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Short communication

Cu–Mn bimetal ion-exchanged SAPO-34 as an active SCR catalyst for removal of NO_x from diesel engine exhausts

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ABSTRACT

Mn/SAPO-34, Cu/SAPO-34, and Cu-Mn/SAPO-34 were prepared through ion-exchanged method and used to remove NO_x from diesel engine exhausts. The original crystal and physical structure of SAPO-34 is maintained in the catalysts. The ion-exchanged amount of Cu in Cu–Mn/SAPO-34 is higher than that in Cu/SAPO-34, and more Cu^+ is formed as active center for low-temperature selective catalytic reduction (SCR). After co-doping of Cu and Mn, the acidic strength of the catalyst increases and formation of NH_3NO_x surface intermediate species is promoted. Cu–Mn/SAPO-34 exhibits high deNO_x activity, hydrothermal stability, and resistance to hydrocarbon (HC).

1. Introduction

Selective catalytic reduction (SCR) of NO_x by ammonia has received extensive research interest for removal of NO_x from diesel engine exhausts [1,2]. The NO_x removal for diesel engines is different from that for gasoline engines, because of the lean-burn condition of diesel engines and wide temperature variation of exhausts (150–550 °C) [3]. Cu/ZSM-5 and Cu/beta exhibit a high catalytic activity and selectivity in SCR reactions for diesel engines [2,4]. However, the hydrothermal stability of these catalysts remains challenging [5] and large amounts of unburned hydrocarbon (HC) in the exhausts leads to poisoning of the catalysts. Therefore, the SCR catalysts used for diesel engines should be able to remove NO_x with high hydrothermal stability and resistance to HC. Ye [2] reported that 80% of NO could be removed within the temperature window of 200–400 °C by using Cu/SAPO-34, and the activity of the catalyst was maintained after hydrothermal treatment and in the presence of HC.

Although Cu/SAPO-34 can effectively remove NO_x with high stability, this catalyst should be more active in the low-temperature range because the normal temperature of exhaust gas from a light duty diesel vehicle ranges from 150 °C to 250 °C [6]. Mn-based catalysts show satisfactory low-temperature SCR performance for stationary sources [7,8]. Some researchers have illustrated that the catalysts that contained Mn with different structures could remove NO_x effectively in the temperature range of 150–250 °C [9–11], and when Mn functioned with Co in the catalysts with hollow and porous structure, NO_x can be effectively removed at even lower temperature [12]. The mechanism study also showed that the co-doping of Mn and a second metal element would greatly improve the reactivity of gaseous NO_2, linear nitrites, and monodentate nitrites [13]. When Mn was co-doped with Fe on ZSM-5 as a SCR catalyst for diesel engines, the low-temperature activity was improved without decreasing the stability of the catalyst [6]. Those findings suggest that co-doping of Cu and Mn on SAPO-34 can be used as an alternative method to obtain SCR catalysts with a high low-temperature activity.

In this study, Cu and/or Mn were doped on SAPO-34 through ion-exchanged method. The physical and chemical properties of the catalysts were characterized. Catalytic activity, hydrothermal stability, and resistance to HC of the catalysts were also investigated.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared through two-step liquid ion-exchanged method [14]. Briefly, 10 g of SAPO-34 zeolites (Tianjin Chemist Scientific Ltd., China; $SiO_2/Al_2O_3 = 0.5$) were added to ammonium nitrate solution (100 mL, 27 wt.%) at 80 °C under continuous stirring for 2 h. The solution was dried to obtain NH_4^+/SAPO-34 powders. Cu and Mn were doped using $Cu(CH_3COO)_2$ and $Mn(CH_3COO)_2$ solutions, respectively. Subsequently, 10 g of NH_4^+/SAPO-34 powders were added to 50 mL of the metal solutions with different ratios of Cu/Mn, and the total concentrations of $Cu(CH_3COO)_2$ and $Mn(CH_3COO)_2$ were

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Table 1
Physical properties of the catalysts.

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
SAPO-34	479.3	0.22	2.2
Mn/SAPO-34	167.4	0.05	3.5
Cu/SAPO-34	154.6	0.05	2.9
Cu-Mn/SAPO-34	259.7	0.12	2.3

Table 2
Atomic concentration on the surface of the catalysts detected by XPS.

Catalysts	Atomic concentration (at.%)					
	Cu	Mn	O	Si	Al	P
SAPO-34	–	–	66.13	10.65	15.23	7.99
Mn/SAPO-34	–	0.50	66.73	8.71	13.96	10.10
Cu/SAPO-34	0.42	–	66.37	8.13	14.90	10.18
Cu-Mn/SAPO-34	0.63	–	66.69	7.68	14.96	10.04

controlled at 0.2 mol/L. The mixture was stirred at 70 °C for 12 h, filtered, and then rinsed with deionized water to get a filter cake. The filter cake was dried at 90 °C for 16 h, and the obtained powders were calcined at 550 °C for 4 h. All catalysts were pressed, rushed, and then sieved to 60–100 meshes.

2.2. Activity test of catalyst

NH_3-SCR activity of the catalysts was carried out in a fixed-bed quartz tubular flow reactor (i.d. 8 mm). The quartz tube contained 2 mL of the catalyst, with a gas hourly space velocity (GHSV) of 30,000 h^{-1}. The composition of typical simulated diesel engine exhausts included the following: 300 ppm_v NO, 300 ppm_v NH_3, 14% O_2, 5.7% H_2O, 2000 ppm_v C_3H_6 (when used), and balance N_2. NO, NO_2, and O_2 concentrations were monitored by using a flue gas analyzer (KM9106 Quintox Kane International Limited, Britain). The activity of the catalysts with different ratios of Cu/Mn is shown in Fig. S1. The highest activity was obtained when the ratio of Cu/Mn was 3:2. Hence, Cu–Mn/SAPO-34 (Cu:Mn = 3:2) was used in subsequent experiments and characterization experiments.

In the investigation of hydrothermal stability, the catalysts were aged in a quartz tube reactor at 650 °C or 750 °C in 10% H_2O/air under a total flow rate of 1 L/min for 24 h before the activity test.

2.3. Characterization

BET surface area, pore volume, and average pore diameter were measured by N_2 physisorption at −196 °C with JW-BK132F instrument (Beijing JWGB Instrument Corporation, China). The physical properties of the catalysts are listed in Table 1.

The X-ray diffraction (XRD) patterns of the catalysts were determined using D/max-rA X-ray diffraction instrument (XD-98) with Cu Kα radiation (λ = 1.5406 Å) at a scanning speed of 1°/min within (2θ) = 5–55°.

The atomic concentrations and the state of the elements on the catalyst surface were analyzed through X-ray photoelectron spectroscopy (XPS) with Al Kα X-ray (Thermo ESCALAB 250Xi, hυ = 1486.6 eV, USA). The binding energy positions were normalized with the standard C 1 s level at 284.8 eV.

Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) analysis were conducted on a Quantachrome Chembet TPR/TPD (p/n 02138-1) equipped with a mass spectrometer (Hiden HAL 201 RC, Britain). Briefly, 100 mg of the catalyst was placed in the quartz reactor, pretreated in He at 500 °C for 1 h, and cooled to 50 °C. TPR experiments were carried out with a ramp of 10 °C/min in 10 vol% H_2/He (120 min/min) from 50 to 800 °C. For NH_3-TPD and NO-TPD experiments, the catalysts were exposed to 4% NH_3/He or 4% NO/He at a rate of 30 mL/min for 30 min, respectively, and then purged with He for 30 min. Desorption was performed to 800 °C in He flow with a rate of 5 °C/min for NH_3-TPD and 10 °C/min for NO-TPD.

3. Results and discussion

3.1. XRD results

The XRD patterns of the catalysts are shown in Fig. 1. The characteristic peaks at 2θ = 9.25°–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 in accordance with the characteristic peaks of SAPO-34 [2]. It means that all of the catalysts possess the CHA structure. Peaks related to CuO, Cu_2O, or MnO_x were not observed, indicating that Cu and Mn species are well dispersed or the concentrations of them are very low [15,16]. The intensity of the peaks decreases after doping of Cu and/or Mn. Thus, the co-doping of Cu and Mn negatively influences the crystal structure of SAPO-34. For Cu–Mn/SAPO-34, the peak intensity is higher than that of Cu/SAPO-34. This finding suggests that co-doping of Cu and Mn on SAPO-34 can weaken the influence of Cu on SAPO-34. Furthermore, Table 1 shows that the physical structure of SAPO-34 is

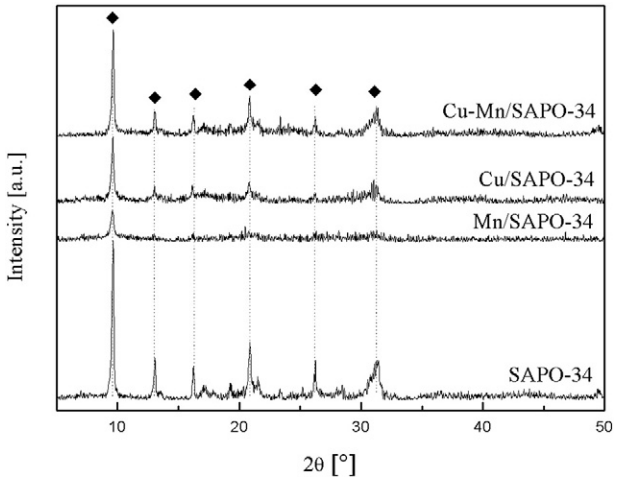

Fig. 1. XRD patterns of the catalysts.

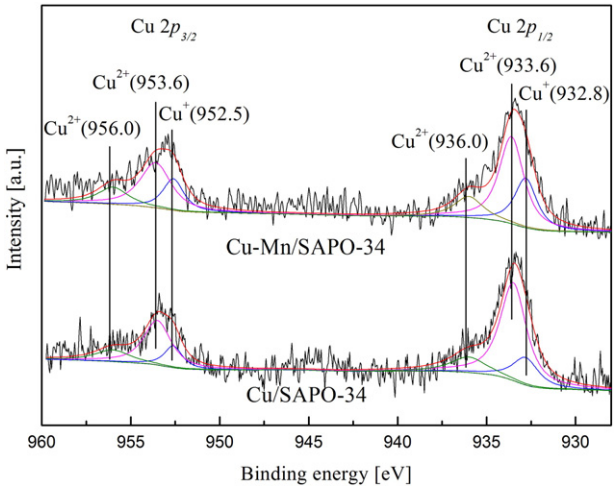

Fig. 2. Cu 2*p* XPS spectra of the catalysts.