species and CuAl_2O_4 -like species during high-temperature calcination. This causes Cu-SAPO-18 to experience micropore blockage and further covers the acidic sites of the catalyst. Finally, the deactivation of Cu-SAPO-18 follows the order of $\text{Cu/K} > \text{Cu/Na} > \text{Cu/Ca} > \text{Cu/Mg-SAPO-18(x)}$, which corresponds to the effect of the contaminants on the acidic sites. Thus, to some extent, the influence of acidic sites on NO conversion seems to be more conspicuous. Finally, the evaluation of NH_3 -SCR dynamics was conducted. It can be concluded that the introduction of contaminants into Cu-SAPO-18 shows little influence on the deNO_x mechanism.

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Graphical Abstract

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Chemical deactivation of Cu-SAPO-18 deNO_x catalyst caused by basic inorganic contaminants in diesel exhaust

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Contaminants (K, Na, Ca, and Mg) with different hydrated ions diameters were impregnated into Cu-SAPO-18, leading to a loss of NH₃-SCR performance of the Cu-SAPO-18 catalyst.

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柴油机尾气中的碱性无机污染物引起Cu-SAPO-18脱硝催化剂的化学失活

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摘要: 选择性催化还原NO_x (NH₃-SCR)已是柴油机尾气处理系统中有效的NO_x减排技术. 铜基分子筛催化剂作为潜在的NH₃-SCR催化剂已被广泛研究, 其中具有AEI结构的Cu-SAPO-18分子筛表现出优异的脱硝活性和水热稳定性, 成为柴油机

尾气后处理系统潜在的替代品。然而在实际的后处理应用中,生物柴油污染物、发动机润滑剂和燃料添加剂中的一些无机组分(K, Na, S, P, Ca和Mg等)可逐渐聚集在催化剂表面,导致催化剂孔道堵塞和活性位点丢失,最终导致SCR催化剂失活。由于碱金属和碱土金属在柴油衍生物中含量较高,因而其对SCR催化剂的影响引起了人们更多的关注。本文采用浸渍法制备了掺杂不同含量碱性无机污染物(K, Na, Ca和Mg)的Cu-SAPO-18催化剂,以阐明这些污染物对Cu-SAPO-18结构、酸性位点和铜物种的影响。

XRD和氮吸附实验结果表明,低含量污染物的掺入造成催化剂孔道堵塞和比表面积下降,而高含量污染物引入导致催化剂部分结构被破坏,其中高含量Na的引入造成催化剂结构破坏最为严重。 H_2 -TPR和EPR结果表明,污染物引入Cu-SAPO-18后,催化剂的 Cu^{2+} 数目减少,这是由于 Cu^{2+} 被 K^+ , Na^+ , Ca^{2+} 和 Mg^{2+} 取代造成的。被取代的 Cu^{2+} 由于无法位于离子交换位点上会在煅烧过程中转变成CuO和 $CuAl_2O_4$, CuO的产生会造成催化剂孔道堵塞甚至部分骨架结构坍塌。另外, NH_3 -TPD结果表明,与新鲜催化剂相比,被污染的Cu-SAPO-18催化剂总酸性位点减少,这是由于 H^+ 和 Cu^{2+} 被 K^+ , Na^+ , Ca^{2+} 和 Mg^{2+} 取代造成Brønsted酸和Lewis酸减少造成的。催化剂比表面积的降低、 Cu^{2+} 数目以及酸含量的减少最终造成催化剂失活,且催化剂失活程度随无机污染物含量的增加而增大。但不同无机组分造成催化剂的失活程度不同,其中K, Na, Ca和Mg造成Cu-SAPO-18催化剂失活程度为 $K > Na > Ca > Mg$ 。此外, K, Na, Ca和Mg造成Cu-SAPO-18催化剂比表面积、 Cu^{2+} 含量以及酸含量的减少程度分别为 $Na > K > Ca > Mg$, $Na > K > Mg > Ca$ 和 $K > Na > Ca > Mg$ 。其中酸含量下降程度与催化剂失活程度一致,表明在某种程度上,酸含量对催化剂 NH_3 -SCR活性的影响高于催化剂结构和 Cu^{2+} 对活性的影响。最后,我们还通过 NH_3 -SCR动力学测试研究了K, Na, Ca和Mg对Cu-SAPO-18催化 NH_3 -SCR反应机理的影响,结果显示新鲜催化剂和被污染催化剂具有相近的活化能,表明无机污染物对Cu-SAPO-18催化 NH_3 -SCR反应机理没有影响。

关键词: Cu-SAPO-18催化剂; 碱性无机污染物; NH_3 选择性催化还原 NO_x ; 酸性位点; 铜离子

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