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NH<sub>3</sub>-SCR activity, hydrothermal stability and poison resistance of zirconium phosphate/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst in simulated diesel exhaust

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**Abstract:**

The ZP/CZ (zirconium phosphate/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>) catalyst exhibits over 80% NO<sub>x</sub> conversion from 250 to 450 °C under a high GHSV of 300,000 h<sup>-1</sup> in the presence of H<sub>2</sub>O, CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>. Mixed with soot leads to a decrease in NO<sub>x</sub> conversion of catalyst at temperatures higher than 350 °C. After hydrothermal aging (760 °C for 48 h) and sulfur aging (400 °C for 48 h), ZP/CZ still owns over 80% NO<sub>x</sub> conversions in 289-450 °C and 297-466 °C respectively, which are significantly better than those of home made Cu-SAPO-34 and vanadium catalysts at higher temperatures. These results indicate that ZP/CZ is a promising catalyst for NO<sub>x</sub> abatement for diesel engine exhaust.

**Key words:** NH<sub>3</sub>-SCR, Zirconium phosphate/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, Anti-poisoning, Diesel exhaust deNO<sub>x</sub>.

## 1. Introduction

As diesel engine has high fuel efficiency, it reduces the fuel consumption and decreases the emission of greenhouse gas – carbon dioxide (CO<sub>2</sub>). However, NO<sub>x</sub>, derives from the combustion of the fuel in oxygen-rich condition, lead to various environmental problems such as acid rain, photochemical smog, ozone depletion and greenhouse effects [1-3]. Among various NO<sub>x</sub> control

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strategies for diesel engines, selective catalytic reduction of  $\text{NO}_x$  by  $\text{NH}_3$  ( $\text{NH}_3$ -SCR) is one of the most promising technology to meet the increasingly stringent standards for  $\text{NO}_x$  emissions [2].  $\text{V}_2\text{O}_5$ - $\text{WO}_3$ (or  $\text{MoO}_3$ )/ $\text{TiO}_2$  catalysts have been widely used in diesel exhaust de $\text{NO}_x$  due to their effectiveness and resistance to  $\text{SO}_2$  poisoning [2, 4]. However, the toxicity of vanadium restrained its application, particularly in the mobile sources [5]. Thus, great efforts have been made to develop environmental-friendly  $\text{NH}_3$ -SCR catalysts with high SCR activity and  $\text{N}_2$  selectivity in a wide temperature range, for controlling the  $\text{NO}_x$  emissions from diesel engines.

The limited volume of vehicle requires de $\text{NO}_x$  catalyst exerting high  $\text{NH}_3$ -SCR performance in case of high space velocity of exhaust. Therefore, transition metal-exchanged zeolites, particularly iron or copper-exchanged zeolites, have received increasing attention in recent years due to their high catalytic activities and selectivities at high space velocity [6-8]. While the insufficient low-temperature activity and/or high cost limit their industrial application. So it is valuable to find other catalysts with high de- $\text{NO}_x$  ability at high space velocity. Massive reports about the SCR catalysts were only characterized in a simple mixture of composing  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{O}_2$ . However, the real work condition of SCR catalyst often includes other compounds such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and unburnt hydrocarbons (HCs). Especially, the hydrocarbons in the exhaust can always be adsorbed by the zeolite catalyst, leading to the poison of catalyst. Therefore, complex gas compounds, containing  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and hydrocarbons (HCs), should be adopted to characterize the SCR catalyst objectively [9].

$\text{CeO}_2$ -based  $\text{NH}_3$ -SCR catalysts, including  $\text{CeO}_2$ - $\text{TiO}_2$  [10-12] and  $\text{CeO}_2$ - $\text{ZrO}_2$  solid acid catalysts [13-16], have received much attention. In our previous report [14], we reported a novel phosphated ceria catalyst with high hydrothermal stability. But, the sulfur resistance of  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{-PO}_4^{3-}$  still needed to be improved to meet the harsh conditions of diesel engine. Furthermore, we reported a zirconium phosphate @  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  catalyst with enhanced  $\text{NO}_x$  conversions in a wider temperature window [16]. However, the overall characterizations of this promising catalyst were not reported.

In this report, gas compounds including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and HCs with a high gas hourly space velocity (GHSV) of  $3 \times 10^5 \text{ h}^{-1}$  are introduced to study the “real” response of ZP/CZ catalyst (with/without soot). Meantime, the hydrothermal stability, sulfur resistance and anti-potassium poisoning ability of the catalyst were also tested to find if it is a suitable  $\text{NH}_3$ -SCR catalyst for

commercial use of diesel engine.

## 2. Experimental

### 2.1 Catalysts preparation

All the materials (AR grade) for synthesizing the catalysts were from Aladdin Industrial Corporation, China.

$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powder was synthesized by a precipitation method which is similar with the routes reported in reference [16]. An appropriate amount of cerium (III) chloride heptahydrate and zirconyl chloride octahydrate were dissolved in deionized water to obtain the salt solution for precipitation. Afterwards, ammonia solution (25%) was added to the salt solution dropwise under magnetic stirring to obtain the precipitate until the pH of the mixed solution reaches 9~10. The mixture was aged at 60 °C for 20 h, followed by spray drying at 200 °C to get the spherical powders. The powders were calcined at 500 °C for 3h to get the  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  microspheres. ZP/CZ catalyst was prepared by impregnating zirconium phosphate (ZrP) (10 wt.%) on  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powder according to the method of reference [14]. ZrP was prepared by co-precipitation method according to the reference [17]. To comprehensively evaluate the performance of the ZP/CZ, VWTi ( $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ ) and Cu-SAPO-34 were prepared as reference materials. The  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst with 2 wt.%  $\text{V}_2\text{O}_5$  and 8 wt.%  $\text{WO}_3$  was prepared by conventional impregnation method using  $\text{NH}_4\text{VO}_3$  and  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  as precursors and commercial  $\text{WO}_3/\text{TiO}_2$  powders as the support. The sample was dried at 100 °C for 5 hours and then calcined at 500 °C for 3 h in air conditions. Cu-SAPO-34 was prepared by ion-exchange method. The commercial H/SAPO-34 molecular sieve ( $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{P}_2\text{O}_5=1:0.3:0.8$ ) powders were stirred in  $\text{Cu}(\text{CH}_3\text{COO})_2$  aqueous solution (0.1 mol/L, 10 ml of solution per g of zeolite) at 60 °C for 10 h. After that, the samples were filtered, washed, and dried at 110 °C for 12 h. Then, the powders were thermally treated in air at 550 °C for 4 h.

Hydrothermal aging of ZP/CZ, Cu-SAPO-34 and VWTi catalysts (ZP/CZ-TA, Cu-SAPO-34-TA and VWTi-TA) were performed at 760 °C in 10 vol%  $\text{H}_2\text{O}/\text{air}$  for 48 h. The sulfur-aged ZP/CZ, Cu-SAPO-34 and VWTi catalysts (ZP/CZ-SA, Cu-SAPO-34-SA and VWTi-SA) was obtained by treating catalyst in air containing 100 ppm  $\text{SO}_2+10\% \text{H}_2\text{O}$  at 400 °C

for 48 h. Potassium-doped catalysts were prepared by impregnation with KCl (0.6 wt.%), followed by dehydration at 100 °C and calcination at 500 °C for 1 h.

## 2.2 Characterizations

H<sub>2</sub>-TPR tests were performed on Micromeritics Auto Chem II. Prior to H<sub>2</sub>-TPR experiment, 50 mg samples were treated by 10% O<sub>2</sub>/He with a total flow rate of 50 ml min<sup>-1</sup> at 500 °C for 30 min. The reactor temperature was raised to 1000 °C at a heating rate of 10 °C min<sup>-1</sup> in H<sub>2</sub> (10 vol%)/Ar (50 ml min<sup>-1</sup>).

## 2.3 Activity measurement

The activity measurement for NO reduction with ammonia was carried out in a fixed bed reactor made of quartz tube. To minimize the mass transfer limitations, the catalyst was sieved with 50-80 mesh size and then charged into the quartz reactor using quartz wool. The reaction gas mixture consisted of 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, 5 vol.% H<sub>2</sub>O, [CO<sub>2</sub>] = 5 vol.% (when used), [C<sub>3</sub>H<sub>8</sub>] = 85 ppm (when used) and N<sub>2</sub> as balance. The total flow of the gas mixture was 0.5 L min<sup>-1</sup> at a gas hourly space velocity (GHSV) of 3×10<sup>5</sup> h<sup>-1</sup>. 0.1 ml oxidized catalysts with/without 1 wt.% soot (mixed by a spatula for 2 min for “loose contact” conditions) were measured at 50 °C intervals in 30 min from 200 °C to 500 °C. The concentrations of nitrogen oxides and ammonia were measured at 200 °C by a thermo Nicolet 380 FTIR spectrometer equipped with a quartz tube (6 mm i.d.). The oxidized catalyst samples were obtained by thermally treating the samples at 500 °C in a 10% (v/v) O<sub>2</sub>/N<sub>2</sub> flow (500 ml min<sup>-1</sup>) for 30 min. The NO<sub>x</sub> conversion was calculated by Eqs. (1).

$$\text{NO}_x \text{ conversion (\%)} = \frac{\text{NO}_{in} - \text{NO}_{out} - \text{NO}_{2out} - 2\text{N}_2\text{O}_{out}}{\text{NO}_{in}} \times 100 \quad (1)$$

## 3. Results and discussion

### 3.1. Anti-poisoning of catalyst

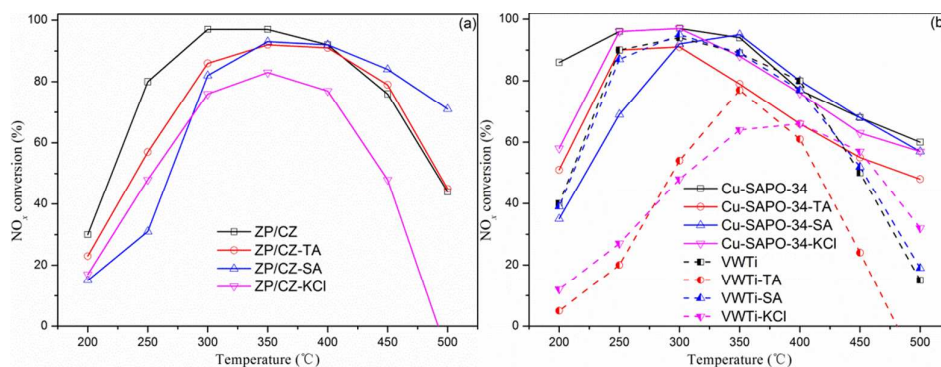


Fig. 1.  $\text{NO}_x$  conversions vs. temperature over (a) ZP/CZ samples, (b) reference samples. (Reaction conditions:  $\text{NO} = \text{NH}_3 = 500$  ppm,  $\text{O}_2 = 5$  vol.%,  $\text{H}_2\text{O} = 5$  vol.%,  $\text{N}_2$  balance,  $\text{GHSV} = 3 \times 10^5 \text{ h}^{-1}$ ).

The  $\text{NH}_3$ -SCR activities of the catalysts are shown in Fig. 1. The fresh ZP/CZ catalyst shows above 80%  $\text{NO}_x$  conversions in a wide temperature region of 250–450 °C.  $\text{N}_2$  selectivity of ZP/CZ catalyst is 100% before 350 °C, but it decreases after 350 °C. The lowest value is 91% at 500 °C. After hydrothermal aging, ZP/CZ-TA shows a deactivation in the temperatures lower than 400 °C. However, ZP/CZ-TA catalyst still owns over 80%  $\text{NO}_x$  conversions in 289–450 °C. In order to study the stability of phosphate at 800 °C, ZP/CZ catalyst was also pretreated at 800 °C in 10 vol%  $\text{H}_2\text{O}/\text{air}$  for 48 h (named ZP/CZ-800°C). ZP/CZ-800°C shows above 80%  $\text{NO}_x$  conversions in a wide temperature region of 291–420 °C. As a result, the phosphate in ZP/CZ catalyst has a good stability up to 800 °C. Compared with the fresh ZP/CZ catalyst, though the de- $\text{NO}_x$  ability of ZP/CZ-SA catalyst decreases before 400 °C, it shows the highest  $\text{NO}_x$  conversions above 400 °C and owns the wide temperature window of 297–466 °C. The potassium poisoning results in the decrease in  $\text{NO}_x$  conversions in the whole temperature region.

According to Fig. 1 (b), the de- $\text{NO}_x$  ability of Cu-SAPO-34 decreases after hydrothermal aging, sulfur aging and potassium poisoning. The  $\text{NO}_x$  conversions window for Cu-SAPO-34-TA, Cu-SAPO-34-SA and Cu-SAPO-34-KCl are 237–350 °C, 272–401 °C, 228–384 °C respectively. Cu-SAPO-34 owns better anti-potassium poisoning than ZP/CZ, while ZP/CZ have better performances in hydrothermal stability and sulfur resistance. As for VWTi catalyst, hydrothermal aging and potassium poisoning make the  $\text{NO}_x$  conversions lower than 80% in the whole temperature region. While, the de- $\text{NO}_x$  ability of VWTi-SA is nearly the same with that of fresh VWTi sample, indicating the highest sulfur resistance of vanadium catalyst.

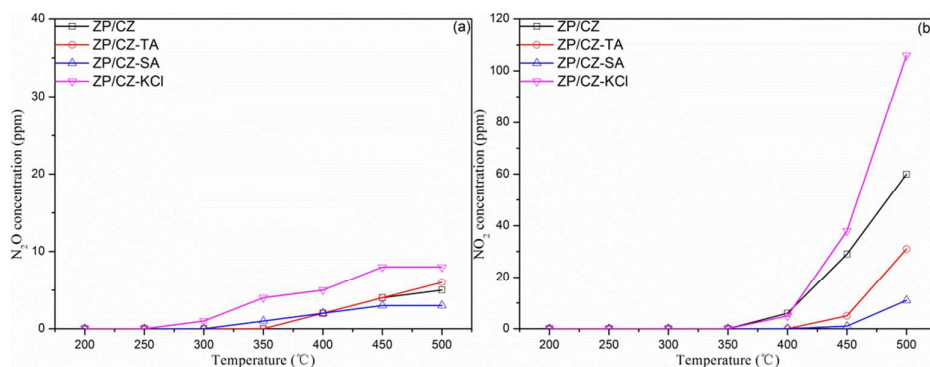


Fig. 2. NH<sub>3</sub>-SCR activities of the catalysts: (a) N<sub>2</sub>O generations and (b) NO<sub>2</sub> generations.

The evolution of N<sub>2</sub>O and NO<sub>2</sub> during NH<sub>3</sub>-SCR reaction is shown in Fig. 2. The outlet N<sub>2</sub>O of catalysts are less than 10 ppm within the whole reaction time. NO<sub>2</sub> is detected at the temperatures higher than 350 °C due to the NH<sub>3</sub> oxidation to NO<sub>x</sub> at high temperatures. The NO<sub>2</sub> generation at 350-500 °C on catalysts follows the sequence of ZP/CZ-KCl >> ZP/CZ > ZP/CZ-TA > ZP/CZ-SA, which is in coordination with the NO<sub>x</sub> conversions at temperatures above 400 °C. Less than 10 ppm NO<sub>2</sub> is detected on ZP/CZ-SA at 500 °C, which indicates that the improved acidity by sulfation results in a significantly high N<sub>2</sub> selectivity of catalyst.

### 3.2. Effect of reaction conditions on catalyst

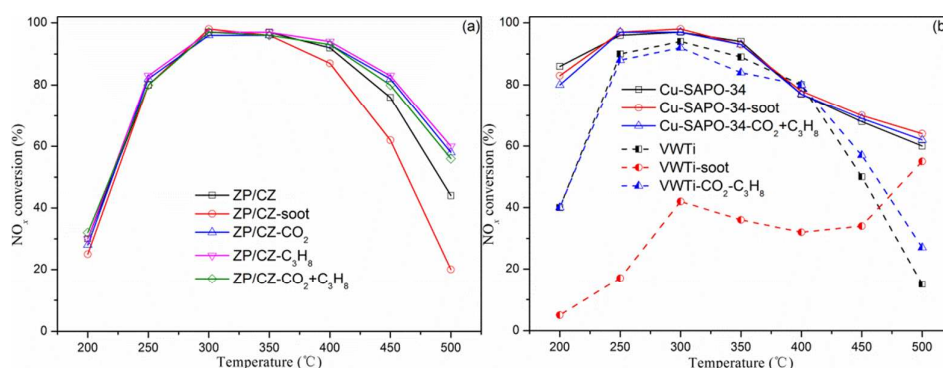


Fig. 3. NO<sub>x</sub> conversions vs. temperatures over (a) ZP/CZ samples, (b) reference samples under different reaction conditions. (Reaction conditions: NO = NH<sub>3</sub> = 500 ppm, O<sub>2</sub> = 5 vol.%, H<sub>2</sub>O = 5 vol.%, [CO<sub>2</sub>] = 5 vol.%, [C<sub>3</sub>H<sub>8</sub>] = 85 ppm, N<sub>2</sub> balance, GHSV = 3 × 10<sup>5</sup> h<sup>-1</sup>).

NH<sub>3</sub>-SCR activities of the ZP/CZ catalyst under different reaction conditions are shown in Fig. 3. The SCR activity of Printex U (soot) was reported in the reference [18]. At higher temperatures (>280 °C), soot was able to selectively oxidize NH<sub>3</sub> to nitrogen while not active for



NO<sub>x</sub> reduction. Similarly, in the present study, lacking enough reductants (NH<sub>3</sub>) for SCR reaction leads to a decreasing NO<sub>x</sub> conversion after 350 °C when soot (1%) is mixed with the PZ/CZ catalyst (shown in Fig. 2 (a)). When CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub> or the combination of the two species are added into the reaction gas, the NO<sub>x</sub> conversions become higher after 350 °C. Our previous work reported that high NH<sub>3</sub> oxidation activity at high temperature led to a low N<sub>2</sub> selectivity and a decrease in NO<sub>x</sub> conversions [14, 19-21]. Since ammonia competes with HCs for the adsorption sites [9] and CO<sub>2</sub> in the inlet also leads to a decreasing NH<sub>3</sub> conversion after 400 °C [22], less ammonia are able to participate in the deep oxidation reaction, leading to slightly higher NO<sub>x</sub> conversions at temperatures higher than 400°C. HCs have no effects on the NH<sub>3</sub> conversion but inhibit the NO<sub>2</sub> generations, especially at higher temperatures (25 ppm at 500 °C). It indicates that the inlet of HCs inhibit the NH<sub>3</sub> participating in the side reactions, leading to better selectivity and activity. The ZP/CZ catalyst exhibits over 80% NO<sub>x</sub> conversion at 250-450 °C and at a high GHSV of 300,000 h<sup>-1</sup> in the presence of H<sub>2</sub>O, CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>, indicating that it is a promising catalyst for NO<sub>x</sub> abatement for the diesel engine exhaust.

For Cu-SAPO-34, adding the combination of CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> or soot into the SCR reaction has little effect on NO<sub>x</sub> conversion. The VWTi in similar reaction conditions presents a lower NO<sub>x</sub> conversions than those of ZP/CZ. Moreover, mixing with soot leads to a serious deactivation of VWTi catalysts at the whole temperatures.

### 3.3. H<sub>2</sub>-TPR

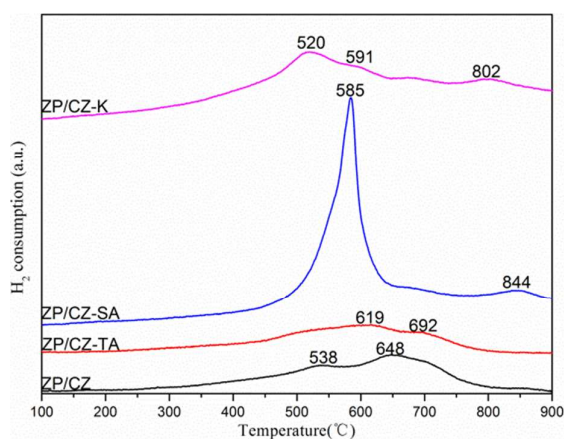


Fig. 4. H<sub>2</sub>-TPR curves of the samples.

Fig. 4 shows the hydrogen consumptions of catalysts versus temperatures. The reduction of



Ce-Zr-O mixed metal oxides typically occurs in two steps, namely, surface reduction followed by subsurface and bulk reduction [23]. Accordingly, the H<sub>2</sub> consumption peaks of ZP/CZ catalyst at 538 and 648 °C are ascribed to the surface/sub-surface lattice oxygen and bulk lattice oxygen respectively.

The hydrothermal aging leads to less reductive surface and bulk oxygen as indicated by the hydrogen consumption peaks shifting from 538 to 619 °C and 648 to 692 °C. According to the literature [14, 23], CePO<sub>4</sub> may lead to the difficulty for the reduction of surface/subsurface oxygen due to the decrease in Ce<sup>4+</sup> ions. The formation of CePO<sub>4</sub> may alter the kinetics of the reduction process of Ce(IV) to Ce(III), inhibiting the mobility of lattice oxygen to the surface of catalyst. In our previous study [16], zirconium phosphate was used for ceria modification rather than phosphate because that the strong pre-combination between zirconium and phosphate may help to reduce the interaction between cerium and phosphate. After hydrothermal aging, the interaction between cerium and phosphate becomes stronger, leading to a decrease in redox ability of catalyst. K atom could facilyly bonded to the CeO<sub>2</sub> surface and reduce the degree of reduction of the cerium species [24]. However, KCl poisoning has little effect on the redox property of ZP/CZ catalyst, which can be ascribed to the special structure of ZP/CZ catalyst. The zirconium phosphate provides acidity sites on the surface of the catalyst and the cerium sites in the core act as the redox sites [16]. The alkali metal is easier to be adsorbed by the acidic shell.

A sharp reduction peak with a tail appears around 585 °C on ZP/CZ-SA corresponding to the reduction of surface oxygen and subsurface oxygen [13], suggesting the occurrence of strong interaction between sulfate species and ZP/CZ. This strong interaction inhibits the mobility of oxygen from bulk to surface, leading to the deactivation of SCR catalyst at low temperatures.

### 3.4. NH<sub>3</sub> adsorption

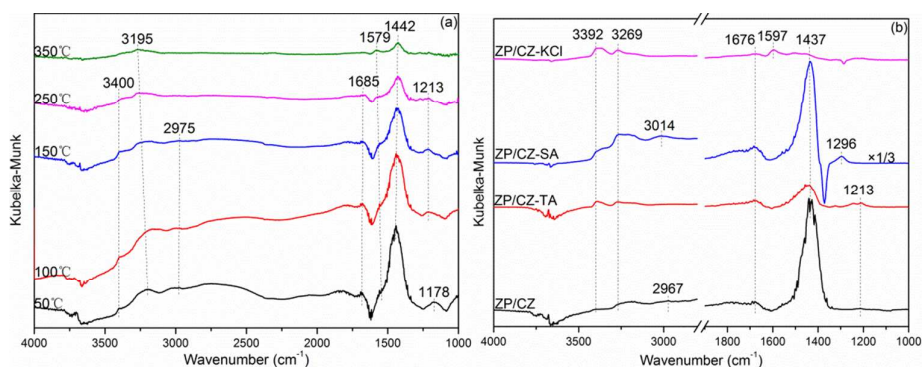


Fig. 5. FTIR spectra of the catalyst arising from contact of  $\text{NH}_3$ : (a) ZP/CZ catalyst, from 50 °C to 350 °C, (b) different catalysts at 150 °C.

Fig. 5 shows the FTIR spectra of the adsorbed species on the catalysts arising from contact with  $\text{NH}_3$  at various temperatures. Bands at 1437-1442, 1676-1685 and 2967-3014  $\text{cm}^{-1}$  are assigned to the  $\sigma_{\text{as}}$  and  $\sigma_{\text{s}}$  of  $\text{NH}_4^+$  on the Brønsted acid sites, respectively. And bands at 1178-1213 and 1579-1597  $\text{cm}^{-1}$  are ascribed to the  $\sigma_{\text{s}}$   $\text{NH}_3$  and  $\sigma_{\text{as}}$   $\text{NH}_3$  on Lewis acid sites. In the N-H region, several bands of  $\text{NH}_3$  on Lewis acid sites appear at 3195-3400  $\text{cm}^{-1}$  [6, 10-12, 25]. On ZP/CZ catalyst, all the bands of ammonia derived species decrease in intensity as the temperature increases. Plenty of acid sites are still detected on ZP/CZ catalyst at 350 °C. The strong acidity and the moderate redox property of ZP/CZ may lead to the excellent activity of catalyst.

According to the results of Fig. 5 (b), after hydrothermal aging, ZP/CZ-TA owns less acid sites and lower acidity. The decreased redox ability and acidity results in the lower  $\text{NO}_x$  conversions of ZP/CZ-TA than the fresh catalyst in the whole temperatures. KCl poisoning leads to a serious poison on the acidity of catalyst as indicated by the nearly disappearance of FTIR spectra at 1437  $\text{cm}^{-1}$ . The potassium ions can strongly bind to the Brønsted acid sites [26-31], leading to a decrease in adsorption sites for ammonia and thereby decreased the de $\text{NO}_x$  ability. The weakest acidity accounts for the lowest  $\text{NO}_x$  conversions of ZP/CZ-KCl.

For ZP/CZ-SA catalyst, the deposition of sulfates brings more acid sites on catalyst, which can help to improve ammonia adsorption on catalyst at high temperature and suppresses the  $\text{NH}_3$  deep oxidation [20, 21, 32]. Thus, ZP/CZ-SA catalyst owns the highest  $\text{NO}_x$  conversions after 400 °C.

#### 4. Conclusion

The fresh ZP/CZ catalyst shows above 80% NO<sub>x</sub> conversions in a wide temperature region of 250-450 °C in simulated diesel exhaust. After hydrothermal and sulfur aging, ZP/CZ catalyst still owns better deNO<sub>x</sub> performance than Cu-SAPO-34 and vanadium catalysts. Although mixed with soot leads to a decrease in NO<sub>x</sub> conversion at temperatures higher than 350 °C, adding H<sub>2</sub>O, CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> into the reaction gas components has little effect on SCR activity of ZP/CZ catalyst. These results show that ZP/CZ is a promising catalyst for NO<sub>x</sub> abatement for diesel engine exhaust.

### Acknowledgements

The authors would like to acknowledge Project 51202126 by the National Natural Science Foundation of China and Project 2013AA065302 supported by the Ministry of Science and Technology, PR China for financial support.

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## Captions

Fig. 1. NO<sub>x</sub> conversions vs. temperature over (a) ZP/CZ samples, (b) reference samples. (Reaction conditions: NO = NH<sub>3</sub> = 500 ppm, O<sub>2</sub> = 5 vol.%, H<sub>2</sub>O = 5 vol.%, N<sub>2</sub> balance, GHSV = 3 × 10<sup>5</sup> h<sup>-1</sup>).

Fig. 2. NH<sub>3</sub>-SCR activities of the catalysts: (a) N<sub>2</sub>O generations and (b) NO<sub>2</sub> generations.

Fig. 3. NO<sub>x</sub> conversions vs. temperatures over (a) ZP/CZ samples, (b) reference samples under different reaction conditions. (Reaction conditions: NO = NH<sub>3</sub> = 500 ppm, O<sub>2</sub> = 5 vol.%, H<sub>2</sub>O = 5 vol.%, [CO<sub>2</sub>] = 5 vol.%, [C<sub>3</sub>H<sub>8</sub>] = 85 ppm, N<sub>2</sub> balance, GHSV = 3 × 10<sup>5</sup> h<sup>-1</sup>).

Fig. 4. H<sub>2</sub>-TPR cures of the samples.

Fig. 5. FTIR spectra of the catalyst arising from contact of NH<sub>3</sub>: (a) ZP/CZ catalyst, from 50 °C to 350 °C, (b) different catalysts at 150 °C.