

## CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS

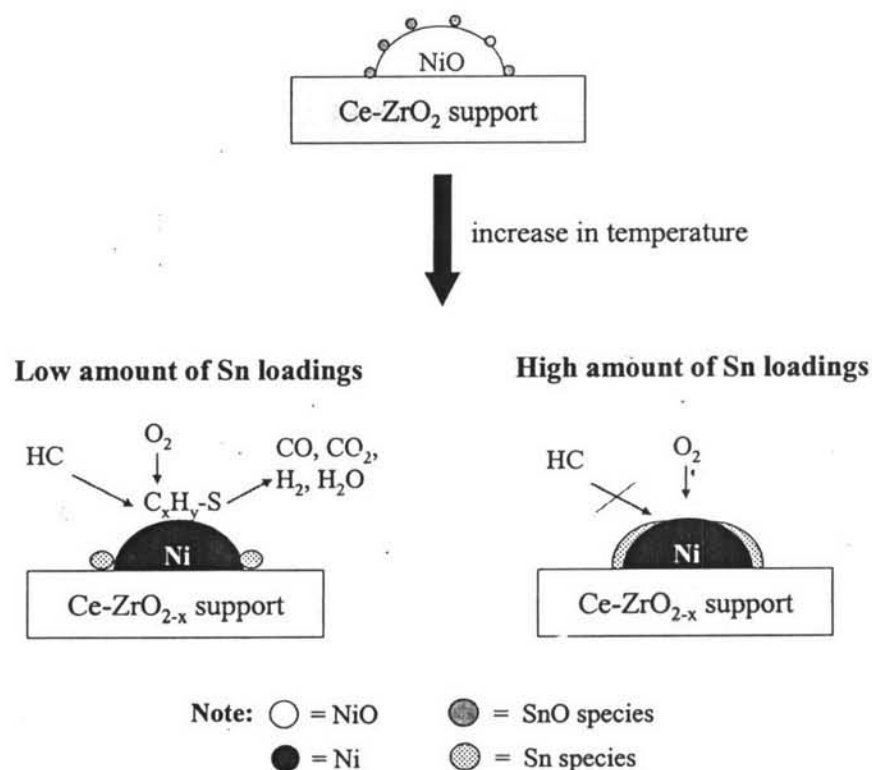
#### 8.1 Conclusions

It can be concluded that the Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalysts showed higher catalytic activity and stability for methane and iso-octane partial oxidation than Ni/CeO<sub>2</sub> and Ni/ZrO<sub>2</sub> catalyst with a little carbon deposition after prolonged reaction time. This might be due to the fact that high metallic Ni dispersion, reducibility and surface oxygen mobility which are the important properties of catalyst for reduction carbon deposition.

The use of reducible support showed an advantage for methane and iso-octane partial oxidation. The β"-Al<sub>2</sub>O<sub>3</sub>, ceramic material with non-stoichiometric (Na<sub>2</sub>O)<sub>(1+x)</sub> Al<sub>22</sub>O<sub>33</sub>, where 0.15 < x < 0.3 and fast Na<sup>+</sup> ion conducting solid electrolyte, as a catalyst support was used to compare with the Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>. The catalytic activity for methane and iso-octane partial oxidation over Ni supported on β"-Al<sub>2</sub>O<sub>3</sub> is lower than Ni supported on Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>. Both catalysts are quite stable when operated under normal conditions, yet the Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst is more stable when rich conditions are applied. According to literature, the addition of alkaline earth oxides could suppress coke formation. However, Ni/β"-Al<sub>2</sub>O<sub>3</sub> with Na<sup>+</sup> conducting ion is not active for methane and iso-octane partial oxidation. Thus, Na<sup>+</sup> cannot promote partial oxidation reaction.

Although 5 wt% Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalysts showed high activity, selectivity, and stability with a resistance to coke formation for methane and iso-octane partial oxidation, some carbon deposition was still observed. The additions of Sn and Nb as the promoters were applied. The results showed that addition of a small amount of Sn (< 0.5 wt%) lowered the catalytic activity for methane and iso-octane partial oxidation by less than 5% while the extent of carbon deposition was decreased by more than 50%. However, Sn loadings higher than 1 wt% caused a massive drop in catalytic activity. This indicates that as long as the Ni surface is only partially covered with Sn species, the active sites for the partial oxidation of methane

and iso-octane remain intact, while the surface site ensembles required for carbon formation are blocked. According to the experimental results, the model of Ni-Sn catalysts might be proposed as shown in Figure 8.1.



**Figure 8.1** Proposed model for Ni-Sn/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalysts.

The addition of NbO<sub>x</sub> (1, 5 and 10 wt%) into Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> lattice of Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst decreased the catalytic activity for methane and iso-octane partial oxidation and increased the amount of carbon deposition. The amount of carbon deposition was increased with an increase of Nb loadings. This might be due to the inhibition of the surface oxygen reduction of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> and weak interaction between NiO and the support from a spillover phenomenon by loading NbO<sub>x</sub> into Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> lattice. Moreover, it can not rule out the high acidity of NbO<sub>x</sub>.

## 8.2 Recommendations

The catalytic partial oxidation of hydrocarbons is the attractive alternative process for hydrogen production. The challenge of this process is how to minimize carbon deposition. In this work, the added small amount of Sn into Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst was successive for reduction of carbon deposition. However, the behavior of Sn at high temperature should be clarified. Development of new atomic scale characterization methods to identify the nature of Sn species, responsible for suppression of coking should be studied.

The further study in oxidation state of Ni related with the activity for these reactions is necessarily.

Once the role of Sn is understood, can promoters other than Tin be developed to avoid coking? We know that large amounts of NbO<sub>x</sub> are not beneficial. However, could very small amounts of NbO<sub>x</sub> doping (< 1%) work, where acidity is not dominant?