Petroleum Research

Petroleum Research, 2019(August-September), Vol. 29, No. 106, 37-41

DOI: 10.22078/pr.2019.3547.2619

The Effect of Spinel Support on the Catalytic Performance of Methanol Reforming Catalysts for Hydrogen Production in a Fixed Bed Reactor

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DOI: 10.22078/pr.2019.3547.2619

Received: November/28/2018 Accepted: April/24/2019

INTRODUCTION

Many attempts have been made in recent years to efficiently use fuels, develop methods and processes for reduction of air pollutants and application of clean fuels, emission of greenhouse gases, increased environmental pollution as a result, diminishing resources and rising prices of fuel oil [1-3]. One of the approaches to achieve clean and cheap energy is application of fuel cells. The fuel cells convert hydrogen feed to electrical energy required for the vehicle driveline [4-5]. The major drawback of this process is the high volume of hydrogen in gas phase for storage and the impossibility of transporting it due to safety reasons, making it necessary to find a method for hydrogen production on the site of consumption. The most appropriate process for the application of methanol as a liquid fuel is methanol reforming process to convert it to hydrogen on site [6]. Copper and zinc containing catalysts are the best available catalysts for methanol reforming. Zinc oxide (ZnO) has a very appropriate synergism with copper, resulting in strong interaction between copper and zinc, which is the main factor contributing to the high activity of these catalysts. Decreased reduction temperature of copper helped by zinc verifies this. In addition, zinc greatly helps improve the suitable distribution and dispersion of copper particles on the catalyst surface. Moreover, aluminum plays a promoting part in increasing the mechanical and thermal strength of the catalyst. Therefore, application of Al_2O_3 structural promoter prevents agglomeration of Cu crystals.

EXPERIMENTAL PROCEDURE

CATALYST PREPARATION

The $ZnLaAlO_4$ support was synthesized according to a gel combustion technique. For this purpose, a solution of $Al(NO_3)_3.9H_2O$, $Zn(CH_3COO)_2.2H_2O$

and $La(NO_3)_3.6H_2O$ in 1:1:1 molar ratio was prepared in distilled water to which a solution of glycerin was added as a fuel, so that the molar ratio of metals/fuel becomes 3:20. The pH of the solution was adjusted to 12 using NH_4OH as a base. Then, the suspension was heated up to 80 °C, and the mixture was stirred for about five hours in order to become concentrated by evaporation of water. The concentrated gel was calcined in a furnace for 10 hours at 800 °C with a heating rate of 5 °C/min.

CATALYTIC ACTIVITY TEST

The system is composed of feed stream flow control, reactor set and gas analysis parts. In this process, the outlet current from the reactor is sent to a condenser in which the temperature is reduced to 0 °C to condense the steam and unreacted methanol in the product. In addition, methanol reforming was carried out using each of Cu-Ni/$LaZnAlO_4$, Cu/$LaZnAlO_4$, Cu/Al_2O_3 and Cu-Ni/Al_2O_3 catalysts in the temperature range of 200-300 °C and feed flow rate of weight hourly space velocity (GHSV) of 11500 h^{-1} at atmospheric pressure in a monolith reactor with a quartz cover (inlet diameter = 14 mm and outlet diameter = 9 mm). The feed mixture for methanol reforming was composed of $N_2/H_2O/CH_3OH$ at a ratio of 1:1:2, which nitrogen gas being used as a diluent.

RESULTS AND DISCUSSION PHASE COMPOSITION ANALYSIS

XRD patterns of $ZnLaAlO_4$ support, Cu-Ni/$LaZnAlO_4$ and Cu / $LaZnAlO_4$ catalysts are shown in Fig. 1. The comparison of XRD patterns of Cu/ $LaZnAlO_4$ and Cu-Ni/$LaZnAlO_4$ catalysts with those of $LaZnAlO_4$, respectively, shows that the peaks corresponding to copper and nickel (active metals) oxide crystals are observable. Debye-Scherrer equation ($d = 0.9\ \lambda/\beta \cos(\theta)$) has been used for obtaining particle sizes, which were 13.24 and 20.18 for Cu/$LaZnAlO_4$ and Cu-Ni/$LaZnAlO_4$ catalysts and support respectively. XRD analysis thus indicates that the $ZnLaAlO_4$ supported synthetic catalysts contain copper and nickel oxide crystals with better distribution and smaller sizes, which will perform better in methanol reforming process.

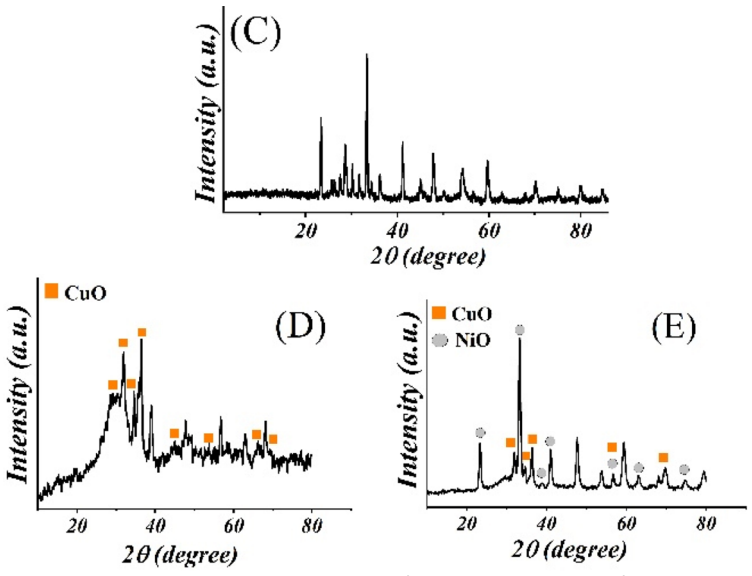

Figure 1: The XRD patterns of (C) $ZnLaAlO_4$ support, (D) Cu/$ZnLaAlO_4$, (E) Cu-Ni/$ZnLaAlO_4$ catalysts.

CATALYTIC PERFORMANCES

Performance of synthetic catalysts in methanol to hydrogen conversion process is shown in Fig. 2. It is observed that $ZnLaAlO_4$ supported catalysts generally have higher conversions than γ-Al_2O_3 supported catalysts. Therefore, the formation of compounds such as aluminates leads to high efficiency of these catalysts in methanol to hydrogen conversion.

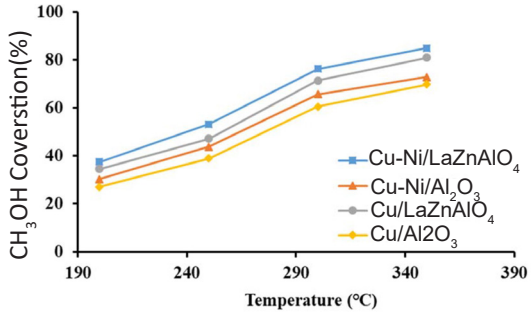

Figure 2: Comparison of methanol conversion using synthetic catalysts.

In addition to high methanol conversion percentage, the synthetic catalysts must have high hydrogen and low carbon monoxide formation efficiencies. Fig. 3 shows the performance of synthetic catalysts with respect to selectivity of hydrogen and other products. In the case of γ-Al_2O_3 supported catalysts relatively high amounts of carbon monoxide were generated whereas $ZnLaAlO_4$ supported catalysts produced very little carbon monoxide. It is generally observed that by increasing the temperature, the possibility and amount of CO formed increased. This is in conformity with CO production mechanism via reverse water-gas shift reaction since rising temperature increases methanol conversion and thus increases concentrations of hydrogen and carbon dioxide, the reactants in water-gas shift reaction, in the reactor and the possibility of CO formation.

CONCLUSIONS

$Cu-Ni/LaZnAlO_4$, $Cu/LaZnAlO_4$, Cu-Ni/γ-Al2O3 and Cu/γ-Al_2O_3 catalysts have been synthesized in order to investigate the effect of $ZnLaAlO_4$ support on the performance of copper and nickel catalysts in the conversion of methanol with steam process; in addition, M/γ-Al_2O_3(M=Cu,Cu-Ni) catalysts have been synthesized in order to investigate the effect of $ZnLaAlO_4$ support on the performance of copper and nickel catalysts in the conversion of methanol with steam process. The results obtained from XRD and FESEM analyses indicated that the active phase particles in M/$LaZnAlO_4$(M=Cu, Cu-Ni) catalyst were smaller, non-agglomerated and appropriately distributed in comparison with those of M/γ-Al_2O_3(M=Cu, Cu-Ni) catalysts. Finally, BET verified the larger volume and pore sizes of M/$LaZnAlO_4$ catalyst compared with M/γ-Al_2O_3.

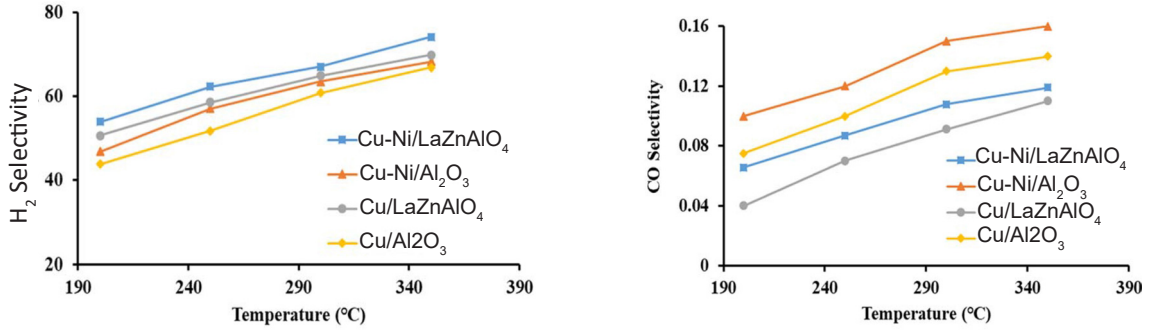

Figure 3: Comparison of the products selectivity using synthetic catalysts.

In addition, TPR analysis indicated the decreased reduction temperature of active metals on $LaZnAlO_4$ support in comparison with alumina. The results obtained from the evaluation of the performance of the four samples also verified that Cu-Ni/$LaZnAlO_4$ catalyst functioned better in terms of high methanol conversion and low CO production in comparison with Cu-Ni/γ-Al_2O_3 catalyst.

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