Effect of mesoporosity of bimetallic Ni-Ru-Al$_2$O$_3$ catalysts for hydrogen production during supercritical water gasification of glucose

Md Zakir Hossain, Muhammad B.I. Chowdhury, Qasem Alsharari, Anil Kumar Jhawar, Paul A. Charpentier *

Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada, N6A 5B9

ABSTRACT

A well-known problem with metal supported alumina catalysts during gasification processes for H$_2$ formation is catalyst deactivation by coke formation and pore plugging. Poorly controlled catalyst structure with low surface area and microporous structure also accounts for low catalyst activity. This work investigated bimetallic Ni-Ru/Al$_2$O$_3$ catalysts that are both effective and durable for glucose gasification in supercritical water with minimal coke formation. Both non-ionic (Pluronic P-123) and cationic (CTAB) templates were examined for mesoporous alumina synthesis with Ni and Ru loadings and compared with a conventional incipient impregnation method. Gas formation during SCWG catalysis was monitored for hydrogen formation while the catalysts were examined both before and after reaction by a variety of physico-chemical techniques including BET surface area, BJH pore size analysis, XRD, TG-DTA, TPR, TPO, Raman spectroscopy & TEM microscopy. The results showed that templating helped disperse both Ni and Ru particles homogeneously inside the pores of mesoporous Al$_2$O$_3$ catalysts; whereas the impregnated catalyst gave poorer dispersion. Comparing with the impregnation method, a six-fold increase of BET surface area was observed using the one-pot synthesis method. Hydrogen production during glucose gasification increased by 25 mol% for both templated catalysts, with the CTAB catalyst showing slightly higher activity. This method provided insignificant coke deposition indicating that the new Ru-Ni/Al$_2$O$_3$ templated catalyst is promising for the development of hydrogen production for an emerging biorefinery.

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1. Introduction

Metal supported on alumina provides attractive catalysts for biomass gasification processes i.e. converting biomass to bioenergy due to their high surface areas and unique porosity [1]. However, coke formation and pore plugging are major concerns for the diffusion of molecules (reactants or products) towards the active sites of the alumina-based catalyst [2]. It is widely known that the rate of deactivation of an Al-based catalyst is largely enhanced by its BET surface area and pore size distribution [3]. Thus, synthesis of mesoporous alumina catalysts having well defined pore structure and size distribution is of significant scientific interest due to their wide ranging applications, including catalysis, separation, molecular sieves, and gas sensors [4]. In most catalyst applications, control of porosity has become a crucial factor for both high activity and selectivity.

For synthesizing porous alumina materials, a variety of approaches have been used including surfactant templates, and solvothermal or hydrothermal processes [5]. Among these, the block copolymers synthesis of well-ordered mesoporous alumina is a reproducible, easily accessible, and scalable method with high surface areas, high thermal stability up to 1000 °C, and a large amount of Lewis acid sites [6]. Well-ordered mesoporous alumina has also been synthesized by ionic (anionic, cataionic or non-ionic) templating methods [7] or by using chemical templates such as carboxylic acids at room temperature [8]. However, these synthesis procedures require several steps which are time-consuming. From the synthesis viewpoint, it is quite a substantial barrier to attain highly ordered mesostructured γ-alumina via a one-step, enviro-friendly, and economical approach. Moreover, catalysis properties and thermal stability of ordered mesoporous alumina have not been studied elaborately. Particularly, very few studies have investigated the growth of alumina with other metals present during synthesis or application.

Supercritical water gasification (SCWG) is an emerging technique of interest to form hydrogen from high water content biomass, primarily due to preventing the high energies required for drying biomass [9]. Nickel (Ni) and alumina have substantial ability to destroy deposited tar by breaking C—C, O—H and C—H bonds during SCWG [10,11]. However, Ni-based catalysts, even after deposition on alumina, favor carbon deposition and metal sintering, which is a major challenge for using them at high temperatures [12]. To maintain catalytic activity and minimize the deactivation of Ni-based catalysts; researchers have added a second metal to the Ni catalyst [13,14]. Ru is reported as an active metal for C—C bond cleavage that may enhance the decomposition of

tars and C and O containing smaller molecules [15]. Sato et al. [16] confirmed that among the four noble metals (platinum, palladium, ruthenium & rhodium), ruthenium and rhodium showed the highest activity for producing methane after 15 min time of alkyl-phenols gasification at 400 °C. Therefore, we hypothesized that supported Ni and Ru on alumina might be a promising catalyst for supercritical water (SCW) biomass gasification. Moreover, previous studies have only investigated catalysts prepared using an impregnation approach, with poor control of porosity. In addition, previous catalysts have shown only poor stability when exposed to the aggressive supercritical water environment [17].

The purpose of this study is to form hydrogen while gasifying carbon in the feed stream instead of liquefaction (tar) or solidification (char). The carbon gasification is measured by carbon gasification efficiency (CGE). This study also examined the preparation and performance of a finely dispersed and thermally stable Ru & Ni loaded mesoporous Al_2O_3 catalysts. Active metals were incorporated during synthesis by examining P123 and CTAB templates. The properties of the fresh and spent catalysts were characterized by using several physico-chemical methods such as BET surface area analysis, BJH pore size distribution, TG-DTA, Hydrogen temperature programmed reduction (H_2-TPR), TPO, X-ray diffraction (XRD), Pulse chemisorption, Transmission electron microscopy (TEM) & Raman spectroscopy. The activity of conventionally impregnated Ni & Ru on alumina catalysts were compared with Ru & Ni incorporated mesoporous alumina catalyst for glucose gasification in SCW.

2. Experimental

2.1. Materials

Aluminum isopropoxide ($C_9H_{21}O_3Al$) (98%), Ruthenium (III) acetyl acetonate ($C_{15}H_{21}O_6Ru$) (97%), isopropanol (purity 99.5%), Nickel nitrate hexahydrate ($NiNO_3·6H_2O$), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P-123, ($C_3H_6O·C_2H_4O$)$_x$, hexadecyltrimethyl ammonium bromide (CTAB) and glucose were obtained from Aldrich (Mississauga, Canada). Nitric acid (68–70%) was obtained from Caledon Laboratory Chemicals (Georgetown, ON, Canada).

2.2. Catalyst preparation

Sol-gel synthesis was examined using two different templates (Pluronic P-123 & CTAB) to control the catalysts mesoporosity. The chemical structure of Pluronic P-123 & CTAB are shown in Fig. 1. The required amount of ruthenium precursor ($(C_5H_7O_2)_3Ru$), nickel precursor ($Ni(NO_3)_2·6H_2O$) and approximately 2 g of Pluronic P-123 or CTAB were dispersed in 20.0 mL of isopropanol and kept stirring continuously for 4 h. Then, 3.2 mL of 68–70 wt% HNO_3 was dissolved in another 10.0 mL of isopropanol and about 20 mmol aluminum isopropoxide was added to the solution. The two solutions were stirred continuously until they were dissolved. Once dissolved, the two solutions were combined. Excess isopropanol (about 10 mL) was used to thoroughly transfer the aluminium isopropoxide. 4–5 mL of H_2O was added slowly into the combined solution to obtain a homogeneous precipitate. The resulting slurry was continuously stirred for another 5 h at ambient temperature. The mixture was then filtered to remove the liquid phase with the solid dried at 60 °C for 48 h in an oven under vacuum. The samples were then calcined at 700 °C for 6 h in a tubular furnace with a ramp rate of 1 °C/min under air to remove the templates. The

catalysts were then reduced with 5% hydrogen balanced with Ar at 600 °C (3 °C/min) for 1 h for activation.

For comparison, an impregnated nickel & ruthenium based alumina catalyst was prepared using a slightly modified approach similar to [18, 19]. $θ$-Al_2O_3 pellets were used as the catalyst support. $θ$-Al_2O_3 was obtained by calcining $γ$-Al_2O_3 in the muffle furnace, the ramp rate of the furnace temperature was set at 10 °C/min and once the temperature reached to 1050 °C, the holding time was 1 h. For a standard synthesis, the desired amount of metal salt was dissolved in deionized water equivalent to 130 vol% of pore volume of alumina (0.19 cm^3/g). All alumina was immersed into the solution at once with Ni and Ru precursors for better metal dispersion. The catalyst was then placed in a closed beaker containing 10 vol% NH_3-H_2O solutions for ammonia vapour treatment for 10 min at 60 °C. This step helped convert metal salts into ammonium salts to increase Ni dispersion. The pellets were then heated from 60 to 250 °C at 2 °C/min to remove ammonium salts attached with the catalyst by sublimation. Hydrogen reduction with 5 vol% H_2 balanced with Ar at 600 °C @ 3 °C/min for 1 h was performed afterwards. The actual loadings (weight difference between support & metal impregnated catalyst) were calculated gravimetrically.

2.3. Catalyst characterization

The BET surface area and pore volume of the fresh and spent catalysts were determined using N_2 adsorption and desorption isotherms (Tristar II 3020, Micromeritics Instrument Corporation) according to the BET and BJH models, respectively. Thermo gravimetric-differential thermal analysis (TG-DTA) was performed by a TGA/SDT A851 model gravimetric analyzer to examine the formation process of mesoporous catalysts and also to determine whether carbon was deposited on the spent catalysts. Characteristics of deposited carbonaceous products during reaction were also confirmed by Temperature programmed oxidation (TPO) of the spent catalysts. The crystallinity of the fresh and spent catalysts was observed using Powder X-ray diffractometry using CuKα radiation ($λ = 1.5408$ Å) in the 2θ range from 0° to 80° with a Bruker D2 Phaser. Reducibility and the optimum reduction temperature of the fresh reduced catalysts were determined with a chemisorption apparatus (Micromeritics Autochem 2920) using Temperature programmed reduction of hydrogen (H_2-TPR). The morphologies of both the fresh and spent catalysts were taken from transmission electron microscopy (TEM) images (model JEOL 2010F). The surfaces of the spent catalysts were also examined by Raman spectroscopy (Kaiser Optical Systems RXNI-785 with an excitation wavelength of 785 nm).

2.4. Catalyst testing and product analysis

The prepared catalysts were tested for glucose gasification in SCW which was carried out using a 600 mL Hastelloy C-276 reactor (Autoclave Engineers, Erie, Penn, U.S.A. with maximum allowable pressure of 5300 psi at 500 °C). A 1.5 kW electric furnace supplied by the same manufacturer was used to heat up the reactor to achieve the desired reaction temperature. The detailed experimental setup and procedure was previously reported by our group [20]. Briefly, for each experiment, 1 g of catalyst was loaded with 70 mL of deionized water into the reactor which was then purged with helium for 10 min at 90 psi. The temperature was then increased to the desired end-point. The required amount of glucose was then dissolved in another 30 mL of deionized water and injected into the reactor at constant pressure using a syringe pump (Isco Model 100DX, Lincoln, NE, USA) with the reaction time started after injection. After reaction, the product was cooled to room temperature by

$$HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H \qquad CH_3(CH_2)_{15}N(Br)(CH_3)_3$$

A   **B**

Fig. 1. Chemical structure of (A) Pluronic P123 (B) CTAB.