

## CHAPTER V

### CONCLUSION

The goal of this research is to search for suitable conditions for copper-catalyzed oxidation of cyclohexane and relevant hydrocarbons and to develop catalytic system for functionalization of saturated hydrocarbons. From this research, it could be found that the oxidation of cyclohexane catalyzed by copper acetate ( $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ), using pyridine-acetic acid as solvent and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an oxidant could proceed at room temperature and atmospheric pressure, with high selectivity for the production of cyclohexanone. The optimum conditions were cyclohexane 20 mmol, pyridine 10-20 mL, acetic acid 1 mL,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  0.2 mmol, and hydrogen peroxide 15 mmol. This condition produced mainly cyclohexanone and trace of cyclohexanol with about 10% conversion of cyclohexane. The catalytic turnover was about 7.5. The reaction rate was very fast. Half-life of this reaction was about 5-10 minutes and the reaction finished within 30 minutes. This reaction time was the fastest for the oxidation of cyclohexane catalyzed by various metal catalysts that have published.

In addition to the main objective which was successful achieved, there were many interesting information from this examination that needed to be further explored. From the results of the comparison of relative reactivity towards cyclic saturated hydrocarbons and chemoselectivity, it was confirmed that the mechanism of this oxidation was occurred by non radical reaction and this oxidation reaction should have cyclohexyl hydroperoxide as an intermediate. On the other hand, using *tert*-butyl hydroperoxide as an oxidant presented the occurrence of a radical intermediate in the oxidation reaction.

It was found that methylenic C-H of alkanes was more reactive than allylic and benzylic C-H bonds. This striking result was in contrast to the order of dissociation bond energy of C-H bond in secondary C-H bond. That made this system

unique. Furthermore, the oxidation of cyclohexene produced only cyclohexenone, not cyclohexene oxide.

Preliminary investigation of the suitable conditions for the functionalization of cyclohexane to produce bromocyclohexane, chlorocyclohexane, and cyclohexyl azide was also achieved.

This system was found to share some common characteristics with iron-based Gif-type systems. For example, the main route of mechanism that occurred *via* a high valent metal-carbon bond and alkylhydroperoxide was believed to take place. The similar trend of reactivity of cycloalkanes and chemoselectivity of the system was also found to be very close to iron-based catalytic systems.

Based upon the tremendous attention devoted to the area of selective functionalization of saturated hydrocarbons, the development of more selective and more practical chemical models to serve in metal-catalyzed functionalization of the most inert chemical compounds will certainly continue.

#### Proposal for the future work

Development of this catalytic system to the large scale experiments that could be applied in a pilot scale is the first thing to be done. In addition, using this copper catalytic system for functionalization of other saturated hydrocarbons should be examined. Moreover, for comparative study other metal catalytic systems for the functionalization of saturated hydrocarbons should be investigated.