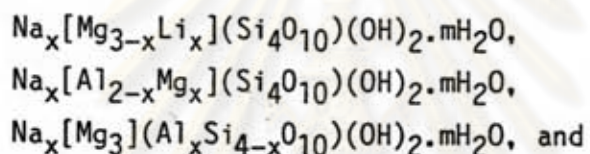


CHAPTER 5

GENERAL CONCLUSIONS

In methanol conversion, methyl formate and dimethyl ether were formed through dehydrogenation and dehydration, respectively, according to the acidic properties of catalysts. Sodium type of layer silicate clays used in this study were laponite, saponite and montmorillonite which the chemical formula were :



respectively. These sodium ions were exchanged with copper ions from copper nitrate solution by means of ion exchange in the catalyst preparation. The catalysts obtained were abbreviated as Cu-Lapo, Cu-Sapo and Cu-Mont. The conversion of methanol was carried out in the temperature range of 200°C to 300°C on these copper-exchanged clay catalysts. Methanol was selectively converted to methyl formate over Cu-Lapo. On the contrary, Cu-Sapo and Cu-Mont catalyzed only dehydration to dimethyl ether and methyl formate was not formed, due to their acidities.

The difference in acidities of each catalyst caused by the difference in the substitution of metal ions in the layer silicates. Saponite is the tetrahedral substitution of Si^{4+} with Al^{3+} while laponite and montmorillonite are octahedral substitutions of Mg^{2+} with Li^+ and Al^{3+} with Mg^{2+} , respectively. Not only the difference in the substitution but also the difference in layer lattice aggregation, surface area, amount of acid sites / area and calculated average electronegativity, are also responsible for the difference in methanol

conversion. X-ray diffraction analysis and nitrogen adsorption studies showed that laponite and saponite possessed macropores due to delaminated face to edge or edge to edge aggregation while face to face aggregation leading to the formation of micropores which was observed on montmorillonite. The NH_3 -TPD spectra also show that acidic properties of catalysts are influenced by the nature of structure of smectite clays.

The dehydrogenation activity of Cu-Lapo increased with reaction temperature. The selectivity for methyl formate was limited by thermodynamic equilibrium and the decomposition of methyl formate to carbon monoxide. Stable catalytic activity and selectivity of Cu-Lapo were obtained at a low reaction temperature (200°C) at time factor of 700 g-cat. At the high temperature of reaction (300°C), catalytic deactivation occurred which may cause from coke formation, sintering or the effect of H_2O formation.

The dehydrogenation activity of Cu-Lapo increased with the treatment temperature in nitrogen atmosphere. Water was found to inhibit the dehydrogenation by replacing to the methanol on the Cu-Lapo which proved by infrared spectrometric measurement.

The effect of thermal treatment can be interpreted from a thermal gravimetric analysis to be a result of desorption of water molecules coordinated to copper in laponite.

The catalytic activity and selectivity in various treatment atmospheres and levels of copper ion exchange were studied to investigate the type of active site. In the treatment atmosphere of hydrogen, reduction of oxidation state of copper ions occurred which was analyzed by electron spin resonance. The catalytic activity of Cu-Lapo treated in hydrogen was higher than that treated in nitrogen or air which the reduction might be occurred later. These results suggested that reduced copper ions might be the active sites in



dehydrogenation of methanol.

The amounts of copper and sodium ions were determined by inductivity coupled argon plasma atomic emission spectroscopy (ICP) measurement and degree of copper ion exchange was calculated. The results showed that the difference species of copper ion could be obtained by the difference in degree of ion exchange and dehydrogenation activity of Cu-Lapo clearly depended upon the degree of ion exchange.

Since the degree of ion exchange effected on the species of copper ion and dehydrogenation activity of Cu-Lapo. These results lead to the conclusion that the dehydrogenation activity of Cu-Lapo depends on the species of copper ion-exchange.

From this research, it is clearly shown that copper-exchanged laponite is an effective catalyst for dehydrogenation of methanol to yield methyl formate, which is one of the key intermediates in methanol-based process in the industries. Due to the limit of researching time, the active sites of this reaction still not clear yet. It will be the great pleasure and progress in the knowledges, if further studies is continued. According to the other aspects in this research, hopefully that the benefits will come to reader as much as possible.

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