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ARTICLE

# Catalysts for the Selective Catalytic Reduction of $NO_x$ with $NH_3$ at Low Temperature

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Selective catalytic reduction of $NO_x$ with $NH_3$ ($NH_3$-SCR) at low temperature is a major challenge in environmental catalysis. In recent years, great efforts have been applied to the development of low-temperature SCR catalysts for both stationary sources and diesel engines. Mn-based catalysts have attracted great attentions due to their excellent low-temperature activity. However, vulnerability to $SO_2$ and $H_2O$ poisoning and preference for $N_2O$ formation make these catalysts still far away from industrial application. $V_2O_5$ loaded on carbon materials have shown both high SCR activity and $SO_2$ tolerance at low-temperature. This type of catalyst is very promising for the applications in low-temperature SCR for stationary sources. Recently, Cu containing small pore zeolites, such as Cu-SSZ-13 and Cu-SAPO-34 with CHA structure and Cu-SSZ-39 and Cu-SAPO-18 with AEI structure, were shown to have very high activity at low temperature and excellent hydrothermal stability at high temperature and thus received much attention for the applications on diesel vehicles. In this review, we will focus on the recent studies of low-temperature $NH_3$-SCR catalysts. In addition, the future directions of low-temperature SCR development will also be discussed.

## 1. Introduction

$NO_x$ (mainly NO and $NO_2$) can induce acid rain, photochemical smog and haze, and can also cause direct damages to the respiratory systems of human bodies. It is mainly produced during the combustion of fossil fuels from stationary sources such as coal-fired power plants and mobile sources such as motor vehicles. In recent years, great efforts have been applied to the development and application of available technologies for the control of $NO_x$ emissions.[1, 2]

Although modifications to the combustion system are extensively utilized to lower $NO_x$ emissions, post-combustion flue gas treatment technologies are still required to meet the ever tightened emission standards. In particular, different catalytic abatement technologies have been used for the $NO_x$ reduction from stationary and/or mobile sources.[3] Among these technologies, selective catalytic reduction of $NO_x$ with $NH_3$ ($NH_3$-SCR: $4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$) is best developed and widely applied for $NO_x$ emission control due to its high efficiency, good selectivity and low cost.[4, 5]

$NH_3$-SCR was initially developed and applied for removing $NO_x$ from stationary sources. This technology has also been introduced into the market for diesel vehicles and is thought to be one of the best technologies for meeting the increasingly stringent standards for $NO_x$ emissions.[6] Catalyst plays key role on the development of $NH_3$-SCR technology.[7] Vanadium-based catalysts, especially $WO_3$ or $MoO_3$ doped $V_2O_5/TiO_2$, have been widely used for the removal of $NO_x$ generated from stationary sources since 1970s.[4] This type of catalyst was also employed as the first generation $NH_3$-SCR catalyst on diesel engines. However, the toxicity of active vanadium species restrained the practical applications of $V_2O_5$-$WO_3(MoO_3)/TiO_2$ on diesel vehicles.[6] Some transition metal exchanged zeolites, such as Fe-ZSM-5 [8, 9], Cu-SSZ-13,[10, 11] and Cu-SAPO-34,[12, 13] and vanadium-free oxide catalysts, such as Ce-based [14-16] and Fe-based oxides [17, 18], were developed as (potential) substitutions. Nevertheless, vanadium-based catalyst with excellent sulfur poisoning resistance is still a preferred choice for diesel vehicles in some developing countries, such as China, due to the high sulfur content in diesel fuel.[19, 20]

There have been strong interests in developing $NH_3$-SCR catalysts with high activity in low-temperature range (100-300 $^oC$).[21] Such a catalyst can be placed in the downstream of the electrostatic precipitator (or baghouse) and/or de-sulfurizer where ash and/or sulfur contents are significantly reduced for stationary applications, especially coal fired power plants. Successful application of low-temperature $NH_3$-SCR catalyst would significantly improve the lifetime of catalyst and the economics of $NH_3$-SCR. Low-temperature $NH_3$-SCR is also very important for diesel vehicles, for example, during cold startup and on traveling short distances.[22] Therefore, we will focus our review on the recent studies of low-temperature $NH_3$-SCR catalysts. In addition, the future directions of low-temperature SCR development will also be discussed.

## 2. Challenges

### 2.1 Inhibition of $H_2O$

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The presence of water vapour or moisture is inevitable for the application of $NH_3$-SCR, no matter whether on stationary sources or diesel engines. Different influences of $H_2O$ on the activity of $NH_3$-SCR catalyst were observed at low temperature and high temperature, respectively.[23, 24] At high temperatures, $H_2O$ could inhibit the unselective oxidation of $NH_3$ and thereby enhance the high-temperature activity. However, $H_2O$ can play a notable role on inhibiting SCR reaction and thereby decrease the activity at low temperatures. It is usually explained as an effect of an adsorption competition between $H_2O$ and $NH_3/NO_x$ molecules on the reaction sites or as modification of the structure of active sites, e.g. the transformation of Lewis acid sites into Brønsted acid sites.[4, 23, 25, 26]

### 2.2 Inhibition of HC

Hydrocarbon (HC) residue in diesel exhaust can induce gradual deactivation of $NH_3$-SCR catalysts, especially zeolite supported catalysts, by coking and deposition.[21, 27] The inhibition effect by HC is related to the structure of the charged catalysts. For example, Cu exchanged medium-pore and cage zeolite, Cu-ZSM-5, is prone to deactivation by HC, while Cu-SSZ-13 and Cu-SAPO-34 with relatively small pores and one-dimensional pore structure showed good HC poisoning resistance.[28, 29]

### 2.3 Poisoning by $SO_2$

$SO_2$ is produced from the combustion of sulfur components in the fossil fuel, such as coal and diesel. The presence of $SO_2$ can significantly impact the $NH_3$-SCR activity of the catalyst. The transformation of $SO_2$ to $SO_4^{2-}$ on the surface of catalyst will increase the surface acidity and thereby enhance the adsorption of $NH_3$, which will significantly improve the high-temperature $NH_3$-SCR activity.[4, 15, 30, 31] In addition, the improvement of low-temperature activity can also be observed on some specific catalysts, such as $V_2O_5$/AC.[32, 33] However, for vanadium-free catalysts, the active metal can be sulfated gradually causing irreversible poisoning,[34-37] and as a result, the low-temperature activity will be sharply decreased. Moreover, the production of ammonium sulphites or sulphates originating from reaction between $NH_3$ and $SO_2$ or $SO_3$ can induce the coverage of active sites and the blockage of pores of the catalyst. This poisoning effect is universal for all of the low-temperature $NH_3$-SCR catalysts.[21, 31] Thermal decomposition of the ammonium sulfates is an effective way to regenerate the deactivated $NH_3$-SCR catalysts. For low-temperature SCR catalysts, periodical washing is another way to solve this problem, particularly for stationary sources.

### 2.4 Poisoning by alkali metals

Alkali metals from fly ash are another major concern for the application of SCR catalyst in coal-fired plants. For diesel vehicles, fuel and lubrication oil additives as well as urea solutions are the origins of alkali metals.[38-40] Accumulation of a small amount of these metals will have a notable poisoning effect on the catalytic activity by decreasing the amount and strength of the Brønsted acid sites.[40-42] Periodical washing is also an effective way to regenerate the alkali metal poisoned catalyst, especially for stationary sources.

### 2.5 Production of $N_2O$

$N_2O$ is a strong greenhouse gas, which can be produced together with $N_2$ during $NH_3$-SCR. The $N_2O$ production is usually notable at high temperatures. But for some low-temperature catalysts, such as Mn-based catalysts, significant amount of $N_2O$ can also be formed even at low temperatures.[43-45] Generally speaking, $N_2O$ formation over Mn-based catalysts at low temperature is due to the non-selective catalytic reduction (NSCR) reaction: $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$.[4] Isotopic labelling study has demonstrated that the two N atoms in $N_2O$ are mainly due to a coupling of one nitrogen atom from $NH_3$ and the other one from NO.[46]

## 3. Mn oxides

Over the last decades, there has been increasing interests in the development of low-temperature SCR catalysts containing transition metal oxide catalysts, such as $V_2O_5$, $Fe_2O_3$, CuO, and $MnO_x$.[21] Among them, Mn-based catalysts attracted great attentions due to their excellent low-temperature activity.

Several oxides of Mn, *i.e.*, $MnO_2$, $Mn_5O_8$, $Mn_2O_3$, $Mn_3O_4$ and MnO, are known to be stable at ambient conditions. Different methods [47] and various precipitants [48] were used to prepare different types of $MnO_x$ as low-temperature SCR catalyst. The influences of crystallinity, oxidation state and structure on its SCR activity and $N_2$ selectivity were investigated. $MnO_2$ appears to exhibit the highest activity per surface area, followed by $Mn_5O_8$, $Mn_2O_3$, $Mn_3O_4$ and MnO, in a reduced order.[49] Amorphous $MnO_x$ prepared by different methods showed superior low temperature activity, which is mainly associated with the amorphous phase and high specific area.[47] Although great efforts have been made to the investigation of $MnO_x$ for low-temperature SCR, high $N_2O$ formation during the reaction is still a general problem.

To improve the catalytic performance of $MnO_x$, some other metal elements were used to modify the catalytic properties of the catalysts, and many support materials were also engaged for Mn-based catalysts. A Mn/$TiO_2$ catalyst with outstanding low-temperature SCR performance was reported in 2001.[50] After that, Mn-based SCR catalysts received great attentions, and various related catalysts were developed. These developed catalysts include Mn-Fe/$TiO_2$,[51] Mn-Ce/$TiO_2$,[52] Mn-Ni/$TiO_2$,[53] Mn/$Al_2O_3$,[54] Mn/$SiO_2$,[55] $MnO_x$/AC,[56] $MnO_x$/$CeO_2$-$ZrO_2$-$Al_2O_3$,[57] Mn-Ce oxide,[58-62] Mn-W oxide,[63] Mn-Fe oxide,[64, 65] Mn-Zr oxide,[66] Mn-Cu oxide,[67] Mn-Fe spinel,[68] and Mesoporous $MnO_2$-$Fe_2O_3$-$CeO_2$-$TiO_2$ [69]. Most of these catalysts were developed for stationary sources. However, the Mn-based catalysts are vulnerable to the poisoning effects of $SO_2$ and $H_2O$, which is still not satisfactorily solved. The relatively high $SO_2$ content in coal fired flue gas prevented the application of Mn-based catalysts.

There were also some investigations of Mn-based catalysts for diesel exhaust treatment. Different dopants including Nb, Fe, W and Zr were selected to improve the catalytic performance of $MnO_x$-$CeO_2$ (Figure 1).[62] Cordierite monoliths coated with the catalysts were tested under the conditions in SCR converters on board of diesel vehicles. Although the Nb-doped catalyst clearly showed improved activity and $N_2$ selectivity, the addition of Nb did not enhance the resistance of the catalyst against $SO_2$

poisoning. Similarly, a $FeMnTiO_x$ catalyst showed excellent low-temperature SCR activity, but an intense and irreversible deactivation occurred after exposure to $SO_2$, because the formation of nitrate species was totally inhibited by the formation of sulfate, resulting in the cut-off of the SCR reaction pathway at low temperatures.[23]

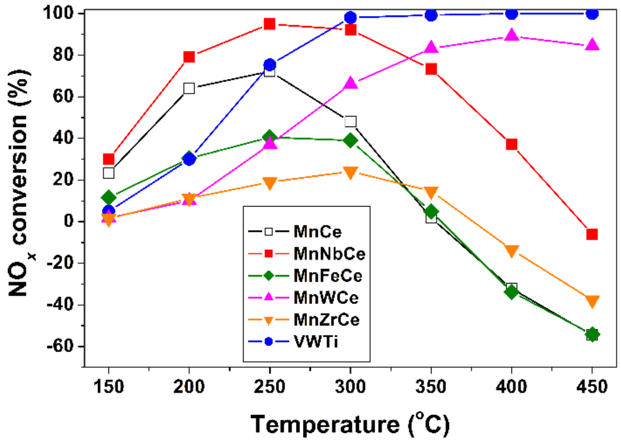

**Fig. 1** $NO_x$ conversions over MnCe, MnNbCe, MnFeCe, MnWCe, and MnZrCe oxides.[62] The $NO_x$ conversion of VWTi oxides is also included for comparison. Catalyst-coated monoliths for the test: 1.2-1.3 g of each catalyst powder were coated with a silica binder on small cordierite monoliths (3.8 cm × 1.7 cm × 1.2 cm) with a cell density of 400 cpsi; Reaction conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10% $O_2$, 5% $H_2O$, and GHSV = volumetric gas flow/coated monolith volume = 52,000 $h^{-1}$. (Reprinted with the permission from the Elsevier Publisher)

Recently, a Mn-Ce mixed oxide catalyst prepared by surfactant-template method showed both higher catalytic activity for $NH_3$-SCR and resistance against $SO_2$ and $H_2O$ than the catalyst prepared by conventional co-precipitation method.[70] In addition, a Mn-Ce-Ti mixed oxide catalyst prepared by hydrothermal method exhibited excellent $NH_3$-SCR activity and strong resistance against $H_2O$ and $SO_2$ in a broad temperature range. The excellent catalytic performance was related to the dual redox cycles ($Mn^{4+} + Ce^{3+} \leftrightarrow Mn^{3+} + Ce^{4+}$ and $Mn^{4+} + Ti^{3+} \leftrightarrow Mn^{3+} + Ti^{4+}$) and the amorphous structure of the catalyst.[71] These results may open new pathways for the development of Mn-based catalysts for low-temperature SCR.

To gain insight into the $NH_3$-SCR reaction over Mn-based catalysts, many mechanistic studies have been carried out. According to the reported reaction pathways, the initial step was usually considered to be the adsorption of $NH_3$ on the Lewis acid sites of the catalysts to form coordinated $NH_3$ and $NH_2$, and then they can react with aerial NO through Eley–Rideal (E-R) mechanism or active nitrite intermediates adsorbed on the surface of the catalysts through Langmuir–Hinshelwood (L-H) mechanism.[21, 72] Based on the investigation on a $MnO_x$-$CeO_2$ catalyst, Qi et al. [60] indicated that all the intermediates during the SCR reaction could transform into $NH_2NO$ and further react to produce $N_2$ and $H_2O$. On the other hand, Liu et al. [23] considered $NH_4NO_3$ as an important intermediate species at low temperatures on a $FeMnTiO_x$ catalyst, and the reduction of $NH_4NO_3$ by NO was suggested as the rate-determining step of the whole SCR reaction. Although spectroscopic investigations, adsorption-desorption studies and kinetic experiments have been widely used to investigate the mechanism of $NH_3$-SCR reaction over Mn-based catalysts, there are still some debates. Different hypotheses proposed by different studies may be related to the different catalyst components, Mn loadings, and test conditions.

## 4. $V_2O_5$-based catalysts

Although $V_2O_5$-based catalysts have been commercialized in $NH_3$-SCR industry since 1970s, there remains continuous interests for the improvement of low-temperature activity under abundant $SO_2$ conditions, both for stationary sources and diesel engines.

$WO_3$ was found to be an excellent promoter and stabilizer for $V_2O_5/TiO_2$.[4] Particularly, the addition of $WO_3$ into $V_2O_5/TiO_2$ could make it more active at low temperatures. The low-temperature activity of $V_2O_5$-$WO_3/TiO_2$ can be further promoted by other dopant, such as Ce. It was found that Ce addition could enhance the $NO_x$ adsorption and oxidation and then accelerate the SCR reaction due to the synergetic interaction between Ce and $V_2O_5$-$WO_3/TiO_2$.[73] In addition, it was also found that Mn can significantly promote the low temperature activity of $V_2O_5/TiO_2$ catalyst.[74]

Although $TiO_2$ was widely used as the support for $V_2O_5$-based catalysts and has proved its excellent property in $NH_3$-SCR industry for several decades, there were still many attempts to improve the support of $V_2O_5$-based catalysts. Several studies reported the application of $V_2O_5$ and $V_2O_5$-$WO_3$ loaded on $TiO_2$-$SiO_2$ in $NH_3$-SCR using various preparation methods.[6, 75, 76] The catalytic performance was further promoted by loading $V_2O_5$ on a $TiO_2$-$SiO_2$-$MoO_3$ support using co-precipitation method.[77] This catalyst exhibited a superior SCR activity and a good sulfur tolerance at lower temperature. Such superior low-temperature SCR activity was mainly attributed to the presence of polymeric vanadate species and high redox property besides high surface area. The $SO_2$ oxidation activity was found to be significantly suppressed with increasing the $SiO_2$ content in the support, which leads to the remarkable improvement of sulfur tolerance of the catalyst and thus is favourable for the industrial applications of low-temperature SCR process.

Carbon is a special catalyst support material with relatively inert property, so that undesired side reactions catalyzed by the support surface hardly occur. Various carbon materials supported vanadium-free catalysts, including $CeO_2$/ACF(activated carbon fiber),[78, 79] $Fe_2O_3$, $Co_2O_3$ or $Mn_2O_3$/ACF,[80] $MnO_x$/CNT (carbon nanotube),[81-83] CuO/CNT,[84] $MnO_x$-$CeO_2$/CNT,[85-88] $Fe_2O_3$, $Cr_2O_3$ or CuO/AC (active carbons),[89, 90] Cu or Mn/active carbon honeycomb,[91] and $MnO_x$-$CeO_2$/ active carbon honeycomb,[34] have been studied for low-temperature SCR reaction. These catalysts exhibited relatively high SCR activities at low temperatures, but the inadequate $SO_2$ tolerance is a fatal problem for their industrial application. However, when $V_2O_5$ with extraordinary inherent resistibility to $SO_2$ was loaded on carbon materials, the obtained catalysts exhibited excellent activity and $SO_2$ tolerance for low-temperature SCR.

When the loading of $V_2O_5$ is relatively low, $SO_2$ even plays a positive effect on the activity. The kinds of $SO_2$ adsorbed on the catalyst surface can be recognized as $SO_4^{2-}$, which can increase the surface acidity and thus benefit $NH_3$ adsorption on the catalyst, and as a result enhance the SCR activity.[33] Although $SO_2$ promotes the SCR activity of the $V_2O_5$/AC catalyst in the absence of $H_2O$, it speeds the deactivation of the catalyst in the presence of $H_2O$ (Figure 2).[32, 92] Under the co-existence of $SO_2$ and $H_2O$, ammonium sulfate salts deposit on the surface of the $V_2O_5$/AC catalyst, block the pores of the catalyst, and cause catalyst deactivation.[32, 93, 94] However, the deposited ammonium sulfate salts can be easily removed, for example by thermal decomposition or by washing.[95] In addition, $H_2O$ inhibits the SCR reaction between the $NH_3$ on the Lewis acid sites and NO, and the inhibition effect increases with increasing $H_2O$ content. The inhibition effect is reversible and $H_2O$ does not poison the $V_2O_5$/AC catalyst.[96] HCl in the flue gas can play a promoting effect on the catalytic activity of $V_2O_5$/AC by increasing the surface acidity of the catalyst, but KCl deactivates the SCR activity by neutralization of acid sites.[97, 98]

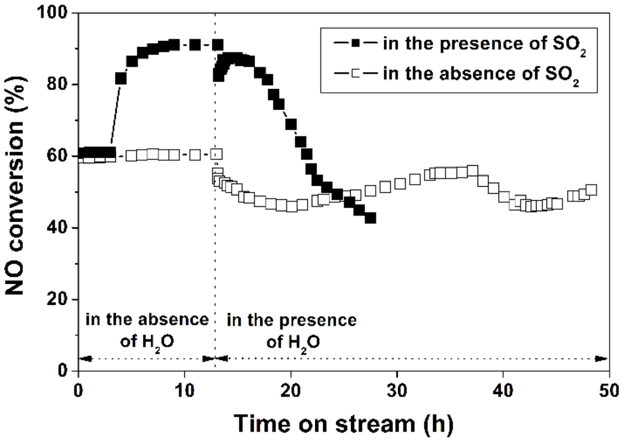

**Fig. 2** Effect of $H_2O$ and $SO_2$ on the NO conversion over 1 wt.% $V_2O_5$/AC catalyst. Reaction conditions: 500 ppm NO, 600 ppm $NH_3$, 500 ppm $SO_2$ (when used), 3.4% $O_2$, 2.5% $H_2O$ (when used), and balance Ar; space velocity of 90000 $h^{-1}$; reaction temperature of 250 °C. (Reprinted with the permission from the Elsevier Publisher)

The commercial catalyst used in SCR is in monolithic form because it is suitable for high gas flow rate with low pressure drop, good gas distribution, and high tolerance to dust and attrition. Therefore, $V_2O_5$ was also directly loaded on active carbon monoliths and carbon-coated monoliths for low-temperature SCR.[99-102]

Similar with Mn-based catalysts, there are still some debates about the mechanism of $NH_3$-SCR reaction over $V_2O_5$-based catalysts. Both Eley–Rideal (E-R) and Langmuir–Hinshelwood (L-H) mechanisms were suggested.[4, 103] When $NO_2$ was added into the reaction for the purpose of promoting $NO_x$ conversion by "fast SCR" reaction ($2\ NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$), the reaction mechanism turns to be more complicated.[104] Based on some transient reactive experiments, Tronconi et al. [104, 105] proposed a ''Nitrate Route'' for the low temperature ''Fast SCR'' reaction over $V_2O_5$-$WO_3$/$TiO_2$ catalyst. The formed $NH_4NO_3$ during the reaction was identified as an important intermediate, and its subsequent reaction with NO was proposed as the rate determining step. Based on this result, they even developed a novel "Enhanced $NH_3$-SCR" Reaction for $NO_x$ abatement at low temperature.[22, 106] Such a reaction involves the selective reduction of NO by $NH_3$ in the presence of nitrate species (e.g., $NH_4NO_3$) to $N_2$ ($2\ NH_3 + 2\ NO + NH_4NO_3 \rightarrow 3N_2 + 5H_2O$). This new reaction has very high DeNO$_x$ efficiency at low temperatures, similar to that of "fast SCR", even though no $NO_2$ is fed to the reaction.

## 5. Zeolites

There are limitations to the catalyst volume that can be placed on board, which requires that the SCR catalyst should present superior $NH_3$-SCR performance under high space velocity conditions.[6] Therefore, Fe (or Cu)-exchanged zeolites, with high adaptability to high space velocity, have received increasing attention for the purpose of mobile application. Starting from 1990s, great efforts have been made to ZSM-5 catalysts.[8, 9] However, the insufficient low-temperature activity of Fe-ZSM-5 and the poor hydrothermal stability of Cu-ZSM-5 restrained their applications on diesel vehicles.[107] Along with these problems, ZSM-5 is susceptible to adsorbing hydrocarbons at low temperatures that can generate heat as the temperature is raised, damaging the zeolite structure.

Recently, Cu containing chabazite type zeolite (Cu-CHA) catalysts, especially Cu-SSZ-13 and Cu-SAPO-34, have been shown to have excellent catalytic activity, especially the low-temperature activity, and hydrothermal stability in $NH_3$-SCR reaction.[28] Furthermore, this type of catalysts is less prone to deactivation by hydrocarbon inhibition and thermal degradation due to their small pore structures. The earliest reports on the excellent $NH_3$-SCR performance of Cu-CHA catalysts were mainly presented in some patent literatures by Johnson Matthey [108] and BASF [109]. Soon after that, many papers on the Cu-CHA catalysts and their $NH_3$-SCR performance were published in the recent years and have attracted more and more attentions.[110]

According to the comparison made by Kwak et al.,[10] Cu-SSZ-13 showed much better low-temperature activity and selectivity than ZSM-5 and beta supported catalysts. Furthermore, the $NO_x$ reduction performance of Cu-ZSM-5 and Cu-beta was significantly reduced at low temperatures after hydrothermal aging, while that of Cu-SSZ-13 was not affected.[111] With similar structure as Cu-SSZ-13, Cu-SAPO-34 also has excellent $NH_3$-SCR performance and stability.[12] Indeed, the hydrothermal stability of Cu-SAPO-34 was better than Cu-SSZ-13, and its low-temperature activity was even increased after hydrothermal aging.[112] Isolated $Cu^{2+}$ ions were identified as both SCR active site and structure protective agent for Cu-CHA catalysts.[113-123] Schmieg et al. [124] systematically assessed the multiple catalytic functions ($NO_x$ conversion, NO and $NH_3$ oxidation, $NH_3$ storage) of a BASF commercial Cu-chabazite (CHA) urea/$NH_3$-SCR catalyst after undergoing different degrees of hydrothermal aging. The decrease in SCR performance was explained by zeolite structure destruction and/or Cu agglomeration. Laboratory aged catalyst (16 h at 800 °C) is very comparable to a 135,000 mile vehicle-aged one in term of its low-temperature $NH_3$-SCR performance, except for the chemically poisoned inlet section of the vehicle-aged catalyst.

Different from other $NH_3$-SCR catalysts, Cu-CHA catalysts were less sensitive to the presence of $NO_2$. Kwak et al. [125] examined the effect of Cu loading on the $NH_3$-SCR performance over a series of Cu ion-exchanged (20–80%) SSZ-13 zeolite catalysts. They found that the NO oxidation over Cu-SSZ-13 was quite low regardless of Cu loading, and during the ‘‘fast’’ $NO/NO_2$-SCR only a slight improvement in low-temperature $NO_x$ reduction activity was obtained. Xie et al. [126] even found that $NO_2$ has an inhibition effect on the low-temperature activity of Cu-SSZ-13 due to the accumulation of $NH_4NO_3$ (Figure 3). In addition to $NO_2$, $SO_2$ can also cause inhibition effect on the low-temperature activity by the formation of ammonium sulfate species, with some contribution from competitive adsorption between $SO_2$ and $NO_x$.[127-129]

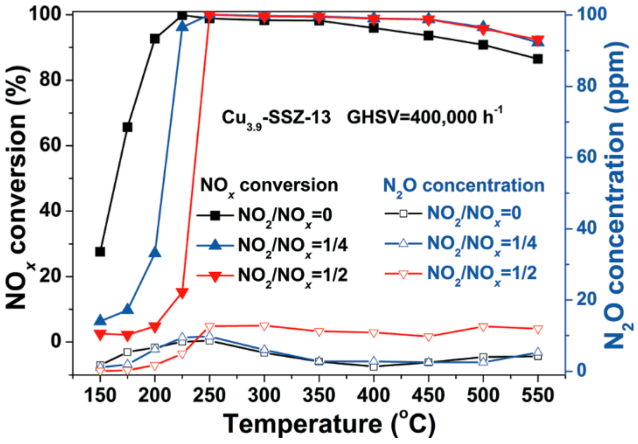

**Fig. 3** $NH_3$-SCR performance of the $Cu_{3.9}$–SSZ-13 catalyst under different reaction conditions.[126] Reaction conditions: 500 ppm $NO_x$ (NO + $NO_2$), 500 ppm $NH_3$, 5 vol.% $O_2$, balance $N_2$, and GHSV = 400 000 $h^{-1}$. (Reprinted with the permission from the RSC Publisher)

To improve the synthesis procedure and reduce the preparation cost of Cu-SSZ-13, a low-cost copper-amine complex (Cu-TEPA) was rationally designed to act as a novel and efficient template for one-pot synthesis of Cu-SSZ-13 zeolites with changeable Si/Al ratios.[11, 130] This methodology allowed the direct introduction of extra-framework copper species in the CHA cages. Soon after that, one-pot direct synthesis of Cu-SAPO-34 was achieved.[13, 117, 118, 131] Recently, Cu-SSZ-13 was even directly prepared on cordierite monolith by *in situ* hydrothermal synthesis method.[132] These improvements of synthesis methods make the Cu-CHA catalysts more applicable in $NH_3$-SCR industry for diesel engines.

Besides Cu-CHA, other Cu-exchanged small pore zeolites containing double 6-ring (D6R) in their structures were also reported as efficient catalysts for the SCR of $NO_x$, such as Cu-SSZ-39 [133] and Cu-SAPO-18 [134] with AEI structure, showing very high catalytic activity, especially low-temperature activity, and hydrothermal stability.

Specific stabilization issues by coordination of extra-framework $Cu^{2+}$ cations to three oxygen atoms of the D6R units present in the CHA structure have been described as the main reason of the excellent catalytic activity and hydrothermal stability of the Cu-CHA catalysts.[110, 134] $Cu^{2+}/Cu^{+}$ redox cycling is required as part of the reaction mechanism.[28] Based on the investigation on a Cu-SSZ-13 containing only isolated $Cu^{2+}$ at 200 °C, Paolucci et al. [135] proposed an $NH_3$-SCR reaction mechanism (Figure 4). In this overall SCR catalytic cycle, the desired product ($N_2$) is formed in both the reduction and oxidation half-cycles, which is an unusual finding among known redox catalytic cycles. In addition, the authors indicated that isolated $Cu^{2+}$ exchange sites on SAPO-34 and other zeolites likely catalyze SCR by a similar mechanism.[135]

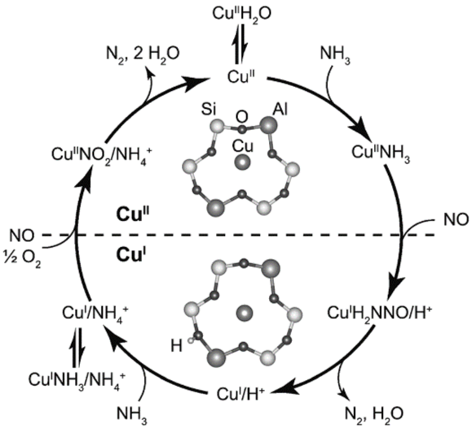

**Fig. 4** Proposed SCR reaction mechanism over Cu-SSZ-13 at 200 °C.[135] The dotted line separates oxidized Cu (top) from reduced (bottom) halves of the redox cycle. (Reprinted with the permission from the Wiley Publisher)

## 6. Summary and perspectives

There have been strong interests to develop $NH_3$-SCR catalysts with high activity and stability in low-temperature range, for the removal of $NO_x$ from both flue gas of stationary sources such as coal-fired power plants and exhaust from mobile sources such as diesel vehicles. Such a catalyst can be placed in the downstream of the de-sulfurizer and/or electrostatic precipitator (or baghouse) for stationary applications, which would significantly improve the lifetime of catalyst and economics of $NH_3$-SCR. Low-temperature $NH_3$-SCR is also very important for diesel vehicles, for example, during cold startup and on traveling short distances.

Over the last decades, there have been increasing interests in the development of low-temperature SCR catalysts containing transition metal oxide catalysts, such as $V_2O_5$, $Fe_2O_3$, CuO, and $MnO_x$. Among them, Mn-based catalysts attracted great attentions due to their excellent low-temperature activity. However, the Mn-based catalysts are vulnerable to the poisoning effects by $SO_2$ and $H_2O$ and the $N_2O$ formation during the SCR reaction is relatively high when this type of catalyst is charged. These problems still inhibit Mn-based catalysts from being industrially utilized. To obtain a catalyst with high catalytic activity and $SO_2$ tolerance for low-temperature SCR, the traditional $V_2O_5/TiO_2$ catalyst was continuously modified, and $V_2O_5$ with extraordinary inherent resistibility to $SO_2$ was loaded on carbon materials. $SO_2$ even plays a positive effect on the low-temperature activity of this type of catalyst. Although the deposition of ammonium sulfate salts can induce deactivation of the catalyst, the catalytic activity can be easily recovered through heating and water washing the deactivated one. With inherent resistibility to the poisoning effects by $SO_2$ on the catalyst components, this type of catalyst is very promising for the applications on $NO_x$ removal from the flue gas of stationary sources.

To promote the $NO_x$ reduction for diesel engines at low temperature, an upstream diesel oxidation catalyst (DOC, containing precious metals) was often used to increase the $NO_2$/NO molar feed ratio and thus promote the “fast SCR” reaction. The recent developed Cu containing small pore zeolites, such as Cu-SSZ-13 and Cu-SAPO-34 with CHA structure and Cu-SSZ-39 and Cu-SAPO-18 with AEI structure, have shown very high activity at low temperature and excellent hydrothermal stability at high temperature. The low-temperature activity enhancement by DOC is desirable for these catalysts, which will significantly reduce the cost and onboard space needed for the aftertreatment system. Therefore, the Cu containing small pore zeolites have received much attention for the applications on $NO_x$ removal from the exhaust of diesel vehicles, and some of the catalysts have already been commercialized.

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## References

1 V. I. Pavulescu, P. Grange and B. Delmon, *Catal. Today*, 1998, **46**, 233-316.

2 S. Roy, M. S. Hegde and G. Madras, *Appl. Energ.*, 2009, **86**, 2283-2297.

3 Z. Liu and S. Ihl Woo, *Cat. Rev.*, 2006, **48**, 43-89.

4 G. Busca, L. Lietti, G. Ramis and F. Berti, *Appl. Catal., B*, 1998, **18**, 1-36.

5 M. Koebel, M. Elsener and M. Kleemann, *Catal. Today*, 2000, **59**, 335-345.

6 P. Granger and V. I. Parvulescu, *Chem. Rev.*, 2011, **111**, 3155-3207.

7 F. Liu, Y. Yu and H. He, *Chem. Commun.*, 2014, **50**, 8445-8463.

8 R. Q. Long and R. T. Yang, *J. Am. Chem. Soc.*, 1999, **121**, 5595-5596.

9 A. Z. Ma and W. Grunert, *Chem. Commun.*, 1999, 71-72.

10 J. H. Kwak, R. G. Tonkyn, D. H. Kim, J. Szanyi and C. H. F. Peden, *J. Catal.*, 2010, **275**, 187-190.

11 L. Ren, L. Zhu, C. Yang, Y. Chen, Q. Sun, H. Zhang, C. Li, F. Nawaz, X. Meng and F.-S. Xiao, *Chem. Commun.*, 2011, **47**, 9789-9791.

12 D. W. Fickel, E. D’Addio, J. A. Lauterbach and R. F. Lobo, *Appl. Catal., B*, 2011, **102**, 441-448.

13 R. Martínez-Franco, M. Moliner, C. Franch, A. Kustov and A. Corma, *Appl. Catal., B*, 2012, **127**, 273-280.

14 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Chem. Commun.*, 2011, **47**, 8046-8048.

15 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Appl. Catal., B*, 2012, **115–116**, 100-106.

16 W. Shan, F. Liu, Y. Yu and H. He, *Chin. J. Catal.*, 2014, **35**, 1251-1259.

17 F. Liu, H. He and C. Zhang, *Chem. Commun.*, 2008, 2043-2045.

18 F. Liu, H. He, C. Zhang, Z. Feng, L. Zheng, Y. Xie and T. Hu, *Appl. Catal., B*, 2010, **96**, 408-420.

19 F. Liu, W. Shan, D. Pan, T. Li and H. He, *Chin. J. Catal.*, 2014, **35**, 1438-1445.

20 B. Guan, R. Zhan, H. Lin and Z. Huang, *Appl. Therm. Eng.*, 2014, **66**, 395-414.

21 J. Li, H. Chang, L. Ma, J. Hao and R. T. Yang, *Catal. Today*, 2011, **175**, 147-156.

22 P. Forzatti, I. Nova and E. Tronconi, *Angew. Chem. Int. Ed.*, 2009, **121**, 8516-8518.

23 F. Liu and H. He, *Catal. Today*, 2010, **153**, 70-76.

24 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *ChemCatChem*, 2011, **3**, 1286-1289.

25 M. D. Amiridis, I. E. Wachs, G. Deo, J.-M. Jehng and D. S. Kim, *J. Catal.*, 1996, **161**, 247-253.

26 L. Lietti, I. Nova and P. Forzatti, *Top. Catal.*, 2000, **11-12**, 111-122.

27 J. Li, R. Zhu, Y. Cheng, C. K. Lambert and R. T. Yang, *Environ. Sci. Technol.*, 2010, **44**, 1799-1805.

28 F. Gao, J. Kwak, J. Szanyi and C. F. Peden, *Top. Catal.*, 2013, **56**, 1441-1459.

29 Q. Ye, L. Wang and R. T. Yang, *Appl. Catal., A*, 2012, **427–428**, 24-34.

30 W. Xu, H. He and Y. Yu, *J. Phys. Chem. C*, 2009, **113**, 4426-4432.

31 Z. Liu, J. Li and A. S. M. Junaid, *Catal. Today*, 2010, **153**, 95-102.

32 Z. Huang, Z. Zhu and Z. Liu, *Appl. Catal., B*, 2002, **39**, 361-368.

33 Y. Hou, Z. Huang and S. Guo, *Catal. Commun.*, 2009, **10**, 1538-1541.

34 Y. Wang, X. Li, L. Zhan, C. Li, W. Qiao and L. Ling, *Ind. Eng. Chem. Res.*, 2015, **54**, 2274-2278.

35 W. Sjoerd Kijlstra, M. Biervliet, E. K. Poels and A. Bliek, *Appl. Catal., B*, 1998, **16**, 327-337.

36 F. Liu, K. Asakura, H. He, W. Shan, X. Shi and C. Zhang, *Appl. Catal., B*, 2011, **103**, 369-377.

37 Y. Cheng, C. Lambert, D. H. Kim, J. H. Kwak, S. J. Cho and C. H. F. Peden, *Catal. Today*, 2010, **151**, 266-270.

38 O. Kröcher and M. Elsener, *Appl. Catal., B*, 2008, **77**, 215-227.

39 M. Klimczak, P. Kern, T. Heinzelmann, M. Lucas and P. Claus, *Appl. Catal., B*, 2010, **95**, 39-47.

40 D. Nicosia, M. Elsener, O. Kröcher and P. Jansohn, *Top. Catal.*, 2007, **42-43**, 333-336.
41 L. Chen, J. Li and M. Ge, *Chem. Eng. J.*, 2011, **170**, 531-537.
42 Y. Peng, J. Li, L. Chen, J. Chen, J. Han, H. Zhang and W. Han, *Environ. Sci. Technol.*, 2012, **46**, 2864-2869.
43 X. Tang, J. Li, L. Sun and J. Hao, *Appl. Catal., B*, 2010, **99**, 156-162.
44 S. Yang, S. Xiong, Y. Liao, X. Xiao, F. Qi, Y. Peng, Y. Fu, W. Shan and J. Li, *Environ. Sci. Technol.*, 2014, **48**, 10354-10362.
45 S. Yang, Y. Fu, Y. Liao, S. Xiong, Z. Qu, N. Yan and J. Li, *Catal. Sci. Technol.*, 2014, **4**, 224-232.
46 P. R. Ettireddy, N. Ettireddy, T. Boningari, R. Pardemann and P. G. Smirniotis, *J. Catal.*, 2012, **292**, 53-63.
47 X. Tang, J. Hao, W. Xu and J. Li, *Catal. Commun.*, 2007, **8**, 329-334.
48 M. Kang, E. D. Park, J. M. Kim and J. E. Yie, *Appl. Catal., A*, 2007, **327**, 261-269.
49 F. Kapteijn, L. Singoredjo, A. Andreini and J. A. Moulijn, *Appl. Catal., B*, 1994, **3**, 173-189.
50 P. G. Smirniotis, D. A. Peña and B. S. Uphade, *Angew. Chem. Int. Ed.*, 2001, **40**, 2479-2482.
51 G. Qi and R. T. Yang, *Appl. Catal., B*, 2003, **44**, 217-225.
52 Z. Wu, R. Jin, Y. Liu and H. Wang, *Catal. Commun.*, 2008, **9**, 2217-2220.
53 B. Thirupathi and P. Smirniotis, *Catal. Lett.*, 2011, **141**, 1399-1404.
54 W. S. Kijlstra, D. S. Brands, E. K. Poels and A. Bliek, *J. Catal.*, 1997, **171**, 208-218.
55 P. G. Smirniotis, P. M. Sreekanth, D. A. Peña and R. G. Jenkins, *Ind. Eng. Chem. Res.*, 2006, **45**, 6436-6443.
56 X. Tang, J. Hao, H. Yi and J. Li, *Catal. Today*, 2007, **126**, 406-411.
57 Q. Zhang, C. Qiu, H. Xu, T. Lin, Z. Lin, M. Gong and Y. Chen, *Catal. Today*, 2011, **175**, 171-176.
58 G. Qi and R. T. Yang, *Chem. Commun.*, 2003, 848-849.
59 G. Qi and R. T. Yang, *J. Catal.*, 2003, **217**, 434-441.
60 G. Qi, R. T. Yang and R. Chang, *Appl. Catal., B*, 2004, **51**, 93-106.
61 F. Eigenmann, M. Maciejewski and A. Baiker, *Appl. Catal., B*, 2006, **62**, 311-318.
62 M. Casapu, O. Kröcher and M. Elsener, *Appl. Catal., B*, 2009, **88**, 413-419.
63 F. Liu, W. Shan, Z. Lian, L. Xie, W. Yang and H. He, *Catal. Sci. Technol.*, 2013, **3**, 2699-2707.
64 R. Q. Long, R. T. Yang and R. Chang, *Chem. Commun.*, 2002, 452-453.
65 Z. Chen, F. Wang, H. Li, Q. Yang, L. Wang and X. Li, *Ind. Eng. Chem. Res.*, 2011, **51**, 202-212.
66 J. Zuo, Z. Chen, F. Wang, Y. Yu, L. Wang and X. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 2647-2655.
67 M. Kang, E. D. Park, J. M. Kim and J. E. Yie, *Catal. Today*, 2006, **111**, 236-241.
68 S. Yang, C. Wang, J. Li, N. Yan, L. Ma and H. Chang, *Appl. Catal., B*, 2011, **110**, 71-80.
69 J. Yu, F. Guo, Y. Wang, J. Zhu, Y. Liu, F. Su, S. Gao and G. Xu, *Appl. Catal., B*, 2010, **95**, 160-168.
70 Z. Liu, Y. Yi, S. Zhang, T. Zhu, J. Zhu and J. Wang, *Catal. Today*, 2013, **216**, 76-81.
71 Z. Liu, J. Zhu, J. Li, L. Ma and S. I. Woo, ACS Appl. Mater. Interfaces, 2014, **6**, 14500-14508.
72 W. S. Kijlstra, D. S. Brands, H. I. Smit, E. K. Poels and A. Bliek, *J. Catal.*, 1997, **171**, 219-230.
73 L. Chen, J. Li and M. Ge, *J. Phys. Chem. C*, 2009, **113**, 21177-21184.
74 Z. Liu, Y. Li, T. Zhu, H. Su and J. Zhu, *Ind. Eng. Chem. Res.*, 2014, **53**, 12964-12970.
75 M. Kobayashi and M. Hagi, *Appl. Catal., B*, 2006, **63**, 104-113.
76 M. Kobayashi, R. Kuma, S. Masaki and N. Sugishima, *Appl. Catal., B*, 2005, **60**, 173-179.
77 M. Kobayashi, R. Kuma and A. Morita, *Catal. Lett.*, 2006, **112**, 37-44.
78 P. Lu, C. Li, G. Zeng, L. He, D. Peng, H. Cui, S. Li and Y. Zhai, *Appl. Catal., B*, 2010, **96**, 157-161.
79 L. Zhu, B. Huang, W. Wang, Z. Wei and D. Ye, *Catal. Commun.*, 2011, **12**, 394-398.
80 M. Yoshikawa, A. Yasutake and I. Mochida, *Appl. Catal., A*, 1998, **173**, 239-245.
81 Y. Su, B. Fan, L. Wang, Y. Liu, B. Huang, M. Fu, L. Chen and D. Ye, *Catal. Today*, 2013, **201**, 115-121.
82 X. Wang, Y. Zheng, Z. Xu, X. Liu and Y. Zhang, *Catal. Commun.*, 2014, **50**, 34-37.
83 X. Wang, Y. Zheng, Z. Xu, X. Wang and X. Chen, *RSC Adv.*, 2013, **3**, 11539-11542.
84 S. Bai, H. Li, L. Wang, Y. Guan and S. Jiang, *Catal. Lett.*, 2014, **144**, 216-221.
85 X. Wang, Y. Zheng and J. Lin, *Catal. Commun.*, 2013, **37**, 96-99.
86 X. Wang, Y. Zheng, Z. Xu, Y. Liu and X. Wang, *Catal. Sci. Technol.*, 2014, **4**, 1738-1741.
87 Y. Wang, C. Ge, L. Zhan, C. Li, W. Qiao and L. Ling, *Ind. Eng. Chem. Res.*, 2012, **51**, 11667-11673.
88 D. Zhang, L. Zhang, L. Shi, C. Fang, H. Li, R. Gao, L. Huang and J. Zhang, *Nanoscale*, 2013, **5**, 1127-1136.
89 J. Pasel, P. Käßner, B. Montanari, M. Gazzano, A. Vaccari, W. Makowski, T. Lojewski, R. Dziembaj and H. Papp, *Appl. Catal., B*, 1998, **18**, 199-213.
90 N. Shigemoto and J. Moffat, *Catal. Lett.*, 2000, **69**, 1-10.
91 M. Ouzzine, G. A. Cifredo, J. M. Gatica, S. Harti, T. Chafik and H. Vidal, *Appl. Catal., A*, 2008, **342**, 150-158.
92 Z. Lei, B. Han, K. Yang and B. Chen, *Chem. Eng. J.*, 2013, **215–216**, 651-657.
93 Z. Huang, Z. Zhu, Z. Liu and Q. Liu, *J. Catal.*, 2003, **214**, 213-219.
94 P. Li, Z. Liu, Q. Li, W. Wu and Q. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 7910-7916.
95 Z. Zhu, H. Niu, Z. Liu and S. Liu, *J. Catal.*, 2000, **195**, 268-278.
96 Z. Huang, Z. Liu, X. Zhang and Q. Liu, *Appl. Catal., B*, 2006, **63**, 260-265.
97 Y. Hou, G. Cai, Z. Huang, X. Han and S. Guo, *Chem. Eng. J.*, 2014, **247**, 59-65.
98 X. Zhang, Z. Huang and Z. Liu, *Catal. Commun.*, 2008, **9**, 842-846.
99 E. García-Bordejé, L. Calvillo, M. J. Lázaro and R. Moliner, *Ind. Eng. Chem. Res.*, 2004, **43**, 4073-4079.

100E. García-Bordejé, L. Calvillo, M. J. Lázaro and R. Moliner, *Appl. Catal., B*, 2004, **50**, 235-242.

101E. García-Bordejé, M. J. Lázaro, R. Moliner, P. M. Álvarez, V. Gómez-Serrano and J. L. G. Fierro, *Carbon*, 2006, **44**, 407-417.

102E. García-Bordejé, M. J. Lázaro, R. Moliner, J. F. Galindo, J. Sotres and A. M. Baró, *J. Catal.*, 2004, **223**, 395-403.

103N. Y. Topsøe, *Science*, 1994, **265**, 1217-1219.

104E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee and M. Weibel, *J. Catal.*, 2007, **245**, 1-10.

105C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee and B. Bandl-Konrad, *Chem. Commun.*, 2004, 2718-2719.

106P. Forzatti, I. Nova and E. Tronconi, *Ind. Eng. Chem. Res.*, 2010, **49**, 10386-10391.

107S. Brandenberger, O. Kröcher, A. Tissler and R. Althoff, *Cat. Rev.*, 2008, **50**, 492-531.

108P. J. Andersen, J. E. Bailie, J. L. Casci, H. Y. Chen, J. M. Fedeyko, R. K. S. Foo and R. R. Rajaram, *WO Pat.,* WO 2008/132452 A2, 2008.

109I. Bull, W.-M. Xue, P. Burk, R. S. Boorse, W. M. Jaglowski, G. S. Koermer, A. Moini, J. A. Patchett, J. C. Dettling and M. T. Caudle, *US Pat.,* US 7601662, 2009.

110U. Deka, I. Lezcano-Gonzalez, B. M. Weckhuysen and A. M. Beale, *ACS Catal.*, 2013, **3**, 413-427.

111J. H. Kwak, D. Tran, S. D. Burton, J. Szanyi, J. H. Lee and C. H. F. Peden, *J. Catal.*, 2012, **287**, 203-209.

112D. Wang, Y. Jangjou, Y. Liu, M. K. Sharma, J. Luo, J. Li, K. Kamasamudram and W. S. Epling, *Appl. Catal., B*, 2015, **165**, 438-445.

113S. T. Korhonen, D. W. Fickel, R. F. Lobo, B. M. Weckhuysen and A. M. Beale, *Chem. Commun.*, 2011, **47**, 800-802.

114U. Deka, A. Juhin, E. A. Eilertsen, H. Emerich, M. A. Green, S. T. Korhonen, B. M. Weckhuysen and A. M. Beale, *J. Phys. Chem. C*, 2012, **116**, 4809-4818.

115J. H. Kwak, H. Zhu, J. H. Lee, C. H. F. Peden and J. Szanyi, *Chem. Commun.*, 2012, **48**, 4758-4760.

116L. Wang, W. Li, G. Qi and D. Weng, *J. Catal.*, 2012, **289**, 21-29.

117U. Deka, I. Lezcano-Gonzalez, S. J. Warrender, A. Lorena Picone, P. A. Wright, B. M. Weckhuysen and A. M. Beale, *Microporous Mesoporous Mater.*, 2013, **166**, 144-152.

118S. Fan, J. Xue, T. Yu, D. Fan, T. Hao, M. Shen and W. Li, *Catal. Sci. Technol.*, 2013, **3**, 2357-2364.

119F. Gao, E. D. Walter, E. M. Karp, J. Luo, R. G. Tonkyn, J. H. Kwak, J. Szanyi and C. H. F. Peden, *J. Catal.*, 2013, **300**, 20-29.

120L. Wang, J. R. Gaudet, W. Li and D. Weng, *J. Catal.*, 2013, **306**, 68-77.

121J. Xue, X. Wang, G. Qi, J. Wang, M. Shen and W. Li, *J. Catal.*, 2013, **297**, 56-64.

122S. A. Bates, A. A. Verma, C. Paolucci, A. A. Parekh, T. Anggara, A. Yezerets, W. F. Schneider, J. T. Miller, W. N. Delgass and F. H. Ribeiro, *J. Catal.*, 2014, **312**, 87-97.

123J. Wang, D. Fan, T. Yu, J. Wang, T. Hao, X. Hu, M. Shen and W. Li, *J. Catal.*, 2015, **322**, 84-90.

124S. J. Schmieg, S. H. Oh, C. H. Kim, D. B. Brown, J. H. Lee, C. H. F. Peden and D. H. Kim, *Catal. Today*, 2012, **184**, 252-261.

125J. Kwak, D. Tran, J. Szanyi, C. Peden and J. Lee, *Catal. Lett.*, 2012, **142**, 295-301.

126L. Xie, F. Liu, K. Liu, X. Shi and H. He, *Catal. Sci. Technol.*, 2014, **4**, 1104-1110.

127L. Zhang, D. Wang, Y. Liu, K. Kamasamudram, J. Li and W. Epling, *Appl. Catal., B*, 2014, **156–157**, 371-377.

128A. Kumar, M. A. Smith, K. Kamasamudram, N. W. Currier, H. An and A. Yezerets, *Catal. Today*, 2014, **231**, 75-82.

129M. Shen, H. Wen, T. Hao, T. Yu, D. Fan, J. Wang, W. Li and J. Wang, *Catal. Sci. Technol.*, 2015, **5**, 1741-1749.

130L. Xie, F. Liu, L. Ren, X. Shi, F.-S. Xiao and H. He, *Environ. Sci. Technol.*, 2014, **48**, 566-572.

131R. Martínez-Franco, M. Moliner, P. Concepcion, J. R. Thogersen and A. Corma, *J. Catal.*, 2014, **314**, 73-82.

132J. Wang, Z. Peng, Y. Chen, W. Bao, L. Chang and G. Feng, *Chem. Eng. J.*, 2015, **263**, 9-19.

133M. Moliner, C. Franch, E. Palomares, M. Grill and A. Corma, *Chem. Commun.*, 2012, **48**, 8264-8266.

134R. Martínez-Franco, M. Moliner and A. Corma, *J. Catal.*, 2014, **319**, 36-43.

135C. Paolucci, A. A. Verma, S. A. Bates, V. F. Kispersky, J. T. Miller, R. Gounder, W. N. Delgass, F. H. Ribeiro and W. F. Schneider, *Angew. Chem. Int. Ed.*, 2014, **126**, 12022-12027.