

Environmentally-benign catalysts for the selective catalytic reduction of NO_x from diesel engines: structure–activity relationship and reaction mechanism aspects

Cite this: *Chem. Commun.*, 2014, 50, 8445

Fudong Liu,[†] Yunbo Yu[†] and Hong He^{*}

Selective catalytic reduction of NO_x using NH₃ or hydrocarbons (NH₃-SCR or HC-SCR) in oxygen-rich exhaust from diesel engines remains a major challenge in environmental catalysis. The development of highly efficient, stable and environmentally-benign catalysts for SCR processes is very important for practical use. In this feature article, the structure–activity relationship of vanadium-free catalysts in the NH₃-SCR reaction is discussed in detail, including Fe-, Ce-based oxide catalysts and Fe-, Cu-based zeolite catalysts, which is beneficial for catalyst redesign and activity improvement. Based on our research, a comprehensive mechanism contributing to the performance of Ag/Al₂O₃ in HC-SCR is provided, giving a clue to the design of a catalytic system with high efficiency.

Received 11th February 2014,
Accepted 4th April 2014

DOI: 10.1039/c4cc01098a

www.rsc.org/chemcomm

1. Introduction

Nitrogen oxides (NO_x) are a major air pollutant that can lead to the formation of acid rain, photochemical smog and haze, thus

endangering the eco-environment and human health.¹ The NO_x emissions resulting from human activity can be ascribed to stationary sources such as coal-fired power plants and mobile sources such as motor vehicles.² With the challenges arising from the energy crisis and global warming, the wide application of diesel engines in vehicles becomes more and more important because of their high fuel efficiency. Two main pollutants from diesel engine exhaust are NO_x and particulate matter (PM). Through the adjustment of heavy-duty diesel engines,

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China. E-mail: honghe@rcees.ac.cn; Fax: +86-10-6284-9123; Tel: +86-10-6284-9123

[†] Authors made equal contributions.



Fudong Liu

Fudong Liu was born in Tianjin, China, in 1982. He received his Bachelor degree in Environmental Engineering from Tsinghua University in 2005 and PhD degree in Environmental Science from Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences (CAS) in 2010. He has been working as assistant professor in RCEES since 2010 and was promoted to associate professor in 2013. He received Excellent

Doctoral Dissertation Award, CAS in 2011 and Young Scientist Award, IACS in 2012. His research interests include environmental catalysis and air pollution control, especially the development of environmental-friendly catalysts for the selective catalytic reduction of NO_x with NH₃.



Yunbo Yu

Yunbo Yu received his PhD degree in Environmental Science from Research Center for Eco-Environmental Science (RCEES), Chinese Academy of Sciences in 2004. He has been an assistant professor of Environmental Science at RCEES since 2004, and was promoted to an associate professor in 2006. He then spent two years as a JSPS postdoctoral fellow in Prof. Haruta's lab at Tokyo Metropolitan University, Japan. His research is concerned with environmental catalysis and air pollution control, especially the development of catalysts for the selective catalytic reduction of NO_x with hydrocarbons.

the emission of PM from diesel engines can be effectively reduced. However, due to the well-known “trade-off” relationship between PM and NO_x emitted from diesel engines, the increasing demand to eliminate NO_x, especially under oxygen-rich conditions, has drawn great attention from both academia and industry.^{3,4} Selective catalytic reduction (SCR) of NO_x using reductants such as NH₃, urea or hydrocarbons (HC) in the oxygen-rich exhausts is a highly efficient way to reduce NO_x emission, although it remains one of the major challenges in the field of environmental catalysis.

The SCR of NO_x with NH₃ (NH₃-SCR) was initially applied in the removal of NO_x from stationary sources, and the commercially used catalyst systems are mainly WO₃ or MoO₃ doped V₂O₅/TiO₂.^{5,6} Vanadium-based NH₃-SCR catalysts have also been successfully used for the deNO_x process from diesel engines, since 2005.^{7,8} However, disadvantages remain for the vanadium-based catalysts, including the toxicity of V₂O₅, the narrow operation temperature window, the easy sublimation of V₂O₅ and phase transformation of the TiO₂ support from anatase to rutile at high temperatures, which greatly restrict their further application, especially when stricter regulations are established for both PM and NO_x for diesel engines, and the SCR converter should be installed downstream of the diesel particulate filter (DPF), with timed thermal shock (~800 °C) in the regeneration processes of the DPF system. Therefore, many researchers are trying to develop vanadium-free NH₃-SCR catalysts with high deNO_x efficiency, high N₂ selectivity, excellent hydrothermal stability and insensitivity to co-existing poisoning components in the SCR atmosphere such as H₂O, SO₂, HC or alkali metals *etc.* Currently, metal oxide catalysts and zeolitic catalysts are two well-studied types of vanadium-free catalysts for the NH₃-SCR process in heavy-duty diesel engines, some of which show great potential in practical use.^{6,9,10} However, despite the numerous studies on SCR performance under different conditions, a comprehensive summarization of the

structure–activity relationship of these catalysts in the NH₃-SCR process is still lacking. In this article, taking Fe-, Ce-based oxide catalysts and Fe-, Cu-based zeolite catalysts as examples, we will discuss the microstructure of active sites, the role of acidity and also the activation of reactants on these catalysts for the NH₃-SCR reaction in detail, which is very important for the design of catalysts and study of reaction mechanisms.

On the other hand, since the pioneering work of Iwamoto *et al.*¹¹ and Held *et al.*,¹² many catalysts such as zeolitic oxide, base oxide/metal and noble metal catalysts have been found to be effective for the SCR of NO_x with hydrocarbons (HC-SCR) in the presence of excess oxygen.^{3,4,7,13–19} Among the catalysts proposed for HC-SCR technology, zeolitic oxide catalysts are effective for NO_x reduction, while their water tolerance has been little improved.⁵ Noble metal catalysts such as Pt/Al₂O₃ exhibit high deNO_x activity in the low temperature range of 200–300 °C while exhibiting a narrow operation temperature window.^{20,21} Up to now, alumina-supported silver (Ag/Al₂O₃) has been known as one of the most effective catalysts for the HC-SCR even in the presence of water vapor and SO₂.^{13,16,22–32} The distinctive advantage of HC-SCR is that the on-board fuel can be used as the reductant for NO_x conversion, thus reducing the cost involved in infrastructure development for delivering the reductant to the automotive engine exhaust system. The past several years have witnessed a growth in research in NO_x reduction by fuel-component hydrocarbons over Ag/Al₂O₃, while the light-off temperature for NO_x reduction is still too high to be used for commercial application in diesel vehicles, even though it has been reported that low temperature activity can be promoted by the addition of H₂.^{24,32–40} More importantly, aromatic hydrocarbons, typically present in diesel fuel, exhibit low activity for NO_x reduction even in the presence of H₂.⁴¹ Indeed, when using diesel fuel (ultra-low sulfur diesel, US06) as the reductant,³⁴ Ag/Al₂O₃ showed high initial activity for NO_x reduction in the presence of 3200 ppm H₂, while its activity gradually decayed with time, reaching a final conversion level similar to that observed in the absence of H₂. These results indicate that the issue of catalyst deactivation by hydrocarbon poisoning still needs to be resolved for the commercial application of HC-SCR. To provide a guideline for developing an ideal HC-SCR system, it is highly desirable to understand the mechanism of NO_x reduction by hydrocarbons at the molecular level.



Hong He

Hong He was born in 1965, Hebei, China. He received his PhD degree in Chemistry at the University of Tokyo in 1994. After working as researcher in Riken Corporation (1994–1997), postdoctoral fellow in University of Southern California and University of Delaware (1997–2000) and visiting scientist in University of Toronto (2000–2001), he became a full professor in 2001 at Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of

Sciences (CAS). His research interests include environmental catalysis and heterogeneous atmospheric chemistry, such as the diesel emission control, indoor air pollution control and study on the formation mechanism and control strategies of haze in China.

2. The structure–activity relationship of vanadium-free catalysts for NH₃-SCR of NO_x

2.1. NH₃-SCR of NO_x over oxide catalysts

Many researchers have focused on the development of vanadium-free oxide catalysts for the NH₃-SCR process, which can be divided into single metal oxide catalysts, supported-type metal oxide catalysts and mixed metal oxide catalysts according to the forms of the catalytic materials. Based on the active components, the vanadium-free oxide catalysts can be further classified as Fe-, Ce-, Mn-, or Cu-based materials, of which the

Fe- and Ce-based catalysts have been well studied in the deNO_x process of diesel engines due to their compatibility with the typical exhaust temperature range. In the following sections, we will systematically summarize the recent research advances in understanding the structure–activity relationship of Fe- and Ce-based oxide catalysts in the NH₃-SCR reaction, which are important for their practical use.

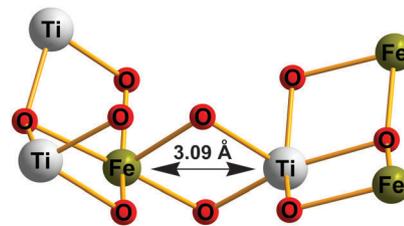
2.1.1. Fe-based oxide catalysts. Early in the 1980s, Kato *et al.*⁴² used Fe₂O₃ as the active phase in a NH₃-SCR catalyst (*i.e.* Fe₂O₃-TiO₂ mixed oxide catalyst) with high SCR activity and N₂ selectivity at relatively high temperatures (350–450 °C), and thereafter numerous types of Fe₂O₃-containing catalysts were developed by researchers, including Fe₂O₃-pillared layered clay (PILC),⁴³ Fe₂O₃-SiO₂,⁴⁴ Fe₂O₃ supported on activated carbon (AC)⁴⁵ or activated carbon fiber (ACF)⁴⁶ *etc.* Yet at that time, no systematic studies of the microstructure of Fe species and its relationship with SCR performance were reported.

Several years ago, Apostolescu *et al.*⁴⁷ developed a new supported-type Fe₂O₃/WO₃/ZrO₂ catalyst achieving total NO_x conversion and high N₂ selectivity in the NH₃-SCR reaction over the temperature range 280–430 °C. Based on a series of characterization results including XRD and H₂-TPR, they pointed out that the Fe species in the Fe₂O₃/WO₃/ZrO₂ catalyst were mainly present in the form of well-crystallized Fe₂O₃ and also small Fe_xO_y particles. During the NH₃-SCR reaction, the Fe³⁺ species catalyzed the dehydrogenation of NH₃ to NH₂ while being reduced to Fe²⁺ species, and thereafter the NH₂ species reacted with gaseous NO to produce N₂ and H₂O, while O₂ could re-oxidize Fe²⁺ species to Fe³⁺ species participating into the next redox cycle. The SCR reaction over this catalyst mainly followed an Eley–Rideal (E–R) mechanism. This is probably the first successful example elucidating the structure–activity relationship of Fe species in the NH₃-SCR reaction for an Fe₂O₃-containing oxide catalyst.

Usually, it is also accepted that NO can be molecularly adsorbed on the transition metal ion or it can dissociatively chemisorb on oxide ion vacancies of the metal oxide catalysts, and react with adsorbed NH₃ or NH₄⁺ species to form SCR reaction intermediates and decompose into N₂ and H₂O afterwards, following a Langmuir–Hinshelwood (L–H) mechanism. To effectively disperse the active species, anatase TiO₂ is usually utilized as the catalyst support for the NH₃-SCR reaction. Although it is inert for NO_x conversion, its acidity can inhibit the formation of sulfate species on the catalyst surface in SO₂-containing atmospheres above 200 °C to avoid the deactivation of SCR catalysts.⁴⁸ Based on the above-mentioned ideas, Roy *et al.*⁴⁹ prepared an Fe ion substituted TiO₂, namely the Ti_{0.9}Fe_{0.1}O_{2-δ} catalyst, by a novel single-step solution combustion method, showing total NO_x conversion at *ca.* 300–425 °C with rather high N₂ selectivity. Compared with the well-crystallized ilmenite phase FeTiO₃ over which the maximum NO_x conversion did not exceed 20%, the catalytic activity of the Ti_{0.9}Fe_{0.1}O_{2-δ} catalyst with ionic metal sites and oxide ion vacancies was much higher, indicating that such defect structures in NH₃-SCR catalysts were important factors influencing their catalytic performance in the deNO_x process.

Over the Ti_{0.9}Fe_{0.1}O_{2-δ} catalyst, Roy *et al.*⁴⁹ considered that the Lewis acid sites were beneficial to the wide SCR operation temperature window, and for the Fe₂O₃/WO₃/ZrO₂ catalyst prepared by Apostolescu *et al.*,⁴⁷ the importance of Lewis acid sites to the E–R mechanism of the NH₃-SCR reaction was also strongly emphasized. However, for the supported-type Fe₂(SO₄)₃/TiO₂ catalyst prepared by Ma *et al.*⁵⁰ with high NO_x conversion at 350–450 °C, they considered that the relatively strong Brønsted acid sites induced by sulfate species contributed substantially to the deNO_x efficiency. Thus, the roles of Lewis acid sites and Brønsted acid sites in the NH₃-SCR reaction over Fe₂O₃-containing catalysts are still in debate, and in future studies, we strongly recommend that the elucidation of the involvement of these two types of acid sites in the NH₃-SCR reaction should be closely correlated to the reaction temperature.

In recent years, we have focused on the investigation of the structure–activity relationship of iron titanate (FeTiO_x) catalysts in the NH₃-SCR reaction. This environmentally-friendly catalyst, when prepared by a co-precipitation method using Fe(NO₃)₃ and Ti(SO₄)₂ as precursors, showed high SCR activity, N₂ selectivity and H₂O/SO₂ durability in the medium temperature range (200–400 °C),⁵¹ and an operation temperature window at least 50–150 °C lower than those of the above-mentioned Fe₂O₃-containing catalysts. Compared with the FeTiO_x catalyst prepared using TiCl₄ as a precursor and a Fe₂O₃/TiO₂ catalyst prepared by an impregnation method, the existence of sulfate species in the preparation process could significantly inhibit the crystallization of mixed metal oxide phases, resulting in the formation of highly dispersed small iron titanate crystallites, which is totally different from the Fe₂O₃ particles normally found in previously reported studies.⁵² A similar promotion effect by sulfate species on the dispersion of Fe species was also observed by Ma *et al.* on their Fe₂(SO₄)₃/TiO₂ catalyst.⁵⁰ Thereafter, the microstructure of iron titanate crystallites in FeTiO_x catalysts was studied in detail using various characterization methods, including N₂ physisorption, Powder XRD, UV-vis DRS, Raman spectroscopy and XAFS *etc.*, and the surface chemical composition and redox behavior were studied using XPS and H₂-TPR. It was definitively concluded that the active iron titanate crystallites in the FeTiO_x catalyst prepared at low calcination temperature were mainly in the form of a specific edge-shared Fe³⁺–(O)₂–Ti⁴⁺ structure (Scheme 1), and had large surface area, pore volume and abundant surface defects supplying rich catalytically active sites



Scheme 1 Proposed model of a homogeneous edge-shared Fe³⁺–(O)₂–Ti⁴⁺ structure in the FeTiO_x catalyst. (Reproduced with permission from Elsevier Inc.)⁵³

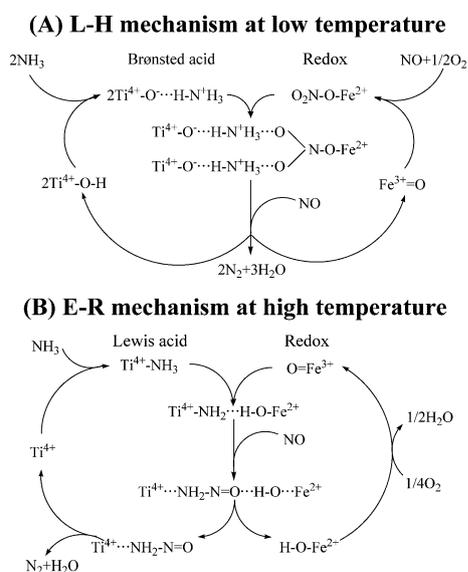
for the NH_3 -SCR reaction. In this specific edge-shared Fe^{3+} - $(\text{O})_2$ - Ti^{4+} structure, the existence of an electronic inductive effect between Fe^{3+} species and Ti^{4+} species was confirmed, leading to higher NO adsorption and oxidation ability for Fe^{3+} species and thus higher SCR activity at low temperatures.^{52,53} Although after high temperature calcination such as at 600 or 700 °C, the specific surface area and reactant adsorption ability of the FeTiO_x catalyst were decreased to a certain extent due to the occurrence of sintering (*i.e.* well-crystallized Fe_2TiO_5 was formed), the intrinsic SCR activity normalized by surface area was actually increased.⁵⁴ In future studies, the deposition of such iron titanate crystallites onto microporous or mesoporous materials with large surface area holds promise as a method to enhance its dispersion and thermal stability for practical utilization in industry.

Using *in situ* DRIFTS, transient response experiments and temperature programmed desorption/surface reaction methods, the NH_3 -SCR reaction mechanism over the FeTiO_x catalyst was well studied (Scheme 2).⁵⁵ At temperatures below 200 °C, on the Fe^{3+} - $(\text{O})_2$ - Ti^{4+} structure, NO can be oxidized into nitrate species on Fe^{3+} sites and then reacts with adjacent adsorbed NH_3 species on Ti^{4+} -OH Brønsted acid sites to form intermediate species (similar to ammonium nitrate species), followed by a subsequent reaction with gaseous NO to produce N_2 and H_2O . An L-H mechanism is proposed accordingly for NH_3 -SCR of NO_x at low temperatures over the FeTiO_x catalyst, in which the formation of reactive monodentate nitrate on Fe^{3+} sites is the rate-determining step.⁵⁵ An efficient method to improve the low temperature SCR activity of the FeTiO_x catalyst is to enhance the NO_x adsorption as monodentate nitrate,⁵⁶ as confirmed by subsequent experimental results in which the low temperature SCR activity was greatly enhanced through partial substitution of Fe species by Mn species in FeTiO_x with considerably enhanced formation of monodentate nitrates.⁵⁷ If SO_2 is

present in the NH_3 -SCR atmosphere, the sulfate species will preferentially adsorb onto Fe sites to form Fe-O-S bonds (as evidenced by EXAFS results) competing with the adsorption of nitrate species, leading to the decline of low temperature SCR activity to a certain extent.⁵⁸ This inhibition effect is more prominent on Mn-substituted FeTiO_x catalysts, mainly due to the easier blocking of the L-H reaction pathway at low temperatures by sulfate deposition on Mn sites.⁵⁹ In future studies, the simultaneous improvement of the low temperature SCR activity and SO_2 durability of Fe-containing catalysts is still a great challenge, unless a completely new reaction pathway different from the L-H mechanism can be opened by catalyst modification or redesign.

Returning to the FeTiO_x catalyst, at temperatures above 200 °C, the Ti^{4+} -OH Brønsted acid sites can be transformed into Lewis acid sites through dehydroxylation, and then adsorb NH_3 to participate in the NO_x reduction process. The adsorbed NH_3 species can be activated into $-\text{NH}_2$ species by neighboring Fe^{3+} sites through dehydrogenation, and thereafter react with gaseous NO to form a NH_2NO intermediate and decompose into N_2 and H_2O . In this process, the Fe^{3+} species is first reduced to Fe^{2+} species and then reoxidized to Fe^{3+} species by gaseous O_2 , completing a redox cycle. A typical E-R mechanism for NH_3 -SCR of NO_x at high temperatures over the FeTiO_x catalyst is proposed accordingly, with the formation of NH_2NO being the rate-determining step.⁵⁵ Although sulfate species may also form on Fe^{3+} sites in this process, the activation of NH_3 to $-\text{NH}_2$ species is not influenced. Therefore, the E-R reaction pathway can still proceed over the sulfated FeTiO_x catalyst, ensuring high deNO_x efficiency at relatively high temperatures.⁵⁸ In brief, this was possibly the first time that different NH_3 -SCR mechanisms over Fe-containing catalysts in the low and high temperature ranges with the involvement of both acid sites and redox sites were demonstrated. Since then, researchers have started to pay attention to the influence of reaction temperature on the NH_3 -SCR mechanism over different types of catalysts, such as the Fe-Ti spinel catalyst,⁶⁰ $\text{CeO}_2/\text{TiO}_2$, CeO_2 - WO_3/TiO_2 catalysts⁶¹ and CuO_x/WO_x - ZrO_2 catalyst⁶² *etc.* In future studies, the hydrothermal stability and resistance to coexisting poisoning pollutants in the SCR atmosphere (*i.e.* H_2O , SO_2 , HC, alkali metals *etc.*) of this FeTiO_x catalyst still need to be investigated in more detail before its practical use in the deNO_x process of diesel engines.

The above-mentioned Fe-containing catalysts are usually in the form of supported-type or mixed oxides, with the second or third component acting as a support or promoter. Actually, the well-designed Fe_2O_3 oxide itself can also show good performance in the NH_3 -SCR reaction, and this type of material has obvious advantages for the investigation of the structure-activity relationship. Very recently, the synthesis of Fe_2O_3 nanomaterials with controlled crystal phase and morphology has achieved great success.⁶³ Over α - Fe_2O_3 samples prepared by Yang *et al.*⁶⁴ by a hydrothermal route with nanocube and nanorod morphologies, the relationship between NH_3 -SCR activity and the exposed crystal facet was established. They concluded that α - Fe_2O_3 nanorods exposing more (110) facets



Scheme 2 Proposed SCR mechanisms over FeTiO_x catalyst in different temperature ranges. (Reproduced with permission from Elsevier Inc.)⁵⁵

with relatively high surface energy and higher density of Fe atoms showed much better NH_3 -SCR activity than $\alpha\text{-Fe}_2\text{O}_3$ nanocubes mainly exposing (012) facets with low surface energy. Mou *et al.*⁶⁵ creatively synthesized novel $\alpha\text{-Fe}_2\text{O}_3$ nanorods and $\gamma\text{-Fe}_2\text{O}_3$ nanorods by aqueous precipitation and calcination/refluxing methods, showing the same morphology but totally different exposed crystal facets. They clearly concluded that the $\gamma\text{-Fe}_2\text{O}_3$ nanorods enclosed by reactive (110) and (100) facets, simultaneously exposing Fe^{3+} and O^{2-} sites, were highly active for the activation of NH_3 and NO, and thus highly active for the NH_3 -SCR reaction. In contrast, the $\alpha\text{-Fe}_2\text{O}_3$ nanorods enclosed by (210) and (001) facets only exposed Fe^{3+} sites and showed relatively poor SCR activity, due to the lack of neighboring oxygen anions for the activation of NH_3 and NO. These studies have significantly elevated the research on the structure–activity relationship of Fe_2O_3 catalysts for the NH_3 -SCR reaction to a new height, and in the near future studies on their practical utilization should be more focused.

2.1.2. Ce-based oxide catalysts. In previous studies, cerium oxide has usually been employed as the promoter or support for NH_3 -SCR catalysts. For example, Chen *et al.*⁶⁶ added *ca.* 10 wt% Ce to a $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst with low vanadia loading (0.1 wt%), which was able to greatly improve the NH_3 -SCR activity in a broad operation temperature window. Long and Yang⁶⁷ found that Ce doping could enhance the stability of Fe-ZSM-5 catalysts, and Carja *et al.*⁶⁸ concluded that the synergistic effect between Fe and Ce in Fe-Ce-ZSM-5 catalysts could greatly improve the deNO_x efficiency. Wu *et al.*^{69,70} concluded that a Ce-promoted Mn/TiO₂ catalyst showed better SO₂ resistance in the low temperature NH_3 -SCR process. Li *et al.*⁷¹ prepared a supported WO₃ catalyst using CeO₂-ZrO₂ mixed oxide as a support, exhibiting excellent NH_3 -SCR activity and thermal stability, as a potential candidate for the deNO_x process of diesel engines.

With the increase of the understanding on the effect of cerium oxide in the NH_3 -SCR reaction, researchers have begun to realize that this material with excellent redox properties can also be used as an active component in SCR catalysts. For instance, Xu *et al.*⁷² reported a novel Ce/TiO₂ catalyst, prepared by a conventional precipitation method, showing high deNO_x efficiency and N₂ selectivity from 250 to 400 °C. Afterwards, Gao *et al.*^{73,74} investigated the influence of preparation methods (including sol-gel, impregnation and co-precipitation methods) and concluded that the catalyst prepared by the sol-gel method showed the best catalytic performance. They considered that the relatively strong interaction between Ce and Ti species and also the high dispersion of CeO₂ crystallites on the TiO₂ surface were important for the NH_3 -SCR reaction. Although the SCR activity of the Ce/TiO₂ catalyst has been proved to be outstanding, the resistance to SO₂ poisoning and high space velocity (GHSV) still need to be enhanced for practical use. For example, the supported Ce/TiO₂ catalyst can be deactivated by SO₂ through the formation of highly thermally stable Ce(SO₄)₂ and Ce₂(SO₄)₃, cutting off the redox cycle between Ce³⁺ and Ce⁴⁺ species.⁷⁵ In addition, with increasing GHSV, the insufficient SCR activity, especially at low temperatures,

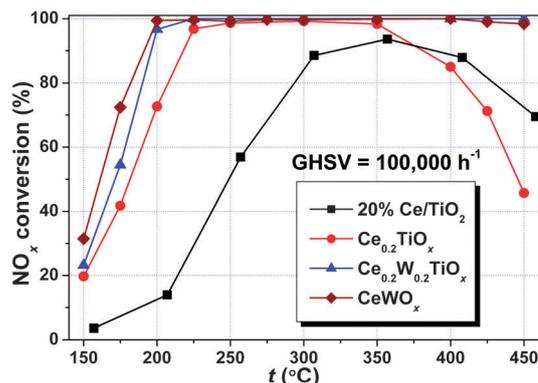


Fig. 1 NH_3 -SCR activity over 20% Ce/TiO₂, Ce_{0.2}TiO_x, Ce_{0.2}W_{0.2}TiO_x, CeWO_x catalysts in simulated diesel engine exhaust.

cannot satisfy the requirements for practical use in diesel engines.^{72,73} To overcome these shortcomings, Shan *et al.*⁷⁶ simply developed a homogeneous precipitation method characterized by a uniform increase of the pH value through decomposition of an organic base (urea in this study) to prepare a CeTiO_x mixed oxide catalyst. During this process, the TiO_x species was first precipitated at the initial stage and afterwards the CeO_x species was precipitated uniformly onto the TiO_x species, forming many catalytically active CeTiO_x crystallites.⁷⁷ This CeTiO_x catalyst showed much higher SCR activity than the supported Ce/TiO₂ catalyst (Fig. 1), with significantly improved resistance to high space velocity.

To better enhance the catalytic performance together with the thermal stability of this CeTiO_x catalyst, doping with W species was carried out (Fig. 1).⁷⁸ Over the optimal Ce_{0.2}W_{0.2}TiO_x catalyst with Ce : W molar ratio of 1 : 1, NO_x conversion could be maintained above 90% from 275 to 450 °C even at a rather high GHSV of 500 000 h⁻¹. The W doping in the Ce_{0.2}W_{0.2}TiO_x catalyst led to a much higher dispersion degree of Ce species, with a larger Ce³⁺/Ce⁴⁺ ratio and more oxygen vacancies, resulting in higher NO oxidation ability and thus better SCR activity at low temperatures. In addition, due to the increased capacity for adsorption of NH₃ species on both Brønsted acid sites and Lewis acid sites induced by W doping, the NH₃ unselective oxidation at high temperatures was also greatly inhibited, thus leading to higher SCR activity and N₂ selectivity simultaneously. A similar promotion effect by W species on CeO₂/TiO₂ supported-type catalysts was also observed by Chen *et al.*,⁷⁹ which they attributed to the strong interaction between Ce and W species.

Actually, for TiO₂-containing NH_3 -SCR catalysts, the activity loss at high temperatures above 600 °C is usually associated with the occurrence of a phase transformation from anatase to rutile. Through analysis of the effect of W species in the Ce_{0.2}W_{0.2}TiO_x catalyst, Shan *et al.*⁸⁰ had the idea to substitute all Ti species by W species. Under this inspiration, a novel and excellent CeWO_x catalyst with high NH_3 -SCR activity, outstanding N₂ selectivity, improved thermal stability, good durability toward co-existing pollutants and especially much higher resistance to space velocity was developed (Fig. 1). Even at a very high GHSV of 500 000 h⁻¹, the NO_x conversion over CeWO_x could be maintained at 100% from 250 to 425 °C, which is very

beneficial for practical use in diesel vehicles with limited installation space for SCR converters. Based on various characterization results, it was concluded that, compared with pristine oxides, the strong interaction between Ce and W species led to higher dispersion of CeO₂ and WO₃ crystallites and more abundant Ce³⁺ species with higher concentration of surface oxygen species, which were important for the oxidation of NO, thus promoting the “fast SCR” reaction. The synergistic effect between Ce and W species produced more Brønsted acid sites and Lewis acid sites for NH₃ adsorption and also maintained enough capacity for NO_x adsorption, achieving a broad operation temperature window in the NH₃-SCR reaction. This CeWO_x catalyst is a fascinating candidate for the deNO_x process from diesel engines, and Chen *et al.*⁸¹ also found this advantageous combination of Ce and W species in a CeO₂-WO₃ mixed oxide catalyst at nearly the same time. Peng *et al.*^{82,83} found that this catalyst could resist greater amounts of alkali metals than V₂O₅-WO₃/TiO₂ and that Mn doping could further improve its low temperature SCR activity. Over this CeO₂-WO₃ mixed oxide catalyst, based on an *in situ* DRIFTS study, Chen *et al.*⁸⁴ proposed two reaction pathways of NH₃-SCR reaction which were similar to the E-R and L-H mechanisms. However, much more work needs to be done to better understand the intrinsic SCR reaction mechanism over this novel material, especially using other characterization methods.

Besides the above-mentioned materials, CeO₂ supported on Al₂O₃,⁸⁵ activated carbon fibers,⁸⁶ and carbon nanotubes⁸⁷ together with a hydrothermally synthesized Ce-P-O catalyst,⁸⁸ were also developed by other researchers, all showing impressive deNO_x efficiency, although the detailed structure-activity relationship of these CeO₂-containing catalysts in NH₃-SCR reaction still needs to be studied. In the aspect of catalyst structure design, Wang *et al.*⁸⁹ developed a novel titanium nanotube-confined CeO₂ catalyst, showing higher NH₃-SCR activity than that of CeO₂ supported on TiO₂ nanoparticles, mainly due to the stronger redox ability and NH₃ adsorption capacity, judging from comparison of the H₂-TPR and NH₃-TPD results, respectively. Owing to the presence of a “shell protection effect”, Chen *et al.*⁹⁰ found that this titanium-nanotube-confined CeO₂ catalyst showed a remarkable resistance to alkali metal poisoning in the deNO_x process. This result provides a new route for synthesis of NH₃-SCR catalysts with higher poisoning resistance for practical use. Recently, the surface modification of CeO₂ by WO_x⁹¹ or sulfate species⁹² and the surface modification of CeO₂-ZrO₂ solid solutions by nickel/sulfate species⁹³ or phosphate species⁹⁴ to promote the NH₃-SCR activity also achieved some progress, in which the roles of acid sites induced by surface modifiers and the inhibition of NH₃ unselective oxidation at high temperatures were carefully addressed. In future studies, the surface modification of CeO₂ or other metal oxides could be a promising way to prepare applicable catalysts that is also convenient for studying their structure-activity relationship in the NH₃-SCR reaction.

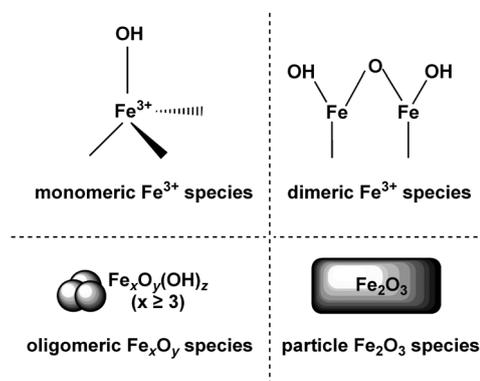
2.2. NH₃-SCR of NO_x over zeolite catalysts

Zeolite catalysts have received much attention in recent years due to their excellent SCR activity and thermal stability for the deNO_x process in diesel engines.³ Owing to the complexity of

zeolite structures (*e.g.* ZSM-5, HBEA, MOR, USY, CHA *etc.*), the difference in preparation methods (*e.g.* aqueous ion-exchange, solid-state ion-exchange, incipient wetness impregnation, chemical vapor deposition, one-pot synthesis *etc.*) together with the differences in active metal sites (*e.g.* Fe, Cu *etc.*), a universally accepted structure-activity relationship for zeolite catalysts in the NH₃-SCR reaction cannot be easily established. Fortunately, many researchers have devoted themselves to relatively fundamental research on zeolite NH₃-SCR catalysts besides work aimed toward their industrially practical use. The enlightening results obtained in this area will be introduced in the following sections classified by the Fe and Cu transition metals commonly used as active sites.

2.2.1. Fe-based zeolite catalysts. Among the numerous Fe-based zeolite catalysts, the application of Fe-ZSM-5 in the NH₃-SCR reaction has attracted much attention from researchers since the end of the last century. In 1999, Ma and Grünert⁹⁵ and Long and Yang⁶⁷ both reported that Fe-ZSM-5 catalysts prepared by over-exchange of Fe into H-ZSM-5 through FeCl₃ sublimation and ion-exchange of Fe into NH₄-ZSM-5 using FeCl₂ as a precursor, respectively, showed excellent NH₃-SCR activity even at high GHSV and in the presence of SO₂. Thereafter, more and more researchers focused on the study of Fe-ZSM-5 catalysts, investigating the influence of preparation methods, Fe exchange level and Si/Al ratio *etc.* on NH₃-SCR activity.¹⁰

Although different research groups reported diverse optimal methods for preparation of Fe-ZSM-5 catalysts with high apparent SCR activity, such as the improved aqueous ion-exchange method by Long and Yang,⁹⁶ the solid-state ion exchange method by Schwidder *et al.*,⁹⁷ and the chemical vapor deposition method by Iwasaki *et al.*,⁹⁸ the researchers eventually concluded that the preparation method was actually not a decisive factor in determining the intrinsic catalytic activity of Fe-ZSM-5 catalysts in the NH₃-SCR reaction (*i.e.* the turnover frequency), but the microstructure of Fe species was.^{10,98} Brandenberger *et al.*⁹⁹ recently systematically studied the different Fe sites located in Fe-ZSM-5 catalysts including monomeric, dimeric, clustered and oligomeric species, and correlated them with the measured NH₃-SCR activity (Scheme 3). They concluded that actually all Fe species in the Fe-ZSM-5 catalyst were active, although they exhibited different



Scheme 3 The Fe species probably present in Fe-zeolite NH₃-SCR catalysts.

temperature dependencies in the SCR reaction. Below 300 °C, only monomeric Fe species contributed to the SCR reaction, and this type of Fe species did not catalyze the NH₃ unselective oxidation below 500 °C, which was beneficial to high N₂ selectivity. The important role of monomeric Fe³⁺ sites was also emphasized by Høj *et al.*¹⁰⁰ in their Fe-BEA catalyst. Above 300, 400 and 500 °C, respectively, the dimeric Fe species, the oligomeric species (*e.g.* trimeric and tetrameric Fe species) and partially uncoordinated Fe sites in the outmost layer of Fe_xO_y particles could also contribute to the NH₃-SCR reaction, and at high temperatures (>500 °C) the contribution of dimeric Fe species dominated. However, the unselective oxidation of NH₃ would occur on Fe_xO_y particles above 350 °C, resulting in low N₂ selectivity, and the dimeric Fe species governed the NH₃ oxidation up to 500 °C. A similar effect by severely clustered Fe_xO_y species on the unselective consumption of the reducing agent NH₃ in the SCR reaction was also proposed by Schwidder *et al.*¹⁰¹ and Devadas *et al.*¹⁰² Therefore, to obtain excellent NH₃-SCR activity at low temperatures together with good N₂ selectivity at high temperatures, an Fe-zeolite catalyst with a maximum quantity of monomeric Fe³⁺ sites should be prepared. Although some other factors may also influence the apparent SCR activity of Fe-zeolite catalysts,¹⁰³ the conclusions drawn by Brandenberger *et al.*⁹⁹ in the above-mentioned study are generally useful for the design, synthesis and application of efficient Fe-zeolite catalysts.

Besides the nature and effect of Fe species in Fe-zeolite catalysts, researchers also have paid close attention to the influence of the acidic properties of zeolite materials on the NH₃-SCR reaction. On Fe-based zeolite catalysts with the same type of framework structure, the SCR activity usually increases with decreasing Si/Al ratio,^{104,105} although the hydrothermal stability of zeolites deteriorates to a certain extent. Early work simply considered that the increase of SCR activity with low Si/Al ratio corresponded to the enhancement of Brønsted acidity induced by aluminium sites (Al-OH),¹⁰⁶ and that the NH₄⁺ species adsorbed on Brønsted acid sites directly participated in the SCR reaction to reduce NO_x.¹⁰⁷ However, after extensive studies, the researchers finally realize that the Brønsted acidic property is actually not a decisive factor for the high NH₃-SCR activity of Fe-zeolite catalysts, because over some zeolite materials without acidic sites, high NO_x conversion rates could still be obtained.¹⁰⁸ Yet, in another aspect, a promotion effect by Brønsted acidity on the NH₃-SCR reaction could still be observed if the catalysts contained the most favorable Fe species, and Schwidder *et al.*¹⁰⁸ concluded that this was probably due to the obvious promotion of an acid-catalyzed intermediate step in the NH₃-SCR reaction (*e.g.* the decomposition of NH₄NO₂) similar to the results reported by Li *et al.*¹⁰⁹ and Savara *et al.*,¹¹⁰ which might be the rate-determining step at low temperatures. In addition, Brandenberger *et al.*¹¹¹ concluded that the Brønsted acid sites might not be required directly in the SCR process for adsorbing or activating NH₃, but they were necessary to bind and disperse the reactive Fe³⁺ ions in the preparation process for Fe-based zeolite catalysts, similar to the results reported by Iwasaki *et al.*¹⁰⁴ Furthermore, the zeolite support with Brønsted acidity could also play a role as an NH₃

reservoir, regardless of the form in which the NH₃ was stored, and in the NH₃-SCR reaction the stored NH₃ could migrate to the active sites so as to undergo a reaction with NO.¹¹¹ A similar spill-over effect of NH₃ on the zeolite support to the active Fe³⁺ sites in the NH₃-SCR reaction was also reported by Klukowski *et al.*¹¹² on their Fe-HBEA catalyst. Therefore, in brief summary, nowadays researchers basically agree that in the standard NH₃-SCR reaction the oxidation function of Fe-based zeolite catalysts and the amount of active Fe species, but not the acidic properties of the zeolite supports, are the main factors controlling the deNO_x efficiency.^{104,111}

Hydrothermal stability is an important factor for the practical use of Fe-based zeolite catalysts, to which the researchers also paid great attention. Hydrothermal treatment could result in the dealumination of zeolite supports, leading to the decrease of Brønsted acid sites or breakdown of the framework structure, and more seriously the migration of active Fe³⁺ species to form clustered Fe_xO_y/Fe₂O₃ species, leading to the decline of NH₃-SCR activity and N₂ selectivity.¹¹³⁻¹¹⁶ The remaining NH₃-SCR activity after hydrothermal aging under different conditions was mainly attributed to the residual monomeric Fe³⁺ species located at ion exchange sites.¹¹⁴ The use of zeolite supports with high Si/Al ratio is expected to result in acceptable hydrothermal stability, but the SCR activity may be negatively affected owing to the presence of fewer Brønsted acid sites to exchange, bind and disperse active Fe³⁺ sites. Recently, Iwasaki and Shinjoh¹¹⁷ successfully improved the hydrothermal stability of Fe-BEA catalysts by sequential ion-exchange of rare earth (RE) metals, and concluded that the improvement was dependent on the ionic radius of the exchanged metals. When using the RE metals with radii of 1.05-1.15 Å such as Ce, Nd, Sm, Gd and Tb, the dealumination of aged Fe-BEA catalyst was clearly reduced. This method could also be useful with other Fe-based zeolite catalysts for the effective improvement of hydrothermal stability in practical use.

Another important deactivation factor for Fe-based zeolite catalysts is hydrocarbon (HC) poisoning, which is closely related to the dimensional structure of zeolite supports. For example, on Fe-ZSM-5 and Fe-BEA catalysts with three-dimensional structure, after HC poisoning the NH₃-SCR activity, especially at low temperatures, was markedly decreased mainly due to carbonaceous deposition. This resulted in the decline of surface area and pore volume together with suppressed NO oxidation ability for blocked Fe³⁺ sites, or the partial reduction of Fe³⁺ species to Fe²⁺ by HC, or the competitive adsorption of HC with NH₃/NO onto the catalyst surface.^{113,118,119} The deactivation effect of HC on NH₃-SCR activity was less on the Fe-MOR catalyst with one-dimensional structure due to the difficulty in HC diffusion, and using this feature Ma *et al.*¹²⁰ effectively improved the HC resistance of a modified Fe-BEA monolith catalyst by coating another layer of MOR zeolite on the outer surface. This useful modification strategy is worthy of application in the preparation of other efficient NH₃-SCR monolith catalysts for the control of emissions from diesel engines.

In practical use, the low temperature NH₃-SCR activity of Fe-based zeolite catalysts still needs improvement to meet the diesel emission standards for cold-start and idle speed processes,¹²¹ especially in the regions where Cu-based zeolite

catalysts cannot be used, such as in Japan.¹²² The relevant methods include the addition of catalyst promoters such as RE metal Ce⁶⁸ and noble metal Pt,¹²³ together with the tuning of the reaction atmosphere, such as raising the NO₂ ratio in NO_x to facilitate the “fast SCR” reaction^{124,125} and adding a small amount of NH₄NO₃ solution as an effective oxidant for NO, creating similar “fast SCR” reaction conditions.¹²⁶ In addition, to enable practical utilization of the catalysts, the deactivation effects of inorganic components contained in diesel exhaust on Fe-based zeolite catalysts are also worthy of investigation, including the combustion products of lubricant oil additives (*i.e.* Ca, Mg, Zn, P, B, Mo), the impurities of biodiesel fuel–urea solution (*i.e.* K, Ca) together with the aerosol particulates from intake air (*i.e.* Na, Cl);¹²⁷ these issues will not be discussed in detail due to the length limit of this article.

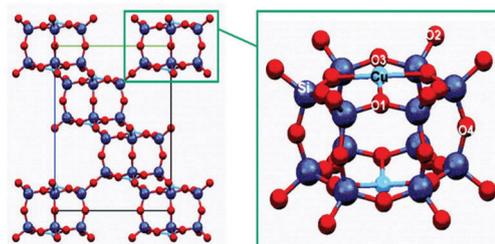
2.2.2. Cu-based zeolite catalysts. Since the use of zeolite catalysts in the NH₃-SCR reaction in the late 1970s, the Cu-based zeolite catalysts (mainly Cu-exchanged Y zeolites) have shown relatively good catalytic performance among the studied materials.⁵ In the 1990s, the Cu-based zeolite catalysts attracted more attention from researchers in the field of catalytic deNO_x from diesel engine exhaust. Cu-ZSM-5 catalysts have been well studied in early studies, and showed excellent low temperature NH₃-SCR activity and a broad operation temperature window even when urea was used as the reductant.¹²⁸ Sjövall *et al.*¹²⁹ concluded that using a zeolite support with low Si/Al ratio and increasing the Cu loading could noticeably enhance the NH₃-SCR activity of Cu-ZSM-5 catalysts. Qi *et al.*¹⁰⁵ reported that Cu-ZSM-5 catalysts showed high deNO_x performance at medium and low temperatures even at high GHSV, but the hydrothermal treatment could result in a decline in activity to a certain extent.

Actually, comparative studies showed that the preparation method, the Cu loading and even the precursors used for ZSM-5 synthesis could influence the hydrothermal stability of Cu-ZSM-5 catalysts.^{105,128,130} It is generally accepted that the active sites in the SCR reaction of Cu-based zeolites, including Cu-ZSM-5, Cu-beta and Cu-FAU, are mainly dimerized Cu²⁺ and Cu⁺ species, and the facility of redox between Cu²⁺ and Cu⁺ is beneficial to high SCR performance.^{10,128,131–135} Through studies on the variation of SCR activity and the alteration of catalytically active sites, Park *et al.*¹³¹ attributed the hydrothermal deactivation of Cu-ZSM-5 catalysts to the migration and re-distribution of Cu²⁺ species, leading to the decrease of active sites and the blockage of zeolite channels by sintered CuO, together with the dealumination and collapse of the zeolite support. After hydrothermal treatment of Cu-beta catalysts under different conditions (500–900 °C, 3% H₂O), Wilken *et al.*¹³⁴ found that the zeolite structure showed no obvious change below 800 °C, yet the oxidation state of Cu species showed apparent change, with a decrease in Cu⁺ species and increase in Cu²⁺ species as indicated by XPS results. Peden *et al.*¹³⁵ found that after severe hydrothermal treatment of Cu-beta catalysts at 900 °C for 2 h with 2% H₂O, the zeolite structure showed clear collapse. Therefore, in brief, the main reasons for the hydrothermal deactivation of Cu-based zeolite catalyst are the instability of active Cu species and of zeolite structures. Interestingly, Moden

*et al.*¹³⁶ reported that the active Cu species in Cu-FER catalysts with smaller pore size (0.42 × 0.54 nm) showed higher hydrothermal stability than that in Cu-beta catalysts with relatively larger pore size (0.66 × 0.67 nm). Nanba *et al.*^{137–139} also observed that in the presence of *n*-decane, NO_x conversion in the NH₃-SCR reaction over the Cu-FER catalyst was less affected than that over Cu-ZSM-5. Thus, it is expected that using a zeolite support with smaller pore size may produce Cu-based zeolite catalysts with exceptional NH₃-SCR activity, outstanding hydrothermal stability and HC resistance simultaneously.

Recently, Kwak *et al.*^{140,141} and Fickel *et al.*¹⁴² reported a series of Cu-chabazite (Cu-CHA) catalysts including Cu-SSZ-13 and Cu-SAPO-34, showing high NH₃-SCR activity, good N₂ selectivity and excellent hydrothermal stability with great application potential in the deNO_x process of diesel engines. Fickel *et al.*¹⁴² considered that the excellent hydrothermal stability of Cu-SSZ-13 and Cu-SAPO-34 catalysts was mainly due to the unique structure of CHA zeolites containing eight-membered-ring pores with small pore size (0.38 × 0.38 nm). For example, the ²⁷Al-NMR results by Kwak *et al.*¹⁴⁰ showed that the hydrothermally treated Cu-SSZ-13 catalyst showed no noticeable change in the peak intensity of AlO₄ species compared with the fresh catalyst; however, the peak intensity of AlO₄ species in Cu-ZSM-5 and Cu-beta catalysts decreased *ca.* 57% and 31%, respectively, suggesting an obvious dealumination process. Based on the commercial Cu-CHA catalyst from BASF Corporation, Schmiege *et al.*¹⁴³ found that even after hydrothermal treatment at 800 °C for 16 h, which was comparable to 135 000 mile vehicle-ageing, this catalyst still exhibited more than 70% NO_x conversion from 200 to 450 °C. The small pore structure in Cu-CHA catalysts was also expected to be more resistant to HC poisoning due to the difficulty in diffusion of HC with larger size, such as isobutane, with a kinetic diameter of 5.5 Å.¹⁴²

Using a variable-temperature XRD method, Fickel and Lobo¹⁴⁴ proved that the ion-exchange of Cu species into NH₄-SSZ-13 could greatly enhance its thermal stability. Through a comprehensive study using Rietveld refinement of the XRD data, *in situ* UV-Vis and XAFS techniques, Fickel and Lobo,¹⁴⁴ Korhonen *et al.*¹⁴⁵ and Deka *et al.*¹⁴⁶ finally concluded that only the isolated Cu²⁺ species located in the six-membered-rings of CHA structure coordinating with three oxygen atoms was the real active species in the NH₃-SCR reaction (Scheme 4). Using *operando* XAFS, density



Scheme 4 The structure of Cu-SSZ-13 obtained from refinements of neutron scattering data, and magnification of the double six member (d6r) unit with Cu present as an isolated ion. (Reproduced with permission from American Chemical Society.)¹⁴⁶

functional theory (DFT) calculations, and first-principles thermodynamics models, Kispersky *et al.*¹⁴⁷ and McEwen *et al.*¹⁴⁸ proposed that under the standard NH₃-SCR conditions at steady state, the active Cu species was actually a mixture of Cu⁺ species and Cu²⁺ species, indicating that the redox cycle between Cu⁺/Cu²⁺ is very important for high NH₃-SCR activity, similar to other Cu-based zeolite catalysts. Very recently, a further study using H₂-TPR and FTIR methods by Kwak *et al.*¹⁴⁹ revealed two distinct cationic positions in Cu-SSZ-13 catalysts at different ion-exchange levels. They concluded that at low ion-exchange levels, the Cu²⁺ ions primarily occupied the sites in the six-membered-rings similar to those identified in early reports, while at high ion-exchange levels, the Cu²⁺ ions were present mostly in the large cages of the CHA structure. The latter Cu²⁺ species were much more easily reduced in the H₂-TPR process, indicating a high redox capability at low temperatures, which might be the main origin of the exceptional NH₃-SCR activity over Cu-SSZ-13 catalysts. Therefore, although the NH₃-SCR performance of Cu-CHA catalysts has been well recognized, the understanding of the intrinsic active Cu sites is still in debate and ongoing. Besides, Kwak *et al.*¹⁵⁰ noticed that regardless of the Cu ion-exchange degree, the NO oxidation ability of Cu-SSZ-13 catalysts was very low; even under “fast SCR” conditions, the NO_x conversion was only slightly improved, with little formation of N₂O. Compared with other Cu-based zeolite catalysts or even other NH₃-SCR catalysts, the above-mentioned “abnormal” results indicate that a totally different NH₃-SCR reaction mechanism may exist over the Cu-SSZ-13 catalyst, which needs to be investigated in detail using various methods in future research. In addition, new types of Cu-based zeolite catalysts are being developed constantly with high deNO_x efficiency, such as the newly reported Cu-SSZ-39 with AEI structure, which also shows extraordinary hydrothermal stability.¹⁵¹ Consequently, study of the structure-activity relationship of Cu-based zeolite catalysts in the NH₃-SCR reaction will always be a hotspot in the field of environmental catalysis.

Nowadays, most Cu-CHA zeolite catalysts are prepared by an ion-exchange method using Cu salt precursors and CHA zeolite supports, usually including ion-exchange, filtration, washing and calcination procedures. Due to the limits in channel size and exchange capacity of CHA zeolites, repeated ion-exchange procedures or longer ion-exchange time is necessary to increase the Cu loading. Furthermore, the synthesis of SSZ-13 zeolites requires the structure-directing agent (SDA) *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH), which is very expensive,¹⁵² limiting the wide application of this material in industry. Therefore, it is highly imperative to improve the synthesis method to reduce the cost of Cu-SSZ-13 catalysts for the NH₃-SCR process. Using the low-cost Cu-tetraethylenepentamine (Cu-TEPA) complex as a novel template, which is stable in a strong alkaline solution and matches the CHA cage structure very well, Ren *et al.*^{153,154} successfully designed a one-pot synthesis method for Cu-SSZ-13 catalysts, obtaining products with high Cu loading and high dispersion of Cu species simultaneously. Through adjusting the starting compositions in the precursor gels, Cu-SSZ-13 zeolites with different Si/Al ratios could be synthesized. The preliminary results showed that the

one-pot synthesized Cu-SSZ-13 catalyst exhibited very good NH₃-SCR activity, especially in the low temperature range, yet much more work should be done to investigate its feasibility in practical use for the deNO_x process of diesel engines. Picone *et al.*¹⁵⁵ used Cu cyclam (1,4,8,11-tetraazacyclotetradecane) and tetraethylammonium (TEA⁺) acting as co-templates to directly synthesize a Cu-SAPO STA-7 catalyst with similar structure to that of Cu-SAPO-34, showing comparable performance in the NH₃-SCR reaction to that of Cu-ZSM-5 prepared by an ion-exchange method and higher performance than that of Cu-SAPO STA-7 with similar Cu content prepared by an aqueous ion-exchange method. The characterization results showed that a more homogeneous distribution of Cu species in Cu-SAPO STA-7 was achieved *via* direct synthesis, which was probably the main reason for its high deNO_x efficiency. The one-pot synthesis methods for Cu-based zeolite catalysts with small pore size using relatively cheap Cu-containing templates allow researchers to tune the Cu content, Cu distribution, and Si/Al ratio and thus the NH₃-SCR activity efficiently, although this approach is restricted to those zeolitic systems that can be prepared using coordination complexes as templates.¹⁵⁶ For practical use of this approach in industry, we believe, there is still a long but exciting way to go.

3. The mechanism responsible for the high performance of Ag/Al₂O₃ for the SCR of NO_x with oxygenated hydrocarbons

It has been widely accepted that the structure of hydrocarbons has a great influence on the activity of Ag/Al₂O₃ for NO_x reduction.^{13,16,157} Oxygenated hydrocarbons such as ethanol, acetaldehyde, and propyl alcohol exhibit excellent NO_x reduction activity on Ag/Al₂O₃,^{158,159} which was also confirmed by our results.^{160–163} More importantly, we attempted to determine the intrinsic property responsible for the NO_x reduction by oxygenated hydrocarbons over Ag/Al₂O₃. As shown in Fig. 2,

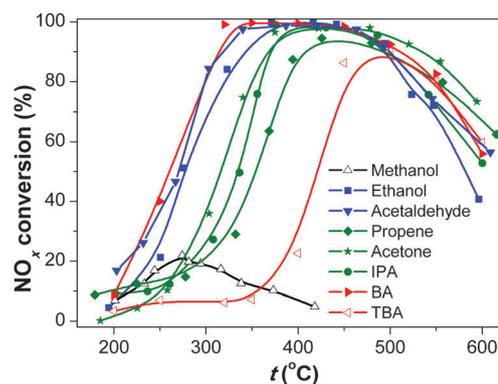


Fig. 2 Activity of 4 wt% Ag/Al₂O₃ for NO_x conversion by various hydrocarbons at different temperatures. Conditions: NO 800 ppm, O₂ 10%, H₂O 10%, reductants (methanol 3030 ppm, or ethanol 1565 ppm, or acetaldehyde 1565 ppm, or propene 1714 ppm, or acetone 1043 ppm, or IPA 1043 ppm, or BA 783 ppm, or TBA 783 ppm), N₂ balance, total flow = 2000 ml min⁻¹, GHSV = 50 000 h⁻¹.

methanol shows the poorest activity for NO_x reduction, while ethanol, acetaldehyde, and butyl alcohol (BA) are most active, giving similar T₅₀ (50% NO_x conversion) at ca. 270 °C with a SV of 50 000 h⁻¹. It should be noted that *tert*-butyl alcohol (TBA) exhibits a much lower NO_x conversion in the temperature range 200–450 °C, providing a T₅₀ for NO_x conversion at around 420 °C, which is ca. 150 °C higher than that of the T₅₀ with BA. The reductants with three carbon atoms (iso-propanol (IPA), and acetone) exhibit moderate activity for NO_x reduction. Clearly, both the carbon chain length and configuration of oxygenated hydrocarbons have a pronounced effect on their properties for NO_x reduction, therefore understanding such differences at the mechanism level may give clues for the design of a HC-SCR system with high efficiency.

3.1. Partial oxidation of oxygenated hydrocarbons over Ag/Al₂O₃

As the initial step of HC-SCR, the partial oxidation of hydrocarbons has attracted much attention. In NO_x reduction by ethanol over Ag/Al₂O₃, it has been proposed that acetate derived from the partial oxidation of ethanol plays a crucial role in the formation of isocyanate species (–NCO), as well as in the global NO_x reduction process.^{13,30,31,167–169} A possible mechanism for NO_x reduction by ethanol over Ag/Al₂O₃ was judged to be similar to that of C₃H₆: approximately, NO + O₂ + C₂H₅OH → NO_x

(nitrate in particular) + C_xH_yO_z (acetate in particular) → R–NO₂ + R–ONO → –NCO + –CN + NO + O₂ → N₂.^{23,24,30,31,167–171} However, this mechanism does not sufficiently explain why ethanol has a much higher efficiency for the SCR of NO_x over Ag/Al₂O₃ than hydrocarbons such as propene (Fig. 2).

In our earlier papers,^{162,172,173} the formation and dynamic performance of partial oxidation products of ethanol over Ag/Al₂O₃ were studied by an *in situ* DRIFTS method, and we found a novel enolic species originating from the partial oxidation of ethanol, with the structural feature of an oxygen atom adjacent to carbon–carbon double bonds (C=C–O). As shown in Fig. 3A, peaks at 1633, 1416 and 1336 cm⁻¹ were assigned to the enolic species adsorbed on the surface of Ag/Al₂O₃. This assignment was confirmed by using 2,3-dihydrofuran as an enolic model compound, which has a structure containing C=C bonded with an oxygen. From a comparison of the intensities of the respective peaks shown in Fig. 3A, we deduced that the enolic species is predominant during the oxidation of ethanol on the Ag/Al₂O₃ surface at low temperatures (within the range of 200–450 °C). However, at high temperatures ranging from 500 to 600 °C, the surface acetate species exhibiting characteristic frequencies at 1570 and 1466 cm⁻¹ becomes dominant.

The partial oxidation intermediates of ethanol over Ag/Al₂O₃ were further identified by synchrotron vacuum ultraviolet (VUV) photoionization mass spectrometry (PIMS), and photoionization

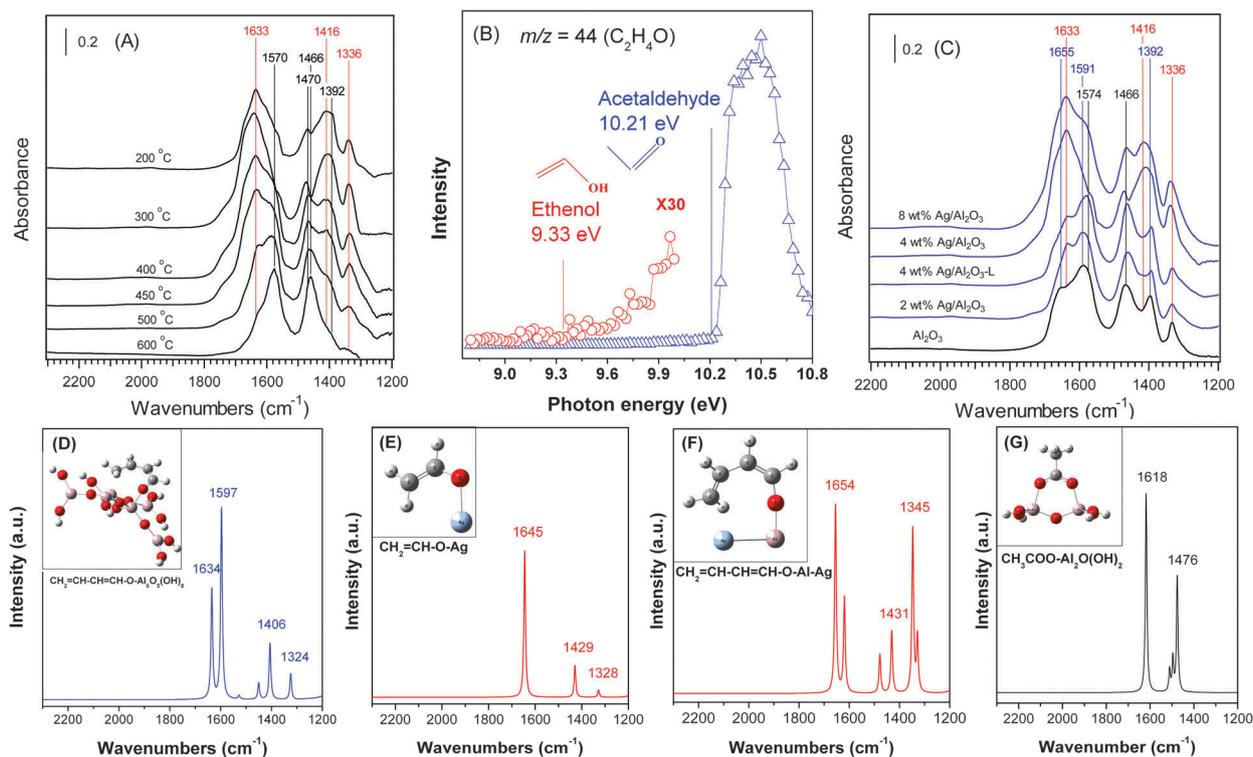


Fig. 3 (A) *In situ* DRIFTS spectra of 4 wt% Ag/Al₂O₃ during partial oxidation of ethanol at different temperatures;¹⁶² (B) the photoionization efficiency (PIE) spectra of *m/z* = 44 (C₂H₄O) measured in a flow of ethanol + O₂ over Ag/Al₂O₃ under low pressure at 330 °C;¹⁶⁴ (C) *in situ* DRIFTS spectra of Ag/Al₂O₃ with different Ag loadings during partial oxidation of ethanol at 250 °C; (D) molecular structure of the calculation model (inset figure) and its calculated FTIR spectrum for the surface C₄ enolic species on Al₂O₃; (E) surface C₂ enolic species on Ag/Al₂O₃; (F) C₄ enolic species on Ag/Al₂O₃;¹⁶⁵ and (G) surface acetate on Ag/Al₂O₃.¹⁶⁶ (Reproduced with permission from Elsevier Inc. and American Chemical Society.)

efficiency (PIE) spectroscopy.¹⁶⁴ The PIE spectra of $m/z = 44$ (C_2H_4O) (Fig. 3B) at low pressure unambiguously illustrate the presence of ethenol ($CH_2=CH-OH$), with an ionization threshold of 9.33 eV.¹⁷⁴ At normal atmospheric pressure, however, this species was hardly observed in the gas phase, indicating a high level of activity. This result also indicates that Ag/Al_2O_3 provides a suitable surface to stabilize the ethenol, because of its strong DRIFTS intensity on the catalyst surface under normal pressure (Fig. 3A). Acetaldehyde, as the stable isomer of ethenol, was detected under low and atmospheric pressure with high ion intensity, giving the characteristic threshold of 10.21 eV.

Meanwhile, propenal ($CH_2=CHCHO$), acetone (CH_3COCH_3), and 2-butenal ($CH_3CH=CH-CHO$) were also measured by VUV-PIMS during the partial oxidation of ethanol over Ag/Al_2O_3 . This indicates that a condensation reaction occurs synchronously during the partial oxidation of ethanol over Ag/Al_2O_3 , which also agrees with our TPD-MS experiment.¹⁷³ The condensation reactions of aldehydes, as well as ketones, are widely used in organic synthesis and are commonly catalyzed by zeolites, Al_2O_3 , and TiO_2 .¹⁷⁵⁻¹⁷⁷

On a detailed mechanistic level, the role of silver species in the HC-SCR of NO_x over Ag/Al_2O_3 was mainly attributed to enhancement of the partial oxidation of reductants to form active intermediates, and their further reaction to produce N_2 .^{16,158,172,178} *In situ* DRIFTS spectra showed that the surface species formed from the partial oxidation of ethanol over Ag/Al_2O_3 (Fig. 3C) were closely related to Ag loading.¹⁶⁵ Over pure Al_2O_3 , the surface enolic species adsorbed on Al sites exhibited characteristic peaks at 1655, 1591, 1392, and 1336 cm^{-1} . After Ag loading, the peaks due to enolic species were observed at 1633, 1416, and 1336 cm^{-1} , the intensity of which gradually increased with increasing Ag content, indicating that this species would be bound on or close to Ag sites.

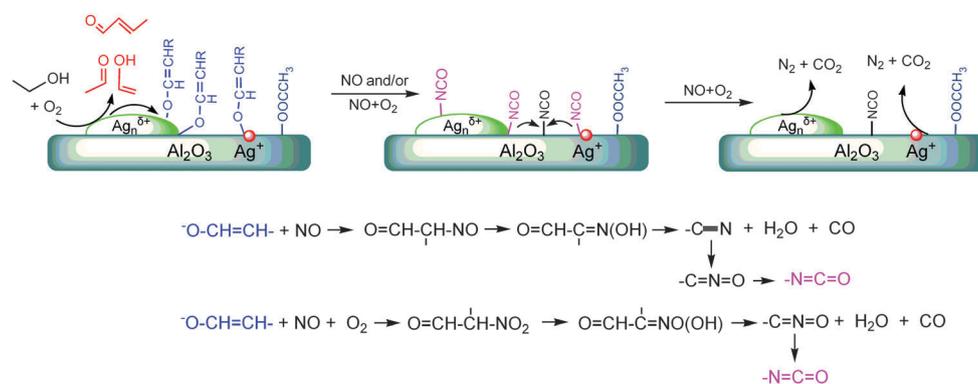
Density functional theory (DFT) calculations were also used to confirm the structure of adsorbed enolic species and acetate on Ag/Al_2O_3 .^{162,165,166,173,179} Two kinds of surface enolic species, adsorbed only on Al sites ($CH_2=CH-CH=CH-O-Al_6O_5(OH)_8$) and bound on or close to Ag ($CH_2=CH-O-Ag$, $CH_2=CH-CH=CH-O-Al-Ag$) were suggested by DFT calculations over Ag/Al_2O_3 and Al_2O_3 , with the simulation molecular structure

model and corresponding FTIR spectrum shown in Fig. 3D–F, respectively.¹⁶⁵ As revealed by ICP measurements,¹⁶⁵ the molar ratio of Al/Ag on 4 wt% Ag/Al_2O_3 was as high as 60, while enolic species bound on Al sites were hardly observed (Fig. 3C), strongly suggesting that the enolic species is preferably adsorbed on or close to silver sites.

On all Ag/Al_2O_3 samples, UV-vis analysis shows that that Ag species are mainly present in the oxidized state (Ag^+ and $Ag_n^{\delta+}$).^{40,180-184} Kinetic measurements confirm that such silver species, particularly strongly bound Ag^+ ions, are the active sites responsible for the reduction of NO_x with ethanol. Thus, we propose that the enolic species on the Ag/Al_2O_3 surface possibly adsorb on or close to isolated Ag^+ ions and/or $Ag_n^{\delta+}$ clusters, exhibiting an intimate contact with the active phase. This enolic species was clearly observed on the leached sample (Fig. 3C), in which Ag^+ ions were predominant, further supporting our assumption.¹⁶⁵ By using precipitable silver compound supported catalysts such as Ag_3PO_4/Al_2O_3 , Ag_2SO_4/Al_2O_3 and $AgCl/Al_2O_3$, we also confirmed that the high dispersion Ag^+ cations were the active silver species for NO_x reduction by ethanol, on which the reactive enolic species was formed having a strong infrared intensity in the typical temperature range of 250–500 °C.¹⁸⁵

During the partial oxidation of ethanol on all samples, meanwhile, the peaks due to surface acetate were also clearly observed, with the characteristic vibrational frequencies (1574 and 1466 cm^{-1}), regardless of silver loading. These results indicate that the acetate species formed during the partial oxidation of ethanol may mainly adsorb on Al sites instead of Ag sites. The adsorption characteristics of acetate on the surface of Ag/Al_2O_3 catalysts have also been investigated by DFT calculations.¹⁶⁶ The calculated vibrational spectrum of acetate adsorbed on Al sites, present as $CH_3COO-Al_2O(OH)_2$, is in good agreement with the experimental one (Fig. 3G), while there is a large error between the calculated and experimental vibrational modes of the acetate species bound on silver sites, further confirming that acetate species over Ag/Al_2O_3 are prone to interact with Al sites.

Based on the above results, the formation mechanism for surface enolic species during the partial oxidation of ethanol over Ag/Al_2O_3 was proposed as shown in Scheme 5. Ethanol



Scheme 5 Hypothesis for adsorbed enolic species formation and mechanism of ethanol-SCR of NO_x over Ag/Al_2O_3 . The intermediates in the gas phase such as acetaldehyde, ethenol, and 2-butenal were confirmed by VUV-PIMS measurement.¹⁶⁴ Surface enolic species, acetate, and $-NCO$ were identified by DRIFTS and DFT calculations.^{165,173} (Reproduced with permission from Elsevier Inc.)¹⁶⁵

principally reacts with oxygen to form acetaldehyde, which is followed by isomerization to ethenol. Subsequently, a C₂ enolic anion (CH₂=CH-O⁻)-M⁺ is formed by hydrogen extraction when ethenol is adsorbed on the surface of Ag/Al₂O₃. Meanwhile, the occurrence of aldol condensation of acetaldehyde, which has been confirmed by PIMS and TPD-MS measurement, may lead to the formation of C₄ enolic species (CH₂=CH-CH=CH-O⁻)-M⁺ as shown in Scheme 5.^{164,173}

Obviously, if the formation of surface enolic species follows the hypothesis described above, two prerequisites must be met. First, the selected reductant must contain at least one C-C bond. This has been clarified by our previous research, in which the enolic species was rarely observed when CH₃OH (Fig. 4A) and CH₃OCH₃ were partially oxidized over Ag/Al₂O₃.^{161,186} Secondly, it is widely accepted that the structural feature H-C-O-H is required for the partial oxidation of alcohols to aldehydes and/or ketones. That is, the OH group must be attached to a carbon atom with at least one hydrogen atom (denoted as α-H). Considering that enols are the tautomers of aldehyde/ketones, the presence of α-H is also a prerequisite for the formation of enolic species during partial oxidation of alcohols over Ag/Al₂O₃. To highlight this issue, butyl alcohol isomers with and without α-H were employed as reductants for NO_x reduction over 4 wt% Ag/Al₂O₃.¹⁶³ 1-Butanol (Fig. 4B), *sec*-butyl alcohol and isobutyl alcohol, containing α-H, are favorable for the partial oxidation to form enolic species while the α-H participated reaction pathway is impossible for *tert*-butyl alcohol (Fig. 4C) due to the absence of α-H.

Previous research further identified that surface enolic species were also produced during the partial oxidation of 1-propanol (and isopropyl alcohol) over Ag/Al₂O₃,^{160,161,187} acetaldehyde over both Ag/Al₂O₃¹⁷² and Co/Al₂O₃,¹⁸⁸ and acetylene over ZSM-5.¹⁸⁹ Interestingly, substantial quantities of enols in the gas phase have been observed by VUV-PIMS during the combustion of hydrocarbons.¹⁹⁰ The above results strongly suggest that adsorbed enolic species and/or enols in the gas phase are common intermediates involved in the partial oxidation

of hydrocarbons and oxygenated hydrocarbons. As a result, identification of their role is a key point in understanding of the pathway of HC-SCR.

3.2. Reactivity of intermediates originating from partial oxidation of oxygenated hydrocarbons over Ag/Al₂O₃

It has been widely accepted that the -NCO species is a vital intermediate for the SCR of NO_x with ethanol and other hydrocarbons, thus much attention has been focused on its formation and reactivity.^{29,178,191-197} With this in mind, the relationship between -NCO formation and the consumption of enolic species and acetate was investigated on Ag/Al₂O₃ via the transient response of the DRIFTS method, and typical results are presented in Fig. 5.¹⁶⁵

After exposure of 4 wt% Ag/Al₂O₃ to C₂H₅OH + O₂ at 400 °C for 60 min, the enolic species bound on or close to Ag sites exhibited strong peaks at 1633, 1412, and 1338 cm⁻¹, while the characteristic vibration modes of the enolic species adsorbed on Al sites were hardly observed. Strong peaks assignable to acetate were also observed at 1573 and 1466 cm⁻¹ (Fig. 5A). Switching the feed gas to NO resulted in a significant decrease in the intensity of peaks due to enolic species, while the decrease in the intensity of acetate peaks was much slower than that of enolic species on the same time scale. Meanwhile, this decrease was accompanied by the appearance of peaks due to -NCO, whose intensity increased with time on stream. These results confirm that the enolic species bound on or close to Ag sites are more active toward NO to form -NCO than acetate at this temperature (Fig. 5B).

Under the same conditions as in the above experiments, we also analyzed the reactivity of enolic species and acetate when NO + O₂ was introduced over 4 wt% Ag/Al₂O₃ (Fig. 5C and D). In this case, a more significant decrease in the concentration of enolic species was observed compared with experiments carried out in the absence of O₂. The trend of -NCO with time on stream follows the typical behavior of a reactive intermediate, increasing its intensity at the beginning, reaching a maximum at 3 min and then decreasing gradually. Meanwhile, the gas phase products such as N₂ and CO₂ were measured by mass

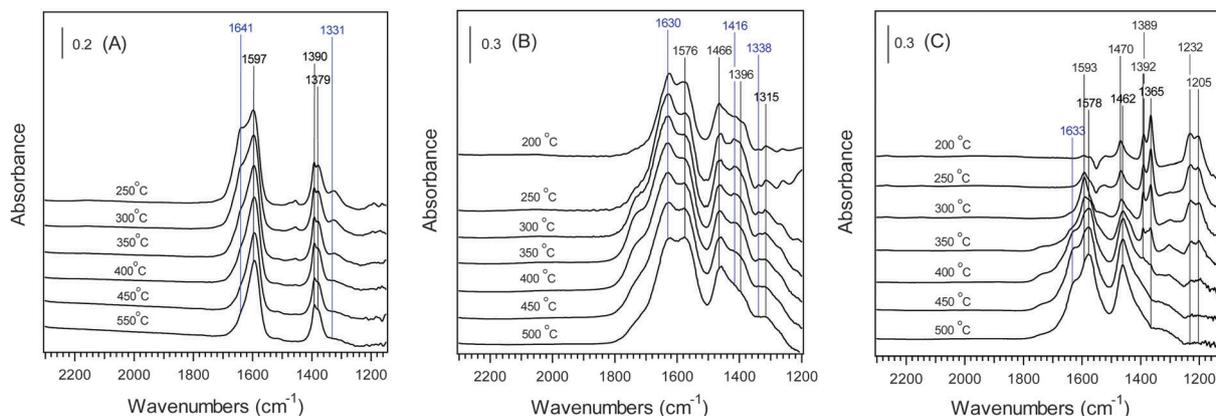


Fig. 4 *In situ* DRIFTS spectra of 4 wt% Ag/Al₂O₃ during partial oxidation of methanol (A),¹⁶¹ 1-butanol (B),¹⁶³ and *tert*-butyl alcohol (C)¹⁶³ at different temperatures. Conditions: the concentrations of reductants are the same as Fig. 2, O₂ 10%, N₂ balance. (Reproduced with permission from Elsevier Inc.)

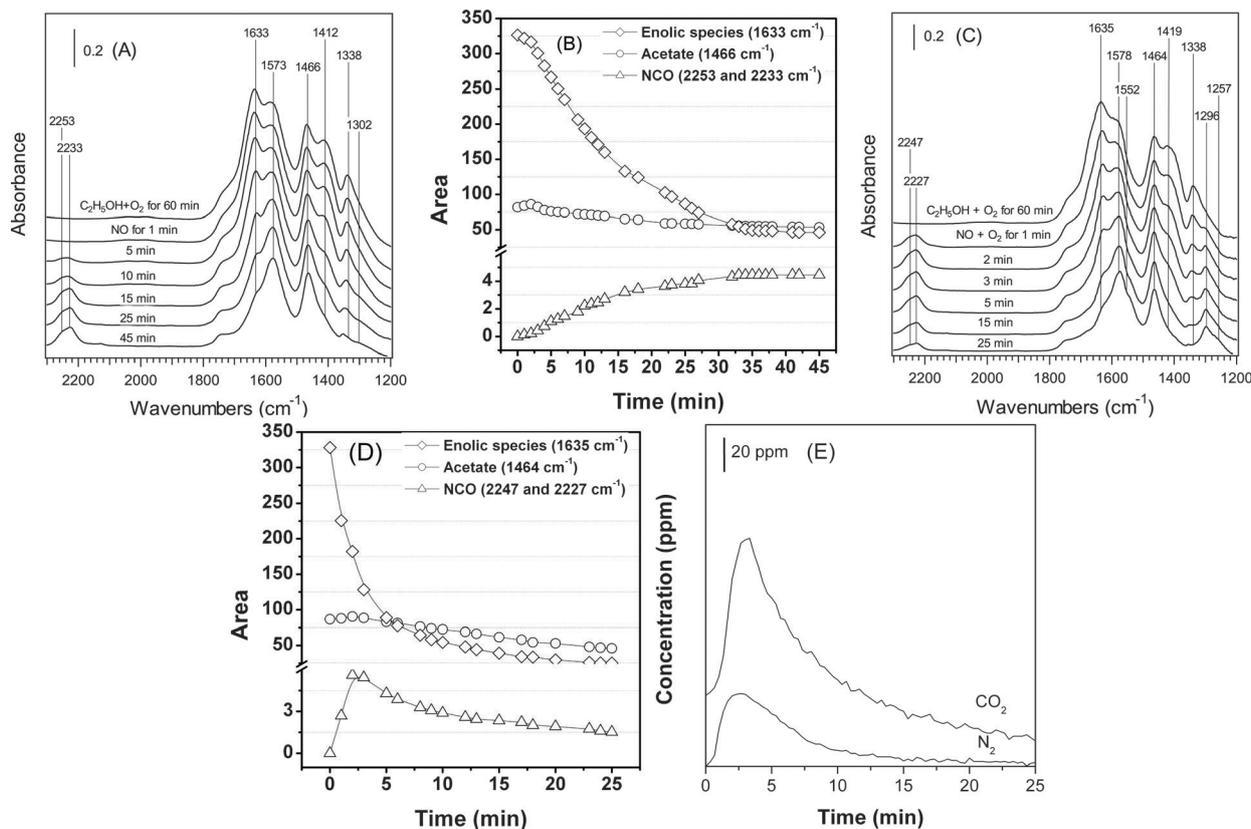


Fig. 5 Dynamic changes of *in situ* DRIFTS spectra over 4 wt% Ag/Al₂O₃ as a function of time in a flow of NO (A), and in a flow of NO + O₂ at 400 °C. (C) Before measurement, the catalyst was pre-exposed to a flow of C₂H₅OH + O₂ for 60 min at 400 °C. Conditions: NO 800 ppm, C₂H₅OH 1565 ppm, O₂ 10% (if used), N₂ or Ar (for the case of (C)) balance. (B) and (D) time dependence of the integrated areas of the peaks of enolic species (◇), acetate (○), and -NCO (△) for the cases of (A), and (C), respectively, and (E) time dependence of N₂ and CO₂ concentration calculated from the mass signals for the cases of (C). (Reproduced with permission from Elsevier Inc.)¹⁶⁵

spectrometry, and the results are shown in Fig. 5E. Based on these data, the consumption of surface enolic species within 25 min was estimated to be 283.1–566.2 μmol g⁻¹-cat, which is fairly close to that of the final product N₂, 204.5 μmol g⁻¹-cat. These results quantitatively confirm that the enolic species in intimate contact with the active phase plays a crucial role in the reduction of NO_x with ethanol. Over this catalyst, meanwhile, H₂-O₂ titration showed that the accessible amount of silver sites was 85.34 μmol g⁻¹-cat, which is lower than that of surface enolic species. This result indicates that not only the Ag sites, but also Al sites closely linked to Ag participate in the formation of surface enolic species, further confirming our assignment for this species.

Further studies confirmed that the enolic species originating from the partial oxidation of butyl alcohol (BA), *sec*-butyl alcohol (SBA), and isobutyl alcohol (IBA), propyl alcohol,¹⁶⁰ isopropyl alcohol (IPA),¹⁶¹ and acetaldehyde¹⁶² over Ag/Al₂O₃ also exhibited high activity toward NO + O₂, and thus are responsible for NO_x reduction by these oxygenated hydrocarbons.

3.3. The reaction pathway of HC-SCR over Ag/Al₂O₃

Based on the above results, a mechanism for NO_x reduction by ethanol over Ag/Al₂O₃ was proposed as shown in Scheme 5. In a typical reaction process, partial oxidation of ethanol results in

the formation of enolic species adsorbed on Al and Ag sites, as well as the formation of acetate on Al sites. Such different features in the adsorption sites for the enolic and acetate species on Ag/Al₂O₃ may contribute to their different reactivity toward NO + O₂ (and/or NO), and their role in the formation of -NCO during the reduction of NO_x with ethanol. The enolic species intimately linked with Ag sites (RCH=CH-O-Ag and RCH=CH-O-Al-Ag), possessing high activity, further react with NO + O₂ (and/or NO) to form Ag-NCO. The acetate bound on Al sites are less active when compared with the enolic species intimately linked with Ag sites, and thus play a minor role in -NCO formation. With an increase in the concentration of Ag-NCO, this species can transfer to Al sites, and as a result, the characteristic frequency of Al-NCO can be observed by the DRIFTS method.

The characteristic IR peaks of -NCO located around 2230 and 2250–2260 cm⁻¹ have been commonly observed on Ag/Al₂O₃ during HC-SCR, while the assignments of their coordination sites are still controversial. Bion *et al.*^{191,192} and Thibault-Starzyk *et al.*¹⁹⁶ observed the characteristic frequencies of -NCO on Ag/Al₂O₃ located at 2255–2265 and 2228–2240 cm⁻¹, which were assigned to -NCO species coordinated with octahedral Al³⁺ ions (Al^{VI}-NCO) and tetrahedral Al³⁺ sites (Al^{IV}-NCO), respectively. During the reduction of NO_x with ethanol and propene on

Ag/Al₂O₃, the two peaks at 2258–2262 and 2230–2235 cm⁻¹ were detected by Ukisu *et al.*,¹⁹⁸ Kameoka *et al.*,^{23,199} and Sumiya *et al.*^{29,168} The high-frequency peak was assigned to Al–NCO, while the low-frequency one was attributed to adsorption on Ag sites (Ag–NCO). To identify the adsorption sites of –NCO on the Ag/Al₂O₃ surface, DFT calculations were performed by Gao and He.¹⁹⁴ The calculated results indicate that the antisymmetric stretching mode of the Al–NCO group is located at 2267 cm⁻¹ with strong intensity, which is in excellent agreement with the experimental value (around 2260 cm⁻¹). The calculated mode of (OH)₂Al–O–Ag–NCO shows the asymmetric stretching frequency of –NCO at 2215 cm⁻¹, also close to the corresponding experimental one (around 2230 cm⁻¹), indicating that the low-frequency peak may correspond to the –NCO species adsorbed on or close to Ag sites. Because of the weak intensity, the symmetric stretching mode for the surface structure containing Ag–NCO or Al–NCO groups has not been observed in the experimental IR spectra, which has also been proved by the DFT calculation. By using an elegant short time-on-stream *in situ* spectroscopic transient isotope experimental technique, more recently, Chansai *et al.*^{178,200} proposed that there may be two types of –NCO species during the reduction of NO_x with hydrocarbons over Ag/Al₂O₃. One is a slowly reacting spectator –NCO species, probably adsorbed on the oxide support of Al₂O₃, while another is related to reactive –NCO, possibly on or close to the active silver phase.

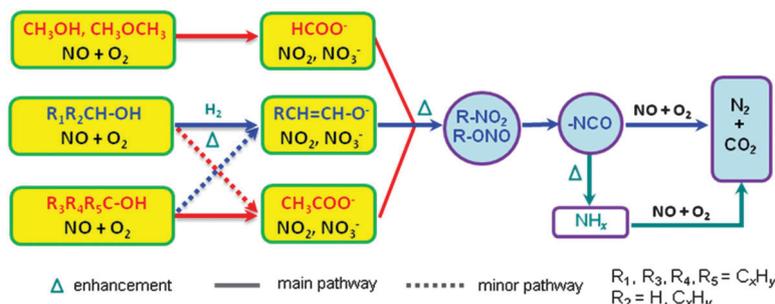
Organo-nitrite and -nitro species (R–ONO and R–NO₂) have been regarded as potential intermediates in the SCR of NO_x with hydrocarbons, which contributed to the formation of –NCO by reaction between the partial oxidation products of hydrocarbons and NO_x (or ad-NO_x).²⁰¹ As for ethanol-SCR over Ag/Al₂O₃, the two species may also participate in the formation of –NCO during exposure of the surface enolic species to NO and NO + O₂. In organic synthesis, enols and/or enolate anions are common intermediates in nitrosation reactions between aldehydes/ketones and substrates containing the NO group such as HONO, NO⁺, NO⁻, neutral NO, C(NO₂)₄, and [Fe(CN)₅NO]₂⁻ to form the initial product of nitroso and nitro compounds.^{202–204} This mechanism permitted us to hypothesize that similar reactions would occur during exposure of enolic species to NO on Ag/Al₂O₃, resulting in the formation of an organo-nitrite compound. Transformation of this organo-NO_x compound to its enol tautomer, –CH=N(OH), with

subsequent dehydration to –CN and transformation to –NCO, has been proposed as a possible route for –NCO formation.^{181,191,205} The presence of O₂ promoted the reaction of enolic species toward NO, possibly resulting in the formation of an organo-nitro intermediate. This compound also contributed to produce –NCO *via* enol and –CNO formation.^{181,191,205}

A general reaction pathway involving the formation of enolic species closely linked to active Ag sites was proposed to explain the NO_x reduction by different alcohols over Ag/Al₂O₃.²⁰⁶ As shown in Scheme 6, both the presence of α-H and at least C–C bonds in alcohols are necessary for the formation of enolic species. The employed alcohols with these two features thus exhibit high efficiency for NO_x reduction, derived from the high concentration of reactive enolic species. As for NO_x reduction by hydrocarbons such as alkanes and alkenes, however, the formation of acetate (or formate in the case of NO_x reduction by CH₄) and its further transformation to –NCO play a crucial role in NO_x reduction. The low reactivity of acetate (or formate) results in a low efficiency for NO_x reduction by hydrocarbons if compared with the NO_x reduction by oxygenated hydrocarbons such as ethanol.

Water vapor is commonly present in diesel engine exhaust, the presence of which has a great influence on the reaction pathway of the HC-SCR.^{13,158,191} Generally, the presence of water vapor usually suppressed the NO_x reduction by hydrocarbons such as propene over Ag/Al₂O₃, while high NO_x conversion was maintained when oxygenated hydrocarbons such as ethanol were employed as reductants. In our previous work,¹⁶ *in situ* DRIFTS results showed that the presence of water vapor promoted the formation of enolic species intimately linked to Ag sites, while it suppressed the formation of acetate species. These opposite effects of water vapor on the two species may derive from their different behaviors on the adsorbed sites, identification of which may provide important implications for understanding the effect of water vapor on the HC-SCR.

From a practical point of view, it is important to develop catalysts or catalyst-reductant systems that are active for NO_x reduction in the presence of SO₂. Numerous studies confirmed that the structure of hydrocarbons (oxygenated hydrocarbons) was not only responsible for the activity of Ag/Al₂O₃ for NO_x reduction, but also contributed to the sulfur tolerance of this silver catalyst.^{13,159,160} In the presence SO₂, the deteriorated



Scheme 6 Mechanism of HC-SCR of NO_x over Ag/Al₂O₃. (Reproduced with permission from CAS/DICP.)²⁰⁶

activity of Ag/Al₂O₃ for HC-SCR was mainly due to the adsorption and accumulation of sulfates on the Al₂O₃ support, before which the oxidation of SO₂ should have occurred on Ag sites.^{13,207,208} As for NO_x reduction by oxygenated hydrocarbons such as ethanol and acetaldehyde, large amounts of enolic species were formed, which adsorbed on or close to the active Ag sites. On the Ag sites covered with enolic species, the oxidation of SO₂ would be suppressed, followed by the adsorption and accumulation of sulfates. Therefore, it is reasonable that the catalyst–reductant system of Ag/Al₂O₃–oxygenated hydrocarbon exhibits high sulfur tolerance. The acetate, as the main product of partial oxidation of hydrocarbons, prefers to interact with Al sites. This situation is of benefit for SO₂ oxidation on Ag sites, and thus a pronounced poisoning effect would be observed during NO_x reduction by hydrocarbons such as C₃H₆ over Ag/Al₂O₃.

Recently, it was found that the presence of H₂ significantly enhanced the low temperature activity of Ag-based catalysts for NO_x reduction by hydrocarbons.^{17,40,209–211} Up to now, however, the interpretation of the H₂ promotional effect on HC-SCR has been under debate. To increase the rate of NO_x conversion, basically, the hydrogen must accelerate the rate(s) of the slow step(s) in the reaction of HC-SCR, while the slow step(s) are likely to vary depending on the reaction temperature and feed conditions.²¹² We were the first to report the pronounced promotional effect of H₂ on NO_x reduction by ethanol over Ag/Al₂O₃ even in the presence of water vapor.²¹³ Evidence provided by *in situ* DRIFTS revealed that the presence of H₂ enhanced the formation of enolic species during the partial oxidation of ethanol over Ag/Al₂O₃ at low temperatures. Such enhancement by H₂ was also confirmed by GC-MS analysis, by promoting the formation of organic nitrogen-containing intermediates such as CH₃-NO₂ and CH₃CN during the ethanol-SCR over Ag/Al₂O₃ at low temperatures. By using *in situ* DRIFTS, we also found that the presence of H₂ increased the activity of –NCO toward NO + O₂ during the NO_x reduction by ethanol over Ag/Al₂O₃. As revealed by VUV-PIMS analysis, meanwhile, the presence of H₂ may trigger the hydrolysis of –NCO to NH₃, providing a new pathway for NO_x reduction.²⁰⁶ As a result, we proposed that the H₂ effect on ethanol-SCR could be attributed to enhancement of the formation of enolic species and their further transformation to –NCO *via* the formation of organic nitrogen-containing species, which has been presented in Scheme 6. Such enhancement was also observed during the NO_x reduction by C₃H₆ over Ag/Al₂O₃ in the presence of H₂.^{160,214}

Typically, most of the studies dealing with the reaction mechanism of HC-SCR have been restricted to surface phenomena. However, Eränen and co-workers^{215,216} proposed that the octane-SCR over Ag/Al₂O₃ not only occurs on the surface of the catalyst but also continues in the gas phase, leading to the final products of N₂, H₂O, CO₂. Such a gas-phase reaction was proved by placing a commercial Pt-supported oxidation catalyst after the Ag/Al₂O₃ catalyst in order to remove CO and unburnt hydrocarbons. When the oxidation catalyst was placed immediately behind the Ag/Al₂O₃, NO_x conversion to N₂ was decreased dramatically. A similar gas-phase reaction was also observed to

occur during NO_x reduction by ethanol over Ag/Al₂O₃.^{24,217,218} The above results strongly suggest that very active N-containing intermediates in the gas phase were created over the Ag/Al₂O₃ catalyst. Identification of these unstable intermediates is thus important in order to understand the mechanism of HC-SCR over Ag/Al₂O₃ and to further optimize the catalysts. However, this may be a difficult task because these gas phase intermediates possess very high reactivity and a short lifetime. Eränen *et al.*²¹⁵ proposed that gas phase reaction behind the silver catalyst may be involved in the reaction of activated NO_x species with amines and ammonia. Organic N-containing species such as R–NO₂, R–NCO, and R–CN are intermediates in the formation of amines and ammonia, which may also take part in this gas reaction. Using a conventional electron-impact (EI) ionization mass spectrometer and liquid nitrogen trap, unfortunately, only R–CN species were detected during the NO_x reduction by octane over Ag/Al₂O₃, together with nitrogen-free species due to the partial oxidation of the reductant.²¹⁵ During the NO_x reduction by ethanol or octane over Ag/Al₂O₃, large amounts of N-containing species such as NH₃ and HCN were detected by a conventional MS technique.²⁴ Considering that the two gas phase species are not so active as to produce N₂ in a catalyst-free system, this may not be the true story. Indeed, the real intermediates would have changed into the final product of N₂ and/or more stable species owing to molecular collision and secondary reaction during the sampling and long retention times of a conventional mass spectrometer.

Recently, synchrotron vacuum ultraviolet (VUV) photoionization combined with molecular-beam mass spectrometry (MBMS), also referred to as synchrotron VUV photoionization mass spectrometry (VUV-PIMS), was successfully applied in detecting reactive intermediates in hydrocarbon combustion chemistry.^{190,219} In this case, molecular-beam sampling and high vacuum downstream can ensure free molecular flow of the sampled gas and reduce collision effects, making it possible to detect both stable and unstable intermediates; the employed vacuum ultraviolet single-photon photoionization can minimize fragmentation of target molecules because the total absorbed photon energy barely exceeds the ionization energy. Both of these advantages of VUV-PIMS may also provide an opportunity for identification of the reactive gas phase intermediates created by Ag/Al₂O₃ during the HC-SCR and give deeper insight into its mechanism if this technique is employed properly. In fact, by using this powerful method, ethanol in the gas phase, an important intermediate during the catalytic oxidation of C₂–C₄ alcohols over the Ag/Al₂O₃ catalyst, was unambiguously identified,^{164,219} further confirming the formation of surface enolic species during the NO_x reduction by ethanol over Ag/Al₂O₃.

4. Conclusions and perspectives

The development of vanadium-free catalysts for the NH₃-SCR of NO_x with high deNO_x activity, N₂ selectivity, hydrothermal stability and durability toward poisoning components is a continuing research hotspot in the field of environmental catalysis.

The study of the structure–activity relationship of these environmentally-benign catalysts in the NH₃-SCR reaction shows that the high dispersion of active species is a very important factor influencing the SCR performance, not only for metal oxide catalysts (such as the high dispersion of Fe³⁺–(O)₂–Ti⁴⁺ species in the FeTiO_x catalyst and CeO_x species in CeTiO_x, CeWTiO_x and CeWO_x catalysts), but also for zeolitic catalysts (such as the isolated Fe³⁺ and Cu²⁺ species located in ion-exchanged sites), which is a quite common view in heterogeneous catalysis. For metal oxide catalysts, the investigation of the effect of exposing different crystal facets in the NH₃-SCR reaction, especially for Fe₂O₃ oxides, has achieved great success, which may be extended to other metal catalyst systems for better understanding of the intrinsic origin of excellent SCR performance on certain materials. The improvement of hydrothermal stability is highly needed for metal oxide NH₃-SCR catalysts, and is a main factor restricting their practical use in the deNO_x process of diesel engines. Although the hydrothermal stability of Fe- and Cu-based zeolite catalysts is higher to a certain extent, due to the long-term operating conditions involving water vapor and timed thermal shock, the migration of isolated active sites can still occur, which requires researchers to develop novel zeolitic materials to meet the increasingly strict NO_x emission standards. The Cu-CHA catalysts such as Cu-SSZ-13, Cu-SAPO-34 and Cu-AEI catalyst such as Cu-SSZ-39 are good examples in this field, and we believe in the near future, more and more novel, efficient zeolitic materials will be developed not only by conventional ion-exchange, chemical vapor deposition methods *etc.* but also by one-pot synthesis using cheaper templates.

The acidity of NH₃-SCR catalysts is always given close attention by researchers, although many debates still remain. On metal oxide catalysts, both the Brønsted acid sites and Lewis acid sites are usually considered to be involved in the NH₃-SCR process, while on zeolite catalysts, only the Brønsted acid sites are proven to be useful for holding active metal sites and storing the reducing agent NH₃. The differences in understanding of the effects of acid sites on metal oxide catalysts and zeolite catalysts may be due to the distinct dispersion, microstructure and neighboring local environments of active sites in these two types of materials. For the metal oxide catalysts, with their relatively large amount of active phase but small amount of acid sites, the proper increase in acidity may be helpful for the deNO_x process; while for the zeolite catalysts, with relatively small quantities of isolated active sites but large amount of acid sites, maintaining the active sites in an isolated state is quite important. In further studies, with more advanced methods including *ex situ*, *in situ*, and *operando* methods, we believe that a universally accepted structure–activity relationship for these vanadium-free catalysts for the NH₃-SCR reaction can be established.

The HC-SCR of NO_x has attracted much attention as a possible alternative to the NH₃/urea-SCR. However, the activity and/or stability of catalysts developed for diesel-SCR are not sufficient to satisfy the demanding conditions of the deNO_x application for diesel engines. On the other hand, the oxygenated hydrocarbons such as ethanol, acetaldehyde, propyl alcohols, and

butyl alcohols exhibit excellent NO_x reduction activity on Ag/Al₂O₃, during which enolic species were formed and identified by *in situ* DRIFTS, VUV-PIMS measurements and DFT calculation. The enolic species originating from the partial oxidation of alcohols over Ag/Al₂O₃ prefer to adsorb on or close to silver sites, in intimate contact with the active phase. This adsorption behavior of the enolic species contributes to their high activity for the formation of –NCO species and the final product N₂ during the NO_x reduction by oxygenated hydrocarbons over Ag/Al₂O₃. A general reaction pathway involving the formation of enolic species closely linked to active Ag sites was proposed to explain the NO_x reduction by different alcohols over Ag/Al₂O₃. The presence of at least one α-H and one C–C bond is indispensable for the employed alcohols to produce enolic species during their partial oxidation over Ag/Al₂O₃. This intrinsic property responsible for NO_x reduction by oxygenated hydrocarbons may provide a guideline for developing diesel-SCR of NO_x systems with high efficiency for diesel engines.

Acknowledgements

The authors express their sincere thanks to the National Natural Science Foundation of China (51221892, 51108446, 21177142, 51278486) and the Ministry of Science and Technology, China (2013AA065301, 2010CB732304) for their support.

Notes and references

- H. Bosch and F. Janssen, *Catal. Today*, 1988, **2**, 369.
- K. Skalska, J. S. Miller and S. Ledakowicz, *Sci. Total Environ.*, 2010, **408**, 3976.
- P. Granger and V. I. Parvulescu, *Chem. Rev.*, 2011, **111**, 3155.
- Z. Liu and S. Ihl Woo, *Catal. Rev.*, 2006, **48**, 43.
- V. I. Parvulescu, P. Grange and B. Delmon, *Catal. Today*, 1998, **46**, 233.
- G. Busca, L. Lietti, G. Ramis and F. Berti, *Appl. Catal., B*, 1998, **18**, 1.
- S. Roy, M. S. Hegde and G. Madras, *Appl. Energy*, 2009, **86**, 2283.
- T. V. Johnson, *Int. J. Engine Res.*, 2009, **10**, 275.
- F. Liu, W. Shan, X. Shi, C. Zhang and H. He, *Chin. J. Catal.*, 2011, **32**, 1113.
- S. Brandenberger, O. Kröcher, A. Tissler and R. Althoff, *Catal. Rev.*, 2008, **50**, 492.
- M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo and N. Mizuno, *Shokubai*, 1990, **1990**, 430.
- W. Held, A. König, T. Richter and L. Pupper, *SAE Tech. Pap. Ser.*, 1990, 900496.
- R. Burch, J. P. Breen and F. C. Meunier, *Appl. Catal., B*, 2002, **39**, 283.
- A. Fritz and V. Pitchon, *Appl. Catal., B*, 1997, **13**, 1.
- M. A. Gómez-García, V. Pitchon and A. Kiennemann, *Environ. Int.*, 2005, **31**, 445.
- H. He and Y. Yu, *Catal. Today*, 2005, **100**, 37.
- F. Klingstedt, K. Arve, K. Eränen and D. Y. Murzin, *Acc. Chem. Res.*, 2006, **39**, 273.
- P. G. Savva and C. N. Costa, *Catal. Rev.*, 2011, **53**, 91.
- K.-i. Shimizu and A. Satsuma, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2677.
- R. Burch and P. J. Millington, *Catal. Today*, 1995, **26**, 185.
- J. Li, J. Hao, L. Fu, T. Zhu, Z. Liu and X. Cui, *Appl. Catal., A*, 2004, **265**, 43.
- K. A. Bethke and H. H. Kung, *J. Catal.*, 1997, **172**, 93.
- S. Kameoka, Y. Ukisu and T. Miyadera, *Phys. Chem. Chem. Phys.*, 2000, **2**, 367.
- J. H. Lee, S. J. Schmiege and S. H. Oh, *Appl. Catal., A*, 2008, **342**, 78.

- 25 L. E. Lindfors, K. Eränen, F. Klingstedt and D. Y. Murzin, *Top. Catal.*, 2004, **28**, 185.
- 26 A. Martinez-Arias, M. Fernández-García, A. Iglesias-Juez, J. A. Anderson, J. C. Conesa and J. Soria, *Appl. Catal., B*, 2000, **28**, 29.
- 27 V. I. Pârvulescu, B. Cojocaru, V. Pârvulescu, R. Richards, Z. Li, C. Cadigan, P. Granger, P. Miquel and C. Hardacre, *J. Catal.*, 2010, **272**, 92.
- 28 K.-i. Shimizu, A. Satsuma and T. Hattori, *Appl. Catal., B*, 2000, **25**, 239.
- 29 S. Sumiya, H. He, A. Abe, N. Takezawa and K. Yoshida, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2217.
- 30 Y. F. Tham, J. Y. Chen and R. W. Dibble, *Proc. Combust. Inst.*, 2009, **32**, 2827.
- 31 Y. H. Yeom, M. Li, W. M. H. Sachtler and E. Weitz, *J. Catal.*, 2006, **238**, 100.
- 32 D. Y. Yoon, J.-H. Park, H.-C. Kang, P. S. Kim, I.-S. Nam, G. K. Yeo, J. K. Kil and M.-S. Cha, *Appl. Catal., B*, 2011, **101**, 275.
- 33 K. Arve, H. Backman, F. Klingstedt, K. Eränen and D. Y. Murzin, *Appl. Catal., B*, 2007, **70**, 65.
- 34 V. Houel, P. Millington, R. Rajaram and A. Tsolakis, *Appl. Catal., B*, 2007, **73**, 203.
- 35 M. K. Kim, P. S. Kim, J. H. Baik, I.-S. Nam, B. K. Cho and S. H. Oh, *Appl. Catal., B*, 2011, **105**, 1.
- 36 T. Nakatsuji, R. Yasukawa, K. Tabata, K. Ueda and M. Niwa, *Appl. Catal., B*, 1998, **17**, 333.
- 37 C. Petitto, H. P. Mutin and G. Delahay, *Chem. Commun.*, 2011, **47**, 10728.
- 38 J. Rodriguez-Fernandez, A. Tsolakis, M. Ahmadinejad and S. Sitshebo, *Energy Fuels*, 2009, **24**, 992.
- 39 B. Sawatmongkhon, A. Tsolakis, S. Sitshebo, J. Rodriguez-Fernández, M. Ahmadinejad, J. Collier and R. R. Rajaram, *Appl. Catal., B*, 2010, **97**, 373.
- 40 P. Sazama, L. Čapek, H. Drobná, Z. Sobalík, J. Dědeček, K. Arve and B. Wichterlová, *J. Catal.*, 2005, **232**, 302.
- 41 C. L. DiMaggio, G. B. Fisher, K. M. Rahmoeller and M. Sellnau, *SAE Paper*, 2009-01-0277.
- 42 A. Kato, S. Matsuda, F. Nakajima, M. Imanari and Y. Watanabe, *J. Phys. Chem.*, 1981, **85**, 1710.
- 43 J. P. Chen, M. C. Hausladen and R. T. Yang, *J. Catal.*, 1995, **151**, 135.
- 44 P. Fabrizioli, T. Bürgi and A. Baiker, *J. Catal.*, 2002, **206**, 143.
- 45 H. Teng, L.-Y. Hsu and Y.-C. Lai, *Environ. Sci. Technol.*, 2001, **35**, 2369.
- 46 G. Marbán and A. B. Fuertes, *Catal. Lett.*, 2002, **84**, 13.
- 47 N. Apostolescu, B. Geiger, K. Hizbullah, M. T. Jan, S. Kureti, D. Reichert, F. Schott and W. Weisweiler, *Appl. Catal., B*, 2006, **62**, 104.
- 48 F. Nakajima and I. Hamada, *Catal. Today*, 1996, **29**, 109.
- 49 S. Roy, B. Viswanath, M. S. Hegde and G. Madras, *J. Phys. Chem. C*, 2008, **112**, 6002.
- 50 L. Ma, J. Li, R. Ke and L. Fu, *J. Phys. Chem. C*, 2011, **115**, 7603.
- 51 F. Liu, H. He and C. Zhang, *Chem. Commun.*, 2008, 2043.
- 52 F. Liu, H. He, C. Zhang, Z. Feng, L. Zheng, Y. Xie and T. Hu, *Appl. Catal., B*, 2010, **96**, 408.
- 53 F. Liu, K. Asakura, P. Xie, J. Wang and H. He, *Catal. Today*, 2013, **201**, 131.
- 54 F. Liu, K. Asakura, H. He, Y. Liu, W. Shan, X. Shi and C. Zhang, *Catal. Today*, 2011, **164**, 520.
- 55 F. Liu, H. He, C. Zhang, W. Shan and X. Shi, *Catal. Today*, 2011, **175**, 18.
- 56 F. Liu and H. He, *J. Phys. Chem. C*, 2010, **114**, 16929.
- 57 F. Liu, H. He, Y. Ding and C. Zhang, *Appl. Catal., B*, 2009, **93**, 194.
- 58 F. Liu, K. Asakura, H. He, W. Shan, X. Shi and C. Zhang, *Appl. Catal., B*, 2011, **103**, 369.
- 59 F. Liu and H. He, *Catal. Today*, 2010, **153**, 70.
- 60 S. Yang, J. Li, C. Wang, J. Chen, L. Ma, H. Chang, L. Chen, Y. peng and N. Yan, *Appl. Catal., B*, 2012, **117–118**, 73.
- 61 L. Chen, J. Li and M. Ge, *Environ. Sci. Technol.*, 2010, **44**, 9590.
- 62 Z. Si, D. Weng, X. Wu, J. Li and G. Li, *J. Catal.*, 2010, **271**, 43.
- 63 X. Mou, Y. Li, B. Zhang, L. Yao, X. Wei, D. S. Su and W. Shen, *Eur. J. Inorg. Chem.*, 2012, 2684.
- 64 X.-Y. Yang, L. Sun, Z.-W. Huang, X.-M. Cheng, T.-W. Zhang, B. Li and X.-F. Tang, *Acta Phys.-Chim. Sin.*, 2012, **28**, 184.
- 65 X. Mou, B. Zhang, Y. Li, L. Yao, X. Wei, D. S. Su and W. Shen, *Angew. Chem., Int. Ed.*, 2012, **51**, 2989.
- 66 L. Chen, J. Li and M. Ge, *J. Phys. Chem. C*, 2009, **113**, 21177.
- 67 R. Q. Long and R. T. Yang, *J. Am. Chem. Soc.*, 1999, **121**, 5595.
- 68 G. Carja, G. Delahay, C. Signorile and B. Coq, *Chem. Commun.*, 2004, 1404.
- 69 Z. Wu, R. Jin, Y. Liu and H. Wang, *Catal. Commun.*, 2008, **9**, 2217.
- 70 Z. Wu, R. Jin, H. Wang and Y. Liu, *Catal. Commun.*, 2009, **10**, 935.
- 71 Y. Li, H. Cheng, D. Li, Y. Qin, Y. Xie and S. Wang, *Chem. Commun.*, 2008, 1470.
- 72 W. Xu, Y. Yu, C. Zhang and H. He, *Catal. Commun.*, 2008, **9**, 1453.
- 73 X. Gao, Y. Jiang, Y. Zhong, Z. Luo and K. Cen, *J. Hazard. Mater.*, 2010, **174**, 734.
- 74 X. Gao, Y. Jiang, Y. Fu, Y. Zhong, Z. Luo and K. Cen, *Catal. Commun.*, 2010, **11**, 465.
- 75 W. Xu, H. He and Y. Yu, *J. Phys. Chem. C*, 2009, **113**, 4426.
- 76 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *ChemCatChem*, 2011, **3**, 1286.
- 77 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Catal. Today*, 2012, **184**, 160.
- 78 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Appl. Catal., B*, 2012, **115–116**, 100.
- 79 L. Chen, J. Li, M. Ge and R. Zhu, *Catal. Today*, 2010, **153**, 77.
- 80 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Chem. Commun.*, 2011, **47**, 8046.
- 81 L. Chen, J. Li, W. Ablikim, J. Wang, H. Chang, L. Ma, J. Xu, M. Ge and H. Arandiyani, *Catal. Lett.*, 2011, **141**, 1859.
- 82 Y. Peng, J. Li, L. Chen, J. Chen, J. Han, H. Zhang and W. Han, *Environ. Sci. Technol.*, 2012, **46**, 2864.
- 83 Y. Peng, Z. Liu, X. Niu, L. Zhou, C. Fu, H. Zhang, J. Li and W. Han, *Catal. Commun.*, 2012, **19**, 127.
- 84 L. Chen, J. Li, M. Ge, L. Ma and H. Chang, *Chin. J. Catal.*, 2011, **32**, 836.
- 85 Y. Shen, S. Zhu, T. Qiu and S. Shen, *Catal. Commun.*, 2009, **11**, 20.
- 86 L. Zhu, B. Huang, W. Wang, Z. Wei and D. Ye, *Catal. Commun.*, 2011, **12**, 394.
- 87 X. Chen, S. Gao, H. Wang, Y. Liu and Z. Wu, *Catal. Commun.*, 2011, **14**, 1.
- 88 F. Li, Y. Zhang, D. Xiao, D. Wang, X. Pan and X. Yang, *Chem-CatChem*, 2010, **2**, 1416.
- 89 H. Wang, X. Chen, X. Weng, Y. Liu, S. Gao and Z. Wu, *Catal. Commun.*, 2011, **12**, 1042.
- 90 X. Chen, H. Wang, Z. Wu, Y. Liu and X. Weng, *J. Phys. Chem. C*, 2011, **115**, 17479.
- 91 Z. Ma, D. Weng, X. Wu and Z. Si, *J. Environ. Sci.*, 2012, **24**, 1305.
- 92 T. Gu, Y. Liu, X. Weng, H. Wang and Z. Wu, *Catal. Commun.*, 2010, **12**, 310.
- 93 Z. Si, D. Weng, X. Wu, J. Yang and B. Wang, *Catal. Commun.*, 2010, **11**, 1045.
- 94 Z. Si, D. Weng, X. Wu, R. Ran and Z. Ma, *Catal. Commun.*, 2012, **17**, 146.
- 95 A. Z. Ma and W. Grünert, *Chem. Commun.*, 1999, 71.
- 96 R. Q. Long and R. T. Yang, *Catal. Lett.*, 2001, **74**, 201.
- 97 M. Schwidder, S. Heikens, A. De Toni, S. Geisler, M. Berndt, A. Brückner and W. Grünert, *J. Catal.*, 2008, **259**, 96.
- 98 M. Iwasaki, K. Yamazaki, K. Banno and H. Shinjoh, *J. Catal.*, 2008, **260**, 205.
- 99 S. Brandenberger, O. Kröcher, A. Tissler and R. Althoff, *Appl. Catal., B*, 2010, **95**, 348.
- 100 M. Høj, M. J. Beier, J.-D. Grunwaldt and S. Dahl, *Appl. Catal., B*, 2009, **93**, 166.
- 101 M. Schwidder, M. S. Kumar, A. Bruckner and W. Grünert, *Chem. Commun.*, 2005, 805.
- 102 M. Devadas, O. Krocher, M. Elsener, A. Wokaun, G. Mitrikas, N. Soger, M. Pfeifer, Y. Demel and L. Mussmann, *Catal. Today*, 2007, **119**, 137.
- 103 S. Brandenberger, O. Kröcher, A. Tissler and R. Althoff, *Ind. Eng. Chem. Res.*, 2011, **50**, 4308.
- 104 M. Iwasaki, K. Yamazaki and H. Shinjoh, *Appl. Catal., B*, 2011, **102**, 302.
- 105 G. Qi, Y. Wang and R. Yang, *Catal. Lett.*, 2008, **121**, 111.
- 106 R. Q. Long and R. T. Yang, *J. Catal.*, 1999, **188**, 332.
- 107 R. Q. Long and R. T. Yang, *J. Catal.*, 2002, **207**, 224.
- 108 M. Schwidder, M. Santhosh Kumar, U. Bentrup, J. Pérez-Ramírez, A. Brückner and W. Grünert, *Microporous Mesoporous Mater.*, 2008, **111**, 124.

- 109 M. Li, Y. Yeom, E. Weitz and W. Sachtler, *Catal. Lett.*, 2006, **112**, 129.
- 110 A. Savara, M.-J. Li, W. M. H. Sachtler and E. Weitz, *Appl. Catal., B*, 2008, **81**, 251.
- 111 S. Brandenberger, O. Kröcher, A. Wokaun, A. Tissler and R. Althoff, *J. Catal.*, 2009, **268**, 297.
- 112 D. Klukowski, P. Balle, B. Geiger, S. Wagloehner, S. Kureti, B. Kimmmerle, A. Baiker and J. D. Grunwaldt, *Appl. Catal., B*, 2009, **93**, 185.
- 113 C. He, Y. Wang, Y. Cheng, C. K. Lambert and R. T. Yang, *Appl. Catal., A*, 2009, **368**, 121.
- 114 S. Brandenberger, O. Kröcher, M. Casapu, A. Tissler and R. Althoff, *Appl. Catal., B*, 2011, **101**, 649.
- 115 X. Shi, F. Liu, W. Shan and H. He, *Chin. J. Catal.*, 2012, **33**, 454.
- 116 L. Ma, J. Li, H. Arandiyani, W. Shi, C. Liu and L. Fu, *Catal. Today*, 2012, **184**, 145.
- 117 M. Iwasaki and H. Shinjoh, *Chem. Commun.*, 2011, **47**, 3966.
- 118 I. Heo, Y. Lee, I.-S. Nam, J. W. Choung, J.-H. Lee and H.-J. Kim, *Microporous Mesoporous Mater.*, 2011, **141**, 8.
- 119 J. Li, R. Zhu, Y. Cheng, C. K. Lambert and R. T. Yang, *Environ. Sci. Technol.*, 2010, **44**, 1799.
- 120 L. Ma, J. Li, Y. Cheng, C. K. Lambert and L. Fu, *Environ. Sci. Technol.*, 2012, **46**, 1747.
- 121 J. Li, H. Chang, L. Ma, J. Hao and R. T. Yang, *Catal. Today*, 2011, **175**, 147.
- 122 B. Moden, J. Donohue, W. Cormier and H.-X. Li, *Top. Catal.*, 2010, **53**, 1367.
- 123 G. Qi and R. T. Yang, *Catal. Lett.*, 2005, **100**, 243.
- 124 A. Grossale, I. Nova, E. Tronconi, D. Chatterjee and M. Weibel, *J. Catal.*, 2008, **256**, 312.
- 125 M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, N. Söger, M. Pfeifer, Y. Demel and L. Mussmann, *Appl. Catal., B*, 2006, **67**, 187.
- 126 P. Forzatti, I. Nova and E. Tronconi, *Angew. Chem., Int. Ed.*, 2009, **121**, 8516.
- 127 P. Kern, M. Klimczak, T. Heinzelmann, M. Lucas and P. Claus, *Appl. Catal., B*, 2010, **95**, 48.
- 128 J. Baik, S. Yim, I.-S. Nam, Y. Mok, J.-H. Lee, B. Cho and S. Oh, *Top. Catal.*, 2004, **30–31**, 37.
- 129 H. Sjövall, L. Olsson, E. Fridell and R. J. Blint, *Appl. Catal., B*, 2006, **64**, 180.
- 130 M. Berggrund, H. Ingelsten, M. Skoglundh and A. Palmqvist, *Catal. Lett.*, 2009, **130**, 79.
- 131 J.-H. Park, H. J. Park, J. H. Baik, I.-S. Nam, C.-H. Shin, J.-H. Lee, B. K. Cho and S. H. Oh, *J. Catal.*, 2006, **240**, 47.
- 132 T. Komatsu, M. Nunokawa, I. S. Moon, T. Takahara, S. Namba and T. Yashima, *J. Catal.*, 1994, **148**, 427.
- 133 G. Delahay, S. Kieger, N. Tanchoux, P. Trens and B. Coq, *Appl. Catal., B*, 2004, **52**, 251.
- 134 N. Wilken, K. Wijayanti, K. Kamasamudram, N. W. Currier, R. Vedaiyan, A. Yezerets and L. Olsson, *Appl. Catal., B*, 2012, **111–112**, 58.
- 135 C. H. F. Peden, J. H. Kwak, S. D. Burton, R. G. Tonkyn, D. H. Kim, J.-H. Lee, H.-W. Jen, G. Cavataio, Y. Cheng and C. K. Lambert, *Catal. Today*, 2012, **184**, 245.
- 136 B. Moden, J. M. Donohue, W. E. Cormier and H. X. Li, in *Studies in Surface Science and Catalysis*, ed. P. M. Antoine Gédéon and B. Florence, Elsevier, 2008, vol. 74, p. 1219.
- 137 T. Nanba, A. Sultana, S. Masukawa, M. Haneda, J. Uchisawa, A. Obuchi and H. Hamada, *Top. Catal.*, 2009, **52**, 1766.
- 138 A. Sultana, T. Nanba, M. Haneda and H. Hamada, *Catal. Commun.*, 2009, **10**, 1859.
- 139 A. Sultana, T. Nanba, M. Sasaki, M. Haneda, K. Suzuki and H. Hamada, *Catal. Today*, 2011, **164**, 495.
- 140 J. H. Kwak, D. Tran, S. D. Burton, J. Szanyi, J. H. Lee and C. H. F. Peden, *J. Catal.*, 2012, **287**, 203.
- 141 J. H. Kwak, R. G. Tonkyn, D. H. Kim, J. Szanyi and C. H. F. Peden, *J. Catal.*, 2010, **275**, 187.
- 142 D. W. Fickel, E. D'Addio, J. A. Lauterbach and R. F. Lobo, *Appl. Catal., B*, 2011, **102**, 441.
- 143 S. 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.
- 144 D. W. Fickel and R. F. Lobo, *J. Phys. Chem. C*, 2010, **114**, 1633.
- 145 S. T. Korhonen, D. W. Fickel, R. F. Lobo, B. M. Weckhuysen and A. M. Beale, *Chem. Commun.*, 2011, **47**, 800.
- 146 U. 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.
- 147 V. F. Kispersky, A. J. Kropf, F. H. Ribeiro and J. T. Miller, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2229.
- 148 J. S. McEwen, T. Anggara, W. F. Schneider, V. F. Kispersky, J. T. Miller, W. N. Delgass and F. H. Ribeiro, *Catal. Today*, 2012, **184**, 129.
- 149 J. Hun Kwak, H. Zhu, J. H. Lee, C. H. F. Peden and J. Szanyi, *Chem. Commun.*, 2012, **48**, 4758.
- 150 J. Kwak, D. Tran, J. Szanyi, C. Peden and J. Lee, *Catal. Lett.*, 2012, **142**, 295.
- 151 M. Moliner, C. Franch, E. Palomares, M. Grill and A. Corma, *Chem. Commun.*, 2012, **48**, 8264.
- 152 S. I. Zones, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3709.
- 153 L. Ren, Y. Zhang, S. Zeng, L. Zhu, Q. Sun, H. Zhang, C. Yang, X. Meng, X. Yang and F.-S. Xiao, *Chin. J. Catal.*, 2012, **33**, 92.
- 154 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.
- 155 A. Lorena Picone, S. J. Warrender, A. M. Z. Slawin, D. M. Dawson, S. E. Ashbrook, P. A. Wright, S. P. Thompson, L. Gaberova, P. L. Llewellyn, B. Moulin, A. Vimont, M. Daturi, M. B. Park, S. K. Sung, I.-S. Nam and S. B. Hong, *Microporous Mesoporous Mater.*, 2011, **146**, 36.
- 156 U. 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.
- 157 J. Lee, S. Song and K. M. Chun, *Ind. Eng. Chem. Res.*, 2010, **49**, 3553.
- 158 T. Miyadera, *Appl. Catal., B*, 1993, **2**, 199.
- 159 K.-I. Shimizu, M. Tsuzuki and A. Satsuma, *Appl. Catal., B*, 2007, **71**, 80.
- 160 H. He, X. Zhang, Q. Wu, C. Zhang and Y. Yu, *Catal. Surv. Asia*, 2008, **12**, 38.
- 161 Q. Wu, H. He and Y. Yu, *Appl. Catal., B*, 2005, **61**, 107.
- 162 Y. Yu, H. He, Q. Feng, H. Gao and X. Yang, *Appl. Catal., B*, 2004, **49**, 159.
- 163 Y. Yu, X. Song and H. He, *J. Catal.*, 2010, **271**, 343.
- 164 Y. Li, X. Zhang, H. He, Y. Yu, T. Yuan, Z. Tian, J. Wang and Y. Li, *Appl. Catal., B*, 2009, **89**, 659.
- 165 Y. Yan, Y. Yu, H. He and J. Zhao, *J. Catal.*, 2012, **293**, 13.
- 166 H. Gao, T. Yan, Y. Yu and H. He, *J. Phys. Chem. C*, 2008, **112**, 6933.
- 167 T. Miyadera, *Appl. Catal., B*, 1997, **13**, 157.
- 168 W. L. Johnson II, G. B. Fisher and T. J. Toops, *Catal. Today*, 2012, **184**, 166.
- 169 Y. H. Yeom, M. Li, W. M. H. Sachtler and E. Weitz, *J. Catal.*, 2007, **246**, 413.
- 170 T. Chafik, S. Kameoka, Y. Ukisu and T. Miyadera, *J. Mol. Catal. A: Chem.*, 1998, **136**, 203.
- 171 A. Martínez-Arias, D. Gamarra, M. Fernández-García, A. Hornés, P. Bera, Z. Koppány and Z. Schay, *Catal. Today*, 2009, **143**, 211.
- 172 Y. Yu, H. He and Q. Feng, *J. Phys. Chem. B*, 2003, **107**, 13090.
- 173 Y. B. Yu, H. W. Gao and H. He, *Catal. Today*, 2004, **93–95**, 805.
- 174 P. J. Linstrom and W. G. Mallard, *NIST Chemistry Webbook*, 2003, NIST Standard Reference Database Number 69, <http://webbook.nist.gov>.
- 175 M. El-Maazawi, A. N. Finken, A. B. Nair and V. H. Grassian, *J. Catal.*, 2000, **191**, 138.
- 176 A. Panov and J. J. Fripiat, *Langmuir*, 1998, **14**, 3788.
- 177 M. I. Zaki, M. A. Hasan, F. A. Al-Sagheer and L. Pasupulety, *Langmuir*, 1999, **16**, 430.
- 178 S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, *J. Catal.*, 2010, **276**, 49.
- 179 H. Gao, H. He, Y. Yu and Q. Feng, *J. Phys. Chem. B*, 2005, **109**, 13291.
- 180 S. T. Korhonen, A. M. Beale, M. A. Newton and B. M. Weckhuysen, *J. Phys. Chem. C*, 2010, **115**, 885.
- 181 F. C. Meunier, J. P. Breen, V. Zuzaniuk, M. Olsson and J. R. H. Ross, *J. Catal.*, 1999, **187**, 493.
- 182 X. She and M. Flytzani-Stephanopoulos, *J. Catal.*, 2006, **237**, 79.
- 183 K.-I. Shimizu, M. Tsuzuki, K. Kato, S. Yokota, K. Okumura and A. Satsuma, *J. Phys. Chem. C*, 2006, **111**, 950.
- 184 A. Sultana, M. Haneda, T. Fujitani and H. Hamada, *Catal. Lett.*, 2007, **114**, 96.

- 185 H. He, Y. Li, X. Zhang, Y. Yu and C. Zhang, *Appl. Catal., A*, 2010, **375**, 258.
- 186 Q. Wu, Y. Yu and H. He, *Chin. J. Catal.*, 2006, **27**, 993.
- 187 Q. Wu, H. Gao and H. He, *Chin. J. Catal.*, 2006, **27**, 403.
- 188 A. Takahashi, M. Haneda, T. Fujitani and H. Hamada, *J. Mol. Catal. A: Chem.*, 2007, **261**, 6.
- 189 Q. Yu, X. Wang, N. Xing, H. Yang and S. Zhang, *J. Catal.*, 2007, **245**, 124.
- 190 C. A. Taatjes, N. Hansen, A. McIlroy, J. A. Miller, J. P. Senosiain, S. J. Klippenstein, F. Qi, L. Sheng, Y. Zhang, T. A. Cool, J. Wang, P. R. Westmoreland, M. E. Law, T. Kasper and K. Kohse-Höinghaus, *Science*, 2005, **308**, 1887.
- 191 N. Bion, J. Saussey, M. Haneda and M. Daturi, *J. Catal.*, 2003, **217**, 47.
- 192 N. Bion, J. Saussey, C. Hedouin, T. Seguelong and M. Daturi, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4811.
- 193 R. M. Ferullo, M. M. Branda, G. R. Garda and N. J. Castellani, *J. Mol. Catal. A: Chem.*, 2001, **167**, 115.
- 194 H. Gao and H. He, *Spectrochim. Acta, Part A*, 2005, **61**, 1233.
- 195 S. Tamm, H. H. Ingelsten and A. E. C. Palmqvist, *J. Catal.*, 2008, **255**, 304.
- 196 F. Thibault-Starzyk, E. Seguin, S. Thomas, M. Daturi, H. Arnolds and D. A. King, *Science*, 2009, **324**, 1048.
- 197 Y. Ukisu, S. Sato, A. Abe and K. Yoshida, *Appl. Catal., B*, 1993, **2**, 147.
- 198 Y. Ukisu, T. Miyadera, A. Abe and K. Yoshida, *Catal. Lett.*, 1996, **39**, 265.
- 199 S. Kameoka, T. Chafik, Y. Ukisu and T. Miyadera, *Catal. Lett.*, 1998, **55**, 211.
- 200 S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, *J. Catal.*, 2011, **281**, 98.
- 201 V. Zuzaniuk, F. C. Meunier and J. R. H. Ross, *J. Catal.*, 2001, **202**, 340.
- 202 R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1996, **61**, 627.
- 203 M. B. Smith and J. March, *March's Advanced Organic Chemistry Reactions, Mechanisms, and Structure*, Wiley-Interscience A John Wiley & Sons, Inc., Sixth edn, 2007, p. 784.
- 204 D. L. H. Williams, in *Advances in Physical Organic Chemistry 19*, ed. V. Gold and D. Bethell, Academic Press Inc., New York, 1983, p. 381.
- 205 A. Obuchi, C. Wögerbauer, R. Köppel and A. Baiker, *Appl. Catal., B*, 1998, **19**, 9.
- 206 H. He, Y. Yu, Y. Li, Q. Wu, X. Zhang, C. Zhang, X. Shi and X. Song, *Chin. J. Catal.*, 2010, **31**, 491.
- 207 F. C. Meunier and J. R. H. Ross, *Appl. Catal., B*, 2000, **24**, 23.
- 208 Q. Wu, H. Gao and H. He, *J. Phys. Chem. B*, 2006, **110**, 8320.
- 209 R. Burch, J. Breen, C. Hill, B. Krutzsch, B. Konrad, E. Jobson, L. Cider, K. Eränen, F. Klingstedt and L. E. Lindfors, *Top. Catal.*, 2004, **30–31**, 19.
- 210 M. Richter, U. Bentrup, R. Eckelt, M. Schneider, M. M. Pohl and R. Fricke, *Appl. Catal., B*, 2004, **51**, 261.
- 211 S. Satokawa, *Chem. Lett.*, 2000, 294.
- 212 J. P. Breen, R. Burch, C. Hardacre, C. J. Hill and C. Rioche, *J. Catal.*, 2007, **246**, 1.
- 213 X. Zhang, H. He and Z. Ma, *Catal. Commun.*, 2007, **8**, 187.
- 214 X. Zhang, Y. Yu and H. He, *Appl. Catal., B*, 2007, **76**, 241.
- 215 K. Eränen, F. Klingstedt, K. Arve, L.-E. Lindfors and D. Y. Murzin, *J. Catal.*, 2004, **227**, 328.
- 216 K. Eränen, L.-E. Lindfors, F. Klingstedt and D. Y. Murzin, *J. Catal.*, 2003, **219**, 25.
- 217 X. Shi, Y. Yu, H. He, S. Shuai, H. Dong and R. Li, *J. Environ. Sci.*, 2008, **20**, 177.
- 218 X. P. Song, C. B. Zhang and H. He, *Chin. J. Catal.*, 2008, **29**, 524.
- 219 Y. Li and F. Qi, *Acc. Chem. Res.*, 2009, **43**, 68.