CHAPTER II

LITERATURE REVIEWS

In this section, special attention of related papers devoted directly to the effect of silicon to aluminium ratio of Ag-zsm-5 zeolite catalysts on silver cluster formation However, the other points are also mentioned so that all information can contribute and lead to some interesting subjects concerned in this thesis.

J.Texter *et al.*[5] examined Ultraviolet absorption of aqueous solutions of tosylate, sulfate, perchlorate and tetrafluoroborate salt of Ag^+. The results of Ultraviolet absorption band at 225, 210 and 192 nm are attributed to isolate Ag^+ ion in the solution.

A.Henglein *et al.* [6] studied Radiolytic reduction of Ag^+ ions in aqueous solution by γ-rays of a Co source and reduction by sodium borohydride in the presence of polyphosphate. The result of Radiolytic reduction showed that when the time of reduction was below 9 minutes Ag^+ ion in aqueous solutions were to converted to silver cluster (Ag^{2+}_4 absorption band in the reduction was 275 nm) so after Radiolytic reduction time was longer than 9 min. rather suddenly two new bands at 300 and 330 appeared (the band at 330 and 330 nm were assigned to Ag_3 and Ag_5 cluster respectively). After 19 min. a band at 345 nm developed (the band at 345 nm was assigned to Ag_8 cluster)

The formation of silver cluster by Radiolytic was

$$Ag^+ + eq^- \rightarrow Ag^0 \tag{1}$$

$$Ag^0 + Ag^+ \rightarrow Ag^+_2 \tag{2}$$

The Ag^+_2 ions dimerized

$$2\,Ag^+_2 \rightarrow Ag^{2+}_2 \tag{3}$$

The absorption spectra of these species has also been observed at 360,310,275 nm assigned to Ag^0, Ag_2^+ and Ag_4^{2+} respectively.

B.G. Ershov et al. [7] Examined Long-lived clusters by pulsing Radiolytic reduction of silver ions in $AgClO_4$ solution which contained 0.1 M 2-proparol. The result showed that the solution contained stronger cluster absorption bands at 295 and 325 nm. when between 1 to 10 pulses were applied. After the absorption of 20 pulses, these bands were no longer present in the spectrum but the plassmon band of larger metallic particles was present. This band was 370 nm. and then after 100 pulses the band at 380 nm appeared , this band was assigned to metallic silver nanoparticle. They reported that a cluster at 325 nm was precursor to the larger particle.

K.A. Bethke and H. Kung [1] studied a lean reduction of NO with C_3H_6 on 2 and 6 wt% Ag/Al_2O_3 catalysts. They reported that high conversions of No were obtained over 2 wt% Ag/Al_2O_3 and conversion of NO to N_2 was much lower than 6 wt% Ag/Al_2O_3. The difference in the behavior of two catalysts was attributed to the much higher Ag dispersion for 2 wt% Ag/Al_2O_3 than 6 wt% Ag/Al_2O_3, and the oxidation states of Ag were different under the reaction conditions. The 2 wt% Ag/Al_2O_3 was believed to contain silver in the +1 oxidation state under the reaction conditions (Ag^+) while 6wt% Ag/Al_2O_3 catalyst contained Ag^0 cluster. For the presence of Ag^0 resulted in a high rate of C_3H_6 combustion while Ag^+ in 2wt% Al_2O_3 resulted in a high conversions of NO to N_2.

Zhijang Li et al. [2] examined the promotion of Ag-ZSM-5 by cerium for selective catalytic reduction (SCR) of NO with methane in the presence of an excess of oxygen. Ce-Ag-ZSM-5 catalysts the CH_4SCR of NOx over the temperature range of 450-600 ^{0}c. The result showed that incorporation of a small amount (1-1.5 wt %) of cerium into Ag-ZSM-5 enhanced the activity and selectivity for SCR with CH_4. The UV-Vis result showed that Silver existed mainly as dispersed Ag^+ ion in a low Ag-

content and conversion of NO to N_2 was much higher than high Ag-content, while nanoparticles of silver of ~ 10nm size were found on the surface of high Ag-content. The dispersed Ag^+ state was more active for SCR reaction while silver particles more effective catalyzed the methane combustion reaction.

Carla Costa *et al.*[8] examined the relation between activity and acidity in variety of ZSM-5 zeolite catalysts with different Si/Al ratio and different photonic content. The acid strength distribution was estimated using temperature program desorption (TPD) of ammonia by applying a digital deconvolution method to the curve. They reported that the most of catalysts had two main peaks of TPD, which show maximum in desorption rate around 450 and 630 K. As the Si/Al ratio increase the number of acid sites decrease and the area below TPD curve were decrease with increase Si/Al ratio.

Ken-ichi Shimizu *et al.* [9] studied selective catalytic reduction (SCR) of NO by n-hexane and n-octane on Ag/Al_2O_3 at the % loading of Ag was 0.6,2,3,5 wt %. The result showed that below 2 wt% of Ag loading , highly dispersed Ag^+ ion were predominant Ag species, while at higher Ag loading above 2wt%, Ag_n cluster were predominant. The Ag^+ ions were responsible for selective reduction for NO to N_2 while Ag_n cluster were responsible for hydrocarbon and N_2o formation. The UV-Vis results showed that the spectrum of the 5 wt% Ag/Al_2O_3 had a broad shoulder around 280-350 nm was assigned to Ag_n clusters.

N.Bogdanchikova *et al.* [4] examined the role of SiO_2/Al_2O_3 molar ratio in the silver cluster stabilization inside mordenite pore. They reported that SiO_2/Al_2O_3 molar ratio regulated silver cluster stabilization by the mean of change of mordenite acid properties. The high concentration and high strength of Brönsted acid site favor the stabilization of silver in the form of clusters inside the pores. In contrast, a low concentration and low strength of Brönsted acid sites and high concentration of Lewis site inside the channels can hinder stabilization of silver clusters. In this case, large silver nanoparticles on the external surface of zeolite were formed.

N.Bogdanchikova *et al.* [10] studied the stability and the declining of silver clusters which have the absorption band at 320 and 285 nm in mordenite having different ratio of SiO_2/Al_2O_3 from 10 to 206. They found that the absence of both

band was the important thing which indicated the difference of silver species. The oxidation reaction would make the peak at 320 and 285 nm change to 310 and 240 nm into silver clusters whose the stability would depend on the ratio of SiO_2/Al_2O_3. The least life time of the cluster at 320 and 285 nm about 40 and 20 days respectively.

N.Bogdanchikova et al. [11] examined the silver phase on Ag/Al_2O_3 catalyst which affected the oxidizing nitric oxide to nitrogen dioxide by C_3H_6. From the study , the conversions of NO to NO_2 by 1.2 wt% Ag/Al_2O_3 were lower than on 10wt% Ag/Al_2O_3. from UV-Vis result showed that both of 1.2 wt% and 10 wt% Ag/Al_2O_3 have major peak at 210, 230 and 350 nm, thus the peaks at 210 and 230 nm are attributed to Ag^+ions , peaks at 290 and 350 nm are tentatively assigned to small Ag_n^{m+} cluster and the absorption at wave lengths > 390 is attributed to metallic silver particle but the signal associated with metallic silver particles in 1.2 wt% Ag/Al_2O_3 was significantly lower than 10 wt% Ag/Al_2O_3. The conversion of NO to No_2 showed that 10 wt% Ag/Al_2O_3 was more active than 1.2 wt% Ag/Al_2O_3.

V.S. Gurin et al. [12] reported that the factor affecting a self-assembling of silver and copper clusters during the reduction of ion exchanged forms of zeolite (mordenite, erionite, L, beta clinoptilolite, ZSM11,Y) in hydrogen. A matching of zeolite void can be easily stabilized in the zeolite with certain pore size in the range of 0.63-0.67 nm. Zeolites had void wider than 0.7 nm stabilize these clusters only for a low reduction temperature small pore (cross section area $\leq$ 0.63 does not stabilize Ag_8 clusters. From the results of UV-Vis showed that, silver-contained mordenite (280.285 and 318.323 nm), erionite (284-293 and 321-322 nm), zeolite beta (290 and splitted peak at 314 and 325 nm), L-zeolite (288-292 and 326 nm) and zeolite Y (single peak at 318-325 nm) can be assigned to Ag_8 clusters.

D.L. Kovalenko et al. [13] studied Silver nanoparticles and cluster produced within the conventional so-gel process with tetraethyl orthosilicate hydrolysis by reduced with hydrogen at different temperatures (150,300 and 500 °c). The result of their study concluded that the increase of Ag concentration results in the formation of larger silver nanoparticles and the silver cluster can be produced only at low temperature of processing in hydrogen. At temperatures more than 150 °c the higher

amount silver is incorporated in the porous silica matrix and the larger nanoparticles are formed.

V.S. Gurin et al. [14] studied an ion-exchangeable zeolite (mordenite) used to control the formation of nanoparticle and clusters within the solid matrix by the hydrogen reduction of metal ions (Ag^+, Cu^{2+} and Ni^{2+}). The result showed that Sio_2/Al_2O_3 molar ratio (15-206) in mordenite appears to be an efficient tool to manage the reducibility of the metal ions. For Ag-mordenite reduced at 200 °c. Intensity of these maxima and their shape depends strongly on MR value but their position of the short wavelength part is almost the same for different MR. The principal peaks are at 280-285 nm and 318-323 nm. In contrast,, in the range of wavelengths 370-450nm,the broad absorption band appears to be dependent from MR remarkably. The most pronounced maxima in the UV range are inherent to the medium valves of MR. while The long-wavelength path develops more for the lowest and highest MR (15 and 206). These UV maxima were assigned to the silver clusters (Ag_8) and the absorption band at above 370 nm was assigned to silver nanoparticles (with sizes in range 1-5 nm)

Shigeo Satokawa et al. [15] studied the effect of H_2 on the selective reduction of NO by light hydrocarbon over Ag/ Al_2O_3 catalyst. The results showed that NO reduction activity at the low temperature region was increased by adding H_2 should act as a promoter of NO reduction by hydrocarbon over Ag/ Al_2O_3. The enhancing effect by H_2 over silver-based catalysts has been explained on the basis of reversible redox behavior between silver cations and silver metal particles in Ag/ Al_2O_3. Therefore, the activity of hydrocarbon oxidation by adding H_2 is speculated to be caused by redox behavior of silver species on alumina surface.

Kazuhito Sato et al. [16] examined the addition of small amount of rhodium enhanced the activity of Ag/ Al_2O_3 catalyst for the selective reduction of NO with decane at low temperatures. The Rh-promoted Ag/ Al_2O_3 showed its high performance even in the presence of low concentrations of SO_2. The result of UV-Vis spectroscopy indicated that the silver species were Ag^+ion (216-238 nm), $Ag_n^{\delta+}$ (238-272 nm) m Ag_{n1}(275-326 nm), Ag_{n2} (330-385 nm). The major silver species on Rh-promoted Ag/ Al_2O_3 were $Ag_n^{\delta+}$ clusters which would be responsible for the high

activity of NO reduction while Ag_{n1}, Ag_{n2} would be responsible for decane combustion.
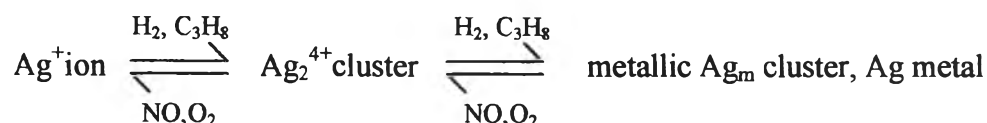
M.A.Ali *et al.* [17] studied about synthesis, characterization and catalytic activity of ZSM-5 zeolite having variable silicon-to-aluminum ratios they prepared ZSM-5 with different Si/Al ratio in the range 15-100 by a rapid crystallization method. They concluded that the acids of catalysts were deceased with increased Si/Al ratio.

Junji Shibata *et al.* [3] studied about Ag cluster as active species for selective catalytic reduction for NO by propane in the presence of hydrogen over Ag-MFI. SCR activity over Ag-MFI was significantly enhanced by addition of H_2 below 673K. Upon the removal of H_2 from reaction gases, NO reduction activity decreased to the same conversion before the addition of H_2 indicating that the promotion effect of H_2 on NO reduction activity was reversible. The UV-Vis spectroscopy was used to identify the active structure of Ag species during the C_3H_8-SCR. Ag^+ion (adsorption bands at 210,232 nm) was mainly in the existence during the C_3H_8-SCR in the absence t of H_2 while $Ag_n^{\delta+}$ clusters ($2 \leq n \leq 4$) (adsorption bands 260,285 nm), together with Ag^+ion, were formed in the presence of H_2. NO reduction rate and band intensity due to $Ag_n^{\delta+}$ cluster increased with an increase in H_2 concentration. On the other hand, the formation of metallic Ag_m cluster ($3 \leq m \leq 5$)(adsorption bands 250,312 nm) and Ag metal (350-380nm) increased the contribution of nonselective hydrocarbon combustion. From the results, it is indicated that a moderately agglomerated $Ag_n^{\delta+}$ cluster is a high active species for SCR by C_3H_8 in the presence of H_2 and that the role of H_2 is the reduction of Ag^+ion to Ag_n^+ cluster. Ag species is markedly influenced by concentrations of gaseous components not only H_2 but also NO and C_3H_8. In addition, the type of Ag species was reversibly changed among Ag^+ion, Ag_n^+cluster and metallic Ag_m clusters together with Ag metal, depending on the reaction atmosphere which suggests that gaseous component control the balance among Ag species on the catalyst.

Beyer and Jacob [18] reported the reduction of Ag^+ ion to (Ag_2^+) m by H_2 as follow.

$$H_2 \rightleftharpoons 2H$$

$$H + Ag^+ \rightleftharpoons [Ag^0H^+]$$

$$[Ag^0H^+] + Ag^+ \longrightarrow Ag_2^+ + H^+$$
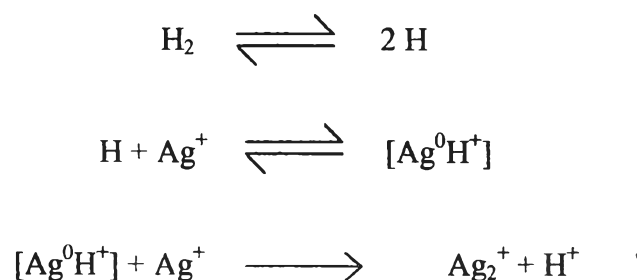
Ag species in MFI zeolite are balanced as described during SCR by C_3H_8 as follow.

$$Ag^+ \text{ion} \underset{NO,O_2}{\overset{H_2, C_3H_8}{\rightleftharpoons}} Ag_2^{4+} \text{cluster} \underset{NO,O_2}{\overset{H_2, C_3H_8}{\rightleftharpoons}} \text{metallic } Ag_m \text{ cluster, Ag metal}$$

V.S. Gurin et al.[19] examined the silver and copper nanostructures within the erionite regular lattice. 14wt%Ag-erionite was reduced with H_2 at the temperature about 100,200,300,400 and 500 °c. The UV-Vis spectroscopy showed that for the reduction temperatures 100-300 °c were presented peaks at 293,322,447 and 683 nm which assigned to Ag_8 cluster. For the reduction temperature 400, 500 °c peaks at 447 and 683 nm were disappeared. The new peak at 380 and 410 nm were developed. They concluded that the silver reduced species associated with the above peaks at 447, 689 nm are transformed to silver nanoparticles between 400 and 500 °c.

Junji Shibata et al. [20] studied the structure of active Ag clusters in the Ag zeolites for SCR of NO by propane in the presence of Hydrogen. Ag-MFI (Si/Al 22) and Ag loading about 1.7, 3.0 and 3.5 wt% were used to compare with H_2-TPR. The H_2-TPR result showed that H_2-TPR were two H_2 consumption peak, the first peak appeared at temperature range from 373 to 573 K. The temperature of the second peak was shifted to a lower temperature with an as increase in Ag content. They concluded that All Ag^+ ions(210,235 nm) are reduced to Ag_{2p}^{p+} cluster first peak and the Ag_{2p}^{p+} cluster are reduced to Ag metal particles at the second peak. And then 3.5 wt% Ag-MFI Si/Al 22 were pretreated in 0.5% H_2 at 573 K for 0.5h and treated in 10% O_2 at

773 K   for 1 h.The UV-Vis result of this section showed that 3.5 wt% Ag –MFI after a H_2 reduction at 573 K where most of Ag species should be present as the Ag_4^{2+} clusters (peak range 280-345 nm). It was confirmed by Ag K-edge XANES spectra. The amount of the clusters increases with an increase of Ag loading. The conversion of NO to N_2 over Ag-MFI is improved by an addition of 0.5% H_2. Its result showed that the present of Ag_4^{2+} clusters after adding 0.5% H_2 in the condition of SCR-C_3H_8 are increased the NO conversions. They concluded that the Ag_4^{2+} clusters in Ag-MFI catalysts are responsible for the selective reduction of NO by C_3H_8.

Junji Shibata *et al.* [21] studied the influence of zeolite support on the activity enhancement by the addition of hydrogen for SCR of NO by propane over Ag-zeolites. The various of Ag containing zeolites (MOR, MFI, BEA and Y) were used to study for SCR- C_3H_8 by the addition of 0.5% H_2 below 673 K. The results showed that NO conversion was increased on Ag-MFI and Ag-BEA while it was not on Ag-MOR and Ag-Y. The C_3H_8-SCR activity was enhanced by the addition of H_2 became large with an increase in Si/Al ratio of MFI. The UV-Vis spectroscopic study exhibited that the state of Ag species differed by zeolite types. From comparison between the C_3H_8-SCR activity and UV-Vis spectra. It was confirmed that $Ag_n^{\delta+}$ $(2 \leq n \leq 4)$(adsorption band at 260, 285 nm) is highly active species for the NO reduction independently on zeolite types except Ag-Y. The balance of Ag species that governed the C_3H_8-SCR activity was shifted to more cationic Ag side with an increase of Si/Al ratio and in order of acid strength (MOR.MFI>BEA). It is suggested that oxidative dispersion of agglomerated Ag species by the increase acid amount and acid strength.