THE EFFECTS OF METAL OXIDES ON THE EFFICIENCY OF HYDROGEN PRODUCTION FROM BIODIESEL WASTE WATER

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Abstract— H_2 production from biodiesel waste water was investigated. The effect of parameter such as the type of mesoporous (SBA-15 and MCM-41) and the type of metallic (Cu and Ni) were determined at space velocity of 16,000 h^{-1}. 2.5% of Nickel and2.5% of Magnesium were incorporated to SBA-15 by wetness impregnation followed by calcination to obtain the corresponding oxides. The optimum condition for the higher hydrogen selectivity from biodiesel waste water by stream reforming was at temperature700◦C for 2 hour by using 2.5Ni-SBA-15.

Keywords— Biodiesel Waste Water, Steam Reforming, SBA-15, Ni catalysts, Mg catalysts.

I. INTRODUCTION

Nowadays, the global energy consumption rises up very year. This trend leads to non-renewable energy resources allocation depletion while it threatens the global environment. To secure the future energy consumption for the sustainability development, the renewable energy is the hope. At the same time, the scientists should seek and develop an alternative energy system which is sustainable, clean, high energy capacity and economical. Using H2 gas as an alternative has been promoted as a future energy resource because hydrogen has a high energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels [10] and is a clean fuel with no CO2 emissions that can easily be used in fuel cells for generation of electricity. Hydrogen can be produce by using different technologies from a wide variety of primary energy sources [8].

Biodiesel is currently one of the promising renewable energy sources. After biodiesel is made, it is often washed with water to remove contaminants, including soap, glycerin, residual methanol and residual catalyst. The characteristic of waste water from conventional washing process were pH =8.5-10.75, chemical oxygen demand (COD) range 360,000 – 600,000mg/L. On preliminary examination glycerin and water is major component. Therefore, it is thought to be used to produce hydrogen by steam reforming reaction generating a H_2-rich mixture

The use of an appropriate catalyst may favor reaction pathways that minimize the formation of undesirable compounds, enhancing selectivity towards main products. Ni catalysts are the most commonly used. Because of its high activity and low cost, although it suffers from a strong deactivation by sintering and coke deposition [12].

In addition, Mg is another a catalyst attractive because decreases coke formation [5].

Besides the selection of metallic phases, the choice of the support is also very important task because it affects: (i) the active surface area by dispersing the metal over the carrier surface; (ii) the stability of the catalyst viametal-support interactions, which may inhibit sintering, and (iii)the reaction pathways according to redox or acid-base proper-ties of the support. Silicate-based mesoporous molecular sieves with stable frameworks (MCM-41, MCM-48, SBA-n, MSU-n) are materials with extremely high surface areas and unique pore size tuning, which make them suitable as supports for accommodating metal particles for catalytic applications [3]. In particular, MCM-41 and SBA-15, has attracted much research attention due to their large surface area and uniform mesoporous channels with controllable size.

In this work, the steam reforming of biodiesel waste water over Ni and Mg catalysts was carried out, in order to study the effect of the support properties, by comparing catalysts supported on MCM-41 and SBA-15 materials.

II. EXPERIMENTAL

2.1. Catalyst preparation

Two series of Ni and Mg catalysts were prepared. Each series consisted of the corresponding metal (2.5 wt.% in the final catalyst)supported on bare SBA-15 and on MCM-41.The synthesis of SBA-15 was carried out by hydrothermal method as described in literature[4,7] with sub-sequent air calcination at 550◦C in static conditions for 5 h at a heating rate of 1.8◦C/min was carried out to eliminate the template agent. Pure silica MCM-41 material synthesis was carried out by a hydrothermal method based on a procedure describe elsewhere[11].

Incorporation of the active phase to the corresponding support was accomplished by incipient wetness impregnation with aqueous solutions of Ni (NO3)2·6H2O (Qrec) or Mg(NO3)2·6H2O (Ajax finechem)and subsequent calcination at 550 °C for 5h.

2.2 Catalyst Characterization

XRD was used to check the porous mesostructure of the sup-ports and to determine crystalline phases in the prepared materials(according to the JCPDS index). The mean sizes of the metallic crystallites and the graphitic domains formed on the used catalysts were calculated by applying Scherrer equation. Data were acquiredon a Philips X'Pert PRO diffractometer, using Cu Kα radiation, a 2θ increment step of 0.020◦and a collection time of 2 s.

2.3. Catalytic tests

The experimental installation to accomplish the steamreforming test was a MICROACTIVITY-PRO unit (PID Eng&Tech.S.L.),as described elsewhere [7]. Outlet flow composition was analyzed using a gas chromatograph (Shimadzu GC 2014). The catalyst (200 mg) was placed in the reactor with silicon carbide and in situ reduced under flowing hydrogen (10 mL/min). Activated catalyst was heated up to 700 ^{O}C and, then, catalytic test was carried out isothermally at atmospheric pressure using nitrogen as carrier gas.A liquid biodiesel waste water reaction was introduced at a flowrate of 0.04 mL/min, vaporized at 150 ^{O}C and further eluted by nitrogen (10 mL/min).

Catalytic activity was evaluated in terms ofselectivity of hydrogen and carbon containing species. Selectivity of hydrogen (S_{H2}) and selectivity ofother product Siwere defined as follows:

$$SH2 = \frac{mol\ of\ H_2\ in\ gas\ product}{mol\ of\ \ C\ atom\ in\ the\ product} x100\%$$

$$S_i = \frac{mol\ of\ i\ \ in\ gas\ product}{C\ atom\ in\ the\ product} x100\%$$

III. RESULTS AND DISCUSSION

3.1. Characterization results

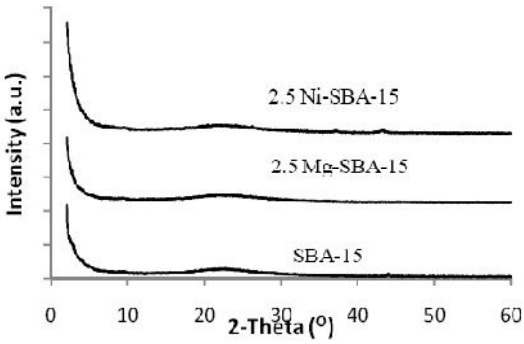
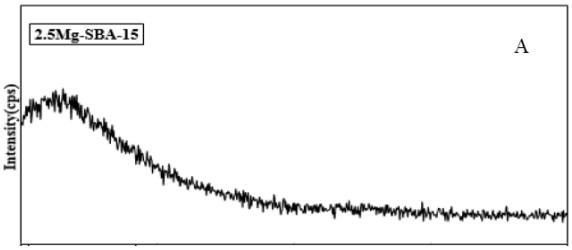


Fig.1 –Low angle X-ray diffraction patterns of 2.5 Mg-SBA-15, 2.5Ni-SBA-15,SBA-15



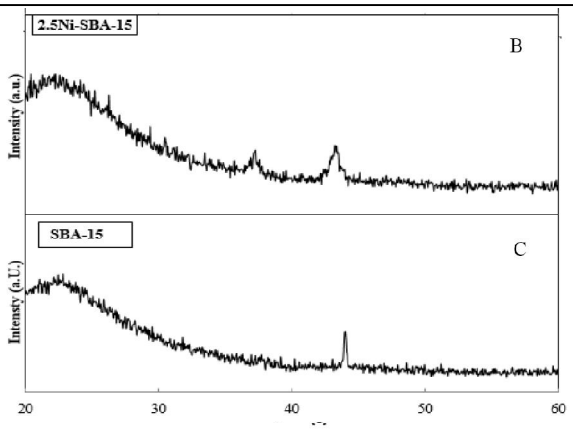


Fig.2 –High angle X-ray diffraction patterns of 2.5 Mg-SBA-15, 2.5Ni-SBA-15,SBA-15

The X-ray diffraction patterns of SBA-15 supporter at high angle shown in Fig. 2. All samples show a broad peak in the 2θ region of 20–30° attributed to the amorphous silica that forms the pore walls of the SBA-15 support. Ni samples (Fig. 2b) exhibit diffraction peaks at 2θ = 37.3°, and 43.3°, corresponding to the planes (1 1 1), (2 0 0) of cubic NiO (JCPDS 78-0643),respectively [12]. For Mg-SBA-15 sample, the characteristic XRD pattern was found to be somewhat distorted after Mg into SBA-15 impregnated catalyst (Fig. 2a). These results indicated that Mg may be in well dispersed amorphous form and crystallite sizes are smaller than the detection limit of XRD[14].

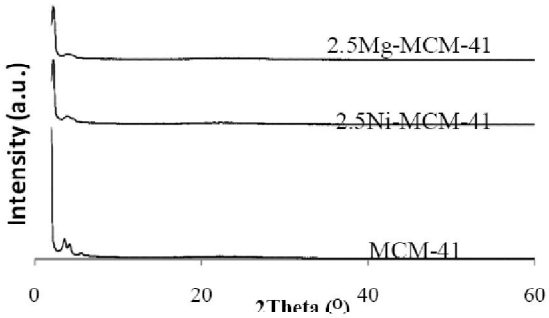
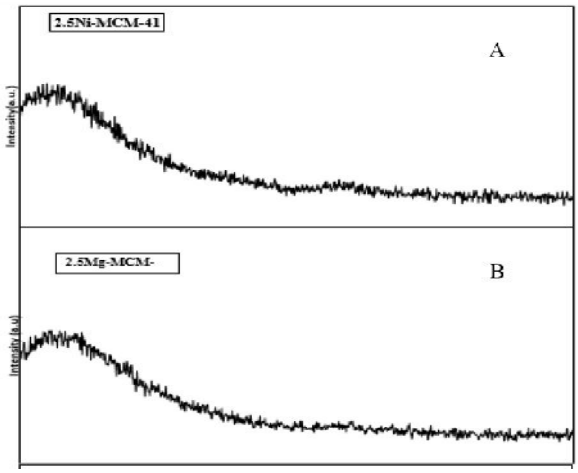


Fig.3 –Low angle X-ray diffraction patterns of 2.5 Mg-MCM-41-15, 2.5Ni- MCM-41, MCM-41



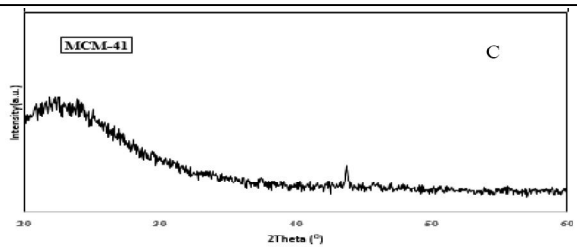


Fig.4 –High angle X-ray diffraction patterns of 2.5 Mg-MCM-41-15, 2.5Ni- MCM-41, MCM-41

The X-ray diffraction patterns of MCM-41 supporter at high angle shown in Fig. 4. For the catalyst containing Ni and Mg, the intensities of these peaks were much less. In fact, for the catalyst containing Ni and Mg, no peak corresponding to Ni (2θ= 44.6°, 51.9° and 76.5° [14]) and Mg were observed, indicating well dispersion and very small size of Ni and Mg crystal within the lattice of MCM-41.

3.2 Catalytic results on biodiesel waste water steam reforming

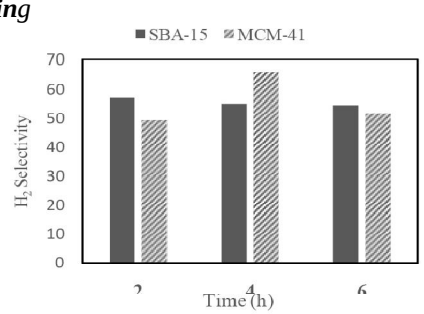


Fig. 5. selectivity of hydrogen in the biodiesel waste water steam reforming over SBA-15 and MCM-41

Effect of support

In order to determine the effect of the support on biodiesel waste water steam reforming reaction, support tests were performed on SBA-15 and MCM-41(in terms of H_2 selectivity and time).

Fig.5 shows the comparison of H2 selectivity it was found that, the H2 selectivity of SBA-15 was higher than MCM-41 and gradual decreasing trend for reaction times longer than 4 h, unlike the MCM-41 decreased rapidly.The reason for the better performance of the SBA because of the possesses uniform hexagonal channels with diameter ranging from 5 to 30 nmand higher hydrothermal stability than MCM-41[7]. Therefore the SBA-15 supporter was most suitable for study catalytic loading.

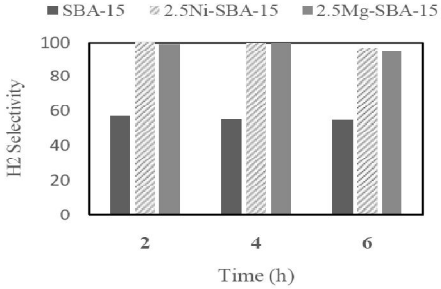


Fig. 5. selectivity of hydrogen in the biodiesel waste water steam reforming over 2.5 Mg-SBA-15, 2.5Ni-SBA-15,and SBA-15.

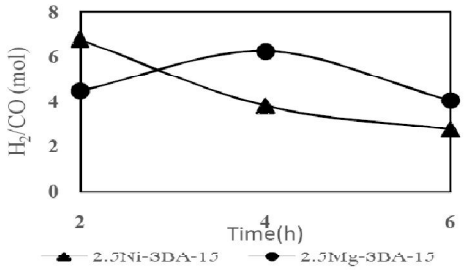


Fig.6. Ratio of H_2 / COover 2.5 Mg-SBA-15, 2.5Ni-SBA-15,and SBA-15.

Effect of nickel and magnesium loading

In order to study the effect of each active phase on biodiesel waste water steam reforming reaction, additional monometallic nickel and magnesium catalysts on SBA-15 were prepared by incipient wetness impregnation

The catalytic results in biodiesel waste water steam reforming are shown in Fig 5 in terms of H2 selectivity and time it was found that, the H2 selectivity of Ni/SBA-15 catalyst to 100% after stabilizing in the 1 h. On the other hand, after 4 h on stream H_2 selectivity significantly decreased. Unlike the Mg/SBA-15 catalyst H2 selectivity to 90% after stabilizing in the 1 h and increase to 100% after 4 h, then gradual decreasing trend for reaction times longer than 6 h,

$$C_3H_8O_3 \rightarrow 3CO + 4H2 \qquad (1)$$

Fig.6. Shows the ratio of H2 / CO it was found that, a variation in the 2.7 to 6.7 range, which is higher than the ratio of the thermal decomposition reaction according to the above equation (H2:CO=4/3=1.33). Therefore, the main reaction were formed during steam reforming reaction is water gas shift reaction, which converts gas into H2 and CO2 resulted in the ratio of H2:CO obtained from the test is higher than 1.33[16].

CONCLUSIONS

According to a study by steam reforming reaction can produce gas Hydrogen from biodiesel wastewater. It was found that the type of mesoporous support achieved leading to the highest hydrogen selectivity due to mesopore structure with extremely high surface areas especially SBA-15

Nickel and Magnesium incorporated SBA-15 like mesoporous catalysts with ordered pore structures were successfully to the highest hydrogen selectivity. Results of this work showed that, the Ni-SBA-15 catalyst relatively high activity, but suffered from deactivation after 6 h on-stream at 700◦C

ACKNOWLEDGMENTS

The authors would like to thank the Department of Chemical Engineering Program in Energy and Environmental Technology Management, Thammasat University Thailandfor supporting this work.The

authors also thank TheThailand Institute of Scientific and Technological Research (TISTR)for instrument and laboratory to conduct this research.

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