

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

There are many issues which are related to this research such as, catalytic removal of NO_x, selective catalytic reduction (SCR) by ammonia, SCR catalysts, pillared clays, and polyoxoanions. Therefore, background and literatures will be reviewed.

2.1. Catalytic Removal of NO_x

Catalytic approach to NO_x de-pollution (DeNO_x) can be classified as (1) Catalytic Decomposition of NO, and (2) Selective Catalytic Reduction.

The catalytic decomposition of NO is the simplest way to remove NO_x. It is follow thermodynamics, but for kinetics, it is inhibited by a high activation energy to decompose NO $\longrightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2$

The selective catalytic reaction (SCR) can be applied in both stationary and non-stationary sources. Different reducing agents can be employed in selective catalytic reduction, for example, ammonia commonly used for stationary sources and hydrocarbons used for automotive sources.

Three way catalyst removes NO_x by selective catalytic reduction with the excess hydrocarbons, and lean when the excess oxygen is used to completely oxidize carbon monoxide and residual hydrocarbons. The amount of power from a diesel engine is not limited by the fuel but by the amount of oxygen available to burn the fuel. Lean burn diesel engines have incredible fuel efficiency advantages over conventional stoichiometric engines. Additionally emissions of carbon monoxide, particulate and hydrocarbon are significantly reduced in these engines, however, they produced far more NO_x than conventional engines. There is not sufficient hydrocarbon in the exhaust to remove NO_x by SCR. Therefore, using the catalyst bed with a large NO_x storage capacity and running the engine in a while to allow SCR occurring (Fritz and Pitchon, 1997).

Nitrogen, nitrous oxide, ammonia and water are detected as reaction products in NO reduction by hydrogen. The association of NO on the catalyst

surface is the crucial step, dominating the overall reaction behavior (Rahkamaa-Tolonen *et al.*, 2002).

2.2 Selective Catalytic Reduction (SCR) by Ammonia

Selective catalytic reduction has been used for post-combustion control in stationary sources, for example, power plants, nitric acid plants, gas turbines, and waste incinerators. For SCR, in general, a reducing agent such as ammonia, urea or light hydrocarbons is co-fed with a flue gas stream, converting nitrogen oxides to water and nitrogen gas. A variety of reducing agents such as CH₄, CO, H₂ and NH₃ have been used. Ammonia is widely used as a reductant in the selective catalytic reduction. The benefit of NH₃ as a reducing agent is its high selectivity towards reaction with NO in the presence of oxygen. (Amiridis *et al.*, 1996). It is injected to the flue gas stream, passing over a catalyst. The optimum temperature is usually between 300°C and 400°C. The efficiency of SCR process reactions at reagent stoichiometry and utilisation of nearly 1.0 allow the effective value, while for a typical Selective Non Catalytic Reduction (SNCR) system, ammonia is required three or four times as much reagents to achieve similar NO_x reductions. The temperature window for efficient SNCR operation typically occurs between 900°C and 1100°C, depending on the reagents and condition of SNCR operation. When the reaction temperature increases over 1,000°C, the NO_x removal rate decreases due to the thermal decomposition of ammonia. Figure 2.1 illustrates the SCR process.

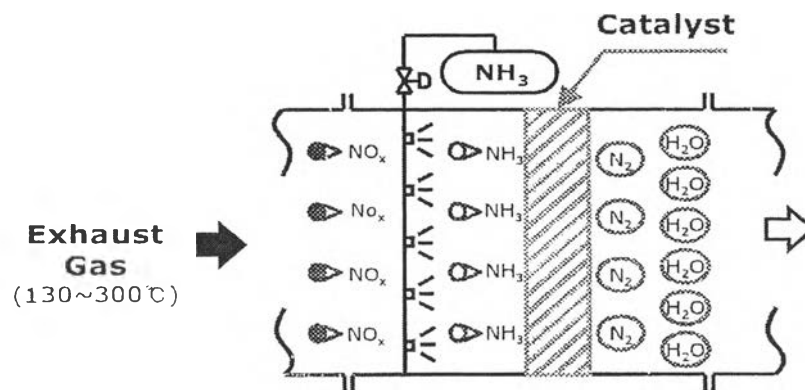


Figure 2.1 Selective catalytic reduction process.

There has been unusual growing and development in flue gas control technologies capable of reducing NO_x emissions to the low levels. SCR offers the advantage of greater NO_x reduction and has, therefore, been widely adopted in industrialized countries with stringent emission limits (Radojevic, 1998). Although the technology was discovered in Japan, the selective catalytic reduction (SCR) of NO with ammonia is a process being commercialized in many decades in United State of America for power plant emission control. The overall reactions over highly selective supported vanadia catalysts are given in Table 1 (Eatl *et al.*, 1998). Marshneva *et al.* (1995) stated that the SCR reaction on titania-supported vanadia hardly depended on the concentration of vanadium atoms. Moreover, the activation energy of the SCR process nearly coincided with the vanadia reoxidation activation energy estimated at 16 kcal/mol. Reoxidation of reduced vanadia species seemed to be the rate-limiting step of the SCR process.

Table 2.1 SCR reactions over the commercial supported vanadia catalyst (Eatl *et al.*, 1998)

No.	Reaction
1	$4\text{NO} + 4\text{NH}_3 + \text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$
2	$4\text{NO} + 4\text{NH}_3 + 3\text{O}_2 = 4\text{N}_2\text{O} + 6\text{H}_2\text{O}$
3	$6\text{NO} + 4\text{NH}_3 = 5\text{N}_2 + 6\text{H}_2\text{O}$
4	$4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$
5	$2\text{NH}_3 + 2\text{O}_2 = \text{N}_2\text{O} + 6\text{H}_2\text{O}$
6	$4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$

2.3 SCR Catalysts

There are many kinds of catalyst that are used in selective catalytic reduction of NO_x by NH_3 , for example, molybdena, tungsten, vanadium oxide monolayer catalysts, platinum, zeolite, WO_3 on TiO_2 , activated carbon and titania-silica honeycombs (Eatl *et al.*, 1998).

Aleman *et al.* (1995) studied the reactivity in the reaction of NO by ammonia of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ concluded that $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts exhibited higher reactivity. EPR, FTIR, FT-Raman, and UV-Vis techniques indicated a strong electronic interaction between vanadium and tungsten oxide surface species at the surface of TiO_2 support. The interaction led to a higher reducibility of the ternary sample. A synergism between vanadium and tungsten oxide surface species was also suggested, accounting for the high reactivity of the ternary sample in the SCR reaction. In addition, the reactivity of ternary $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ De- NO_x catalysts examined by transient and steady-state techniques is higher than that of the binary $\text{V}_2\text{O}_5/\text{TiO}_2$ samples having the same V_2O_5 loading (Lietti *et al.*, 1996).

Van Den Brink *et al.* (2002) studied a stack of a Co-ZSM-5 catalysts and a Pd/Fe-ZSM-5 catalyst. It is possible to remove NO_x and N_2O in a single reactor by SCR with propane.

Series of pillared clays study on SCR by ammonia were accomplished by Yang's group. A cationic montmorillonite clay was intercalated with titania (TiO_2) between its layers to expand and maintain its clay sheets. Vanadia and iron were further exchanged for studying the activity on SCR (Yang *et al.*, 1995).

2.4 Pillared Clay

Pillared interlayer clays (PILCs) or pillared clays are two-dimensional zeolite-like materials prepared by exchanging the charge-compensating cations between the clay layers with large inorganic hydroxycations, which are polymeric or oligomeric hydroxy metal cations formed by hydrolysis of metal oxides or salts. Upon heating, the metal hydroxy cations undergo dehydration and dehydroxylation, forming stable metal oxide clusters which act as pillars keeping the silicate layers separated, creating interlayer space of molecular dimensions. Since pillared clays have a number attractive features such as high porosity, high thermal stability and exchangeable cations, they have been widely studied as catalysts and adsorbents (Li *et al.*, 1997).

The PILC based catalysts have been found to be excellent and $\text{H}_2\text{O}/\text{SO}_2$ resistant catalysts for the selective catalytic reduction (SCR) reactions by NH_3 and by hydrocarbons (Yang *et al.*, 1998).

Li *et al.* (1997) studied Cu^{2+} ion-exchanged pillared clays for SCR of NO by hydrocarbons. The results showed that the catalysts yielded substantially higher SCR rates than both Cu^{2+} -exchanged pillared clay and Cu^{2+} -ZSM-5 at temperatures above 400 °C. H_2O and SO_2 caused only mild deactivation.

The Fe-Cr/ TiO_2 -PILC with the ratio of Fe/Cr of 3 showed the highest activity for the selective catalytic reduction (SCR) of NO with NH_3 . Compared with commercial $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts, the activity of the doped pillared clay was about twice as much under H_2O -and- SO_2 -free conditions, and was around 40% higher under conditions with H_2O and SO_2 (Cheng *et al.*, 1996).

Yang *et al.* (1998) stated that Cu-Ti-PILC showed the highest activities at temperatures below 370°C, while Cu-Al-PILC was much active at above 370°C. H_2O and SO_2 only slightly deactivated the SCR activity of Cu-Ti-PILC. The doping of

0.5 wt% Ce_2O_3 on Cu-Ti-PILC increased the activities from 10% to 30% while 1.0 wt% of Ce_2O_3 decreased the activity.

The Fe-TiO₂-PILC catalysts showed high activities in the reduction of NO_x by NH₃ in excess oxygen. SO₂ further increased the catalytic activities at above 350°C, whereas H₂O decreased the activity slightly. The catalysts were about twice as active as commercial type V₂O₅-WO₃/TiO₂ catalyst in the presence of H₂O and SO₂, moreover, it had higher N₂/N₂O product selectivity. Ce further increased the activity over three times (Long *et al.*, 1999).

Long *et al.* (2000a) stated that the V₂O₅/TiO₂-PILC catalysts were highly active in SCR of NO_x by ammonia, shown a broad temperature window, and the maximum NO conversion was higher than that on V₂O₅/TiO₂ catalysts. The V₂O₅/TiO₂-PILC catalysts also had higher N₂/N₂O product selectivity. Addition of WO₃ to V₂O₅ further increased the activities.

Small amount (less than 2 wt%) of CeO₂ and PrO_{1.83} added to Fe-TiO₂-PILC can increase the activity on selective catalytic reduction of nitric oxide by ammonia (by 35%) both in the absence and presence of H₂O and SO₂, but TbO_{1.75} did not improve the SCR activity significantly (Long *et al.*, 2000b).

Later in 2000, VO-TiO₂-PILC showed high activity for the selective catalytic reduction of nitric oxide by ammonia in the presence of oxygen. The maximum activity was obtained with 2.1–3.5 wt% vanadium (Long *et al.*, 2000c).

All above pillared clay catalysts are summarized in Table 2.2 showing conversion and selectivity.

Table 2.2 Catalysts which have been studied for SCR of NO by ammonia

Catalyst	NO conversion	N ₂ selectivity	Conditions
Fe-Cr/TiO ₂ - PILC	99% 96%	100% 100%	375°C, absence H ₂ O /SO ₂ 375°C, presence H ₂ O /SO ₂ Fe/Cr =3
Cu ²⁺ -Ti-PILC	90% 75-85%	100% 100%	550°C , absence H ₂ O /SO ₂ 550°C , presence H ₂ O /SO ₂
Cu-Ti-PILC Cu-Al-PILC	55% 55%	100% 100%	>370°C <370°C
Fe ³⁺ -TiO ₂ -PILC	91.5% 98.1%	100% 100%	5.45%wt Fe, 400°C, absence H ₂ O /SO ₂ 4.32%wt Fe, 400°C, presence H ₂ O /SO ₂
V ₂ O ₅ -TiO ₂ -PILC	93.4%	99.5%	4.4% V ₂ O ₅ +8.2%WO ₃ /TiO ₂ - PILC,375°C
CeO ₂ /Fe-TiO ₂ -PILC	92% 98.5%	99% 99.1%	1%wt CeO ₂ ,375°C, absence H ₂ O/SO ₂ 1%wt CeO ₂ ,400°C, presence H ₂ O/SO ₂
VO-TiO ₂ -PILC	94.5%	98.8%	3.5%wt vanadium,375°C absence & presence H ₂ O /SO ₂ are same results
WO ₃ +V ₂ O ₅ /TiO ₂	93%	95%	375°C

Note : The last catalyst is a commercial catalyst.

2.5 Hydrotalcite Clay

Normally pillared clays are clays whom the interlayers are modified from those of original clay minerals. Clay minerals are composed of infinite layers of metal or non metal oxides and hydroxides stacked on top of each other. The far less common anionic clays, hydrotalcite(HT), have positively charged metal oxide layers with anions located interstitially. Many of these are based on double hydroxides of the main group (Mg, Al) and the transition metal (Fe, Co, Ni, Cr) hydroxides. The structure of these materials is very similar to that of brucite (Mg(OH)₂). In brucite, OH⁻ ions are hexagonally close packed and Mg²⁺ ions occupy alternate layers of octahedral sites resulting in a stacking of charge-neutral layers of the composition Mg(OH) (P_{3ml}, a=3.01 Å and c= 4.8 Å). Anion and water molecules are incorporated

in the interlayer region for charge balance and stability leading to an increased interlayer spacing. Figure 2.1 demonstrates the hydrotalcite clay structure (Cavani, F. *et al.*, 1991).

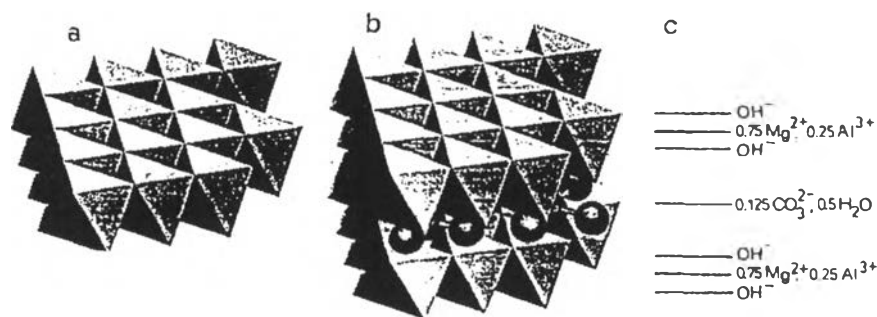


Figure 2.2 The hydrotalcite clay structure (Cavani, F. *et al.*, 1996).

Hydrotalcite clay ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$) has also modified as catalysts for SCR of NO. Hydrotalcite –based catalysts exhibits a promoted low temperature NO SCR activity as well as in the NO reduction, while the NO oxidation was mainly governed by the oxygen activation on the oxidic support (Fornasari *et al.*, 2002).

Hydrotalcite-type clay is different from hydrotalcite clay in the role of pillaring agent. Generally, hydrotalcite clay has carbonate group intercalated between clay layers, whereas hydrotalcite-type clay has other pillaring agent, for example, organic group or aromatic group. Therefore, if there are not carbonate group between clay sheets in hydrotalcite clay, that clay should be called hydrotalcite-type clay.

2.6 Polyoxoanions

Oxo anions have two, three, or four oxygen atoms attached to a central atom to give a discrete anion. However, it is possible for one or more of these oxygen atoms to be shared between two atoms to give an ion with a bridge oxygen. The oxoanion of V^v, Nb^v, Ta^v, Mo^{VI} and W^{VI} from extensive series are called isopoly anions which contain only the element and oxygen such as Nb₆O₁₉⁸⁻ and heteropoly

anions which contain additional metal or nonmetal atom $[\text{Co}^{\text{II}}_2\text{W}_{12}\text{O}_{42}]^{8-}$ (Cotton, 1995).

Polyoxometalates (POMs) could be ideal pillaring agents. These anions generally possess structures consisting of multiple layers of space-filling oxygens as well as a wide range of charge densities. Robust POMs should impart large spacing, and those with suitably high charge densities should give rise to large lateral anion spacings, thereby providing approach to the intracrystalline surfaces (Pinnavaia *et al.*, 1988).

Payen *et al.* (1987) showed that the surface chemistry of alumina-supported molybdate and heptamolybdate remained stable during preparation, reduction and reoxidation using Laser Raman Spectroscopy. At pH 4.4-5, the dominant species was MoO_4^{2-} , and at pH 11, $\text{Mo}_7\text{O}_{24}^{6-}$ was dominant.

Synthesis of heptamolybdate-and decavanadate-pillared hydrotalcite-type clays has been accomplished on organic-anion -pillared clay precursors that were subsequently exchanged with the appropriate isopolymetalate under mildly acidic conditions as illustrated in Figure 2.2 (Drezdron,1988).

Twu *et al.*,(1989) studied the structure and reactivity of oxovanadate anions in layered lithium aluminate material over wide range of pH ion-exchange by Raman spectroscopy. All of the conditions used to prepare different types of oxoanions are summarized in Table 2.3.

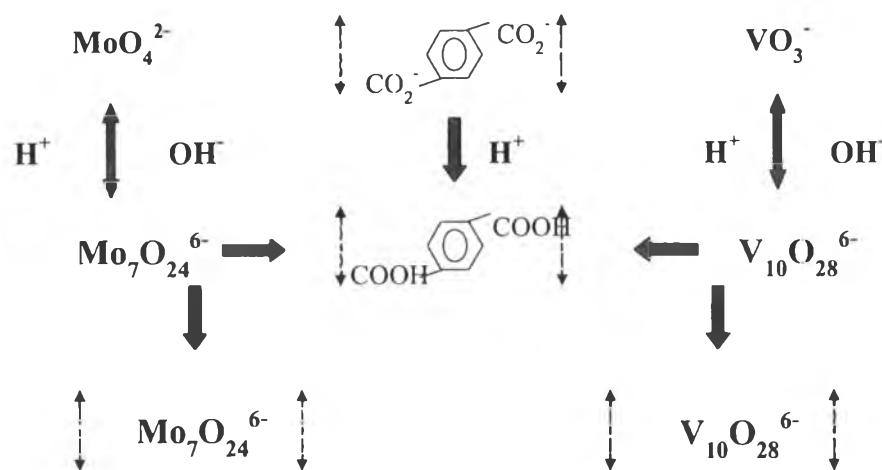


Figure 2.3 Schematic representation of terephthalate anion exchanged with heptamolybdate and decavanadate inside the layer of a hydrotalcite-type clay (Drezdzon, 1988).

Table 2.3 Conditions in Preparation of Different Types of Polyoxoanions

Polyoxoanions		pH	Drying temp (°C)	Time	Remark
Polyvanadate ^a	$\text{V}_2\text{O}_7^{6-}$	8-11	<80	overnight	
	$\text{V}_4\text{O}_{12}^{4-}$	5-8	80-100	overnight	
	$\text{V}_{10}\text{O}_{28}^{6-}$	3-5/4.4*	125	overnight	
Polymolybdate ^b	MoO_4^{2-}	11	110	overnight	Also calcined
	$\text{Mo}_7\text{O}_{24}^{6-}$	4.4*/5	110	overnight	2hr in air 500°C

a : Twu *et al.*, (1989)

b : Payen *et al.* (1987)

* : Drezdzon (1988)

Therefore, it would be interesting and promising to use a new type of catalysts prepared by intercalating polyoxoanions of vanadium and molybdenum into the layers of hydrotalcite-type clay as catalysts for selective catalytic reduction of nitric oxide by ammonia. Effect of Fe loadings was also investigated.