

Review

Current Catalyst Technology of Selective Catalytic Reduction (SCR) for NO_x Removal in South Korea

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Abstract: Recently, air pollution has worsened throughout the world, and as regulations on nitrogen oxides (NO_x) are gradually tightened many researchers and industrialists are seeking technologies to cope with them. In order to meet the stringent regulations, research is being actively conducted worldwide to reduce NO_x-causing pollution. However, different countries tend to have different research trends because of their regional and industrial environments. In this paper, the results of recent catalyst studies on NO_x removal by selective catalytic reduction are reviewed with the sources and regulations applied according to the national characteristics of South Korea. Specifically, we emphasized the three major NO_x emissions sources in South Korea such as plant, automobile, and ship industries and the catalyst technologies used.

Keywords: environmental regulation; emission gas; nitrogen oxide; selective catalytic reduction; NO_x removal catalyst

1. Introduction

Climate change as a result of the promotion of industrialization and urbanization through economic growth around the world has increased awareness of the atmosphere. As a result, regulations are being tightened to release air pollutants to protect the air environment and the world faces mandatory challenges to reduce air pollutants [1–6].

Figure 1 shows the results of the measurement of particulate matter (PM_{2.5}) exposure concentration in Organization for Economic Cooperation and Development (OECD) countries in 2017. The average PM_{2.5} concentration from Figure 1 was about 12.5 µg/m³, which actually exceeds the average value of 34%, and South Korea recorded the highest concentration of PM_{2.5} [2].

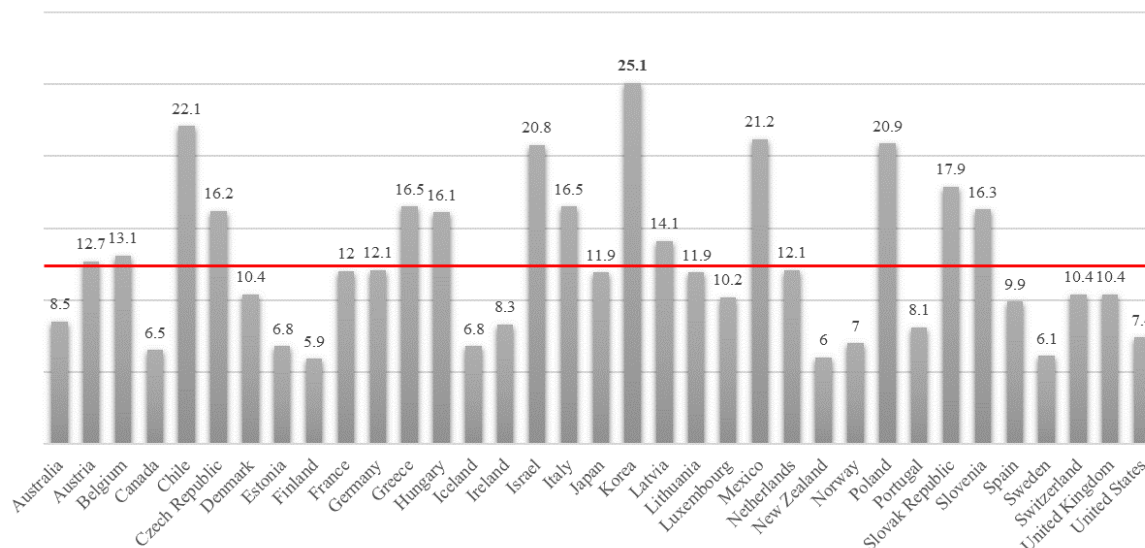


Figure 1. Concentration of PM 2.5 as per the Organization for Economic Cooperation and Development (OECD) countries in 2017 (Units: $\mu\text{g}/\text{m}^3$).

The atmospheric condition of South Korea is threatened by the increase of high concentration of fine dust. In particular, in March 2019, Seoul's monthly average PM 2.5 concentration reached its highest level since the observation, and an emergency reduction measure for high concentrations of fine dust was issued for seven consecutive days. With this issue, the human body is not only exposed to fine dust, but also crops and ecosystems and so on. A survey on the severity of fine dust among the people found that about 30% face very serious problems, and more than 60% are serious [3]. The public's anxiety also seems to increase because fine dust, an air pollutant, is the most easily and frequently encountered part of life. In response to this anxiety, the government's response is also strengthening in South Korea.

As a result of this, the world is working to reduce the substances that cause air pollution. BBC research predicts that the management market to reduce air pollution will grow by 2019, with DeNO_x systems the highest growth rate of 6.3% (Table 1). This aims to prevent the generation of additional particulate matter through the secondary chemical reaction of precursor materials (SO_x, NO_x, etc.) as well as the direct release of particulate matter.

Table 1. Recent history on global air pollution control equipment market by product type (\$ millions).

Type	2012	2013	2014	2019	CAGR *% 2014–2019
Flue gas desulfurization	14,882.1	15,523.1	16,850.2	21,573.0	5.1
Electrostatic precipitators	11,781.1	12,152.9	12,512.3	15,893.1	4.9
DeNO _x systems	10,482.0	11,089.9	12,538.3	17,044.0	6.3
Fabric filters	10,139.4	10,478.5	11,685.4	15,101.6	5.3
Scrubbers	4284.8	4324.1	4245.7	5230.3	4.3
Others	2877.6	2985.1	3106.3	3594.7	3.0
Total	54,447.0	56,553.6	60,938.2	78,436.7	5.2

* CAGR: Component Annual Growth Rate.

Nitrogen oxide (NO_x) is one of the secondary sources of fine dust (components: 59.3% of sulphates, nitrates, etc., carbon and soot 16.8%, minerals 6.3%, and other substances 18.6%), which causes chemical reactions in the atmosphere. The air pollution process due to NO_x is summarized in Figure 2. After

reaction with water, NO_x forms nitric acid in the atmosphere, causing acid rain, and in addition, photochemical smog, tropospheric ozone, and ozone layer destruction [1,5,6].

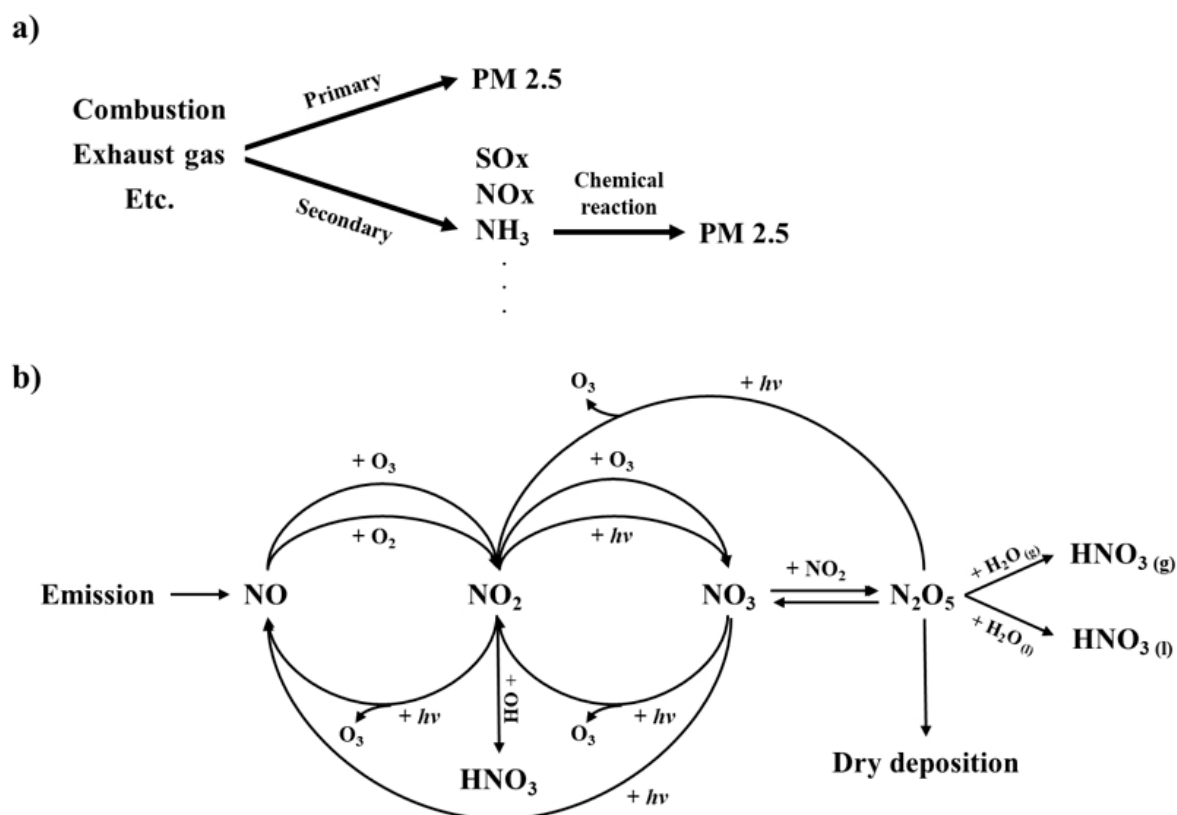


Figure 2. (a) PM 2.5 formation (b) atmospheric NO_x reactions [1].

The causes of NO_x emissions vary, so it is important to develop technologies to reduce NO_x , taking into account the local and industrial characteristics of each country. In South Korea, fine dust concentration mainly result from the influence of neighboring countries [7]. However, in order to reduce air pollutants emitted according to the industrial characteristics of South Korea, it is necessary to solve the problem through technology development.

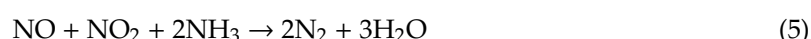
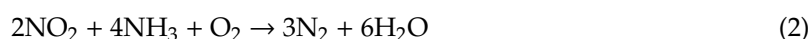
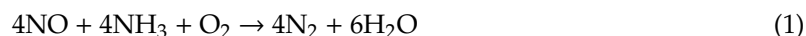
In this paper, we summarized the selective catalytic reduction (SCR) reaction that is commonly used and commercialized among many De NO_x technologies. In order to examine trends in NO_x reduction technology in consideration of the regional and industrial characteristics of South Korea, the changes in emission and environmental regulations according to emission sources in South Korea are examined. Moreover, the SCR catalytic technologies for NO_x removal in South Korea and the future research directions are discussed.

2. Selective Catalytic Reduction (SCR) for Nitrogen Oxide (NO_x) Removal

There are several technologies under investigation to remove NO_x , but the most standard removal of NO_x is the SCR process [8]. The SCR process is one of catalytic reactions, where single metal oxide, mixed metal oxides and supported metal oxides, and pure or metal-exchanged zeolites catalysts are generally used to convert nitrogen oxides (NO_x) into nitrogen molecule (N_2) and water (H_2O), which are harmless not only to human being but also the environment, by using suitable reducing agents such as ammonia, urea, hydrocarbon and hydrogen [9]. Although these reducing agents have their own advantages and disadvantages, they induce a strong decrease in the Gibbs free energy values. Likewise, the free energy values can be further reduced by the introduction of oxygen [10]. In order to protect the injected reducing agent, the SCR system is generally kept after a diesel oxidation catalytic bed. The reducing agents used for SCR process are summarized below with their mechanism.

2.1. Ammonia (NH₃-SCR Process)

The most common SCR process is the use of ammonia (NH₃) as the reducing agent. NH₃-SCR process is already commercialized around the world including South Korea and has many advantages such as flexible operating temperature, excellent redox properties and high thermodynamic stability over other reducing agents [11]. NH₃-SCR reaction may vary depending on the content of NO and NO₂ in the NO_x of the exhaust gas and the main chemical reactions in NH₃-SCR process are given below [12]:



Equations (1)–(5) are reactions of NH₃ and NO and NO₂ in the presence and absence of O₂, respectively, that result in decomposition of NO_x. The standard reaction is Equation (1), which occurs when NO_x consists only of NO. If there is only NO₂ in the exhaust gas, NH₃ reacts as in Equation (4), which is generally a slow reaction. In the case of Equation (5), NO_x substance is a fast reaction that occurs when NO and NO₂ are mixed in equimolar.

Many researchers suggested that metal oxides-based catalysts having both Lewis and Brønsted acid sites are good for the NH₃-SCR process [13]. NH₃ can be adsorbed on Lewis and/or Brønsted acid sites of the metal oxides and intermediates like adsorbed NH₃ or NH₄⁺ formed on Brønsted acid sites which were reacted with NO through Langmuir–Hinshelwood (L-H) mechanism producing N₂ and H₂O. The physically adsorbed NO is oxidized by metal ions to form nitrate as shown in the following reaction pathway (Figure 3) [14,15].

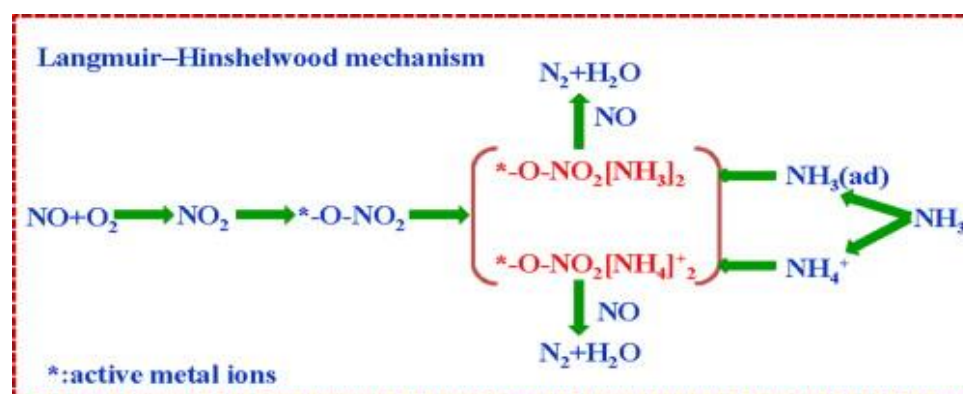


Figure 3. General reaction pathway for ammonia selective catalytic reduction (NH₃-SCR) on metal oxide catalysts. (Reprinted with permission from [15]. Copyright (2011) Elsevier).

The NH₃-SCR reaction mechanism (Figure 4) was proposed by Liu et al. for the FeTiO_x catalyst using different analytical techniques such as in-situ DRIFTS, transient response experiments and temperature programmed desorption of NH₃ [16]. In more detail, Brønsted acid sites were higher than Lewis acid sites at 200 °C, whereas the former sites transformed into Lewis acid sites at >200 °C through dehydroxylation on FeTiO_x. L-H mechanism is proposed at 200 °C (Figure 4A). NO oxidized into nitrate species on Fe³⁺ which was reacted with adjacent adsorbed NH₃ species on Ti⁴⁺-OH Brønsted acid sites to intermediate species (like ammonium nitrate), followed by a subsequent reaction with NO to produce N₂ and H₂O. At high temperature, a typical Eley–Rideal (E-R) mechanism is proposed for NH₃-SCR of NO_x (Figure 4B). In this mechanism, Fe³⁺ firstly reduced to Fe²⁺, which then re-oxidized to Fe³⁺ by O₂, to complete a redox cycle. In parallel, adsorbed NH₃ species activated into -NH₂ species

by Fe^{3+} via dehydrogenation, which react with NO to form an intermediate (NH_2NO), followed by a subsequent conversion into N_2 and H_2O .

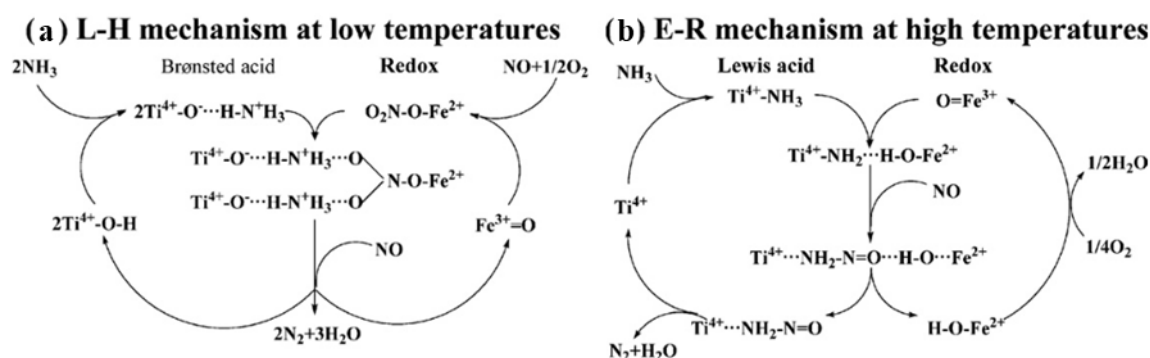


Figure 4. Representative NH_3 -SCR mechanisms over FeTiO_x catalyst at low (a) and high (b) temperatures. (Reprinted with permission from [16]. Copyright (2011) Elsevier).

Beside metal oxide catalysts, protonic and metal incorporated zeolites were also used for the NH_3 -SCR process whose reaction mechanism is explained well in a previous review paper [13]. For a representative reaction mechanism on zeolite-based catalysts, NH_3 -SCR reaction for NO/ NO_2 over a commercial Fe-ZSM-5 catalyst was shown in Figure 5. Results were demonstrated that the intermediates of NH_4NO_2 or NH_4NO_3 species, in which NH_4NO_2 decomposes to N_2 and H_2O . On the other hand, NH_4NO_3 can directly decomposed to generate N_2O and H_2O [17].

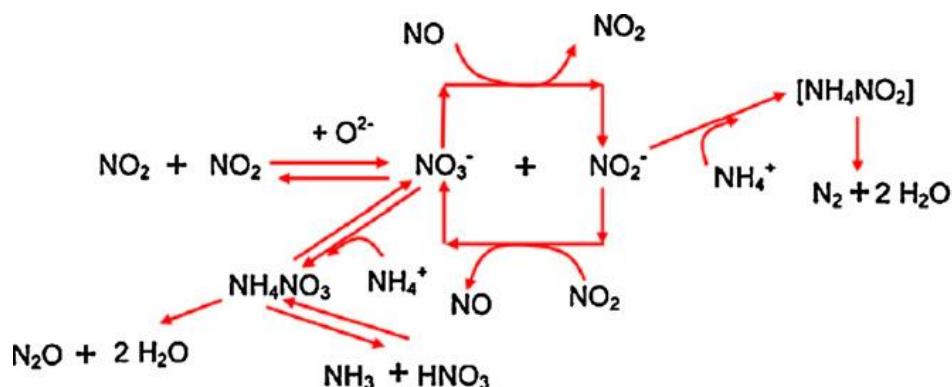


Figure 5. Proposed reaction scheme for NO and NO_2 NH_3 -SCR over commercial Fe-ZSM-5. (Reprinted with permission from [17]. Copyright (2008) Elsevier).

Although this NH_3 -SCR process is a well-established technology in the various parts of South Korea (for instance Pyeongtaek, Incheon and Ulsan) [18], the use of an expensive reductant, and transportation and storage of NH_3 , besides some toxic unwanted products, are problems related to the process [8,19].

2.2. Urea (Urea-SCR Process)

To avoid handling hazardous and corrosive NH_3 , urea can be used as a reducing agent that is easy to handle as aqueous solutions (Iskan City of South Korea used 40% aqueous urea-based SCR technology [18]). Urea, a large-scale commodity chemical, was considered as an NH_3 precursor for SCR technology. Generally, urea solution decomposes at elevated temperature to NH_3 in the hot exhaust gas via two-step reactions as shown in the following Figure 6:

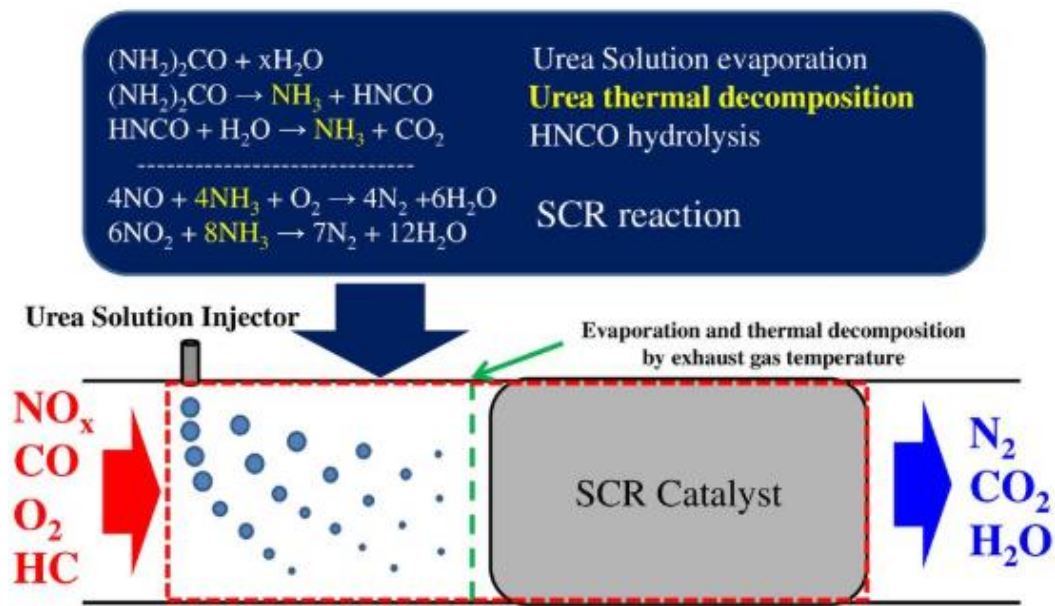


Figure 6. General reaction pathway for urea-SCR process [20].

Also, as shown in Figure 7, the concept adopted by Kwangsung Co. Ltd. (Gimhae, Korea) for marine/offshore using urea-SCR system [21].

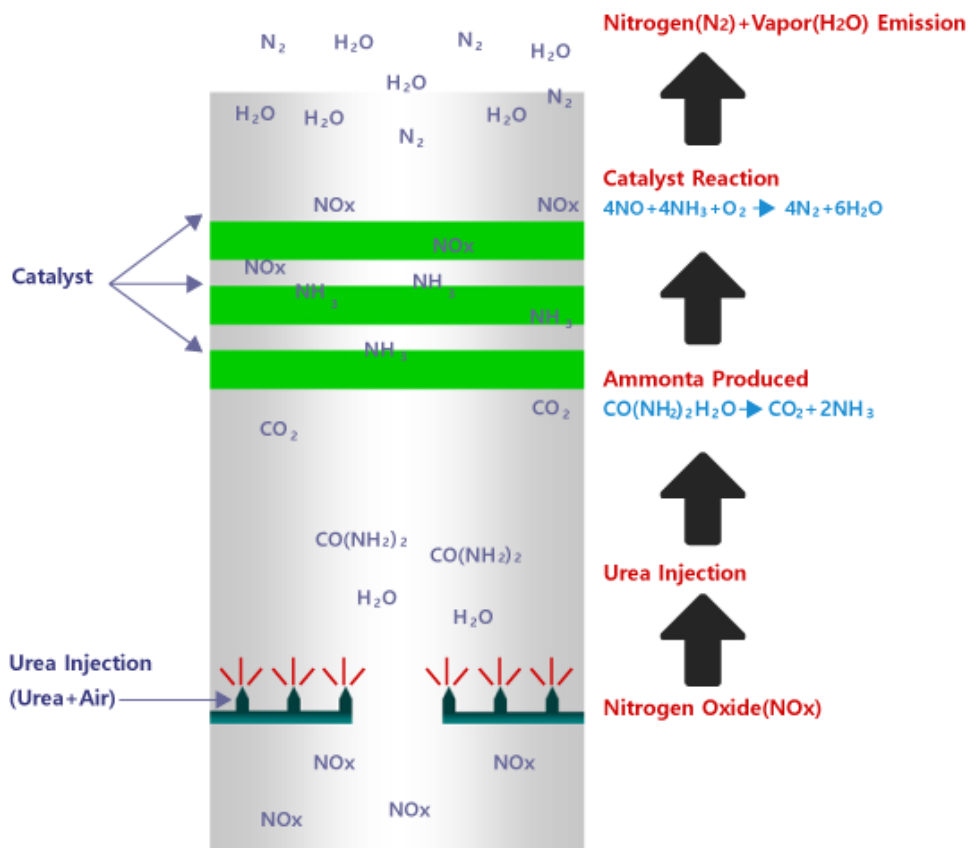


Figure 7. Conceptual design of Kwangsung Co. Ltd. for marine/offshore using urea-SCR process [21].

Figure 8 shows a urea decomposition reaction to ammonia and isocyanic acid (HNCO), which usually occurs under thermal reaction even without any catalysts [22], along with two byproducts namely biuret and cyanuric acid at moderate temperature of 300 °C. HNCO is a stable intermediate

species in the gas phase but hydrolyzes to NH_3 and CO_2 on the $\text{TiO}_2/\text{ZrO}_2$ -based SCR catalyst. Also, smaller amounts of undesired stable products, for instance ammeline, ammeline and melamine were formed by substitution of the OH groups of cyanuric acid with one, two and three NH_3 groups respectively [23].

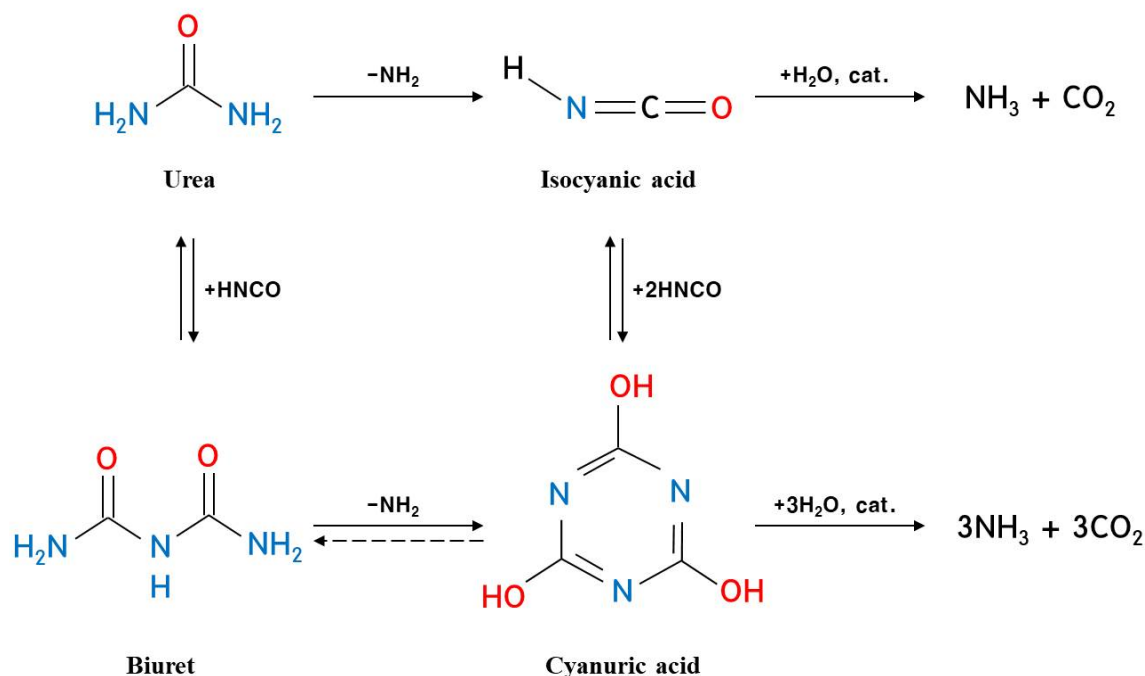


Figure 8. Reaction scheme for urea decomposition, including the two byproducts biuret and cyanuric acid [22].

Different catalytic activities were observed with and without water on urea hydrolysis and thermolysis [24,25]. The order of catalyst activities according to the reaction is:

Urea thermolysis: $\text{TiO}_2 > \text{H-ZSM-5} \approx \text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{SiO}_2$

Urea hydrolysis: $\text{ZrO}_2 > \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{H-ZSM-5} > \text{SiO}_2$

Although urea is non-toxic and cheaper than NH_3 , aqueous solution of urea is more difficult to dose and to mix with the exhaust gas than NH_3 which make urea decompose incompletely and deactivate the SCR catalyst [22].

2.3. Hydrocarbon (HC-SCR Process)

Hydrocarbons added to or contained in emissions can also be used as an alternative reducing agents [26]. Hydrocarbons such as methane, propane and propene appear to have excellent catalytic activity, and in particular, the selectivity of nitrogen is excellent [9,10]. The main advantage is the use of a hydrocarbon gas or its mixture very similar to that found in exhausts besides low cost and feasibility. Generally, three major reaction steps are involved during the hydrocarbon-SCR (HC-SCR) process [27]. As shown below, (a) NO decompose into N_2 (Equation (6)) and then hydrocarbons attack by the surface oxygen, or hydrocarbon oxidation to adjust the oxidation state of metal ion catalyst (Equation (7)), (b) the hydrocarbon intermediate (HC^*) formed is able to reduce NO_x selectively (Equations (8) and (9)), and (c) NO_2 , formed from NO and O_2 , reduced preferentially by hydrocarbon species to form N_2 (Equations (10) and (11)).





Zeolites containing a Modernite Framework Inverted (MFI) structure seems to be good for the HC-SCR process, although few studies on Ferrierite structure was also reported [19]. For instance, Mn-ZSM-5 and Fe-ZSM-5 were used to remove NO_x with methane and propane as the reducing agents, respectively. Lobree et al. proposed a possible mechanism on Fe-ZSM-5 for the reduction of NO by propane (C_3H_8) in the presence of O_2 (Figure 9) [28]. Fe^{2+} (actually $\text{Fe}^{2+}(\text{OH}^-)$) reacts with O_2 to form $\text{Fe}^{3+}(\text{O}_2^-)$. NO is oxidized to NO_2 which is then adsorbed on the Fe^{3+} catalysts surface, followed by reaction with propane. Intermediates of CN and NCO were formed from $\text{C}_x\text{H}_y\text{NO}$, of which CN react faster with NO_2 to form N_2 and carbon-containing combustion products via the oxidation or the hydrolysis reaction [9].

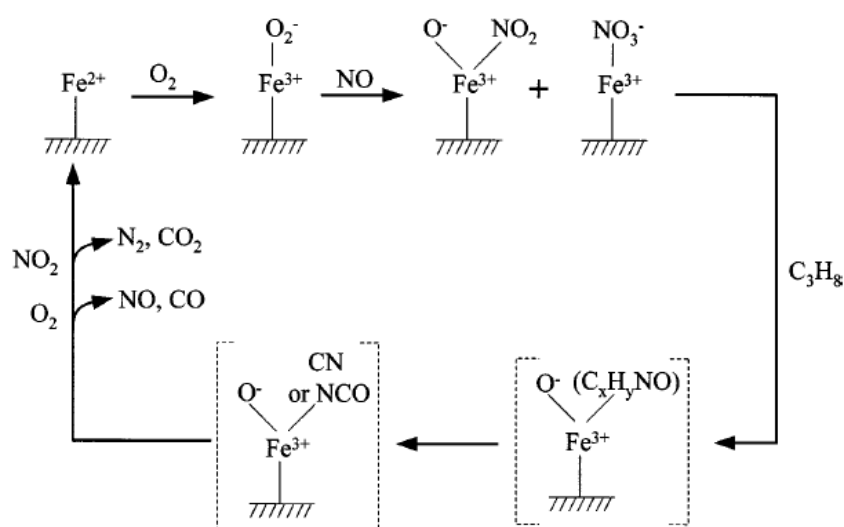


Figure 9. Proposed mechanism for the reduction of NO by propane (C_3H_8) over Fe-ZSM-5. (Reprinted with permission from [28]. Copyright (1999) Elsevier).

Some studies on alumina-based catalysts ($\text{Cu-Al}_2\text{O}_3$ and $\text{Ag-Al}_2\text{O}_3$) were also reported for the removal of NO_x [29]. Nitrates obtained from NO_x adsorbed on the $\text{Cu-Al}_2\text{O}_3$. The acetate species may form via the partial oxidation of propene (C_3H_6) with O_2 and possibly with nitrates. The acetate formed acts as a surface reductant that reduces nitrates to N_2 via the well-known possible CN and NCO intermediates (Figure 10) [30]. The different catalysts used and their deactivation phenomena for HC-SCR process can be found in a recent review article [10].

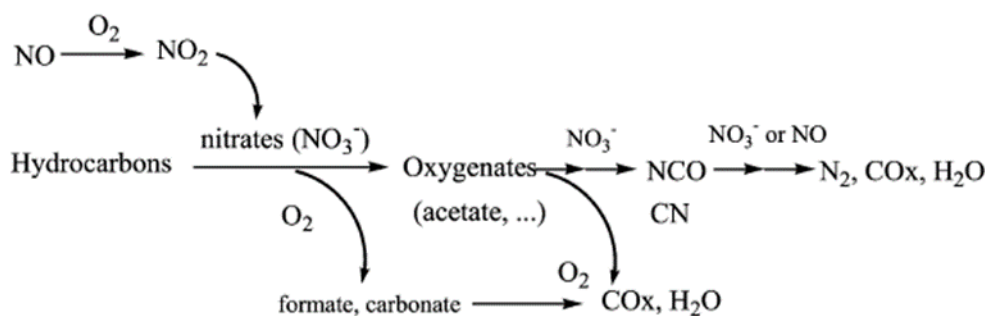


Figure 10. Proposed mechanism of C_3H_6 -SCR over $\text{Cu-Al}_2\text{O}_3$ catalysts [30].

2.4. Hydrogen (H_2 -SCR Process)

Compared with the NH_3 -, urea- and HC-SCR processes, H_2 -SCR has attracted more attention for NO_x removal. Hydrogen (H_2), a clean environmental fuel, generates only water without inducing secondary pollutants such as CO_2 , after its combustion with air [31]. Hydrogen can be produced from the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) in the realistic exhaust gas [32]. During the H_2 -SCR process, the main reactions that can occur are as follows [31]:



Equation (12) is the most desired reaction as NO reacts with H_2 to produce N_2 and H_2O . However, as per Equations (13) and (14), N_2O produced as a byproduct during reactions of two NO molecules with three H_2 molecules. NH_3 and/or NH_4^+ species were considered as an important intermediate species (Equation (15)) for the H_2 -SCR reaction, although the presence of oxygen can inhibit its formation on selective catalysts [31,32]. Shibata et al. [33] used in-situ IR studies and found that the intensity of the NH_4^+ band on the Brønsted acid sites of Pt/MFI was closely related to the H_2 -SCR catalytic activity. However, NH_4^+ band intensity decreased quickly when the hydrogen gas supply was cut off, attributed that NH_4^+ species highly active with NO and O_2 . The NH_4^+ species likely to be formed between the reaction of adsorbed N, which was obtained from the dissociation of NO, and the active hydrogen on the Pt sites. The complete reaction scheme of H_2 -SCR over Pt/MFI is shown in Figure 11.

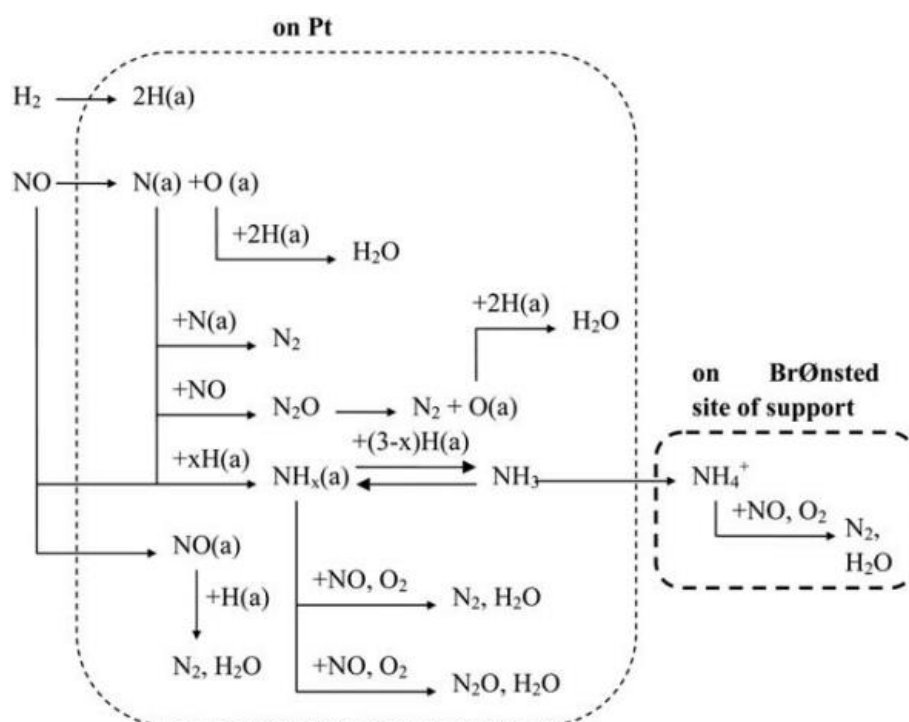


Figure 11. Proposed reaction scheme for H_2 -SCR over Pt/Modernite Framework Inverted (MFI) catalyst [33].

Pt and Pd metals show a high activity for H₂-SCR at low temperature. The nature of supports and their intrinsic acidity greatly affect the activity of NO_x reduction and selectivity to N₂/N₂O [34]. The details of the active metals, and their supports and degree of deactivation rate for H₂-SCR were already covered in past review papers [31,32,34]. As far as we know, no South Korean industries have utilized both HC- and H₂-SCR processes until now. However, with strict regulation by the government, we are anticipating some initiation from heavy industries of using those processes which will reduce unwanted pollutants such as CO₂, a key greenhouse gas.

3. Recent SCR Technology Status for NO_x Removal in South Korea

3.1. NO_x Emission Sources

South Korea's Clean Air Policy Support System (CAPSS) source classification system for nitrogen oxides (NO_x) has been adopted based on the European CORINAIR Source Classification System (SNAP 97). The classification system has been changed to 13 major categories according to the NO_x emission conditions in South Korea since 2007, and is summarized in Table 2 along with the source classification codes (SCC) and details for each item. Figure 12 shows the NO_x emissions of South Korea from 2010 to 2016 according to the CAPSS source classification system [35]. As a result, total NO_x emissions are estimated to increase by 31,183 tons per year from 1,061,210 ton/yr (2010) to 1,248,309 tons/yr (2016). According to the type of source, the results in 2016 show that the ratio of mobile pollutant sources (on-roads (07) and non-roads (08)) was the highest, accounting for 61% (89,000 tons), the largest increase in the last six years, which led to the increases of the total NO_x emissions. NO_x emitted through the combustion process (energy industry (01), non-industry (02), manufacturing industry (03)), which account for the second highest NO_x emissions with about 33% of the total emissions, maintaining more than 400,000 tons annually. Other production processes (04), waste treatment (09) and cotton pollutants (11) produced approximately 78,000 tons of NO_x, and no NO_x emissions for SCC (05), (06), (10), and (12) were calculated. The results of NO_x emissions discussed above are based on air pollutant classification, and when the NO_x emissions are classified by different regions of South Korea, the order of the sources that emit the NO_x may partially change. Therefore, Lim et al. [36] pointed out that there is a need for an efficient air-quality management policy, not a policy focused only on urban areas, because of regional differences in emission characteristics.

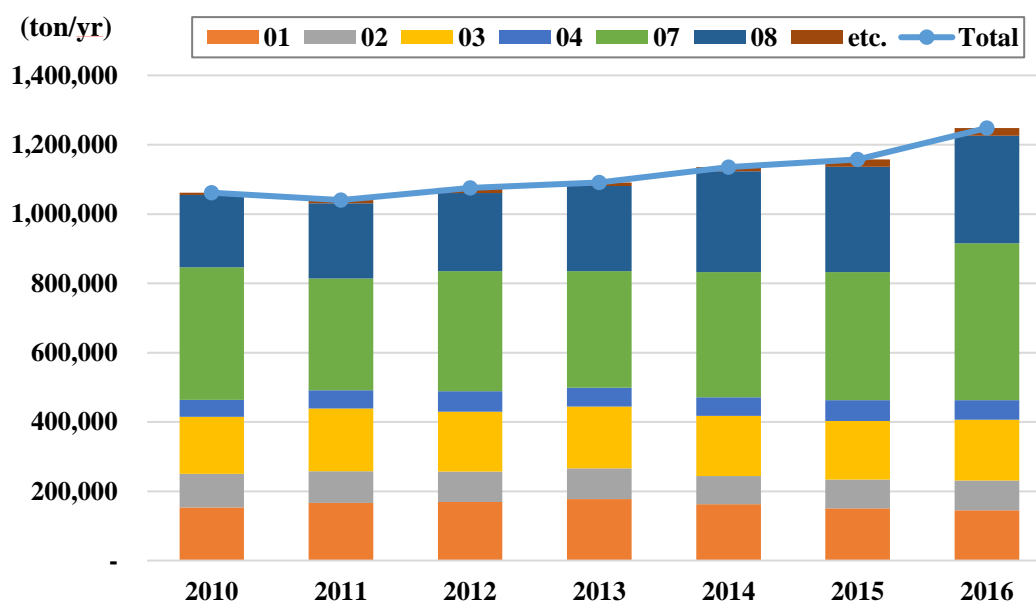


Figure 12. NO_x emission sources in South Korea from 2010 to 2016 [35].

Table 2. Categories of NO_x emission sources in South Korea [35].

SCC	Major Categories of Emission Sources	Details
(01)	Energy industrial combustion	Public and private power generation facilities, district heating facilities, oil-refining facilities
(02)	Non-industrial combustion	Commercial and public institutions, residential facilities, agriculture, livestock and fisheries facilities
(03)	Manufacturing combustion	Combustion facilities, furnaces, etc.
(04)	Production process	Petroleum products, industry, steelmaking, inorganic chemicals manufacturing, organic chemicals manufacturing, wood, pulp manufacturing, food and beverage processing, other manufacturing
(05)	Energy transport and storage	gasoline supply
(06)	Use of organic solvents	Painting facilities, washing facilities, laundry facilities, other organic solvents
(07)	On-road vehicles	Passenger cars, taxis, vans, buses, vans, special vehicles, motorcycles
(08)	Non-road vehicles	Railway, ship, aviation, agricultural machinery, construction equipment
(09)	Waste incineration	Incineration, other waste disposal
(10)	Agriculture	
(11)	Other sources	Other things
(12)	Scattering dust	dust road, construction activity
(13)	Bio-combustion	

SCC: Source Classification Codes.

3.2. NO_x Environmental Regulations

Regulations for NO_x in South Korea follow the legislation amended by international organizations or the Korean Ministry of Environment. In general, fixed sources such as the chemical industry and power generation units have strong regional characteristics, so they follow emission allowances issued by environmental ministries in each country, but mobile sources (i.e., on-roads and non-roads vehicles) are not limited by the regulations of one country.

The Air Environment Conservation Act promulgated by the Ministry of Environment is followed for the fixed pollution sources. Recent revisions of regulations show a significant reduction in emission limits of NO_x and SO_x from 2020, as compared to 2019, as shown in Figure 13. Emission allowance standards applied to workplaces may vary depending on the nature of installed facilities. Under the current law, the NO_x emission limit was 20–530 ppm, but according to the revised law from 2020, the value is strengthened about 28%. The details of DeNO_x facilities and their fuel type can be found in Appendix 8 of the Enforcement Regulations of the Air Quality Conservation Act (Table 3). In addition, due to the higher NO_x emission level than the actual allowance standard, the air emission control panel fixed the penalty amount of 2130 won/kg of NO_x [37]. In South Korea, the regulations in plant industry (boilers and power generation) were established at 2000, though the regulations are gradually strengthened every year. For instance, the allowable concentration of NO_x for power generation facilities (shown in Table 3) has been significantly reduced since 2015, which is more than twice the previous year's limit of NO_x emission.

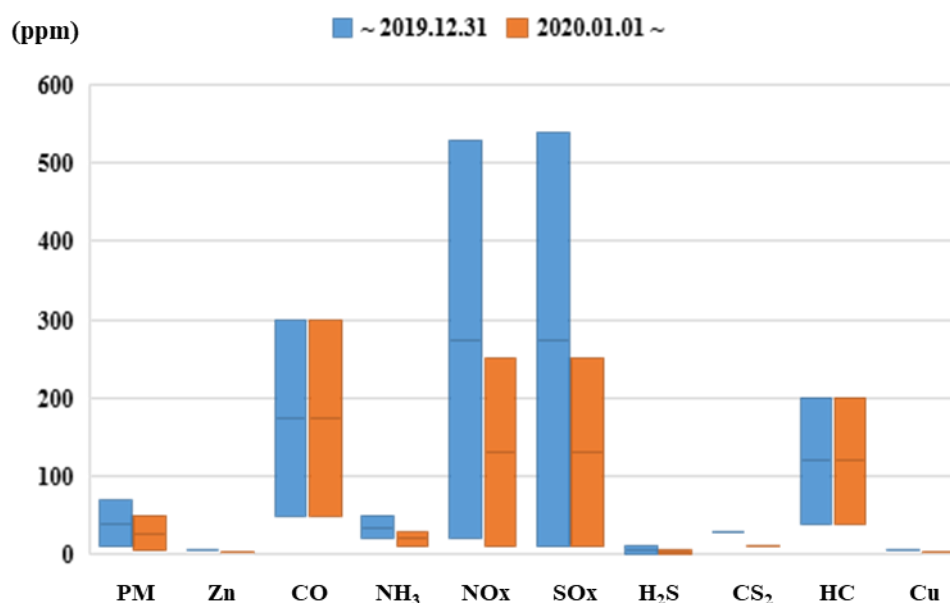


Figure 13. General air pollutants with emission standards in South Korea.

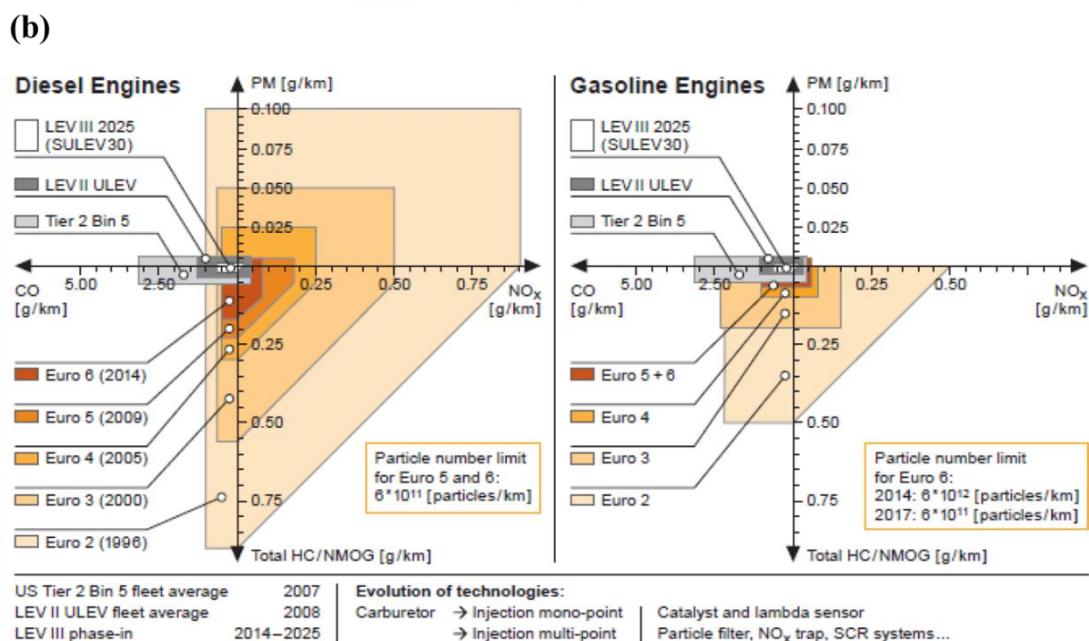
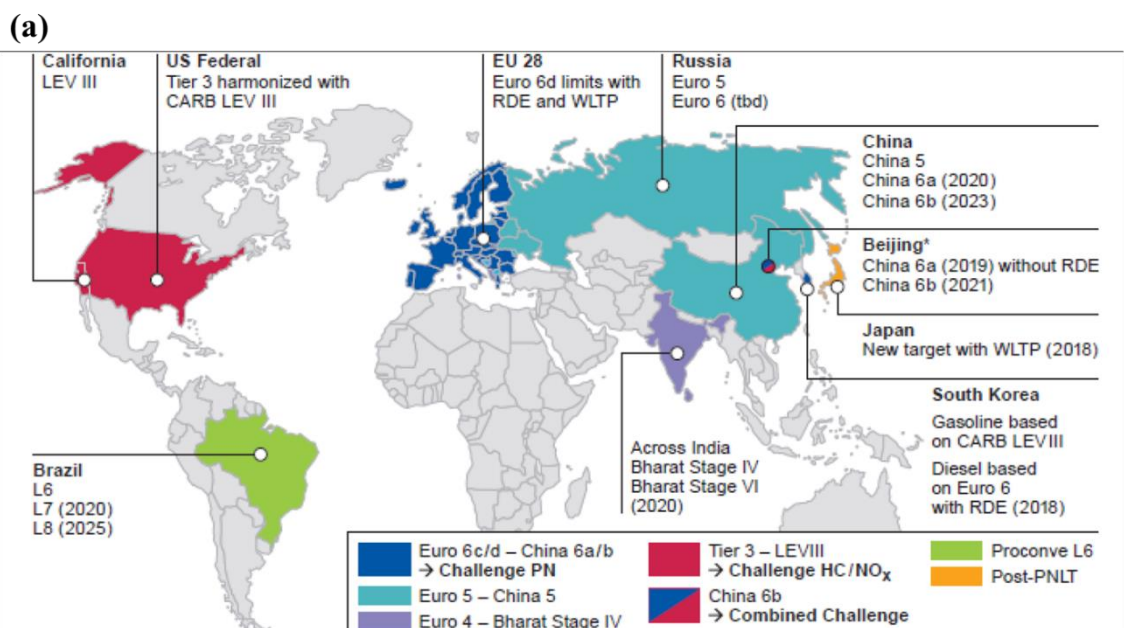
Table 3. The standard for the emission of NO_x in South Korea.

Facility	Fuel Type	Installation Period	NO _x Emission Standard [ppm]
Boiler	Liquid ⁽¹⁾	~2001.06.30	130
		2001.07.01~2014.12.31	70
		2015.01.01~	50
	Solid	~2007.01.31	120
		2007.02.01~	70
	Gas ⁽¹⁾	~2014.12.31	150
2015.01.01~		40	
Power generation	Liquid ⁽²⁾	~2001.06.30	530
		2001.07.01~2014.12.31	270
		2015.01.01~	90
	Solid ⁽³⁾	~1996.06.30	70
		1996.07.01~2014.12.31	50
		2015.01.01~	15
	Gas ⁽⁴⁾	~2001.06.30	80
		2001.07.01~2014.12.31	50
		2015.01.01~	20

Source: Clean Air Conservation Act (Article 16 Appendix 8) in South Korea. ⁽¹⁾ For the case of evaporation rate is over the 40 tons/h or calorific quantity is over the 24,760 kcal/h. ⁽²⁾ For case of internal combustion engine for power generation (diesel). ⁽³⁾ For the case of generation capacity is over the 100 MW. ⁽⁴⁾ For the case of the internal combustion engine for power generation (include gas turbine).

Mobile pollution sources, namely on-road and non-road vehicles, are the largest producers of NO_x emission in South Korea. Automobiles are mainly responsible for the on-road pollution sources, whereas ships are majorly contributors to the non-road pollution sources. The emission standards for automobiles and ships in South Korea are typically in accordance with international regulations specified by the United States (US) and Europe (Figure 14a,b). Regulations for automobiles are based on the Super Ultra-Low Emission Vehicle (SULEV) standard, which is the ultra-low emission vehicle

standard for Californian gas emissions of gasoline and gas vehicles. This is the world’s strongest standard, aiming to reduce 90% of the existing models. In the case of diesel cars, the European Union’s standards are applied, which are in line with the recent rise in the regulatory level [37–39].



(c)

Fuel type	Emission Standards														
	~	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
Gasoline		ULEV								SULEV					
LPG		ULEV								SULEV					
Diesel		EURO 4			EURO 5				above EURO 6						

Figure 14. NO_x Emission standard of on-road vehicles on worldwide (a,b) and South Korea (c) [37–39].

In 2000, the regulation standards of emission control from the United States and Europe were introduced to Korea, and they were applied almost similar to Korea since 2010. NO_x emission regulations have been significantly strengthened since 2006, with the emission standards of vehicles classified as gasoline, liquefied petroleum gas (LPG) and diesel vehicles (Figure 14c). The certification test methods applied in the same New European Driving Cycle (NEDC) modes as Europe, starting with the introduction of Euro-3 in 2002 and the application of Euro-4 criteria in 2006 (Figure 15) [40].

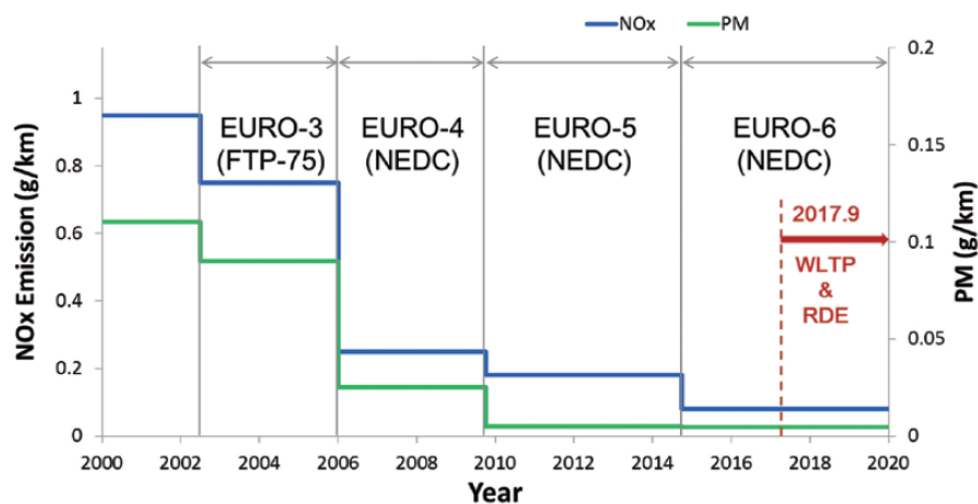


Figure 15. NO_x emission standard for lightweight diesel vehicles in South Korea [41].

In the case of regulations applied to ships, the total tonnage of ships that enter and leave in South Korean ports was increased to 5.6% in 2016 as compared to the previous years. Of the total, the portion of oceangoing ship amounts are 89% (Figure 16). Therefore, due to the nature of foreign ships that have to pass through various countries and international waters, the regulations on the emission of NO_x for domestic ships also relate to international regulations.

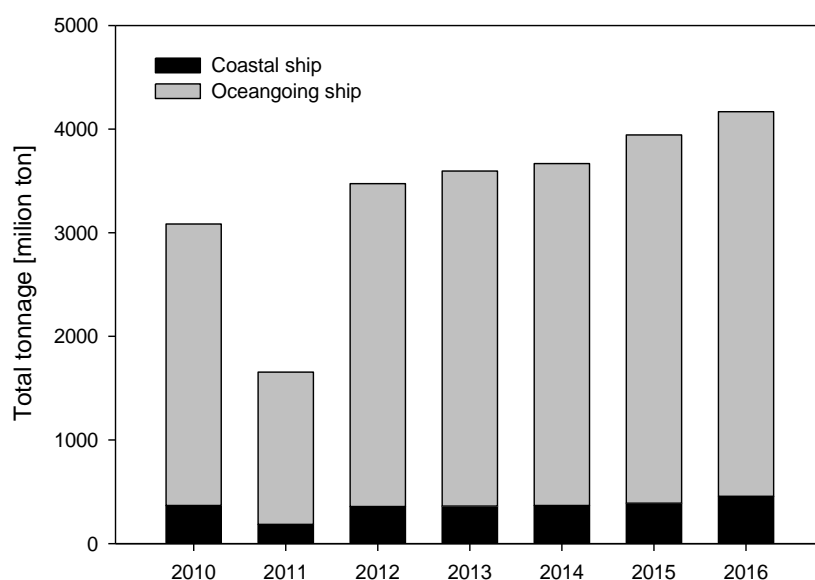


Figure 16. Status of ship entry and exit in South Korea [42].

As per Annex VI of the Convention on the Prevention of Marine Pollution (MARPOL), the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO) has applied the emission regulations of NO₂ from diesel engines at international ports since 1 January 2000. The regulatory standard has been applied to reduce nitrogen oxide emissions by 78%, which

may be less than 3.4 NO_x g/kWh, or less than the amount emitted by the existing Tier II (Table 4 and Figure 17). In addition, according to the Annex VI of MARPOL, the North American and Caribbean waters are now designated as a nitrogen oxide control area and are considering further expansion to the North Sea and Baltic Sea [43].

Table 4. The status of emission regulations of NO_x in the Convention on the Prevention of Marine Pollution (MARPOL).

Period		~2000.01.01	2011.01.01~2015.12.31	2016.01.01~
Classification	RPM (n)	Tier I	Tier II	Tier III
Outside ECA	$n < 130$	17.0	14.4	
	$130 \leq n < 2000$	$45.0 \times n (-0.2)$	$44.0 \times n (-0.23)$	
	$2000 \leq n$	9.8	7.7	
ECA (North America, Puerto Rico, Virgin island)	$n < 130$	17.0	14.4	3.4
	$130 \leq n < 2000$	$45.0 \times n (-0.2)$	$44.0 \times n (-0.23)$	$9.0 \times n (-0.2)$
	$2000 \leq n$	9.8	7.7	2.0

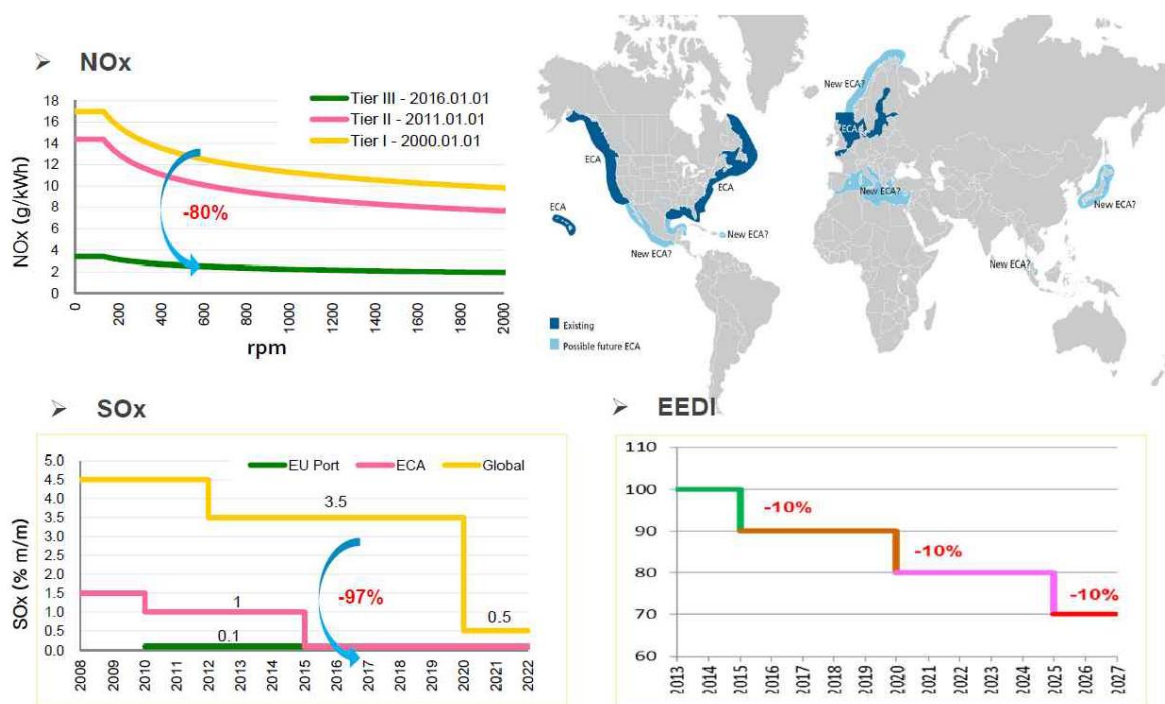


Figure 17. The status of NO_x and SO_x emission limitation [43].

In the case of the SCR system for NO_x reduction, not only is the regulation different for each emission source but also the composition of exhaust gas is different. To remove NO_x, the catalytic technology can be classified into three broad categories: environmental catalysts (to remove NO_x emitted after chemical processes), automotive catalysts (to remove NO_x from automotive exhaust gases), and marine catalysts (for NO_x reduction in the marine industry). Therefore, the technology trends of South Korea responding to the tightened NO_x emission regulations are summarized in the following section.

3.3. Research Trends of SCR Catalysts for DeNO_x

3.3.1. Power Plants

In power plants, an increase of DeNO_x catalyst layer is directly proportional to the efficiency of nitrogen oxide removal. The power plants of South Korea are removing nitrogen oxides in the exhaust gas using SCR method. Most SCR plant units are often designed to be equipped with four-layer catalysts, though only two layers are now filled with catalyst to satisfy the emission criteria. A four-layer SCR catalytic system also displayed a good efficiency for removal of NO_x. However, they suffered a pressure drop, due to additional catalytic layers, which increased not only the overall cost of the DeNO_x process but also the ammonia distribution in the nozzle of ammonia injection facility [44].

According to the Korea Electric Power Exchange's statistics in 2018, the capacity of thermal power plants using gas and coal as raw materials accounts for about 69% of the total capacity (Table 5). While the number of thermal power generators using gas and coal as raw materials, accounting for 73% of the total number of main power generators. With this power industry environment, the thermal power has a higher number of operating days as compared to other sources of power generation, especially 81.53% for coal-fired power generation (Table 6) [45].

Table 5. Status of main power generator in South Korea [45].

Classification	The Capacity of Facility [MW]	Number of Generator
Nuclear	21,850	23
Coal	35,408	61
Gas	37,837	236
Water	6282	57
Oil	4104	31
Total	105,481	408

Table 6. Rate of operation by power generator in South Korea [45].

Classification	Total	Nuclear	Coal	Gas	Water	Oil
2014	70.01%	82.39%	90.07%	61.53%	20.32%	27.81%
2015	66.85%	84.82%	90.33%	48.82%	16.12%	38.02%
2016	67.80%	81.26%	87.54%	49.85%	26.86%	48.52%
2017	65.33%	73.82%	85.44%	50.32%	30.66%	31.95%
2018	63.98%	65.31%	81.53%	55.16%	37.68%	26.39%

The exhaust gas treatment facility of coal-fired power generation requires stable performance for a long period of time. In order to preserve long-term stability, the presence of proper catalysts in coal-fired power-generating SCR facilities is highly recommended. Therefore, long-term stability of operation is required for catalyst injection into power-generating SCR facilities. In addition, for boilers used in thermal power generation, the temperature of the boiler exhaust is higher than 500 °C which is enough to operate any catalyst. However, due to its higher temperature, the SCR catalyst may deactivate during long-term operation. Therefore, since 2000s, when SCR facilities were supplied to South Korea, various studies have been conducted for stable operation of the SCR catalyst.

The catalysts used in the SCR process are V₂O₅-WO₃ (or MoO₃)/TiO₂ have honeycomb and plate type structures (Figure 18). In particular, the V₂O₅-WO₃ (or MoO₃)/TiO₂ monolith catalyst of the honeycomb type has been consistently used as it has advantages such as high heat and mass transfer rates besides high contact area [46].

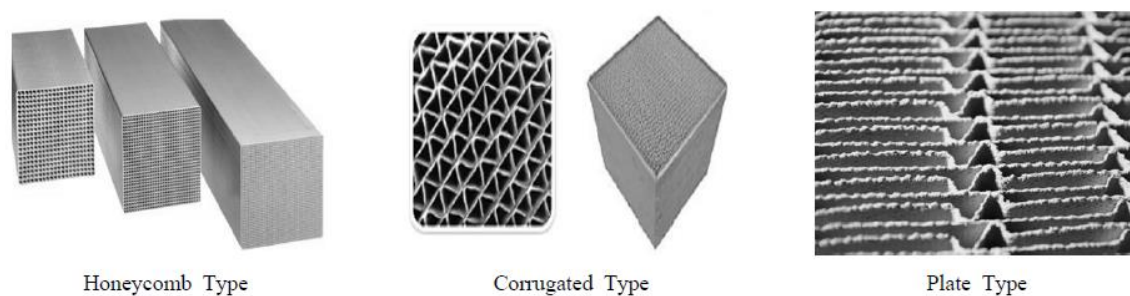


Figure 18. General types of SCR catalyst [47].

Looking at the amount of installation of SCR catalyst in South Korea in 2015 (Table 7), the subsidiary power plant of the Korea Electric Power Corporation (KEPCO) is approximately 21,758 m³, and third-party power plant usage is estimated to be around 4786 m³. The total use of SCR catalyst for domestic power plants and incinerators is roughly around 26,660 m³ [47].

Table 7. The status of installed SCR catalyst in South Korea (2015) [47].

Classification	Cat. Type	Total Amount of Installed SCR Catalysts [m ³]
KEPCO and Subsidiary	Honey comb	6462
	Plate	13,125
	Corrugate	2171
Other company	-	4786
Incineration plant	-	95
Total		26,660

Huang et al., according to V₂O₅ content, investigated the thermal behavior of V₂O₅/TiO₂ catalyst. They changed the pretreatment temperature of the catalyst from 250 to 500 °C. Through this experiment, they reported that at temperatures above 400 °C the phase transition of V₂O₅ occurred and condensation caused the decrease of the specific surface area (Figure 19) and hence of the catalytic activity [48].

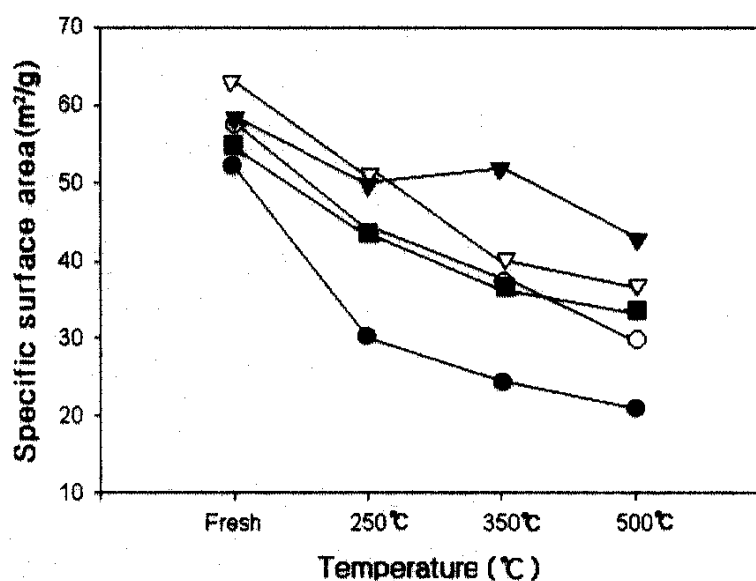


Figure 19. Effect of catalyst sintering temperature on specific surface area: (■) 0 wt%, (●) 1.0 wt%, (○) 3.0 wt%, (▼) 5.0 wt% and (▽) 10.0 wt% with V₂O₅ content in the catalyst [48].

Cha et al. investigated the thermal deactivation characteristics of $V_2O_5-WO_3/TiO_2$ catalyst of plate-type. They reported that when the catalyst calcined at temperatures above 600 °C, the NO_x conversion rate was dramatically reduced (Figure 20). The XRD analysis results showed that the crystalline structure of TiO_2 changed from anatase to rutile, and the surface area and the contribution of the catalyst was significantly reduced at those temperatures due to the formation of $CaWO_4$ and TiO_2 crystals, which were confirmed by scanning electron microscope (SEM) images (Figure 21) [49].

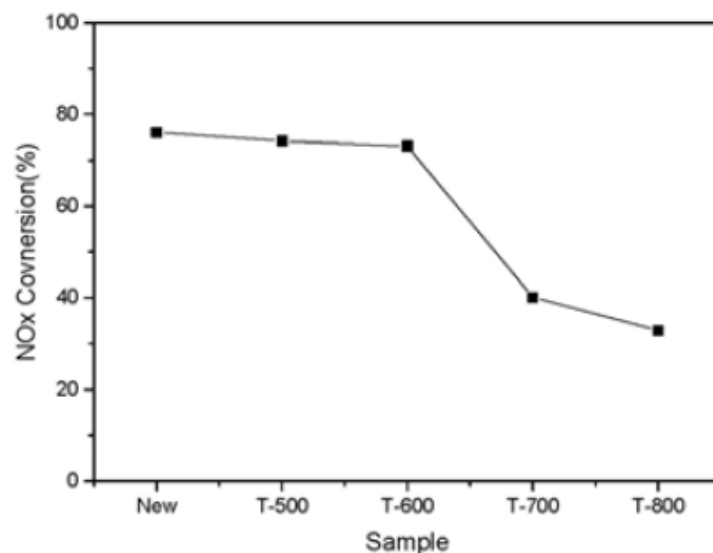


Figure 20. NO_x conversion of plate type SCR catalyst at different calcination temperature [49].

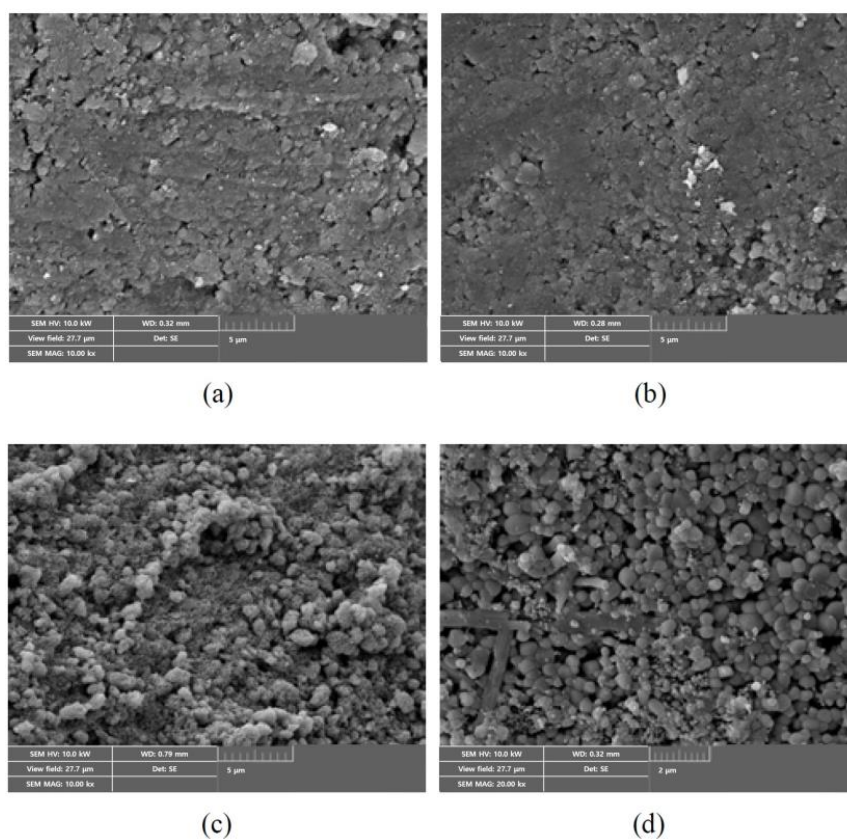


Figure 21. Microstructure of catalysts surface at different calcination temperature: (a) new, (b) T-600, (c) T-700, (d) T-800 [49].

Nam et al. conducted a study on the high-temperature SCR reaction using W/TiO₂ catalyst. They found that TiO₂ alone showed a conversion rate of NO_x of less than 50% at temperatures above 500 °C. However, addition of W with 13 wt% into TiO₂ showed an increased SCR efficiency, but more than 13 wt% content of W on TiO₂ led to lower efficiency. W(13)/TiO₂(B) (where W content is 13 wt% and B = pure anatase) catalyst was pretreated at 600 °C and then loaded SCR reaction operated at 500 °C and 550 °C. The catalytic activity was stable even after more than 900 h (Figure 22) [50].

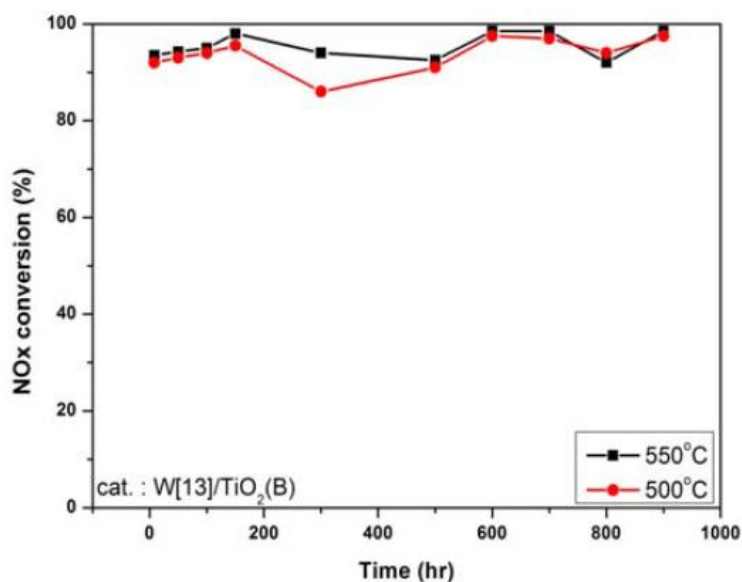


Figure 22. The effect of thermal aged on NO_x conversion over W [13]/TiO₂(B) (Reaction condition: NO_x: 400 ppm, NH₃/NO_x: 1.0, O₂: 8 vol%, H₂O: 8 vol%, Space velocity (S.V): 60,000 h⁻¹) [50].

Except for liquefied natural gas (LNG), most fossil fuels contain significant amount of sulfur dioxide within the exhaust gas after combustion of these fuels. SO₂ may be oxidized into SO₃ in the presence of catalysts, which converted again into SO₄⁻ species on the catalyst surface. The new species formed inhibits the catalytic active sites, or SO₄²⁻ species may be combined with NH₄⁺ to create salt, NH₄HSO₄. This salt also made it possible to cover the catalyst active species, and thus greater catalytic deactivation was observed in the presence of SO₂ [51].

Lee et al. carried out studies to enhance SCR reactivity in the presence of SO₂ on the V/TiO₂ catalyst. They showed different SCR conversion rates and SO₂ durability results depending on the vanadium content. The NO_x conversion was increased by increasing the vanadium amount (from 0.5 to 3.0 wt%) on TiO₂, whereas the relative activity for SCR of NO_x in the presence of SO₂ followed an opposite trend (Figure 23). They have also tested the relative activity for SCR after the addition of 5 wt% W into the optimized V[2]/TiO₂ (i.e., V[2]W[5]/TiO₂) catalyst which displayed an improved performance of NO_x in the presence of SO₂ 500 ppm (Figure 24a) [52]. It was observed from SO₂-Temperature Programed Desorption (TPD) (Figure 24b) that the desorption peak was shifted to lower temperature on V[2]W[5]/TiO₂ catalyst as compared with that of W-free catalyst (V[2]/TiO₂).

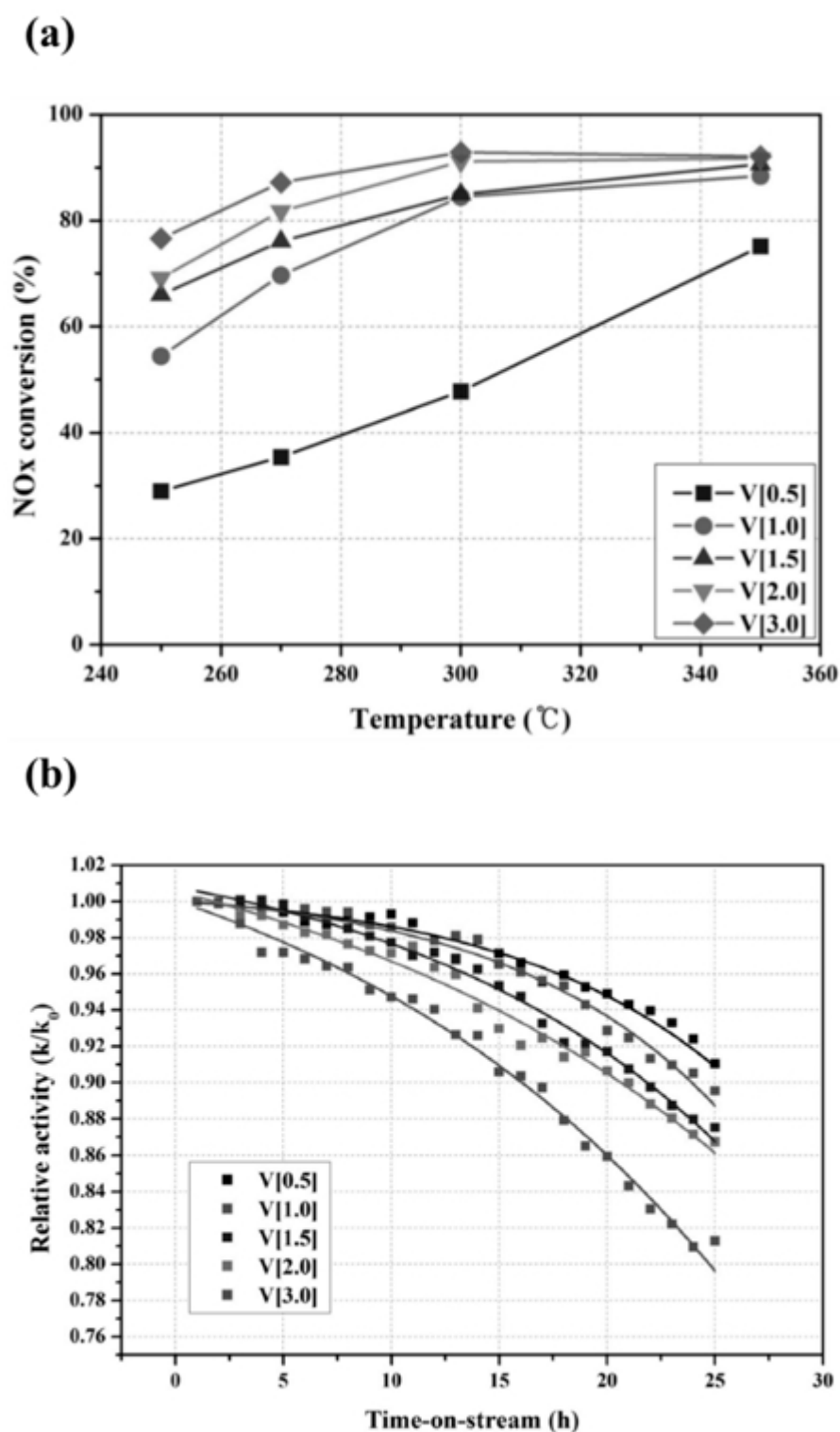


Figure 23. (a) Effect of vanadium contents of V[x]/TiO₂ catalysts on NO_x conversion (reaction conditions: NO: 748 ppm, NO₂: 55 ppm, O₂: 3%, H₂O: 6%, NH₃/NO_x: 1.0, S.V: 60,000 h⁻¹). (b) Relative activity in the present of SO₂ for the SCR of NO by NH₃ with V[x]/TiO₂ catalysts [52].

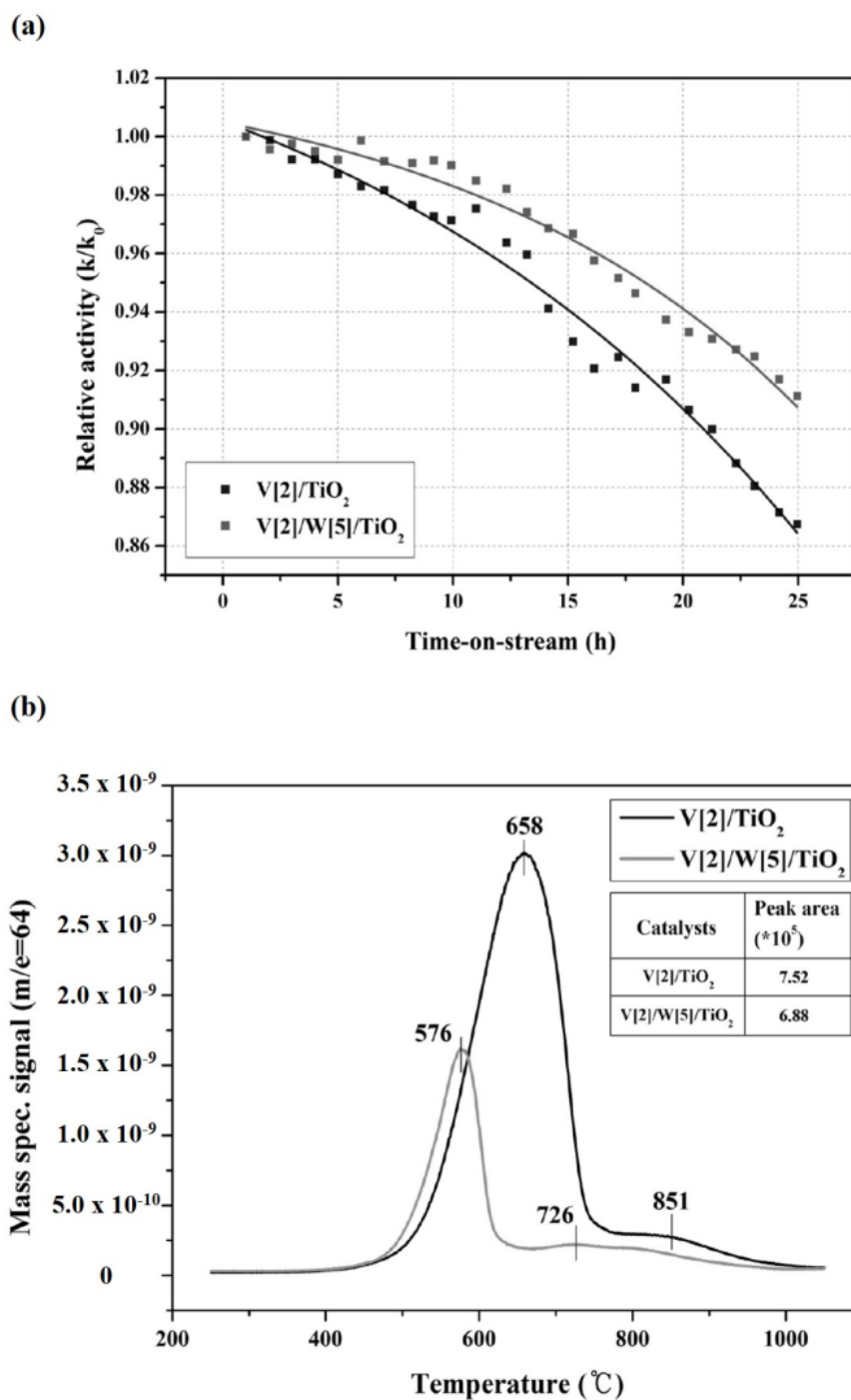


Figure 24. (a) Relative activity in the present of SO_2 for the SCR of NO by NH_3 with $V[2]/TiO_2$ and $V[2]/W[5]/TiO_2$ catalyst (reaction conditions: reaction temperature: $250^{\circ}C$, NO: 748 ppm, NO_2 : 55 ppm, O_2 : 3%, H_2O : 6%, SO_2 : 500 ppm, NH_3/NO_x : 1.0, S.V: $60,000 h^{-1}$) (b) SO_2 -TPD pattern of $V[2]/TiO_2$ and $V[2]/W[5]/TiO_2$ catalysts. [52].

Park et al. found that over 90% of catalytic activity was recovered when spent catalyst was washed by acidic solution in the field regeneration of SCR waste catalyst, and the concentration of acidic solution was 3~5 M (Figure 25). When the acidity of the solution exceeds the optimal point, the dissolution effects of the impurity component deposited on the catalyst surface that caused the catalyst deactivation. Moreover, the leaching rate of vanadium and tungsten, which are the main active components, increases and eventually lead to catalyst deactivation [53].

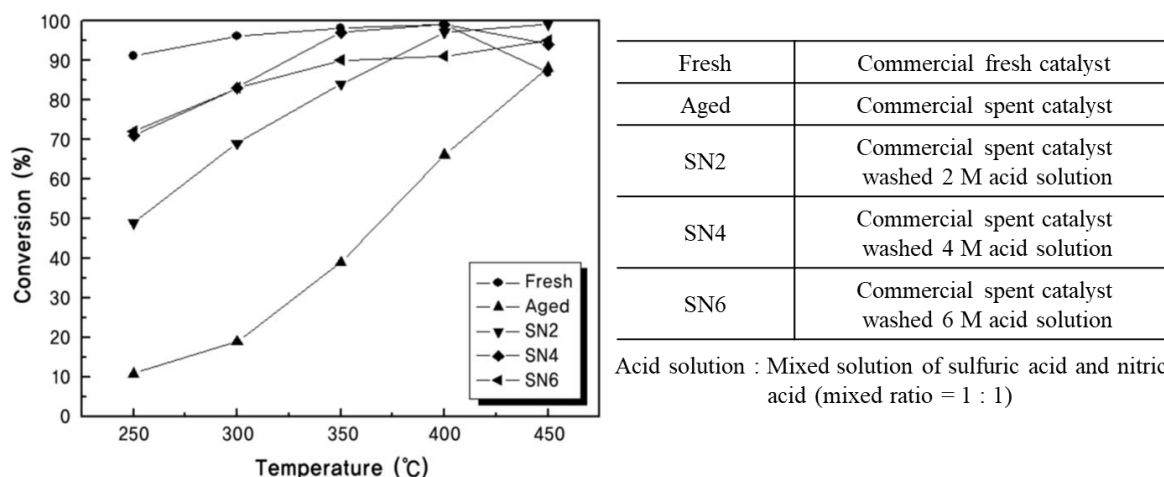


Figure 25. Conversion rate of NO over the prepared catalysts with sulfuric + nitric acid solution washing as a function of reaction temperature (space velocity = 6000 h^{-1} , NO/NH₃ ratio = 1:1, O₂ = 3.6 % (v/v), NO = 300 ppm, SO₂ = 400 ppm) [53].

Despite many efforts being made to increase the life and stability of the SCR catalysts, they have a limited life depending on the operation conditions applied. The life of the catalyst used in the NH₃-SCR process is usually 3–5 years depending on the operating conditions of catalyst at each process site. In addition, only a few years ago, the activity of the SCR catalyst, which markedly deteriorated and reached the end of its life, was mostly treated by reclaiming the waste. Although research is being conducted worldwide to regenerate and use it, the currently studied regeneration method is to desorb the catalyst from the reactor and transport it to a regeneration plant to regenerate the degraded catalyst. In order to retain the original activity of the degraded catalyst, acid is used to remove the adsorbed coke and other particulate matters on the surface of the catalyst which was generally reported to be a time-consuming process [53].

3.3.2. Car Engines

Hydrocarbons, carbon monoxide and nitrogen oxides emitted by gasoline engines can be reduced by using three-way catalysts. Diesel engines also emit those reducing gases, although they need to be operated in excess oxygen environments. Due to the dominant concentration of reducing agents such as hydrocarbons and carbon monoxide in the exhaust gas, which actually need to be reduced to N₂ from NO_x, they reacted with excess oxygen. The diesel engine produces higher emissions of particle matter (PM) and NO_x than gasoline engines [54]. In South Korea, diesel oxidation catalyst (DOC) and diesel particulate filter (DPF) were used to reduce the NO_x as per the Euro-5 regulation. However, Euro-6 regulations, which applied from 2015, require a separate technology called SCR to reduce NO_x as the emission volume of NO_x is significantly strengthened, compared to Euro-5 (Figure 15). The reduction technique of NO_x can be divided into two methods such as pre-processing technology (engine application technology, where both fuel and oxygen ratio adjust within engine) and post-processing technology (actual SCR catalytic technology) [54].

Among the post-processing technologies, the lean NO_x trap (LNT) and SCR are the representative technologies that reduce nitrogen oxides. Urea-SCR is the most excellent device for removing NO_x by spraying urea solution into the exhaust pipe to create ammonia by thermal hydrolysis (Figure 7). However, it should be considered that the system is complex and has problems such as low efficiency at low temperatures, the generation of solid byproducts and the use of low-grade elements, etc. These problems can be avoided by uniform mixing of the urea solution [55]. The driving characteristics of the vehicle cause a sudden change in engine load, resulting in different exhaust gas temperatures and concentrations of NO_x (Figures 26 and 27) [56].

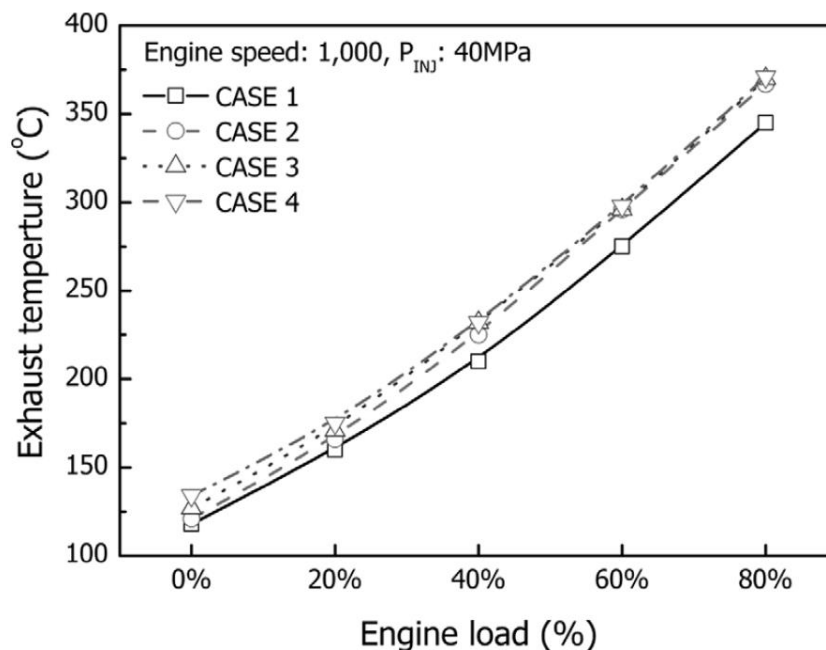


Figure 26. Comparisons of injection strategy of exhaust gas temperature [56].

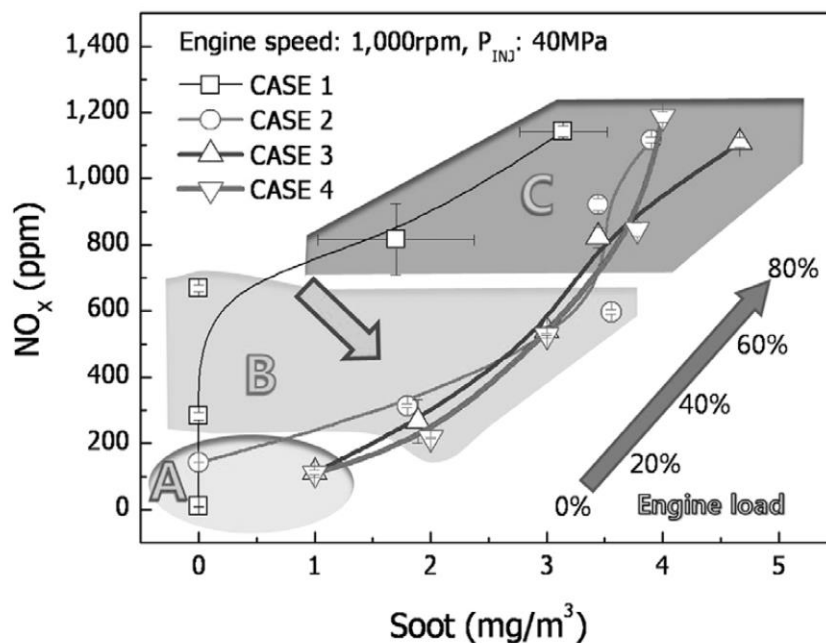


Figure 27. Effect of injection strategy on Soot and NO_x emissions [56].

The most likely and effective deployment of the current vehicle SCR system is in the order of DOC and DPF followed by SCR. The SCR catalyst will also be exposed to high temperature exhausts during the forced regeneration of DPF PM combustion [57]. V₂O₅/WO/TiO₂ catalysts, widely used in plant industries, show excellent efficiency in the range of 300–400 °C, but the reaction activity and selectivity are significantly reduced at low temperature (below 200 °C) and high temperature (above 400 °C) [58]. The Cu-ZSM-5, a typical example of non-V₂O₅ based catalytic system, has also received an attention due to its fast rate of NO decomposition [59].

The vanadium catalyst generally used in the SCR process has a low deactivation at moderate reaction temperature even in the presence of sulfur, although the catalyst deactivated at high temperature. By contrast, the adsorption amount of ammonia is excellent on the zeolite catalysts in the wide reaction temperature range, but sulfur resistance is low. Han et al. investigated the performance

of the catalyst to overcome the shortcomings of vanadium catalyst and zeolite catalyst and maximize the catalyst life time as well as catalytic activity. They reported high temperature stability from the Fe-zeolite catalyst and sulfur resistance from the V_2O_5 catalytic system (Figure 28). Both the catalyst stability and sulfur resistance were enhanced when V_2O_5 was loaded into the Fe-zeolite catalyst (Figure 29) [60].

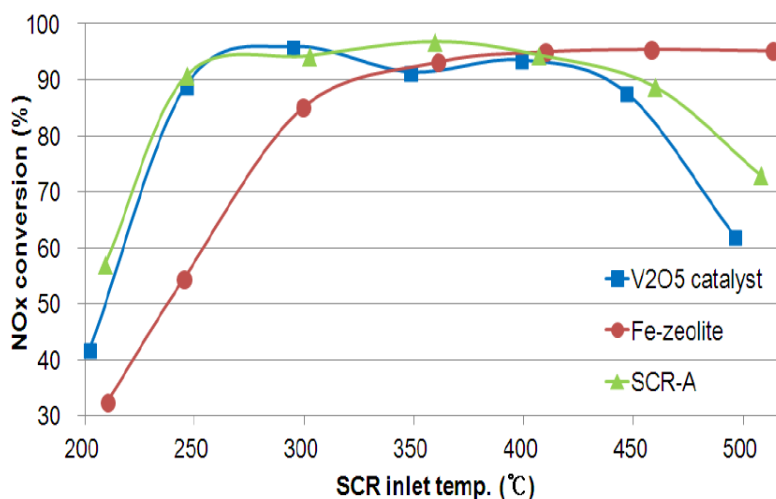


Figure 28. Comparison of DeNO_x activity of SCR-A catalyst which was combined with V_2O_5/TiO_2 and Fe-zeolite [60].

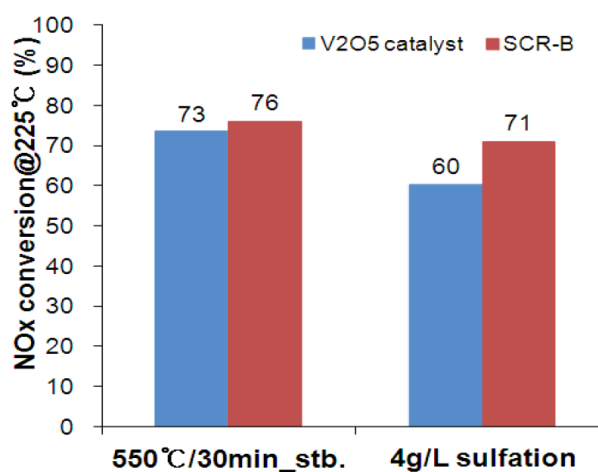


Figure 29. Steady-state engine test results at 225 °C before and after 4 g/L sulfation [60].

Huang et al. investigated the NH_3 -SCR catalytic reaction on the zeolite catalyst with different structures. In more detail, using commercial zeolite catalyst (Clariant Co., Ltd. Daegu, Korea), they exchanged cations such as Cu and Fe to BEA (zeolite β) and MFI (ZSM-5) respectively. The BEA exchanged with Cu ions displayed a greater low temperature activity, and thus higher NO conversion rate than Fe exchanged on MFI. Furthermore, as shown Figure 30, NH_3 desorption peaks of BEA zeolite (B) was greatly influenced by the type of ion exchange metal ions rather than the structure of the zeolite's structure [61].

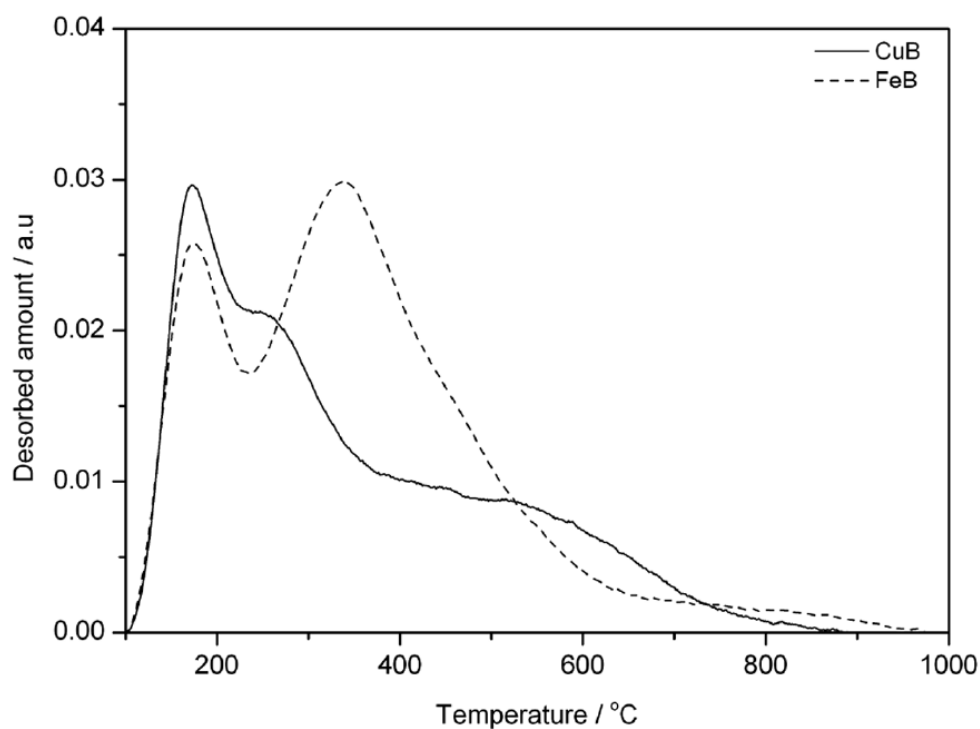


Figure 30. NH_3 -TPD curves of CuB and FeB [61].

In another research, Seo studied the iron exchanged with Cu, Co, Ni, Mn, and Co in the zeolite, and investigated catalytic performance of DeNO_x . Also, the effects of the catalyst were investigated by adding some cations like Ba, K and Ca to the Cu-zeolite catalyst. The researcher reported that Cu and Mn showed a high NO_x conversion at low reaction temperature of 200 °C (Figure 31). The Ba-modified zeolite showed a high activity at 500 °C, as compared with that of K- and Ca-modified catalysts, by inhibiting the agglomeration of Cu particles on the zeolite catalyst (Figure 32) [62].

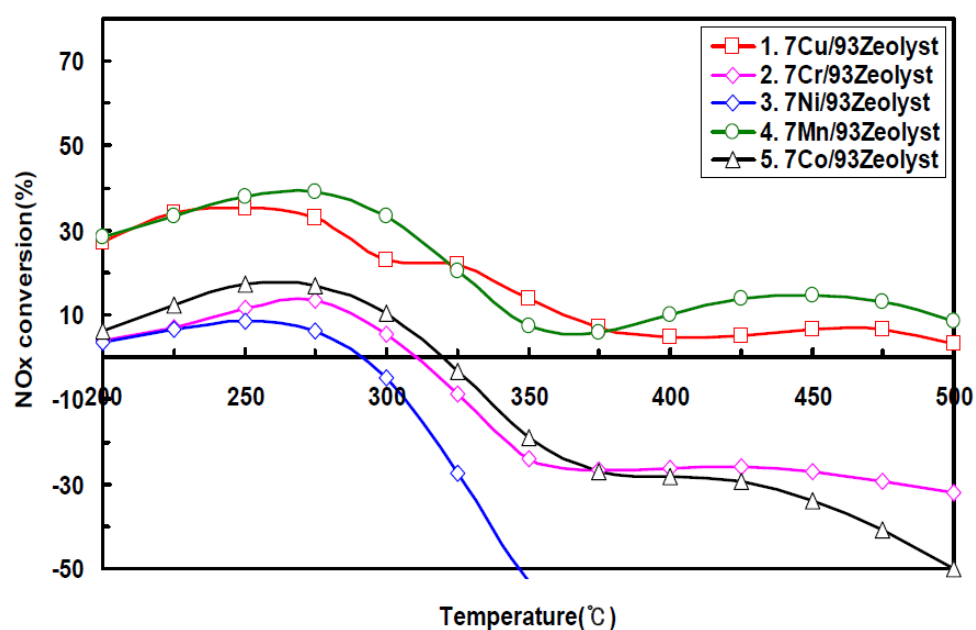


Figure 31. Conversion rate according to kind of transition metal [62].

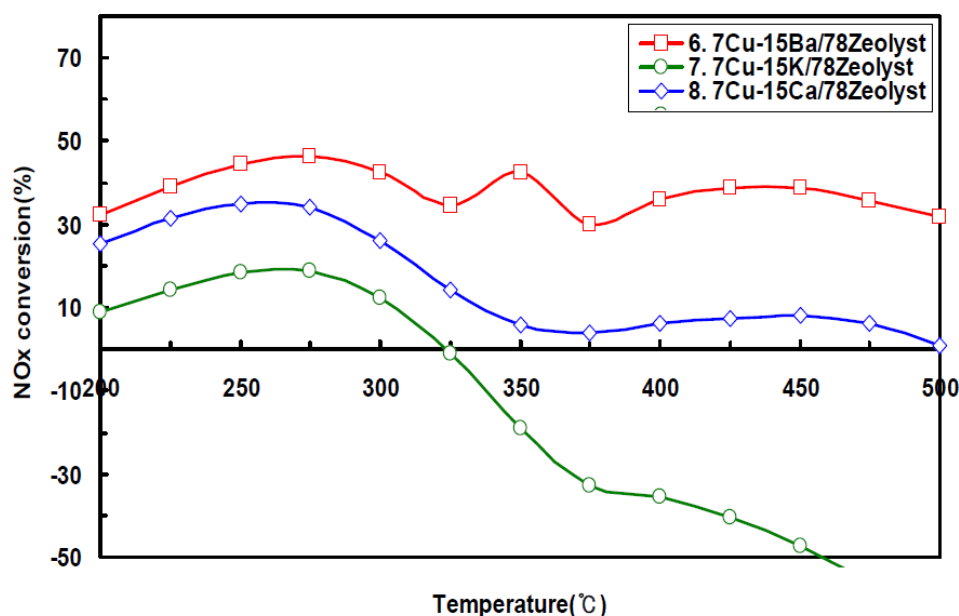


Figure 32. Conversion rate according to NO_x storage material [62].

In the case of the direct ammonia-injection SCR system, the solid phase ammonia storage material is heated to generate ammonia gas, a reducing agent, and sprayed directly into the exhaust pipe in a gaseous phase. There is no discharge of solid byproducts, and the shape of the exhaust system required for uniform mixing of reducing agent is relatively free. In addition, since a series of processes such as thermal decomposition and hydrolysis are not required in low-temperature areas, which is advantageous in terms of reactivity and efficiency, this technique could be applied in the future [55].

The characteristics of NO_x reduction rate, reaction rate, and ammonia slip of ammonia gas injection system were evaluated by Jung et al. via preparing ammonia gas injection system, which can replace the existing urea-SCR, using low temperature Cu-ZSM-5 catalyst. They reported that, unlike the urea solution, the response rate of ammonia gas was significantly improved due to the injection of reducing agents, with less stable adsorbed-phase occurring in the SCR catalyst (Figure 33) [63].

3.3.3. Marine Engines

The generation of nitrogen oxides and power supply for ships results from the internal combustion engines of ships. The exhaust emission characteristics of a heavy-duty diesel engine with real time analysis are shown in Figure 34 [64]. Since engine optimization alone does not satisfy Tier III's regulatory parameters on the reduction of nitrogen oxide emissions, the development of ship's exhaust gas post-processing device has become required to satisfy the enhanced emissions regulations of IMO [65].

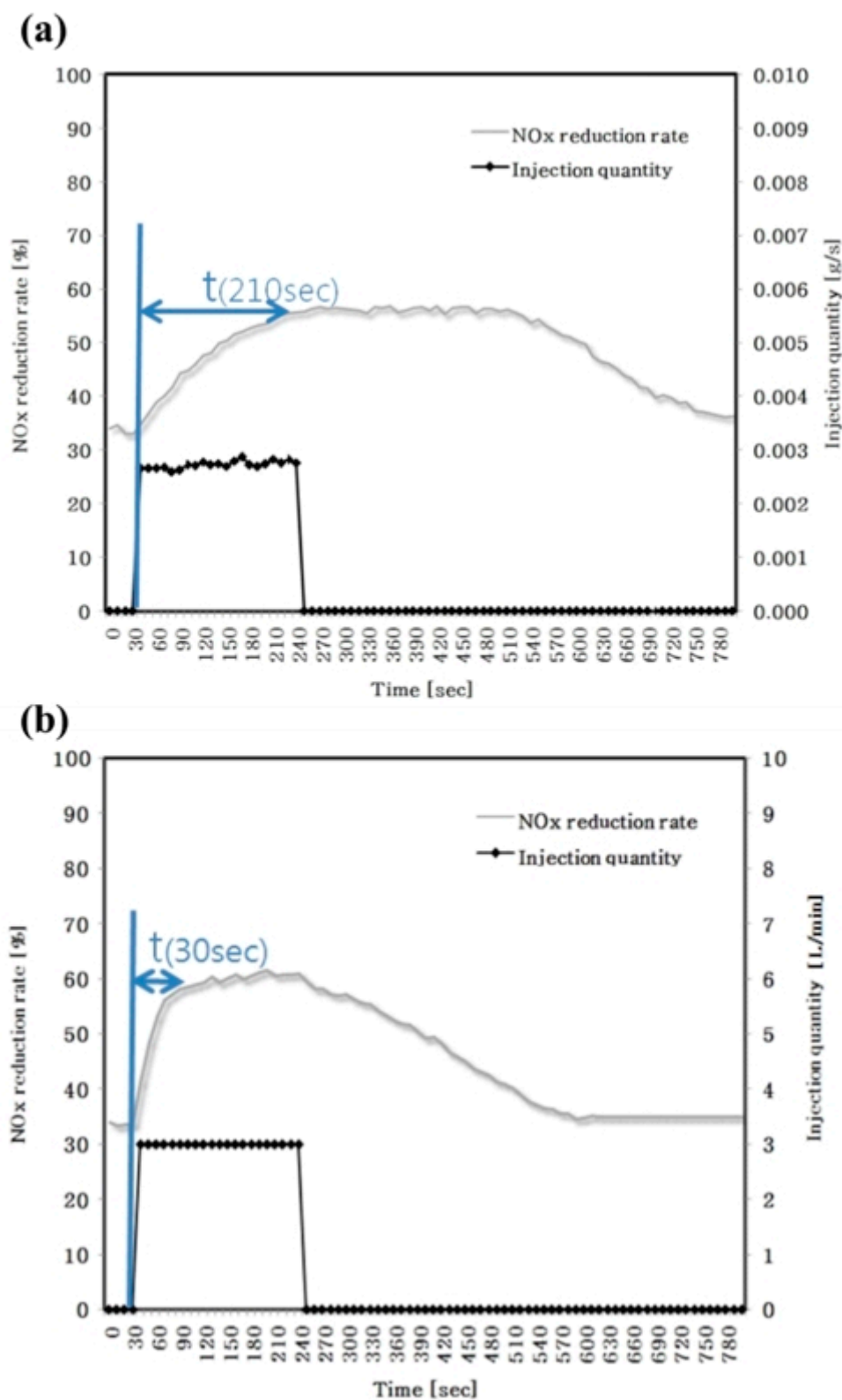


Figure 33. NO_x reduction rate vs. time. Operating at 1500 rev/min, bmp 2 bar, (a) urea-SCR, (b) NH₃-SCR.

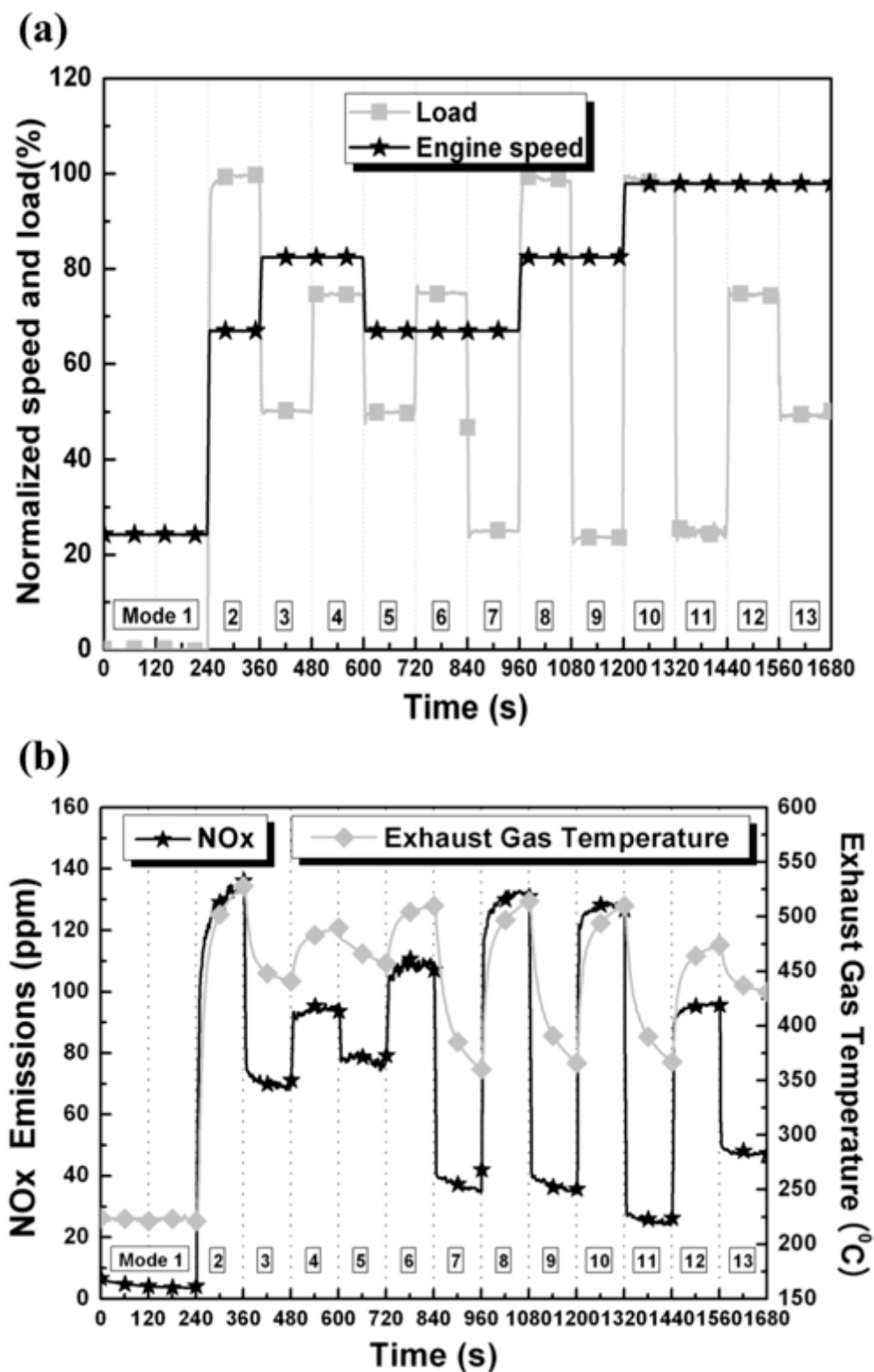


Figure 34. Exhaust emission characteristics of heavy-duty diesel engine: (a) real-time ECS (European Steady-State Cycle) test mode, (b) real-time NO_x emission characteristics [64].

Most diesel engines for propulsion use a 2-stroke engine that is simple in structure and has good momentum. Diesel engines for power generation are mainly used with 4-stroke engines [66]. However, unlike automobile engines which have a temperature of 300 to 400 °C, the 2-stroke diesel engine for

ships only has a temperature of 200 to 300 °C, making it difficult for the SCR system to be applied to the system [65].

In addition, the catalyst used in the ship SCR process built within the ship, so the vibration resistance to withstand the internal engine, operation, and vibration caused by waves must be considered. Great importance should be given to the prevention of catalyst poisoning and the formation of ammonium bisulfate in the presence of SO₂ [67]. In order to solve this problem, various catalysts having nitrogen oxide reduction performance suitable for ship SCR process environment have been studied.

Kwon et al. studied the low temperature SCR reaction on Mn/TiO₂ catalyst using various commercial TiO₂ as supports (Figure 35). They reported that low MnO_x surface density caused by high dispersion manganese oxides increased low-temperature SCR activity besides lowering the reduction temperature (from MnO₂ to Mn₂O₃) of surface MnO_x on TiO₂ [68].

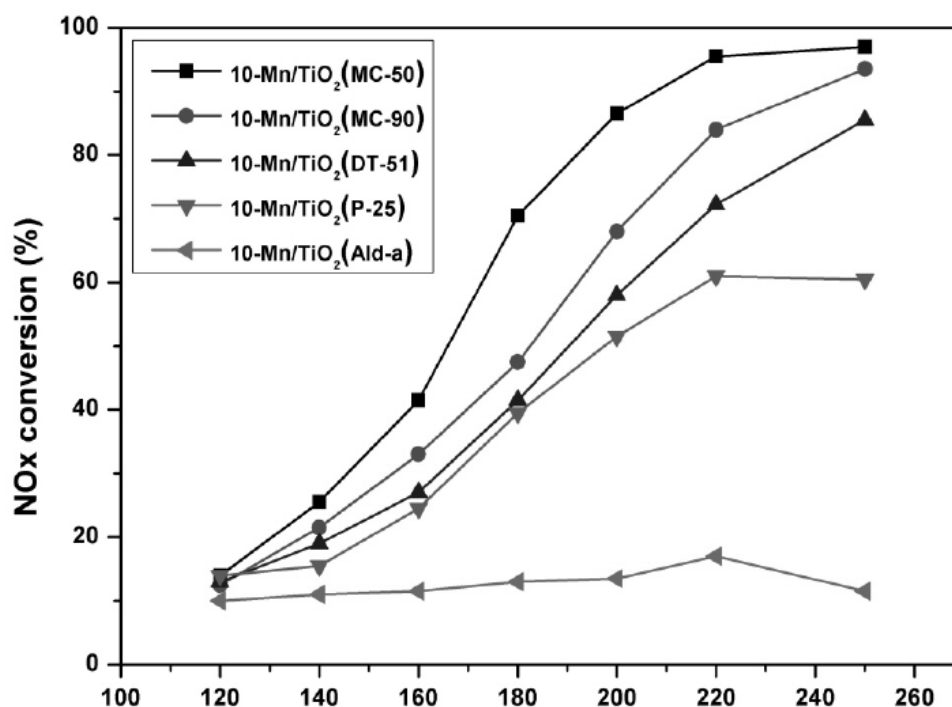


Figure 35. The effect of reaction temperature on NO_x conversion over 10-Mn/TiO₂ catalysts (NO_x: 200 ppm, NH₃/NO_x: 1.0, O₂: 8%, S.V: 60,000 h⁻¹) [68].

As shown in Figure 36, Kang et al. investigated the NO_x reduction rate using the single Cu and Mn oxide, and Cu-Mn mixed oxides catalyst. The presence of small amounts of copper oxide showed 100% NO_x conversion compared with single metal oxide catalysts such as CuO and MnO_x at wide temperature range (323–473 K) [69].

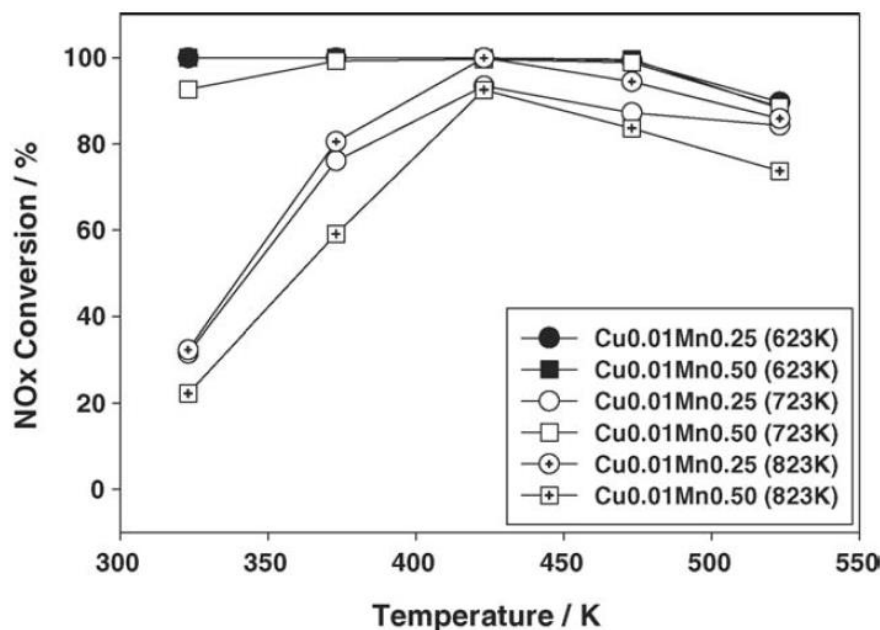


Figure 36. NO_x conversions over Cu0.01Mn0.25 and Cu0.01Mn0.50 catalysts calcined at 623, 723 and 823 K. Reactants: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂ in N₂, S.V: 30,000 h⁻¹. (Reprinted with permission from [69]. Copyright (2006) Elsevier).

Ship diesel fuel contains sulfur (Table 8), which will go through the combustion process and form SO₂, which is a known catalytic poisoning gas for the active species of the SCR catalysts. In more detail, SO₂ is the biggest problem for cold NH₃-SCR catalysts [70]. Many research efforts have been made to reduce the poisoning of SCR catalyst in the presence of sulfur.

Table 8. Properties of diesel fuel used in Korea naval vessels [71].

Items	Standards	Results	Test Methods
Flash point (°C)	40~	63.0	KSM ISO 2719:2003
Viscosity (40 °C, mm ² /s)	1.5~6.0	3.301	KSM ISO 3104:2008
Sulfur (%)	~1.0	0.028	KSM ISO 8754:2003
Cetane number	40~	53.0	KSM ISO 4264:2003
Density@15 °C (kg/m ³)	815–855	84.6	KSM ISO 12185:2003

Ha et al. investigated the effects of moisture and SO₂ in gases (5% H₂O and 100 ppm SO₂) on the selective catalytic recuperative activity of NO at low temperatures on Fe/zeolite catalyst. Additives such as Mn, Zr, and Ce were added into Fe/zeolite catalysts to check their catalytic efficacy. The NO conversion rate of Fe/BEA catalyst was reduced to 47% at 200 °C, which slightly increased to 53% on the MnFe/BEA in the presence of moisture and SO₂. The modified catalyst also displayed a greater stable activity than the Fe/BEA catalyst. Mn showed the effect of increasing the dispersion on Fe as compared to that of Zr and Ce, and also preventing the formation of a valuable aggregate of Fe [72].

Using the Cu-chabazite SCR catalyst, Nam investigated the effect of reducing nitrogen oxides by SO₂ poisoning at low temperatures between 150 and 300 °C. The researcher was able to measure NO_x reduction for two hours at 150 °C, and then again at the same temperature for another two hours. Although the reduction rate of NO_x was reduced by 50% compared to the new one, it was reported that the higher temperature near to 300 °C, the effect of sulfur poisoning was almost eliminated [73].

Lee et al. [74] investigated the effect of ceria loading over Sb-V₂O₅/TiO₂ catalyst for the selective catalytic reduction of NO_x by NH₃. The V₂O₅-Ce/TiO₂ and Sb-V₂O₅-Ce/TiO₂ catalysts were prepared

by incipient wetness co-impregnation of vanadia and antimony on the pre-prepared CeO₂/TiO₂ support, which was synthesized by deposition precipitation method by hydrolysis with ammonium hydroxide. The addition of 10% ceria to Sb-V₂O₅/TiO₂ significantly enhanced the total acidity and redox properties, and thus the NO_x conversion as well as N₂ selectivity (>95%) at wide temperature range of 220–500 °C (Figure 37). The X-ray diffraction (XRD) results indicated the active components of Sb and V were homogeneously dispersed over CeO₂/TiO₂. The results of NO and SO₂ TPD of 10% ceria-loaded Sb-V₂O₅/TiO₂ catalyst showed enhancement of NO adsorption and SO₂ inhibition properties, which is thought to play a significant role in the long-term stability of the catalyst during an SO₂ on-off study for 38 h at 240 °C.

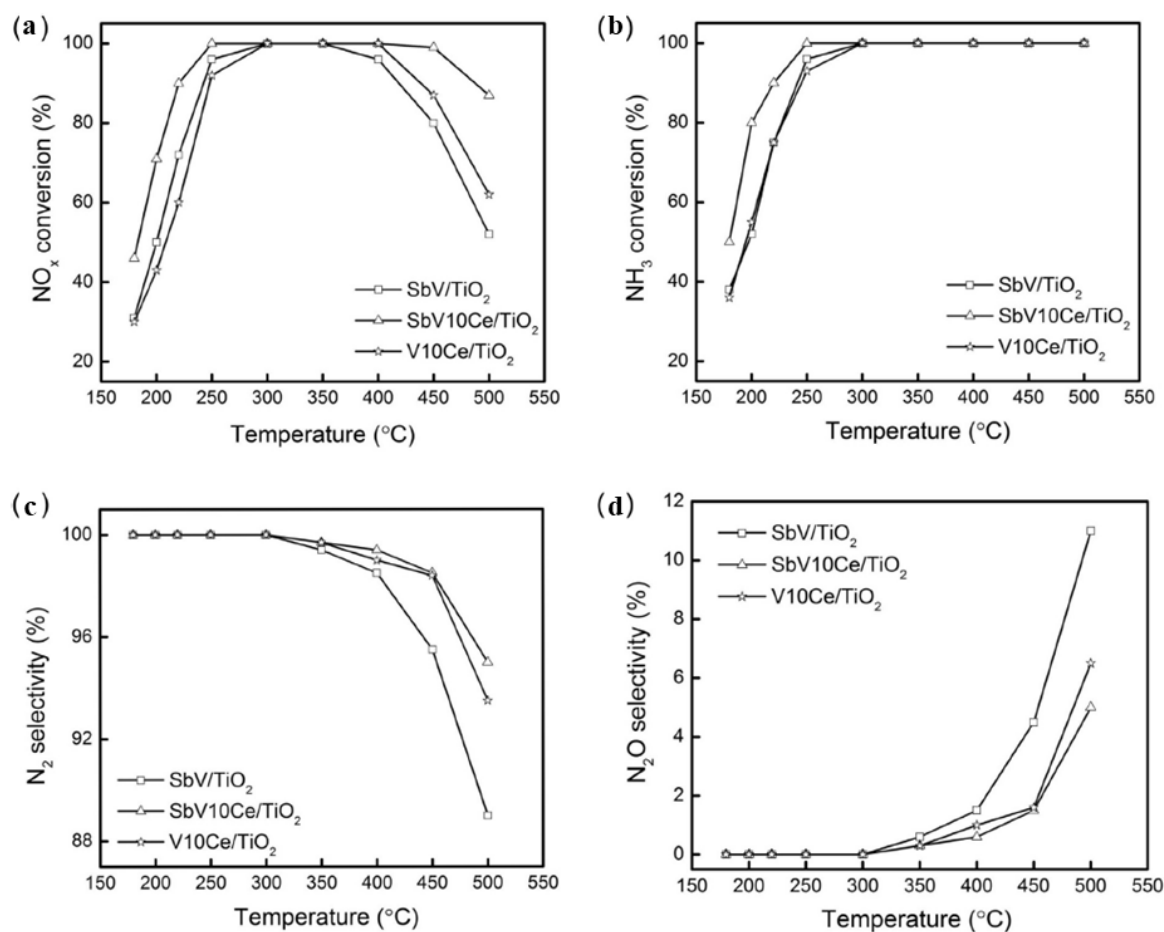


Figure 37. Activity of SbV/TiO₂, SbV10Ce/TiO₂ and V10Ce/TiO₂ samples calcined at 500 °C under H₂O and SO₂ (A) NO_x conversion (B) NH₃ conversion (C) N₂ selectivity and (D) N₂O selectivity. (Reaction conditions: [NO_x] = [NH₃] = 800 ppm, [O₂] = 3 vol%, [H₂O] = 6 vol%, [SO₂] = 800 ppm, N₂ balance, S.V = 60,000 h⁻¹). (Reprinted with permission from [74]. Copyright (2013) Elsevier).

To investigate the effect of pore structure of TiO₂ on sulfur poisoning, Youn et al. studied 5 wt% V₂O₅ supported on the two types of TiO₂ (VT) having distinctive pore, mesopore (DT-51) and micropore (microporous TiO₂) structures for selective catalytic reduction of NO_x with NH₃ (NH₃ SCR). The catalyst prepared by the wet impregnation method of vanadium solution on TiO₂. During the SCR reaction in the presence of SO₂ for 12 h, 5 wt% VT (DT-51) showed more drastic decrease in activity than 5 wt% VT (micro). They reported that a larger amount of SO₂ was desorbed over the DT-51 catalyst used during the temperature-programmed decomposition with the elemental analysis. The 5 wt% VT (micro) having V=O bonds that showed stronger sulfur resistance, but 5 wt% VT (DT-51) having V–O–V bonds that lost their activity more severely than the former. They also summarized

that the different vanadium species on the pore structure of TiO₂ have a significant effect on the sulfur poisoning during SCR reaction [75].

4. Conclusions

In this paper, we reviewed the results of the selective catalytic reduction (SCR) process to remove nitrogen oxide (NO_x), an air pollutant, in South Korea. Plant industry, car engines and marine engines are the main NO_x producers. The technologies used to reduce the NO_x emission are summarized in the following section.

Power plants: in the case of power plants, steady operating performance is required among SCR catalytic performances. Coal-fired power plants generate the high-temperature along with exhaust gases, which may deactivate and inhibit the stable operation of the SCR catalyst. Therefore, the SCR technology is focused on the identification of the direction of increasing the catalyst stability at high temperature operation for large-scale equipment. In South Korea, power plants under KEPCO account for about 81% SCR catalytic system for fixed pollutants. Therefore, SCR catalyst research on fixed pollutants has been conducted in response to the requirements of the power plant. On the other hand, thermal power plant is responsible for 69% of power generation, of which about 46% is fueled by coal. Therefore, SCR catalysts for fixed pollutants are being studied to reflect the characteristics of coal-fired power plants. As of 2015, the regulation of nitrogen oxide emission for these fixed sources has been greatly strengthened, so it is required to increase the reduction rate of nitrogen oxides in SCR units. In recent years, research has been conducted to improve the economy and reduce waste of power plants by regenerating large amounts of deactivated catalysts obtained from thermal power plants.

Car engines: automobile engines are divided into gasoline engines and diesel engines. There are differences in the composition of air pollutants (gasoline: hydrocarbons, carbon monoxide, nitrogen oxides/diesel: oxygen, nitrogen oxides, oxidizing substances), which are emitted from them. Three-way catalytic gasoline engines (number of SCR units; lower oxygen conditions rarely used) and diesel engines (exist always oxygen) are two separate device technologies. In particular, in the case of diesel engine, the generation of NO_x is high due to the combustion characteristic of excessive oxidizing agent, and thus, SCR technology for automobiles is mainly focused and researched on diesel engine. In South Korea's automobile industry, the regulation of nitrogen oxides from diesel engines is adopted from European emission regulations, and the introduction of these regulations has led to the need for automotive SCR devices. The emission regulation is applied regardless of the load of the diesel engine, so the ability to remove NO_x in the low-temperature zone, which is the initial starting point of the vehicle, is required. In addition, due to particle matter (PM) regulation, the diesel particle filter (DPF) is mounted on the vehicle in which high-temperature exhaust gases are generated. Therefore, SCR catalytic technology is suitable to be installed after the DPF device so that the catalytic system can remove NO_x in the low-temperature region and also resist the heat generated during the high temperature exhaust gas. In this regard, automotive SCR catalysts have also been studied in response to this demand. In addition, the research on SCR catalysts by direct injection of ammonia is required in the future, which may provide a high performance NO_x removal, according to the Real Driving Emission (RDE) measurement method.

Marine engines: SCR denitrification catalysts are generally used in marine engines. The exhaust gas temperature of ship engine is below 300 °C, so the catalyst should be active in the low-temperature range. The proportion of international ships arrival or passing through the area of seas in between countries contribute larger emissions of NO_x than Korean domestic ships. The capacity of international ships is also very high as compared to domestic ones and, therefore, they emit higher amounts of NO_x. These ships are required to comply with international regulations centered on IMO rather than domestic regulations. Since 2016, the IMO's regulation of nitrogen oxides has been greatly strengthened to Tier III, which requires the introduction of additional SCR facilities for exhaust gas to reduce nitrogen oxides through optimization of existing combustion conditions and engine technology. Accordingly, domestic SCR catalysts for ships have also been revived to meet these demands, and research on

SCR catalysts for ship engines is currently underway. In particular, the fuel for ships is high in sulfur content and exhaust gases are generated even at low-temperature due to low load operation. Therefore, SCR catalysts targeting domestic ships are also being studied for catalysts having activity against low temperature SCR reaction and poison resistance to sulfur.

Many efforts have been made to develop South Korea's own technology to reduce the amount of nitrogen oxide. We hope that the SCR technology developed will definitely have a positive impact on air pollution.

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