

H₂ Production from Partial Oxidation of *iso*-Octane over Ni/Ce_{0.75}Zr_{0.25}O₂ and Ni/β"-Al₂O₃ Catalysts

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Abstract

In this study, the partial oxidation of *iso*-octane over Ni/Ce_{0.75}Zr_{0.25}O₂ and Ni/β"-Al₂O₃ catalysts was investigated. The results indicated that Ni/Ce_{0.75}Zr_{0.25}O₂ is more active than Ni/β"-Al₂O₃. The partial oxidation products are mainly H₂ and CO for Ni/Ce_{0.75}Zr_{0.25}O₂ with hydrogen selectivity up to 85%. The H₂/CO ratio is in the range of 1.3-2.0 depending on the operating temperature. It was noticed that at temperature above 700°C, the presence of methane was detected. On the other hand, the main products of *iso*-octane partial oxidation over Ni/β"-Al₂O₃ are CO₂ and *i*-C₄H₈ at temperature below 650°C. Above 650°C, the main products are H₂ and CO. The H₂/CO ratio is about 1.3. However, the hydrogen selectivity was found to be lower than that of Ni/Ce_{0.75}Zr_{0.25}O₂ due to the formation of other hydrocarbons such as CH₄, C₂H₄, C₂H₆ and C₃H₆. These hydrocarbons are the products of catalytic cracking of *iso*-octane and methane coupling. The reaction mechanism of *iso*-octane partial oxidation over Ni/β"-Al₂O₃ catalyst might be explained by β-elimination. For both catalysts, the hydrogen and carbon monoxide selectivity was found to decrease with increasing C/O ratio. The Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst can be operated in a wider range of C/O ratios than the Ni/β"-Al₂O₃ catalyst.

Introduction

There is currently great interest in fuel cells as a potential replacement of conventional combustion engines or as auxiliary power units in automobiles. The most promising fuel cells would seem to be the ones equipped with proton exchange membrane (PEM) using hydrogen (Avci et al., 2001; Moon et al., 2001). However, the distribution and

on-board storage of hydrogen are major hurdles. Therefore, compact and efficient devices to convert liquid transportation fuels to hydrogen are needed, either in the form of on-board reformers or in stationary facilities supplying refueling stations with hydrogen. It is very likely that for the foreseeable future, we will have to rely on the existing gasoline distribution infrastructure as source of hydrogen for fuel cell equipped vehicles. Hydrogen can be produced from natural gas, naphtha, vacuum residue, refinery off-gas, etc. In transportation, methanol, gasoline or diesel are suitable fuels (Ahmed and Krumpelt, 2001). Some studies have been focused on the conversion of methanol to hydrogen (Peppley et al., 1999) but an effective distribution infrastructure for this fuel is not in place. The generation of hydrogen from the other fuels, including natural gas, liquefied petroleum gases (LPG), gasoline, and diesel represents attractive alternatives.

There are three main methods for producing hydrogen from heavy hydrocarbons, namely steam reforming, partial oxidation, and autothermal reforming. In this study, we will focus on partial oxidation. The conversion of heavy hydrocarbons, which are major constituents of gasoline and diesel, to hydrogen by partial catalytic oxidation tends to suffer from coke deactivation. Hence, there has been emphasis on the development of highly active and coke resistant catalysts for partial oxidation (Moon et al., 2001). Nickel-based catalysts are attractive due to their low cost. Thanks to the redox properties of mixed oxide $\text{CeO}_2\text{-ZrO}_2$, Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst showed high catalytic activity and resistance to coke formation in methane partial oxidation (Pengpanich et al., 2004). The use of ion conducting solid electrolytes as a catalyst support is also of interest. It was reported that several ion-conducting solid electrolytes, namely H⁺, Li⁺, Na⁺, K⁺, Au⁺, Ag⁺ β"-Al₂O₃ act as good supports for oxidation catalysts (Harkness et al., 1996; Agrawal et al., 1999; Guillet et al., 2003). By conducting ions to the metal surface, the rate of hydrocarbon oxidation is improved. The use of β"-Al₂O₃ in fuel cell applications was found to be advantageous since it yields higher value chemicals and electricity simultaneously (Kiwi et al., 1991).

In this study, we investigate the activity, selectivity, and stability of both the 5 wt% Ni/Ce_{0.75}Zr_{0.25}O₂ and 5 wt% Ni/β"-Al₂O₃ catalysts for *iso*-octane partial oxidation over the temperature range of 400-800°C at atmospheric pressure.

Experimental

Catalyst preparation

5 wt% Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst and 5 wt% Ni/β"-Al₂O₃ catalyst were prepared by conventional impregnation method with nickel salt solutions. The β"-alumina (with Na⁺ ion conductor) used as support was supplied from Ionotec (England) while Ce_{0.75}Zr_{0.25}O₂ support was prepared by urea hydrolysis following the method published by Pengpanich et al. (2002). The catalyst was thermally treated in air at the temperature of 500°C for 4 h.

Catalyst characterizations

The surface areas of the samples were determined by the BET method using a Quantachrome Corporation Autosorb instrument. The samples were outgassed at 250°C for 4 h prior to analysis.

Temperature Programmed oxidation (TPO) carried out in a TPO reactor analyzer coupled with an FID was used to quantify the amount of coke formation in the spent

catalysts. Typically, about 40 mg of sample was heated with a constant rate of 10°C/min from room temperature to 900°C using 2%O₂ in He as an oxidizing gas at a flow rate of 40 ml/min. The output gas was passed to a methanation reactor using 15 wt% Ni/Al₂O₃ as a catalyst prior to FID detector. After the temperature reached to 900°C, 100 µl of CO₂ pulses was injected in order to calculate the amount of coke formed on the catalysts.

Catalytic activity tests

A fixed-bed quartz tube microreactor (i.d. Ø 6 mm) was used to test the catalytic activity for *iso*-octane partial oxidation. Typically, ca. 10 mg of catalyst sample diluted in 90 mg of α-Al₂O₃ was packed between layers of quartz wool. The reactor was placed in an electric furnace equipped with K-type thermocouples. The catalyst bed temperature was monitored and controlled by Shinko temperature controllers. *iso*-Octane was vaporized from a saturator at 10 °C using He as carrier gas. The concentration of *iso*-octane was maintained at 0.8% by mole. Typically, feed composition was altered to obtain C/O ratios in the range between 0.6 and 1.6, balanced with He. The total flow rate of feed gases was kept at 150 ml/min (GHSV = 80,000 h⁻¹) using Aalborg mass flow controllers. Measurements were carried out at furnace temperatures adjusted sequentially to 400 - 800°C. The product gases were chromatographically analyzed using a Shimadzu GC 14A equipped with a CTR I (Alltech) column for the TCD detector and Porapak® Q (Alltech) column for the FID detector. The selectivities (S) reported in this work were calculated by the ratio of the specific product yield (Y) to the conversion (X) of *iso*-octane, with all products scaled by their numbers of C or H atoms.

Results and discussion

Partial Oxidation of *iso*-Octane

The conversion of *iso*-octane, oxygen consumption, and the product selectivities of *iso*-octane partial oxidation over Ni/β"-Al₂O₃ and Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts are shown in Fig.1. Over the Ni/β"-Al₂O₃ catalyst, the *iso*-octane conversion started to increase rapidly as the temperature increased from 600 to 700°C whereas the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst gave nearly 100 % conversion at much lower temperature (ca. 550°C), indicating that Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst has higher catalytic activity than Ni/β"-Al₂O₃ catalyst. It should be noted, though, that the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst had a much higher BET surface area than the Ni/β"-Al₂O₃ catalyst, as presented in Table 1.

For the 5 wt% Ni/β"-Al₂O₃ catalyst (see Fig. 1(a)), CO₂ and *i*-C₄H₈ were the dominant products at temperatures < 650°C. Above 650°C, the CO₂ and *i*-C₄H₈ selectivities were found to decrease, and other products including CO, H₂, CH₄, C₂H₄, C₂H₆ and C₃H₆ products were observed. At these conditions, the oxygen was completely consumed and a H₂/CO molar ratio of ca. 1.3 was obtained. This suggests that at temperatures < 650°C CO₂ was produced by total oxidation while *i*-C₄H₈ was produced by a cracking reaction. At higher temperatures, the light hydrocarbons produced by cracking reactions are then reformed with either H₂O or CO₂ to yield CO and H₂ products (Pacheco et al., 2003). The olefinic products, C₃H₆ and *i*-C₄H₈, observed in *iso*-octane partial oxidation over Ni/β"-Al₂O₃ catalyst, might be due to β-elimination. The *i*-C₄H₈ resulted from abstraction of the tertiary hydrogen followed by β-scission of the parent molecule into isobutylene and isobutyl radical. The isobutyl radical can undergo either abstraction of a

primary H atom leading to another isobutylene molecule (O'Connor et al., 2000), or β -methyl elimination to form propylene (Huff and Schmidt, 1995).

The C_2H_4 and C_2H_6 products formed over Ni/ β'' - Al_2O_3 catalyst at temperatures above $700^\circ C$ may be due to oxidative coupling of methane. From our earlier results for methane partial oxidation (data not shown), not only CO_2 , CO and H_2 products, but also C_2H_4 and C_2H_6 products were observed over this catalyst. This suggests that oxidative coupling of methane over Ni/ β'' - Al_2O_3 may occur. A similar finding was observed by Kiwi et al. (1991) reporting that β'' - Al_2O_3 is capable of producing CH_3 radical precursors to generate C_2H_4 and C_2H_6 products. Therefore, the presence of C_2 products observed in the *iso*-octane partial oxidation might stem from this reaction.

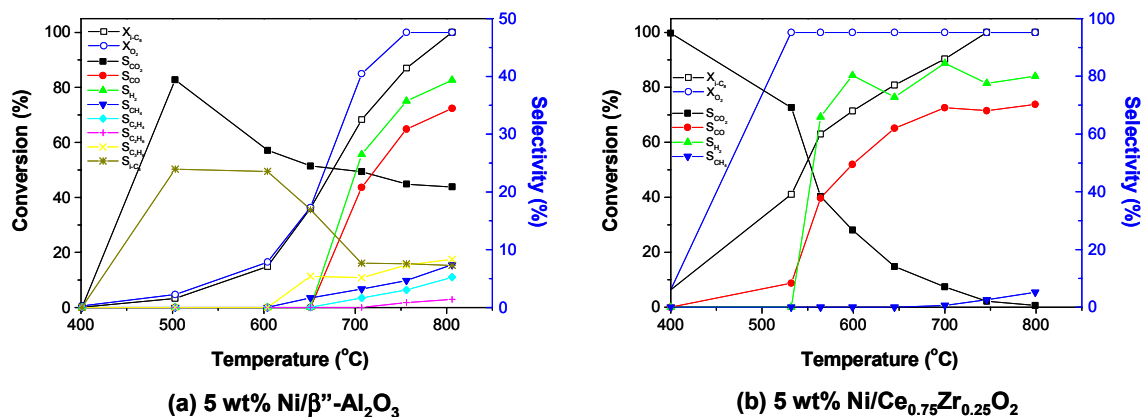


Figure 1 *iso*-Octane conversion, oxygen consumption and product selectivities over 5 wt% Ni supported catalyst at the condition of space velocity = $80,000\text{ h}^{-1}$ and feed molar ratio of C/O ratio = 1.

Table 1 BET surface area of the Ni supported catalysts

Catalyst	BET surface area (m^2/g)
5 wt% Ni/ β'' - Al_2O_3	5.5
5 wt% Ni/ $Ce_{0.75}Zr_{0.25}O_2$	112.0

On the 5 wt% Ni/ $Ce_{0.75}Zr_{0.25}O_2$ catalyst (see Fig. 1(b)), at temperatures $< 550^\circ C$, only CO_2 was observed as product, while CO and H_2 products became dominant at temperatures above $550^\circ C$. No $C_2 - C_4$ products were found over this catalyst. After complete consumption of O_2 , CO and H_2 started to reach significant levels in the product stream. This infers that the CO and H_2 were produced by reforming rather than by partial oxidation (Praharso et al., 2003). The H_2/CO ratio was in the range of 1.3-2.0 depending on the operating temperature. It was found that the H_2/CO ratio decreased with increasing operating temperature. From stoichiometry, the H_2/CO ratio from steam reforming is about 2.1 while that of dry reforming is about 0.6. It is apparent that the dry reforming dominates at higher temperature. The small amount of CH_4 present in the product stream at temperatures above $700^\circ C$ is believed to be due to the methanation reaction (Ming et al, 2002; Krummenacher et al., 2003).

The effect of C/O ratio

In this study, the C/O feed ratio was varied from 0.6 to 1.6 at a GHSV = 80,000 h⁻¹ and the reaction temperature of 700 - 800°C. Table 2 shows the effect of C/O ratio on the *iso*-octane conversion, oxygen consumption, and product selectivities over 5 wt% Ni/ β'' -Al₂O₃ and 5 wt% Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts at temperatures of 700, 750, and 800°C, respectively. For 5 wt% Ni/ β'' -Al₂O₃ catalyst, it was found that CO, H₂, and CO₂ selectivities were decreased with increasing C/O feed ratio while the selectivity to hydrocarbons (C₂'s, C₃'s) increased. It appears that with increasing C/O feed ratio, adsorbed alkane and/or surface carbon concentration on the catalyst surface should increase, further inhibiting O₂ adsorption. An increase in selective formation for olefins was indeed found at higher C/O ratios (Dietz III et al., 1996).

As shown in Table 2, similar results were found in 5 wt% Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst but higher hydrocarbons (C₂'s, C₃'s) were not observed. At C/O feed ratios > 1.0, CO and H₂ selectivities decreased while CH₄ selectivity increased. The decrease in CO and H₂ selectivities might be due to the onset of methanation with increasing C/O feed ratios.

Coke formation

The carbon formation over these catalysts was investigated after 6 h of reaction time at 800°C and C/O ratios of 0.6, 1.0 and 1.6, respectively. The TPO profiles of the catalysts are shown in Fig. 2. The TPO profiles of 5 wt%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst show a peak centered at ca. 620°C. The peak area increased with increasing C/O ratio. For the TPO profiles of 5 wt% Ni/ β'' -Al₂O₃, a very small peak was observed for the catalysts operated under C/O ratio ≤ 1.0, while a peak centered at ca. 650°C was observed for the catalysts operated at C/O ratio of 1.6. The amounts of carbon deposited on the catalysts are shown in Table 3.

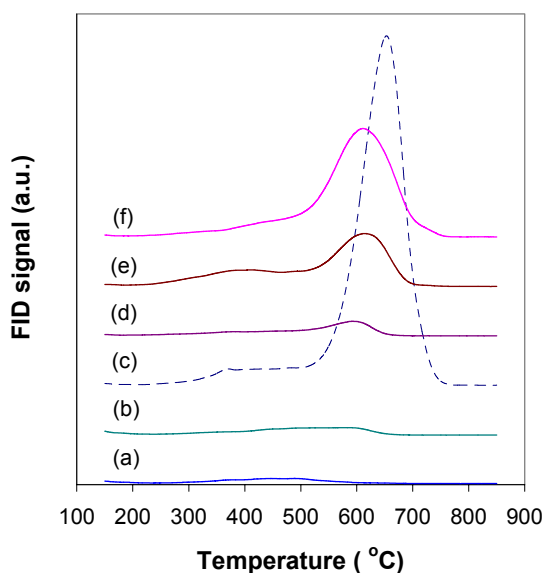


Figure 2 TPO profiles of spent catalysts after exposure to reaction at 800°C for 6 h with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min: (a) 5 wt%Ni/ β'' -Al₂O₃ (C/O ratio = 0.6), (b) 5 wt%Ni/ β'' -Al₂O₃ (C/O ratio = 1.0), (c) 5 wt%Ni/ β'' -Al₂O₃ (C/O ratio = 1.6), (d) 5 wt%Ni/Ce_{0.75}Zr_{0.25}O₂ (C/O ratio = 0.6), (e) 5 wt%Ni/Ce_{0.75}Zr_{0.25}O₂ (C/O ratio = 1.0), (f) 5 wt%Ni/Ce_{0.75}Zr_{0.25}O₂ (C/O ratio = 1.6).

Table 2 *iso*-Octane partial oxidation over 5 wt%Ni/Ce_{0.75}Zr_{0.25}O₂ and Ni/ β -Al₂O₃ catalysts using varied C/O feed ratios

Temp. (°C)	C/O Feed ratio	Ni/Ce _{0.75} Zr _{0.25} O ₂							Ni/ β -Al ₂ O ₃										
		X _{i-C8} (%)	X _{O2} (%)	S _{CO2} (%)	S _{CO} (%)	S _{H2} (%)	S _{CH4} (%)	H ₂ / CO	X _{i-C8} (%)	X _{O2} (%)	S _{CO2} (%)	S _{CO} (%)	S _{H2} (%)	S _{CH4} (%)	S _{C2H4} (%)	S _{C2H6} (%)	S _{C3H6} (%)	S _{IC4} (%)	H ₂ / CO
700	0.6	100	100	48	49	82	0	1.7	70	43	26	19	14	3.4	2.6	0	4.8	0.2	1.2
750	0.6	100	100	44	54	84	0.6	1.7	95	69	24	28	39	6.1	4.9	1.1	10.4	7.8	1.5
800	0.6	100	100	40	57	86	1.6	1.7	100	94	24	45	85	8.3	6.8	1.3	4.5	0.2	1.2
700	0.8	94	100	27	68	84	0.6	1.3	69	45	30	18	19	3.3	2.4	0	4.8	5.4	1.2
750	0.8	100	100	27	70	81	1.7	1.3	94	73	25	35	52	6.9	5.2	1.1	9.4	9.1	1.5
800	0.8	100	100	27	68	86	2.3	1.2	100	94	25	46	80	10.8	8.7	1.2	5.5	0.9	1.7
700	1.0	90	100	16	69	84	0.6	1.3	68	80	22	20	22	3.2	1.4	0	5.1	7.6	1.2
750	1.0	100	100	16	68	80	2.6	1.3	92	100	26	29	51	5.4	3.8	1.1	6.9	10.5	1.2
800	1.0	100	100	17	70	84	5.1	1.2	100	100	17	34	59	7.4	5.2	1.4	8.3	9.3	1.3
700	1.3	85	100	9	60	78	0.8	1.4	58	85	18	15	19	2.7	1.3	0	8.3	16.2	1.4
750	1.3	94	100	4	60	78	2.8	1.4	88	100	18	23	40	5.2	2.9	1.2	9.9	13.4	1.4
800	1.3	100	100	3	64	76	6.8	1.4	100	100	13	29	53	7.5	4.7	1.7	10.4	11.4	1.7
700	1.6	75	100	8	65	78	1.0	1.4	57	87	14	11	11	2.9	1.4	0	8.7	17.8	1.2
750	1.6	87	100	4	58	78	4.1	1.5	85	100	16	18	38	5.6	3.3	1.6	11.7	16.1	1.5
800	1.6	100	100	3	52	75	10.1	1.6	100	100	12	20	42	7.8	5.1	2.1	12.3	14.7	2.0

Table 3 Amounts of carbon deposited on the catalysts, as determined by TPO, using 2%O₂ in He and heating rate of 10°C/min, after 6 h of reaction time at 800°C and C/O ratios of 0.6, 1.0 and 1.6

Catalyst	C/O ratio	<i>iso</i> -Octane conversion ^a (%)	Percent of carbon (wt%)
5%Ni/ β -Al ₂ O ₃	0.6	100	0.13
	1.0	100	0.19
	1.6	100	3.88
5%Ni/Ce _{0.75} Zr _{0.25} O ₂	0.6	100	0.23
	1.0	100	0.85
	1.6	100	1.30

^a conversion at the end of reaction time (6 h)

The amount of carbon deposition over the Ni/ β -Al₂O₃ catalyst was less than that of the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst under C/O feed ratio \leq 1.0. On the other hand, the amount of carbon deposition over Ni/ β -Al₂O₃ catalyst increased by a factor of more than 20 when the C/O ratio was larger than 1.0. This indicates that the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst is more stable under rich conditions due to its good redox properties

Summary

It can be concluded that Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst is more active than Ni/ β -Al₂O₃ catalyst for partial oxidation of *iso*-octane. Under the reaction conditions, synthesis gas was produced at temperatures above 550°C on the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst, whereas Ni/ β -Al₂O₃ required temperatures above 650°C. Interestingly, alkanes and olefins (CH₄, C₂'s, C₃'s and C₄'s) were produced over the Ni/ β -Al₂O₃ catalyst, but only CH₄ was formed over the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst. This suggests that Ni/ β -Al₂O₃ may be used for the simultaneous production of H₂ for fuel cells and of value-added chemicals. Both catalysts are quite stable when operated under normal conditions, but the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst is more stable when rich conditions are applied.

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