Effect of Calcination Temperature on Hydrogen Production via Ethanol Dry Reforming Over Ni/Al_2O_3 Catalyst

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Abstract— **Ni/Al_2O_3 catalysts were prepared by the wet-impregnation method and calcined at different temperatures (500°C, 600°C and 700°C) to obtain NiAl-1, NiAl-2 and NiAl-3 respectively. NiAl-1, NiAl-2, NiAl-3 represent catalysts calcined at 500°C, 600°C and 700°C respectively. The catalysts were characterized using different techniques, XRD, BET and TGA. XRD results revealed the presence of NiO phase on all the catalysts during calcination, however, the presence of spinel, $NiAl_2O_4$, was more pronounced on the catalyst calcined at 600°C (i.e. NiAl-2), indicating the existence of strong metal-support interaction. BET results showed that NiAl-1 has the highest surface area of about 190cm^2/g. All the catalysts were tested for ethanol dry reforming in a tubular stainless steel fixed-bed reactor at 700°C and CO_2/ethanol ratio of 3 under atmospheric pressure and were evaluated in terms of reactants conversion and selectivity of H_2 to see the effect of the different calcination temperatures on the catalysts' activities. Ethanol conversion was 100% for all the three catalysts and NiAl-2 has the highest CO_2 conversion with an average value of about 57%. The three catalysts have almost the same performance in terms of H_2 selectivity. The presence of multi-walled carbon nanofibers (MWCNFs) were confirmed on all the catalysts as revealed by the TGA result. The catalyst calcined at 600°C (i.e. NiAl-2) displayed the best relative catalytic activity**

Index Terms—**Ethanol, XRD, BET, TGA, Carbon dioxide, wet-impregnation, calcination, spinel, MWCNFs**

I. INTRODUCTION

Change in the climate and a shortage of energy is the main challenge the world is facing at the moment. The unwanted increase in greenhouse gas emission resulting from the combustion of fossil fuels has led ultimately to global warming and consequently climate change. The overwhelming dependence on crude oil based energy, which is fast depleting, couple with the undesirable carbon dioxide (CO_2) emission have awaken mankind's consciousness to search for alternative source that is renewable, clean and causes less or no pollutants. Hydrogen gas is a good substitute; it burns without releasing any pollutant and can serve a number of purposes. It can be used in fuel cell, in Haber process to there is limited information about dry reforming of ethanol in literature, therefore giving room for more exploration.

manufacture ammonia, in the oil refining process, as coolant in generator, above all, as syngas to produce other important chemicals. Syngas, a mixture of CO and H_2, has gained much recognition because it can be used as feedstock to produce clean synthetic fuels and important petrochemicals via Fischer-Tropsch Synthesis (FTS) [1].

With these, hydrogen is known to be a promising an alternative energy that will reduce the world's dependence on the usage of environmentally harmful fossil fuels. Conventional and large scale production of H_2 has been through steam reforming [2], partial oxidation [3] and auto-thermal reforming [4] of methane. Among all, dry reforming of methane is considered the most attractive, efficient and suitable method for hydrogen production, which is subsequently used to generate synthetic fuel, when combined with CO, that is aimed to replace petroleum based energy source [5, 6]. This method employs the conversion of the two main greenhouse gases, methane (CH_4) and CO_2 to produce valuable products. On the contrary, CH_4 is also from a non-renewable source (i.e. natural gas, a kind of fossil fuel) and therefore makes the method nonsustainable. Ethanol dry reforming happens to be a better alternative for H_2 production.

This method uses ethanol that can be obtained from a number of renewable biological materials and undesirable CO_2 as feedstocks [7]. Wang and Wang used the Gibbs energy minimization approach to investigate dry reforming of ethanol and discovered that high reaction temperature and CO_2-rich reactants enhanced both C_2H_5OH and CO_2 conversions as a result of reduction of carbon deposit. Gleicielle, Raimundo, Lisiane, Mariana and Fabio studied the effect of preparation method of MgO on the performance of Ni/MgO catalysts for steam reforming of ethanol [8]. Precipitation, decomposition and Precipitation and aging methods were used to prepare Mg/O. They found that the latter method gave the easiest reducible catalyst with the least amount of carbon deposit after reaction. Steam reforming of ethanol over noble and nonnoble metals has been well studied and reported, however,

$$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO \quad \Delta H^0_{298} = 296.80\ kJmol^{-1} \qquad (1)$$

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Dry reforming of ethanol is as represented in the above reaction equation. Nickel (Ni) based catalysts has been reported to exhibit high catalytic activity in CO_2 reforming of ethanol due to their high C-C cleavage, ability to withstand high temperature, also Ni-is relatively cheap [9]. Hu and Lu also discovered that DRE over Ni supported on Al_2O_3 catalyst possessed high activity, selectivity and desirable H_2/CO ratio [10].

The aim of this research is to investigate the effect of calcination temperature on the catalytic activity of Ni/Al_2O_3 catalysts calcined at 500^0C, 600^0C and 700^0C for CO_2 reforming of ethanol. Also the performance of the catalysts was compared.

II. EXPERIMENTAL

A. Catalyst Preparation

Nickel catalysts supported on Al_2O_3 were synthesized via the impregnation method using $Ni(NO_3)_2.6H_2O$ as precursor. Alumina (Al_2O_3; SA6175) purchased from Norton, USA, was added to a uniform solution of Nickel nitrate and water. At first, 0.495g of $Ni(NO_3)_2.6H_2O$ was added to 30ml of H_2O, followed by 0.9g of Al_2O_3 to prepare 1.0g of the catalyst. The solution was placed over magnetic stirrer hot plate with continuous stirring until there was slurry. Nickel loading was 10% of the support. After impregnation, the samples were dried at 110^0C for 14hrs in the furnace and calcined at 500^0C, 600^0C and 700^0C for 4hrs at a heating rate of 2^0C/min to obtain *Ni/Al-1*, *Ni/Al-2* and *Ni/Al-3* respectively. The catalysts were characterized, activated and tested for catalytic CO_2 reforming of ethanol.

B. Characterization

The crystalline structure of the catalyst was determined by recording *XRD* (X-ray diffractogram) patterns using a Rigaku (Miniflex) diffractometer equipped with a Cu Kα radiation source operating at 40kV and 40mA. The scanning was over a 2θ range of $10\text{-}85^0$ with a step of 0.01^0. The results were compared with JCPDS data base for the phase's identification.

Multi-point *BET* (Brunauer Emmet Teller) surface area and pore volume measurement for the catalyst was carried out using N_2 physisorption at 77K in a Micrometric Tristar II 3020 analyser. Each sample was degassed at 300°C for 3h to remove moisture and adsorbed gases from the catalysts' surface. Thermogravimetric analysis (*TGA*) was carried out on the spent catalyst for the quantitative analysis of carbon deposited on the catalyst. It was done in air atmosphere using TGA-15 SHIMADZU Thermogravimetric analyzer by heating 10-15mg of the spent catalyst from room temperature to 1000°C at a heating rate of 20°C.

C. Catalyst Testing

Catalysts were tested in a stainless steel fixed-bed tubular (9.1 mm i.d. and 30 cm long) micro-reactor (PID Eng & Tech MICROACTIVITY) under atmospheric pressure. The obtained gaseous products were analyzed by gas chromatography, connected in-line, GC-2014 Shimadzu gas chromatograph having TCD and columns that detects the effluents from Molecular Sieve and Porapak N columns that are in parallel. Before the start of the reaction, 0.1g of the catalysts was fed into the reactor on a glass wool acting as a bed for the catalyst in the reactor. Activation was performed under the flow of hydrogen gas (20.0ml/min) at 600^0C for 65 minutes. A thermocouple was positioned in the center of the reactor for temperature monitoring. After activation, there was purging with pure nitrogen (5ml/min). This was carried out for 25 minutes, in order to remove any remnant unused hydrogen.

Therefore, the reaction began with a hydrogen-free feed; ethanol was injected with the aid of a pump, CO_2 and N_2 by mass flow controller (MFC). The total feed was maintained at 60.0ml/min and CO_2/ethanol=3. The catalysts samples were tested for dry reforming of ethanol at 700^0C, reactants conversion and H_2 selectivity were calculated based on the expressions below:

$$X_{r'}(\%) = \frac{F_{r'}in - F_{r'}out}{F_{r'}in} \times 100\% \quad (2)$$

$$S_p(\%) = \frac{p}{H_2 + CH_4 + CO} \times 100\% \quad (3)$$

Where F_{in} and F_{out} are the molar flow rates in and out respectively, r' could be any substance in the feed (e.g. C_2H_5OH and CO_2) and "p" represents amount of the specie in question present in product stream.

III. RESULTS AND DISCUSSION

D. Textural properties

The N_2-physisorption results such as the *BET* surface areas, pore volumes (*P.V*) and pore diameter (*P.D*) for fresh *NiAl-1, NiAl-2* and *NiAl-3* are summarized in table I. The pore volume and pore size are taken from the desorption section of the corresponding N_2 isotherm that resulted from the Barret, Joyner and Halenda (*BJH*) method applied. The adsorption isotherm and pore size distribution are presented in Fig. 3a and 3b.

From the results it is obvious that *NiAl-1* has the highest relative *BET* surface area compare to the others prepared at higher calcination temperature. It can also be deduced that the *BET* surface areas are inversely proportional to the calcination temperature for these catalysts. The adsorption-desorption isotherms for all the catalysts is type IV, in accordance with the IUPAC isotherm classification. All isotherms showed H1 hysteresis loop at higher relative pressure. This characterizes capillary condensation in mesoporous structures.

Table I. N_2 Physisorption Results For The Catalysts

Catalyst	N_2 physisorption parameters		
	BET (cm^2/g)	*P.V* (cm^3)	*P.D* (cm)
NiAl-1	190.00	0.57	9.16
NiAl-2	182.92	0.590	9.54
NiAl-3	180.00	0.60	10.10

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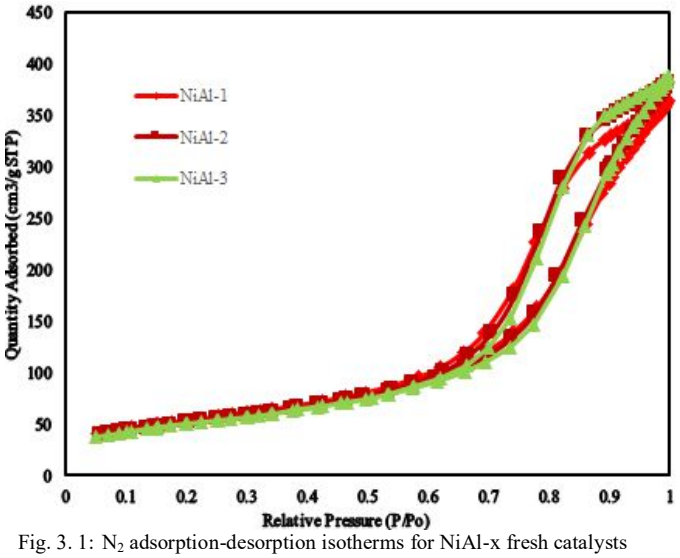


Fig. 3. 1: N_2 adsorption-desorption isotherms for NiAl-x fresh catalysts

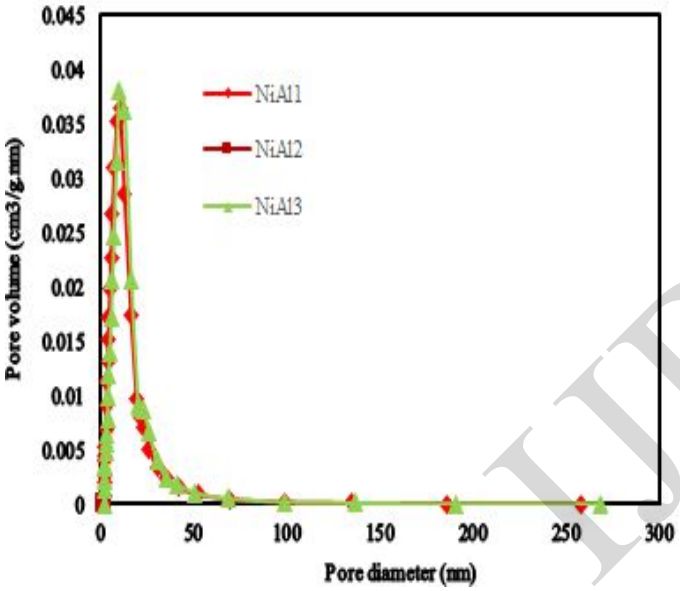


Fig. 3. 2: Pore size distribution for NiAl-x catalysts

E. X-ray diffraction measurement

The crystal structures of *NiAl-1*, *NiAl-2* and *NiAl-3* were identified by *XRD* as in Fig. 4. Joint Committee on Powder Diffraction Standards (*JCPDS*) database was used to analyze all the *XRD* patterns [12]. As in Fig. 4 the typical peaks for γ-alumina at 2θ angle of 19.45°, 32.30°, 37.61°, 46.52° and 67.13° were detected on *NiAl-1, NiAl-2*, and *NiAl-3*. The three catalysts possessed NiO phase at 2θ angle of 43.64°, 37.10° and 62.85°. Also spinel phase ($NiAl_2O_4$) seems to be well noticed only on *NiAl-2* (i.e. the catalyst calcined at 600°C) at 76.98°. This indicates a strong metallic interaction between the catalyst and the support.

F. Thermo-gravimetric (TGA) studies

TGA was used to observe changes in physical and chemical properties of the used catalysts, containing deposited carbonaceous species, by varying temperature. Also, TGA can reveal the stability of used catalyst in an oxidative environment. There was no removal of carbon prior to the start of the analysis.

Figure 5 shows the weight loss as the catalysts were being heated for TGA analysis. It can be seen from the curves that a shoulder appeared just before the sharp loss in weight. This indicates the presence of multi-walled carbon nano-fibers (MWCNFs) as in [13, 14]. The loss in weight is as a result of gasification of the carbonaceous species deposited on the catalysts' surface. The weight loss began at temperature around 500°C and ended close to 800°C. Thus, stable MWCNFs were formed at 800°C and above.

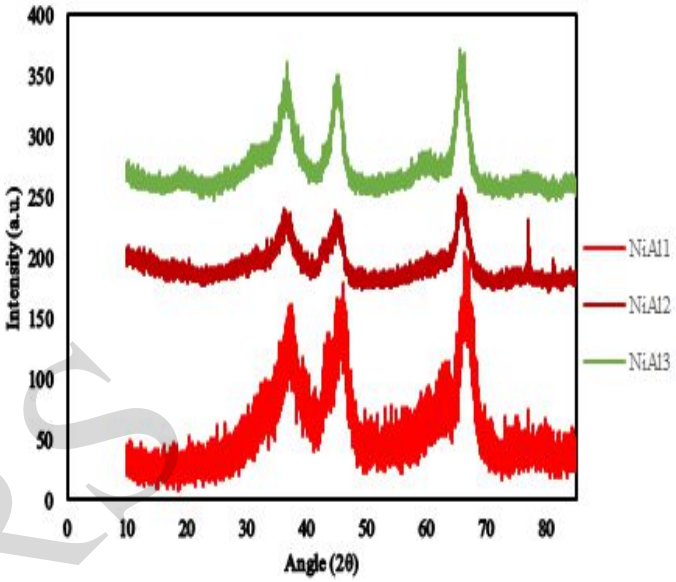


Fig. 4: XRD patterns of fresh NiAl-1, NiAl-2, NiAl-3

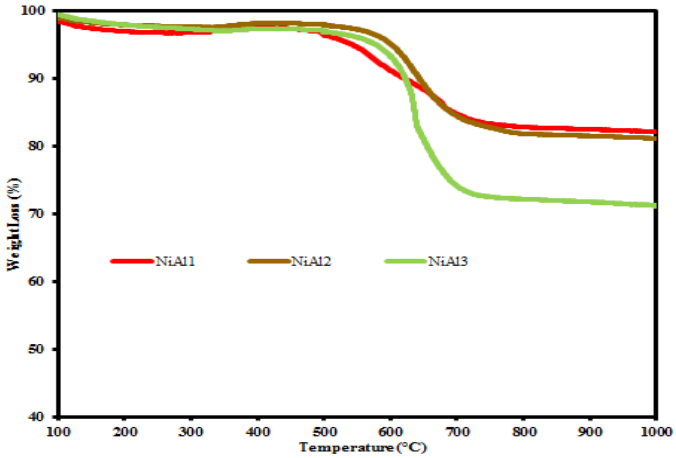


Fig. 5: TGA profile for used NiAl-1, NiAl-2, NiAl-3

G. Catalytic activity

The activity of the Ni catalysts supported on Al_2O_3 and calcined at three different temperatures (500°C, 600°C and 700°C) was determined in terms of reactants conversion and product selectivity (H_2). Hu and Lu performed CO_2 reforming of ethanol over Ni/Al_2O_3 catalyst at different temperature and

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feed ratio [15]. They obtained the maximum conversion of ethanol, but low CO_2 conversion at 700°C and CO_2/Ethanol=1. Thus, the reactions in this research were performed at the reported optimum operating conditions and feed ratio.

H. Reactants conversion

Figure 6 shows the conversion of the reactant. Ethanol conversion attains 100% for the three catalysts as in [15]. NiAl-2 catalyst calcined exhibited the highest conversion, with the average value of 57%.

I. H_2 Selectivity

Figure 7 shows that the catalysts appear to have about the same value which is also quasi-static, NiAl-2 still has a little edge above others.

II. CONCLUSION

The dry reforming of ethanol was performed on Ni/Al_2O_3 catalysts that were calcined at three different temperatures. The catalyst calcined at 600°C (*NiAl-2*) showed the greatest activity in terms of reactant conversion and H_2 selectivity, therefore providing the highest H_2 yield and selectivity. This might be connected to the observed spinel phase on the catalyst which is an indication of strong metal support interaction.

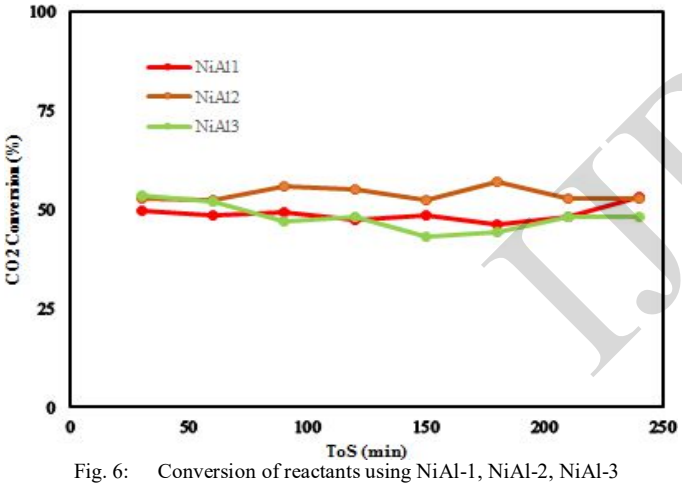


Fig. 6: Conversion of reactants using NiAl-1, NiAl-2, NiAl-3

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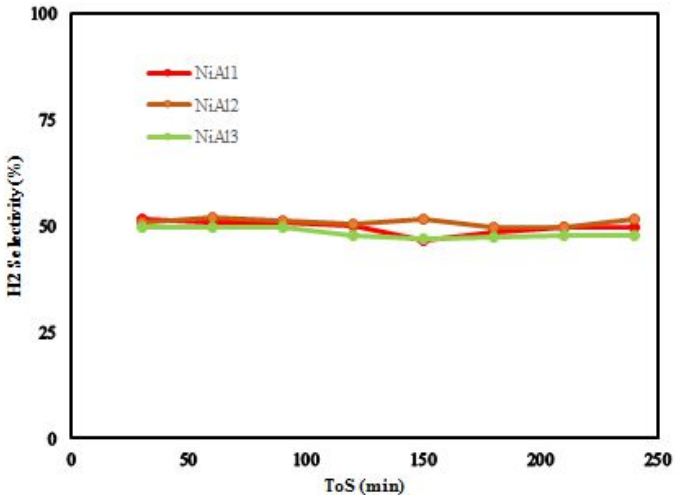


Fig. 7: H2 selectivity of NiAl-1, NiAl-2, NiAl-3

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