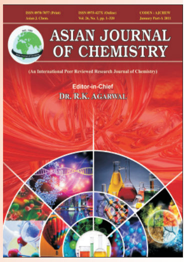
Asian Journal of Chemistry; Vol. 26, No. 7 (2014), 2099-2104

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16224



One Pot Optimized Synthesis of Cu-SAPO-34/Cordierite with HF and the Properties of NH_3-SCR for NO_x Removal

HUI QIAO, JIANCHENG WANG, ZHIJUAN GAO, YING CHEN, ZHIQIANG LIU, LIPING CHANG and WEIREN BAO*

State Key Laboratory Breeding Base of Coal Science and Technology, Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, Shanxi Province, P.R. China

*Corresponding author: Tel/Fax: +86 351 6010482; E-mail: baoweiren@tyut.edu.cn; wangjiancheng@tyut.edu.cn

Received: 24 August 2013; *Accepted*: 9 December 2013; *Published online*: 22 March 2014; AJC-14970

Cu-SAPO-34/cordierite catalysts, prepared *via in situ* hydrothermal synthesis technique with various HF content, of which the morphology and crystal structure were characterized by XRD and SEM, respectively. The activity of the catalysts prepared above for selective catalytic reduction (SCR) of NO_x was evaluated with a fixed-bed reactor in simulated diesel vehicle exhaust. The results indicated that HF content played great roles on crystallization and catalytic properties of the samples. Loading amount and relative crystallinity of Cu-SAPO-34 were both increased along with the increasing n(HF)/n(Al_2O_3) ratio in the range of 0.01-0.03. The grain size became smaller and more uniform. The samples, crystallized for 24 h, have already showed a higher de-NO_x activity and a stronger anti-aging property, over which the NO_x conversion rate at the space velocity of 12 000 h^{-1} could reach higher than 95 % from 320 to 600 °C. As for the sample of n(HF)/n(Al_2O_3) = 0.03, NO_x conversion rate could reach higher than 80 % from 380 to 560 °C at the space velocity of 36 000 h^{-1} and reached higher than 50 % from 460 to 580 °C after the aging treatment.

Keywords: HF, Cu-SAPO-34, Cordierite, de-NO_x, Selective catalytic reduction, Aging treatment.

INTRODUCTION

The growing demand for fuel-efficient vehicles has resulted in the widespread application of diesel engines due to the advantages of strong power, higher thermal efficiency, lower oil consumption, longer service life and the products of hydrocarbon and carbon monoxide can be significantly reduced. However, the diesel vehicle also emits lot of NO_x to the atmosphere[1,2]. Now, more and more restrictive legislations for diesel exhaust emissions promote the development and application of the exhaust after-treatment techniques[3]. Up to now, selective catalytic reduction technology with reductant (such as NH_3) is considered as a leading control method for NO_x emission[3-6].

High oxygen content and the presence of water vapor in the diesel exhausts contribute to the low catalytic activity of the conventional three-way catalyst that can remove carbon monoxide, hydrocarbons, nitrogen oxides effectively at the same time[7,8]. Therefore, the urgent and challengeable task is aimed at developing a new catalyst, with high NO_x-SCR activity, good hydrothermal stability and excellent anti-aging performance in the presence of excess oxygen and water vapor. Due to small-pore, medium acidity as well as excellent thermal and hydrothermal stability[9,10], SAPO-34, a silicoaluminophosphate molecular sieve, has been widely studied. As a promising candidate for the potential application in diesel engine exhaust treatment, it has been reported that Cu-SAPO-34 powder exhibited a higher activity for NO_x-SCR. Our previous studies have found that NO_x conversion rate in C_3H_6-SCR could reach higher than 60 % from 500 to 650 °C over Cu-SAPO-34/cordierite monolithic catalysts, moreover, the samples had a higher Cu-SAPO-34 loading as well as excellent hydrothermal stability. Meanwhile, the effects of oxygen concentration and space velocity on the de-NO_x activity of the catalysts in NH_3-SCR were also investigated[11]. It has been proven that the addition of appropriate amount of HF could remarkably improve the crystal structure and morphology as well as the crystal size of Cu-SAPO-34 molecular sieve. During the crystallization process of molecular sieve, hydrofluoric acid plays a role in not only the mineralization but also the structure directing like the template, which promoted the dissolution of the silica and aluminum source of the initial gel and accelerated the crystallization rate[12,13].

In this paper, Cu-SAPO-34/cordierite was prepared by in suit hydrothermal method. Copper(II) oxide and morpholine were used as the copper source and structure directing agent, respectively. The catalysts were characterized by X-ray diffraction and scanning electron microscopy. Meanwhile, the effect of HF content on morphology, structure and catalytic properties of the samples was investigated.

EXPERIMENTAL

Preparation of catalyst: Cu-SAPO-34/cordierite was prepared *via* one step in-suit hydrothermal method. A commercial honeycomb cordierite (200 cpsi), after appropriately acid-treated, was used as support for monolithic catalyst. The pretreating procedure and synthetic process of Cu-SAPO-34/cordierite is similar to that reported in our previous work[11]. Copper(II) oxide, morpholine, silica gel (30.4 wt % SiO_2), aluminum hydroxide [64.5 wt % $Al(OH)_3$] and phosphoric acid (85 wt % H_3PO_4) were used as active metal source, template, silicon source, aluminum source and phosphorus source, respectively. The initial gel was prepared according to the molar compositions of 0.08 CuO: 0.2 SiO_2: 0.3 Al_2O_3: 0.45 P_2O_5: 1.25 C_4H_9NO: 50 H_2O: x HF. The ratio of n(HF)/n(Al_2O_3) varied from 0, 0.01, 0.02, 0.03, 0.05, 0.10 to 0.20 by changing HF content. A series of catalysts were obtained by changing the crystallization time (3, 6, 12, 24, 36 and 48 h) for every one ratio of n(HF)/n(Al_2O_3).

Activity evaluation of the catalysts: The NO_x-SCR activity tests of different samples were carried out in a fixed bed quartz reactor in ordinary pressure. The feed gas, total flow rate of 420 mL/min composed of 0.05 vol. % NO_x, 0.05 vol. % NH_3 (used as reductant), 7 vol. % O_2, 10 vol. % water vapors and N_2 as the balance gas, was controlled by the mass flow meters and the space velocity was 12 000 or 36 000 h^{-1} through changing the monolithic catalyst volume. The NO_x concentrations in both inlet and outlet were detected by a flue gas analyzer (British, Kane-9106) and the NO_x conversion rate was calculated by the following equation:

$$NO_x \text{ conversion} = (1-C_o/C_i) \times 100\ \% \qquad (1)$$

where, C_o and C_i were the concentrations of NO_x in the outlet and inlet gas, respectively.

The aging experiments were carried out using N_2 as balance gas, the Cu-SAPO-34/cordierite catalysts were treated at 720 °C for 10 h in the presence of 10 % vapor and 0.02 % SO_2 at the total flow rate of 420 mL/min.

Characterization of the catalysts: X-ray diffraction (XRD) measurements were recorded on Rigaku D/max2500 diffractormeter with a CuK_α (λ = 0.154056 nm) radiation and a graphite monochromator. The tube voltage was 40 kV and the tube current was 100 mA. The data of 2θ from 5 to 65° were recorded at 8°/min with the step size of 0.01°. In addition, the samples were grinded into powder before tested.

The surface morphology and elemental composition were examined by scanning electron microscopy (SEM, Jeol Jsm-6700 F). The corresponding samples were sprayed with a thin gold layer before the detection and the accelerating voltage was 10 kV.

The computing method of Cu-SAPO-34 loading amount in the catalysts is similar that in our previous work[11]. The mass of loading was calculated by weighing the cordierite before and after the hydrothermal synthesis.

RESULTS AND DISCUSSION

Characteristics of Cu-SAPO-34/cordierite prepared using different HF content: The crystal structure of Cu-SAPO-34/cordierite with different HF content at the crystallization time of 24 h were analyzed *via* XRD in order to investigate the effect of different HF content on the structure of Cu-SAPO-34/cordierite. Moreover, the results are shown in Fig. 1 and the other XRD results at crystallization time of 3, 6, 12, 36 and 48 h are shown in Fig. 1(S). The characteristic peaks of SAPO-34 are hardly detected in the samples at the crystallization time of 3 and 6 h, indicating no SAPO-34 crystal was formed within such a short time. When the crystallization time is over 12 h, the obvious characteristic peaks of both SAPO-34 and cordierite are detected, which indicated that the SAPO-34 molecular sieve has been growth on the cordierite support. The samples with that n(HF)/n(Al_2O_3) equaled from 0 to 0.10 all had a higher relative crystallinity and purity and the intensities of the corresponding characteristic peaks of SAPO-34 rose along with the increasing HF content in the initial gel. The intensities of the characteristic peaks of SAPO-34 reached a maximum when n(HF)/n(Al_2O_3) was 0.05 and then remained unchanged when n(HF)/n(Al_2O_3) became higher, however, decreased sharply when n(HF)/n(Al_2O_3) was boosted to 0.20, which probably suggested that there were no regular and order Cu-SAPO-34 crystallites structure except the amorphous on cordierite substrates.

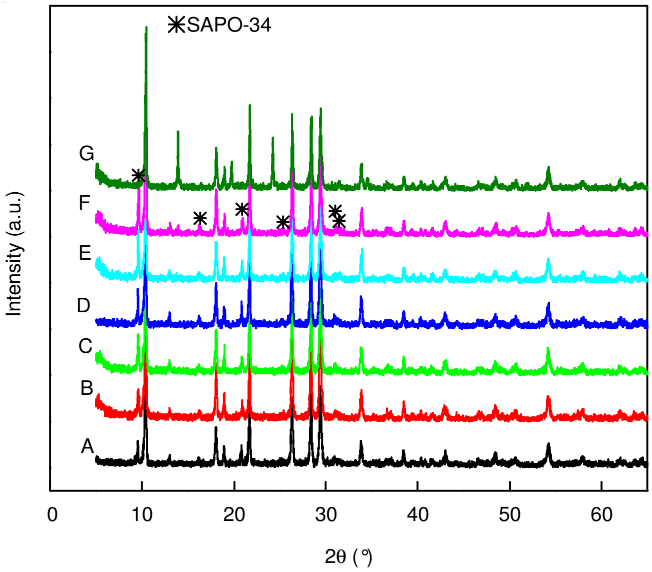


Fig. 1. XRD patterns of Cu-SAPO-34/cordierite with the different HF contents at crystallization time 24 h n(HF)/n(Al2O3) equals to 0, 0.01, 0.02, 0.03, 0.05, 0.10 and 0.20 in A, B, C, D, E, F and G, respectively

In order to intuitively analyze the effect of HF content on the crystallization of SAPO-34, the main characteristic peak intensity (2θ = 9.5°) of SAPO-34 with different HF content at different crystallization time (12, 24, 36 and 48 h) are analyzed in Fig. 2. It was showed that the characteristic peak intensity increased along with the increasing crystallization time. A better crystal type and structure of SAPO-34 could be available when the crystallization time was 24 or 36 h. For all samples at the same crystallization time, the characteristic peak intensity increased firstly then decreased along with the increasing HF content, which are consistent with the above discussion.

Obviously, the relative crystallinity of Cu-SAPO-34 crystallites can be significantly improved when the ratio of n(HF)/

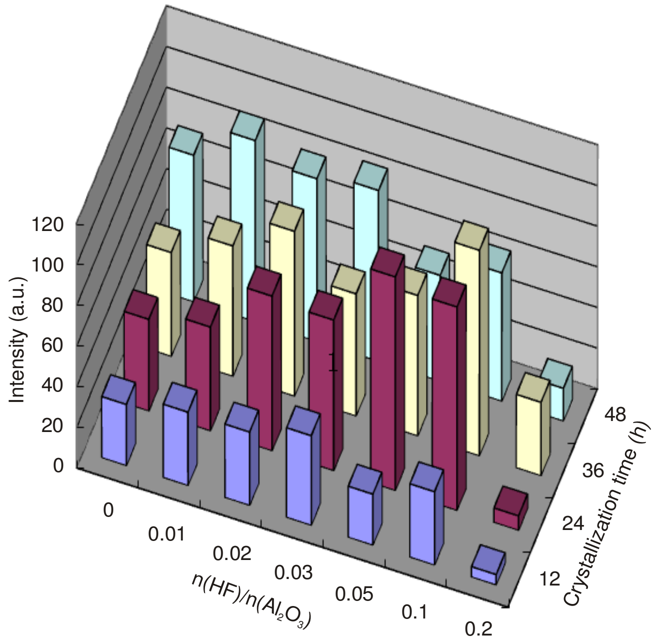


Fig. 2. Characteristic peak intensity (2θ = 9.5°) of SAPO-34 with different HF contents at different crystallization time

$n(Al_2O_3)$ ranged from 0.01 to 0.10. On the contrary, excess HF [$n(HF)/n(Al_2O_3) = 0.20$] could seriously hinder the growth of Cu-SAPO-34 crystallites and destroy its crystal texture, which contribute to the growth of amorphous on the cordierite substrates. This would be further confirmed by the corresponding SEM results.

To some extent, the loading amount of active component was the main factor influencing the activity of catalyst. The Cu-SAPO-34 loading amounts of different samples are shown in Fig. 3. It is obviously found that the loading amount of Cu-SAPO-34 varied with the change of the ratio of $n(HF)/n(Al_2O_3)$ from 0.01 to 0.10, but they were all higher than 13.6 % without HF. The loading amount reached the maximum of 20.3 % when $n(HF)/n(Al_2O_3)$ equal to 0.03 and then gradually dropped to 15 % when $n(HF)/n(Al_2O_3)$ increased to 0.10. The corresponding data for that $n(HF)/n(Al_2O_3)$ of 0.20 is not given in Fig. 3 because no Cu-SAPO-34 crystallites with neat structure was found on the cordierite substrates, which was consistent with the XRD results (Fig. 1). Therefore, it is known that appropriate amount of HF is favorable for the growth of Cu-SAPO-34 crystallites, but excess amount of HF has an adverse effect.

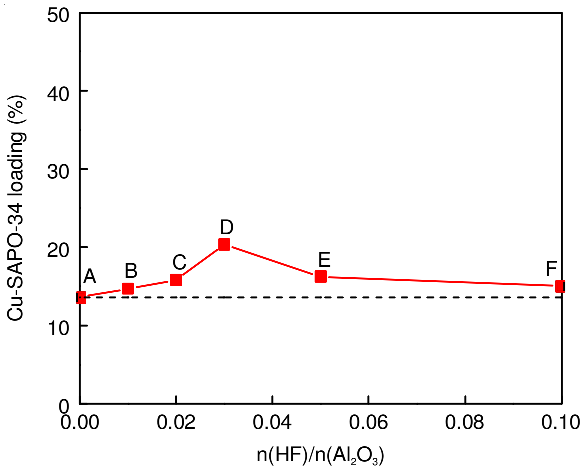


Fig. 3. Cu-SAPO-34 loading amounts of the samples with different HF

The effect of HF content on the morphology of Cu-SAPO-34 was investigated by SEM and the results corresponding to crystallization time of 6 and 24 h are shown in Fig. 4. From the SEM images, it can be easily seen that there are only a few Cu-SAPO-34 crystallites on the surface of cordierite when the crystallization time was 6 h and more crystallites were formed when $n(HF)/n(Al_2O_3)$ reached 0.02 or 0.03. Coincidentally, appropriate HF content could also improve the crystal morphology and size of the samples at the crystallization time of 24 h. Among which, the crystal size of Cu-SAPO-34 with the presence of HF was concentrated near 15 µm, which were obviously less than that of 20-35 µm without HF. It can be indicated that a certain amount of HF could promote the formation of Cu-SAPO-34 crystal with uniform structure and accelerate the crystallization rate. However, the quantity of the crystallites gradually tapered off along with further increasing of HF content and the morphology had changed by different degrees. There was only a small amount of Cu-SAPO-34 crystal on the cordierite substrates when $n(HF)/n(Al_2O_3)$ equal to 0.10 and the morphology became irregular, even more, there were only amorphous formed when $n(HF)/n(Al_2O_3)$ reached 0.20. Consequently, during the preparing process of Cu-SAPO-34/cordierite, the excess HF was adverse for the formation of Cu-SAPO-34 crystallites, which was consistent with the XRD results (Fig. 1). This might be because, the substitution of phosphorus and silicon were both badly affected by the over addition of HF during the formation process, which further destroyed the framework. Compared with those without HF, the Cu-SAPO-34 crystal with appropriate HF content ($n(HF)/n(Al_2O_3) = 0.01$-0.03) exhibited the characteristics of numerousness, small size and uniform distribution[13,14].

Effect of HF content on the de-NO_x activity of Cu-SAPO-34/cordierite catalyst: The de-NO_x properties of Cu-SAPO-34/cordierite monolithic catalysts with different HF content at the crystallization time of 6, 12, 24, 36 and 48 h were investigated at the space velocity of 12 000 h^{-1} and the results are displayed in Fig. 5 and Fig. 2 (S). It should be noted that the de-NO_x activity data of all samples at the crystallization time of 3 h and the sample with excess HF content ($n(HF)/n(Al_2O_3) = 0.20$) of 6 h are not given because almost no activity was observed. The temperature windows for the NO_x conversion rates above 95 % for all samples are summarized in Table-1.

From Fig. 5 and Table-1, it is observed that the de-NO_x properties of the catalysts increased along with the increasing crystallization time and then kept stable when the crystallization time reached above 12 h. The temperature windows with the NO_x conversion rates of above 95 % over Cu-SAPO-34/cordierite monolithic catalysts with appropriate HF content [$n(HF)/n(Al_2O_3] = 0.03$) at the crystallization time of 12 h or even longer were 340-600 °C, which were much broader than those without HF (420-560 °C). Inconceivably, compared with the catalyst without HF at the same crystallization time, the de-NO_x properties disappeared or reduced by different degree along with the further increasing HF content. However, the sample with excess HF [$n(HF)/n(Al_2O_3) = 0.20$] at the crystallization time of 48 h was an exception and it was probably

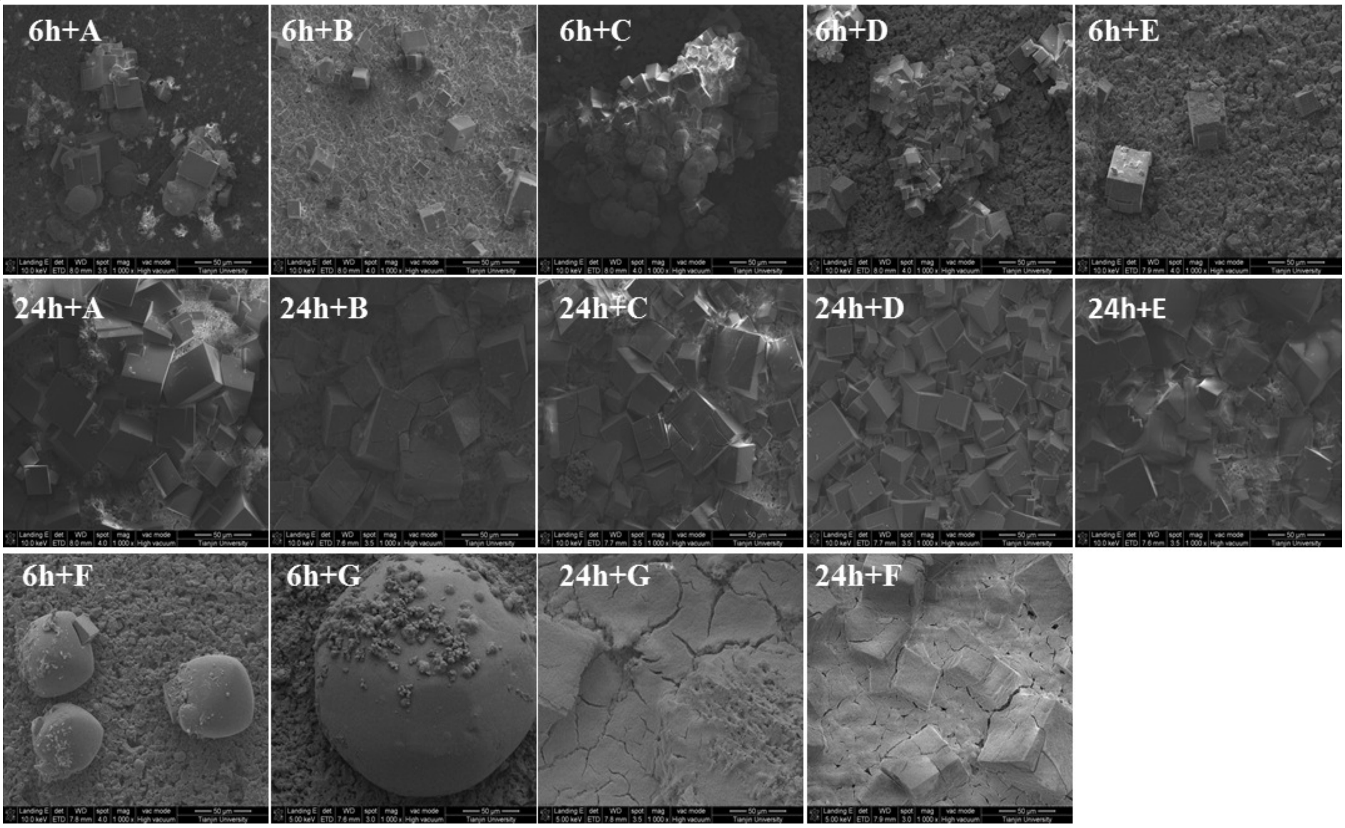


Fig. 4. SEM images of Cu-SAPO-34/cordierite with different HF at the crystallization time of 6 h and 24 h; $n(HF)/n(Al_2O_3)$ equals to 0, 0.01, 0.02, 0.03, 0.05, 0.10 and 0.20 in A, B, C, D, E, F and G, respectively

TABLE-1
ACTIVE TEMPERATURE WINDOWS OF PREPARED CATALYSTS WITH NO_x conversion rates of Above 95 %

Samples	Crystallization time			
	12 h	24 h	36 h	48 h
$n(HF)/n(Al_2O_3) = 0$	420-560 °C	440-560 °C	420-580 °C	420-540 °C
$n(HF)/n(Al_2O_3) = 0.01$	420-620 °C	340-620 °C	360-600 °C	360-600 °C
$n(HF)/n(Al_2O_3) = 0.02$	420-520 °C	340-600 °C	380-620 °C	380-600 °C
$n(HF)/n(Al_2O_3) = 0.03$	320-600 °C	320-600 °C	340-600 °C	340-600 °C
$n(HF)/n(Al_2O_3) = 0.05$	420-560 °C	380-520 °C	340-560 °C	n/a
$n(HF)/n(Al_2O_3) = 0.10$	n/a	480-500 °C	400-580 °C	n/a
$n(HF)/n(Al_2O_3) = 0.20$	n/a	n/a	460-500 °C	340-580 °C

attributed to the Cu particles on cordierite support. To sum up, compared with the samples without HF, the addition of appropriate HF content [$n(HF)/n(Al_2O_3) = 0.03$] can improve the de-NO_x performance of Cu-SAPO-34/cordierite monolithic catalysts and the excess HF are doing the NH_3-SCR activities a disservice, which echoed the analysis results of XRD and SEM.

It is a challenge to develop a selective catalytic reduction catalyst presenting superior de-NO_x performance under the conditions of high space velocity[1]. Fig. 6(a) shows the de-NO_x activity over Cu-SAPO-34/cordierite monolithic catalyst with different HF content at the crystallization time of 24 h under the reaction condition of high space velocity (36 000 h^{-1}). Both the highest NO_x conversion rate and active temperature window were weakened at the space velocity of 36,000 h^{-1}. Even so, the samples with the HF content that $n(HF)/n(Al_2O_3)$ equal to 0.01, 0.02, 0.03 and 0.05 still presented a better NH_3-SCR de-NO_x performance. Especially, the sample for that $n(HF)/n(Al_2O_3)$ equal to 0.03 had higher de-NO_x activity than the others and the corresponding NO_x conversion rate was kept above 80 % from 380 to 560 °C.

Anti-aging property of different samples: The de-NO_x activity of the samples with different HF content after aging treatment under 720 °C for 10 h in 10 % vapor and 0.02 % SO_2 was investigated and the results are shown in Fig. 6(b). By comparing, it is found that the catalytic activity, after some time, was decreased and the temperature windows were narrowed for all samples. However, the sample for that $n(HF)/n(Al_2O_3)$ equal to 0.03 had the slightest activity decrement and its NO_x conversion rate was kept above 40 % from 460 to 540 °C. It is shown that appropriate amount of HF could enhance the anti-aging performance of Cu-SAPO-34/cordierite.

The morphology of the aged samples was examined by SEM and the results are shown in Fig. 7. For all samples, it is shown that Cu-SAPO-34 crystals were somewhat cracked and obscured after the aging treatment and that may be one of the

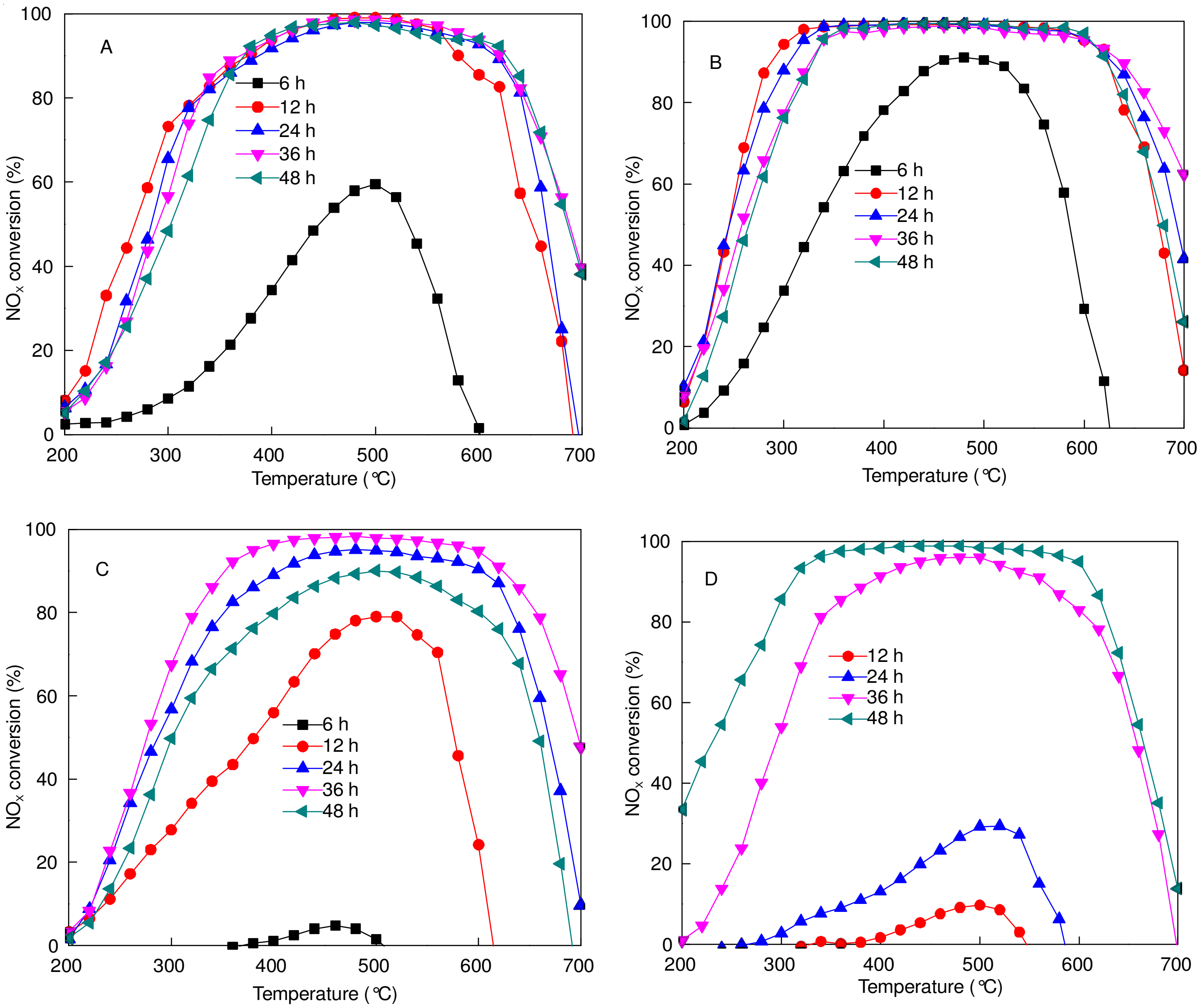


Fig. 5. De-NO$_x$ activity of Cu-SAPO-34/cordierite with different HF A: n(HF)/n(Al_2O_3) = 0; B: n(HF)/n(Al_2O_3) = 0.03; C: n(HF)/n (Al_2O_3) = 0.10; D: n(HF)/n (Al_2O_3) = 0.20. Reaction conditions: 0.05 % NO$_x$, 0.05 % NH_3, 7 % O_2, 10 % H_2O, balance N_2, total gas flow of 420 mL/min and SV = 12,000 h^{-1}

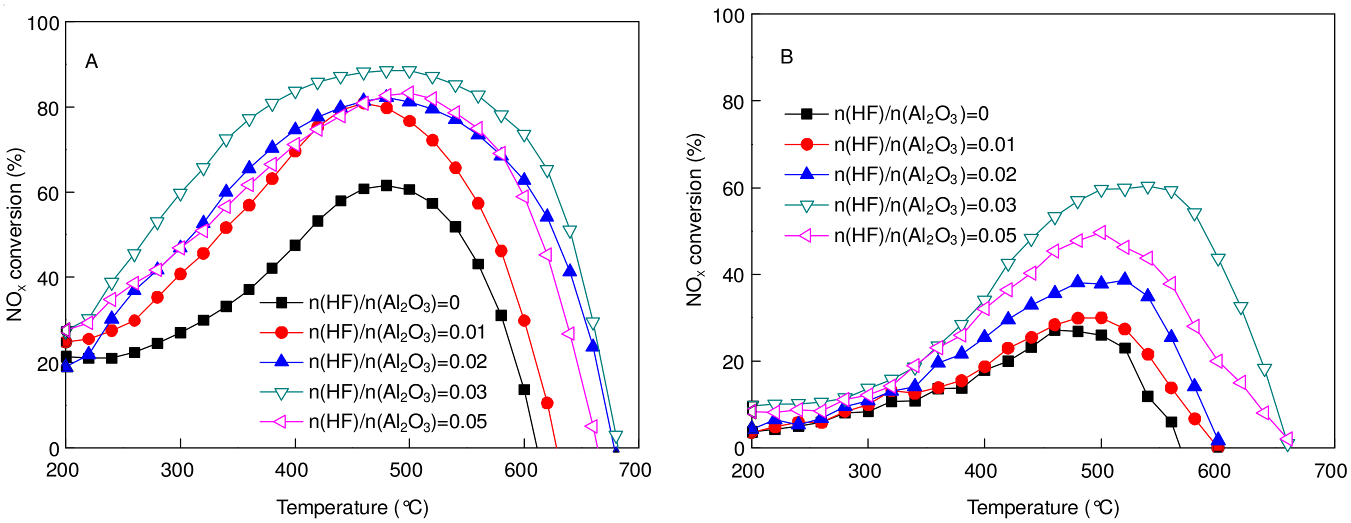


Fig. 6. De-NO$_x$ activity of different samples (crystallization time of 24 h) at SV 36,000 h^{-1}. A: Fresh samples, B: Aged samples. Reaction conditions: 0.05 NO$_x$, 0.05 NH_3, 7 O_2, 10 % H_2O, total gas flow of 420 mL/min and SV = 36,000 h^{-1}. Aging condition: 10 H_2O, 0.02 SO_2 %, 720 °C, 15 h

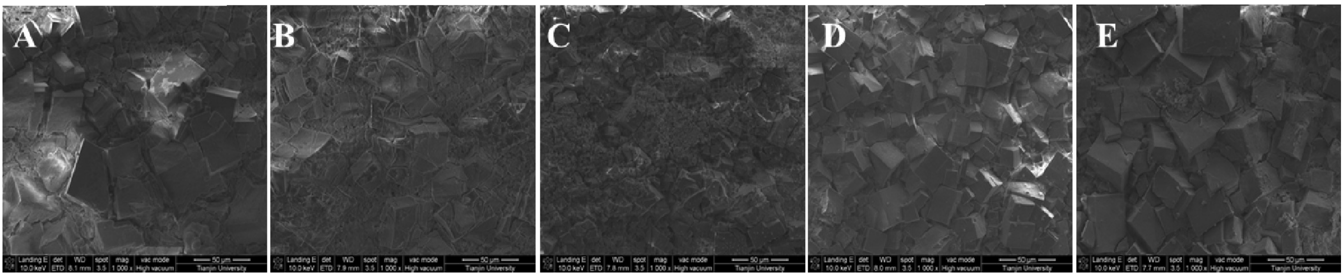


Fig. 7. SEM images of the different samples at crystallization time of 24 h after the aging treatment n(HF)/n(Al_2O_3) equals to 0, 0.01, 0.02, 0.03 and 0.05 in A, B, C, D and E

reasons for the decrease of de-NO_x activity. However, for the sample of n(HF)/n(Al_2O_3) = 0.03, the cracked and obscure degree were the lightest, which could further explain its strongest anti-aging property.

Conclusion

HF content in the initial gel had an obvious effect on the crystallization and catalytic properties of Cu-SAPO-34/cordierite. Reasonable amount [n(HF)/n(Al_2O_3) = 0.01-0.03] of HF addition could significantly improve the relative crystallinity and loading amount of Cu-SAPO-34 as well as the de-NO_x activity and anti-aging properties. Whereas, excess HF [n(HF)/n(Al_2O_3) = 0.20] negatively influenced the formation of Cu-SAPO-34, which further adversely affected the de-NO_x activity and anti-aging properties. As for the samples of n(HF)/n(Al_2O_3) = 0.03, NO_x conversion could reach higher than 95 % between 320 and 600 °C at the space velocity of 12000 h^{-1}. Moreover, under the reaction condition of high space velocity (36000 h^{-1}), the NO_x conversion rate could reach over 80 % between 380 and 560 °C and still higher than 50 % from 460 to 580 °C after the aging treatment.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from NSFC (20906067), CPSF (2011M500543) and the Program for the Top Young Academic Leaders of Higher Learning Institutions of Shanxi.

REFERENCES

1. W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Catal. Today*, **184**, 160 (2012).
2. J. Hu, Y. Wu, Z. Wang, Z. Li, Y. Zhou, H. Wang, X. Bao and J. Hao, *J. Environ. Sci. (China)*, **24**, 865 (2012).
3. T.V. Johnson, *SAE Int. J. Engines*, **4**, 143 (2011).
4. H. Sjövall, R.J. Blint and L. Olsson, *Appl. Catal. B*, **92**, 138 (2009).
5. S. Shwan, J. Jansson, J. Korsgren, L. Olsson and M. Skoglundh, *Catal. Today*, **197**, 24 (2012).
6. Z. Zhen, *Chin. J. Catal.*, **29**, 303 (2008).
7. J. Kašpar, P. Fornasiero and N. Hickey, *Catal. Today*, **77**, 419 (2003).
8. J. Wang, Y. Ji, U. Graham, C. Cesar Spindola De Oliveira and M. Crocker, *Chin. J. Catal.*, **32**, 736 (2011).
9. M. Kang, *J. Mol. Catal. Chem.*, **161**, 115 (2000).
10. G. Liu, P. Tian, Y. Zhang, J. Li, L. Xu, S. Meng and Z. Liu, *Micropor, Mesopor, Mater.*, **114**, 416 (2008).
11. Z. Liu, L. Tang, L. Chang, J. Wang and W. Bao, *Chin. J. Catal.*, **32**, 546 (2011).
12. H. Liu, Z. Xie, C. Zhang and Q. Chen, *Chin. J. Catal.*, **24**, 279 (2003).
13. R.M. Shayib, N.C. George, R. Seshadri, A.W. Burton, S.I. Zones and B.F. Chmelka, *J. Am. Chem. Soc.*, **133**, 18728 (2011).
14. Ø.B. Vistad, E.W. Hansen, D.E. Akporiaye and K.P. Lillerud, *J. Phys. Chem. A*, **103**, 2540 (1999).