Steam reforming of tar from pyrolized biomass over supported Ni-Mn catalyst at lower temperature

Nwaynay Hlaing[1], Kazuya Kawahara[1], Osamu Nakagoe[1], Hideaki Sano, Guobin Zheng, Shuji Tanabe [1]
[1]*Division of Chemistry and Material Science, Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan*
E-mail: s-tanabe@nagasaki-u.ac.jp

Abstract: The catalytic steam reforming of biomass was investigated in a two-stages fixed bed reactor with Ni-Mn/SBA-15 catalysts which were synthesized via an wet impregnation method by adding ethylene glycol. All the bimetallic catalysts showed high activity at 773 K as well as that of Ni catalysts. The synthesize procedure provided the small metal particles (< 5 nm) and high dispersion in the SBA-15 supports according to TEM analysis. The supported Ni-Mn catalysts showed high activity because of the synergy effect between Ni and MnOx although the supported Mn catalyst showed low performance.

Keywords: Ethylene glycol assisted method, Biomass gasification, Ni-Mn bimetallic catalyst.

1. Introduction

Ni metal catalysts are promising candidates for the steam reforming of tar. Although the Ni catalysts showed high activity, they are easily deactivated by the carbon deposition on the catalyst surface and sintering of Ni^0 species.[1, 2]

To improve catalytic activity and stability of Ni-based catalysts, most studied have focused on the addition of the second metal and many articles have been published on the use of Ni-based bimetallic in the steam reforming of biomass gasification tar and tar model compounds.[3-6] In general, small Ni particle size and strong metal-support interaction can effectively suppress coking and sintering.[10-12] Therefore, synthesize technique and the choice of support material are also important for obtaining active catalyst.

Only one study have been published about the use of Ni-Mn/Al_2O_3 catalyst in the steam reforming of biomass tar.[7] Therefore, this research aim to develop highly dispersed Ni and Ni-Mn catalysts using ethylene glycol assisted impregnation technique. SBA-15 was used as support to their advantages of high surface area and uniforms pore size. The catalytic activity and selectivity in steam reforming of biomass tar were investigated at low temperature, 773 K.

2. Experimental

The large pore mesoporous SBA-15 support material was synthesized using hexane as a micelle expender, as reported in the literature.[8, 9] The SBA-15 supported monometallic Ni and bimetallic Ni-Mn catalysts were synthesized via an ethylene glycol (EG) assisted impregnation procedure. Totally, 10 wt % of metal loading was chosen in all catalysts. The molar ratio of metal species to EG was fixed 10.

The catalytic steam reforming of sawdust experiments was carried out in a two-stage fixed-bed quartz reactor. Prior to examine the activities, the catalyst was reduced with an H_2/N_2 (30/30 ml/min) mixed gas at 773 K for 1 h. The catalyst bed temperature was maintained at 773 K and sawdust pyrolysis was carried out at 973 K under the 50 ml/min of N_2. The 80 mg/min of steam was directly supplied into the sawdust bed with feeder. The product gases were analyzed by the gas chromatographs (GC). The water gas shift reaction was conducted with catalyst amount of 0.3 g, the CO, and H_2O flow rate was 12 ml/min and 40 mg/min, and the 12 ml/min of N_2 flow at 773 K.

3. Results and discussion

The loading of Ni and Mn on the SBA-15 support decreased the textural properties due to these metals take placed within the porous structure (Table 1). There is no significant peak of metallic and metal oxide in XRD measurement because metal particles were very small and highly dispersed in the SBA-15 supports.[3] This results were agreed by TEM observation (Figure 1-a-d and Table 1).

All Ni-Mn/SBA-15 and Ni/SBA-15 catalysts showed high catalytic activities in the steam reforming of the biomass tar into the gaseous product, C_{GAS}, even at 773 K while the Mn/SBA-15 catalysts exhibited low activity in the tar reforming (Table 2). The Ni-Mn catalysts resulted in higher CO formation and lower CH_4 and CO_2 formation than Ni catalyst because the CO reaction/ water gas shift reaction (WGSR) was decreased by addition Mn metal (Table 2 and Figure 2). If the possibility of WGSR was decreased, the H_2 formation would also be decreased. However, the H_2 gas formation of the Ni-Mn catalysts was maintained the same as the Ni catalyst (Figure 2). It could be suggested that the synenergy effect between Ni and MnO_x maintained the H_2 formation (Figure 3). Therefore, the addition of Mn on the Ni steam reforming catalyst has both promoting and suppressing effects.

Table 1. The physical properties of the catalysts

Material	BET surface area (m^2/g)	Avg. particle size (nm)*
SBA-15	666	-
10Ni/SBA-15	629	2.60
9Ni-1Mn/SBA-15	590	2.53
8Ni-2Mn/SBA-15	573	3.00
7Ni-3Mn/SBA-15	553	4.68

*Measured by TEM

Table 2. The carbon balance in steam reforming and activities of WGSR

Material	C_{GAS} (%)^	C_{CHAR} (%)^	C_{TAR} (%)^	CO conversion (%)#
10Ni/SBA-15	70	30	0	91
9Ni-1Mn/SBA-15	68	30	2	76
8Ni-2Mn/SBA-15	68	31	1	67
7Ni-3Mn/SBA-15	68	29	3	70
10Mn/SBA-15	19	31	50	1.3

^Catalytic steam reforming experimental results calculated by carbon balance equation

Water gas shift reaction experimental results

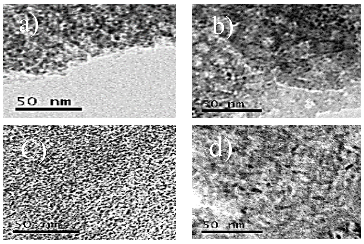

Figure 1. TEM image of the calcined catalysts a)10Ni/SBA-15, b)9Ni-1Mn/SBA-15, c)8Ni-2Mn/SBA-15 and d) 7Ni-3Mn/SBA-15.

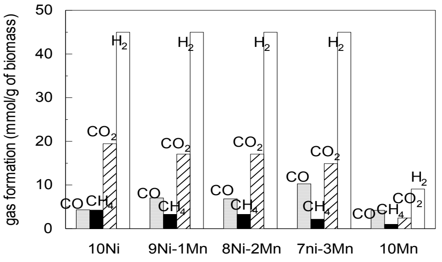

Figure 2. The gaseous product formation amount of supported SBA-15 catalysts; pyrolysis temp., 973 K and catalyst bed temp., 773 K.

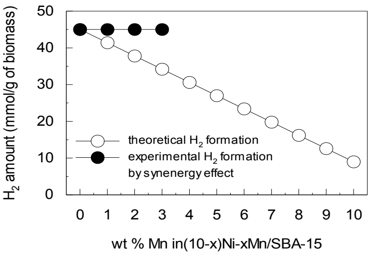

Figure 3. Comparison of H_2 formation by synenergy effect between Ni and Mn metal.

4. Conclusion

The catalysts with small particles and high dispersion were obtained by the ethylene glycol assisted impregnation technique. The Ni/SBA-15 and Ni-Mn/SBA-15 the catalysts showed high catalytic activity even at low temperature, 773 K. The tar conversion activity was slightly decreased in Ni-Mn compared to Ni catalysts because the active site of Ni metal might be reduced by Mn metal addition. The water gas shift reaction was decreased by the Mn metal addition on the Ni metal. The H_2 production was still maintained the same as Ni catalyst by the synenergy effect between the two metals.

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