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Catalytic steam reforming of tar derived from steam gasification of sunflower stalk over ethylene glycol assisting prepared Ni/MCM-41

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ABSTRACT

Ethylene glycol (EG) assisted impregnation of nickel catalyst on MCM-41 (Ni/MCM-41-EG) was performed and applied for steam reforming of tar derived from biomass. The catalyst was characterized by SEM–EDX, BET, XRD, and TPR. It is found that smaller nickel particles were well dispersed on MCM-41 and better catalytic activity was shown for the Ni/MCM-41-EG when compared with the catalyst of Ni/MCM-41 prepared by using the conventional impregnation method. H_2 yield increased approximately 8% when using 20 wt.% Ni/MCM-41-EG instead of 20 wt.% Ni/MCM-41 for the steam reforming of tar derived from sunflower stalk. The catalyst reusability was also tested up to five cycles, and no obvious activity reduction was observed. It indicates that EG assisted impregnation method is a good way to prepare metal loaded porous catalyst with high catalytic activity, high loading amount and long-term stability for the tar reforming.

1. Introduction

Fossil fuels such as natural gas, petroleum and coal have been consumed for a long time and resulted in serious environmental problem. Nowadays, it is the time to consider using renewable energy resources such as waste biomass instead of a part of traditional fossil energy resources [1]. To date, many agricultural residues and other waste biomass are not used properly and effectively. For example, in 2011, the total area of sunflower cultivation in the world was up to 26 million hectares [2], but most of sunflower stalk from harvest is not effectively utilized. It is a potential resource for bioenergy production. Recently, hydrogen is regarded as one of clean energy in the future [3]. To obtain H_2-rich gas, steam gasification of biomass is the most effective way [4]. During the gasification, steam reforming reactions and water–gas shift (WGS) reaction can enhance H_2 gas yield [5,6]. However, during steam gasification of biomass, one of the most significant problems is the formation of tar together with syngas. The tar is complex compound mixture, which contains single-ring to multiple-ring compounds along with many oxygen containing hydrocarbons [7,8]. The tar is easily polymerized in the gasification system, leading to the blockage and attrition of reactor and pipelines [9,10]. To reduce the amount of tar in the system, there are many physical techniques such as scrubber and electrostatic techniques [8]. However, these techniques are not recommended due to extravagant energy expenditure and a large amount of solvent disposal. Catalytic cracking and/or reforming of tar offer alternative ways for the reduction of tar amount and simultaneously producing syngas and other useful chemicals [11].

Various catalysts such as calcite, dolomite, olivine and metal oxide have been investigated for the tar reforming [12–16]. Nickel is one of catalysts for O–H, C–H and C–C cracking during the tar reforming. It is considered as one of the most promising catalysts for the tar reduction [17–21]. Kimura et al. [22] found that nickel-based catalyst prepared by co-impregnation method exhibited high performance in the steam gasification of biomass. Hu and Lu [23] reported that nickel metal exhibited better performance in terms of H_2 production when compared with other metals such as Co and Fe for the steam reforming of acetic acid. They found that the coke is difficult to be formed on its surface and metal sintering rate is also slow. Nickel metal sometimes showed the similar catalytic activity as some noble metals such as Pt and Pd [17,24]. Rh is found to have higher catalytic performance and coke resistant ability than Ni in the steam reforming of tar, but it

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is limited by its high cost for large-scale applications [25]. On the other hand, support materials have been identified to have important role on catalytic activity due to the interactions between the catalyst and support materials. Many researchers have tried to develop excellent support materials. One of suitable support materials for Ni is α-Al_2O_3. Simell et al. [26] reported that Ni loaded α-Al_2O_3 exhibited good chemical and physical stability with excellent mechanical properties. Koike et al. and Wang et al. [27,28] reported that adding MnO_x on Ni/Al_2O_3 or combining of Co with Ni/Al_2O_3 resulted in higher catalytic performance and longer stability when comparing with Ni/Al_2O_3 itself for the steam reforming of toluene and the real tar derived from cedar wood. Moreover, many support materials for Ni catalyst such as ZrO_2, TiO_2, CeO_2, Al_2O_3 and MgO were also investigated [29]. It is found that Ni/CeO_2 showed more excellent catalytic activity and lower coke deposition in partial oxidation and steam reforming of tar than other catalysts. Nickel sintering and coke deposition generally occurred during the reforming of tar [30]. To solve this problem, high dispersion and high loading of catalyst on the support materials are required. In general, the support materials with low surface area (mostly less than 200 m^2/g) easily lead to the sintering of supported metal during the thermal treatment period due to low dispersion with high accumulation of metal [31]. Recently, mesoporous molecular sieves such as HMS, KIT-1, SBA-15 and MCM-41 with high BET surface area have been attracted considerable interest as catalyst supports [24,32]. Among them, MCM-41 is widely utilized as adsorbents, catalyst support and hydrogenation catalyst. Since the homogeneous hexagonal pore arrays with pore diameters ranged from about 2 to10 nm and high specific surface area higher than 1000 m^2/g [33], it is possible to use it as catalyst support for high catalyst loading. Todorova et al. [34] and Szegedi et al. [35] reported that the large pore size and high surface area of MCM-41 promoted catalyst particles to disperse on it, and more effective mass transfer was realized within the porous structure. As such, the sintering of supported metals can be reduced. Herein, the metal loading method sometimes has great effect on the metal dispersion in the porous structure of such kinds of supports. Zhao et al. [31] found that H_2 and syngas yields decreased during the tar reforming when Ni loading amount on MCM-41 was increased from 5 to 20 wt.% when using traditional impregnation method to prepare the catalysts. Therefore, development of novel metal loading method is important for the improvement of the dispersion quality and decrease particle size in order to obtain higher catalytic activity and longer activity stability. Recently, it is found that ethylene glycol (EG) assisted impregnation method can improve the interaction between the metals and support materials due to the redistribution of active phase on the support body, resulting in the formation of more uniform and smaller metal particles on the supports [36]. Furthermore, it is also avoid using too much organic solvent, expensive chelating agents and complex preparation process. However, to date, this method is still not widely applied [37].

In this work, EG-assisted impregnation method was applied for the preparation of Ni-doped MCM-41 catalysts (Ni/MCM-41-EG) with different Ni doping amounts from 5 to 40 wt.% and used for the steam reforming of tar derived from sunflower stalk. As-prepared catalysts were characterized by BET, XRD, TPR and SEM–EDX. Long-term stability of the catalysts were also investigated. It is expected to obtain a kind of Ni-based catalyst with high catalytic activity, high catalyst loading and long-term stability.

2. Experimental

2.1. Biomass materials

Sunflower stalk was collected from Aomori, Japan and used as biomass feedstock in this study. It is crushed and sieved with a size in a range of 1–2.8 mm and dried at 105 °C overnight in oven. Proximate analysis was carried out to determine the moisture, volatile matter, ash and fixed carbon of biomass using a thermogravimatric analyzer (TGA, DTG-60H, Shimadzu, Japan) based on ASTM D5142-04. Ultimate analysis was performed to determine the elemental composition (C, H, N, S and O) by using an elemental analyzer (Vario EL cube elemental analyzer). Ash composition was determined using an energy dispersive X-ray spectrometer (EDX-800HS, Shimadzu, Japan). The results of proximate, ultimate and ash composition are shown in Table 1.

2.2. Catalyst preparation

MCM-41 was synthesized using the procedure reported by Roik and Belyakova [38]. In a typical synthesis process, 7.28 g of cetyltrimethylammonium bromide (CTAB, Wako, Japan) was dissolved in 259.2 mL of deionized water and mixed with 32.4 mL of ethanol (Wako, Japan) under stirring at 25 °C for 30 min. After complete dissolution, 20.9 mL of ammonia (Kanto Chemical, Japan) was added and followed by adding 22.3 mL of tetraethyl orthosilicate (TEOS, Kanto Chemical, Japan). The sol was formed with a molar composition of 0.1TEOS: 0.02CTAB: 2.4NH_4OH: 5.2C_2H_2OH: 14.4H_2O and remained under stirring at 25 °C for 2 h. After finishing, the sol was transferred to a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. Finally, the precipitated white product of MCM-41 was filtered, washed with deionized water, dried at 105 °C in oven and then calcined in air at 550 °C for 4 h.

Ni/MCM-41 catalysts with different Ni loadings (5, 10, 20 and 40 wt.%) were prepared by EG-assisted co-impregnation as well as conventional impregnation methods. In the co-impregnation procedure, a certain amount of EG (Kanto Chemical, Japan) and $Ni(NO_3)_2{\cdot}6H_2O$ (Wako, Japan) were dissolved together with a molar ratio of Ni:EG = 1:1 in ethanol (Wako, Japan). Then MCM-41 powder was added to the mixture and stirred for 2 h. Thereafter, the mixture was dried at 80 °C followed by calcination at 550 °C for 4 h. For comparison, EG unmodified Ni/MCM-41 was prepared by using the conventional impregnation method. SiO_2 (Saint-Gobain, Norpro, Japan) was also selected as support and

Table 1
Proximate, ultimate and ash compositions of biomass.

Biomass	Sunflower stalk
Proximate analysis (wt.%)[a]	
Moisture	2.31
Volatile matter	85.06
Ash	11.40
Fixed carbon[b]	1.23
Ultimate analysis (wt.%)[c]	
Carbon	39.57
Hydrogen	5.39
Nitrogen	1.18
Sulfur	0.25
Oxygen[b]	53.61
Ash composition analysis (wt.%)	
K_2O	71.69
CaO	16.30
P_2O_5	9.01
SO_3	2.81
SrO	0.10
CuO	0.04
Rb_2O	0.06
ZnO	0.05
Br	0.03

[a] Dry basis.
[b] Mass difference.
[c] Dry and ash-free.