

## CHAPTER II

### LITERATURE REVIEW

Zeolite materials and metallosilicate are known to be related to the degree of substitution of aluminum and metals for silicon in the framework. The modification of catalytic properties through dealumination of zeolite lattice by various treatments has therefore been a matter of considerable interest. So, some of the more prominent studies of the modified zeolite and metallosilicate were summarized below.

For the preparation, the pH effect on the preparation of MFI type ferrisilicate zeolites was proposed by Young-Hoon and et al. [10]. They suggested that ferrisilicate with MFI type structure were hydrothermally synthesized under the different pH of the final synthesis gel and the relation between the content of the framework incorporated iron and the pH effect was examined. The structural environments of iron in the ferrisilicates were characterized by XRD, SEM, IR, EPR and ammonia-TPD. It has been shown that pH of the final gel mixture during the synthesis affects the crystal size, morphology, chemical composition and catalytic activity. The results of the lattice parameters, IR and EPR indicate the existence of a framework iron and the content of framework iron depend on pH of the synthesis gel. By iron cation can be incorporated into the tetrahedral framework sites of a molecular sieve structure during the ferrisilicate synthesis. The degree of iron substitution is generally very low. However, the amount of iron incorporated is dependent on the synthetic condition. Iron does not necessarily occupy exclusively the framework site of ferrisilicate. It can also exist in the ion exchange sites as the charge balancing cation and also in the ferrisilicate cavities as the small iron oxide particle. Moreover they found that when the pH of the gel mixtures is maintained at 9, regular twinned and elongated crystals are found with a size about 30  $\mu\text{m}$  in length. Small cube-shaped crystals of 2  $\mu\text{m}$  were obtained when the pH of the gel mixtures was increased to 11. It is well known that more nuclei are formed in the higher alkalinities in the synthesis MFI type silicalite-1. Therefore, the crystal size of ferrisilicates decrease with increasing the pH of the synthesis gel. Therefore, they can conclude that the content of framework iron is increased with decreasing the pH of the final synthesis gel.

However, Bellussi et al. [11] prepared vanadiumsilicates by varying concentration of NaOH in the gel mixture during the synthesis and suggested the Na<sup>+</sup> ions affect the state of the vanadium contained in the crystalline solid and its stability to the thermal treatments, Dewar et al. [12] prepared Al- and Ga- substituted MFI zeolites from a sodium-free system in the presence of fluoride ions. They confirmed that the compositions of the products have the least value for Si/M ratio, when the pH of the synthesis gels is near to neutral. In the case of the synthesis of aluminosilicate zeolites, alumina-rich zeolites crystallize preferably at a higher pH in the mean while silica-rich zeolites crystallize preferably at a lower pH [13]. Szostak et al. [14] also suggested that initial ferrisilicate complex in the synthesis had to be prepared under an acidic condition to avoid precipitation of rust-red iron hydroxides and, once iron was complexed in this manner, the formation of ferric hydroxides appeared to be suppressed at elevated pH. In that work, they only focused on the formation of initial ferrisilicate complex and they discussed that the pH for the successful preparation of ferrisilicate was needed to be adjusted between 8 and 11 required for the hydrothermal crystallization. However, they did not consider a systematic study between the framework iron content and the pH of the final synthesis gel. Moreover, they did not recognize that the pH of the final gel mixture plays a critical role in the framework incorporation of iron.

For the hydrothermal treatment, Kanchanawanichkun P. and et al. [15] proposed the effect of Pd on the durability improvement of Co/HZSM-5 for NO removal under hydrothermal treatment. The durability of catalysts subjected to hydrothermal treatment with a He stream containing 10% steam at 600°C for 24 h. was investigated. The loss of catalytic activity for NO conversion after hydrothermal treatment on Co/HZSM-5 was due to framework dealumination of the zeolite. The Pd-modification of Co/HZSM-5 resulted in improved durability against the hydrothermal treatment when loading Pd approximately 0.4% wt. From NMR spectra, dealumination of tetrahedral aluminum in the zeolite framework was completely prevented when loading Pd from 0.4% wt or higher. The effect of water on the activity of SCR of NO by methane over Co-ZSM-5 was investigated by Armor et al [16]. They also conclude that the water effect was a kinetic phenomenon, and that Co/HZSM-5 catalysts were not durable under long steam aging. The reduction of low concentrations of nitric oxide with methane under wet conditions on Co/HZSM-5, Pd/H-ZSM-5. And Pd/



Co/H-ZSM-5 catalysts has been investigated by Kikuchi et al. It was found that the reduction of NO<sub>x</sub> with CH<sub>4</sub> hardly proceeded on Co/HZSM-5 under wet conditions. Kikuchi suggested that the activity loss of the catalysts in wet condition was mainly due to adsorption of H<sub>2</sub>O molecules formed during the reaction on the surface and to the change of the surface mechanism of the NO reaction on Co/HZSM-5. Armor [16], who reported that the loss of catalytic activity could be reversed by eliminating water from the system. On the other hand, severely wet conditions might damage the catalyst structure, besides preventing complete adsorption. Moreover Kanchanawanichkun P. and et al. [15] found that according to the XRD profile of the fresh catalysts, the crystallinity of HZSM-5 and Co/HZSM-5 was considerably reduced following hydrothermal treatment, in the case of the Pd modified Co/HZSM-5, there was only a slight decrease following hydrothermal treatment, especially in the case of 0.4% Pd/ Co/HZSM-5, consequently, it definitely appeared that the 0.4% Pd/ Co/HZSM-5 catalyst under hydrothermal treatment with respect to crystallinity. The results for the <sup>27</sup>Al MAS NMR spectra of the catalysts before and after pretreatment. The spectra confirmed that the severe steam treatment caused dealumination. This is consistent with another report of loss in activity and stability after steam pretreatment due to framework dealumination of zeolite (Budi and Howe) [17]

Nevertheless, Rungsimanop J. and et al [18] suggested that Effect of Pd on the stability improvement of Cu/H-MFI for NO removal under hydrothermal pretreatment conditions. The stability of the catalysts subjected to hydrothermal treatment with a He stream containing 10% steam at 800°C was investigated. The Cu/H-MFI catalyst markedly lost its activity for NO conversion after the hydrothermal pretreatment. The Pd-modification of the Cu/H-MFI resulted in improved stability against the hydrothermal treatment when loading Pd approximately 0.2-0.3 wt%. The dealumination of tetrahedral Al in MFI framework was completely prevented when loading Pd from 0.3 wt% or higher. Further loading of Pd higher than 0.3% caused the larger crystallite size upon pretreatment as seen from the scanning electron micrographs (SEM). It has been suggested that there may be some changes in Pd and Cu on H-MFI, such as alloying/or palladium oxides formation, leading to some loss of Cu<sup>2+</sup> active species for NO removal. This results in the limitation of NO conversion improvement for the pretreated Pd/Cu/HMFI with the loading amount of Pd higher than approximately 0.3%. Other kinds of metal ion-exchanged MFI such as

galium [19, 20] iron [21, 22], cobalt [13-25], cerium [26, 27], platinum [28], palladium [29] were also studied for the reaction of NO removal under the hydrothermal pretreatment. In addition, other groups of active catalysts such as transition metal and/or metal oxide (Cu, Co Mn, Fe, Cr, V, Ag) were also concerned [30-34]. Nevertheless, those types of catalyst referred above suffer from the deactivation under the condition of high temperature and the presence of steam possibly occurred in practical use [35-37]. On the other hand, platinum group metal catalysts have also been studied for NO conversion [38, 39] and it is known that platinum group metal catalysts are highly resistant to the presence of steam [40]. H-MFI and Cu/H-MFI considerably lost their crystallinity after pretreatment due to the structural collapse. Such tendency of loss in crystallinity was reduced with the presence of Pd, and no significant loss of crystallinity was observed on Pd/ Cu/HMFI catalysts with the amount of Pd up to 0.2 wt% or more. This should be noted that though some loss of structure occurred after pretreatment, especially for the catalysts without Pd, the content of Cu or Pd loaded was not significantly changed by the pretreatment as seen from the ICP data. This indicated that there was no significant loss of metal species such as evaporation of metal due to the hydrothermal treatment. The result of  $^{27}\text{Al}$  MAS NMR of the catalysts before and after pretreatment shown that hydrothermal treatment of H-MFI, Cu-MFI and 0.1% Pd/ Cu/HMFI caused the appearance of new signal assigned to extra-framework Al atoms in octahedral coordination [41-43]. This is consistent with the previous report of loss in activity and stability after steam pretreatment due to framework dealumination [42]. However, after loading 0.3 wt% Pd and after pretreatment found that no peak relating to octahedral aluminum. This suggests that the presence of a certain amount of Pd, approximately 0.3 wt% loading as observed here could stabilize the MFI framework structure by preventing the occurrence of dealumination.

However, Dangsawai T. and et al. [44] proposed that Enhancement of activity for NO removal of MFI-type H-Co-Silicate by hightemperature pretreatment. By the activity of Cu/H-ZFM-5 decreased with an increase of pretreatment temperature. Incontrast with Cu/H-ZSM-5, the activity of H-Co-Silicate for NO removal increased with the pretreatment temperature. As for H-Co-Silicate, the pretreatment at 1000°C was the optimum condition to enhance the conversion that was four times higher than that without pretreatment. Some parts of cobalt species migrated from the



framework and became active sites that enhance the activity for NO removal. And found that XRD patterns of H-Co-Silicates and Cu/H-ZSM-5 after pretreatment, H-Co-Silicate maintains the MFI structure even at 1100°C. However, the intensity of X-ray diffraction lines of H-Co-Silicate after pretreatment at 1100°C is lower than the without pretreatment. It can be indicated that, after pretreatment at 1100°C, H-Co-Silicate has lower crystallinity causing the loss of performance for NO removal. But for Cu/H-ZSM-5, the XRD pattern after pretreatment at 1000°C changes visibly, compared with that without pretreatment. The intensity of identified diffraction lines at around 23.1, 8.03, 23.94° 2θ which are ascribed to Silicon oxide as cristobalite form appeared after pretreatment at 1000°C. Therefore, it means that MFI-type structure of Cu/H-ZSM-5 is destroyed by the high temperature pretreatment, as supported by a previous paper [45].



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