

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

4.1.1 BET Surface Area

The fresh catalysts were measured their surface areas by the multiple point BET method. The effects of Ce and Cr loading on the BET surface areas of catalysts were given in Table 4.1. It is found that addition of Ce and Cr decrease the surface area of catalysts when compared with the Ni catalyst. The surface area of catalyst was lost due to the interaction between active metal and promoter. Ni-Cr catalyst has the lowest surface area. Although the particle size of Cr is smaller than Ce, Ce has higher surface area. Because ceria is a high surface area material, it is interesting to use it as support of catalysts (Cheng *et al.*, 1996, Tiernan and Finlayson, 1998).

Table 4.1 BET surface areas of catalysts prepared

Catalyst	BET surface area (m ² /g)
15% Ni /Al ₂ O ₃	92
15% Ni 5%Ce /Al ₂ O ₃	75
15% Ni 5%Cr /Al ₂ O ₃	70

4.1.2 Temperature-Programmed Reduction

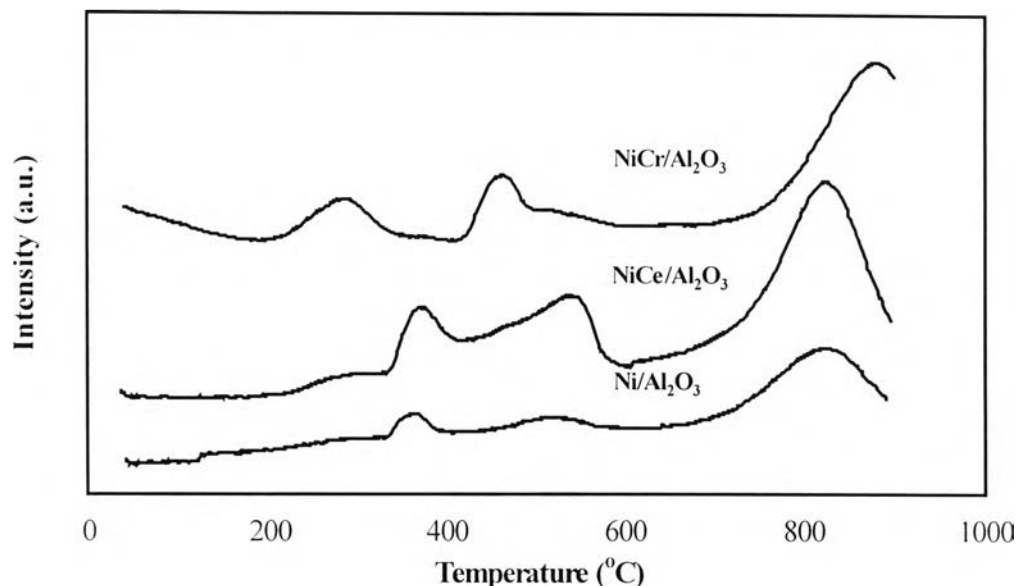


Figure 4.1 TPR results of 15%Ni/Al₂O₃, 15%Ni5%Ce/Al₂O₃, and 15%Ni5%Cr/Al₂O₃

A comparison of the TPR profiles (Figure 4.1) for the catalysts show the influence of the addition of Ce and Cr. The TPR of the Ni catalyst is started above 170°C. The TPR of Ni-Ce catalyst and Ni-Cr catalyst are started above 225°C and 220°C, respectively. As shown in Figure 4.1, two peaks are observed on the Ni catalyst. A low temperature peak at 380°C is identified and attributed to the reduction of nickel oxide. A high temperature peak is located at 820°C. This result is similar to that of the De Bokx study and the Chen study (Chen and Chen, 1990). The occurrence of the low temperature peak is attributed to the reduction behavior of NiO for a physical mixture of nickel oxide and alumina. This is regarded as “free nickel”. The occurrence of the high temperature peak is due to the reduction of the nickel oxide that has interacted with alumina and regarded as “fixed nickel.”

For TPR profiles of Ni-Ce and Ni-Cr catalysts, it is seen that the addition of Ce and Cr influences the change in TPR curves of both catalysts. Since the presence of the low temperature peak is attributed to the reduction of free oxide, it can be seen from Figure 4.1 that more free nickel oxide is present in the promoted nickel catalyst samples. Thus the more the nickel is present as a form of free nickel, the easier the reduction of the promoted nickel catalyst sample. Moreover, it is observed that Ni-Cr catalyst is easier to reduce than Ni-Ce in the low temperature regime. At temperatures above 600°C, Ni-Ce catalyst is reduced more than Ni-Cr Catalyst as indicated by a larger area of the reduction in low temperature region and the lower temperature of the high temperature peak.

4.1.3 X-Ray Diffraction (XRD)

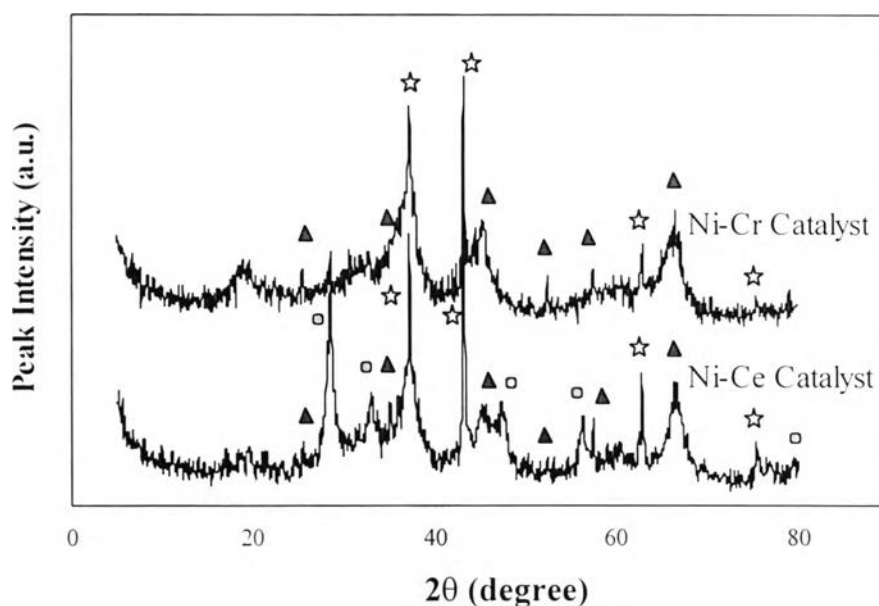


Figure 4.2 XRD patterns of fresh Ni-Ce/Al₂O₃ and Ni-Cr/Al₂O₃ catalysts: (☆) NiO; (▲) Al₂O₃; and (◊) CeO₂.

XRD analysis was carried out for Ni-Ce and Ni-Cr catalysts. The result shows that there exists obvious NiO phases in both Ce promoted catalyst and Cr promoted catalyst. The fresh Ni-Ce catalyst consists of NiO, CeO₂, and Al₂O₃. The fresh Ni-Cr catalyst is composed of NiO and Al₂O₃. There is no existence of the Cr phase peak on the XRD pattern of Ni-Cr catalyst. This reveals that such chromium is formed in amorphous phase or a highly dispersed state.

4.2 Light Off Temperature

4.2.1 The Effect of O₂/C Ratios on Light off Temperature over Ni-Cr Catalyst

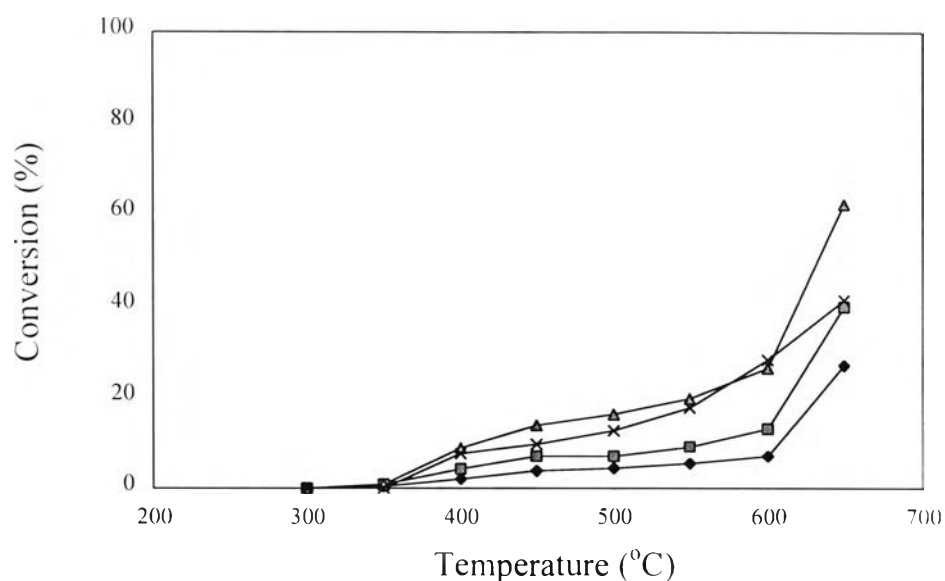


Figure 4.3 Effect of O₂/C on light off temperature of iso-octane over Ni-Cr catalyst; O₂/C ratios: (◆) 0.13/1, (■) 0.25/1, (▲) 0.5/1, and (×) 1/1

The effect of O₂/C ratios on the light off temperature during C₈H₁₈ oxidation over Ni-Cr /Al₂O₃ is presented in Figure 4.3. Generally, the same light off pattern, a sudden increase in temperature with the attainment of a constant temperature at steady state, was observed for each of the ratios studied. Light off temperatures of 610, 560, 420 and 450°C were observed for O₂/C ratios of 0.13, 0.25, 0.5, and 1, respectively.

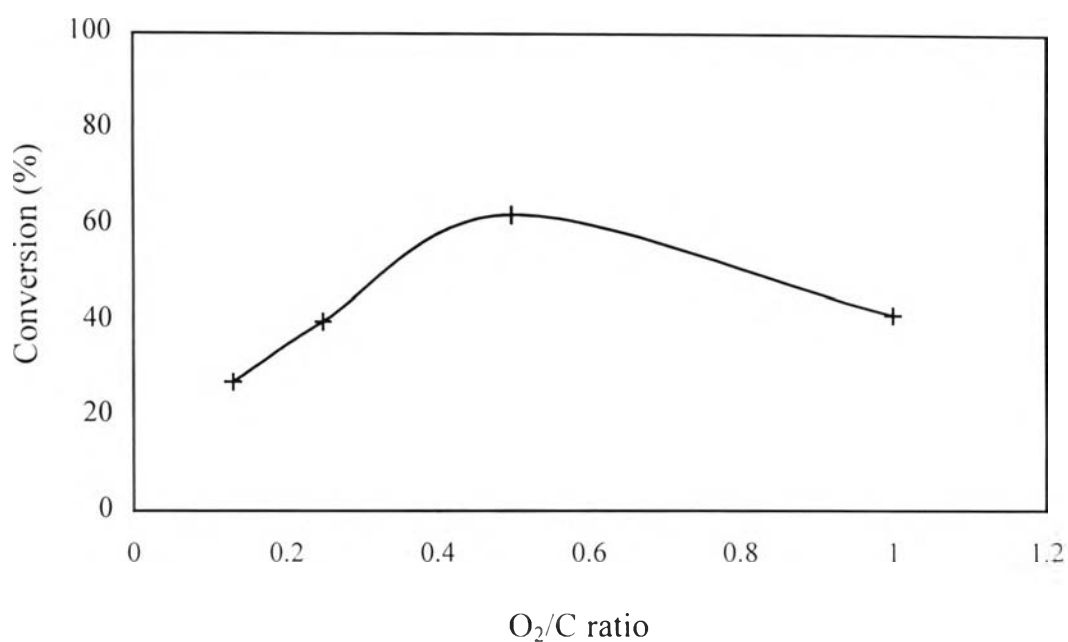


Figure 4.4 Effect of O₂/C ratios on conversion of iso-octane oxidation at 650°C over Ni-Cr catalyst

Figure 4.4 shows the effect of O₂/C ratios on the conversion of iso-octane. It was found that the optimum value of O₂/C ratio that gives the highest iso-octane conversion was 0.5. The decrease in conversion with increasing O₂/C ratio to 0.5 and then decreased when the oxygen ratio more than 0.5. This result is similar to the reported behavior of the oxidation reactions (Ma *et al.*, 1996). The oxidation reaction show a non-monotonic dependence on oxygen pressure with the order with respect to oxygen from positive to negative, depending on oxygen partial oxidation.

4.2.2 The Effect of O₂/C Ratios on Light Off Temperature over Ni-Ce Catalyst

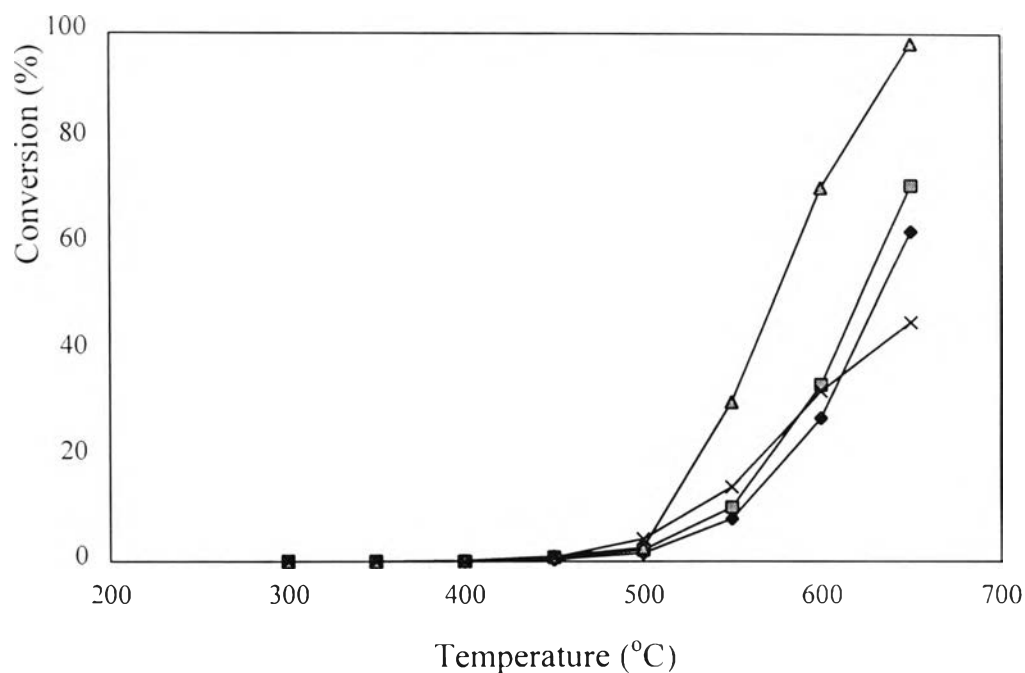


Figure 4.5 Effect of O₂/C on light off temperature of iso-octane over Ni-Ce catalyst: O₂/C ratios: (♦) 0.13/1, (■) 0.25/1, (▲) 0.5/1, and (×) 1/1

The effect of O₂/C ratios on the light off temperature during C₈H₁₈ oxidation over Ni-Ce /Al₂O₃ is shown in Figure 4.5. Light off temperatures of 565, 560, 520 and 545°C were observed for O₂/C ratios of 0.13, 0.25, 0.5, and 1, respectively.

The effect of O₂/C ratios on the conversion of iso-octane over Ni-Ce catalyst is shown in Figure 4.6. It was observed that the optimum value of O₂/C ratio that gives the highest iso-octane conversion is 0.5. This result is similar to the observed patterns of light off temperature and the optimum O₂/C ratios of Ni-Cr catalyst.

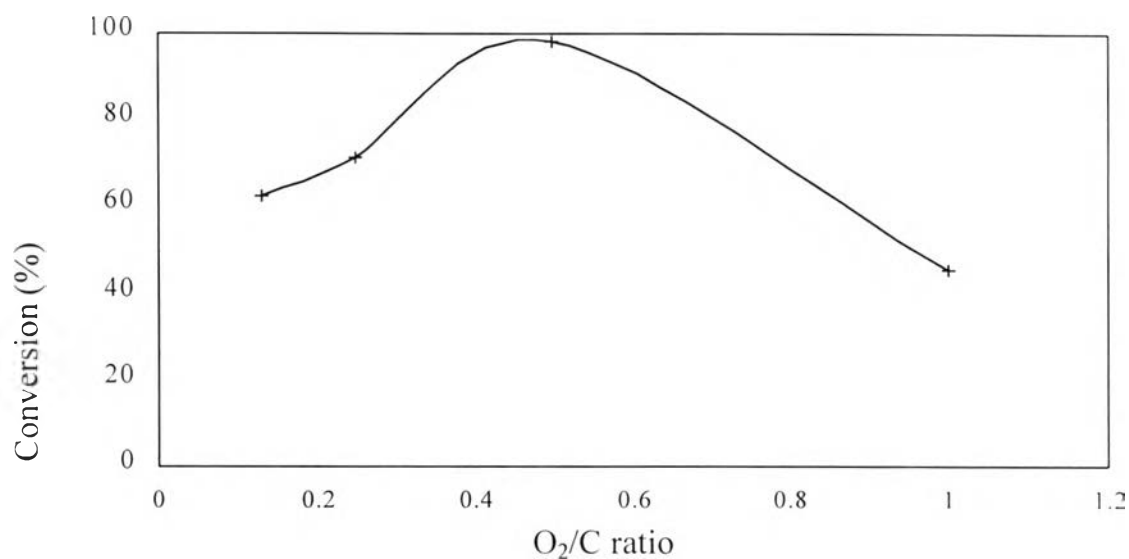


Figure 4.6 Effect of O₂/C ratios on conversion of iso-octane oxidation at 650°C over Ni-Ce catalyst

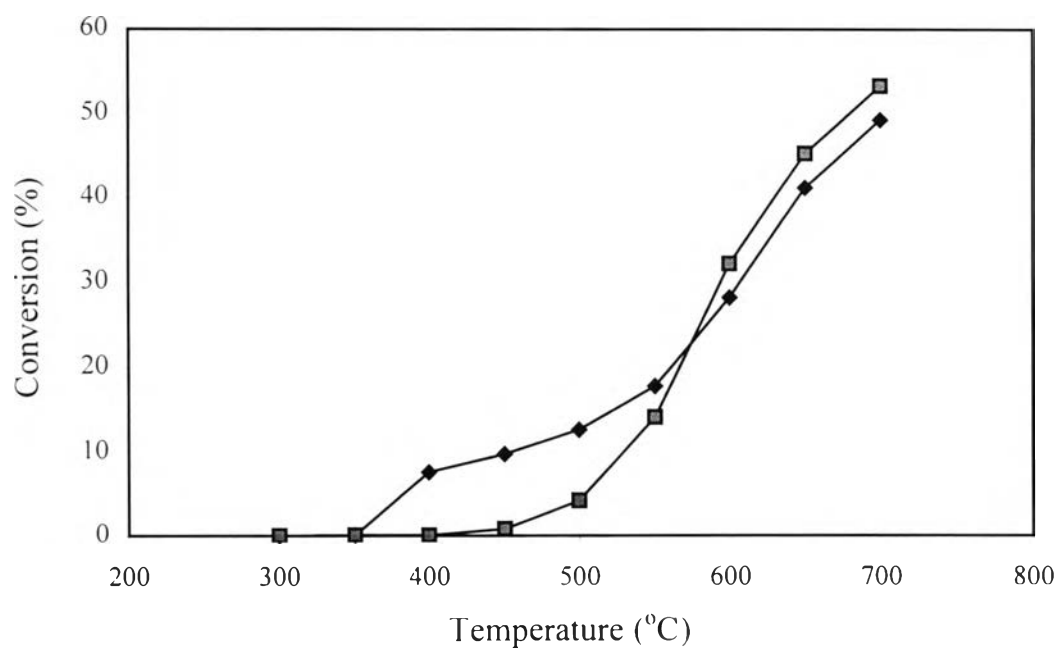


Figure 4.7 Light off temperature of iso-octane over Ni-Cr and Ni-Ce catalysts at O₂/C ratios: 1/1; (◆) Ni-Cr catalyst, and (■) Ni-Ce catalyst

4.2.3 Light Off Temperatures of Ni-Ce and Ni-Cr Catalysts

The light off temperatures of iso-octane over Ni-Cr and Ni-Ce catalysts at O₂/C ratios: 1/1 are presented in Figure 4.7. It was observed that Ni-Cr catalyst has lower light off temperature than that of Ni-Ce catalyst. However, at high temperatures, the higher conversion of iso-octane can be obtained from Ni-Ce catalyst.

4.3 The Effect of Steam/Carbon Ratios

4.3.1 The Effect of Steam/Carbon Ratios over Ni-Cr Catalyst

Result in Figure 4.8 shows the influence of steam/ carbon ratios on the H₂/CO product ratio in steam reforming with autothermal system of iso-octane over NiCr/Al₂O₃ catalyst. Hydrogen can be produced at 450°C. The observed values of H₂/CO ratios (~0.7-1.5) shows that at the low temperature (450-550°C) hydrogen mainly produced by partial oxidation reaction. The effect of H₂/C on the conversion of iso-octane had the same trend with the effect of steam ratio on H₂/CO (Figure 4.10). The H₂/CO ratio and iso-octane conversion were depending on the concentration of steam and it is observed the optimum value of steam/carbon ratio, which is 2 to give the highest H₂/CO ratio and conversion (from Figure 4.10). The H₂/CO ratio decreases when the steam/carbon ratio is above two. From the result shown in Figure 4.9, it was observed that the CO selectivity strongly decreased in the low temperature region (450 and 500°C) while this of high temperatures slightly decreases with increasing steam ratio. These results indicated that water would inhibit the rate of partial oxidation especially at low temperature region which the partial oxidation is the main reaction and these reduce the rate of hydrogen production from partial oxidation.

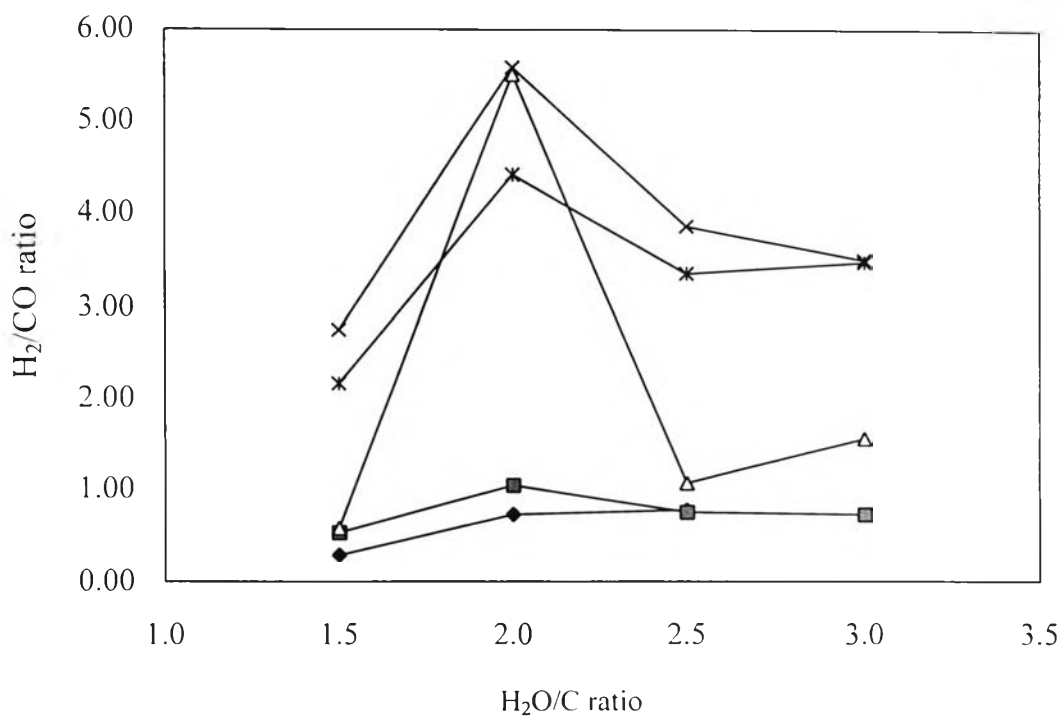


Figure 4.8 Effect of H₂O/C ratio on H₂/CO ratio at 450 °C (◆), 500 °C (■) 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCr/Al₂O₃ catalyst

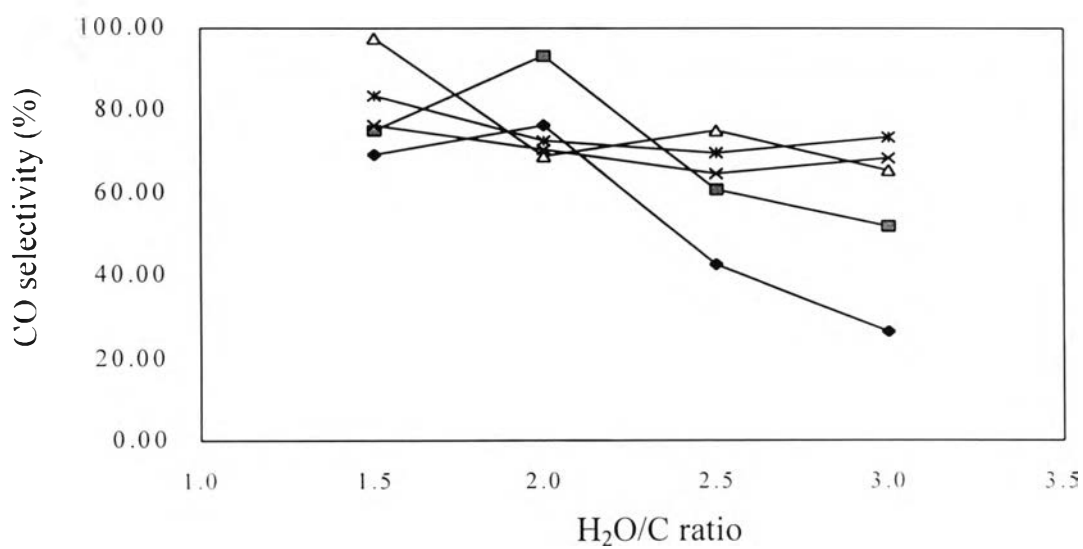


Figure 4.9 Effect of H₂O/C ratio on CO selectivity at 450 °C (◆), 500 °C (■) 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCr/Al₂O₃ catalyst

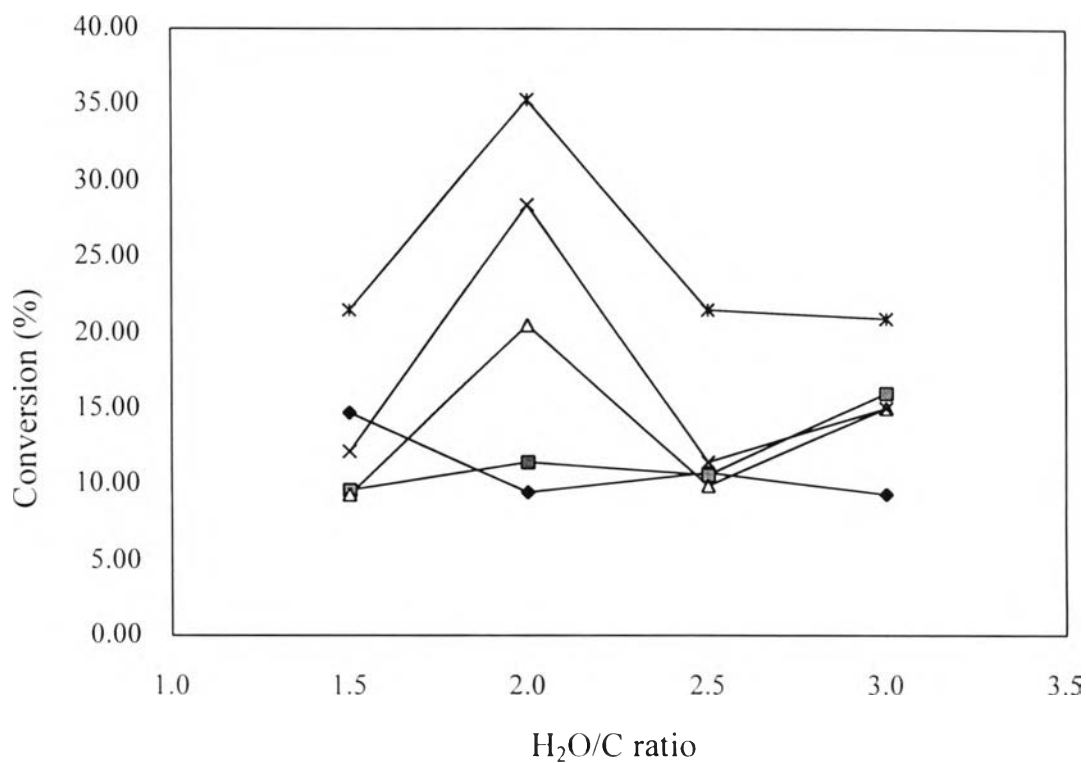


Figure 4.10 Effect of H₂O ratio on conversion of iso-octane at 450 °C (◆), 500 °C (▲), 550 °C (■), 600 °C (×) and 650 °C (·) of NiCr/Al₂O₃ catalyst

The effect of temperature shows in Figure 4.8. The result shows that the H₂/CO ratio increases with increasing temperature. This is because increasing temperature increases the rate of steam reforming. However when the temperature is higher than 600 °C the ratio of H₂/CO decreases because of the decreasing rate of water gas shift.

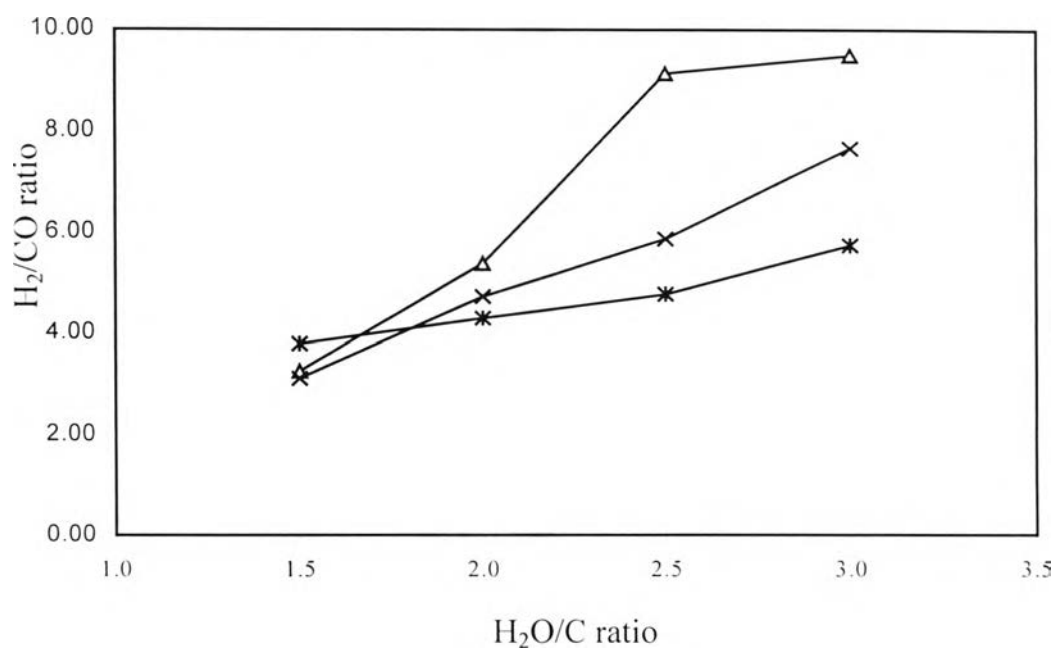


Figure 4.11 Effect of H₂O/C ratio on H₂/CO ratio at 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCe/Al₂O₃ catalyst

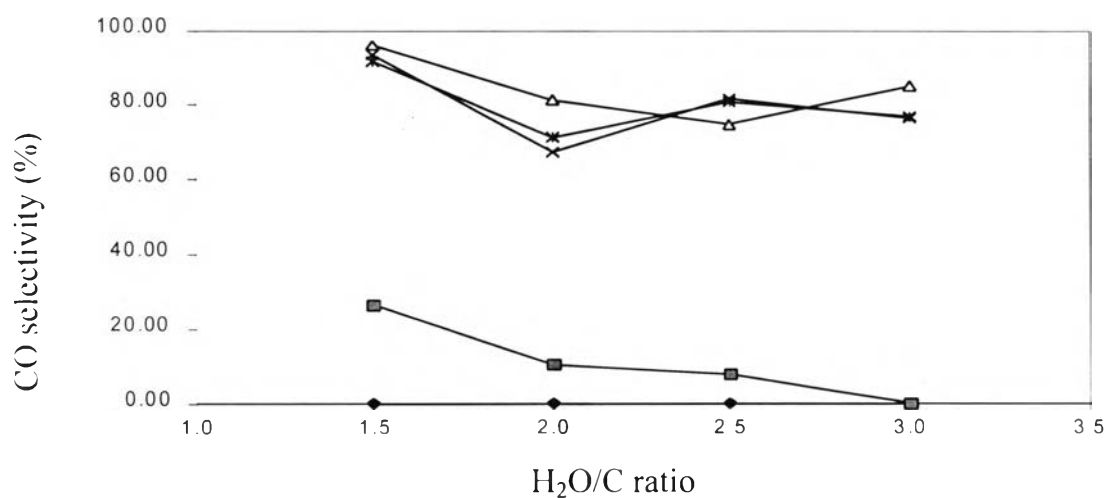


Figure 4.12 Effect of H₂O ratio on CO selectivity (%) of iso-octane at 450 °C (◆), 500 °C (■), 550 °C (▲), 600 °C (×) and 650 °C (-) of NiCe/Al₂O₃ catalyst

Influence of temperature and steam/carbon ratios on the H₂/CO product ratio in steam reforming with autothermal system of iso-octane over NiCe/Al₂O₃ catalyst are presented in Figure 4.11. As seen hydrogen can be produced at temperature above 550°C. The observed higher H₂/CO ratio (> 2.125) indicates that a water gas shift reaction occurs simultaneously with steam reforming reactions. Moreover, it was observed that the H₂/CO ratios strongly depend on steam concentration, thereby the H₂/CO ratio increases as an increase in H₂O/C ratio.

Figure 4.11 shows the effect of temperature on H₂/CO product ratios. The decrease in H₂/CO ratio with increasing temperature is correspondent with the fact that a water gas shift reaction is not thermodynamically favored at high temperatures (Choudhary *et al.*, 1998). The effect of H₂O/C on CO selectivity is shown in Figure 4.12. The CO selectivity decreases with an increasing H₂O/C. It is indicated that the partial oxidation decreases with increase in the steam concentration. Moreover, the increasing steam ratio increases water gas shift reaction rate and then the concentration of CO decrease because CO was the reactant in this reaction.

The above observations indicate the water gas shift reaction plays a significant role on hydrogen production on NiCe/Al₂O₃. Ceria is excellent promoter of the water gas shift reaction (WGS). In the oxy-steam reforming (autothermal system) Ceria enhances the role of nickel by increasing the activity of the metals both in oxidation and in WGS. It shows the high performance catalyst to produce hydrogen in steam reforming reaction with autothermal system. The same effect of ceria promoter was also observed in steam reforming of propane in present of oxygen (Maillet *et al.*, 1997).

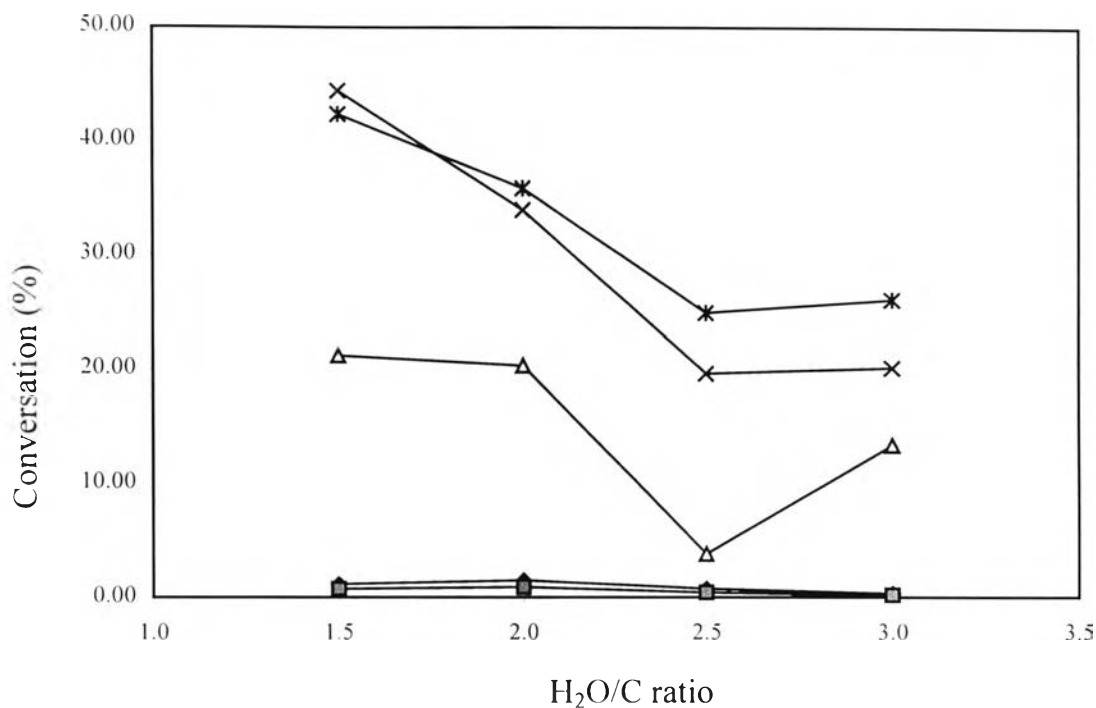


Figure 4.13 Effect of H₂O ratio on conversion of iso-octane at 450 °C (◆), 500 °C (■), 550 °C (▲), 600 °C (×) and 650°C (·) of NiCe/Al₂O₃ catalyst

The effect of H₂O/C ratio on the conversion over Ni-Ce catalyst is shown in Figure 4.13. It was observed that the iso-octane conversion decreases with increasing steam concentration. This may be due to the water inhibites the oxidation rate and conversion and this can conclude that the main iso-octane conversion might be due to partial oxidation.

4.4 The Effect of Oxygen/Carbon Ratios

4.4.1 The Effect of Oxygen/Carbon Ratios over Ni-Cr Catalyst

Results showing the influence of temperature and oxygen/carbon ratios on the H₂/CO product ratio in steam reforming with autothermal system of iso- octane over NiCr/Al₂O₃ catalyst are presented in Figure 4.14.

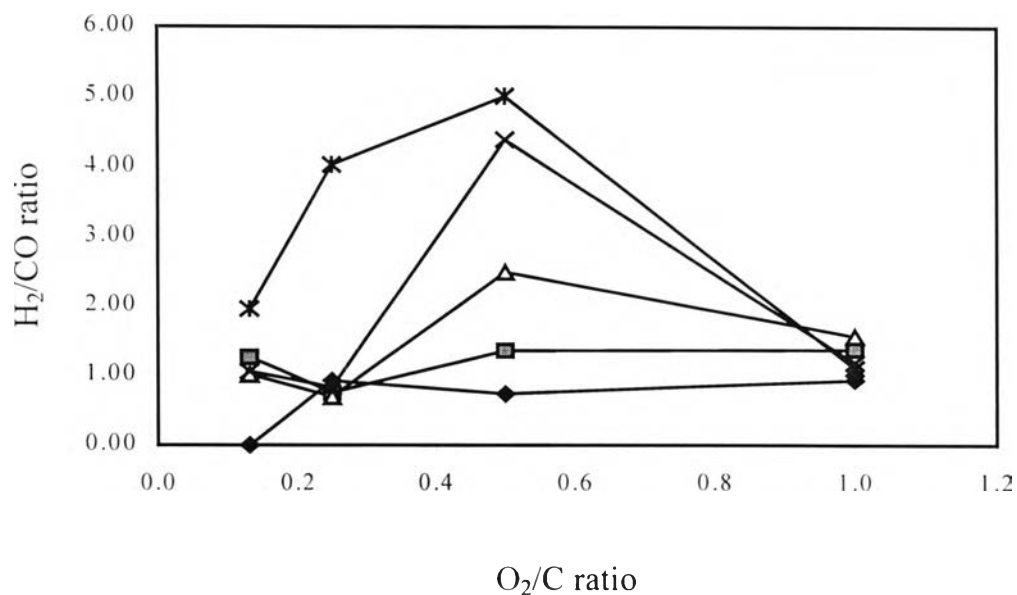


Figure 4.14 Effect of O₂/C ratio on H₂/CO ratio at 450 °C (◆), 500 °C (■) 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCr/Al₂O₃ catalyst

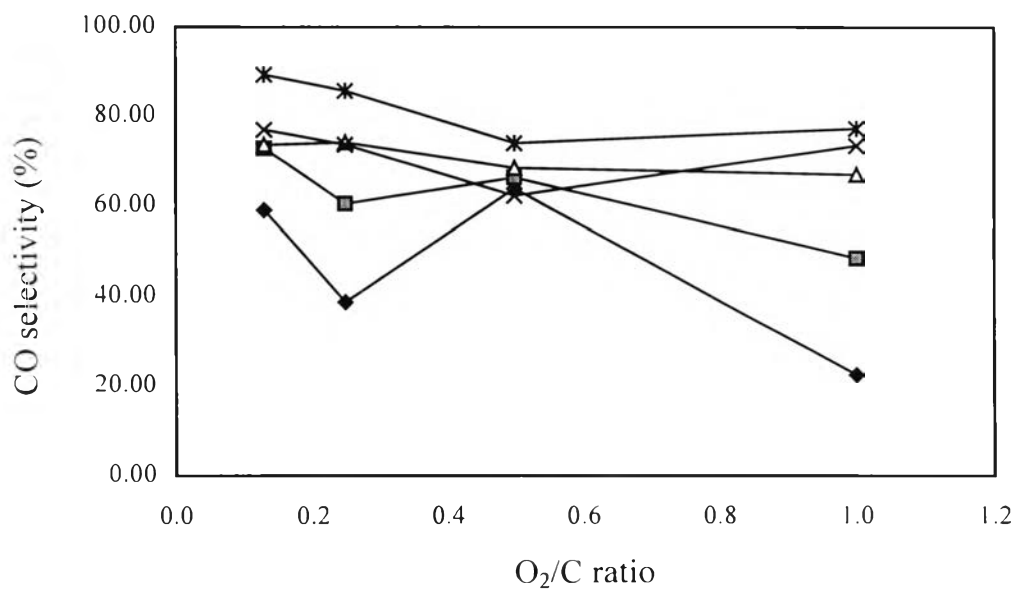


Figure 4.15 Effect of O₂ ratio on CO selectivity (%) of iso-octane at 450 °C (◆), 500 °C (■) 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCr/Al₂O₃ catalyst

The optimum value of oxygen ratio is 0.5. When increasing the oxygen concentration the H_2/CO ratio increases because the rate of oxidation is promoted and it gives the more heats to the steam reforming reaction which is a strongly endothermic reaction. However, increasing oxygen/carbon ratio more than 0.5 would decrease the H_2/CO ratio. This is because increasing the oxygen ratio results that the rate of partial oxidation is more favored and it can be determined from the ratio of H_2/CO ratio ($\sim 1-1.7$).

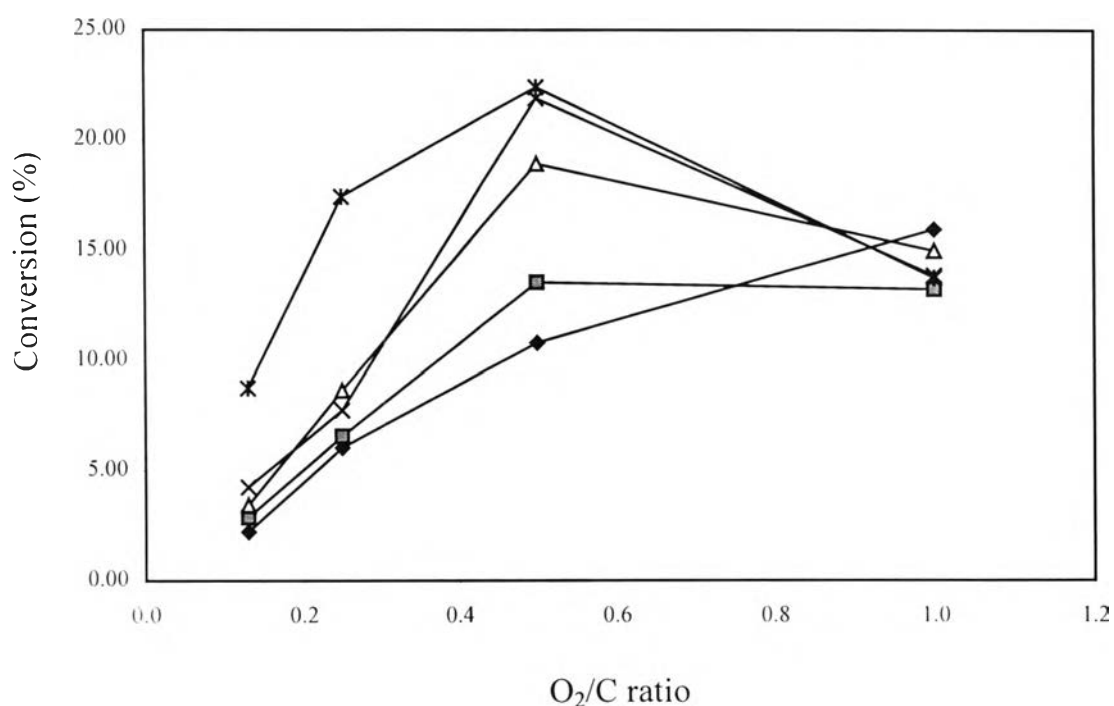


Figure 4.16 Effect of O_2/C ratio on conversion of iso-octane at 450 °C (◆), 500 °C (■) 550 °C (▲), 600 °C (×) and 650 °C (+) of $NiCr/Al_2O_3$ catalyst

The effect of O_2/C ratio on the conversion of iso-octane of $NiCr/Al_2O_3$ catalyst is shown in Figure 4.16. The optimum value of oxygen ratio is 0.5. It indicates that the main reactions that occur is partial oxidation.

This is because the oxidation reaction rate show the non-monotonic dependence on oxygen pressure and this result is similar to the light off temperature of Ni-Cr catalyst.

4.4.2 The Effect of Oxygen/Carbon Ratios over Ni-Ce Catalyst

The experiments were carried at 450-650°C and used the constant H₂O/C ratio at 2. The oxygen ratios were varied from 0.33 to 1. Results showing the influence of temperature and oxygen/carbon ratios on the H₂/CO product ratio in steam reforming with autothermal system of iso-octane over NiCe/Al₂O₃ catalyst are presented in Figure 4.17. The results indicate that concentration of oxygen has slightly affect on the H₂/CO ratio over NiCe/Al₂O₃ catalyst.

Figure 4.18, the CO selectivity decreases with increasing oxygen pressure. The increasing oxygen increases the rate of CO oxidation and the CO is in turn convert in to CO₂.

Because ceria is a good oxygen storage material and it provides oxygen when the oxygen is not sufficient. Increasing temperature increases the rate of steam reforming and then increases the H₂/CO ratio. However, at high temperature (650°C) the H₂/CO decrease because of decreasing in rate of water gas shift reaction.

The effect of oxygen ratios on the conversion of iso-octane is shown in Figure 4.19. The conversion decreases with increasing oxygen concentration. The result showed is similar with the effect of oxygen on the oxidation of iso-octane. This indicates that the main reaction occurred in the experiment is partial oxidation.

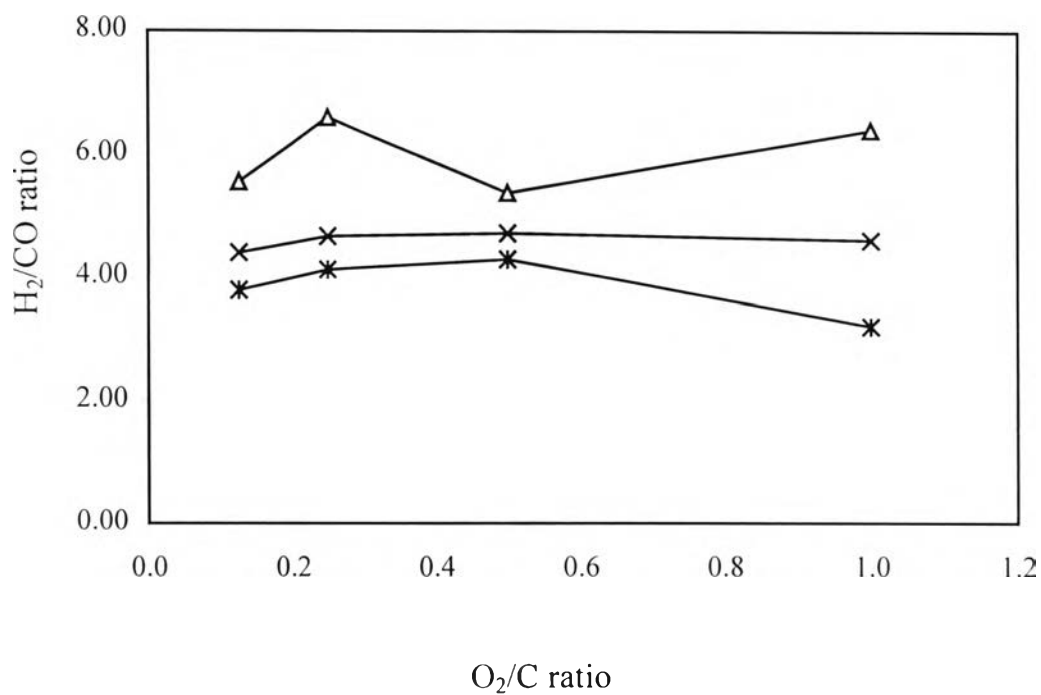


Figure 4.17 Effect of O₂/C ratio on H₂/CO ratio at 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCe/Al₂O₃ catalyst

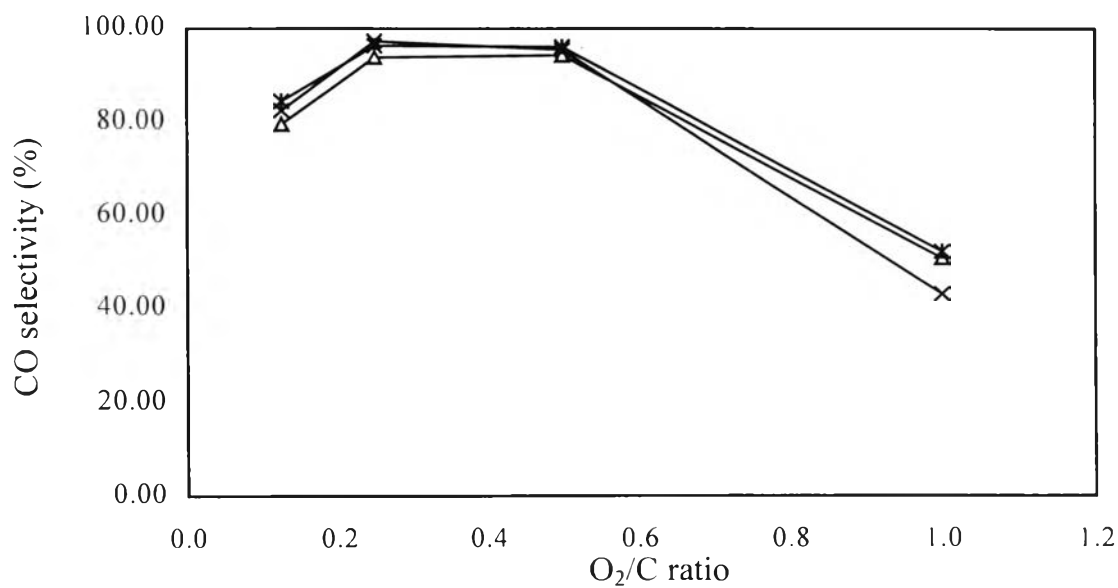


Figure 4.18 Effect of O₂ ratio on CO selectivity (%) of iso-octane at 550 °C (▲), 600 °C (×) and 650 °C (*) of NiCe/Al₂O₃ catalyst

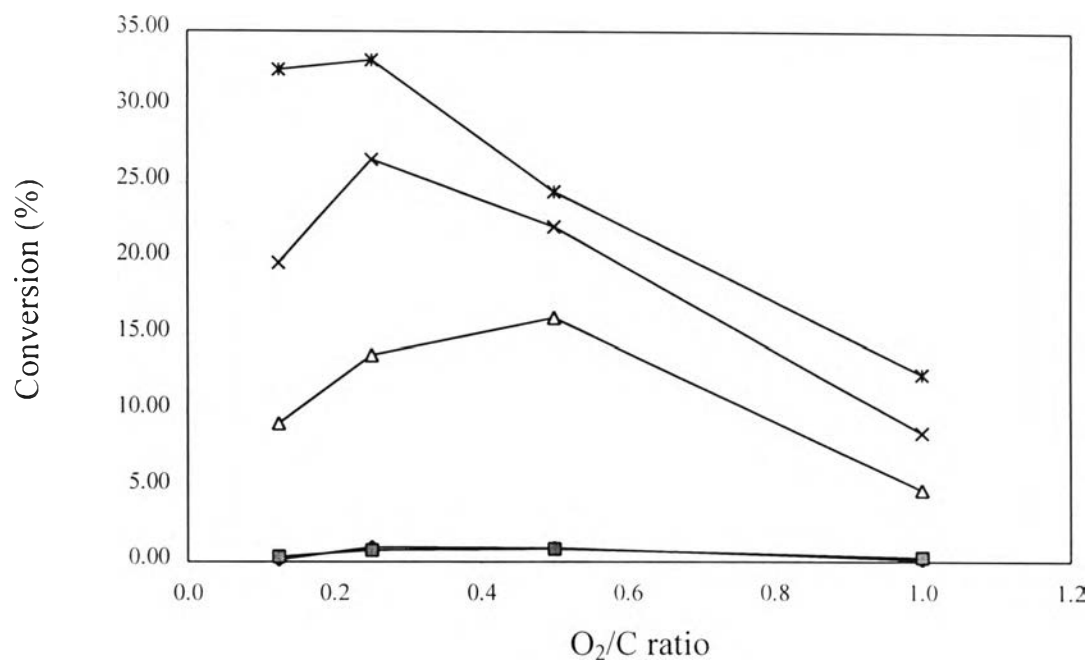


Figure 4.19 Effect of O₂/C ratio on conversion of iso-octane at 450 °C (◆), 500 °C (■), 550 °C (▲), 600 °C (×) and 650 °C (·) of NiCe/Al₂O₃ catalyst

4.4.3 The Effect of Ce loading

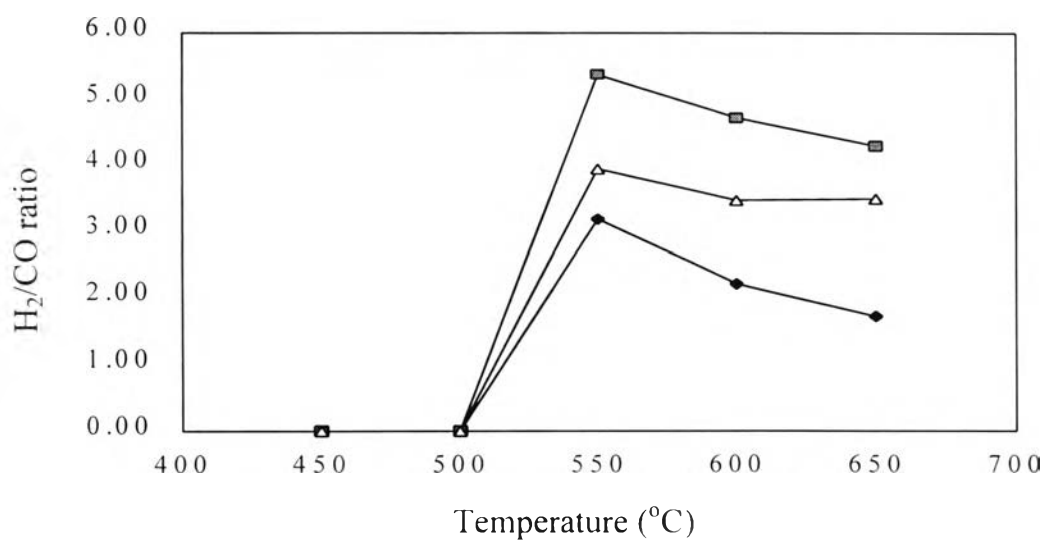


Figure 4.20 Effect of Ce loading on H₂/CO ratio at 650 °C, O₂/C: 0.5, H₂O/C: 2; 5%Ni15%Ce/Al₂O₃ (◆), 10%Ni10%Ce/Al₂O₃ (▲), and 5%Ni15%Ce/Al₂O₃ (■)

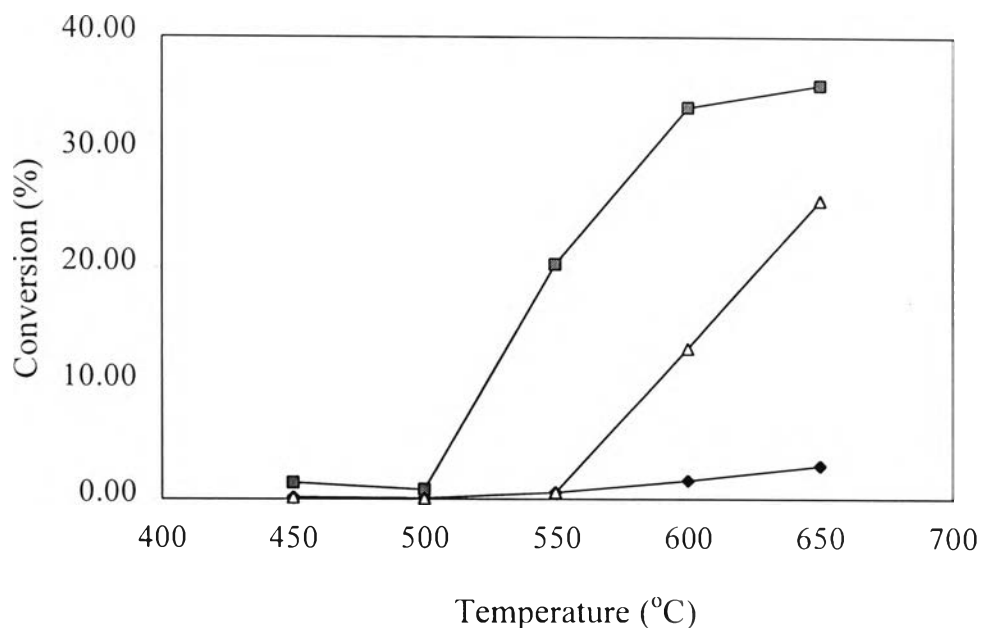


Figure 4.21 Effect of Ce loading on the conversion at 650 °C, O₂/C:0.5, H₂O/C:2; 5%Ni15%Ce/Al₂O₃ (◆), 10%Ni10%Ce/Al₂O₃ (▲), and 5%Ni15%Ce/Al₂O₃(■)

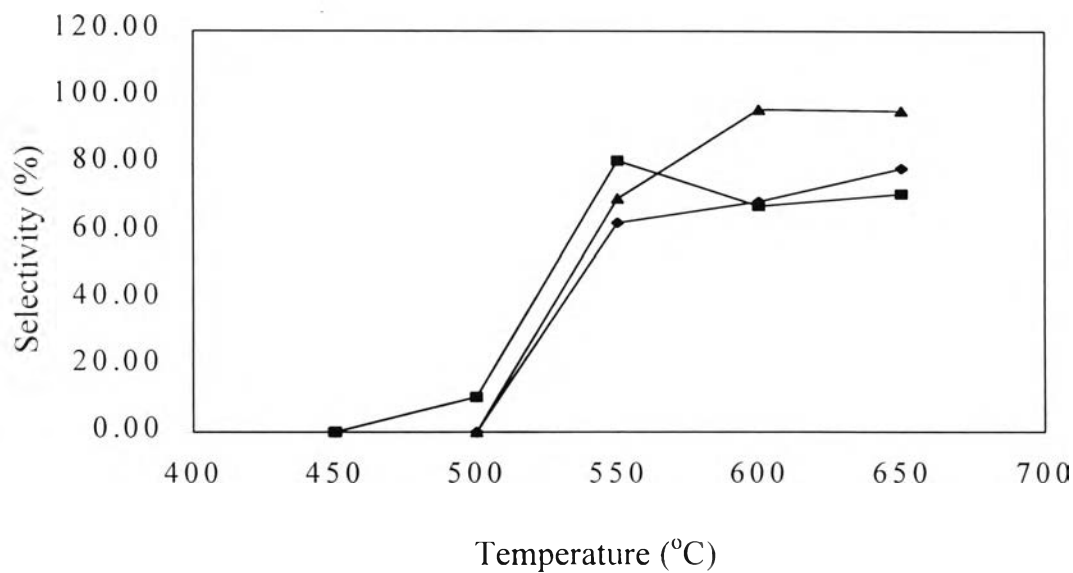


Figure 4.22 Effect of Ce loading on the selectivity at 650 °C, O₂/C: 0.5, H₂O/C: 2; 5%Ni15%Ce/Al₂O₃ (◆), 10%Ni10%Ce/Al₂O₃ (▲), and 5%Ni15%Ce/ Al₂O₃(■)

The effects of Ce loading are shown in Figure 4.20-4.22. The H_2/CO ratio decreases with increasing Ce loading. This result indicates that increasing content of Ce increases the oxidation reactions. As shown in Figure 4.21, the conversion increase when decrease Ce content. This shows that the steam reforming reaction decreases and the rate of CO oxidation increases with increasing the Ce loading.

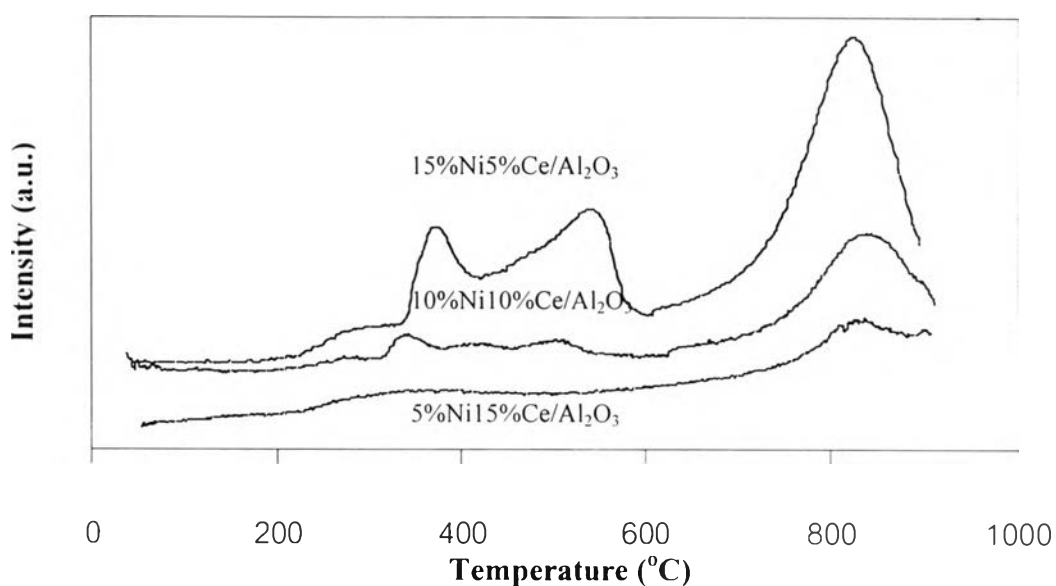


Figure 4.23 TPR profiles of 5%Ni15%Ce/Al₂O₃, 10%Ni10%Ce/Al₂O₃, and 15%Ni5%Ce/Al₂O₃

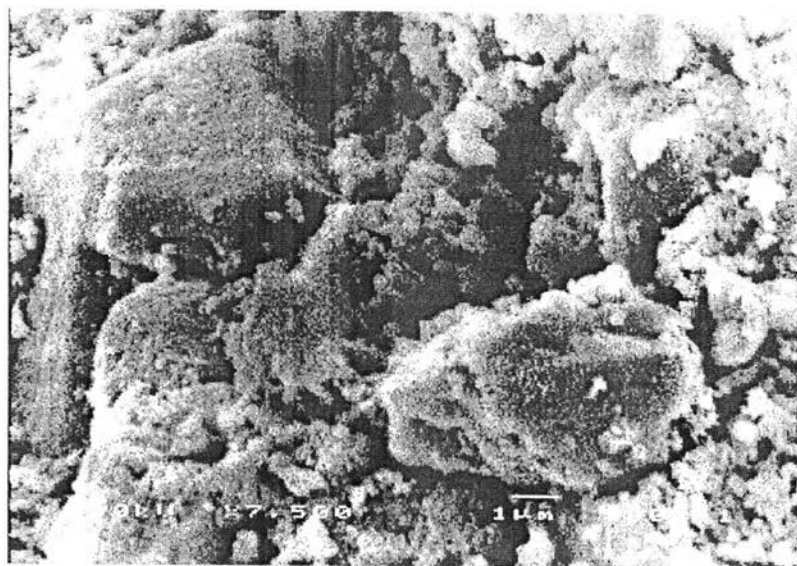
Table 4.2 BET surface areas of Ni-Ce catalysts

Catalyst	BET surface area (m ² /g)
15% Ni 5% Ce/Al ₂ O ₃	75
10% Ni 10%Ce /Al ₂ O ₃	75
5% Ni 15%Ce /Al ₂ O ₃	76

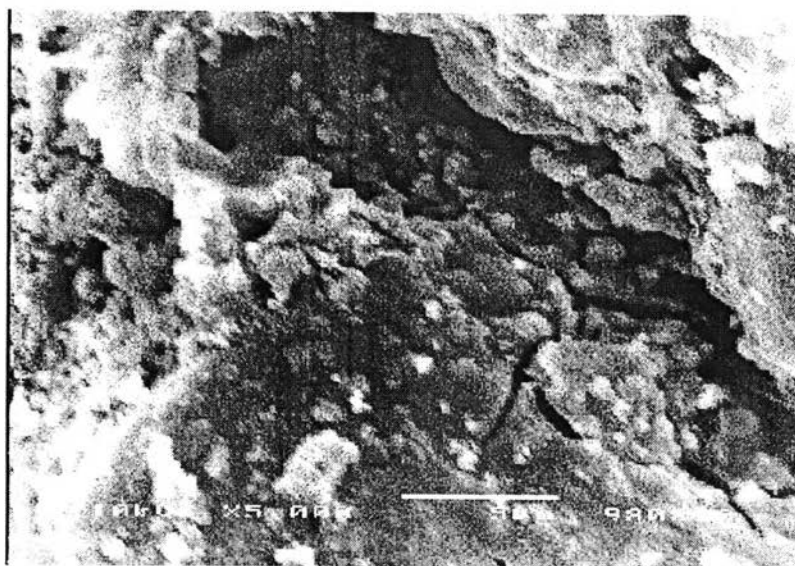
As shown in Figure 4.23, the TPR patterns of catalyst show that the percentage of Ce loading reduces the reductivity of catalyst. The “free NiO” phase was reduced by increasing the content of Ce. However, high percentage of Ce catalysts might have higher surface areas. This is because Ce is the high surface area promoter. Table 4.2 shows that the surface area of Ni-Ce with varying percentage of Ce loading is not significant different because all the catalysts are loaded in the same supporter, alumina which has high surface area.

4.6 The Coke Formation

The coke formation was studied in this study by using TGA and SEM analysis. The reaction carried at 650°C, H₂O/C ratio: 2 and O₂/C ratio: 0.5 for 20 hrs. After running the experiment, used catalyst was investigated coke formation by TGC. The result shows that there is no coke formation because TGA can not detect the TPO peak and this result can be confirms by the SEM pictures of catalysts. From Figure 4.24 and 4.23, the pictures show that there is no coke formation on both of Ni-Cr and Ni-Ce catalysts. This indicated that Cr and Ce would be good promoters that give high activity and reduce coke formation.

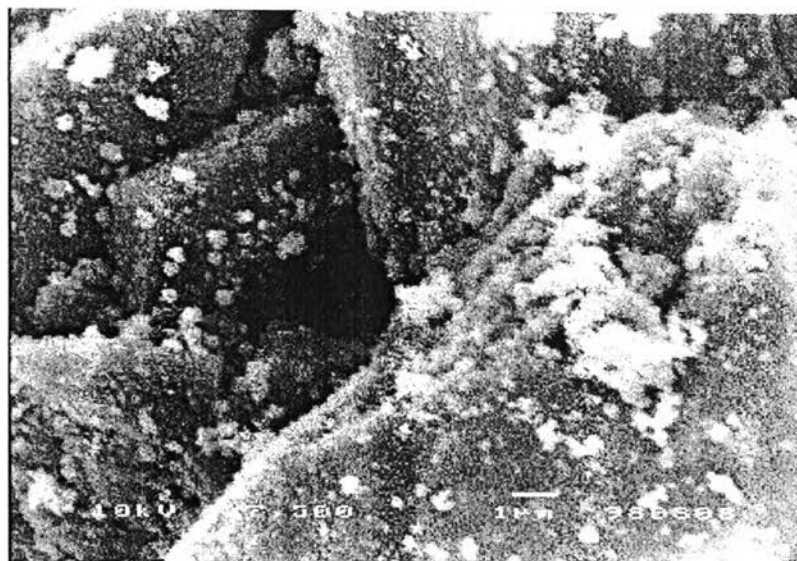


(a)



(b)

Figure 4.24 SEM pictures of fresh 15%Ni 5%Cr/Al₂O₃ (a) and used 15%Ni 5%Cr/Al₂O₃ (b)



(a)



(b)

Figure 4.24 SEM pictures of fresh 15%Ni 5%Ce/Al₂O₃ (a) and used 15%Ni 5%Ce/Al₂O₃ (b)