



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

## Enhancing hydrogen production from the pyrolysis-gasification of biomass by size-confined Ni catalysts on acidic MCM-41 supports

Mengjing Ye<sup>a,1</sup>, Yongwen Tao<sup>a,1</sup>, Fangzhu Jin<sup>a</sup>, Huajuan Ling<sup>a</sup>, Chunfei Wu<sup>c,\*</sup>, Paul T. Williams<sup>b,\*</sup>, Jun Huang<sup>a,\*</sup>

<sup>a</sup> School of Chemical and Biomolecular Engineering, the University of Sydney, NSW 2006 Australia

<sup>b</sup> School of Chemical & Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

<sup>c</sup> School of Engineering and Computer Science, University of Hull, Hull, HU6 7RX, UK

### ARTICLE INFO

#### Keywords:

Biomass gasification  
Hydrogen production  
Wood sawdust  
Ni catalysts  
Support acidity  
MCM-41

### ABSTRACT

Hydrogen, currently produced from the reforming of fossil fuel resources, is a significant source for clean energy and the chemical industry. It is promising to develop a high-efficiency hydrogen production process from renewable biomass for sustainable development. This research reports that catalyst support acidity could strongly enhance the hydrogen production from the biomass gasification of wood sawdust. For minimizing the influence of the Ni particle size for the biomass gasification, the uniform Ni nanoparticles around 2–3 nm were loaded into one type of mesoporous support MCM-41 with various acidity. Ni/H-[Al] MCM-41 with a large amount of Brønsted acid sites contributed 2–3 times higher hydrogen yield (21.6 mmol H<sub>2</sub> g<sup>-1</sup> sample) than that on Ni/H-[Si]MCM-41 with a small amount of very weak acidic surface SiOH groups (9.8 mmol H<sub>2</sub> g<sup>-1</sup> sample) and that on nonacidic Ni/Na-[Si]MCM-41 (6.7 mmol H<sub>2</sub> g<sup>-1</sup> sample). The surface acid sites on supports could generate bifunctional catalysts and were proposed to show two functions for enhancing the hydrogen production: 1) help to crack and transfer the pyrolysis chemicals into smaller compounds for more efficient reforming on the Ni surface inside nanopores; 2) enhance the support and Ni interaction for better reduction property and surface activity of Ni nanoparticles and improve the reforming performance. The obtained Ni/MCM-41 catalysts were quite stable and no sintering has been observed after the gasification at 800 °C, and only a low coke deposition has been detected.

### 1. Introduction

Hydrogen has been increasingly promoted as a clean energy source since its combustion product is only water without any greenhouse gases (GHG) emission. Nowadays, hydrogen is mainly produced from carbon-rich fossil fuel resources such as natural gas, coal, and crude oil, with a significant amount of GHG emissions discharged to atmosphere [1]. To find a renewable resource for hydrogen production, many approaches have been investigated where biomass gasification has provided a very promising option. This is due to the fact that biomass is abundant in nature and it is a CO<sub>2</sub>-neutral resource [2]. Catalysts play an essential role to improve the hydrogen production in biomass gasification and Ni-based catalysts have been frequently studied because of their acceptable activity and low cost compared with noble metal catalysts [3–6].

It has been reported from the literature that catalysts with smaller particle size and high dispersion shows higher catalytic activity and

lower deactivation [7–10]. Silva et al. [11] suggested that reducing Co particle size (< 3 nm) decreased the deactivation rate and demonstrated the lower amount of carbon deposition (0.71 mg carbon/mg catalyst) for ethanol steam reforming. Wu et al. [12] reported that NiO particles located inside the MCM-41 mesopores demonstrated higher hydrogen production from biomass gasification and suggested that smaller Ni particles (3 nm) inside the MCM-41 mesopores promoted water gas shift reaction and reforming reactions of hydrocarbons and methane due to the longer residence time of reactants inside the MCM-41 pores. Therefore, nano-porous supports are popular for reforming reactions due to its high surface area, well-defined structure for small metal nanoparticles [13–17].

Apart from particle size, the chemical property and surface functional groups of supports also play an important role in the performance of catalysts due to the various reaction pathways by multifunctional groups or support-metal interactions [18,19]. It should be noted that surface acidity exists on nearly all of current supports, which have a

\* Corresponding authors.

E-mail addresses: [C.Wu@hull.ac.uk](mailto:C.Wu@hull.ac.uk) (C. Wu), [p.t.williams@leeds.ac.uk](mailto:p.t.williams@leeds.ac.uk) (P.T. Williams), [jun.huang@sydney.edu.au](mailto:jun.huang@sydney.edu.au) (J. Huang).

<sup>1</sup> Co-first authors.

<http://dx.doi.org/10.1016/j.cattod.2017.05.077>

Received 30 September 2016; Received in revised form 17 April 2017; Accepted 28 May 2017  
0920-5861/ © 2017 Elsevier B.V. All rights reserved.

significant effect for reactions [20–26]. Youn et al. [20] investigated Ni catalysts supported on  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$  and  $\text{ZnO}$  with different surface acidity and reported that  $\text{Ni}/\text{Ti}_{0.2}\text{Zr}_{0.8}\text{O}_2$  with intermediate acidity of support showed the best catalytic performance for hydrogen production during ethanol reforming. However, Emma et al. [21] reported the Ni catalyst on the acid support showed lower methane conversion compared to that on the neutral support during methane dry reforming. Therefore, there is still a debate as to whether the acidity of support has positive or negative influence for reactions.

For biomass gasification, the effect from support acidity has not been well investigated. In this paper, we address whether the existence of surface acidity of catalyst supports significantly influences the catalytic performance of the supported metal nanocatalysts in biomass gasification using supported Ni catalysts as an example. One type of support MCM-41 with uniform nano-pores has been applied to size the Ni nanoparticles and minimize the effects from the Ni particle size for the reaction. MCM-41 supports have been synthesized with the acidity (Al form), without acidity (neutral form, may exist as very weak acidic surface OH groups), and without acidity (Na form) [27,28]. Ni particles could be impregnated into uniform nanopores to realize uniform particle sizes. The obtained Ni/MCM-41 catalysts with and without support acidity were investigated for hydrogen production from biomass gasification.

## 2. Experimental

### 2.1. Materials

Wood sawdust was used with particle size of less than 0.2 mm with a moisture content of 5.7 wt.%, volatile content of 74.8 wt.%, fixed carbon content of 18.3 wt.% and ash content of 1.2 wt.%.

MCM-41 support was prepared according to the procedure reported by Cheng et al. [29] For H-[Al]-MCM-41 and Na-[Si]-MCM-41 supports, the mole ratio of Al/Si and Si/Na are equal to 1:10 and 1:2 respectively. Calculated amounts of aluminum sulfate and sodium carbonate were added to the MCM-41 materials. The obtained gels were completely mixed with vigorous stirring for 1 h. The resulting solids were collected by filtration, washed with distilled water, and then dried in an oven at 80 °C. Finally, the obtained cake was calcined at 550 °C with a heating rate of 1 °C min<sup>-1</sup> in the presence of static air for 6 h.

Wet impregnation method was used to synthesize catalysts by loading Ni on porous H-[Si]-MCM-41, H-[Al]-MCM-41, Na-[Si]-MCM-41,  $\text{SiO}_2$  supports, respectively (The mole ratio is Ni/Al = 1:1). The required amount of Ni ( $\text{NO}_3$ )<sub>2</sub>·6H<sub>2</sub>O was dissolved in ethanol to form 1 mol L<sup>-1</sup> of solution. The impregnation was employed by the addition of powdered H-[Si]-MCM-41, H-[Al]-MCM-41, Na-[Si]-MCM-41,  $\text{SiO}_2$  supports to the nickel precursor solution. The mixture was stirred overnight followed by evaporation of the mixture at 80 °C. The obtained solids were calcined at 550 °C with a heating rate of 1 °C min<sup>-1</sup>, then maintained at 550 °C for 6 h in static air.

### 2.2. Pyrolysis-Gasification of wood sawdust

The biomass gasification experiments were carried out in a two-stage fixed bed reaction system, which has been reported in our previous work [30]. Biomass sawdust was pyrolyzed in the first reactor, the derived gaseous pyrolysis products are passed directly to the second reactor where catalytic steam reforming occurred. For each experiment, about 1.0 g sawdust and 0.5 g catalyst were used. Sawdust was placed inside the first reactor, and the catalyst was placed inside the 2nd reactor. Both reactors were separately externally electrically heated. The temperatures of the two reactors were controlled separately using two temperature controllers. Initially, the temperature of the catalyst bed (2nd reactor) was heated and stabilized at 800 °C. Then the first pyrolysis reactor was started to be heated up to 550 °C with a heating rate of 40 °C min<sup>-1</sup>. Water was injected to the top of the 2nd reactor with a

flow rate of 4.74 ml h<sup>-1</sup> by a syringe pump when the pyrolysis temperature reached around 200 °C.  $\text{N}_2$  was used as carrier gas for each experiment with a flow rate of 80 ml min<sup>-1</sup>. The derived gaseous products after the second reactor were condensed with dry ice cooled condensers to produce the liquid products and the non-condensed gases were collected with a Tedlar gas sample bag for later analysis. It is noted that the whole catalytic reaction time was about 40 mins for each experiment. Selected experiment was repeated to ensure the reliability of the data. Mass balance close to 100% was used as an indicator of an acceptable experiment.

### 2.3. Products analysis and characterization

The non-condensed gases were analyzed off-line by gas chromatography (GC). The  $\text{CO}_2$  gas was analyzed by Varian 3380 GC with a Hysep 80–100 mesh column and argon as carrier gas.  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{N}_2$  gases were determined by another Varian 3380 GC equipped with a 60–80 mesh molecular sieve column with argon carrier gas.  $\text{C}_1$ – $\text{C}_4$  hydrocarbons were detected using a further Varian 3380 GC with a flame ionization detector while  $\text{N}_2$  is working as carrier gas.

Surface area, average pore size, and total pore volume of the fresh catalysts were determined by  $\text{N}_2$  adsorption and desorption isotherms on a Quantachrome Autosorb<sup>-1</sup>. Each sample (50 mg) was degassed at 423 K for 12 h under vacuum before measurements and then recorded at 77 K.

X-ray diffraction (XRD) patterns of the fresh catalysts were obtained on a SIEMENS D6000 instrument in the range of 1.5–70° with a scanning step of 0.02 using  $\text{CuK}\alpha$  radiation (0.1542 nm wavelength). A high resolution scanning electron microscope (SEM) (LEO 1530) was used to obtain the surface morphology of the fresh and reacted catalyst. Transmission electron microscopy (TEM) (Philips CM200) was used to characterize and examine the fresh catalysts.

Temperature-programmed oxidation (TPO) of the reacted catalysts was utilized to obtain the degree of coke deposition by using a Stanton-Redcroft thermogravimetric analyser (TGA and DTG). About 10 mg of the reacted catalyst was heated in air at 15 °C min<sup>-1</sup> to a final temperature of 800 °C, with a dwell time of 10 min. Temperature programmed reduction (TPR) of the prepared catalysts were carried out using a modified thermogravimetric analyzer (SDTQ600) coupled with a mass spectrometer (ThermoStar GSD301). Prior to the commencement of TPR, the sample was heated at 20 °C min<sup>-1</sup> in pure  $\text{N}_2$  (500 ml min<sup>-1</sup>) from room temperature to 500 °C. The pre-treated catalysts were cooled to room temperature before heating to 1000 °C at a rate of 10 °C min<sup>-1</sup> in a  $\text{H}_2$  atmosphere. During the reduction process, variance of generated gas and mass loss were respectively monitored by MS and TGA through a heated capillary delivery.

$\text{NH}_3$ -TPD was performed on Chem BET TPR/TPD Chemisorption Analyzer, CBT-1, QuantaChrome instruments. Typically, 30 mg of the samples were pretreated at 500 °C for 1 h in He flow at a flow rate of 120 ml min<sup>-1</sup> to purge the gas or moisture adsorbed on the samples, then the temperature was cooled to adsorption temperature of 100 °C, followed by adsorption of the gas mixture of  $\text{NH}_3$  and He (8.16%, mol/mol) for 30 min or 15 min, respectively. After adsorption, pure He flow (120 ml min<sup>-1</sup>) was passed through the samples which were heated from 100 to 1100 °C at a heating rate of 10 °C min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Characterization of fresh catalysts

The same type of mesoporous silica material MCM-41 has been prepared and impregnated with Ni particles as described in the above experimental section. Their XRD patterns have been listed in Figs. 1 and 2. As shown in the XRD patterns of the small angle region ( $2\theta = 1.5$ – $10^\circ$ ), all Nicalysts expressed a typical pattern of MCM-41 material with a hexagonal framework of strong (100) reflection at 2-

Download English Version:

<https://daneshyari.com/en/article/6504436>

Download Persian Version:

<https://daneshyari.com/article/6504436>

[Daneshyari.com](https://daneshyari.com)