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Article

Effect of CuSAPO-34 catalyst preparation method on NO_x removal from diesel vehicle exhausts

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ABSTRACT

CuSAPO-34 samples prepared by hydrothermal synthesis (HS), pore-volume impregnation (PVI), and ion-exchange (IE) methods were characterized using X-ray diffraction, scanning electronic microscopy, atomic absorption spectroscopy, temperature-programmed reduction with hydrogen, X-ray absorption near-edge structure spectroscopy, X-ray photoelectron spectroscopy, and N₂ adsorption. The selective catalytic reduction (SCR) ability over CuSAPO-34 for NO_x from a simulated diesel exhaust was investigated through C₃H₆-SCR and NH₃-SCR, before and after aging of the CuSAPO-34 catalyst. The results indicated that the sample prepared by IE had significantly better activity compared with those prepared using HS and PVI, especially in C₃H₆-SCR at temperatures below 300 °C. The activity of CuSAPO-34 in NO SCR was affected by the preparation method as a result of changes in the specific area (*A*_{BET}), pore-size distribution, and the valence state of the active component. The active component of the catalyst prepared by HS was mainly Cu²⁺, whereas those of samples prepared by IE and PVI were mainly Cu⁺. Aging treatment can destroy the structure of the catalyst, decrease its surface area, and reduce the number of active Cu components on the catalyst surface, leading to a visible decrease in catalytic activity. The CuSAPO-34 prepared using the PVI method had the smallest decrease in NO SCR activity after aging, showing that it had better anti-aging properties.

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1. Introduction

Diesel vehicles have attracted much attention and their use has increased sharply because they have advantages such as high thermal efficiency, high power, and low emissions of CO and hydrocarbons (HCs) [1]. As is well known, NO_x is one of the main pollutants contained in diesel vehicle exhausts, and this high content is very harmful to people and to the environment. Some measures must therefore be taken to reduce this harm.

The regulations on diesel vehicle emissions have become much more stringent, especially with respect to NO_x. Because of the high oxygen content, however, traditional three-way catalysts do not work well in this case [2].

In recent decades, many researchers have focused on the removal of NO_x from diesel vehicle exhausts. Selective catalytic reduction (SCR) is regarded as the best way to remove NO_x and NH₃-SCR is already a highly commercialized technology used for denitration of fixed pollutant sources under lean-burn con-

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ditions. The use of NH_3 , however, makes the denitration process complicated. For mobile sources, such as vehicles, avoiding and controlling NH_3 leaks and erosion are the main problems restricting the use of this efficient technology. It is known that the exhausts from lean-burn engines consist of about 0.05% NO_x , 5–10% O_2 , 10% H_2O , and 0.05–0.1% HCs. Based on this gas composition, the HCs can theoretically reduce NO_x completely to N_2 , and the key point is to find an appropriate catalyst. Because of their high activities and wide activity temperature windows, zeolite-based catalysts have been widely considered [3–8], but their activities are greatly restricted when exposed to atmospheres containing O_2 , H_2O , and SO_2 . Cu-ZSM-5 was at one time considered to be an ideal catalyst for the removal of NO_x , and O_2 has a positive effect on its activity at low temperatures ($< 250\text{ }^\circ\text{C}$). However, its activity is severely reduced at high temperatures [9]. Furthermore, Park et al. [10] found that its structure collapsed after exposure to vapor, and its activity could not be recovered. Iwamoto et al. [11] investigated the effects of SO_2 on Cu-ZSM-5 in both HC-SCR and NO_x decomposition. They found that SO_2 caused partial loss of Cu-ZSM-5 activity in HC-SCR, but the catalyst was completely deactivated in NO_x decomposition. Because of their high thermal and hydrothermal stabilities [12–14], metal-SAPO-34 catalysts overcome these problems; furthermore, their suitable pore structures make them popular for purifying vehicle exhausts [15]. In supported catalysts, the catalytic activity is crucially affected by the preparation method [16–19]. Zeolite-supported catalysts, which are usually prepared using ion-exchange (IE) methods, give excellent catalytic performances. However, the amount of exchanged metal greatly influences the zeolite properties. Catalysts with high metal loadings can be obtained using an impregnation method, but the pores are easily blocked by the reactive metal. In-situ hydrothermal synthesis, in which a reactive metal component is introduced during the preparation process, not only simplifies the preparation but also introduces the active metal into the zeolite framework. Each of these methods has its own advantages and disadvantages, but there has been no systematic analysis and comparison of the effects of the preparation conditions on the physicochemical properties and SCR activities of catalysts. The aim of the present study is to investigate the effect of the Cu loading method on the SAPO-34 physical structure. The performance of CuSAPO-34 for SCR removal of NO in simulated diesel vehicle exhaust atmospheres, using C_3H_6 and NH_3 as reductants, was also studied. Fresh and aged catalysts were characterized using scanning electron microscopy (SEM) and other analytical techniques, and the influence of the aging process on the activity and structure of CuSAPO-34 was investigated to explore the feasibility of reducing NO_x with HCs contained in diesel exhaust gases.

2. Experimental

2.1. Catalyst preparation

SAPO-34 powder, supplied by the Nankai University Catalyst Plant, was used as a support for preparing catalysts by IE

and pore-volume impregnation (PVI) methods. The IE method was as follows. First, the support was ion-exchanged with ammonium nitrate ($w = 27\%$), forming a slurry, which was stirred vigorously at $80\text{ }^\circ\text{C}$ for 2 h. The mixture was then filtered on a Bucher filter, washed with distilled water until the pH of the filtrate was neutral ($\text{pH} = 7$), and then dried at $90\text{--}100\text{ }^\circ\text{C}$ for 16 h. The ammonium-exchange process was repeated twice. Cu was then introduced into the NH_4 -SAPO-34 by IE with CuSO_4 solution (1 mol/L). The slurry was stirred vigorously, using mechanical agitation, at $70\text{ }^\circ\text{C}$ for 2 h. The mixture formed was filtered, washed with distilled water until the filtrate became neutral, dried at $90\text{--}100\text{ }^\circ\text{C}$ for 16 h and calcined at $550\text{ }^\circ\text{C}$ for 4 h. Finally, the above process, including IE, filtering, washing, drying, and calcination, was repeated. The PVI preparation process was as follows. SAPO-34 was impregnated with a Cu precursor solution, which was made by dissolving cupric acetate ($w \geq 99\%$), to give a 1% Cu loading on the catalyst. The mixture was kept stationary for 12 h, dried for 3 h at $120\text{ }^\circ\text{C}$, and calcined at $600\text{ }^\circ\text{C}$ for 3 h.

The in-situ hydrothermal synthesis (HS) procedure was as follows. CuO , H_3PO_4 , $\text{Al}(\text{OH})_3$, and silica gel were used as sources of Cu, P, Al, and Si. Morpholine was used as a template. A crystallization gel was prepared with the molar ratios of $0.08\text{CuO}:0.2\text{SiO}_2:0.92\text{Al}(\text{OH})_3:0.9\text{H}_3\text{PO}_4:1.25\text{morpholine}:50\text{H}_2\text{O}:0.01\text{HF}$. The preparation method has been described in details in the literature [20]. The initial gel was crystallized at $190\text{ }^\circ\text{C}$ for 72 h. The solid product was washed three times, dried at $120\text{ }^\circ\text{C}$ in air for 3 h, and calcined at $600\text{ }^\circ\text{C}$ for 3 h to remove the template. Finally, the CuSAPO-34 catalyst was obtained.

2.2. Characterization

The X-ray diffraction (XRD) patterns of powder samples were obtained with a Rigaku D/MAX2500, using a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154056\text{ nm}$), a tube voltage of 40 kV, and a tube current of 100 mA. The scanning rate and range were $8^\circ/\text{min}$ and $5^\circ\text{--}85^\circ$, respectively. SEM images were obtained using a JEOL JSM-6700F with an accelerating voltage of 10 kV. Before scanning, all samples were sprayed with gold. The Cu content was measured using atomic absorption spectroscopy (AAS; Varian AA240FS, USA) with a 324.7 nm Cu testing wavelength, a 3.0 mA lamp current, and a fuel gas of C_2H_2 (1700 ml/min). Temperature-programmed reduction with hydrogen (H_2 -TPR) experiments were conducted using a TP-5000 equipment with a thermal conductivity detector, developed by the Tianjin Xianquan Institute. A 0.05 g sample of CuSAPO-34 catalyst was first loaded and pretreated at $150\text{ }^\circ\text{C}$ for 0.5 h in a N_2 atmosphere. After cooling to ambient temperature, the gas was switched to the reducing gas (5% H_2/He , 30 ml/min) and the sample was heated to $510\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$. The X-ray absorption near-edge structure (XANES) spectra of the samples (K-edges of Cu and P) and Cu reference samples (CuO , Cu_2O , and Cu) were obtained using the soft X-ray micro characterization beam line at Canadian Light Source. X-ray photoelectron spectroscopy (XPS) was carried out with a Vacuum Generators Escalab-250 (VG Scientific Ltd., UK), using $\text{Al K}\alpha$ ($h\nu$

= 1486.6 eV) radiation. The vacuum during spectra acquisition was 1.3×10^{-6} Pa and the X-ray power was limited to 120 W (12 kV $\times$ 10 mA). The textural properties of the samples were studied using N_2 adsorption–desorption at -196°C (JW-BK122W, JWGB Sci. & Tech. Co., Ltd., Beijing). Prior to the measurements, all samples (0.1–0.2 g) were evacuated at 150°C for 3 h. The pore-size distributions of different samples were calculated by the Barrett–Joyner–Halenda method using the N_2 -adsorption branch. The specific area (A_{BET}) was assessed by the Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure range from 0.05 to 0.35. The total pore volume (V_t) was calculated by converting the amount of N_2 adsorbed at a relative pressure of 0.99 to the volume of liquid adsorbate.

2.3. Activity and anti-aging tests of catalysts

Catalysts prepared using the three different methods were evaluated using temperature-programmed reactions (TPRs). Using NH_3 and C_3H_6 separately as the reducing gas, the activity was investigated by detecting the conversion of NO to N_2 . The catalysts were tableted, ground, and sieved to 40–60 mesh before evaluation. Catalyst powder (0.6 ml) was placed at the center of a quartz reactor ($\Phi = 8.5$ mm). He gas at a flow rate of 100 ml/min was used to clean the reactor for 2 h before testing, and then the gas was switched to the simulated exhaust gas (0.6% NO, 0.7% C_3H_6/NH_3 , 5% O_2 , with He as the balancing gas and a total flow rate of 100 ml/min). Before the TPR experiment, the system was heated to 50°C for 0.5 h to mix the reactant gases well. The activity test temperature varied from 100 to 500°C at a heating rate of $7^\circ\text{C}/\text{min}$. The outlet gas was automatically sampled and analyzed using an on-line gas chromatograph (GC-9890A, Linghua Instrument Co., Ltd., Shanghai, China) equipped with a Porapak Q column for separating N_2O and CO_2 , and a column with 5A molecular sieves for separating N_2 , O_2 , and CO. The NO conversion was calculated based on the yield of N_2 in the product gas.

With the purpose of studying the effect of SO_2 and water on the activity, catalyst samples were exposed to a stream of gas containing 0.03% SO_2 and 10% water vapor, balanced with Ar, at a flow rate of 400 ml/min, and heated for 10 h at 720°C . The same evaluation conditions as those described above were used to test the activity of the aged catalyst in the removal of NO from simulated exhaust gas.

3. Results and discussion

3.1. Characterization

The XRD patterns of CuSAPO-34 samples prepared using different methods are shown in Fig. 1. The characteristic peaks of SAPO-34 at $2\theta = 9.45^\circ$ – 9.65° , 16.0° – 16.2° , 17.85° – 18.15° , 20.55° – 20.9° , 24.95° – 25.4° , and 30.5° – 30.7° appeared for all three catalyst types. The results for the samples before aging show that all the fresh samples had all the diffraction peaks of the SAPO-34 molecular sieve, and had quite high crystallinities and crystal regularities. It should be pointed out that the char-

Fig. 1. XRD patterns of CuSAPO-34 samples.

acteristic peaks of CuSAPO-34 prepared by the in-situ method very nearly coincided with those of the commercial product, i.e., the reactive metal precursor CuO had almost no effect on the crystallization process and the final crystalline form. There was no obvious Cu characteristic peak in the CuSAPO-34 XRD patterns, which may be the result of small crystal domains and/or low Cu loadings [21].

Figure 2 shows the SEM results of different CuSAPO-34 samples before and after aging. Despite the different preparation methods, all the samples had cubic crystal grains of size 1–2 μm covered with different amounts of amorphous material. The crystallinity and morphology of the PVI sample were better than those of the HS and IE samples. The IE sample, however, performed better in the activity tests and this might be because the catalyst produced using the PVI method had smoother and more regular crystals, offering fewer active sites for reaction. The other samples, with rough surfaces, had larger numbers of active sites. It was found that the crystal form was damaged after aging; this coincides with the XRD results. Unlike the PVI sample, there were almost no intact crystal forms in the other two samples after aging, which indicates that the PVI sample had strong anti-aging abilities.

The Cu loadings in the CuSAPO-34 samples are listed in Table 1. As the results show, the HS sample had the highest loading (1.15%), followed by IE and then PVI (0.89%). The similar contents of Cu in the catalysts obtained using the three methods (close to 1%) provided a reference for comparisons in further characterization and activity tests.

Figure 3 shows the H_2 -TPR profiles of different CuSAPO-34 samples before and after aging. For all the samples, before aging, an obvious broad peak from H_2 consumption was detected at nearly the same temperature, i.e., 310°C . This is the mixed peak from Cu^{2+} and Cu^+ reduction to Cu^0 . Of the three samples, the HS sample had the largest peak, followed by the IE sample, and last the PVI sample. The differences in the peak areas can be ascribed to the different Cu loadings on SAPO-34. The peak temperatures of the three catalyst samples were all somewhat higher compared with those in the literature [22,23]; this could be caused by strong interactions between CuO and SAPO-34 in the prepared samples. No H_2 consumption peak was detected

Fig. 2. SEM images of CuSAPO-34. a-d, b-e, and c-f: HS, IE, and PVI samples before and after aging.

Table 1

Cu loadings and $\text{Cu}^{2+}/\text{Cu}^+$ ratios in CuSAPO-34 prepared using different methods.

Sample	w/%	$\text{Cu}^{2+}/\text{Cu}^+$
HS	1.15	3/2
IE	1.04	2/3
PVI	0.89	1/1

w—the loading amount of Cu; $\text{Cu}^{2+}/\text{Cu}^+$ —the fitting results of XANES.

for the samples after aging, although repeated experiments were carried out. It is therefore assumed that a Cu species (CuSO_4), which is difficult to reduce, was formed during the aging process because of the existence of SO_2 and water vapor in the aging gas, thus causing the activity to decrease.

The XANES spectra of Cu and P are shown in Fig. 4. The spectra shows that the samples prepared using different methods had distinct Cu states. Peaks A, B, and D show that the PVI and IE samples had more Cu^+ and Cu^0 , whereas more Cu^{2+} was found in the HS sample. The results are in agreement with the H_2 -TPR results; the differences among the Cu valence states would certainly affect the denitration activities of the catalysts. According to the XANES results for P, all the samples had similar tetrahedral structures consisting of P–O combined with Al, except for small differences among the intensities, suggesting that the molecular structure was not significantly affected by the in-situ preparation method and subsequent metal loading.

To study the valence states of the Cu species present on the CuSAPO-34 surface, the Cu $2p_{3/2}$ transitions were monitored by XPS, and the results are shown in Fig. 5. For all three samples before and after aging, two peaks appeared at around 933 eV and 952 eV, corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. There was, particularly for HS, a very weak shake-up

satellite peak at about 943 eV, from bivalent Cu [24–27]; this is in accord with the H_2 -TPR results. Because of the low Cu loading (1.15% maximum), the Auger spectra were not clear enough to determine the ratio of Cu^+ to Cu accurately. A comparison of the peak areas before and after aging shows a decrease, implying a decrease in the amount of Cu on the SAPO-34 surface; this could be because a proportion of the Cu^{2+} species migrated into the pore canals of SAPO-34. More importantly, the peak corresponding to Cu $2p_{3/2}$ moved to a higher binding energy; this may be caused by sintering of some of the Cu, or CuSO_4 formation during the aging process (caused by water vapor and SO_2 in the aged gas). The activity decreased as a result of a decrease in the number of reactive components.

The pore-structure parameters of the different samples are

Fig. 3. H_2 -TPR profiles of CuSAPO-34 prepared using different methods before and after aging.

Fig. 4. Cu (a) and P (b) K-edge XANES spectra of fresh samples.

Fig. 5. XPS profiles of different CuSAPO-34 samples before and after aging.

listed in Table 2. It is clear that for the samples before aging, the HS sample had the largest A_{BET} and V_t , followed by the IE and PVI samples, in that order. It is known that a larger A_{BET} would favor catalytic reactions, and this proved to be in accord with the activity tests. However, for the samples after aging, there was not such a regular trend as that described above. A comparison showed that the A_{BET} and V_t values decreased by different degrees; the HS sample showed the sharpest decrease, followed by the IE sample. The values for the PVI sample decreased slightly, indicating its strong resistance to aging. These results indicate that the pore structure and anti-aging ability of CuSAPO-34 are both affected by the preparation method. The D

Table 2

Pore structure results from N_2 adsorption of CuSAPO-34 samples prepared using different methods before and after aging.

Sample		$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_t/(\text{cm}^3/\text{g})$	D/nm
Before	HS	166.79	0.095	2.51
aging	IE	155.00	0.090	2.53
	PVI	148.64	0.079	2.32
After	HS	59.53	0.043	3.16
aging	IE	105.13	0.063	2.62
	PVI	106.06	0.061	2.50

values of the samples prepared using the three methods, however, all increased after aging. Combined with the SEM results, this suggests that extra mesopores are formed during the aging process, along with destruction of the crystalline shape, reducing the number of micropores and decreasing the A_{BET} , which will have a further impact on the activity of the aged samples.

The N_2 adsorption-desorption and pore-size distribution curves are shown in Fig. 6. The results in Fig. 6(a) show that the N_2 adsorption-desorption curves of all the samples before aging were type IV in the IUPAC classification, a characteristic of mesopore materials. In the initial stage of the isotherms, the steep rise in N_2 adsorption suggests the presence of micropores. When the relative pressure, p/p_0 , is over a certain value, a hysteresis loop can be seen, showing that CuSAPO-34 has a complex pore structure and a wider-pore-size distribution region. This might be because some crystallographic defects formed during synthesis result in imperfect crystal units or amorphous material in the crystals. These results are in agreement with the SEM results, which also detected the presence of amorphous materials. From Fig. 6(b), it is found that there are no visible differences between the N_2 isotherm adsorption-desorption curves of the catalyst samples before and after aging, and the hysteresis loop still exists. This suggests that the aging process had no obvious effect on the pore composition. The quantity of N_2 adsorption-desorption, however, decreased obviously after aging. The decrease is most obvious in the HS sample; the amounts for the PVI and IE samples decreased slightly, and were similar to each other. These results indicate that the aging treatment had the greatest effect on the pore structure of the sample prepared by the HS. The pore-size distribution profiles of CuSAPO-34 before aging are shown in Fig. 6(c). There is only one visible peak, appearing at 3.40 nm, for HS, reflecting the fact that the pore size of HS is mainly around 3.40 nm, i.e., mesopores. The absence of an obvious peak at around 2.00 nm reflects the small number of micropores. For the samples from PVI and IE, the multimodal pore-size distributions, with peak values at 2.21 and 8.21 nm, and 2.49 and 5.84 nm, corresponding to micropores and mesopores, indicate a mixture of micro- and meso-pores in the

Fig. 6. N_2 adsorption-desorption isotherms (a, b) and pore-size distributions (c, d) of fresh and aged samples.

samples prepared by PVI and IE. After aging, the pore size of the HS sample increased sharply from 3.40 to 6.42 nm; for both PVI and IE, the proportion of mesopores increased somewhat and that of micropores decreased. These results suggest that the different preparation methods led to different pore-size distributions, and the aging process could destroy the micropore structure.

3.2. Effect of preparation method on activity of CuSAPO-34 catalyst

The effect of the preparation method on the conversion of NO_x over CuSAPO-34 at different temperatures, from 100 to 500 °C, is shown in Fig. 7. No detectable N_2O was found during the tests, which implies that the main product from the reduction of NO over CuSAPO-34 was N_2 . In both C_3H_6 -SCR and NH_3 -SCR, the NO conversion increased with increasing temperature. In particular, for C_3H_6 -SCR, the sample prepared using IE (56% maximum) had distinctly better denitration activity than those of the HS and PVI samples at reaction temperatures below 300 °C. As the reaction temperature increased from 300 °C to 400 °C, the catalytic activity of the HS sample increased more significantly, by nearly 30%. For the IE sample NH_3 -SCR, there was no increase in catalytic activity with increasing temperature; this was ascribed to the strong reducing properties of NH_3 . It should be noted that the improved activity of the IE sample compared with that of HS gradually disappeared in both reactions at high temperatures (≥ 300 °C),

which indicates that the superior activity of the PVI sample can only be exploited at high temperatures. The conversion of NO over both HS and PVI samples decreased slightly when the temperature was over 400 °C. A comparison showed that the conversion of NO_x over CuSAPO-34 in NH_3 -SCR was much higher than that in C_3H_6 -SCR. In addition, the IE sample had the highest catalytic activity, and the PVI sample had the lowest, for the C_3H_6 reducing agent, similar to the results for NH_3 .

The XANES and XPS results show that Cu^{2+} and Cu^+ were present in the samples prepared using the different methods, which confirms that the activity of the catalyst is related to the valence state of its active component Cu. There is an oxidation-reduction cycle between Cu^{2+} and Cu^+ , in which Cu^+ is used as the active center [28]. Active species are formed through NO adsorption on Cu^+ and then transformed into N_2 . The differences at different temperatures are mainly caused by different ratios of Cu^+ to Cu^{2+} in the Cu^+/Cu^{2+} system. It can be seen from the linear fitting results (listed in Table 1) for XANES that the Cu^{2+}/Cu^+ ratio for the three fresh catalysts are 3:2, 2:3, and 1:1, corresponding to the HS, IE, and PVI samples. The IE sample, with a higher content of Cu^+ , performs better in de- NO_x . A comparison of the curves before and after aging shown in Fig. 7 shows a decrease in NO conversion. According to the XRD and XPS results, the crystal structure of the aged sample changed, and there was a reduction in the amount of active Cu, along with formation of $CuSO_4$. Wilken et al. [29] found that a decrease in the amount of Cu^+ and an increase in the amount of Cu^{2+} during the aging process were the main factors for partial

Fig. 7. NH_3 -SCR (a) and C_3H_6 -SCR (b) over CuSAPO-34.

deactivation of Cu-based catalysts. The activity reductions for the samples after aging are therefore the result of the combined actions of the different factors discussed above.

4. Conclusions

Three different CuSAPO-34 samples were prepared using HS, PVI, and IE loading methods, and their SCR de- NO_x activities using C_3H_6 and NH_3 were investigated. The results suggested that in C_3H_6 -SCR, the IE sample gave the highest NO conversion, generally above 30%, and 56% maximum. Regardless of whether C_3H_6 or NH_3 was used as the reducing agent, the IE sample exhibited the highest usage ratio of the active component, followed by the HS sample, and then the PVI sample. The crystal structure, content, and chemical form of the reactive component were, to some extent, destroyed or affected by aging, resulting in a decrease in the catalytic activity, but the catalytic activity for de- NO_x over all three samples still remained quite high.

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Graphical Abstract

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Effect of CuSAPO-34 catalyst preparation method on NO_x removal from diesel vehicle exhaustsZUO Yongquan, HAN Lina*, BAO Weiren, CHANG Liping, WANG Jiancheng*
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CuSAPO-34 catalysts were prepared by hydrothermal synthesis, ion exchange, and pore-volume impregnation. The de-NO_x activity of CuSAPO-34 strongly depended on the preparation method, and the sample prepared using ion exchange performed best in selective catalytic reduction in both NH₃-SCR and C₃H₆-SCR.

Cu的负载方法对CuSAPO-34脱除柴油车尾气中NO_x的影响左永权^a, 韩丽娜^{a,b,*}, 鲍卫仁^a, 常丽萍^a, 王建成^{a,#}^a太原理工大学 煤科学与技术山西省和教育部重点实验室, 山西太原030024^b太原理工大学 材料科学与工程学院, 山西太原030024

摘要: 采用X射线衍射、扫描电镜、原子吸收、程序升温还原、X射线吸收近边吸收谱、X射线光电子能谱、氮吸附等手段对水热合成(HS)、等体积浸渍(PVI)与离子交换(IE)法制备的CuSAPO-34样品进行了表征, 并评价了老化前后催化剂上C₃H₆-SCR与NH₃-SCR脱除模拟柴油车尾气中NO_x的反应活性。结果表明, IE法制得的催化剂活性最高, 尤其在C₃H₆-SCR低温阶段; PVI法制得的催化剂活性最差。制备方法影响CuSAPO-34催化剂的比表面积、孔径分布和活性组分价态从而改变其催化活性。各催化剂均存在Cu⁺和Cu²⁺, 但比例明显不同。HS样品以Cu²⁺为主, 另两种样品则含较多的Cu⁺。老化不仅部分破坏了分子筛的形貌、降低了分子筛的比表面积, 尤其是表面Cu含量, 而且有部分Cu生成了CuSO₄, 使得老化后催化剂的脱硝活性降低。PVI法制得的催化剂老化后活性下降幅度最小, 表明该分子筛抗老化能力较强。

关键词: CuSAPO-34; 水热合成; 离子交换; 等体积浸渍; 选择性催化还原; 老化

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1. 前言

柴油车因具有热效率高、功率大、CO及碳氢化合物(HC)排放低^[1]等优点而备受关注, 使用量急剧增加。众所周知, 柴油车尾气中NO_x含量较高, 对人类及环境造成严重的危害; 高效脱除柴油车尾气中的NO_x势在必行。然而, 由于柴油车尾气中含氧量较高, 使传统三效催化

剂脱除法几近失效^[2]。

目前, 选择性催化还原(SCR)被公认是脱除柴油车尾气中NO_x最合理的方法。贫燃条件下用NH₃-SCR脱除固定污染源NO_x已经是一项高度商业化的技术, 然而NH₃的利用使得脱除NO_x装置非常复杂。另外对诸如交通工具等移动污染源而言, NH₃泄露控制以及腐蚀仍然是制约该技术应用的主要因素。贫燃发动机尾气一般含

有大约 0.05% NO_x , (5%~10%) O_2 , 10% H_2O 与 (0.05%~0.1%) HC , 理论上 HC 完全可以将 NO_x 还原为 N_2 , 但选择合适催化剂至关重要. 沸石基分子筛因高活性与宽活性温度窗口备受关注^[3~8]; 但在 O_2 , H_2O 与 SO_2 存在条件下, 分子筛活性受到严重抑制. 人们一度认为, Cu-ZSM-5 是 NH_3 -SCR脱除 NO_x 的理想催化剂, 且 O_2 在低温时对其活性有促进作用; 但较高温度时则有较严重的抑制作用^[9]. 此外, Park等^[10]还发现, 经 H_2O 处理后, Cu-ZSM-5 结构坍塌, 进而造成不可逆失活. Iwamoto等^[11]研究了 SO_2 对 Cu-ZSM-5 在 HC -SCR和分解脱除 NO_x 的影响, 结果发现, 在 HC -SCR中, SO_2 造成 Cu-ZSM-5 局部不可逆失活; 而在分解脱除 NO_x 过程中通入 SO_2 后, Cu-ZSM-5 几乎完全失活. 金属- SAPO-34 分子筛的高热稳定性与水热稳定性^[12~14]则可能弥补这一缺陷, 而且该分子筛适宜的孔结构使其在净化汽车尾气中表现出较好的性能^[15]. 对于负载型催化剂, 活性金属负载方法对其催化性能几乎起决定性作用^[16~19]. 目前分子筛基负载型催化剂常采用离子交换法制备, 所得催化剂性能高, 但金属交换量受分子筛性质的影响较大. 浸渍法可以制备金属含量较高的催化剂, 但活性金属易堵塞载体的孔道. 原位负载(in-situ)是指在分子筛合成过程中将活性金属引入, 可简化制备步骤, 而且活性金属可能进入分子筛骨架. 上述三种常用的催化剂制备方法各有千秋, 制备条件对所制催化剂的物化性能及其对选择性催化还原 NO_x 反应活性的影响尚未见报道. 本文考察 Cu 的负载方法对 CuSAPO-34 分子筛物理性质的影响, 并通过模拟柴油车尾气, C_3H_6 或 NH_3 还原剂, 考察 CuSAPO-34 催化剂上 NO -SCR性能; 结合老化前后催化剂活性的变化及其形貌、活性组分组成及还原性、催化剂孔结构等表征结果, 讨论老化对 CuSAPO-34 活性影响的作用机理, 以探索柴油车尾气中 HC 还原 NO_x 的可行性.

2. 实验部分

2.1. 催化剂制备

离子交换法(IE)制备催化剂. 首先用硝酸铵溶液($w = 27\%$)与 SAPO-34 (南开大学催化剂厂)粉末进行离子交换, 将形成的浆料在 80°C 强烈搅拌2 h; 利用Bucher过滤器对混合物进行过滤洗涤, 直至滤液呈中性, 所得粉末在 $90\sim 100^\circ\text{C}$ 干燥16 h. 重复以上铵离子交换过程两次. 其次, 通过与 CuSO_4 溶液(1 mol/L)进行离子交换, 将 Cu 引入 NH_4 - SAPO-34 内, 在 70°C 机械搅拌该浆料2 h; 经过滤、洗涤直至滤液 $\text{pH} = 7$; 所得滤饼在 $90\sim 100^\circ\text{C}$ 干燥16

h, 550°C 焙烧4 h, 即制得IE样品.

按 Cu 负载量为1%计算, 配制乙酸铜溶液, 加入 SAPO-34 进行等体积浸渍(PVI); 然后静置12 h, 120°C 干燥3 h, 600°C 焙烧3 h, 即制得PVI样品.

原位水热法(HS)合成 CuSAPO-34 ^[20]. 以吗啉为模板剂, CuO 为铜源, H_3PO_4 为P源, $\text{Al}(\text{OH})_3$ 为Al源, 硅胶为硅源. 依照 0.08 CuO :0.2 SiO_2 :0.92 $\text{Al}(\text{OH})_3$:0.9 H_3PO_4 :1.25吗啉:50 H_2O :0.01 HF (摩尔比)配置晶化液, 在 190°C 晶化72 h. 固相产物洗涤3次, 120°C 下干燥3 h, 然后在 600°C 焙烧3 h, 即制得HS样品.

2.2. 催化剂表征

催化剂的X射线衍射(XRD)测试在日本Rigaku D/MAX2500型X射线衍射仪上进行, Cu 靶 K_α 辐射($\lambda = 0.154056\text{ nm}$), 管电流100 mA, 管电压40 kV, 扫描范围 $2\theta = 5^\circ\sim 85^\circ$, 扫描速率 $8^\circ/\text{min}$. 扫描电镜(SEM)测试在日本Jeol Jsm-6700F型SEM上进行, 加速电压10 kV, 扫描前先对样品表面进行喷金处理, 然后选择不同区域进行扫描. Cu 含量采用原子吸收(AAS, 美国VARIAN AA240FS)测量, 铜的测定波长324.7 nm, 灯电流3.0 mA, 燃气(C_2H_2)流量1700 ml/min. H_2 程序升温还原(H_2 -TPR)利用天津先权研究所的TP-5000型仪器测试, 先将0.05 g样品于 150°C 下用 N_2 吹扫30 min, 冷却至室温后切换为5% H_2 -95% He , 以 $10^\circ\text{C}/\text{min}$ 升至 510°C . 利用加拿大光源中心的SXRMB(the Soft X-ray Micro characterization Beam line)对样品和 Cu 标样(CuO , Cu_2O 和 Cu)的同步辐射X射线吸收谱以及 Cu 和 P 的K边近边谱进行研究. X射线光电能谱(XPS)分析采用英国VG公司的Escalab-250型多功能表面分析仪, 使用 $\text{Al } K_\alpha(h\nu = 1486.6\text{ eV})$ 作激发源, 功率为120 W ($12\text{ kV} \times 10\text{ mA}$), 工作室真空度为 $1.3 \times 10^{-6}\text{ Pa}$. 孔结构分析在北京精微高博科技有限公司生产的JW-BK122W型吸附仪上进行, N_2 为吸附质, 吸附温度 -196°C , 所有样品吸附前均在 150°C 下真空干燥3 h, 样品用量0.1~0.2 g. 孔径分布通过BJH公式计算恒温吸附曲线数据获得, 比表面积利用标准BET公式计算相对压力为0.05~0.35恒温吸附数据得到, 总孔容通过将相对压力为0.99时 N_2 的吸附量转化为液体吸附质计算得到.

2.3. 催化剂活性及抗老化性评价

分别以 NH_3 与 C_3H_6 为还原剂, 通过检测 NO 转化成 N_2 的转化率考察催化剂的活性. 先将催化剂压片, 研磨, 筛选40~60目. 将0.60 ml样品固定于内径为8.5 mm石英反应管中, 常温通入 He 吹扫2 h排净管路中残留空气, 然后

切换为反应气(0.60% NO-0.70% C₃H₆(或NH₃)-5.00% O₂, He为平衡气, 总流量100 ml/min)稳定0.5 h后, 从常温开始以7 °C/min的速率升温至100~500 °C进行反应. 采用配有TCD检测器的气相色谱仪(GC-9890A, 上海灵华仪器有限公司)对尾气进行在线分析. 其中Porapak Q填充柱用于检测N₂O和CO₂, 5A柱检测N₂, O₂和CO, 以N₂生成量计算NO转化率.

为了考察SO₂和H₂O对催化剂活性的影响, 在0.03% SO₂-10% H₂O, Ar为平衡气, 总流量是400 ml/min, 720 °C条件下将催化剂连续老化10 h, 再同上进行活性评价.

3. 结果与讨论

3.1. 催化剂的表征

图1为不同方法制得的CuSAPO-34催化剂老化前后的XRD谱. 由图可见, 三种催化剂在 $2\theta = 9.45^\circ \sim 9.65^\circ$, $16.0^\circ \sim 16.2^\circ$, $17.85^\circ \sim 18.15^\circ$, $20.55^\circ \sim 20.9^\circ$, $24.95^\circ \sim 25.4^\circ$ 与 $30.5^\circ \sim 30.7^\circ$ 处均出现SAPO-34的特征衍射峰. 老化前各样品均有完好的晶体结构与较高的结晶度和晶体规整性, 但老化后各样品衍射峰明显减弱, 表明结晶度降低. 应特别指出, 原位水热合成制备的CuSAPO-34的特征峰几乎和商业购买品的重合, 说明在分子筛制备过程中, 活性金属前驱体CuO对晶化过程和最终的晶型基本没有影响. 另外, 各样品均未出现明显的Cu特征峰, 可能是由于晶粒较小或者Cu负载量低的缘故^[21].

图2为不同方法制备的CuSAPO-34催化剂的SEM照片. 由图可见, 各样品均呈正方形形貌, 晶粒粒径为1~2 μm , 且各分子筛表面有不等量无定形物. 比较后发现, PVI样品的形貌与结晶度好于HS和IE样品, 但却表现出较低的催化活性(见下文), 很可能是因为PVI样品晶形更加平滑规整, 提供的活性位反而更少; 其余样品的晶面附着较多的无定形物导致表面比较粗糙, 可为催化反应提供较多的活性位. 另外, 样品老化后其晶体形貌受到明显破坏, 除PVI样品之外, 另两种样品几乎没有完整的晶形存在, 说明PVI样品有较强的抗老化能力.

表1为各分子筛样品中Cu负载量. 可以看出, HS样品中Cu负载量最高, 为1.15%, IE次之, PVI的最低, 只有0.89%; 但均量均接近于1%.

图3是不同方法制备的CuSAPO-34样品老化前后的H₂-TPR谱. 由图可见, 老化前各样品几乎均在310 °C处出现明显的耗氢峰, 其中HS峰面积较大, IE次之, PVI最小. 这与它们的Cu负载量一致. 我们推测, 该耗氢峰是Cu²⁺和Cu⁺还原为单质Cu⁰的复合峰, 但峰值与文献

[22,23]结果有所延迟. 这可能是因为铜的氧化物与载体SAPO-34之间存在较强相互作用所致. 老化后各样品未出现任何还原峰, 可能是经老化后Cu以较难还原的物种形式存在. 因为老化过程中有SO₂和水, 故猜测可能是部分铜以铜盐的形式存在, 从而导致老化催化剂活性降低.

图4为不同方法制得的CuSAPO-34样品的Cu和P的近边谱. 可以看出, 各样品中Cu的价态差别较大, A, B, D处的峰显示IE和PVI样品具有较多的Cu⁺和Cu⁰, 而HS样品中在C处的主峰则表现出了更多的Cu²⁺, 与H₂-TPR结果一致. P的XANES结果显示, 三种催化剂都是和Al结合的P氧四面体结构, 且仅强度稍有不同, 说明原位制备和后续金属的负载对分子筛骨架影响不大.

图5为各CuSAPO-34样品老化前后的XPS谱. 由图可见, 各样品均在933与952 eV附近分别出现Cu 2p_{3/2}和Cu 2p_{1/2}特征峰. HS催化剂在943 eV附近出现较弱的振动伴峰, 表明样品表面存在Cu²⁺^[24~27], 与TPR结果一致. 由于所制样品中Cu的负载量总体较低, 样品的Auger谱图较差, 所以不能准确判定样品表面是否有低价态Cu⁺和Cu⁰的存在及比例. 对比后发现, 老化后样品表面Cu含量明显降低, 其原因可能是Cu物种发生迁移进入SAPO-34孔道内部. 更重要的是, Cu 2p_{3/2}向高的结合能移动, 这可能是因为高温老化过程中(老化气氛中有H₂O和SO₂)表面部分Cu物种烧结或者形成较难还原的CuSO₄, 活性物的减少势必会降低老化后催化剂活性.

表2为各样品老化前后的结构性质. 可以看出, 对于老化前的样品, HS样品的A_{BET}与V_t较大, IE居中, PVI较小; 较大的A_{BET}无疑更有利于进行催化反应. 另外, 经老化后, 各样品的V_t与A_{BET}都有所降低, 其中HS降低幅度最大, IE次之, PVI最小, 说明PVI样品抗老化能力较强, 与SEM结果一致. 综上所述, 制备方法对CuSAPO-34的孔结构和抗老化能力均有影响. 老化使不同CuSAPO-34样品的平均孔径有所增加. 结合SEM结果, 我们分析可能是老化对晶形破坏较严重, 微孔数量减小的同时形成了具有较大孔径的孔道, 降低了A_{BET}, 从而影响了老化后催化剂的活性.

图6为各样品的N₂吸附-脱附曲线及孔径分布图. 由图可见, 老化前各样品的等温线均呈IV型, 在p/p₀初始阶段, N₂吸附量急剧上升, 说明样品存在微孔; 当p/p₀大于一定值后, 均有滞后环出现, 表明CuSAPO-34样品孔径分布加宽, 孔道结构复杂, 可能是由于在合成样品过程中有结晶缺陷存在, 造成结构单元不完整; 也可能是样

品中存在无定形杂质所致. 老化后各样品的 N_2 吸附-脱附曲线类型没有变化, 仍然存在滞后环, 只是吸附-脱附量明显减少, 其中HS减少量最大, 表明老化对HS样品孔结构的影响较大, 而对孔类型影响不明显. 图6(c)为老化前各样品的孔径分布图. 由图可见, HS样品主要为孔径集中于3.40 nm附近的介孔材料, 微孔所占比例较少; 而PVI与IE除分别在2.21和2.49 nm左右出现微孔外, 还分别在8.21与5.84 nm附近出现较多的介孔. 比较后发现, 老化后, HS样品的峰值明显增加, 而PVI与IE样品的介孔所占比例有所增加, 但微孔所占比例减小. 由此可见, 不同的制备方法形成不同的孔径分布, 老化能破坏微孔结构从而增加介孔的比例.

3.2. 制备方法对CuSAPO-34活性的影响

图7为不同方法制得的CuSAPO-34样品上 NO_x 转化率随温度的变化. 实验过程中没有检测到 N_2O , 可以认为NO转化反应的主要产物是 N_2 . 由图可见, 在 C_3H_6 -SCR与 NH_3 -SCR反应中, 随着温度升高, 各CuSAPO-34分子筛上NO转化率均上升. 对于 C_3H_6 -SCR反应, 低温($< 300^\circ\text{C}$)阶段IE样品上NO转化率明显高于HS和PVI(活性相当); 当温度由 300°C 上升至 400°C 时, 相对于IE和PVI样品, HS样品上NO转化率明显增加; 在 NH_3 -SCR低温阶段, IE样品活性不太高, 这归因于 NH_3 较强的还原性. 应注意的是, 在高温($\geq 300^\circ\text{C}$)阶段, HS样品的活性明显升高; 至 400°C 以上后, 除IE外, 样品的NO转化率均小幅下降. 对比后发现, 以 NH_3 作还原剂时, 各分子筛样品上NO转化率明显高于 C_3H_6 作还原剂时的转化率; 但总体上PVI样品的活性均较低, 而IE样品的活性较高.

结合XANES和XPS结果可知, 各样品中均含有 Cu^{2+}

和 Cu^+ , 催化剂脱硝活性与活性组分存在价态密切相关, Cu^{2+} 与 Cu^+ 之间氧化还原循环可逆, 其中 Cu^+ 作为活性中心^[28], 在吸附NO后形成活性物种进一步反应生成 N_2 . 各样品在不同温度阶段的活性差异, 主要是 $\text{Cu}^+/\text{Cu}^{2+}$ 比例不同所致. 由表1可见, IE, PVI和HS新鲜样品的 $\text{Cu}^{2+}/\text{Cu}^+$ 分别为2/3, 1/1和3/2. 结果表明, IE催化剂中较高的 Cu^+ 使其具有最高的脱硝活性. 对比图7发现, 老化后各分子筛样品上NO转化率均有所下降. 上文结果显示, 老化部分改变了分子筛晶形结构, 表面Cu活性组分减少, 且有部分 CuSO_4 生成. Wilken等^[29]认为, 老化过程中 Cu^+ 减少, 而 Cu^{2+} 相应增加会使样品的活性降低. 因此, 老化样品活性的降低应该是上述因素共同作用的结果.

4. 结论

采用三种负载方法制备了CuSAPO-34催化剂, 并考察了它们在 C_3H_6 和 NH_3 的选择性催化还原NO反应中的催化性能. 结果表明, C_3H_6 -SCR中IE样品上NO转化率最高, 总体维持在30%以上, 最高达56%; 在 C_3H_6 和 NH_3 作还原剂时, 该样品活性组分利用率最高, 而PVI样品的性能最差. 老化在一定程度上由于破坏了分子筛的晶体结构, 改变了表面活性组分的Cu含量和化学形态, 从而导致样品活性均有所降低, 但仍然保持了较高的脱硝活性.

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