CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Selective Catalytic Reduction (SCR) of NO_x by Ammonia

The selective catalytic reduction (SCR) of NO_x is the most efficient post-combustion technology for NO_x reduction from stationary sources such as electrical generating plants and nitric acid plants. In the SCR of NO_x, reducing agents such as ammonia and hydrocarbons can be used to convert NO_x selectively to nitrogen and water.

Ammonia (NH_3) is widely used as a reducing agent in the SCR process. The benefit of NH_3 as the reducing agent is its high selectivity to react with NO, producing element N_2 over metal oxide catalyst in excess amount of oxygen (Heck and Farrauto, 1995) while the noble-metal three way catalysts are not effective in the presence of excess oxygen (Yang, 1995). The major desired reactions over selective metal catalysts such as vanadia catalyst (Janssen, 1987) and platinum catalyst (Heck *et al.*, 1995) are:

$$4\,NH_3 + 4\,NO + O_2 \longrightarrow 4\,N_2 + 6\,H_2O\text{ , or}$$

$$4\,NH_3 + 2\,NO_2 + O_2 \longrightarrow 3\,N_2 + 6\,H_2O$$

The others reactions are

$$4\,NH_3 + 4\,NO + 3\,O_2 \longrightarrow 4\,N_2O + 6\,H_2O$$

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

$$2\,NH_3 + 2\,O_2 \longrightarrow N_2O + 3\,H_2O$$

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$

At temperatures below 200°C, ammonia can also react with the NO_2 possibly present in the effluent gas producing explosive NH_4NO_3.

$$2\,NH_3 + 2\,NO_2 + H_2O \longrightarrow NH_4NO_3 + NH_4NO_2$$

2.2 SCR Catalysts

There are many kinds of catalysts used in SCR of NO_x by NH_3, depending on an operating condition in order to optimize the abatement process. The active component and temperature ranges may be classified as follow:

Low temperature (175-250°C); platinum
Medium temperature (300-450°C); vanadium
High temperature (350-600°C); zeolite

One of the most effective catalysts and presently used for flue gas application is medium temperature range vanadia-based catalysts or V_2O_5/TiO_2-based catalysts (Yang, 1995 and Willi *et al.*, 1996). In commercial use, WO_3 and/or MoO_3 are usually added as promoters (Long and Yang, 2000a). Wach *et al.*(1996) investigated SCR of NO_x with NH_3 over a series of supported vanadia catalysts to obtain additional insight into these important industrial reactions. It was found that the SCR selectivity toward N_2 formation varied with the immediate environment of the surface vanadia species, and the selectivity depended on the specific oxide support (TiO_2>Al_2O_2>SiO_2).

V_2O_5/TiO_2 catalysts showed the decrease of SCR turnover frequency of approximately 40-50% when H_2O was added to the reacting gas mixture, independent on vanadia surface coverages while the presence of SO_2 resulted in a significant increase of the turnover frequency at low vanadia surface coverages. (Amiridis *et al.*, 1996).

Although the vanadia-based catalysts are highly active, major disadvantages of these catalysts still remained, such as their toxicity, high activity for oxidation of SO_2 to SO_3, and formation of N_2O at high temperatures (Long and Yang, 1999b). Hence, the high temperature range zeolite catalysts have been also interested. Long and Yang (1999b) studied a series of Fe-exchanged molecular sieves as catalysts for SCR of NO with NH_3. It was found that nearly 100% NO conversions were obtained at 400-500°C over Fe-ZSM-5 and Fe-mordenite catalysts, producing only N_2 and giving lower activity for oxidation of SO_2 to SO_3.

2.3 Pillared Clay Catalysts for SCR of NO_x by NH_3

Pillared clays or pillared interlayer clays (PILCs) catalysts are another interesting catalysts because they are inexpensive as compared to the catalysts that have been discussed. PILC catalysts have been studied extensively for a number of catalyzed reactions and found to be H_2O/SO_2 resistant catalysts with high activities for SCR of NO by NH_3 (Yang *et al.*, 1995). They also have attractive features such as high porosity, high thermal stability and exchangeable cations (Long and Yang, 1999a).

PILC catalysts derived from cationic clays such as bentonite clay is the one that has been studied the most for SCR of NO (Yang *et al.*,1992; Cheng *et al.*,1996, Long and Yang, 1999a, 2000a, 2000b, 2000c). Initially Yang *et al.*(1992) defined the cationic PILCs as the two-dimensional zeolite-like materials prepared by exchanging the charge-compensating cations between the clay layers with larger inorganic hydroxycations. The compensating cations were formed by hydrolysis dehydration and dehydroxylation of metal salts to form stable metal oxide clusters which acted as pillars keeping the silicate layers separated and creating interlayer spacing (gallery) of molecular dimension. Five PILCs have been synthesized and tested for their activities in the SCR of NO by NH_3 in the temperature range of 250-450°C. The activities were in the decreasing order: Cr_2O_3-PILC, Fe_2O_3-PILC, TiO_2-PILC, ZrO_2-PILC, and Al_2O_3-PILC. Only Cr_2O_3-PILC exhibited higher activity than a commercial WO_3-V_2O_5/TiO_2 catalyst, but its activity was severely decreased by SO_2.

Cheng *et al.* (1996) studied Fe_2O_3 and Cr_2O_3 supported on Titania-PILC as catalysts for the SCR of NO_x by NH_3. The results showed the highest activity on the catalyst whose the ratio of Fe/Cr was 3. The activity of the Fe_2O_3 and Cr_2O_3 doped pillared clays was about twice as much as commercial V_2O_5/TiO_2 catalysts under H_2O- and SO_2-free conditions, and was approximately 40% higher under conditions with H_2O and SO_2. In addition, their activity for SO_2 oxidation to SO_3 was only 20 - 25% of the V_2O_5-based catalysts.

The Fe-exchanged TiO_2-PILC catalysts have been studied and showed high activities in the reduction of NO_x by NH_3 in excess oxygen. The catalysts were about twice as active as the commercial type V_2O_5-WO_3/TiO_2 catalyst, and had higher N_2/N_2O selectivity in the presence of H_2O and SO_2. SO_2 further increased the catalytic activities at above 350°C, whereas H_2O decreased the activity slightly (Long and Yang, 1999a).

Long and Yang (2000a) investigated SCR of NO with NH_3 over a series of vanadia doped TiO_2-PILC catalysts, and found that the V_2O_5/TiO_2-PILC catalysts provided higher NO conversion than V_2O_5/TiO_2 catalyst, and also had higher N_2/N_2O selectivity. In addition, H_2O and SO_3 slightly increased the activities at the temperature of more than 350°C. Addition of WO_3 to V_2O_5 further increased the activities.

Rare earth oxides, i.e., CeO_2 and $PrO_{1.83}$ have been found to be promoters for Fe-TiO_2-PILC catalysts. Adding a small amount (less than 2 %wt) of these oxides can increase the activity on SCR of NO by NH_3 (by 35%) both in the absence and presence of H_2O and SO_2 (Long and Yang, 2000b).

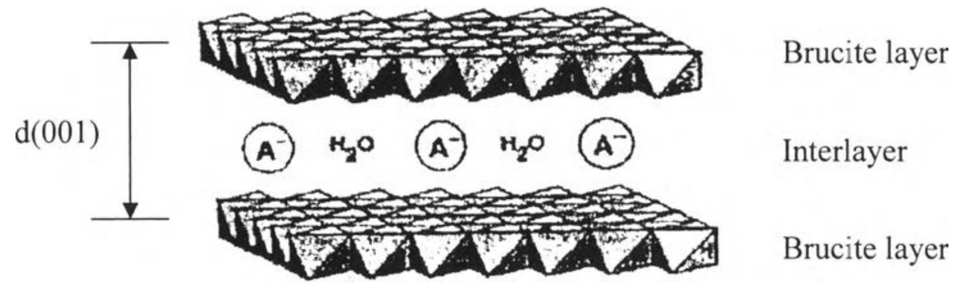
VO^{2+}exchanged-TiO_2-PILCs were latter investigated. These catalysts showed high activity for the SCR of NO by NH_3 in the presence of oxygen and resistance to H_2O and SO_2 at high temperature. The maximum activity was obtained with 2.1 – 3.5 %wt vanadium (Long and Yang, 2000c).

2.4 Hydrotalcite-type Clay

Hydrotalcite clays have been used in recent years as catalysts and as precursors of oxide catalysts and catalyst supports (Shen *et al.*, 1994). Hydrotalcite is an anionic clay found in nature, and can be easily synthesized in the laboratory. It is composed of mixed layers of brucite or $Mg(OH)_2$ and Al, $[Mg_{1-x}Al_x(OH)_2]^{x+}$, with interlayer anions and water to provide overall charge neutrality. Layered double hydroxides (LDHs) were also called in order to represent the compounds having general formula similar to hydrotalcite compound,

$$M_x^{2+}M^{3+}(OH)_{2x+2}(A^-).yH_2O$$

where x may vary from 2 to 5 depending upon the particular combination of divalent and trivalent element, M^{2+} and M^{3+}.



$A^- = CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-$

$x \ = 2\text{-}5$

Figure 2.1 Schematic drawing for the structure of hydrotalcite clays (Townsend, 2001).

2.5 Polyoxometalate-pillared Hydrotalcite-type Clay

Polyoxometalates (POMs) are suitable pillaring agents for hydrotalcite clays. 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 gallery heights, and give rise to large lateral anion spacings, thereby providing access to the intracrystalline gallery surfaces (Kwon *et al.*, 1988).

However, there may be some difficulty in intercalating such large species. The first strategy made use of the fact that Cl^- anion was easier to displace than, for example, CO_3^{2-}. For this reason, Kwon *et al.* (1988) synthesized $V_{10}O_{28}^{6-}$-pillared hydrotalcite (d = 11.9Å) by directly exchange of decavanate anion ($V_{10}O_{28}^{6-}$) with Cl^- interlayer anion. Then, Drezdzon (1988) synthesized $Mo_7O_{24}^{6-}$ (d = 12.17 Å) and $V_{10}O_{28}^{6-}$ (d = 11.8 Å)-hydrotalcite type clays started from organic-anion-pillared clay (terepthalate dianion-pillar) precursor that was subsequently exchanged with appropriate POMs under mildly acidic conditions. The third procedure for synthesizing POM-pillared hydrotalcite presented by Chibwe *et al.* (1989) was achieved by direct exposure of a calcined-hydrotalcite clay to a solution of the pillaring species, i.e., $Mo_7O_{24}^{6-}$(d = 12.0 Å) and $V_{10}O_{28}^{6-}$(d = 11.8 Å).

From previous work (Rochanutama, 2003), $V_{10}O_{28}^{6-}$and $Mo_7O_{24}^{6-}$pillared hydrotalcite have been firstly studied as catalysts for SCR of NO_x by NH_3. These POM catalysts were similarly synthesized by the method established by Drezdzon (1988). The results showed high N_2/N_2O selectivity over commercial-type catalysts, and some catalysts exhibited high activity for reduce NO_x. Therefore, these results demonstrated that $V_{10}O_{28}^{6-}$and $Mo_7O_{24}^{6-}$pillars intercalated in the hydrotalcite clay can be effective catalysts for NO removal. Moreover, these clays with large basal spacing d(001) can adsorb a large amount of NO as indicated on TPD of NO experiments. Pillared derivatives with even larger gallery height and pore sizes are desired for catalytic reactions.

Vanadate-exchanged hydrotalcite clays have been investigated by Ulibarri *et al.* (1993). Pre-swelling with glycerol was also performed. It was found that pore size distribution was broader than that of the samples prepared via a terepthalate intermediate and so was the surface area.

In the search for advanced materials, polyacid anions are interesting for using as the pillaring agents. Triborate-pillared hydrotalcites (d = 10.8 Å) have been synthesized in one step by adjusting the pH of the coprecipitation to favor formation of desired anion (Bhuttachurry *et al.*, 1992). Tetraborate pillared hydrotalcites have been studied next, and the d-spacing of 11.0 Å and high surface area were achieved (Li *et al.*, 1996). Recently, Ogawa and Asai (2000) successfully synthesized deoxycholate interlayer compounds by novel hydrothermal reactions. The d-value of 32.9 Å was observed with a bilayer form of deoxycholate.

Research on heteropoly acids and related POM compounds is a field of increasing importance. Complex proton acid that incorporates polyoxometalate anion having metal-oxygen octahedra as the basic structural unit known as a Keggin heteropolyanion typically represented by the formula $XM_{12}O_{40}^{x-8}$ have several advantages as a catalyst.

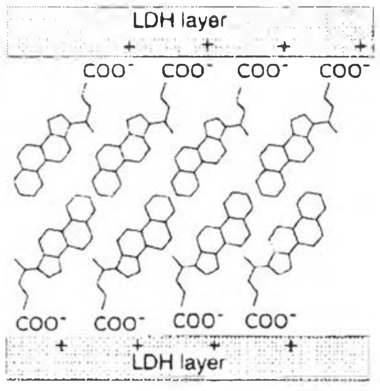


Figure 2.2 Schematic drawing for the microstructure of deoxycholate- intercalation compound (Ogawa and Asai, 2000).

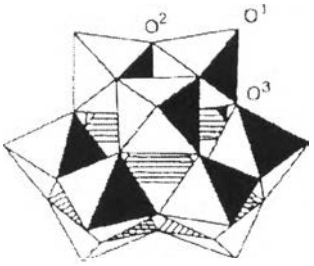


Figure 2.3 The Keggin structure of the $XM_{12}O_{40}^{x-8}$ anion (α-isomer): terminal (O^1), edge-bridging (O^2), and corner-bridging (O^3) oxygen atoms (Kozhevnikov, 1997).

Dimotakis *et al.* (1990) prepared Keggin-type POM pillared hydrotalcite, i.e., $H_2W_{12}O_{40}^{6-}$ (d = 14.8 Å) from terephthalate interlayer precursors. Together with Wang *et al.* (1992), the POM ion with Keggin-type structure-, $PV_3W_9O_{40}$, pillared hydrotalcites (d ~ 13.0 Å) were prepared in an aqueous in one-step reactions. Several starting materials and treatment conditions were also studied.

Keggins are the most stable and often appear as demonstrated in literatures. Therefore, it would be interesting to use polyacid- and POM- (Keggin ions) pillared hydrotalcite clays as catalysts for SCR of NO with NH_3. In this work, POM-pillared clays were prepared by using deoxycholate-pillared clay as precursor. All pillared clays were characterized and used as precursors (or support) to prepare catalysts for SCR of NO by NH_3.