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Impact of diesel emission fluid soaking on the performance of Cu-zeolite catalysts for diesel NH_3-SCR systems*

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Abstract: Diesel emission fluid (DEF) soaking and urea deposits on selective catalytic reduction (SCR) catalysts are critical issues for real diesel engine NH_3-SCR systems. To investigate the impact of DEF soaking and urea deposits on SCR catalyst performance, fresh Cu-zeolite catalyst samples were drilled from a full-size SCR catalyst. Those samples were impregnated with DEF solutions and subsequently hydrothermally treated to simulate DEF soaking and urea deposits on real SCR catalysts during diesel engine operations. Their SCR performance was then evaluated in a flow reactor with a four-step test protocol. Test results show that the DEF soaking leached some Cu from the SCR catalysts and slightly reduced their Cu loadings. The loss of Cu and associated metal sites on the catalysts weakened their catalytic oxidation abilities and caused lower NO/NH_3 oxidation and lower high-temperature N_2O selectivity. Lower Cu loading also made the catalysts less active to the decomposition of surface ammonium nitrates and decreased low-temperature N_2O selectivity. Cu loss during DEF impregnation released more acid sites on the surface of the catalysts and increased their acidities, and more NH_3 was able to be adsorbed and involved in SCR reactions at medium and high temperatures. Due to lower NH_3 oxidation and higher NH_3 storage, the DEF-impregnated SCR catalyst samples showed higher NO_x conversion above 400 °C compared with the non-soaked one. The negative impact of urea deposits during DEF impregnation was not clearly observed, because the high-temperature hydrothermal treatment helped to remove the urea deposits.

Key words: Diesel engine emission control, Selective catalytic reduction (SCR), NO_x reduction, Cu-zeolite catalyst, Diesel emission fluid (DEF) soaking
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1 Introduction

Diesel engines have attracted much attention around the world because of their higher power output and better fuel efficiency compared with their gasoline counterparts. However, the in-cylinder lean-burn combustion of diesel engines also generates significant NO_x emissions (Heywood, 1988). Substantial NO_x emissions can result in acid rain, photochemical smog, and ozone depletion. To meet the increasingly stringent NO_x emission regulations, diesel engines have started to be required to have exhaust NO_x aftertreatment systems (Johnson, 2015). The selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is one of the most effective ways to abate NO_x emissions from diesel engine exhaust (Naseri *et al.*, 2014; 2015).

Diesel NH_3-SCR systems use a 32.5% (in weight) aqueous urea, known as diesel emission fluid (DEF), as a reducing agent to reduce NO_x selectively with SCR catalysts (Wurzenberger and Wanker, 2005). As DEF is injected into the hot diesel exhaust gas, it undergoes water evaporation Eq. (1), urea thermolysis Eq. (2), and hydrolysis Eq. (3) to form

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the real reducing agent of NH_3, which is then involved in the subsequent SCR reactions inside the SCR catalyst.

$$CO(NH_2)_2\ (aq)\rightarrow CO(NH_2)_2\ (s/l)+6.9H_2O, \tag{1}$$

$$CO(NH_2)_2\ (l)\rightarrow NH_3\ (g)+HNCO\ (g), \tag{2}$$

$$HNCO\ (g)+H_2O\rightarrow NH_3\ (g)+CO_2\ (g). \tag{3}$$

However, DEF injection and decomposition in real diesel NH_3-SCR systems are more complicated. Because of the low diesel exhaust gas temperature and high exhaust flow velocity, it is usually difficult for the injected DEF to completely decompose to NH_3 before entering the SCR catalyst (Munnannur *et al.*, 2012; Weeks *et al.*, 2015). The unevaporated DEF can cause liquid-wall interaction on the exhaust wall, the exhaust mixer, and even the inlet face of SCR catalyst. Part of the wall-interaction DEF may form DEF liquid films along the exhaust pipe in extreme cases. This phenomenon causes the SCR catalyst to have a high risk of being soaked by DEF, causing urea deposits and catalyst deactivation issues. Previous studies have shown that the unevaporated and undecomposed DEF has a great tendency to generate high molecular solid byproducts, such as biuret, cyanuric acid, ammelide, and ammeline (Smith *et al.*, 2014; Weeks *et al.*, 2015). Most of them need a higher temperature to decompose again, leaving urea deposits in the diesel exhaust system. The urea deposits, if occurring on the SCR catalyst surface because of DEF soaking, will change the catalyst performance and its durability.

Numerous studies have concerned the potential reaction pathways of urea decomposition as well as the impact of SCR catalysts on them (Bernhard *et al.*, 2012; Ebrahimian *et al.*, 2012; Brack *et al.*, 2014; Ku and Hong, 2015). Several studies have also focused on the deactivations of SCR catalysts caused by steam, sulfur, phosphorus, hydrocarbon, and other impurities or additives in commercial diesel and lubricating oils (Kern *et al.*, 2010; Klimczak *et al.*, 2010; Lezcano-Gonzalez *et al.*, 2014; Ummel and Price, 2014). However, only a few publications have considered the impact of DEF and urea deposits on the performance of SCR catalysts. Among them, Cheng *et al.* (2008) investigated the effect of hydrothermal aging on the reactivity of Cu-zeolite SCR catalysts with DEF exposure, and found that DEF caused obvious deteriorations of the performance of the SCR catalyst. Eichelbaum *et al.* (2010a; 2010b) impregnated Fe-beta zeolite powder with DEF followed by hydrothermal treatments at different temperatures, and found that DEF and urea deposits reduced the catalyst performance drastically but the high temperature helped to restore the performance after the removal of urea deposits. Therefore, DEF has been proved to be another cause of SCR catalyst deactivation beyond traditional knowledge. However, most recent studies simply ascribe the DEF-induced catalyst deactivation to the urea deposits on the catalyst, and almost no one has noticed the impact of DEF solution itself; the detailed catalyst deactivating mechanism during DEF soaking is still unclear, especially for those Cu-zeolite SCR catalysts like Cu-SAPO-34. Due to the inevitable interaction between DEF and SCR catalysts in real diesel SCR design, the impact of DEF soaking and urea deposits on the SCR catalyst performance needs to be considered during the whole SCR lifetime.

This study was mainly to investigate the impact of DEF soaking and urea deposits on the performance of Cu-zeolite SCR catalysts. To simulate DEF soaking and urea deposits on real SCR catalysts during diesel engine operations, several fresh SCR catalyst samples were impregnated with DEF for certain times and then blown dry with heated indoor lab air. Subsequently, all the impregnated samples were hydrothermally treated on a flow reactor with typical feeding gas in diesel exhaust to simulate the behavior of DEF and urea deposits in real applications. Finally, NO_x conversion, N_2O selectivity, NH_3 oxidation, NO oxidation, and NH_3 storage of each SCR catalyst sample were evaluated on the flow reactor with a four-step test protocol (Kamasamudram *et al.*, 2010). Test results and data analysis have been illustrated to clarify the impact of DEF soaking and urea deposits on the performance of Cu-zeolite SCR catalysts.

2 Experimental

2.1 SCR catalyst samples

An integrated diesel after-treatment system from a Champaign-Urbana Mass Transit District (CUMTD) bus at Urbana, USA had attracted our attention, because the Cu-zeolite SCR catalyst in the system had encountered DEF soaking and urea deposit issues in the extremely cold winter of 2014. All the Cu-zeolite

SCR catalyst samples in this study were drilled from a new full-size SCR catalyst with the same formulation of Cu-SAPO-34 as used on the bus. Each sample had a diameter of 2.54 cm, a length of 5.08 cm and a cell density of 400 CPSI. The entire experimental procedure for those samples in this study is shown in Fig. 1. At the beginning of the experiments, all the catalyst samples were hydrothermally treated in a flow reactor at 700 °C for 4 h with the feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), and a balance gas of N_2, to ensure their stable performance in the subsequent tests.

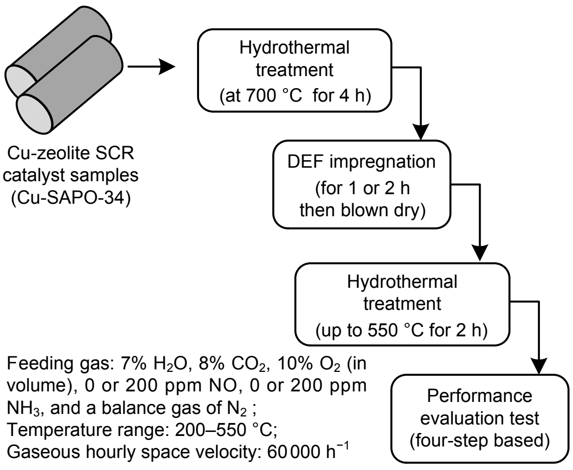

Fig. 1 Schematic diagram of the entire experimental procedure (1 ppm=1×10^{-6})

2.2 DEF soaking and hydrothermal treatment

After hydrothermal pretreatment, two catalyst samples were impregnated with DEF solutions for 1 h and 2 h separately to simulate DEF soaking and urea deposits formation on the catalyst surface during diesel engine operations. Moreover, to investigate the potential physical and chemical interactions between the soaking liquid and the catalysts, one additional sample was also impregnated with distilled water as a comparison. All the DEF and water impregnated samples were then blown dry with heated indoor lab air. The DEF-impregnated samples were subsequently treated hydrothermally in a flow reactor at temperatures of up to 550 °C for 2 h, with a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), and a balance gas of N_2, to simulate the behaviors of DEF and urea deposits on the catalyst in real applications. The water-impregnated sample was also hydrothermally treated in the same flow reactor with the same conditions as above as a comparative reference.

2.3 SCR performance evaluation tests

All the performance tests of catalyst samples were conducted on the same flow reactor above. The flow reactor has a synthetic exhaust gas mixture delivery device, in which different gas species from high-pressure gas bottles can be regulated and mixed by their mass flow controllers. A high-pressure pump is used to deliver a desired amount of water stream into the mixtures. The synthetic gas mixtures are then fed directly to a tube resistance furnace based reactor, in which the testing catalyst sample is placed in a quartz tube inside the furnace and the catalyst temperature can be controlled. All the stainless steel gas lines in the flow reactor are heated up to at least 190 °C to avoid potential water condensation and NH_3 adsorption. The gas species and their concentrations both upstream and downstream of the catalyst sample are measured and recorded by an MKS MultiGas 2030 FTIR gas analyzer (USA).

A four-step integrated test protocol was used to conduct the performance tests for those SCR catalyst samples based on the flow reactor above (Kamasamudram *et al.*, 2010). During each four-step test cycle with a certain temperature, the basic feeding gas species were kept fixed as 7% H_2O, 8% CO_2, and 10% O_2 (in volume), which represented the typical diesel exhaust environment. However, the NO_x and NH_3 concentrations in the feeding gas were switched periodically between 0 ppm and 200 ppm, as shown in Fig. 2. Four individual steps with different combinations of inlet feeding NO and NH_3 concentrations existed in each isothermal cycle, including NO oxidation, standard SCR, NH_3 saturation, and clean. Each step could be used to summarize different performances of the test catalyst sample, such as NO_x conversion, N_2O selectivity, NO and NH_3 oxidations, and NH_3 storage amount. The isothermal four-step test cycle was conducted at different temperatures to evaluate the entire SCR performance under different diesel exhaust conditions. In this study, the experimental temperature was ramped down from 550 °C to 200 °C with a decrement of 50 °C for each four-step test cycle, and the gaseous hourly space velocity (GHSV) was kept at 60 000 h^{-1} all the time.

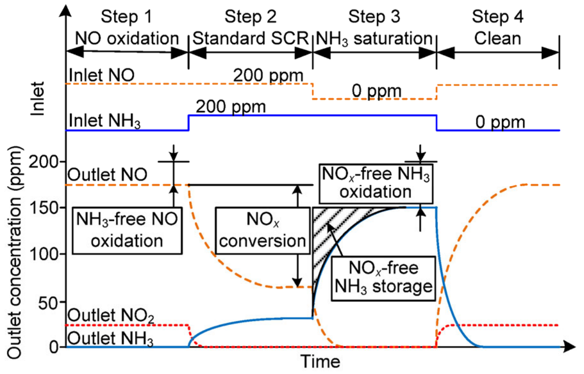

Fig. 2 Schematic diagram of the four-step based SCR catalyst performance test protocol

3 Results and discussion

3.1 Catalyst DEF soaking behavior

To simulate DEF soaking and urea deposits formation on the SCR catalyst during diesel engine operations, two SCR catalyst samples were impregnated with DEF for 1 h and 2 h separately. It was observed that the original clear DEF solutions were all found to have a blue hue after impregnating the SCR sample each time. It seems that some Cu was dissolved and leached down from the catalyst samples, and the largest change in blue color occurred during the first hour. To exclude the DEF's physical dissolution effect, one additional catalyst sample was also impregnated in the same volume of distilled water as a comparison. However, no obvious blue hue in the water was found at all. To be clear, it is the urea in the DEF solution that caused some Cu to leach out from those SCR catalyst samples through potential chemical processes.

For further verification of the loss of Cu from catalyst samples during liquid impregnation, DEF and water that had impregnated catalyst samples were collected and used for inductively coupled plasma (ICP) analysis. During ICP analysis, Cu concentration was clearly detected in the DEF solution, but none was found in water. From the ICP results, it can also be inferred that the Cu detected in the DEF solution probably came from the structure of zeolite rather than the free Cu in the catalyst pores. There must be potential chemical reactions, in which parts of Cu ions on the zeolite structure were replaced and dissolved into the DEF solution.

In fact, urea can decompose easily in aqueous solutions such as DEF, yielding ammonium (NH_4^+) and cyanate (OCN^-) ions (Okazaki and Funazukuri, 2008). Therefore, when the Cu-zeolite SCR catalyst samples were impregnated into such an ion solution, the ammonium ions could replace some Cu^{2+} ions from the catalyst zeolite structure and leave copper ammonia complex ions ($[Cu(NH_3)_4]^{2+}$) in the DEF solution. The copper ammonia complex ions would show an obvious blue hue even at a low ion concentration. Thus, besides there being urea deposits, DEF soaking will also definitely slightly change catalyst Cu loading. Each can drastically influence the activity and durability of SCR catalysts. In the following sections, the SCR catalytic performance of those DEF-impregnated samples will be illustrated and analyzed to investigate the impact of DEF soaking and urea deposits.

3.2 Catalyst NO_x conversions

Fig. 3 shows the NO_x conversions of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NO, 200 ppm NH_3, and N_2 as a balance gas. All the NO_x conversion data were obtained from the standard SCR segment of the four-step test at each temperature point (Fig. 2). For different SCR catalyst samples, the NO_x conversions show almost the same trend of single-peak curves. The NO_x conversions of each sample can exceed 90% in a wide medium temperature range from 250 °C to 400 °C and begin to decrease at low and high temperatures. The low NO_x conversions at low temperatures (<250 °C) are caused by the low catalytic activity, whereas at high temperatures (>400 °C) it is mainly ascribed to the strong NH_3 oxidation process.

From the NO_x conversions over different DEF-impregnated SCR catalyst samples, the DEF impregnation has almost no impact on NO_x conversions at low and medium temperatures, but it can drastically increase high-temperature NO_x conversions above 400 °C, as illustrated in Fig. 3. The catalyst sample impregnated by DEF for 2 h has the highest NO_x conversions in the high temperature range, almost doubling the value of the non-soaked sample at 550 °C. DEF impregnation was thought to have a negative effect on the catalyst NO_x conversions because of the potential urea deposits on the catalyst surface (Eichelbaum *et al.*, 2010a; 2010b). However, in this study, those DEF-impregnated SCR catalyst samples have nearly the same level or even higher NO_x conversions in the high temperature range. There are probably two reasons. First, the high-temperature hydrothermal treatment (up to 550 °C) after DEF impregnation helped to remove the urea deposits from the catalyst surface and recovered their performance according to the urea decomposition properties (Brack *et al.*, 2014). Second, the catalyst Cu loading change during DEF impregnation also altered their catalytic activities. A more detailed influence mechanism will be given in the following sections.

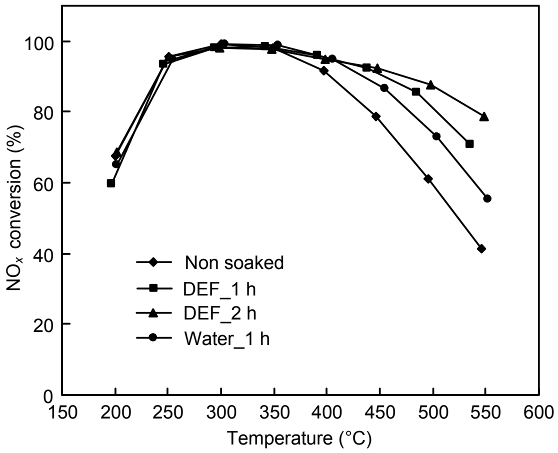

Fig. 3 NO_x **conversions of SCR catalyst samples at a space velocity of 60000** h^{-1} **and a feeding gas of 7%** H_2O**, 8%** CO_2**, 10%** O_2 **(in volume), 200 ppm NO, 200 ppm** NH_3**, and** N_2 **as a balance gas**

Fig. 3 also shows the NO_x conversions of a distilled-water-impregnated SCR catalyst sample as a comparison. The water impregnation also has almost no impact on the NO_x conversions at low and medium temperatures, but it can slightly increase the high-temperature NO_x conversions as well. That is because physical effects such as water flushing and dissolution can remove isolated impurities inside the catalyst samples and increase their reaction surface area. However, compared with those DEF-impregnated SCR catalyst samples, the NO_x conversions of the water-impregnated sample at high temperatures are much lower. Therefore, besides the physical effects, there must be additional reasons that could affect the NO_x conversions of SCR catalyst samples during DEF impregnation. From the ICP analysis above, the catalyst Cu loading change during DEF impregnation is probably the root cause of the improvement in NO_x conversations.

3.3 Catalyst NO oxidations

During the reduction process of NO_x with NH_3, the oxidation of NO to NO_2 is a rate-determining step. If the catalyst can oxidize a significant amount of NO to NO_2, the fast SCR reaction will be dominant over the standard SCR reaction, which helps to improve the entire SCR performance over a wide temperature range (Wurzenberger and Wanker, 2005). Fig. 4 shows the NO oxidations of SCR catalyst samples at a space velocity of 60000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NO, and N_2 as a balance gas. All the NO oxidation data were obtained from the NH_3-free NO oxidation segment of the four-step test at each temperature point (Fig. 2). The NO oxidation capability of the non-soaked SCR catalyst sample shows one single-peak curve with the maximum value at approximately 450 °C. However, for those DEF-impregnated samples, their NO oxidation performance decreases drastically, and the longer the impregnation time is, the greater the degradation of NO oxidation becomes.

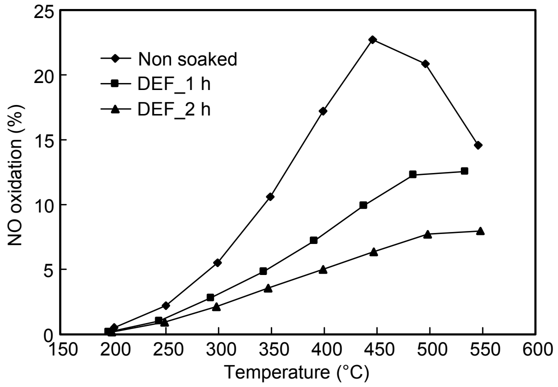

Fig. 4 NH_3**-free NO oxidations of SCR catalyst samples at a space velocity of 60000** h^{-1} **and a feeding gas of 7%** H_2O**, 8%** CO_2**, 10%** O_2 **(in volume), 200 ppm NO, and** N_2 **as a balance gas**

In fact, for metal-exchanged zeolites SCR catalysts like Cu-SAPO-34, previous studies have found that the oxidation reaction of NO to NO_2 always takes place on the metal sites, which are essential for SCR reactions (Ma *et al.*, 2012). Therefore, the decrease of NO oxidations of those DEF-impregnated SCR catalyst samples may be ascribed to the Cu loss during DEF impregnation, as discussed in Section 3.1. Some researchers also believe that the metal sites as well as the active sites on the catalyst surface may be blocked by urea deposits after DEF impregnation, which can decrease NO oxidations (Eichelbaum *et al.*, 2010a; 2010b). However, from the relatively high NO_x conversion results in Fig. 3, the active sites responsible for SCR reactions were not blocked by urea deposits at all after high-temperature hydrothermal treatment. Therefore, Cu loss during DEF impregnation is the main reason for the decrease in catalyst NO oxidations.

3.4 Catalyst NH_3 oxidations

Fig. 5 shows the NO_x-free NH_3 oxidations of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NH_3, and N_2 as a balance gas. All the NH_3 oxidation data were obtained from the NO_x-free NH_3 oxidation segment of the four-step test at each temperature point (Fig. 2). For the non-soaked SCR catalyst sample, the NH_3 oxidations are almost less than 20% below 300 °C, gradually increasing through the medium temperatures and reaching nearly 100% above 450 °C. The NO_x-free NH_3 oxidation results above indicate that NH_3 can effectively participate in SCR reactions below 300 °C, but as the temperature increases above 350 °C, the NH_3 oxidation process gradually becomes dominant, decreasing the NO_x conversions in the high temperature range, as shown in Fig. 3.

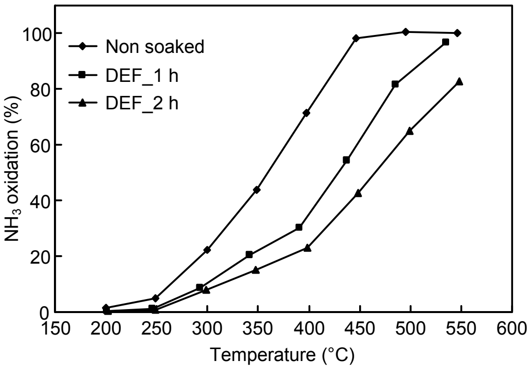

Fig. 5 NO_x-free NH_3 oxidations of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NH_3, and N_2 as a balance gas

For those DEF-impregnated SCR catalyst samples, the NO_x-free NH_3 oxidations have the same trend as for the non-soaked sample, almost all less than 20% below 300 °C, and begin to increase gradually above 300 °C. However, the absolute NH_3 oxidations of those DEF-impregnated samples are much lower than the non-soaked sample at each temperature point, especially at high temperatures, and the longer the impregnation time, the larger the NH_3 oxidation decreases. The above results indicate that the oxidation abilities of catalyst samples were weakened after DEF impregnation, and more NH_3 could be involved in SCR reactions, which helped to increase the NO_x conversions in the high temperature range.

Fig. 6 shows the NO and NH_3 oxidations of SCR catalyst samples at 400 °C with different DEF impregnation times. It is clear that both NO and NH_3 oxidations exponentially decrease with DEF impregnation time, because the Cu loss during DEF impregnation reduced the metal sites and weakened the catalyst's oxidation ability. Since NO is the main product in the NH_3 oxidation reaction (Ma *et al.*, 2014), the Cu loss-induced degradation of NO oxidation also inhibits the oxidation process of NH_3.

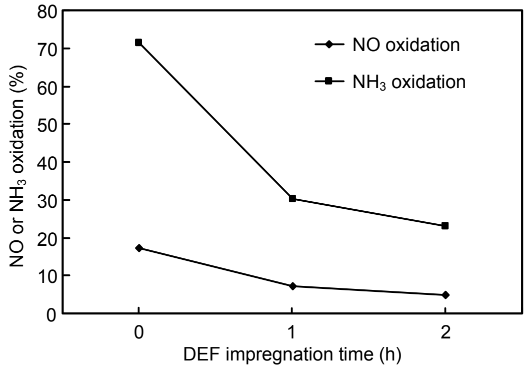

Fig. 6 NO and NH_3 oxidations of SCR catalyst samples with different DEF impregnation time at the testing temperature of 400 °C

3.5 Catalyst NH_3 storage level

It is well established that NH_3 should be adsorbed on the SCR catalyst surface before it reduces the gaseous NO_x (Wurzenberger and Wanker, 2005). Therefore, the SCR performance is greatly affected by the catalyst NH_3 storage capability. Fig. 7 shows the NH_3 storage level of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NH_3, and N_2 as a balance gas. All the NH_3 storage data were obtained from the NO_x-free NH_3 oxidation segment of the four-step test at each temperature point (Fig. 2), by integrating the difference of inlet and outlet NH_3 concentrations. Although the total NH_3 storage should also contain the dynamic NH_3 storage in the standard SCR segment of the four-step test, the NO_x-free NH_3 storage, to some extent, can also reflect the NH_3 storage capacities of those test SCR catalyst samples.

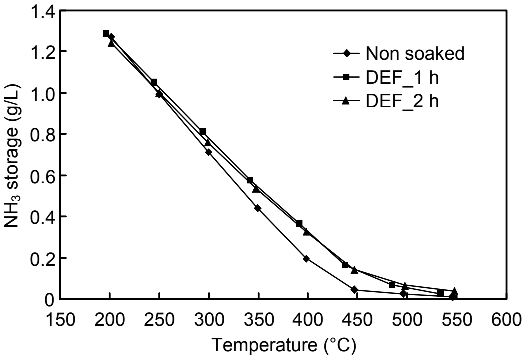

Fig. 7 NO_x-free NH_3 storage level of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NH_3, and N_2 as a balance gas

As illustrated in Fig. 7, the NH_3 storage capacities of all test SCR catalyst samples decrease drastically with increasing temperature. However, compared with the non-soaked sample, those DEF-impregnated SCR catalyst samples appear to have a slightly higher NH_3 storage capacity, especially in the medium and high temperature ranges. In fact, for metal-exchanged zeolite SCR catalysts, NH_3 can be adsorbed on either metal sites or acid sites, such as Lewis/Bronsted sites. NH_3-TPD (temperature programmed desorption) tests on Cu-zeolite catalysts in many studies have demonstrated that the storage NH_3 is mainly adsorbed on acid sites above 200 °C, whereas the NH_3 adsorption on Cu sites usually happens at low temperatures (Ma *et al.*, 2013; 2014). Thus, the NH_3 storage capacity at a normal SCR reaction temperature range (above 200 °C) is mainly determined by the number of acid sites on the catalyst surface. The Cu loss during DEF impregnation tests released more acid sites for NH_3 adsorption on the catalyst surface. Therefore, DEF impregnation actually slightly improved the catalyst acidity and NH_3 storage capability (Fig. 7). The higher NH_3 storage capability at medium and high temperatures is another reason for the higher high-temperature NO_x conversions of those DEF-impregnated SCR catalyst samples.

3.6 Catalyst N_2O selectivity

N_2O selectivity is another important practical issue for SCR catalysts. For metal-exchanged zeolite SCR catalysts, N_2O is usually produced in two ways, low-temperature ammonium nitrates decomposition and high-temperature NO/NH_3 oxidation (Kamasamudram *et al.*, 2012; Kumar *et al.*, 2015). Fig. 8 shows the N_2O selectivity of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NO, 200 ppm NH_3, and N_2 as a balance gas. All the N_2O selectivity data were obtained from the standard SCR segment of the four-step test at each temperature point (Fig. 2). As expected, all the SCR catalyst samples have a similar qualitative behavior of N_2O selectivity with two N_2O production peaks. One is located at approximately 250 °C, and the other at around 500 °C. The two N_2O peaks correspond to the two processes of N_2O generation as mentioned above.

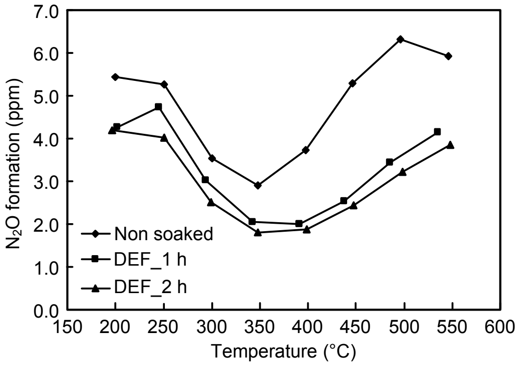

Fig. 8 N_2O selectivity of SCR catalyst samples at a space velocity of 60 000 h^{-1} and a feeding gas of 7% H_2O, 8% CO_2, 10% O_2 (in volume), 200 ppm NO, 200 ppm NH_3, and N_2 as a balance gas

However, compared with the non-soaked SCR catalyst sample, those DEF-impregnated samples have a relatively low N_2O selectivity across the entire temperature range. As mentioned above, DEF impregnation slightly reduced the Cu loading and Cu metal concentration on the catalyst surface. The decrease of Cu loading made those DEF-impregnated

SCR catalyst samples less active to the decomposition of surface ammonium nitrates during SCR reactions and reduced N_2O formation in the low temperature range (Kamasamudram *et al.*, 2012; Kumar *et al.*, 2015). Moreover, it also has been proved that the Cu oxocations, such as $[CuOCu]^{2+}$, act as the catalytic active sites for the NO/NH_3 oxidation and N_2O formation at high temperatures (Beutel *et al.*, 1996). Therefore, the Cu loss during DEF impregnation also gave those SCR catalyst samples a lower N_2O selectivity in the high temperature range.

From the results and discussion above, it is clear that DEF impregnation will definitely slightly change the catalyst Cu loading besides the urea deposit issue. The negative effect of urea deposits on the performance of SCR catalysts was not clearly observed, because the high-temperature hydrothermal treatment (up to 550 °C) helped to remove the urea deposits. In contrast, the Cu loading change of those catalyst samples due to DEF impregnation had caused a great effect on the SCR performance, as shown in Figs. 3–8. The Cu loss of catalyst reduced the metal active sites on the catalyst surface and weakened the catalytic oxidation ability, which caused lower NO/NH_3 oxidation and lower high-temperature N_2O formation. Lower Cu loading also slowed down the decomposition of surface ammonium nitrates during SCR reactions, leading to lower N_2O selectivity at low temperatures. Furthermore, the replaced Cu during DEF impregnation also released more acid sites on the catalyst surface and increased the catalyst acidity, and more NH_3 was able to be adsorbed at medium and high temperatures for SCR reactions. Both the higher NH_3 storage and lower NH_3 oxidation helped to involve more NH_3 into SCR reactions for NO_x reduction, especially at high temperatures, leading to higher NO_x conversions at high temperatures as shown in Fig. 3.

4 Conclusions

DEF soaking and urea deposits on SCR catalysts are critical issues in real diesel engine NH_3-SCR systems. To investigate the impact of DEF soaking and urea deposits on the SCR performance of Cu-zeolite catalysts, several fresh catalyst samples were drilled from a new full-size SCR catalyst with a formulation of Cu-SAPO-34. Those catalyst samples were impregnated with DEF solutions for certain times and dried, and subsequently hydrothermally treated for the simulation of DEF soaking and urea deposits on real SCR catalysts during diesel engine operations. Their SCR performance was finally evaluated in a flow reactor with a four-step test protocol.

Test results show that DEF impregnation caused some Cu to leach out from the SCR catalyst samples and slightly reduced their Cu loadings. The Cu loss of catalysts reduced the metal active sites on the catalyst surface and weakened the catalytic oxidation abilities, which caused lower NO/NH_3 oxidation and lower high-temperature N_2O formation. Lower Cu loading also slowed down the decomposition of surface ammonium nitrates during SCR reactions, thus decreasing N_2O selectivity at low temperatures. Cu loss during DEF impregnation released more acid sites on the catalyst surface and increased the acidity of the catalyst, which caused more NH_3 to be adsorbed and involved in SCR reactions at medium and high temperatures. The lower NH_3 oxidation and higher NH_3 storage gave those DEF-impregnated SCR catalyst samples higher NO_x conversions, especially in the high temperature range. Urea deposits due to DEF impregnation should have a negative impact on SCR performance because of the potential blocking effect on the micro pores and catalytic active sites (Eichelbaum *et al.*, 2010a; 2010b). However, in this study, the urea deposits were probably removed during the high-temperature hydrothermal treatment after DEF impregnation; thus, their negative impact was not clearly observed.

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中文概要

题　目： **尿素水溶液浸渍对柴油机 NH_3-SCR 后处理铜基分子筛催化剂性能的影响**

目　的：柴油机 NH_3-SCR 系统在实际使用中容易出现 SCR 催化剂被尿素水溶液（DEF）浸渍和催化剂表面尿素结晶的问题，导致催化剂失活和老化。以铜基小孔分子筛 Cu-SAPO-34 为对象，研究 DEF 浸渍和尿素结晶对催化剂性能的影响，并分析 DEF 浸渍和尿素结晶影响催化特性的深层机理。

创新点： 1. 通过小样 DEF 浸泡和水热处理模拟柴油机 NH_3-SCR 系统在实际使用中催化剂表面被 DEF 浸渍、尿素结晶生成及演变的情况；2. 采用四步法在流动反应器上对被 DEF 浸泡和水热处理后的催化剂小样进行性能评估和分析。

方　法：1. 对全尺寸铜基分子筛 SCR 催化剂取小样并进行 700 °C 和 4 小时的水热预处理使其性能稳定；2. 通过 1~2 小时 DEF 浸泡和高达 550 °C 的水热处理，模拟柴油机 NH_3-SCR 系统在实际使用中催化剂表面 DEF 浸渍、尿素结晶生成与演变情况；3. 采用四步法在流动反应器上对被 DEF 浸泡和水热处理后的催化剂小样进行 NO_x 转化率、N_2O 选择性、NO 和 NH_3 氧化性以及 NH_3 存储等性能评估；4. 以新鲜催化剂小样为参照，分析 DEF 浸渍和尿素结晶对铜基分子筛 SCR 催化剂性能的影响。

结　论：1. DEF 浸渍会轻微减小铜基分子筛 SCR 催化剂的铜载量；2. 铜载量的降低削弱了催化剂的氧化性，导致较低的 NO/NH_3 氧化性和高温 N_2O 选择性；3. 铜载量的降低减缓了催化剂表面硝酸氨的分解，导致较低的低温 N_2O 选择性；4. DEF 浸渍引起铜载量变化的同时增强了催化剂表面酸性，使更多 NH_3 可以被吸附和参与 SCR 反应；5. DEF 浸渍过的催化剂小样由于具有较低的 NH_3 氧化性和较高的 NH_3 存储能力，所以在 400 °C 以上具有更好的 NO_x 转化率；6. 尿素结晶对催化剂性能影响不明显，主要是因为 DEF 浸泡后的高温水热处理已经去除了催化剂表面大部分的尿素结晶。

关键词： 柴油机排放控制；选择性催化还原；NO_x 还原；铜基分子筛催化剂；尿素水溶液浸渍