

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

This section shows the effects of Ni loading amount and the loading methods on the $Ce_{0.75}Zr_{0.25}O_2$ catalyst characterizations, which are the BET surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR) and Transmission Electron Microscope (TEM).

4.1.1 BET Surface Area

The surface areas of Ce/Zr mixed oxides with different Ni loading catalysts (5, 10, 15 % by weight of Ni on Ce/Zr mixed oxides with the Ce/Zr of 75/25) were measured by multiple point BET method. The results showing effects of Ni amounts and loading methods on the BET surface area of catalysts are given in Table 4.1.

Table 4.1 BET surface areas of all fresh catalysts

% Ni loading on $Ce_{0.75}Zr_{0.25}O_2$	BET surface area (m^2/g)	
	Sol-Gel Method	Impregnation Method
0	104.50	-
5	102.30	73.60
10	89.87	59.58
15	90.39	63.37

The unloaded $Ce_{0.75}Zr_{0.25}O_2$ had the highest BET surface area. It was found that the addition of Ni by both sol-gel and impregnation method decreased the surface area of the catalysts when compared with the unloaded $Ce_{0.75}Zr_{0.25}O_2$. The explanation of this surface area lost can be counted on the interaction between Ni

active metal and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ support. BET surface area of sol-gel catalysts showed slightly higher surface area than impregnation on sol-gel catalysts. This result supported the hypothesis that the catalysts prepared by sol-gel technique normally have a higher surface area compared to the conventional methods.

Table 4.2 Pore volume and pore size of all fresh catalysts

% Ni loading on $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	Pore Volume (cc/g)		Pore Size (nm)	
	Sol-Gel Method	Impregnation Method	Sol-Gel Method	Impregnation Method
0	0.0953	-	3.58	-
5	0.0361	0.0208	1.628	1.430
10	0.0325	0.0232	1.484	1.440
15	0.0374	0.0193	1.518	1.424

The effects of Ni loading and catalyst preparation method on pore volume and pore size of catalysts are illustrated in Table 4.2. The highest pore volume and pore size belongs to the unloaded $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. The addition of Ni by both sol-gel and impregnation method decreased the pore volume and pore size of the catalysts. These results can be explained by the Ni particle deposition into the active pore of catalysts. The sol-gel catalysts had slightly higher pore volume and pore size than the impregnation catalysts. However, the pore sizes of loading catalysts were not significantly different.

4.1.2 X-Ray Diffraction (XRD)

The XRD patterns of samples with different Ni loading by sol-gel and impregnation methods are given in Figure 4.1 and 4.2, respectively. The XRD pattern of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ shows that there was no peak of ZrO_2 while the CeO_2 phase peak was found, corresponding to the (111), (200), (200), (311), (222) and (400) planes (at about 29° , 33° , 48° , 56° , 60° and 70° (2θ)).

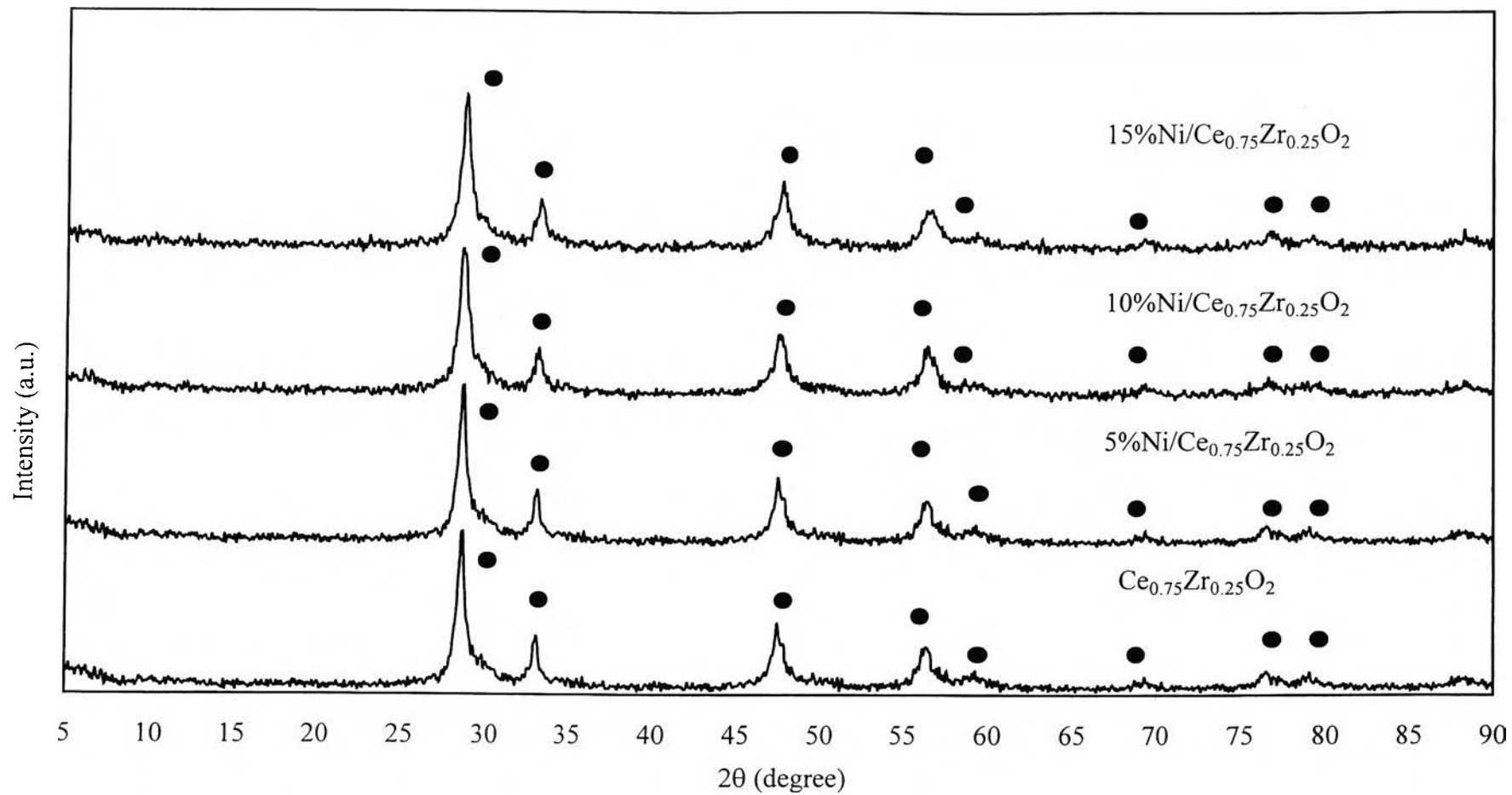


Figure 4.1 XRD patterns of 5%, 10% and 15%Ni over Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method in comparison with Ce_{0.75}Zr_{0.25}O₂; (●) CeO₂

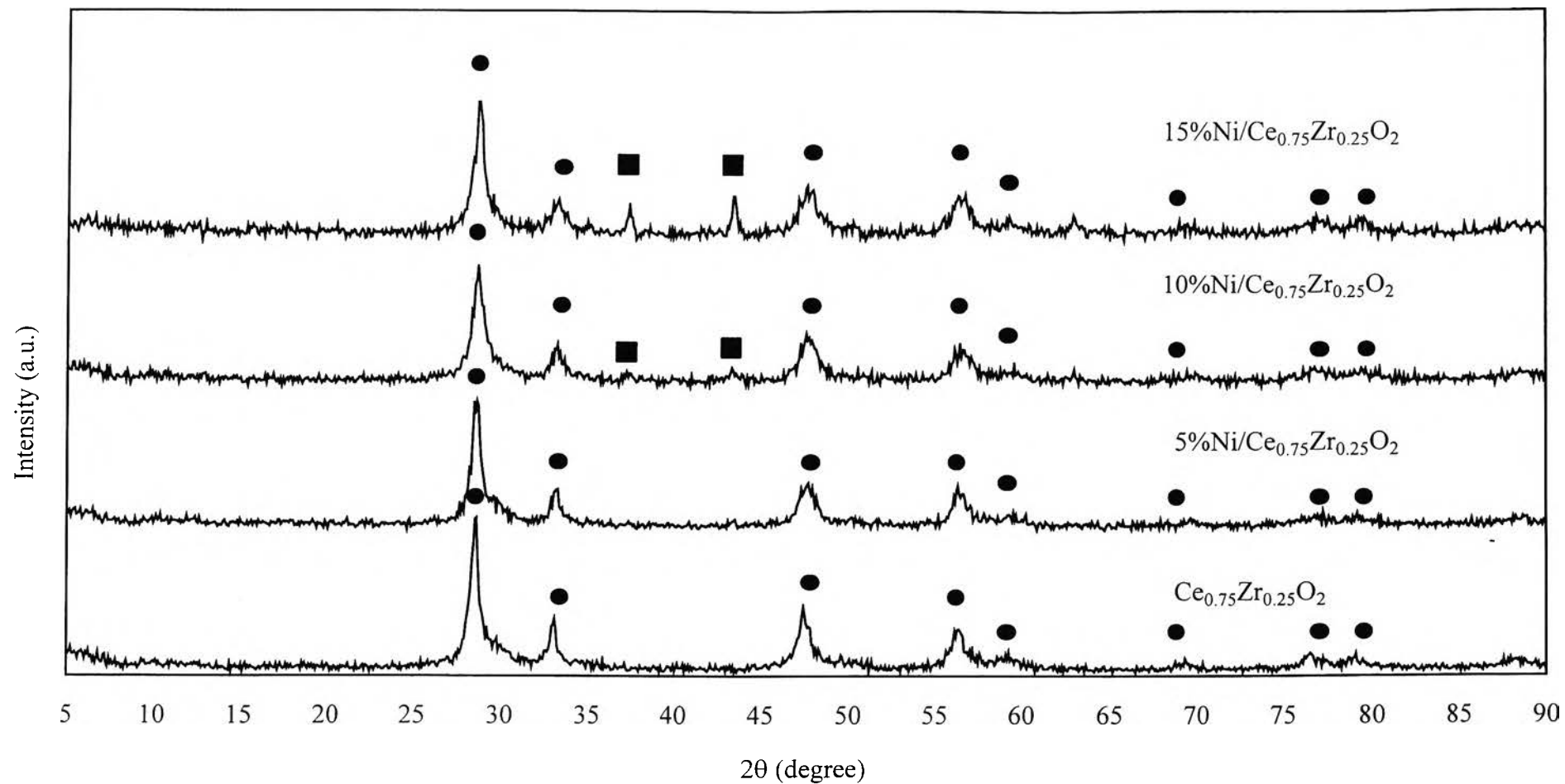


Figure 4.2 XRD patterns of 5%, 10% and 15% Ni over Ce_{0.75}Zr_{0.25}O₂ prepared by impregnation method in comparison with Ce_{0.75}Zr_{0.25}O₂; (●) CeO₂, (■) NiO

CeO₂ has the fluorite (CaF₂) structure made of a close packed cubic array of metal atoms in which all tetrahedral holes are filled by oxygen (Travarelli *et al.*, 1997). Normally, ZrO₂ has the tetragonal phase with the splitting of the (111), (200) and (220) at about 30°, 35° and 50°, (2θ), respectively. For the XRD pattern of Ce_{0.75}Zr_{0.25}O₂, Zr was incorporated into CeO₂ lattice to form a solid solution. In other words, this result can be concluded that Ce_{0.75}Zr_{0.25}O₂ was the cubic fluorite-structured phase.

The comparisons of the XRD patterns of different Ni catalysts by sol-gel loading method with Ce_{0.75}Zr_{0.25}O₂ are shown in Figure 4.1. The XRD patterns were entirely similar to that of Ce_{0.75}Zr_{0.25}O₂. There was no NiO observed in the XRD spectra of all sol-gel loading catalysts suggesting that Ni is highly dispersed on Ce_{0.75}Zr_{0.25}O₂ or Ni is incorporated into CeO₂ by the loading method.

For impregnation, the difference was not found for 5%Ni/Ce_{0.75}Zr_{0.25}O₂. However, there was the addition of the NiO phase spectra for 10% and 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst. Actually, NiO has also the fluorite (CaF₂) structure made of a close packed cubic array of metal atoms in which all tetrahedral holes are filled by oxygen. The peak intensity of NiO phase was increased with the increase in the percentage of nickel due to the higher NiO concentration. Therefore, the crystal structure of impregnation catalysts is still the cubic fluorite-structured phase. It can be concluded from these results that both Ni loading methods did not change the structure phase.

4.1.3 Temperature-Programmed Reduction (TPR)

A comparison of the TPR profiles (Figure 4.3 and 4.4) for all fresh catalysts shows the influence of nickel addition. The TPR of Ce_{0.75}Zr_{0.25}O₂ catalyst started above 170°C. There were two peaks observed on the Ce_{0.75}Zr_{0.25}O₂ catalyst. First, A low temperature peak at 550°C is attributed to the reduction of the easily reducible surface oxygen. Second, A high temperature peak at approximately 850°C relates to the partial reduction of Ce⁴⁺ to Ce³⁺ (Fornasiero P. *et al.*, 1995) and bulk oxygen. For sol-gel catalysts, the TPR of 5, 10, 15% Ni over Ce_{0.75}Zr_{0.25}O₂ catalysts were started above 87, 85 and 70°C as shown in Figure 4.3, respectively.

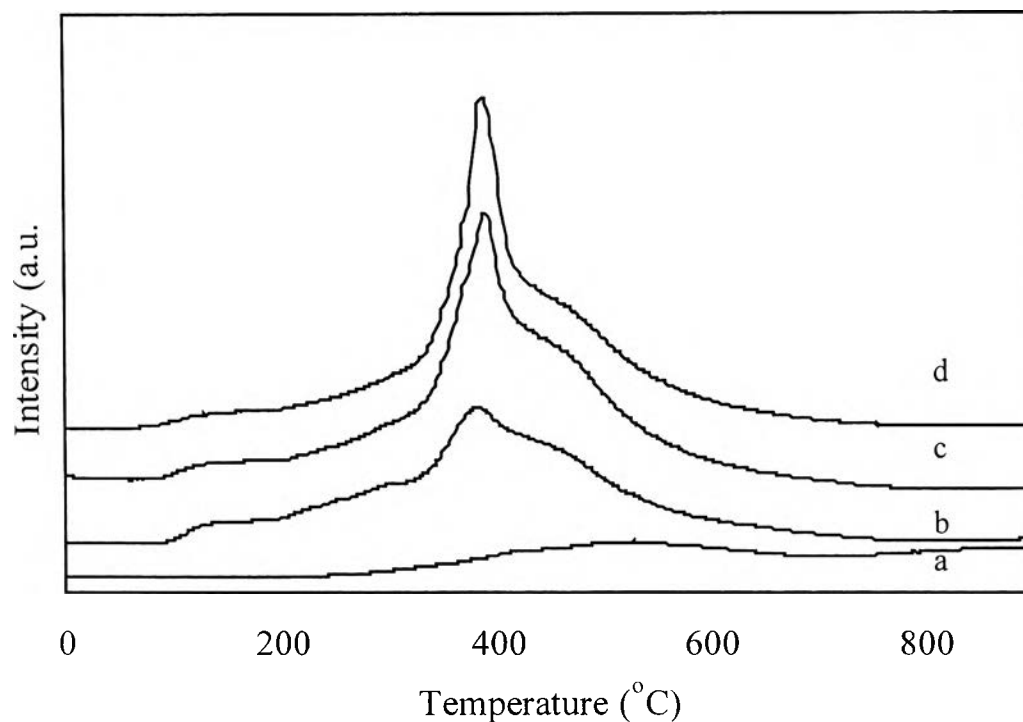


Figure 4.3 CO TPR results of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (a), 5%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (b), 10%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (c) and 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (d) prepared by the sol-gel method

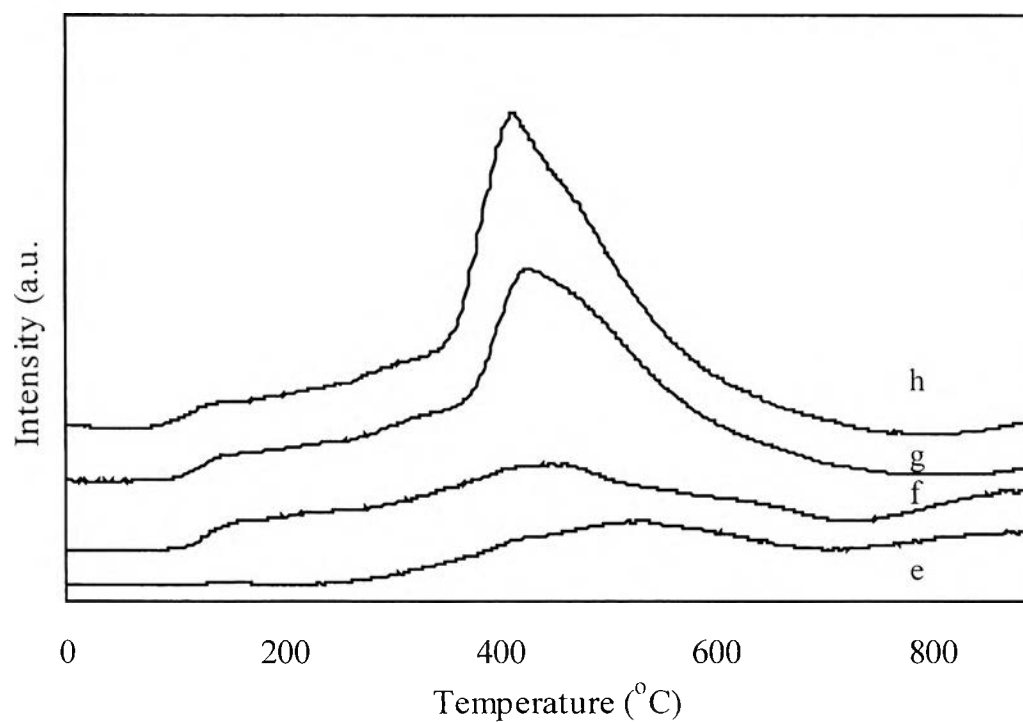


Figure 4.4 CO TPR results of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (e), 5%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (f), 10%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (g) and 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (h) prepared by impregnation method

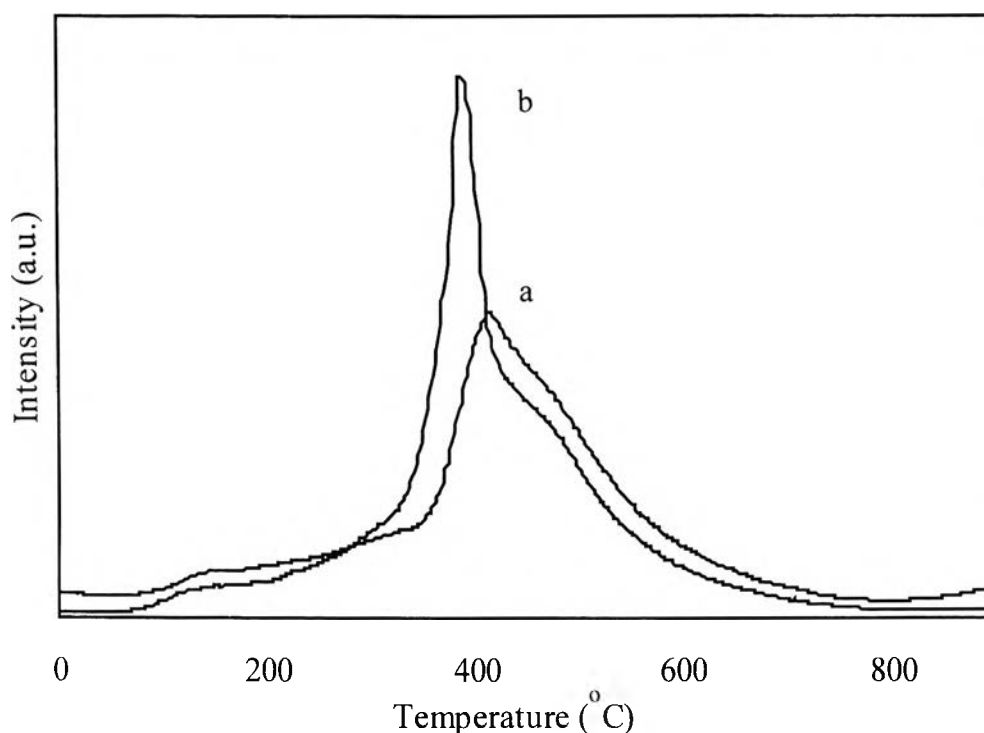


Figure 4.5 CO TPR results of 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ compared between sol-gel (a) and impregnation method (b)

It means that the higher percentage of Ni in catalyst caused the easier reduction. A sharp peak at about 430°C and other low-broad peak at 850°C were obtained. The first peak is associated with the reduction of NiO to Ni^0 , and the peak at 850°C is the reduction peak of CeO_2 support (Montaya J.A. *et al.*, 2000). The sharp peak obtained at 430°C corresponds to high uniformity in NiO crystallite size. There was a stronger Ni-support interaction for the more Ni content because the peak was slightly shifted to a higher temperature.

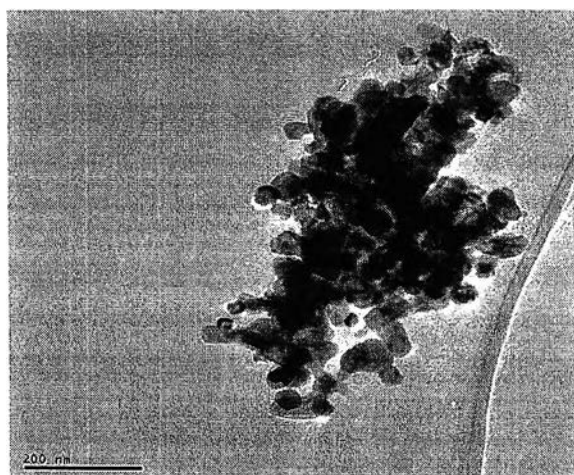
As shown in Figure 4.4, the TPR of 5, 10, 15% Ni over $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalysts were started above 73 , 68 and 64°C for impregnation catalysts, respectively. The higher percentage of Ni attributed to the easier reduction. It was found a broad TPR profile, which consisted of two peaks. These were a low temperature peak at 390°C and a high temperature peak at 460°C . The first peak is associated with the reduction of NiO alone, and the peak at 390°C is the reduction peak of NiO-CeO_2

support interaction (Montaya J.A. *et al.*, 2000). There was a more free NiO for the more Ni content because the larger area of TPR peak.

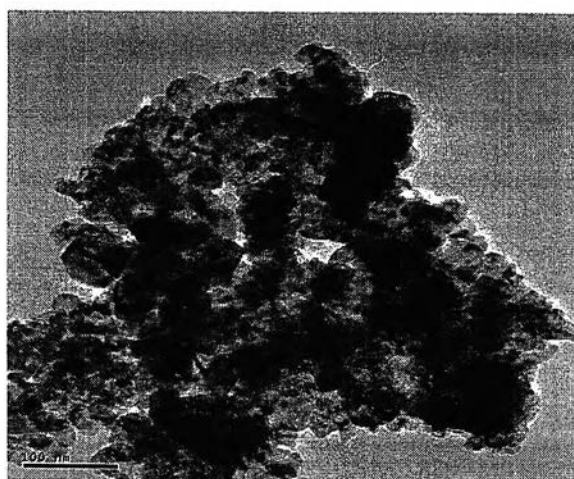
Figure 4.5 shows the TPR of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by both sol-gel and impregnation methods. At temperature above 400°C, sol-gel catalyst is reduced more than impregnation catalyst as indicated by a larger area of the reduction in this temperature region.

4.1.4 Transmission Electron Microscopy (TEM)

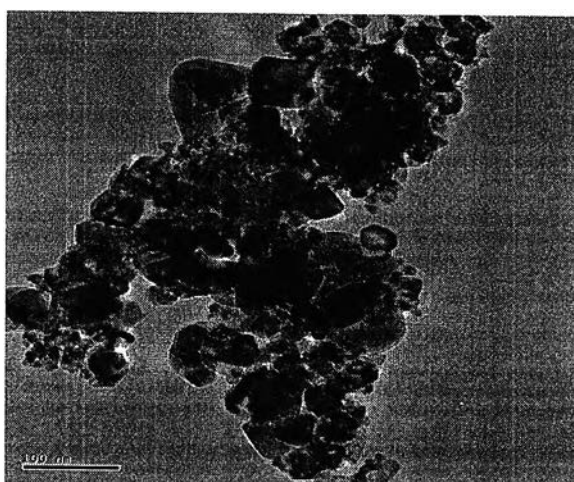
The homogeneity of all different nickel loading catalysts were also investigated by TEM results as illustrated in Figure 4.6(a)-(c) and 4.7(e)-(f). The sol-gel catalyst had the nearly uniform grain while the impregnation catalyst had the big black particle inside which was covered by other textures. Therefore, the sol-gel catalysts have higher homogeneity than impregnated ones. Since we loaded Ni metal before the Ce/Zr mixed oxide formed a stable solid solution.



a

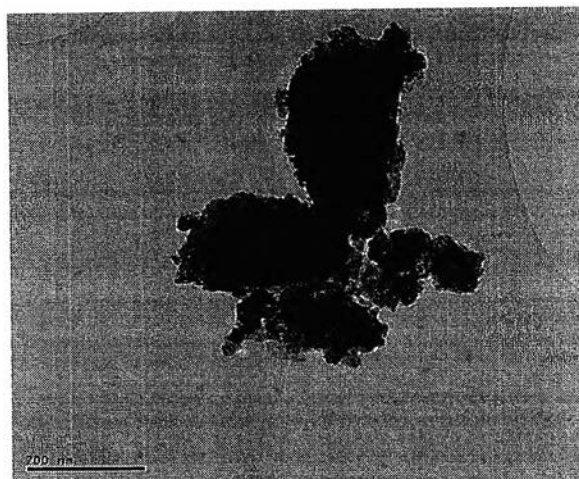


b

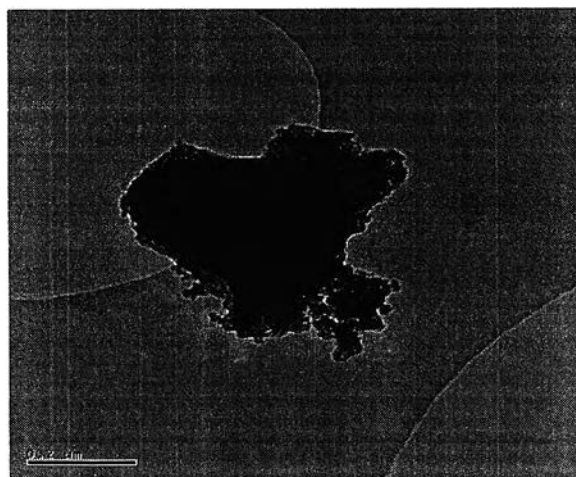


c

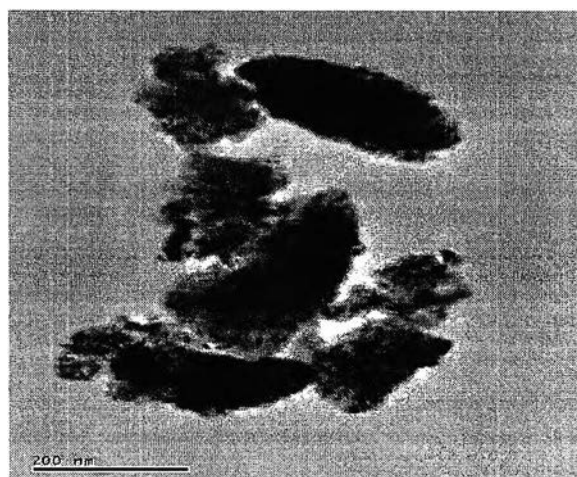
Figure 4.6 TEM pictures of Ni loading on $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ by sol-gel method with 5%Ni(a), 10%Ni(b) and 15%Ni(c)



d



e



f

Figure 4.7 TEM pictures of Ni loading on $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ by impregnation method with 5%Ni(d), 10%Ni(e) and 15%Ni(f)

4.2 Light Off Temperature

Light off temperature or the temperature obtained at 50% conversion is used to study the effect of iso-octane partial oxidation. This experimental part reported the effect of all catalysts and O_2/C ratio (reactant ratio) on light off temperature.

4.2.1 The Effect of Ni Loading Over $Ce_{0.75}Zr_{0.25}O_2$ By Sol-gel Method

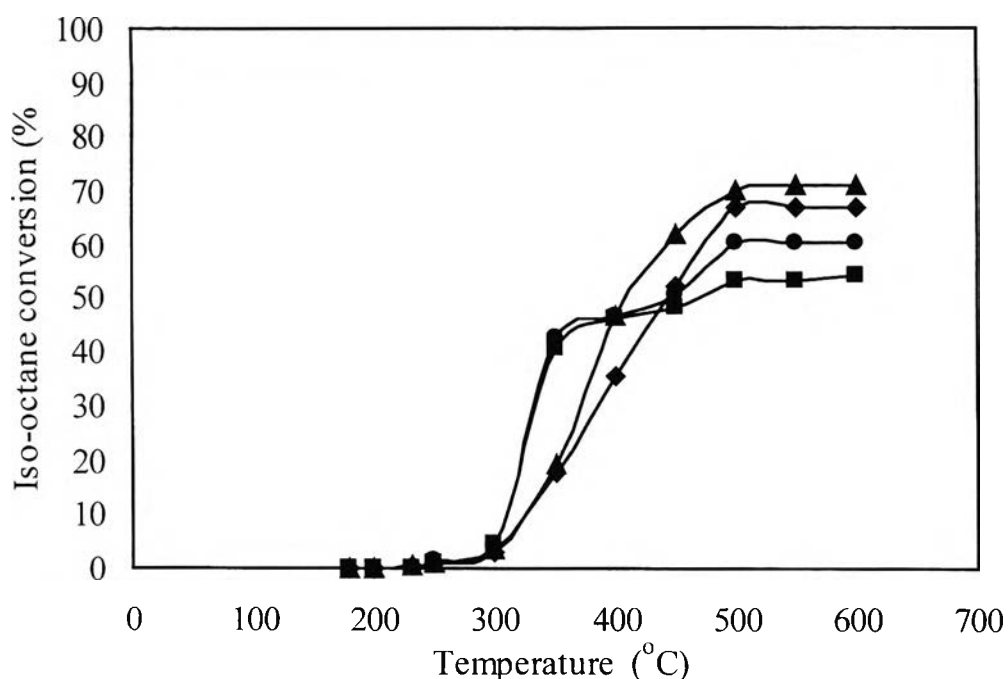


Figure 4.8 Iso-octane conversion as a function of reaction temperatures over different nickel loading on $Ce_{0.75}Zr_{0.25}O_2$ by sol-gel method; %Ni loadings: (■) 0, (●) 5, (◆) 10 and (▲) 15 with reaction condition: O_2/C ratio = 1/1, total flow rate = 160 ml/min and space velocity = $64,000\text{ h}^{-1}$

The effect of different nickel loadings (0, 5, 10 and 15 wt%) by sol-gel method over the $Ce_{0.75}Zr_{0.25}O_2$ catalyst was tested for the catalytic activity on iso-octane oxidation at O_2/C of 1/1. The light off patterns of all catalysts were the same as presented in Figure 4.8, which could be divided into 3 parts. Firstly, the iso-octane conversion starts above 200°C and slightly increases at the temperatures below

However, the higher conversion of iso-octane can be obtained from 15%Ni sol-gel catalyst at high temperature above 450°C.

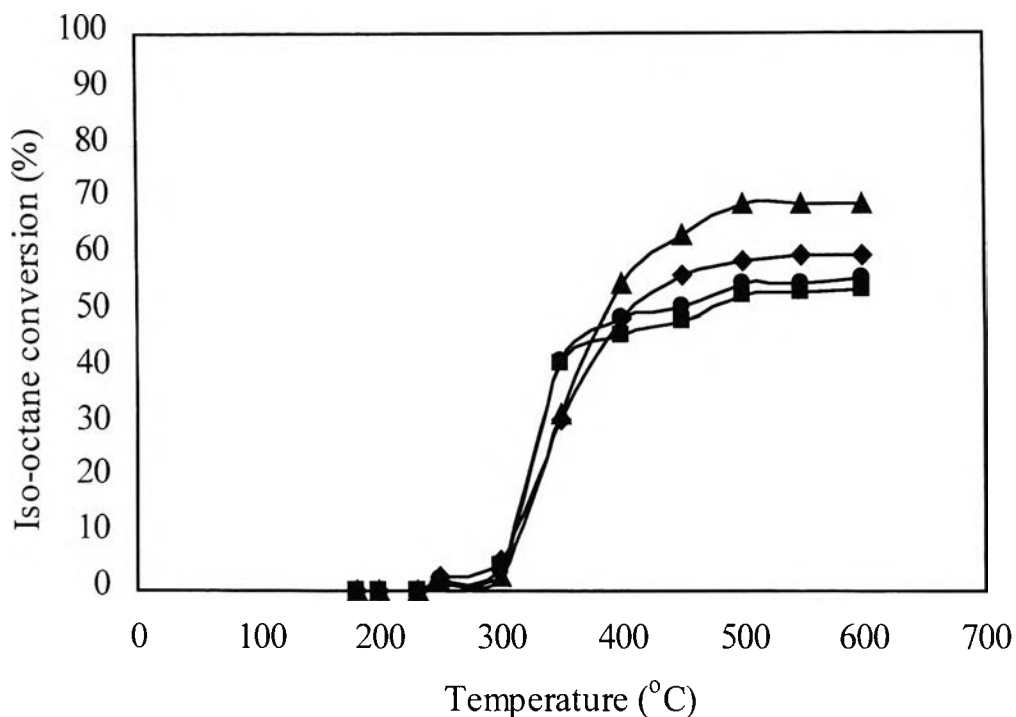


Figure 4.9 Iso-octane conversion as a function of reaction temperatures over different nickel loadings on $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ by impregnation method; %Ni loadings: (■) 0, (●) 5, (◆) 10 and (▲) 15 with reaction condition: O_2/C ratio = 1/1, total flow rate = 160 ml/min and space velocity = $64,000 \text{ h}^{-1}$

The product selectivities of iso-octane oxidation over 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ prepared by sol-gel and impregnation method show in Figure 4.11 and 4.12, respectively. At low temperature range ($< 300^\circ\text{C}$), the main product from both catalysts was CO_2 . There was a little amount of CO observed in the range of ca. $300\text{-}450^\circ\text{C}$ as shown in Figure 4.11 and 4.12, which caused a drop in CO_2 selectivity. Next, CO_2 , CO and H_2 products were observed was more than 450°C . These results are similar to the behavior of Pt/ ZrO_2 catalyst for methane oxidation reported by Hegarty *et al.* (1998). However, the H_2 product selectivity of sol-gel catalyst is higher than that of impregnation catalyst.

4.2.4 The Effect of O₂/C on Light Off Temperature Over Ce_{0.75}Zr_{0.25}O₂ and 15%Ni/Ce_{0.75}Zr_{0.25}O₂ Prepared By Both Sol-gel and Impregnation Method

The effect of O₂/C ratios was interesting to study because, in autothermal system, heat generated from partial oxidation will be supplied to steam reforming reaction. The effects of O₂/C ratios on the light off temperature during iso-octane oxidation over Ce_{0.75}Zr_{0.25}O₂ are presented in Figure 4.13 to 4.15. The O₂/C ratio was varied from 0.125, 0.25, 0.50 and 1 because it was not exceeded the O₂/C stoichiometric ratio for iso-octane partial oxidation (O₂/C=1/2). Due to the best activity of iso-octane oxidation, 15%Ni catalysts from both loading methods were used in this experiment.

The light off patterns of each O₂/C ratio was the same for all catalysts as shown in Figure 4.13 to 4.15. The conversion were increased with higher O₂/C ratio. For iso-octane oxidation, the highest catalytic activity was then obtained at O₂/C of 1/1 for all catalysts.

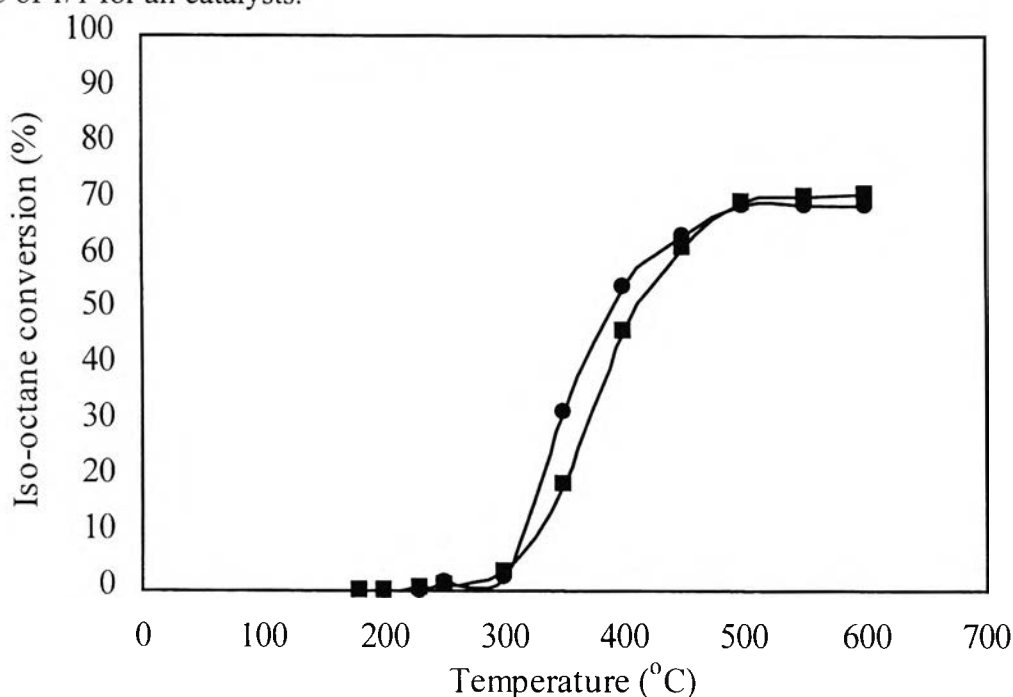


Figure 4.10 Iso-octane conversion as a function of reaction temperatures on 15%Ni/Ce_{0.75}Zr_{0.25}O₂; Ni loadings method: (■) sol-gel method and (●) impregnation method with reaction condition: O₂/C ratio = 1/1, total flow rate = 160 ml/min and space velocity = 64,000 h⁻¹

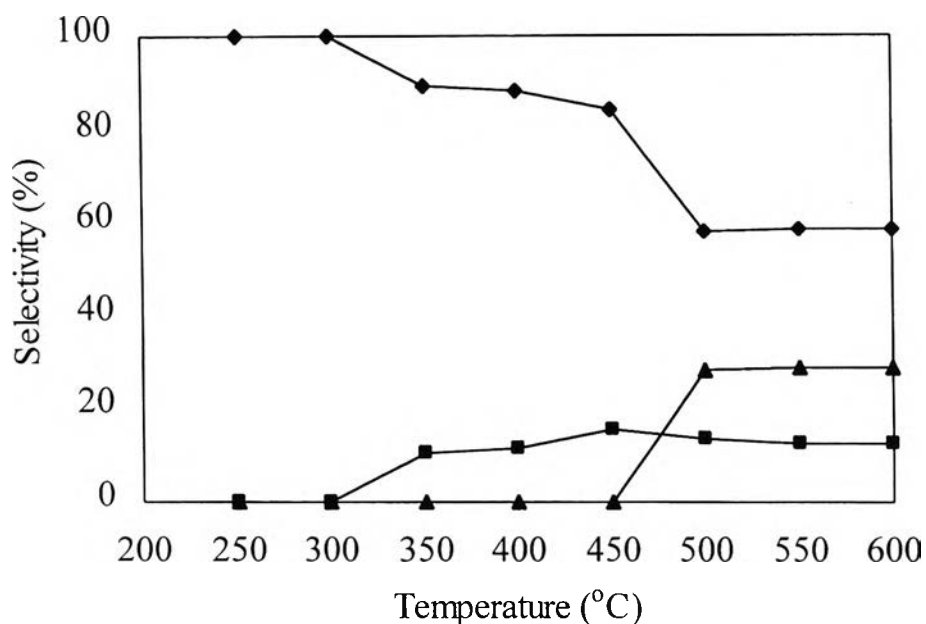


Figure 4.11 Selectivity of CO₂, CO and H₂ product from iso-octane oxidation over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method; (◆) CO₂, (■) CO and (▲) H₂ with reaction condition: O₂/C ratio = 1/1, total flow rate = 160 ml/min and space velocity = 64,000 h⁻¹

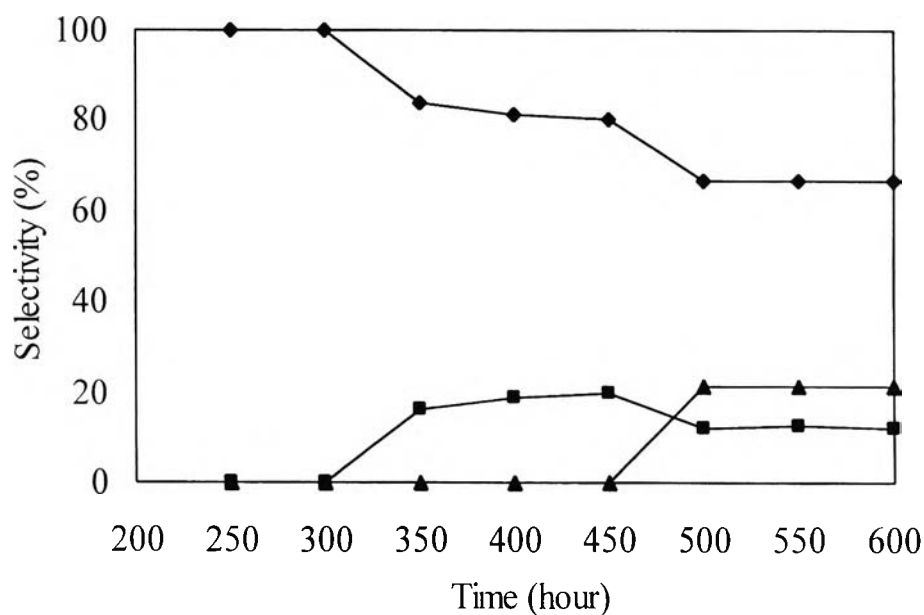


Figure 4.12 Selectivity of CO₂, CO and H₂ product from iso-octane oxidation over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by impregnation method; (◆) CO₂, (■) CO and (▲) H₂ with reaction condition: O₂/C ratio = 1/1, total flow rate = 160 ml/min and space velocity = 64,000 h⁻¹

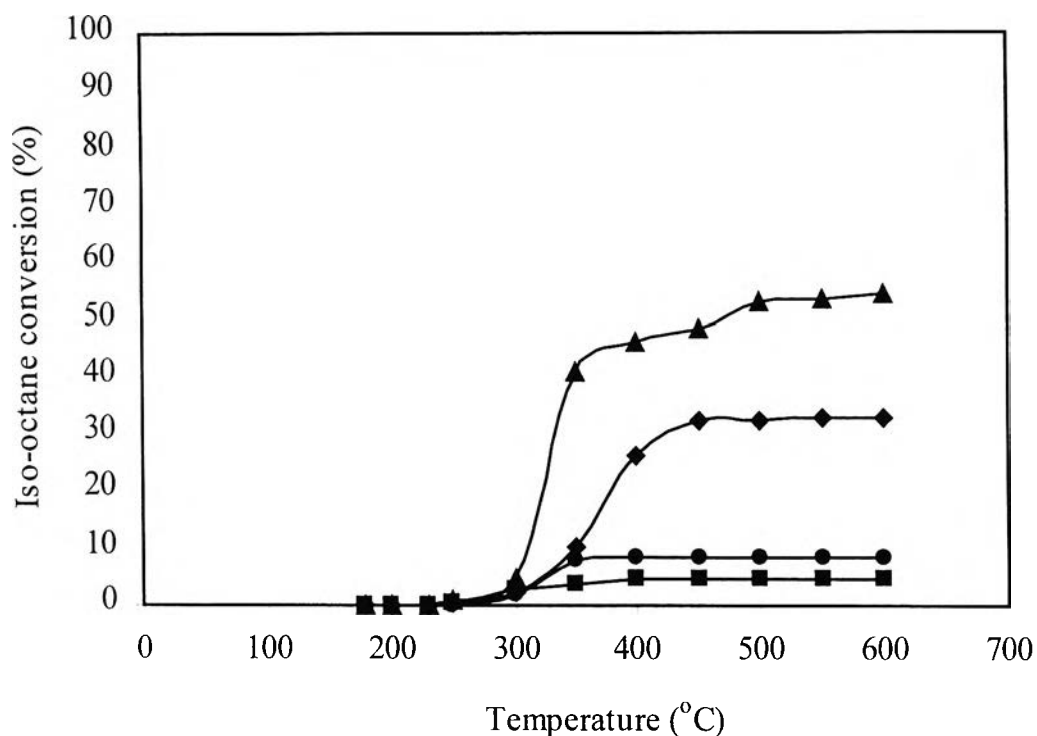


Figure 4.13 The effect of O₂/C on light off temperature of iso-octane oxidation over Ce_{0.75}Zr_{0.25}O₂; O₂/C ratios: (■) 0.125/1, (●) 0.25/1, (◆) 0.50/1 and (▲) 1/1 with reaction condition: total flow rate = 160 ml/min and space velocity = 64,000 h⁻¹

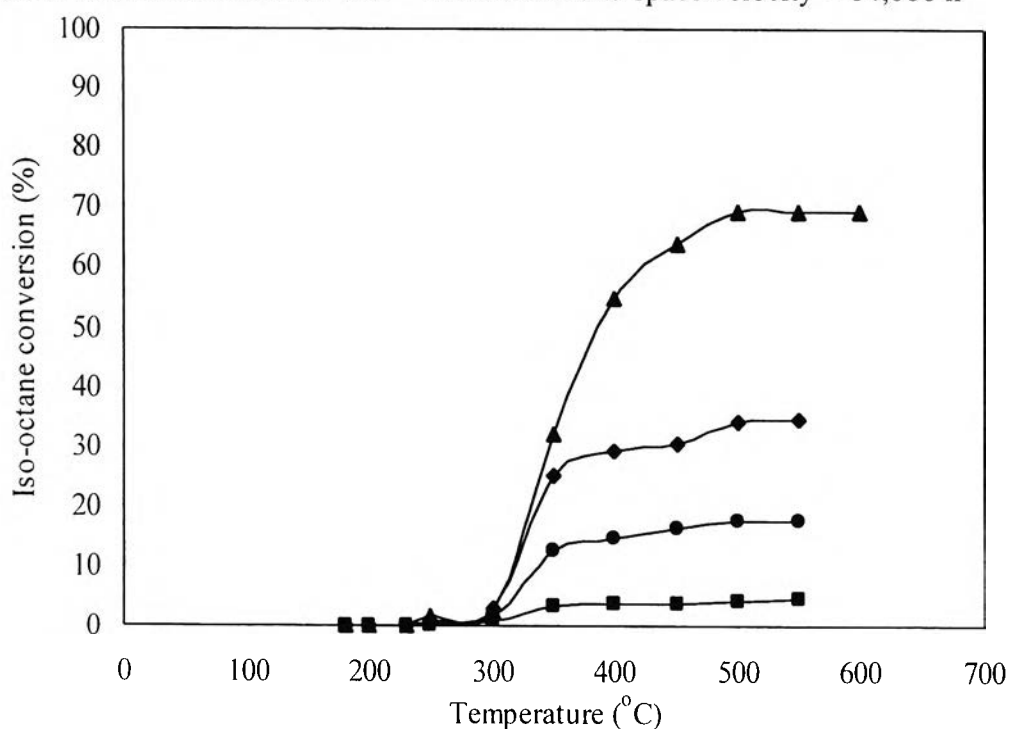


Figure 4.14 The effect of O₂/C on light off temperature of iso-octane oxidation over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method; O₂/C ratios: (■) 0.125/1, (●) 0.25/1, (◆) 0.50/1 and (▲) 1/1 with reaction condition: total flow rate = 160 ml/min and space velocity = 64,000 h⁻¹

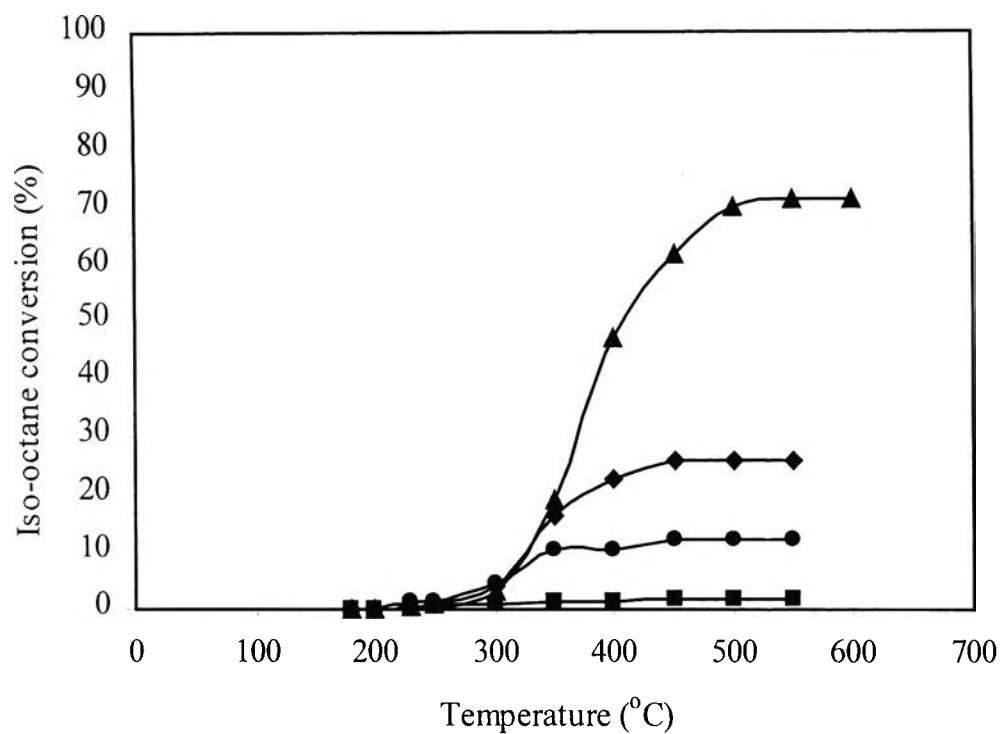


Figure 4.15 The effect of O₂/C on light off temperature of iso-octane oxidation over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by impregnation method; O₂/C ratios: (■) 0.125/1, (●) 0.25/1, (◆) 0.50/1 and (▲) 1/1 with reaction condition: total flow rate = 160 ml/min and space velocity = 64,000 h⁻¹

4.3 The Effect of Steam/Carbon Ratios

The effects of steam/carbon ratios on H₂/CO ratios, CO selectivity and iso-octane are shown in this section. The autothermal system experiments were done with 15%Ni with Ce_{0.75}Zr_{0.25}O₂ catalytic prepared by sol-gel and impregnation method due to their good activity, as mentioned in the light off temperature part.

4.3.1 The Effect of Steam/Carbon Ratios Over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ Prepared By Sol-gel Method

Results showing the influence of steam/carbon ratios on the H₂/CO product ratio in the autothermal system of iso-octane over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by the sol-gel method are presented in Figure 4.16. The experiments were done at a constant O₂/C ratio = 1/1 on account of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ exhibited the highest catalytic activity of sol-gel loading catalysts for iso-octane oxidation at O₂/C of 1/1.

As seen, hydrogen can be produced at the temperature above 450°C. All values of observed H₂/CO ratios, which are higher than 9.9/1, indicated that the water-gas shift reaction occurs simultaneously with steam reforming reaction. At low temperature range (450-500°C), it was observed that the H₂/CO ratios strongly depend on steam concentration, thereby the H₂/CO increases as an obvious increase in H₂/CO ratio. While the H₂/CO ratios was slightly increased with the addition of H₂O/C ratio at high temperature range (550-600°C). Moreover, H₂/CO ratio decreased with increasing temperature. It corresponds with the fact that water-gas shift reaction is not thermodynamically favored at high temperature (Choudhary *et al.*, 1998).

Figure 4.17 shows the effect of H₂O/C ratio on the CO selectivity. The CO selectivity increased with increasing temperature, but the CO selectivity decreased with increasing steam concentrations. It is implied that the increase in steam/carbon ratio enhanced the water-gas shift reaction rate, but decreased the concentration of CO. Since CO is the reactant in the water-gas shift reaction. The

increase in CO selectivity with a rise in temperature was from the decrease of the rate of water-gas shift, which is not thermodynamically favored at high temperatures.

The iso-octane conversion is rarely effected by H_2O/C ratio as shown in Figure 4.18. When the temperature increased, The iso-octane conversion increased because of the increasing rate of both steam reforming and partial oxidation. The iso-octane conversion slightly drops at H_2O/C ratio above 2. This might be explained that the addition of steam decreased the partial oxidation rate, which was the exothermic reaction, resulting in the decrease in the rate of steam reforming reaction (Hegarty et al., 1998).

4.3.2 The Effect of Steam/Carbon Ratios Over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ Prepared By Impregnation Method

Influence of temperature and steam/carbon ratios on the H_2/CO product ratios with autothermal system of iso-octane over the 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst prepared by impregnation method are demonstrated in Figure 4.19. As seen, hydrogen can be produced at temperature above 450°C. The observed higher H_2/CO ratio (>7.301) indicates that a water gas shift and steam reforming reaction appeared concurrently. The result was the same tendency as 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method. The decrease in H_2/CO ratio with increasing temperature because a water gas shift reaction is not preferred at high temperature (exothermic reaction).

The effect of H_2O/C on the CO selectivity over the 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst by impregnation method is shown in Figure 4.20. The CO selectivity decreases with an increasing H_2O/C , which is implied that the partial oxidation decreases with increase in the steam concentration. Moreover, the increasing steam ratio increases water gas shift reaction rate, and the selectivity of CO decreases because CO was the reactant in this reaction. 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 the presence of oxygen (Maillet et al., 1997).

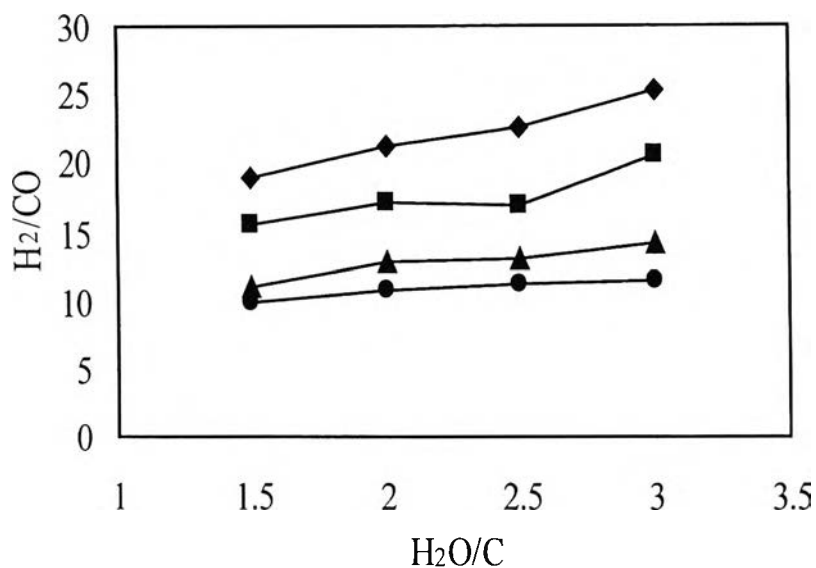


Figure 4.16 The effect of H₂O/C ratios on H₂/CO product ratio at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: O₂/C = 1/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

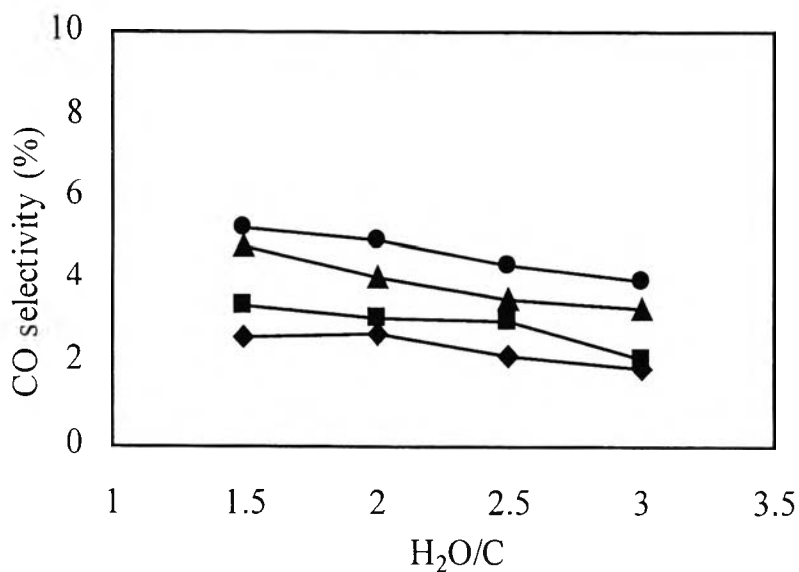


Figure 4.17 The effect of H₂O/C ratios on CO selectivity at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: O₂/C = 1/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

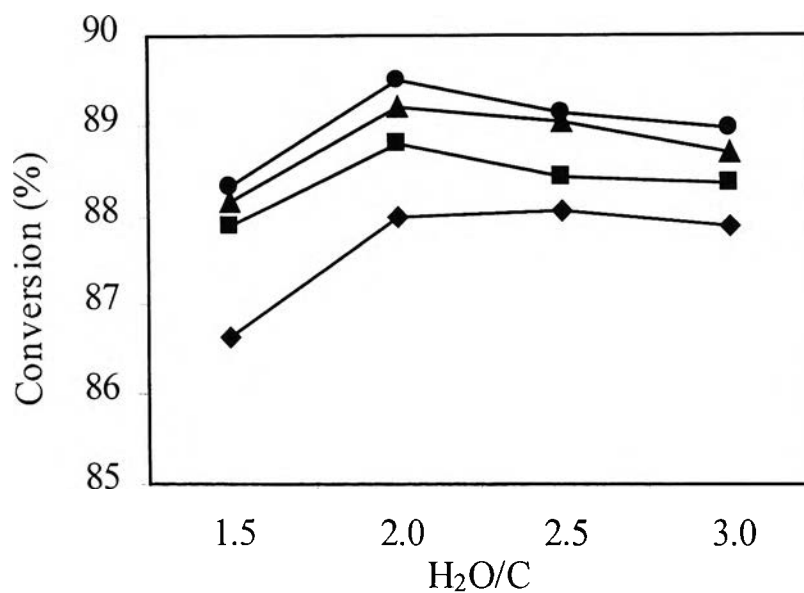


Figure 4.18 The effect of H₂O/C ratios on iso-octane conversion at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: O₂/C = 1/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

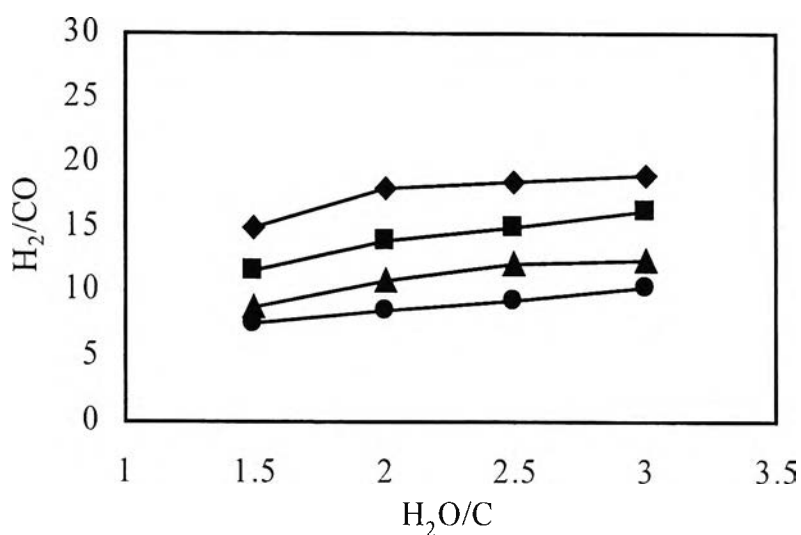


Figure 4.19 The effect of H₂O/C ratios on H₂/CO product ratio at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: O₂/C = 1/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

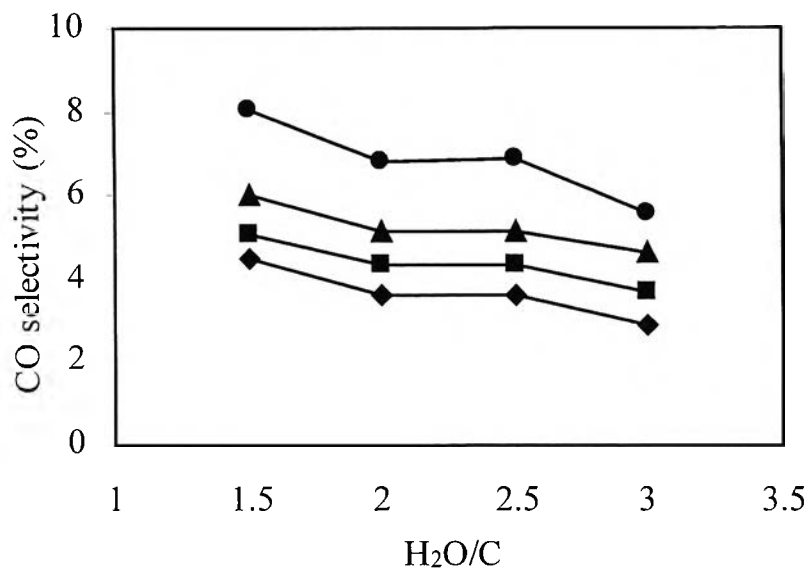


Figure 4.20 The effect of H₂O/C ratios on CO selectivity at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: O₂/C = 1/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

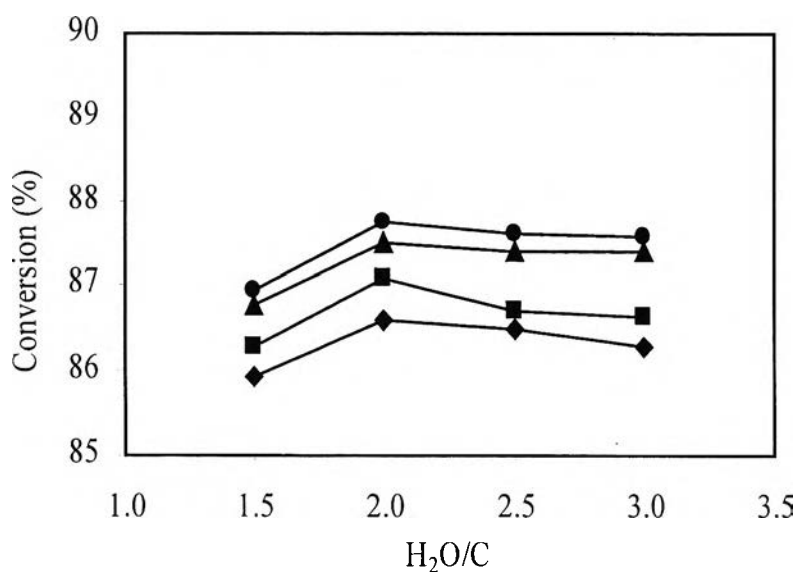


Figure 4.21 The effect of H₂O/C ratios on iso-octane conversion at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: O₂/C = 1/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

The effect of H_2O/C ratio on the conversion over catalyst is shown in Figure 4.21. At steam/carbon below 2.0, the iso-octane conversion rises with increasing temperature, because the rate of steam reforming and partial oxidation increased. At steam/carbon above 2.0, it was observed that the iso-octane conversion slightly dropped with increasing steam concentration. This may be due to water inhibits 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 15%Ni/Ce_{0.75}Zr_{0.25}O₂ Prepared By Sol-gel Method

The effect of temperature and oxygen/carbon ratios on the H_2/CO product ratio with autothermal system of iso-octane over 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method are presented in Figure 4.22 to 4.24. The experiments were carried at 450-600 °C and used the constant H_2O/C ratio at 2.0 because the highest iso-octane conversion was achieved at this H_2O/C ratio.

The H_2/C ratio was hardly affected by the O_2/C ratio. The increase in H_2/CO ratio corresponds to the decrease in CO selectivity (Fig 4.22). The observed H_2/CO ratio (>6.203) shows that steam reforming and water gas shift reaction appeared coincidentally. The H_2/CO ratio, which decreased with a rise in temperature, was caused by the decrease in the rate of water-gas shift reaction at high temperature.

As shown in Figure 4.23, the increasing of oxygen/carbon ratio dropped CO selectivity. It can be suggested that the increase in O_2/C ratio inhibited the rate of partial oxidation reaction, resulting in the decrease in CO selectivity. Temperature also influences on the CO selectivity. The increase in temperature increases CO selectivity, due to CO is the reactant in the water-gas shift reaction. The increase in the temperature suppresses the rate of water-gas shift that enhances the increase in CO concentration.

The influence of O_2/C ratio on the conversion over $15\%Ni/Ce_{0.75}Zr_{0.25}O_2$ prepared by sol-gel method is illustrated in Figure 4.24. The iso-octane conversion was significantly effected by O_2/C ratio. It can be concluded that the main reaction in the autothermal system with $15\%Ni/Ce_{0.75}Zr_{0.25}O_2$ is iso-octane oxidation. Moreover, the increase in temperature increases the conversion of iso-octane. It is showed that the rate of iso-octane oxidation and steam reforming was enhanced at high temperature.

4.3.2 The Effect of Oxygen/Carbon Ratios Over $15\%Ni/Ce_{0.75}Zr_{0.25}O_2$ Prepared By Impregnation Method

As shown in Figure 4.25, the H_2/C ratio was gradually increased with the O_2/C ratio. The increase in H_2/CO ratio corresponds to the decrease in CO selectivity (Fig 4.25 and 4.26). The observed H_2/CO ratio (>5.9) shows that steam reforming including water gas shift reaction occurred at once. The H_2/CO ratio, which decreased with a rise in temperature, was caused by the decrease in the rate of water-gas shift reaction at high temperature.

The increasing of oxygen/carbon ratio dropped CO selectivity as shown in Figure 4.26. It can be suggested that the increase in O_2/C ratio inhibited the rate of partial oxidation reaction, resulting in the decrease in CO selectivity. Temperature also influences on the CO selectivity. The increase in temperature increases CO selectivity because CO is the reactant in the water-gas shift reaction. The increase in the temperature suppresses the rate of water-gas shift that enhances the increase in CO selectivity.

Figure 4.27 represents the effect of O_2/C ratio on the conversion over $15\%Ni/Ce_{0.75}Zr_{0.25}O_2$ prepared by impregnation method. The iso-octane conversion was significantly effected by O_2/C ratio. It is showed that the rate of iso-octane oxidation and steam reforming was enhanced at high temperature.

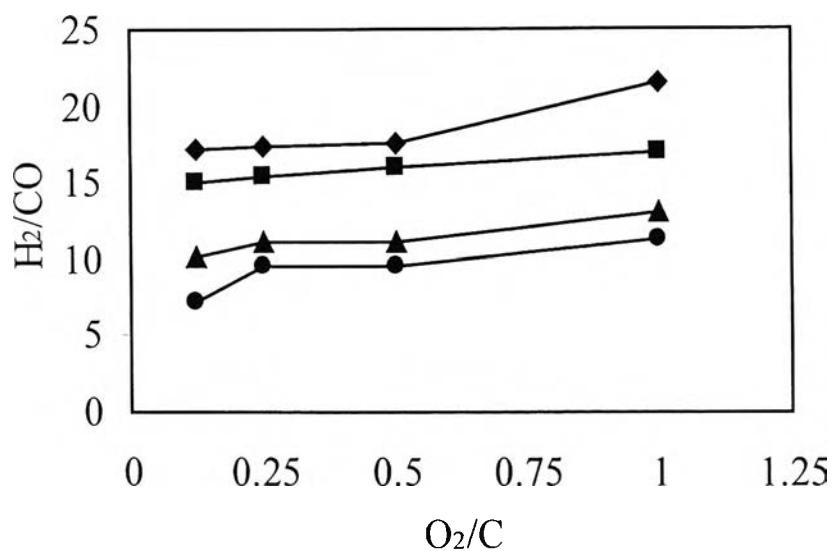


Figure 4.22 The effect of O₂/C ratios on H₂/CO product ratio at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: H₂O/C = 2/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

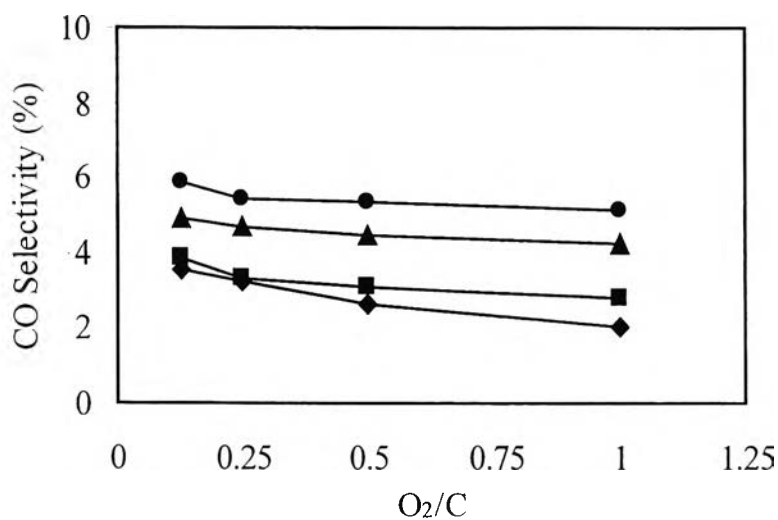


Figure 4.23 The effect of O₂/C ratios on CO selectivity at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: H₂O/C = 2/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

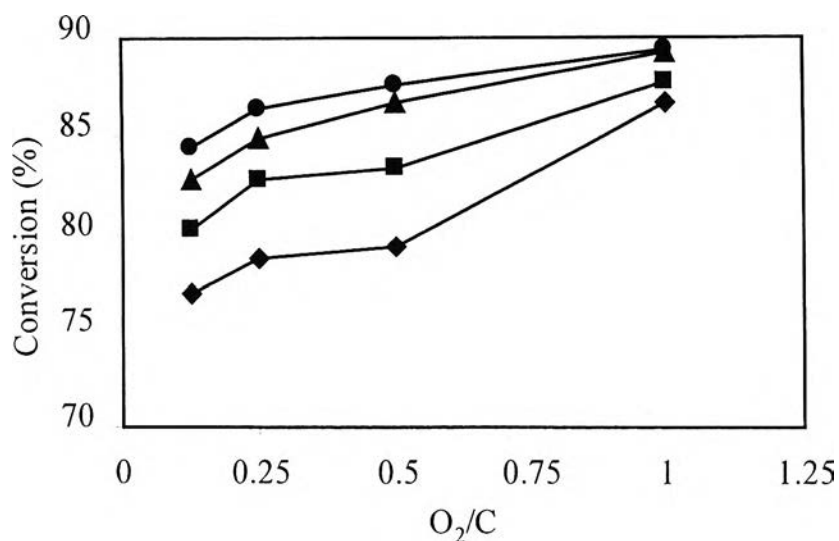


Figure 4.24 The effect of O₂/C ratios on iso-octane conversion at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: H₂O/C = 2/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

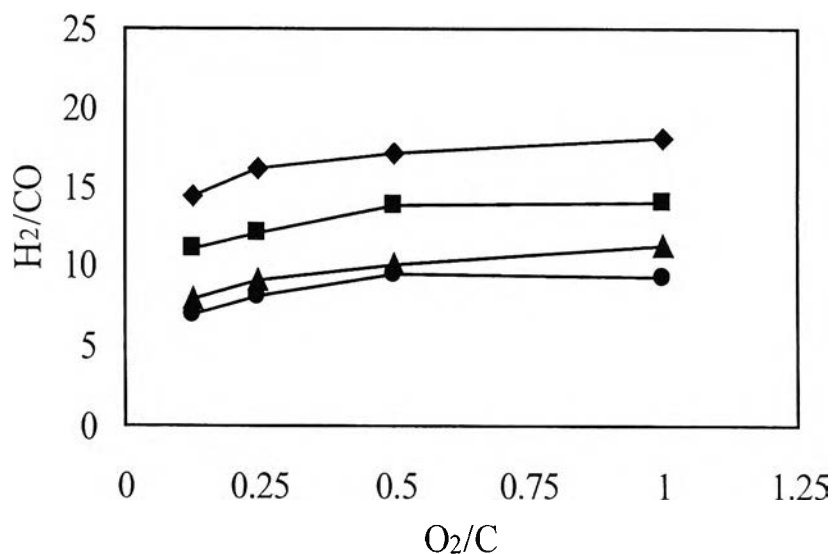


Figure 4.25 The effect of O₂/C ratios on H₂/CO product ratio at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel with reaction condition: H₂O/C = 2/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

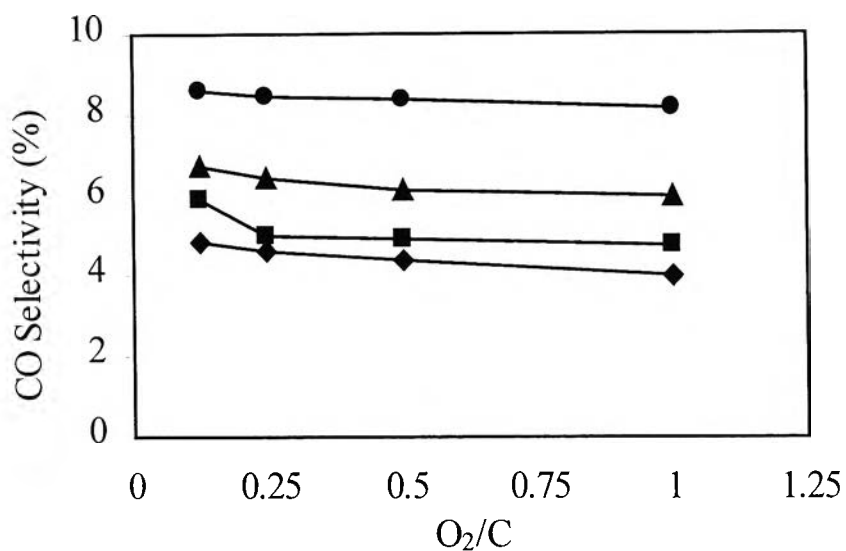


Figure 4.26 The effect of O₂/C ratios on CO selectivity at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: H₂O/C = 2/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

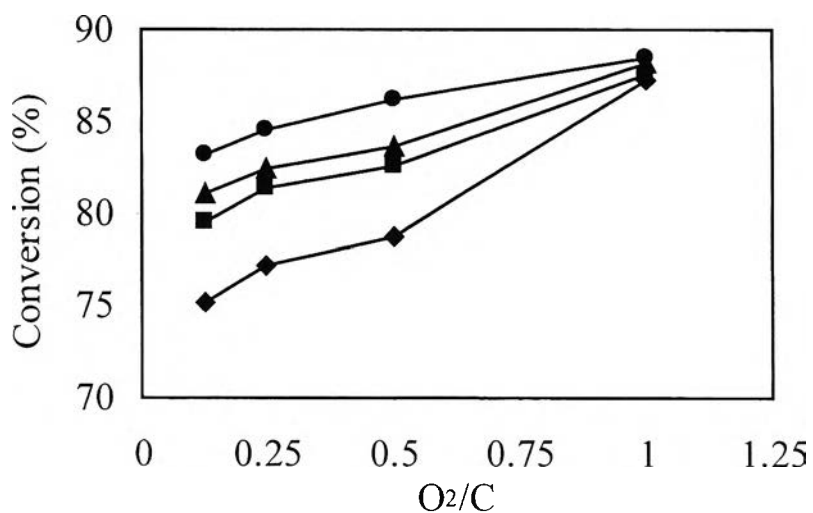


Figure 4.27 The effect of O₂/C ratios on iso-octane conversion at (◆) 450°C, (■) 500°C, (▲) 550°C and (●) 600°C of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ by sol-gel method with reaction condition: H₂O/C = 2/1, total flow rate = 160 ml/min and space velocity 64,000 h⁻¹

4.5 Coke Formation Study

The used catalysts were investigated their differences types, amounts and forms of carbon deposition by temperature programmed oxidation (TPO) and transmission electron microscopy (TEM) and catalyst decomposition.

4.5.1 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation (TPO) for all used catalysts tested were conducted by Gas Chromatography (GCMS). When the carbon is oxidized, GC will record the amount of carbon monoxide gas increases as a function of temperature and time. As shown in Figure 4.28 and 4.29, the TPO spectra of the unloaded $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and the sol-gel catalysts showed two obvious peaks: a first low temperature peak(at around 350°C) and a second one at high temperature peak(at about 450°C). It suggests that these peaks may be due to deposit of a graphitic carbon(Swaan H.M., 1994). Moreover, this implies that the types of carbon on the used sol-gel catalysts had the same stability as from the support catalyst because of the same location of TPO peaks.

The TPO spectra for the impregnation catalysts showed one extremely sharp peak at about 600°C , which is attributed to the combustion of whisker carbon fibers(Michael C.J. *et. al*, 1996). This implies that the types of carbon on the used sol-gel catalysts may be different from those on the impregnation catalyst because the TPO peaks were in the different location. The carbon deposited on the sol-gel catalysts should be easilier to remove than that on the impregnation ones due to the lower in oxidation temperature peak.

On different Ni loading catalyst, there were the differences in the amount of carbon formed on each catalyst. % carbon on three catalysts are in the following order: $0\% > 5\% > 10\% > 15\%$, which is related to the surface area under TPO patterns. It means that the higher Ni loadings perform the lower carbon deposition.

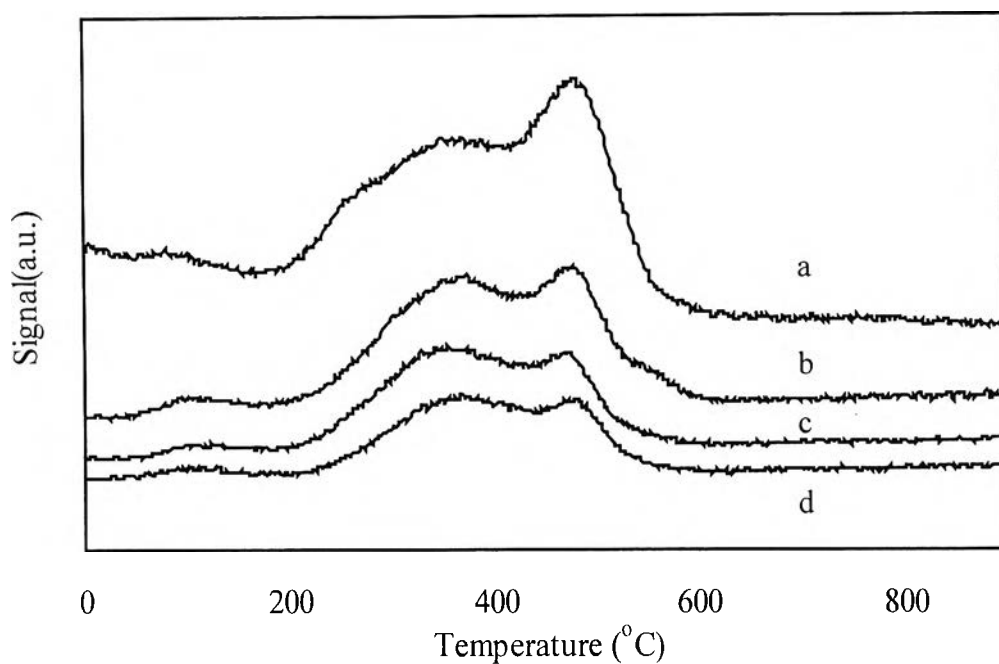


Figure 4.28 TPO results of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (a), 5%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (b), 10%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (c) and 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (d) which prepared by sol-gel method

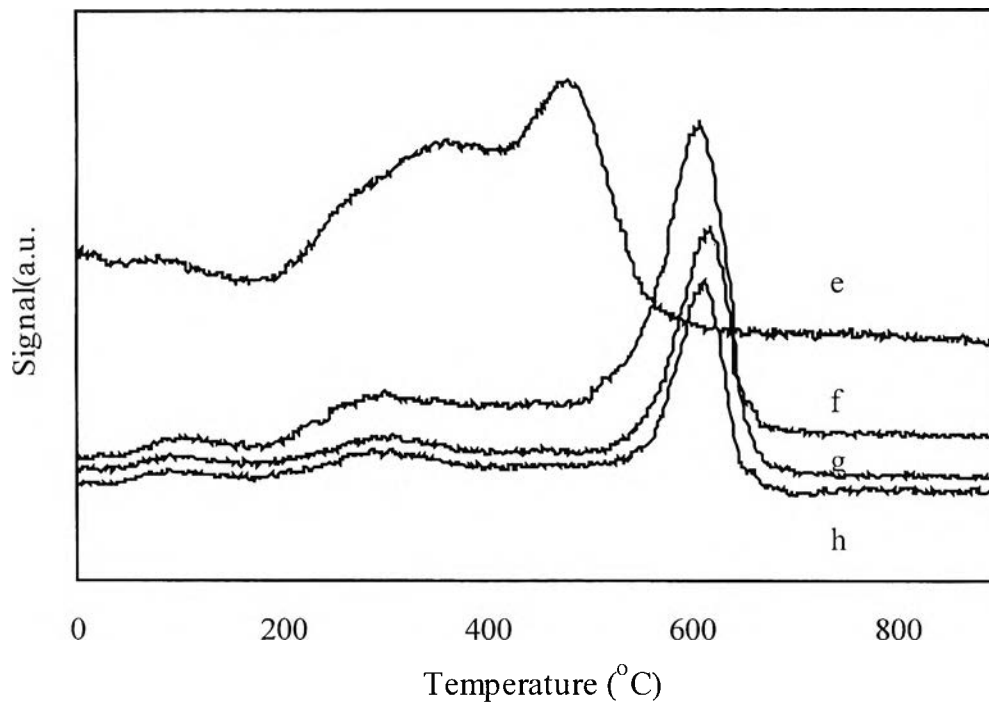


Figure 4.29 TPO results of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (e), 5%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (f), 10%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (g) and 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (h) which prepared by impregnation method

4.5.2 Transmission Electron Microscopy (TEM)

After catalysts were used, transmission electron microscopy or TEM was employed to investigate the coke formation. TEM results of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by both sol-gel and impregnation methods were shown in Figure 4.30(a) and 4.30(b), respectively.

It was found that there was the difference in the coke formation because the shapes of formed coke were not the same. As shown in Figure 4.30(a), the carbon deposition on 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method is in an amorphous form, which is easier to reduce at low temperature corresponding to low temperature peak of TPO results. Whereas the coke formation on 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by impregnation method was in a fiber or whisker form, which is harder to reduce as shown in Figure 4.30(b) corresponding to the high temperature peak of the TPO results. Furthermore, there are filaments of different diameters indicating the presence of a distribution of Ni crystallite sizes (Montaya J.A. *et al.*, 2000).

4.5.3 Catalyst Decomposition

The 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts prepared by both techniques were studied their decomposition with the reaction time as shown in Figure 4.31. The reaction was carried at 600°C, H₂O/C ratio = 2/1 and O₂/C ratio = 1/1 for 10 hours. Figure 4.31 shows the activity of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts during 10 hours. The activity of the sol-gel catalyst had nearly no change while, for impregnation catalyst, the activity gradually decreased. It is suggesting that 15%Ni/Ce_{0.75}Zr_{0.25}O₂ prepared by sol-gel method is a suitable catalyst for autothermal system since it gave more constants in the activity. In other word, the coke was easilier to form on the impregnation catalyst than on the sol-gel one.

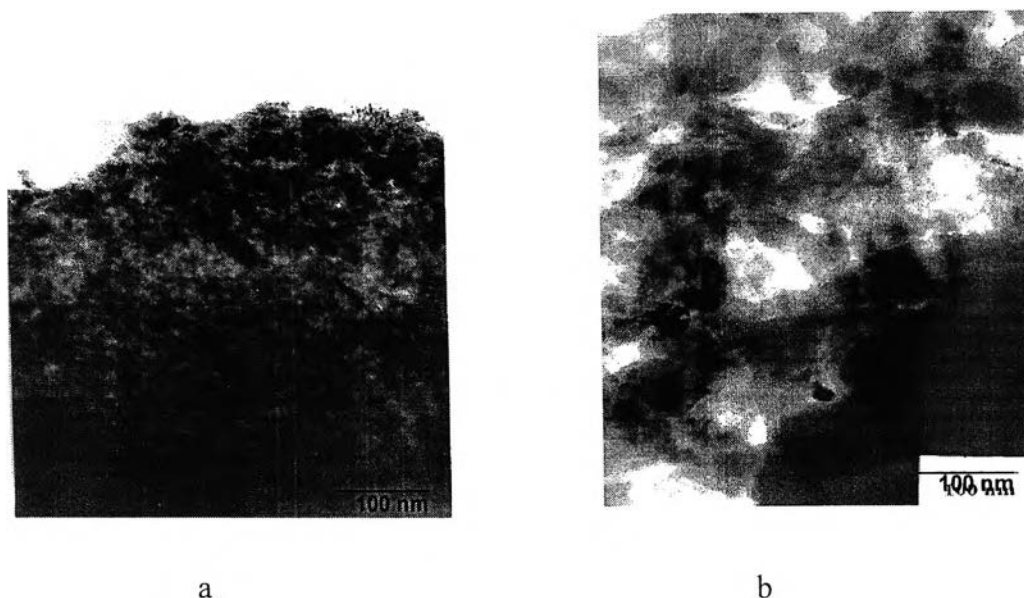


Figure 4.30 TEM results of used 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ which prepared by sol-gel method (a) and impregnation method (b), respectively

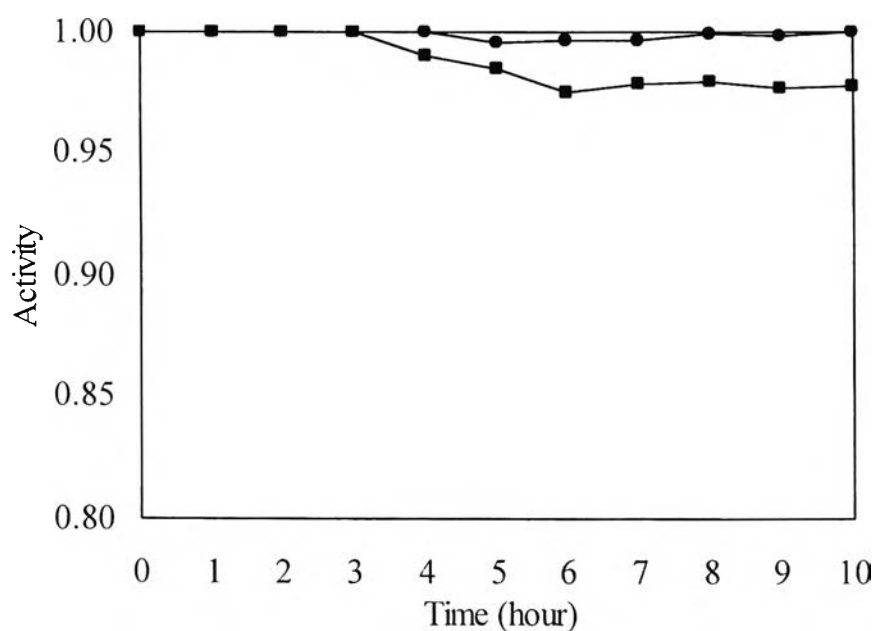
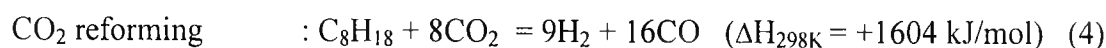
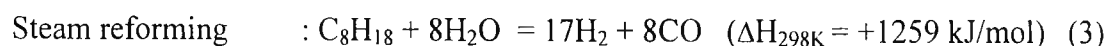
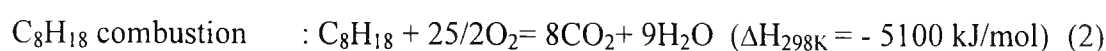
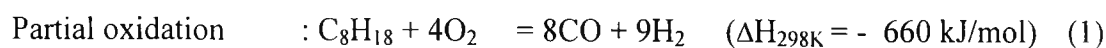


Figure 4.31 The activity of 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ versus time for coke formation study carried under autothermal system with reaction condition: $\text{H}_2\text{O}/\text{C} = 2/1$, $\text{O}_2/\text{C} = 1/1$, 600°C , total flow rate = 160 ml/min and space velocity = $64,000 \text{ h}^{-1}$

4.6 Catalyst Bed Temperature Profile

Catalyst bed temperature profiles were determined in order to help elucidate the reaction pathway. The catalyst bed temperature profiles obtained for reaction at 600°C are shown in Figure 4.32. The experiments were carried out individually with three concerned reactions: steam reforming, partial oxidation and autothermal system reactions. From the definition of the temperature difference, the positive value (exotherm) means the exothermic reaction occurred inside the catalyst bed because the temperature of bed is higher than that of furnace. In the same way, the negative temperature difference (endotherm) means the endothermic reaction occurred inside the bed.

In the case of steam reforming, there is a large endotherm of > 40°C at the start of catalyst bed but the temperature decreases magnitude further down the bed. The detected endotherm from steam reforming reaction corresponded with its thermodynamic property, which has the positive enthalpy change of reaction. For partial oxidation, an exotherm was found at the start of the catalyst bed and this was followed by a large endotherm later in the bed. This suggests that the partial oxidation mechanism was iso-octane partial oxidation or combustion (Eq.(1)) followed by steam or carbon dioxide reforming (Eq.(3) and (4)) due to the same tendency of temperature profile received by Hegarty *et al.* (1998).



For autothermal system, both the endotherm associated with steam reforming or carbon dioxide reforming and the exotherm associated with partial oxidation or combustion were reduced. This is advantageous as it reduced the temperature of the “hot spots” in the catalyst bed. It is suggesting that these proposed reactions could be used for predicting the reaction mechanism and rate which further utilize for having the best performance in a reactor design.

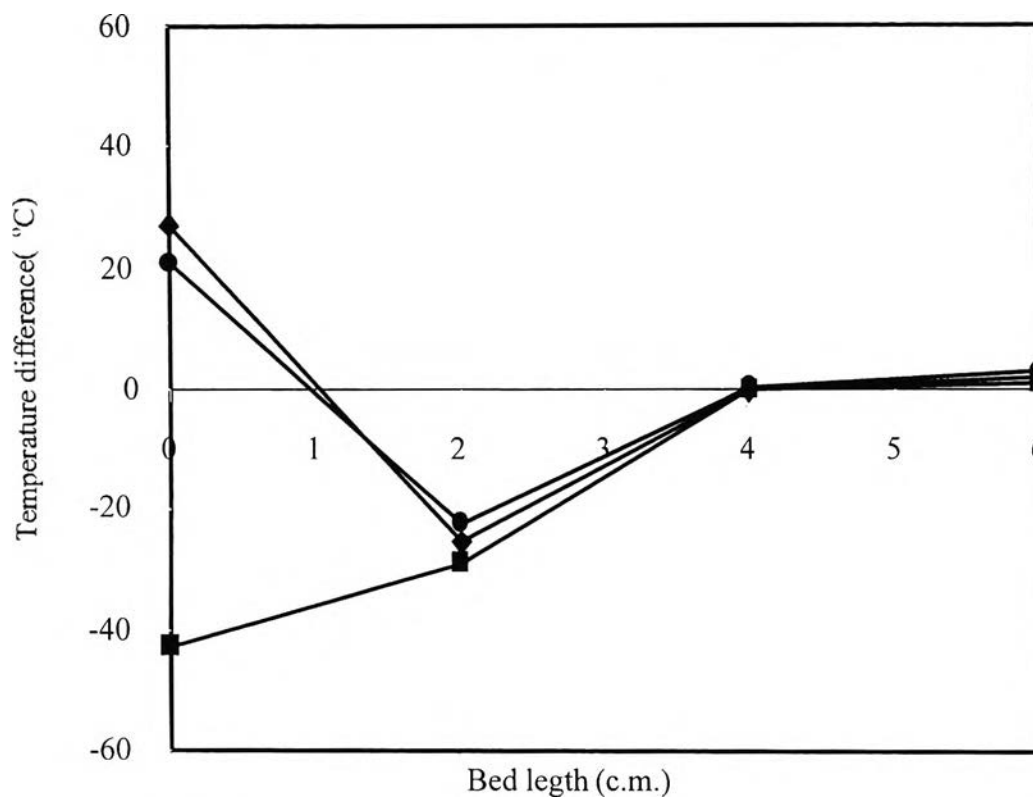


Figure 4.28 Catalyst bed temperature profiles measured at the furnace set-point of 600°C for steam reforming(■), partial oxidation(◆) and autothermal system(●); the temperature difference refers to the measured bed temperature minus the furnace set-point temperature