

Chapter 4

Conclusions

This thesis presents studies of manganese oxide catalysts supported on silica and alumina whashcoated on foam substrates. The studies include including preparation, characterization, and activity tests. The performance of the foam supported manganese oxide catalysts during acetone oxidation reaction using ozone, and the structural properties of the manganese catalysts during ozone decomposition reaction were investigated in depth. The main conclusions of these studied can be summarized as follows:

- The manganese active phase was well dispersed for the 10 wt % silica- and alumina-supported foam catalysts with no discernable manganese XRD features.
- Complete oxidation of acetone was observed over the manganese oxide catalysts. The introduction of ozone reduced the reaction temperature substantially, which indicates that ozone was a stronger oxidant than oxygen.
- The alumina-supported catalyst was more active than the silica-supported catalyst with higher acetone and ozone conversion TOFs.
- The application of foam substrates gave small pressure drops at high flow rates, indicating that the foam substrates are good supports for reactions of high flow rate.
- *In situ* steady-state Raman spectroscopy measurements showed the presence of an adsorbed acetone species and a peroxide species due to ozone during acetone catalytic oxidation reaction, and also showed the competition for the active

catalyst sites between the two reactants. This can help to better understand the mechanism of the reaction.

- According to the reactivity and steady-state Raman spectroscopy results, a mechanism for the acetone oxidation reaction was proposed. On the 10 wt % $\text{MnO}_x/\text{Al}_2\text{O}_3$ the rate of reaction of ozone with acetone was higher than the rate of decomposition, while on the 10 wt % $\text{MnO}_x/\text{SiO}_2$ the decomposition rate of ozone was slightly higher than the oxidation rate. This indicates that at least for the alumina-supported catalyst, the reactive intermediate for acetone oxidation is the atomic oxygen form.
- For the silica-supported samples the XAS results showed that the ozone decomposition reaction gave rise to an apparent shift of the absorption edge energy (E_0) position to the higher energy region (XANES) with the coordination number of Mn-O being increased (EXAFS). For the alumina-supported samples, however, there was only a small shift of the E_0 position for the 3 wt % sample and nearly no shift for the 10 wt % sample (XANES) with the coordination number of Mn-O being barely increased (EXAFS).
- Alumina-supported catalysts are more active than the silica-supported catalysts due to a higher electron-accepting ability for the alumina-supported catalysts.
- For the samples of the same support, the higher loading sample was more active than the lower loading sample due to the lower oxidation state of the clusters and the Mn atoms in the clusters are more positively charged.