

## Ni/Ce-Al<sub>2</sub>O<sub>3</sub> for maximum hydrogen production from biomass/tar model compounds: Role of support type and Ce modification

Sagir Adamu<sup>1</sup>, Idris A. Bakare<sup>2</sup>, Mohammad M. Hossain<sup>1\*</sup>

*1 Department of Chemical Engineering, 2 Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

*\*Corresponding author: mhossain@kfupm.edu.sa*

### Highlights

- Ce modification has significant catalytic effects of Ni/Ce-meso-Al<sub>2</sub>O<sub>3</sub> and Ni/Ce- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>
- Ni dispersion is higher on synthesized Ce(x)-meso-Al<sub>2</sub>O<sub>3</sub> than on Ce(x)- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>
- Desorption kinetics shows that Ce helps to alter metal-support interaction and reduce acidity
- Ni(20)/Ce-meso-Al<sub>2</sub>O<sub>3</sub> gave highest hydrogen yield and least CO<sub>x</sub> species

### 1. Introduction

A sustainable future requires clean renewable energy resources. Biomass offers zero net carbon to the environment. Therefore, several processes have been developed for biomass conversion to more useful biofuels and chemicals. Nickel based catalyst are investigated by a number of researchers using various biomass feedstocks [1]. Coking, thermal degradation and presence of tarry compounds are the major challenges with the Ni/Al<sub>2</sub>O<sub>3</sub> based catalysts [2]. In this work, we investigated the role of ceria dopant and support type (i.e. commercial gamma alumina and a mesoporous alumina synthesized in our laboratory[3]) on steam gasification of mixed glucose/toluene feed for optimal hydrogen production in a CREC riser simulator (at 500 - 700 °C) and fluidized bed conditions [4]. Glucose and toluene were used as biomass and tar model compounds, respectively.

### 2. Methods

Ce modified Ni(20)/Ce-meso-Al<sub>2</sub>O<sub>3</sub> and Ni(20)/meso-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using Ce(1)-doped or bare mesoporous Al<sub>2</sub>O<sub>3</sub> support, which was synthesized according to a template-free technique established in our laboratory. On the other hand, Ni(20)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ce modified Ni(20)/Ce- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by impregnating nickel onto commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. In all cases, we utilized successive incipient wetness impregnation method to achieve the desired 20wt% Ni loading. NH<sub>3</sub>-TPD was used to determine catalysts acidity, and to study the desorption kinetics of each catalyst system. XRD was used to determine the crystalline properties of the catalysts. The performance of the catalysts for biomass model compounds (glucose + toluene) gasification was evaluated in a CREC Riser Simulator under fluidized bed conditions [4]. In order to study the metal support interactions, we applied a temperature dependent first order rate of desorption of NH<sub>3</sub> from the catalyst surface. The governing equation is given by [3].

$$\frac{dV_{des}}{dT} = \frac{k_{des}}{\beta} \left( 1 - \frac{V_{des}}{V_m} \right) \exp \left( -\frac{E_{des}}{R} \left( \frac{1}{T} - \frac{1}{T_c} \right) \right) \quad (1)$$

where,  $V_{des}/V_m$  is the fractional volume of NH<sub>3</sub> desorbed,  $T_c$  is the centering temperature,  $\beta$  is the heating rate,  $k_{des}$  is the first order rate constant,  $E_{des}$  is the activation energy.

### 3. Results and discussion

XRD analysis (Figure 1) shows that the catalysts supported on commercial gamma alumina (i.e. Ni(20)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni(20)/Ce- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) showed relatively narrower peak than those supported on our new Al<sub>2</sub>O<sub>3</sub> (i.e. Ni(20)/meso-Al<sub>2</sub>O<sub>3</sub> and Ni(20)/Ce-meso-Al<sub>2</sub>O<sub>3</sub>). Hence, nickel dispersion was better in the case of the meso-Al<sub>2</sub>O<sub>3</sub> catalysts. Table 1 gives the result for the acidity of the four catalysts, plus the results of NH<sub>3</sub> desorption kinetics. The parameters (i.e.  $k_{des}$  and  $E_{des}$ ) were obtained by solving Equation 1 numerically in Mathematica, and then regressing the model against the experimental data using Runge Kutta method. Ni(20)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> shows the highest total acidity of 0.284 mmol NH<sub>3</sub>/g-catayst, and lowest activation energy

for ammonia desorption. On the other hand, Nickel supported on the newly prepared Ce-Al<sub>2</sub>O<sub>3</sub> showed moderate acidity (0.202 mmol NH<sub>3</sub>/g) and exhibited a higher activation energy for ammonia desorption.

Table 1: NH<sub>3</sub> desorption parameters

Catalyst	(mmol NH <sub>3</sub> /g-sample)	$E_{des}$ (kJ/mol)	$k_{des}$ (cm <sup>3</sup> /min)*10 <sup>3</sup>	$R^2$
Ni(20)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.284	4.47 ± 0.39	34 ± 0.95	0.99
Ni(20)/Ce- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.270	5.28 ± 0.56	29.2 ± 1.36	0.99
Ni(20)/meso-Al <sub>2</sub> O <sub>3</sub>	0.251	8.593 ± 0.30	45.2 ± 2.11	0.98
Ni(20)/Ce-meso-Al <sub>2</sub> O <sub>3</sub>	0.202	9.61 ± 0.26	35.7 ± 1.93	0.98

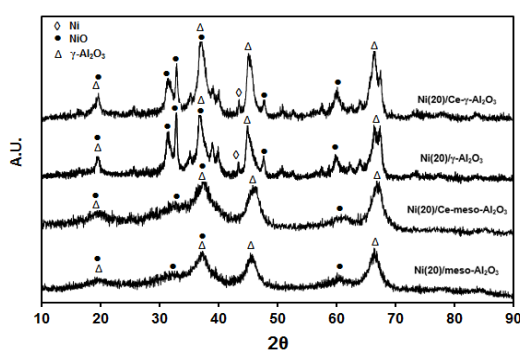


Figure 1: XRD patterns of the prepared catalysts

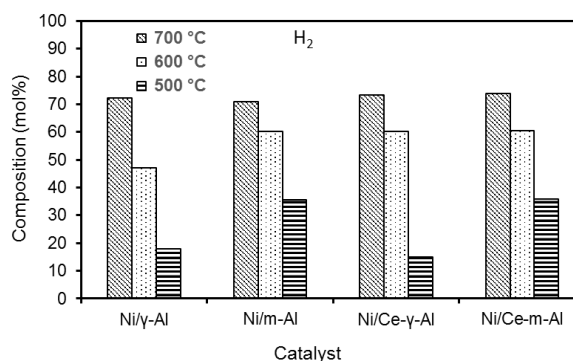


Figure 2: Effect of support type and Ce on H<sub>2</sub> composition (feed: 12.5 wt% glucose + 2.5 wt% toluene; time: 30 seconds)

Figure 2 illustrates the result of catalysts performance for 12.5 wt% glucose + 2.5 wt% toluene mixed feed, for a reaction time of 30 seconds. The four catalysts showed similar performances in terms of hydrogen production at 700 °C. However, at lower temperature (600 and 500 °C), there is significant difference (about two fold) between hydrogen production from meso-Al<sub>2</sub>O<sub>3</sub> supported catalysts as compared to that of commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts. The lower performance of the Ni(20)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts is related to the formation of coke and/or stable carbonaceous compounds such as nickel carbide [5,6]. As regards the ceria modification, we see that doping 1.0 wt% Ce did not significantly alter the rate of hydrogen production from the 15 wt% glucose/toluene mixed feed at 700 °C. However, addition of ceria enhanced the catalyst resistance against coking, and CO<sub>x</sub>, HC's (C<sub>1</sub>, C<sub>2</sub> and C<sub>2</sub><sup>=</sup>) formation especially at low reaction temperature.

#### 4. Conclusions

The combined template free method for meso-Al<sub>2</sub>O<sub>3</sub> synthesis with the subsequent metal impregnation via incipient wetness impregnation is a promising method for highly active, moderately acidic and well dispersed Ni/Al<sub>2</sub>O<sub>3</sub> for biomass gasification. Ni(20)/Ce-meso-Al<sub>2</sub>O<sub>3</sub> was the best in terms of hydrogen production, indicating the synergistic effect of both ceria promoter and our methodology for synthesizing Ce-doped-Al<sub>2</sub>O<sub>3</sub> support. For a 15 wt% mixed glucose/toluene feed at 700 °C and 30 seconds reaction time, the product composition was 74.33 mol% H<sub>2</sub>, 22.60 mol% CO<sub>x</sub> and 3.06 mol% HC's (i.e. C<sub>1</sub>, C<sub>2</sub> and C<sub>2</sub><sup>=</sup>).

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#### Keywords

Template free Ce-Al<sub>2</sub>O<sub>3</sub>; Desorption kinetics; Hydrogen production; Coke resistance