**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. H₂ 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.

Keywords: Catalytic steam gasification; Tar reforming; Sunflower stalk; Ni/MCM-41; Ethylene glycol; Co-impregnation.

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 H₂-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 H₂ 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 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 $\alpha-Al_2O_3$. Simell et al. [26] reported that Ni loaded $\alpha-Al_2O_3$ 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 $200\text{ m}^2/\text{g}$) 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 to 10 nm and high specific surface area higher than 1000 m²/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 H₂ 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 thermogravimetric 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: 2.4NH₄OH: 5.2C₂H₅OH: 14.4H₂O 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 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 20 wt.% Ni/ SiO_2 -EG was prepared the same co-impregnation method.

2.3. Catalyst characterization

Specific BET surface areas, pore volumes and pore diameters of catalysts were determined by N_2 adsorption-desorption using a Quantachrome instrument (NOVA 4200e, USA). Crystalline structures of catalysts were analyzed by a X-ray diffractometer (XRD, Rigaku Smartlab, Japan) in the 2θ range of 10-70° with a scanning step of 0.02° using Cu K α radiation ($\lambda = 0.1542$ nm). Reduction behaviors of catalysts were investigated by temperature-programmed reduction (TPR) using a BET-CAT catalyst analyzer (BEL, Japan). Particle surface morphologies of catalysts were characterized with a scanning electron microscope (SEM, SU8010, Hitachi, Japan) coupled with energy dispersive X-ray detector (EDX). The amount of coke deposition on catalyst was analyzed using a thermogravimetric analyzer (TGA, DTG-60H, Shimadzu, Japan) at a heating rate of 10 °C/min to a temperature of 800 °C under air flow.

2.4. Catalytic steam reforming testing

Catalytic activity of as-prepared catalyst was evaluated using a fixed bed reactor system, which was described in details elsewhere [39]. Ar flow ($50 \text{ cm}^3/\text{min}$) and steam flow (0.09 g/min) were used as carrier gas and gasifying agent, respectively. In a typical run, 0.6 g of biomass and 1 g of catalyst were separately packed in the reactor. Different reaction temperatures in the range of 550-750 °C with a heating rate of 20 °C/min were selected. For comparison, the reaction time was fixed at 2 h for each experiment. The products at the outlet of the reactor were condensed with a cold trap to collect the liquid at first and the non-condensed gases were purified and collected in a gas bag for further analysis.

2.5. Analysis of gas products

The collected non-condensed gases were analyzed off-line using a gas chromatography (Agilent 7890A GC system, USA) equipped with thermal conductivity detector (TCD) and 3 packed columns (1 molecular sieve 5A column + 1 HayeSep Q column + 1 molecular sieve 5A column) for separation of CO, CH₄ and CO₂ using He as a carrier gas, while a molecular sieve 5 A for H₂ detection using Ar as a carrier gas. The gas yield was quantitatively determined from peak area obtained by GC. The average value of three times measurements of each gas sample was determined. All of the gas yields were expressed in unit of mmol/g of carbon.

3. Results and Discussion

3.1. Characterization of catalyst before reaction

N₂ adsorption-desorption isotherms and pore size distributions of catalysts are shown in Fig. 1. As shown in Fig. 1A and C, it can be seen that the Ni/MCM-41 and Ni/MCM-EG prepared with different Ni loadings (5, 10, 20 and 40 wt.%) exhibited IUPAC type IV

isotherms corresponding to the typical mesoporous structure [40]. Fig. 1B and D show the narrow pore size distributions with an average pore size of 3 nm. The textural properties of catalysts are summarized in Table 2. The surface areas of catalysts were successively decreased from about 1200 to 850 m²/g with the increasing of Ni loading from 5 to 40 wt.%. The significant decrease of specific surface area and pore volume with the increase of the Ni loading content indicated that the NiO particle was dispersed in the porous structure of MCM-41. It should be noted that Ni/MCM-41-EG catalysts showed slight different pore size distributions when compared with Ni/MCM-41 catalysts.

Fig. 2A and C show XRD patterns of the catalysts before reaction. The diffraction peaks at 37.5°, 43.4° and 63.0° were ascribed to NiO crystalline phase [41]. It can be seen that Ni/MCM-41-EG exhibited broad and weak diffraction peaks while Ni/MCM-41 showed sharp and strong diffraction peaks, especially in 40 wt.% Ni loading, indicating that NiO particles on MCM-41-EG had smaller size with better dispersion. Its crystallite size determined by Scherrer's equation are summarized in Table 2. It is found that NiO particle size increased with the increasing of Ni loading from 5 to 40 wt.%. Fig. 3 shows SEM images of catalysts. Interestingly, as observed in Fig. 3B-D, the bulk NiO particles were obviously observed on the surface of Ni/MCM-41 prepared in the Ni loading of 10 to 40 wt.%. Moreover, with the increase in the Ni loading amount, the amount of bulk NiO particle also increased, indicating that NiO particles on MCM-41 were accumulated due to the sintering during the thermal treatment when too much NiO was loaded on MCM-41. On the contrary, the bulk NiO particle was not observed in the case of 5 wt.% Ni/MCM-41 as shown in Fig. 3A, indicating that NiO was well-dispersed on MCM-41. In contrast, as shown in Fig. 3E-H, for Ni/MCM-41-EG even with high Ni loading amounts, no bulk NiO particle was observed, demonstrating that EG assisted impregnation improved the dispersion of Ni catalyst on MCM-41 support. The possible mechanism of EG assisting prepared Ni/MCM-41 can be

proposed as following: when EG is applied for Ni/MCM-41 preparation, EG molecules will combine and disperse in the porous structure of MCM-41 at first and then, a complex will be formed between $\text{Ni}(\text{NO}_3)_2$ and EG, where NO_3^- ions combine with EG molecule, and Ni^{2+} ions could disperse deeply into the pore channels of MCM-41. In this case, EG molecule will assist Ni^{2+} ions to disperse in the porous structure of MCM-41, and hold Ni element during the following thermal treatment to hinder NiO sintered. For Ni/MCM-41 prepared without EG, Ni^{2+} ions can also be dispersed into the pore channels of MCM-41. However, in this case, Ni^{2+} ions can be move freely in the pore channels. More Ni^{2+} ions could exist on the outer surface of MCM-41 due to the diffusion resistance in the pore, and thus the loading amounts on the surface depend on the concentration of initial $\text{Ni}(\text{NO}_3)_2$ solution. If the concentration is too high, more Ni element will gather on the surface of MCM-41, leading to sintering under high thermal treatment. As such, the pore channels might be easily blocked. Therefore, in the presence of EG assisting prepared Ni/MCM-41, NiO particles will separately dispersed in the porous structure of MCM-41, and will not be so easy to grow. As a result, NiO particles will be better dispersed in the porous structure of MCM-41 with smaller size.

TPR profiles of catalysts are shown in Fig. 4. As shown in Fig. 4A, it can be seen that three reduction peaks for NiO on MCM-41 with high loadings were observed. The first reduction peak occurred at a low temperature range of about 260 to 340 °C was attributed to the free NiO or the superficial NiO species, which had no or less interaction with MCM-41 support. The second reduction peak at about 340 to 420 °C was assigned to the reduction of bulk NiO particles. The third reduction peak exhibited at higher temperature of about 600 °C suggested the existence of small NiO particles with a strong interaction with MCM-41 support [42-44]. In contrast, as shown in Fig. 4B, for Ni/MCM-41-EG, the reduction peak at low temperature range shifted to lower temperature, indicating that the free NiO or the

superficial NiO species on Ni/MCM-41-EG were more easily reduced due to its smaller particle size. On the other hand, the reduction peak at high temperature range shifted to higher temperature, indicating that many smaller NiO species on Ni/MCM-41-EG had stronger interaction with the MCM-41 support so that they were not so easy to be reduced. It also indicated that the NiO particles formed by the assistance of EG had uniform and smaller particle size and stronger interaction with MCM-41 supports when compared with Ni/MCM-41 [43]. It was noted that the third reduction peak was shifted towards higher temperature. This trend can be explained to the hard reducibility of some NiO particles as well as probably due to increasing of amount of NiO particle with interaction on MCM-41.

The amounts of H₂ uptake used for the catalyst reduction were calculated from TPR peak area by assuming that NiO species were directly reduced to metallic Ni, and the results are summarized in Table 2. One can see that the amount of H₂ uptake increased with the increasing of Ni loading amount from 5 to 40 wt.% on both the MCM-41 and MCM-41-EG, resulting from the increase in the active surface of nickel metal on support.

3.2. Catalytic steam reforming of tar

In the fixed bed reactor, the steam gasification of biomass and steam reforming of tar occurred simultaneously. All of the following reactions could be included:

Fig. 5 shows the effect of reaction temperature on the steam gasification of sunflower stalk alone. A dramatic increase in the gas yield as the reaction temperature increased from 550 to 750 °C, in which H₂ gas yield increased from 18.63 to 92.15 mmol/g-carbon. This indicates that higher temperature could promote thermal cracking and decompositions of biomass and tar. However, it should be noted that the gas yield slightly increased in the reaction temperature range from 650 to 750 °C, indicating that the steam gasification of sunflower stalk was almost complete in this temperature range. It has reported that a reaction temperature over 850 °C is enough for the steam gasification of biomass [45]. However, in this study, sunflower stalk was more easily gasified due to the existence of higher volatile matter and AAEM contents in its structure. As shown in Fig. 5B, only a small amount of liquid product (tar and water) was generated while char yield remained almost constant when the gasification temperature was over 650 °C. Here, in order to identify the catalytic activity of the as-prepared catalysts, a lower reaction temperature, i.e., 600 °C, was selected.

Fig. 6 shows the gas yield from the steam gasification of sunflower stalk together with the steam reforming of tar in the presence of Ni/MCM-41-EG and compared with the presence of Ni/MCM-41 as well as without catalyst. Here, the generated tar from biomass was pass through catalyst layer and reformed there by steam. Moreover, in this study, catalyst was not reduced by H₂ at first before use. It is expected that the H₂ and CO generated by the steam gasification of sunflower stalk could reduce NiO to metal Ni at first during the reaction process, which has been identified in our previous study [10]. Fig. 2B and D also indicated that some NiO were reduced to Ni during the reaction. For Ni/MCM-41 catalysts, one can see that the H₂ yield increased from 68.03 to 81.78 mmol/g-carbon when Ni loading amount on MCM-41 increased from 5 to 20 wt.%. However, further increase of Ni loading amount resulted in the decrease of H₂ yield, probably due to the disastrous effect of sintering and dispersion of Ni on MCM-41. In general, sintering is easy to occur in the case of high metal

loading for the catalyst prepared by conventional method. For Ni/MCM-41-EG, the trend of gas yield variation with the Ni loading amount was similar to that of Ni/MCM-41, but gas yield in each condition was higher, indicating that Ni/MCM-41-EG had higher catalytic activity for the reforming of sunflower stalk tar, and the H₂ yield increased from 77.49 to 88.64 mmol/g-carbon with the increase of Ni loading content from 5 to 20 wt.% on MCM-41-EG, and then the H₂ yield decreased to some extent when Ni loading amount increased to 40 wt.%. As stated above, the EG assisted impregnation resulted in better dispersion of the smaller particles and more catalytic sites, which led to higher gas yield, especially higher H₂ production. However, overloading of Ni on support decreased the gas yield, it is possible that the saturation loading of Ni could occur for any mesoporous materials [31]. Here, it should be noted that no significant difference of the catalyst performance was observed for Ni loading amount from 10 to 40 wt.%. Thus, it is possible to decrease the Ni loading amount in a practical process. For comparison, SiO₂ (Saint-Gobain, Norpro, Japan) was also selected as support and 20 wt.% Ni/SiO₂-EG was prepared the same co-impregnation method and applied for the steam reforming of tar. As shown in Fig.6, 20 wt.% SiO₂-EG provided lower catalytic performance than 20 wt.% Ni/MCM-41-EG. It is probably due to its lower surface area (as indicated in Table 2), which could lead to larger NiO particle supported on MCM-41 with weaker interaction between the catalyst and support when compared with 20 wt.% Ni/MCM-41-EG. XRD and TPR analyses as shown in Fig. 7 indicated that larger particle formed on SiO₂-EG.

The effect of catalyst amount on the gas yield was investigated using 20 wt.% Ni/MCM-41-EG. As shown in Fig. 8, one can see that the total gas yield increased with the increasing of catalyst amount from 0.2 to 1.4 g. It should be noted that the gas yield sharply increased from 0.2 to 1 g and then, increased gradually from 1 to 1.4 g, suggesting that the

generated tar from the biomass was almost converted completely due to more active sites provided by the larger amount of catalyst.

3.3. Catalyst reusability

In this work, 20 wt.% Ni/MCM-41 and 20 wt.% Ni/MCM-41-EG were reused without regeneration at the same operation conditions for 5 cycles. As shown in Fig. 9, no serious reduction on gas yield was observed for both catalysts. Interestingly, at the second cycle, both Ni/MCM-41 and Ni/MCM-41-EG exhibited the increase of gas yield when compared with the fresh catalysts, indicating that the reused catalysts had a better catalytic activity. This phenomenon might be explained as followings: the AAEM species in the biomass moved to the catalyst surface with the tar, which promoted the catalytic activity of catalyst [10]. Fig. 10 shows SEM-EDX results of 20 wt.% Ni/MCM-41-EG after the reaction (5th reuse). It is clearly seen that K species (AAEM) existed on the surface of the catalyst. Many researchers proposed the mechanism of K metal-catalyzed steam reforming of biomass and tar [46,47]. The possible reaction could be described as following:

Eqs. (7)-(10) construct a redox cycle that seems reasonable to clarify the catalytic ability of K_2CO_3 . Moreover, at high temperatures of about 500 to 600 °C, it was proven that K_2CO_3 could be decomposed to K_2O with the existence of carbon. The catalytic mechanism of the K_2CO_3 for steam reforming could be described as following:

338 The complicated potassium intermediates such as $\text{K}_2\text{O-C}$ and $\text{K}_2\text{O}_2\text{-C}$ could dominate
 339 the catalytic process. From above reactions, two redox cycles of K_2CO_3 and reduced K_2CO_3
 340 promote the carbon conversion and enhance H_2 yield for steam gasification of biomass or tar.

341

342 3.4. Characterization of catalysts after reaction

343 Table 2 also shows the BET surface areas of catalysts after the reaction at 600 °C for 2
 344 h. One can see that the surface area and pore volume decreased after reaction, which could be
 345 resulted by the coke deposition, metal sintering and accumulation. Moreover, it might be also
 346 from K and other species deposited on the surface of catalyst during reaction. Fig. 2B and D
 347 also show XRD patterns of catalysts after reaction at 600 °C for 2 h. Two new diffraction
 348 peaks appeared at 44.7° and 52°, corresponding to the Ni metal crystalline phase [48].
 349 Furthermore, the intensities of three diffraction peaks at 37.5°, 43.4° and 63.0° decreased,
 350 suggesting that certain amount of NiO on catalyst was reduced to Ni metal as following:

352 where H_2 was produced from the steam gasification of sunflower stalk. One can see that the
 353 intensities of new peaks of Ni crystalline phase became stronger than that of NiO crystalline
 354 phase in Ni/MCM-41 after the reaction, especially for the cases of 20 and 40 wt.% Ni
 355 loadings, which should be resulted from the agglomeration and sintering of catalyst.
 356 However, Ni/MCM-41-EG with new peaks of Ni crystalline phase exhibited more stability

when compared with Ni/MCM-41. The amounts of coke deposition on spent catalyst were calculated from TGA analysis. The results are shown in Table 2. It is clearly seen that the amount of coke deposition seems to be successively increased with the increasing of Ni loading from 5 to 40 wt.%, suggesting that the increased coke deposition was related with the amount and size of NiO particle on the support. Comparing Ni/MCM-41 with Ni/MCM-41-EG, less amount of coke deposition was found in EG assisting prepared Ni/MCM-41, suggesting that EG assisting prepared Ni/MCM-41 can resist the coke formation and improve the stability of catalyst.

4. Conclusions

Ni/MCM-41-EG was prepared by EG-assisted co-impregnation method, and applied for the steam reforming tar derived from biomass. Comparing with the Ni/MCM-41 prepared by conventional method, it is found that NiO particles were better dispersed on MCM-41 with smaller particle size. TPR analysis results indicated that NiO particle on MCM-41-EG had stronger interaction with the support. Moreover, Ni/MCM-41-EG showed higher catalytic activity and excellent reusability for the steam reforming of tar derived from steam gasification of sunflower stalk.

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Table captions

Table 1 Proximate, ultimate and ash compositions of biomass.

Table 2 Textural properties of catalysts.

Figure captions

Fig. 1. (A) N₂ adsorption-desorption isotherms and (B) pore-size distributions of 5 - 40 wt.% Ni/MCM-41, (C) N₂ adsorption-desorption isotherms and (D) pore-size distributions of 5 - 40 wt.% Ni/MCM-41-EG.

Fig. 2. XRD patterns of (A) 5-40 wt.% Ni/MCM-41 before reaction, (B) 5-40 wt.% Ni/MCM-41 after reaction, (C) 5-40 wt.% Ni/MCM-41-EG before reaction and (D) 5-40 wt.% Ni/MCM-41-EG after reaction.

Fig. 3. SEM images of (A)-(D) 5-40 wt.% Ni/MCM-41 and (E)-(H) 5-40 wt.% Ni/MCM-41-EG.

Fig. 4. TPR profiles of (A) 5-40 wt.% Ni/MCM-41 and (B) 5-40 wt.% Ni/MCM-41-EG.

Fig. 5. (A) Gas yield and (B) mass balance obtained from steam gasification of sunflower stalk alone. Reaction condition: reaction time of 2 h; water flow rate of 0.9 g/min; and reaction temperatures of from 550 to 750 °C.

Fig. 6. (A) Gas yield and (B) mass balance obtained from steam reforming of tar derived from steam gasification of sunflower stalk using various catalysts Reaction condition: reaction temperature of 600 °C; reaction time of 2 h and water flow rate of 0.9 g/min.

Fig. 7. (A) XRD patterns and TPR profiles of 20 wt.% Ni/MCM-41-EG and 20 wt.% Ni/SiO₂-EG.

549 **Fig. 8.** Effect of catalyst amount on the steam reforming of tar derived from steam
550 gasification of sunflower stalk using 20 wt.% Ni/MCM-41-EG. Reaction condition: reaction
551 temperature of 600 °C; reaction time of 2 h and water flow rate of 0.9 g/min.

552 **Fig. 9.** Catalyst reusability of (A) 20 wt.% Ni/MCM-41 and (B) 20 wt.% Ni/MCM-41-EG
553 for the catalytic steam reforming of tar derived from the steam gasification of sunflower
554 stalk. Reaction condition: reaction temperature of 600 °C; reaction time of 2 h and water flow
555 rate of 0.9 g/min.

556 **Fig. 10.** (A) SEM image and (B) EDX mapping image of 20 wt.% Ni/MCM-41-EG after
557 reaction (5th reuse). EDX spectra were inserted in (B).

558

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 ₂ O	71.69
CaO	16.30
P ₂ O ₅	9.01
SO ₃	2.81
SrO	0.10
CuO	0.04
Rb ₂ O	0.06
ZnO	0.05
Br	0.03

^a Dry basis; ^b Mass difference; ^c Dry and ash-free

Table 2 Textural properties of catalysts.

Fresh catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	H ₂ uptake ^a (mmol/g)	NiO crystallite diameter ^b (nm)
5 wt.% Ni/MCM-41	1217	0.86	3.12	0.08	< 4.0
10 wt.% Ni/MCM-41	900	0.70	3.11	1.41	13.4
20 wt.% Ni/MCM-41	870	0.68	3.11	2.47	21.0
40 wt.% Ni/MCM-41	824	0.61	3.12	4.23	28.8
5 wt.% Ni/MCM-41-EG	1283	0.94	3.11	0.08	< 2
10 wt.% Ni/MCM-41-EG	1095	0.85	3.09	1.37	< 2
20 wt.% Ni/MCM-41-EG	906	0.71	2.98	2.48	< 3
40 wt.% Ni/MCM-41-EG	849	0.52	2.97	4.23	5.5
20 wt.% SiO ₂ -EG	188	0.53	3.91	2.40	9.2
Spent catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Coke deposition (%)	Ni and NiO crystallite diameter ^b (nm)
5 wt.% Ni/MCM-41	853	0.75	3.11	0.9	< 4.0
10 wt.% Ni/MCM-41	767	0.64	3.11	1.8	13.8
20 wt.% Ni/MCM-41	600	0.43	3.06	3.0	24.7
40 wt.% Ni/MCM-41	543	0.17	2.89	3.5	32.0
5 wt.% Ni/MCM-41-EG	899	0.88	3.11	0.5	< 2.0
10 wt.% Ni/MCM-41-EG	770	0.69	3.11	1.0	< 2.0
20 wt.% Ni/MCM-41-EG	632	0.47	2.96	1.5	< 3.0
40 wt.% Ni/MCM-41-EG	561	0.35	2.90	2.2	6.0

^a H₂ uptakes were calculated from TPR curves.

^b Mean Ni and NiO crystallite diameters were determined from XRD patterns using Scherrer's equation.

Figure-2

Figure-3

Figure-4

Figure-5

Figure-6

Figure-7

Figure-8

Figure-9

Figure-10