Partial oxidation of ethanol over supported Ni catalysts: Effect of support

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Abstract

In this study, the effect of supports on the catalytic activity of Ni based catalysts for the partial oxidation of ethanol was investigated in a fixed bed reactor over the temperature range of 300-650^{o}C. The results showed that the product distribution depended on the type of supports. At C/O molar ratio of 1, the main products of the partial oxidation reaction were H_2 and CO_2 for all catalysts. Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst presents the highest catalytic activity and selectivity towards H_2. The amount of carbon deposited on Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst was less than the other catalysts due to its good redox properties.

Introduction

Hydrogen is forecasted to become a major energy carrier for the future since it can reduce pollution and greenhouse gas emissions. Therefore, the large amounts of hydrogen will be required in a hydrogen economy.

Hydrogen can be produced from hydrocarbons such as natural gas, naphtha, vacuum residue, refinery off-gas, gasoline, diesel, methanol etc. Among these, ethanol is a very promising candidate because it is a renewable raw material that can be obtained from biomass and addresses the CO_2 emission. Furthermore, the infrastructure needed for ethanol production and distribution has already been established in Thailand for producing gasohol.

There are three main methods for producing hydrogen from HCs, namely steam reforming, partial oxidation and autothermal reforming. Partial oxidation of ethanol is an attractive process for hydrogen production because it enables fast start up and does not need the addition of heat. However, this process has some disadvantages such as formation of by-products and catalyst deactivation (Fatsikostas and Verykios, 2004). Hence, the catalysts which are highly active, selective and stable under reaction conditions are needed. Nickel-based catalysts are attractive for partial oxidation of HCs due to their low cost. Since support plays a significant role on performance of supported metallic catalysts on this reaction (Ni et al., 2007; Mattos and Noronha, 2005), the study concerning the effects of metal and support on partial oxidation of ethanol is needed.

In this study, Ni supported on different supports (Al_2O_3, $Ce_{0.75}Zr_{0.25}O_2$, ZrO_2 and MgO) was investigated for the partial oxidation of ethanol in a fixed bed reactor over the temperature range of 300-650^{o}C.

Experimental

Catalyst Preparation

The $Ce_{0.75}Zr_{0.25}O_2$ and ZrO_2 used as supports were synthesized by urea hydrolysis method as reported in Pengpanich et al. (2002) while commercial α-Al_2O_3 and MgO supports were supplied from Alfa Aesar.

The catalysts were prepared by incipient wetness impregnation method using an aqueous solution of $Ni(NO_3)_2.6H_2O$ (99.0%, Fluka). The amount of Ni loading was controlled at 5 wt %. The catalysts were then calcined in air at 500^{o}C for 4 hr.

Catalyst Characterization

The catalysts were characterized by H_2 pulse chemisorption, XRD, and H_2-TPR. The amount of carbon deposition on the spent catalyst was quantified by TPO technique using 2% O_2 in He.

Catalytic Activity Tests

Partial oxidation of ethanol was carried out in a packed-bed quartz (i.d. 6 mm) reactor. Typically, ca. 0.1 g of the catalyst was diluted with 0.1 g of α-Al_2O_3. The Ethanol was vaporized from a saturator at 40 ^{o}C using Ar as carrier gas and mixed with air to obtain the desired C/O molar ratio of 1.0. The total flow rate of feed gases was kept at 60 ml/min (GHSV = 36,000 ml/h-g of cat) using Aalborg mass flow controllers. Measurements were carried out at furnace temperatures adjusted sequentially to 400 - 650^{o}C. The gaseous products were chromatographically analyzed to separate H_2, O_2, N_2, CO, CO_2, CH_4, C_2H_4, acetaldehyde and acetone.

Results and Discussion

The main products of ethanol partial oxidation are H_2, CO_2 and CO with a trace of CH_4, C_2H_4, acetaldehyde and acetone for all catalysts. The ethanol conversion and product distribution over these catalysts are shown in Figure 1. The results showed that $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst presents the highest catalytic activity and selectivity towards H_2 than the other catalysts. This might be due to the highest metal dispersion of this catalyst.

The product selectivities are varied depending on the catalysts. At temperature below 450^{o}C, acetaldehyde was found in most catalyst systems and decreased with increasing temperature. This suggested that the dehydrogenation takes place over these catalysts at low temperature. It was found that a significant amount of acetaldehyde was obtained over Ni/MgO and Ni/ZrO_2 catalysts suggesting that dehydrogenation reaction of ethanol is more favour on MgO and ZrO_2 supports. Above 450^{o}C, the amount of acetaldehyde was relatively low and other products including CO, H_2 and CO_2 products were more pronouced. This suggests that the partial oxidation was the main reactions at temperatures above 450^{o}C.

As shown in Table 1, the amount of carbon deposition varies with type of supports decreasing in the order of Ni/α-Al_2O_3 > Ni/ZrO_2 > Ni/MgO > $Ni/Ce_{0.75}Zr_{0.25}O_2$. This might be due to the fact that $Ce_{0.75}Zr_{0.25}O_2$ has the highest oxygen storage capacity and good reducibility.

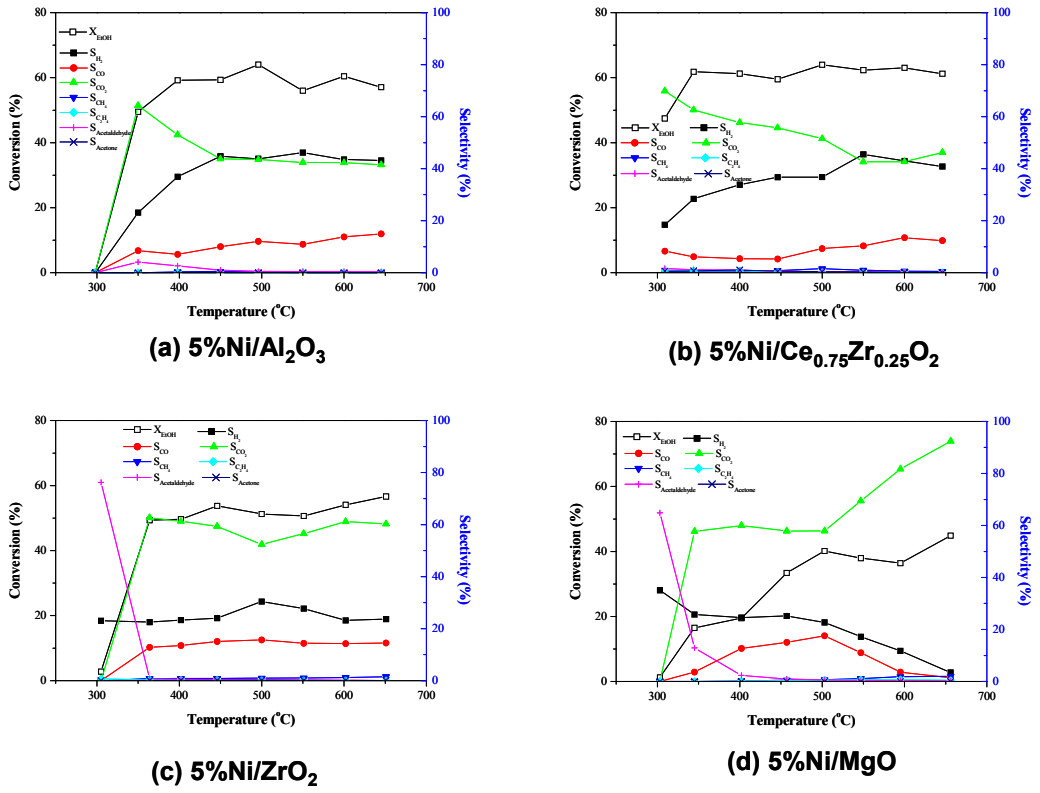

Figure 1 Ethanol conversion and product selectivities over 5 wt% Ni supported catalysts at the condition of GHSV = 36,000 ml/h-g of cat and feed molar ratio of C/O ratio = 1.

Table 1 The Amount of Carbon Deposition Quantified by TPO over The Spent Catalysts after 6 hr of Reaction at 500°C and C/O Ratio of 1.0

Catalyst	EtOH Conversion[1] (%)	Amount of carbon deposition (wt%)
$Ni/Ce_{0.75}Zr_{0.25}O_2$	59.5	15.2
Ni/ZrO_2	50.7	28.6
$Ni/\alpha\text{-}Al_2O_3$	56.0	42.3
Ni/MgO	36.4	13.7

[1]at the end of reaction time (6 h)

Conclusions

It can be concluded that the catalytic activity of partial oxidation of ethanol depended on the nature of support. The main products of the reaction were H_2 and CO_2 for all catalysts. $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst presents a good catalytic activity and selectivity for ethanol partial oxidation. The amount of carbon deposition on the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst was less than the other catalysts due to its good redox properties. This suggests that $Ce_{0.75}Zr_{0.25}O_2$ is a promising support for partial oxidation of ethanol.

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