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Stability of Cu–Mn bimetal catalysts based on different zeolites for NO_x removal from diesel engine exhaust

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ABSTRACT

Cu–Mn bimetal catalysts were prepared to remove nitrogen oxides (NO_x) from diesel engine exhaust at low temperatures. At a Cu/Mn ratio of 3:2, the NO_x conversions at 200 °C reached 65% and 90% on Cu–Mn/ZSM-5 and Cu–Mn/SAPO-34, respectively. After a hydrothermal treatment and reaction in the presence of C₃H₆, the activity of Cu–Mn/SAPO-34 was more stable than that of Cu–Mn/ZSM-5. No obvious variations in the crystal structure or dealumination were observed, whereas the physical structure was best maintained in Cu–Mn/SAPO-34. The atomic concentration of Cu on the surface of Cu–Mn/SAPO-34 was quite stable, and the consumption of octahedrally coordinated Cu²⁺ could be recovered. Conversely, the proportion of octahedrally coordinated Cu²⁺ on the surface of Cu–Mn/ZSM-5 significantly decreased. Therefore, besides the structure, the redox cycle between Cu⁺ and octahedrally coordinated Cu²⁺ played an important role in the stability of the catalysts.

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1. Introduction

Diesel engines are more fuel-combustion efficient than traditional stoichiometric engines. In recent years, the number of diesel vehicles has increased continuously with emissions of nitrogen oxides (NO_x). Selective catalytic reduction (SCR) of NO_x is the most widely used technology for NO_x removal [1]. Three-way catalysts that are successfully used for petroleum vehicles do not work for lean-burn engine exhaust because of the wide range of temperatures and high concentration of oxygen in diesel engine exhaust. Therefore, it is critical to develop an effective SCR catalyst to remove NO_x from diesel engine exhaust. Although Cu based zeolites [2,3], such as Cu/ZSM-5 and Cu/SAPO-34, show a high deNO_x activity when the temperature of the diesel engine exhaust is higher than 200 °C, their low catalytic activity below 200 °C is the main problem that limits their application to diesel engines. The typical temperature of

light-duty diesel engine exhaust ranges from 150 °C to 250 °C, and the temperature of the exhaust gas from advanced diesel engines with a high fuel efficiency is expected to be even lower [4]. Therefore, catalysts are required to be more active at low temperatures. Since Mn-based catalysts show a good SCR performance at low temperatures for stationary sources [5,6], and Mn was already added to Fe/ZSM-5 as the SCR catalyst for diesel engines to improve the low-temperature activity without decreasing the stability of the catalyst [4], the co-doping of Cu and Mn might provide an alternative solution to obtain an SCR catalyst with a high activity at low temperatures as well as high stability. Mn doping could increase the NO conversion on Cu–Mn/SAPO-34 from 40% to 90% at 200 °C [8]. The stability of the catalysts has not been thoroughly discussed.

The hydrothermal stability of Cu/ZSM-5 poses problems when the temperature of the diesel engine exhaust rises above 650 °C, with high moisture, during the regeneration of diesel

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particulate filters (DPFs), because of dealumination or aluminum migration [2]. Cu/SAPO-34 catalysts with a chabazite (CHA) structure show a higher hydrothermal stability than Cu/ZSM-5 [7]. Also, deactivation by hydrocarbons (HCs) remains an important issue for catalysts because HCs lead to coke deposits on the active sites and destroy the structure of the catalysts. For Cu–Mn bimetal catalysts based on zeolites, the effect of Mn on the hydrothermal stability and resistance to the HCs of the catalysts has not been studied, and the factors that influence the stability are ambiguous.

In this paper, Cu and Mn were co-doped on ZSM-5 and SAPO-34 by the ion-exchange method to reveal Cu–Mn bimetal catalysts for NO_x removal from diesel engine exhaust. The catalytic activity and hydrothermal stability of the catalysts, and their resistance to HCs were investigated. The physical and chemical properties of Cu–Mn/ZSM-5 and Cu–Mn/SAPO-34 were characterized, and the key factors that influence the stability are discussed.

2. Experimental

2.1. Materials

Zeolites (H/ZSM-5, SiO₂/Al₂O₃ = 38; H/SAPO-34, SiO₂/Al₂O₃ = 0.5) were purchased from Tianjin Chemist Scientific Ltd., China. Ammonium nitrate, Cu(CH₃COO)₂·H₂O, and Mn(CH₃COO)₂·4H₂O were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Catalyst preparation

Cu–Mn bimetal catalysts with different ratios of Cu/Mn were prepared by a two-step liquid ion exchange method [9]. Zeolites (10 g of H/ZSM-5) were added to ammonium nitrate (100 mL, 1 mol/L) and stirred continuously in a 500-mL three-neck flask at 90 °C for 2 h. The NH₄⁺/ZSM-5 powders were obtained by filtration and rinsed thoroughly with deionized water. After the ion-exchanged procedure was repeated three times, the solid was dried at 120 °C for 12 h. Cu and Mn were ion-exchanged to NH₄⁺/ZSM-5 by mixing the powder with a solution of Cu(CH₃COO)₂·H₂O and Mn(CH₃COO)₂·4H₂O. NH₄⁺/ZSM-5 (10 g) was added to 50 mL of the solution with different ratios of Cu and Mn, and the total metal concentration was controlled at 0.2 mol/L. The mixture was stirred vigorously at room temperature for 6 h and was filtered and rinsed thoroughly with deionized water. After the ion-exchange procedure was repeated two times, the solid was dried at 110 °C for 12 h and then calcined at 500 °C for 5 h to obtain Cu–Mn/ZSM-5. The preparation of Cu–Mn/SAPO-34 was similar to that for Cu–Mn/ZSM-5, as described in a previous study [8]. The Cu–Mn/ZSM-5 and Cu–Mn/SAPO-34 catalysts were finally pressed, crushed, and sieved to 60–100 mesh.

To investigate the hydrothermal stability, the catalysts were aged in a quartz tube reactor at 750 °C in 10% H₂O/air with a total flow of 1000 cm³/min for 24 h.

2.3. Activity tests of the catalyst

The NH₃-SCR activity of the catalysts was analyzed in a fixed-bed quartz tubular flow reactor (i.d., 8 mm). The quartz tube contained 2 mL of catalyst, with a gas hourly space velocity (GHSV) of 30 000 h^{−1}. Typical simulated diesel engine exhaust consists of 300 ppm NO, 300 ppm NH₃, 14% O₂, 5.7% H₂O, 2000 ppm C₃H₆ (when used), and balanced N₂. The tubing of the reactor system was heated to prevent the formation of ammonium nitrate deposits and water condensation. The NO, NO₂, and O₂ concentrations were monitored by a flue gas analyzer (KM9106 Quintox, Kane International Ltd., Hertfordshire, UK). N₂O was analyzed by an infrared gas analyzer (PGD-100, Madur E-commerce Co., Ltd., EU). The NO_x conversion and N₂ selectivity were calculated using Eqs. (1) and (2), respectively.

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% \quad (1)$$

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

[NO_x]_{in} and [NO_x]_{out} represent the concentration of NO_x in the inlet and outlet gas, respectively. [N₂O]_{out} represents the concentration of N₂O in the outlet gas.

2.4. Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were measured using a D/max-rA XRD instrument (XD-98, PERSEE, Beijing, China) with Cu K_α radiation (λ = 0.15406 nm) and were scanned from 2θ = 10°–55° with a step of 1°/min.

The morphologies of the catalysts were observed by scanning electron microscopy (SEM; UHR FE-SEM SU8020, Hitachi, Tokyo, Japan), and the accelerating voltage was 15 kV.

The Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore diameter of the catalysts were measured by N₂ adsorption-desorption isotherms at −196 °C using a physical adsorption instrument (JW-BK132F, JWGB, Beijing, China). The physical properties of the samples are listed in Table 1.

Solid-state ²⁷Al nuclear magnetic resonance (NMR) spectra were recorded on an Avance III 400 spectrometer (Bruker, Billerica, MA, USA). All ²⁷Al NMR spectra were recorded at a spinning rate of 12 kHz.

The atomic state at the surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with Al K_α X-rays (ESCALAB 250Xi, Thermo, Waltham, MA, USA; hν = 1486.6 eV). The shift of the binding energy caused by relative surface charging was corrected using the C 1s level at 284.8 eV as an internal standard. The concentrations of elements, such as Cu, Mn, O, Si, Al, and P, were calculated from the integrated peak areas of the XPS data.

3. Results and discussion

3.1. SCR performances of different catalysts

The SCR activities of Cu–Mn/ZSM-5 and Cu–Mn/SAPO-34 with different ratios of Cu/Mn are shown in Fig. S1. Among the samples, Cu–Mn/ZSM-5 and Cu–Mn/SAPO-34 showed the

Fig. 1. Catalytic performance for SCR of NO_x with ammonia on the Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 catalysts. Reaction conditions: 300 ppm NO, 300 ppm NH_3 , 14% O_2 , 5.7% H_2O , balance N_2 , GHSV = 30000 h^{-1} .

highest activities when the ratio of Cu/Mn was 3:2. Therefore, the two samples were chosen for the following investigation. Fig. 1 shows the improvement in the catalytic activity by Cu-Mn co-doping. The activity of Cu/ZSM-5 was much higher than that of Cu/SAPO-34 below 280 °C, whereas the activity of Cu/SAPO-34 was easier to maintain at high temperatures. When Cu and Mn were co-doped, the promotional effect on the low-temperature activity of Cu-Mn/SAPO-34 was more significant. NO_x conversion on Cu-Mn/SAPO-34 reached approximately 90% at 200 °C, which is more than twice that on Cu/SAPO-34, and NO_x conversion on Cu-Mn/ZSM-5 only increased by 10% with respect to that of Cu/ZSM-5, reaching approximately 65% at 200 °C. Hence, Cu-Mn/SAPO-34 was more active for NO_x removal than Cu-Mn/ZSM-5 at low temperatures. When the temperature ranged from 240 °C to 320 °C, the Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 catalysts showed similar de NO_x activities. When the temperature was above 320 °C, the NO_x conversion on Cu-Mn/SAPO-34 was higher than that on Cu-Mn/ZSM-5. The concentration of N_2O as a by-product in the outlet gas was measured. The results showed that N_2O was not detected in the outlet gas of the reactor in the SCR reaction, and the selectivity to N_2 was almost 100%. In tests of the temperature tolerance (Fig. S2), both Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 maintained high de NO_x activities during cycles of temperature variation. Along with the measurements, low-temperature NO_x conversion was improved on the two catalysts, reaching more than 80% when the temperature was above 170 °C. The activity of Cu-Mn/SAPO-34 was more stable than that of Cu-Mn/ZSM-5, and it showed a higher NO_x conversion below 200 °C and between 320 °C and 550 °C.

3.2. Hydrothermal stability and resistance to hydrocarbons

Hydrothermal stability remains an important issue for SCR catalysts because the temperature of diesel engine exhaust rises above 650 °C when large amounts of H_2O are present during the regeneration of DPFs [10]. The samples were treated at 750 °C for 24 h with flowing wet air containing 10% H_2O

during the hydrothermal aging treatment, and the catalytic activities are shown in Fig. 2. Although the two fresh samples showed good activities within the temperature range of the diesel engine exhaust, the activity and stability differed entirely after the hydrothermal aging treatment. Significant loss of activity was observed on aged Cu-Mn/ZSM-5, especially below 360 °C, and the NO_x conversion was below 50%. Unlike Cu/ZSM-5 [2], Cu-Mn/ZSM-5 has a lowest point at 280 °C, and NO_x conversion declined by nearly 80%. For Cu-Mn/SAPO-34, the hydrothermal aging treatment did not cause any negative effects, and it improved the activity. The aged sample showed a higher NO_x conversion than fresh Cu-Mn/SAPO-34 below 240 °C, and the NO_x conversion could reach nearly 100% at 200 °C. Furthermore, the rate of deterioration in the activity above 360 °C was also relieved, and the NO_x conversion remained above 84%. Therefore, the hydrothermal stability of Cu-Mn/SAPO-34 was much higher than that of Cu-Mn/ZSM-5.

The resistance to HCs is another important property of the catalysts because the diesel engine exhaust might contain large amounts of unburned HCs, which can deactivate the catalysts [2]. Fig. 3 shows the activity of the catalysts in the SCR reaction with and without 2000 ppm C_3H_6 . After C_3H_6 was injected into the mixed reactant gas, the NO_x conversion curve of Cu-Mn/ZSM-5 showed an apparent double-peak shape with the lowest point at approximately 360 °C. The activity lost approximately 50% at 360 °C, and the highest NO_x conversions were only 75.2% at 280 °C and 71.6% at 440 °C. For Cu-Mn/SAPO-34, the NO_x conversion decreased by only 5% from 160 °C to 200 °C in the presence of C_3H_6 . When temperatures were between 240 °C and 440 °C, the NO_x conversion was almost the same as that for the reaction without C_3H_6 . Above 440 °C, the presence of C_3H_6 reduced the NO_x conversion by less than 5%. Therefore, C_3H_6 had little effect on Cu-Mn/SAPO-34. To further study the effect of C_3H_6 on the activity, the reacted samples were used for the SCR reaction without C_3H_6 for three cycles of temperature variation (Fig. S3). The catalytic activity of Cu-Mn/ZSM-5 decreased in the first cycle and was approximately 30% less than that of fresh

Fig. 2. Catalytic performance for SCR of NO_x with ammonia on the Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 catalysts. Reaction conditions: 300 ppm NO, 300 ppm NH_3 , 14% O_2 , 5.7% H_2O , balance N_2 , GHSV = 30000 h^{-1} .

Fig. 3. Catalytic performance for SCR of NO_x with ammonia over the Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 catalysts. Reaction conditions: 300 ppm NO, 300 ppm NH_3 , 14% O_2 , 5.7% H_2O , 2000 ppm C_3H_6 (when used) balance N_2 , GHSV = 30000 h^{-1} .

Cu-Mn/ZSM-5 at 200 °C after three cycles. Although the low-temperature activity ($T < 240$ °C) of Cu-Mn/SAPO-34 also decreased in the first cycle, it recovered with only a 6% rate of deterioration at 200 °C compared to fresh Cu-Mn/SAPO-34 in the second and third cycles. Therefore, Cu-Mn/SAPO-34 showed a higher resistance to C_3H_6 than Cu-Mn/ZSM-5, and the catalytic activity could recover quickly after being poisoned by C_3H_6 .

3.3. SEM results and physical properties

The morphology of the Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 catalysts was analyzed by SEM. As shown in Fig. 4, aggregation was observed on Cu-Mn/ZSM-5 after the hydrothermal aging treatment, and it also occurred after the SCR reaction in the presence of C_3H_6 . For Cu-Mn/SAPO-34, SEM images showed a

Table 1
Physical properties of the Cu-Mn-doped catalysts.

Sample	A_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Cu-Mn/ZSM-5 ^a	279.9	0.102	3.1
Cu-Mn/ZSM-5 ^b	274.6	0.079	3.5
Cu-Mn/ZSM-5 ^c	173.5	0.060	3.1
Cu-Mn/SAPO-34 ^a	259.7	0.115	2.3
Cu-Mn/SAPO-34 ^b	250.3	0.171	2.7
Cu-Mn/SAPO-34 ^c	189.1	0.135	2.8

^a Fresh samples.

^b Catalysts after aging at 750 °C for 24 h in a gas flow containing 10% H_2O /air with a total flow of 1000 cm^3/min .

^c Catalysts after reacting with 300 ppm NO, 300 ppm NH_3 , 2000 ppm C_3H_6 , 14% O_2 , 5.7% H_2O , and balance N_2 .

cubic-like rhombohedral morphology, and the catalyst became smoother than the fresh sample after the hydrothermal aging treatment. When the catalyst was used for the SCR reaction in the presence of C_3H_6 , the surface seemed rough, and some particles were observed on the surface. However, the variation of the morphology of Cu-Mn/SAPO-34 was less apparent than that for Cu-Mn/ZSM-5. With the CHA framework, aggregation barely occurred on Cu-Mn/SAPO-34.

As given in Table 1, the fresh catalysts had large BET surface areas and pore volumes, and the hydrothermal aging treatment and reaction in the presence of C_3H_6 had a different influence on the physical properties of Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34. After the hydrothermal aging treatment, although the BET surface area of Cu-Mn/ZSM-5 did not decrease significantly, the pore volume became less than 80% of that for the fresh one, and the average pore diameter increased from 3.1 nm to 3.5 nm. Therefore, the aggregation observed in Fig. 4(b) was accompanied by the collapse of micropores in the structure. Contrary to Cu-Mn/ZSM-5, the BET surface area and pore volume of Cu-Mn/SAPO-34 remained nearly the same after the

Fig. 4. SEM images of Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34. (a) Cu-Mn/ZSM-5-fresh; (b) Cu-Mn/ZSM-5-aged; (c) Cu-Mn/ZSM-5- C_3H_6 ; (d) Cu-Mn/SAPO-34-fresh; (e) Cu-Mn/SAPO-34-aged; (f) Cu-Mn/SAPO-34- C_3H_6 .

hydrothermal aging treatment, and the pore volume increased with an increase in average diameter. This finding indicated that, although the pores in Cu-Mn/SAPO-34 became larger, they remained in the skeleton structure.

After the SCR reaction in the presence of C_3H_6 , the BET surface areas of Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 decreased, whereas variations of Cu-Mn/ZSM-5 were more significant. C_3H_6 can be adsorbed onto the surface of catalysts and form carbonaceous deposits, leading to a decrease in the BET surface area, and C_3H_6 can diffuse into the skeleton structure and deposit inside the zeolites, resulting in decreased pore volumes [5,11]. The data in Table 1 show that after the SCR reaction in the presence of C_3H_6 , the pore volume of Cu-Mn/ZSM-5 decreased significantly, whereas that of Cu-Mn/SAPO-34 increased. This difference is related to the structures of the catalysts. The kinetic diameter of C_3H_6 is 0.4678 nm, which is smaller than the opening pore size of ZSM-5 (0.55 nm) and larger than that of SAPO-34 (0.372 nm). Therefore, C_3H_6 could diffuse into the internal channel of ZSM-5 and cover the Cu active sites, which reduced the pore volume and catalytic activity. For Cu-Mn/SAPO-34, C_3H_6 barely diffused into the CHA cage. The decreased BET surface areas were caused by carbon deposits on the surface of Cu-Mn/SAPO-34; the pore volume and active sites located inside the cage were maintained. The CHA structure was the main contribution to the high resistance of Cu-Mn/SAPO-34 to HCs.

3.4. XRD results

The XRD patterns of the Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 catalysts are shown in Fig. 5(a) and (b), respectively. The Cu-Mn/ZSM-5 catalysts exhibited typical XRD patterns and remained intact after the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 [12]. For Cu-Mn/SAPO-34, the characteristic peaks at $2\theta = 9.25^\circ$ – 9.90° , 12.80° – 13.45° , 16.05° – 16.50° , 16.95° – 17.60° , 20.45° – 22.10° , 25.75° – 26.60° , 30.10° – 31.80° , and 49.45° – 49.80° are the characteristic peaks of the CHA structure; this suggests that all the Cu-Mn/SAPO-34 catalysts maintained their CHA structure [13]. Also, peaks of the copper-related phases (Cu, Cu_2O , and CuO) or MnO_x were not observed on the Cu-Mn/ZSM-5 and Cu-Mn/

SAPO-34 catalysts, indicating that the loading of Cu and Mn species was very low or well dispersed in the samples on the ion-exchange sites under these conditions [14,15]. The intensity of the XRD peaks of Cu-Mn/ZSM-5 after the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 did not change. This finding indicates that the crystal structure of Cu-Mn/ZSM-5 was maintained during the two reactions and, thus, would not be the main reason for the loss in activity. The peak intensity of Cu-Mn/SAPO-34 slightly increased after the hydrothermal aging treatment. Considering the SEM image of Fig. 4(e), the hydrothermal aging treatment enhanced the crystallinity of the catalyst and was favorable for the activity, especially in the low-temperature range. The reaction in the presence of C_3H_6 also increased the crystallinity of Cu-Mn/SAPO-34; it showed that the crystal structure of the sample was not damaged. Therefore, the slight decrease in the activity of Cu-Mn/SAPO-34 in the presence of C_3H_6 should be attributed to variations in the morphology and the physical properties of the catalysts.

3.5. NMR results

Al in the AlO_x species in the catalysts was monitored by ^{27}Al NMR. Some zeolites can dealuminate under high-temperature hydrothermal conditions without incurring significant damage to their crystal structures, and Al^{3+} ions were transferred from tetrahedral positions to octahedral coordination [16]. Thus, the decreased intensity of peaks associated with tetrahedrally coordinated Al atoms or the increased intensity of those associated with octahedrally coordinated Al atoms were considered dealumination. As shown in Fig. 6(a), all Cu-Mn/ZSM-5 catalysts showed a main peak at a chemical shift of 52.5 ppm, which is attributed to the tetrahedrally coordinated Al atom [17]. Another peak at approximately 0 ppm seemed to be caused either by an artifact from the instrument or by data processing [18]. The lack of octahedrally coordinated Al in Cu-Mn/ZSM-5 was attributed to the strong influence of paramagnetic Cu ions [19]. The intensity of the tetrahedral aluminum peak was not significantly less than that of the fresh Cu-Mn/ZSM-5 sample after the hydrothermal aging treatment or the NH_3 -SCR reaction in the presence of C_3H_6 , which meant that the Cu-Mn/ZSM-5 cat-

Fig. 5. XRD patterns of Cu-Mn/ZSM-5 (a) and Cu-Mn/SAPO-34 (b).

Fig. 6. ^{27}Al NMR spectra of Cu-Mn/ZSM-5 (a) and Cu-Mn/SAPO-34 (b).

alyst did not dealuminate significantly after the two treatments described above. The findings were unlike those from previous studies of Cu/ZSM-5, which reported that the number of tetrahedrally coordinated Al atoms decreased significantly without incurring damage to the crystal structures [19]. Therefore, the dealumination of the catalyst could be relieved and the stability of the catalyst could be enhanced by co-doping Cu-Mn to ZSM-5. Combined with the XRD and SEM results, the findings indicated that, after the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 , the collapse of the skeleton structure should be one of the main factors attributable to the decreased activity of Cu-Mn/SAPO-34.

The ^{27}Al NMR spectra of Cu-Mn/SAPO-34 consisted of three signals. As shown in Fig. 6(b), the peak between 37.16 ppm and 42.51 ppm could be ascribed to tetrahedrally coordinated Al atoms; the peak at a chemical shift of 11.96 ppm was attributed to pentacoordinated Al atoms; the peak between -14.38 ppm and -12.86 ppm could be ascribed to octahedrally coordinated Al atoms that were partially coordinated to water molecules [20]. After the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 , the intensity of the octahedrally coordinated aluminum signal was reduced significantly. Because the octahedrally coordinated aluminum was partially

coordinated to water, the decrease in this peak intensity might be caused by water loss [21]. In addition to the results shown in Figs. 2 and 3, these findings indicate that the reduced octahedrally coordinated aluminum atoms had little effect on the SCR activity of Cu-Mn/SAPO-34. The number of octahedrally coordinated aluminum atoms decreased, and the intensity of the peak caused by tetrahedrally coordinated Al atoms remained almost the same, which indicated that dealumination did not occur in Cu-Mn/SAPO-34 after the hydrothermal aging treatment and SCR reaction in the presence of C_3H_6 .

3.6. XPS results

To provide insight into the different SCR activities of Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34, XPS analysis was used to examine the valance states and atomic concentrations of the elements on the surfaces of the two catalysts. As presented in Table S1, the doping amount of Cu was less than 1%, and the concentration of Mn was below the detection limit. Although the concentrations of Cu and Mn were the same in the precursor solution of the two catalysts, the amount of Cu on the surface of Cu-Mn/SAPO-34 was higher than that of Cu-Mn/ZSM-5. This finding indicated that the ion-exchange ability of Cu with

Fig. 7. XPS spectra of Cu-Mn/ZSM-5 (a) and Cu-Mn/SAPO-34 (b). (1) Fresh; (2) Hydrothermal aging; (3) SCR reaction in the presence of C_3H_6 ; (4) Three SCR reaction cycles without C_3H_6 after (3).

NH_4^+ on $\text{NH}_4^+/\text{SAPO-34}$ was stronger than that on $\text{NH}_4^+/\text{ZSM-5}$. The XPS profiles are shown in Fig. 7. The peaks of $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$, located at 932.8 ± 0.2 eV and 952.5 ± 0.2 eV, could be ascribed to Cu^+ [22,23]. Other $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$ peaks should correspond to isolated Cu^{2+} species with different exchange sites in the zeolite framework [24]. The $\text{Cu } 2p_{3/2}$ peaks at 933.6 eV were caused by isolated Cu^{2+} in the tetrahedrally coordinated sites, and the peak at 936.0 eV was attributed to isolated Cu^{2+} in the octahedrally coordinated sites [25]. A satellite peak at approximately 940.0–950.0 eV, and 10 eV higher than that of the $\text{Cu } 2p_{3/2}$ peak, was observed for Cu^{2+} , which further proved that a large amount of surface Cu was present as Cu^{2+} in the catalysts [26–28]. The relative proportions of Cu^+ and Cu^{2+} , according to the fitting results, were calculated and are listed in Table 2. Clearly, Cu ions existed mainly as isolated Cu^{2+} on the surfaces of Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34 ; this was confirmed to be the active center of the catalysts for the SCR reaction [29]. CHA-type zeolites favored the formation of copper ions, especially in generating more Cu^+ than other zeolites [11]. This study showed that more Cu^+ was detected on the surface of fresh Cu-Mn/SAPO-34 than Cu-Mn/ZSM-5 . Cu^+ was confirmed to play an important role in NH_3 -SCR below 200 °C [11], and the enrichment of Cu^+ on the surface of fresh Cu-Mn/SAPO-34 might be the reason for its better low-temperature activity than that of Cu-Mn/ZSM-5 (Fig. 1).

After the hydrothermal aging treatment and SCR reaction in the presence of C_3H_6 , the variations of concentration of Cu differed for the two catalysts. As presented in Table S1, a small decrease in the Cu concentration from 0.53% to 0.49% was observed on the surface of Cu-Mn/ZSM-5 , and the Cu concentration increased to 0.85% after the SCR reaction in the presence of C_3H_6 . The doping of Cu was unstable on the surface of Cu-Mn/ZSM-5 . The Cu concentration was much higher on the surface of Cu-Mn/ZSM-5 than on the catalyst after the SCR reaction without C_3H_6 because of the presence of C_3H_6 . Therefore, the existence of Cu was significantly affected by C_3H_6 during the reaction, causing Cu to migrate to the surface of the

catalyst, which would produce copper oxide or copper aluminum compounds [30] and deteriorate the activity. The proportion of Cu species on the surface of Cu-Mn/ZSM-5 also varied notably after the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 (Table 2). After the hydrothermal aging treatment, the proportion of Cu^+ was nearly the same as that of the fresh Cu-Mn/ZSM-5 sample, whereas the proportion of octahedrally coordinated Cu^{2+} was reduced from 29.59% to 9.37%, and approximately two-thirds of the octahedrally coordinated Cu^{2+} was transformed to tetrahedrally coordinated Cu^{2+} . When Cu-Mn/ZSM-5 was used in the SCR reaction in the presence of C_3H_6 , part of the Cu^{2+} was transformed to Cu^+ , and the proportion of Cu^+ increased from 19.74% to 44.57%. Furthermore, octahedrally coordinated Cu^{2+} could not be detected, and all the octahedrally coordinated Cu^{2+} transformed to Cu^+ and tetrahedrally coordinated Cu^{2+} . When the catalyst from the SCR reaction in the presence of C_3H_6 was then used for the SCR reaction without C_3H_6 for three cycles of temperature variation, octahedrally coordinated Cu^{2+} was still not detected, and 7.84% of Cu^+ was transformed to tetrahedrally coordinated Cu^{2+} .

Cu was more stable on the surface of Cu-Mn/SAPO-34 than Cu-Mn/ZSM-5 . The concentration of Cu remained nearly the same before and after the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 . Although Mn was not detected in the fresh Cu-Mn/SAPO-34 sample, it was detected when Cu-Mn/SAPO-34 was used in the SCR reaction in the presence of C_3H_6 (Table S1), and the ratio of Cu/Mn was approximately 3:2, which was equal to the ratio in the precursor solution. The proportion of Cu^+ and tetrahedrally coordinated Cu^{2+} decreased with increases in the octahedral coordination of Cu^{2+} after the hydrothermal aging treatment. Some of the Cu^+ was transformed to Cu^{2+} , and the transformation from tetrahedrally coordinated Cu^{2+} to octahedrally coordinated Cu^{2+} was much stronger. After the SCR reaction in the presence of C_3H_6 , the octahedrally coordinated Cu^{2+} was also transformed to Cu^+ and tetrahedrally coordinated Cu^{2+} . However, it was different from Cu-Mn/ZSM-5 ; octahedrally coordinated Cu^{2+} appeared again after the SCR reaction without C_3H_6 for three cycles of temperature variation. The concentration of Cu^+ was 27.12%, which was slightly lower than that of the fresh sample, whereas the concentration of octahedrally coordinated Cu^{2+} remained at a high level of 23.15%.

The major difference between the two catalysts was the existence of Cu. The concentration of Cu on the surface of Cu-Mn/SAPO-34 was kept at approximately 0.64%, whereas that of Cu-Mn/ZSM-5 varied from 0.49% to 0.85%. Cu^+ ions were suggested to play an important role in NO_x removal when the temperature was below 200 °C. A previous study demonstrated that octahedrally coordinated Cu^{2+} was also an important factor in the low-temperature activity [10]. In Cu-Mn/ZSM-5 , both the hydrothermal aging treatment and the SCR reaction in the presence of C_3H_6 led to a significant decrease in the amount of octahedrally coordinated Cu^{2+} , which was consistent with the decrease of the activity of the catalyst. The further SCR reaction without C_3H_6 did not cause octahedrally coordinated Cu^{2+} to appear again. The redox cycle of the

Table 2
XPS characterization of the copper species.

Sample	Distribution of different copper species (%)		
	Cu^+	Tetrahedrally coordinated Cu^{2+}	Octahedrally coordinated Cu^{2+}
Cu-Mn/ZSM-5^a	19.56	50.85	29.59
Cu-Mn/ZSM-5^b	19.74	70.89	9.37
Cu-Mn/ZSM-5^c	44.57	55.43	—
Cu-Mn/ZSM-5^d	36.73	63.27	—
Cu-Mn/SAPO-34^a	28.64	55.86	15.50
Cu-Mn/SAPO-34^b	23.80	42.73	33.47
Cu-Mn/SAPO-34^c	31.66	68.36	—
Cu-Mn/SAPO-34^d	27.12	49.73	23.15

^a Fresh samples.

^b Catalysts after aging at 750 °C for 24 h in a flowing gas containing 10% $\text{H}_2\text{O}/\text{air}$ with a total flow of 1000 cm^3/min .

^c Catalysts after reacting with 300 ppm NO , 300 ppm NH_3 , 2000 ppm C_3H_6 , 14% O_2 , 5.7% H_2O , and balance N_2 .

^d Three cycles of temperature variation with 300 ppm NO , 300 ppm NH_3 , 14% O_2 , 5.7% H_2O , and balance N_2 after reaction c.

Cu species only took place between Cu^+ and tetrahedrally coordinated Cu^{2+} , which was accompanied with a low activity at low temperatures (Fig. S3). Therefore, the decrease in octahedrally coordinated Cu^{2+} should be another reason for the low hydrothermal stability and low resistance to HCs of Cu-Mn/ZSM-5 besides the variations in its physical properties. In Cu-Mn/SAPO-34, the effect of the decrease of Cu^+ was balanced by the increases of octahedrally coordinated Cu^{2+} after the hydrothermal aging treatment, and the physical properties were almost maintained, revealing the increased low-temperature activity. When Cu-Mn/SAPO-34 was used for the SCR reaction in the presence of C_3H_6 , the octahedrally coordinated Cu^{2+} disappeared with the increase of Cu^+ and tetrahedrally coordinated Cu^{2+} . However, Cu^+ and tetrahedrally coordinated Cu^{2+} on Cu-Mn/SAPO-34 could be transformed to octahedrally coordinated Cu^{2+} again after the SCR reaction without C_3H_6 . The existence of octahedrally coordinated Cu^{2+} as well as the redox circle between Cu^+ and octahedrally coordinated Cu^{2+} played more important roles in the low-temperature activity of Cu-Mn/SAPO-34 than that of Cu-Mn/ZSM-5. Although carbonaceous deposits that formed during the SCR reaction in the presence of C_3H_6 reduced the BET surface area, Cu-Mn/SAPO-34 could still maintain a high level of activity (Fig. 3) with the redox cycle between Cu^+ and Cu^{2+} . Therefore, besides the physical properties, the differences in the variations of Cu spe-

cies were a main reason for the different levels of stability between Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34.

4. Conclusions

During the SCR reaction, a Cu/Mn ratio of 3:2 was the most favorable for both Cu-Mn/ZSM-5 and Cu-Mn/SAPO-34. The NO_x conversion on the two catalysts could reach more than 70% at 200 °C, and Cu-Mn/SAPO-34 had a much higher hydrothermal stability and resistance to HCs than Cu-Mn/ZSM-5. There was no significant variation in the crystal structure of the two catalysts after the hydrothermal aging treatment or the reaction in the presence of C_3H_6 , and the dealumination of Cu-Mn/ZSM-5 could be relieved by the addition of Mn. For physical properties, the aggregation of Cu-Mn/ZSM-5 as well as decreases in the BET surface area and pore volume might be some of the reasons for its lower stability than that of Cu-Mn/SAPO-34. Furthermore, the Cu species were the main parameters that influenced the stability of the catalysts. On Cu-Mn/ZSM-5, a significant decrease in the amount of octahedrally coordinated Cu^{2+} was caused by both the hydrothermal aging treatment and the reaction in the presence of C_3H_6 , and the redox cycle between Cu^+ and octahedrally coordinated Cu^{2+} was significantly inhibited. On the surface of Cu-Mn/SAPO-34, the atomic concentration of Cu was highly stable, and the redox

Graphical Abstract

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Stability of Cu-Mn bimetal catalysts based on different zeolites for NO_x removal from diesel engine exhaust

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The redox cycle of Cu^+ and octahedrally coordinated Cu^{2+} significantly affected the high hydrothermal stability and resistance to hydrocarbons of Cu-Mn/SAPO-34.

cycle of Cu^+ and Cu^{2+} during the SCR reaction was well maintained. Therefore, the physical properties and Cu species are two important factors for the stability of the catalysts.

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分子筛负载Cu–Mn双金属柴油机尾气脱硝催化剂的稳定性

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摘要: 近年来柴油车尾气排放了大量的氮氧化物(NO_x), 其治理技术目前主要基于选择性催化还原(SCR)。但是, 由于柴油车尾气的温度波动范围较宽, 氧气浓度高, 汽油车三效催化剂不能用于柴油车尾气脱硝, 因此开发一种有效的SCR催化剂去除柴油机尾气中的 NO_x 至关重要。Cu/分子筛催化剂在尾气温度高于200 °C时表现出高的脱硝活性, 但低温(<200 °C)催化活性仍有待提高。此外, 当柴油颗粒过滤器再生时催化剂处于高温高湿环境, 而且柴油车尾气中有未完全燃烧的碳氢化合物(HCs)存在。因此, 水热稳定性和抗HCs失活性也是催化剂性能的一个重要指标。Cu–Mn共负载可以有效提高催化剂在200 °C以下对 NO_x 的脱除性能, 但其稳定性尚未讨论。

本文采用离子交换法将Cu–Mn双金属体系负载在ZSM-5和SAPO-34上, 考察了Cu–Mn双金属催化剂去除柴油车尾气 NO_x 的效果, 以及催化剂的温度敏感性、水热稳定性和抗HCs性能。通过X射线衍射(XRD)、扫描电镜(SEM)、 N_2 吸附、 ^{27}Al 固体核磁共振(^{27}Al NMR)和X射线光电子能谱(XPS)等手段分析了催化剂活性和稳定性差异的原因, 探讨了影响稳定性的关键因素。

研究发现, 当Cu/Mn比为3:2时, 200 °C时Cu–Mn/ZSM-5和Cu–Mn/SAPO-34的 NO_x 转化率分别达到65%和90%。当催化剂水热老化处理后, 或在反应气体中通入 C_3H_6 后, Cu–Mn/SAPO-34对 NO_x 的去除率比Cu–Mn/ZSM-5稳定。SEM和物理结构分析结果表明, 水热老化处理和含 C_3H_6 气氛的SCR反应后, Cu–Mn/ZSM-5发生了明显的团聚, 且BET比表面积和孔容减小; 而Cu–Mn/SAPO-34未发生团聚现象, 且保持较好的物理结构。因此, Cu–Mn/ZSM-5的团聚以及物理结构的破坏可能是其稳定性低的原因之一。XRD结果表明, 水热老化处理后Cu–Mn/ZSM-5晶体结构无明显变化, Cu–Mn/SAPO-34的结晶度有所

提高. 含 C_3H_6 气氛的SCR反应后, 两种催化剂仍然保持分子筛结构的特征峰, 表现出较好的晶型结构, C_3H_6 不会对催化剂的结晶度和晶体结构产生破坏作用. 结合SEM图像发现水热老化处理提高了Cu–Mn/SAPO-34的结晶度并提高其低温活性. ^{27}Al NMR结果表明, 两种催化剂在水热老化处理和含 C_3H_6 气氛的SCR反应后, 四面体配位Al的峰面积几乎没有明显的改变, 表明反应后催化剂并未发生明显的脱铝现象, 仍然保持较好的结构稳定性. 这与之之前研究中Cu/ZSM-5反应后四面体配位的Al原子明显减少的结果不同. 因此, Mn的加入可以缓解催化剂的脱铝, 提高稳定性. XPS结果表明, 水热老化处理和含 C_3H_6 气氛的SCR反应均使得Cu–Mn/ZSM-5上八面体配位的 Cu^{2+} 明显降低, Cu^+ 和八面体配位的 Cu^{2+} 之间的氧化还原循环受到明显抑制. 而在Cu–Mn/SAPO-34表面, Cu原子浓度高度稳定, SCR反应中 Cu^+ 和 Cu^{2+} 保持良好的氧化还原循环. 因此, 稳定的物理结构和Cu物种是催化剂稳定性的两个重要因素.

关键词: Cu–Mn/SAPO-34; Cu–Mn/ZSM-5; 柴油车尾气; 水热稳定性; 抗烃类性能

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