A structured nickel-based catalyst with high performance and tolerance to coke deposition in naphthalene steam reforming for biomass-gasification process

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Abstract: In order to construct a biomass gasification process, our group developed a catalyst for steam reforming of naphthalene which is main component of tar. The Ni/Al_2O_3 structured catalyst prepared by electroless plating showed high activity and long lifetime even under sever condition. The obtained performance was the world champion data. From physicochemical measurement, such advantage feature was brought about using electroless plating. Namely, a strong interaction was formed between Pd nuclei used in plating and Ni deposited around them, and such interaction formed special facet-surface on deposited Ni particles, which is caused of high performance and tolerance to coke deposition.

Keywords: Naphthalene steam reforming, Structured catalyst, Electroless plating.

1. Introduction

The development of the gasification process of biomass resources is important in ensuring the future energy. Our group now is developing a gasification system of wood chips and agricultural residues combining gasifier and gas engine under the support of MITI program. Figure 1 shows such gasification system. The key point in constructing this gasification system is to efficiently gasify the tar component generated in the gasification process and what kind of powerful catalyst should be developed for that purpose. In the previous study[1)], the Ni/Al_2O_3 structured catalyst prepared by electroless plating had high activity and strong tolerance to coke deposition in methane dry reforming, in which coke deposition is more a problem than steam reforming. Therefore, it is conceivable to apply the Ni/Al_2O_3 structured catalyst for tar reforming in the gasification system.

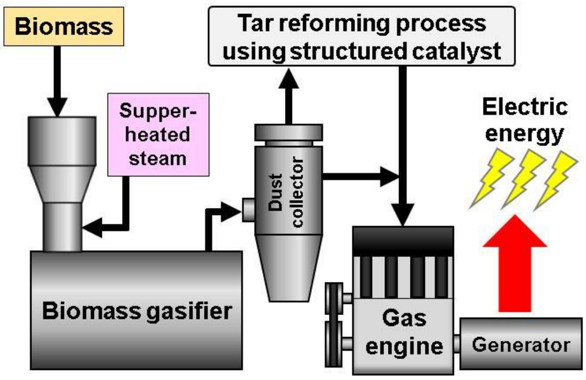

Figure 1. Overview of developing gasification system.

In this study, the reforming property of the Ni/Al_2O_3 structured catalyst for steam reforming of naphthalene (eq.1), which is the main component of tar, was investigated under sever reforming condition.

$$C_{10}H_8 + 10H_2O \rightarrow 10CO + 14H_2 \qquad \Delta H = 1675\ kJ\cdot mol^{-1} \qquad (1)$$

In addition, since it was found that this catalyst exhibited high reforming properties and a long lifetime, its performance factors were investigated from the viewpoint of physicochemical properties.

2. Experimental

The Ni/Al_2O_3 structured catalyst was prepared by electroless plating combining with sol-gel method. After being activated a stainless steel substrate (20 mmϕ x 50 mmL) by HCl aq. at 303 K for 20 min, the aluminum-gel was uniformly coated on the substrate and calcined at 1073 K to form γ-Al_2O_3 layer. The substrate was alternately immersed in $SnCl_2$ and $PdCl_2$ baths at 308 K with 20 times to form Pd nuclei for plating on the Al_2O_3 layer. After reducing Pd nuclei by hydrazine aq. for 15 min, the substrate was immersed in nickel plating bath with $NaBH_4$ as the reducing agent at 328 K for 30 min. $Ni(NO_3)_2$ were used as nickel precursors. The amount of deposited catalyst component, including Ni and Al_2O_3, was about 230 mg.

After being reduced the prepared catalyst using a conventional flow reactor, the raw material (naphthalene: 4.8-9.6×10^{-5} mol/min, H_2O: 7.2-14.2×10^{-4} mol/min, H_2: 5.6-11.2×10^{-4} mol/min, N_2: 1.7-3.4×10^{-4} mol/min) was fed at 700°C or more. The ratio of steam to carbon (S/C) was 1.5.

3. Results and discussion

Fig.2 indicates a high activity (nearly 100%) and a long lifetime (over 50 hours) of the Ni/Al_2O_3 structured catalyst even under sever naphthalene reforming condition. The composition of the product gas at 50 hours was mainly H_2 and CO in both temperature. Also, even if the reforming was repeatedly shut-down and restart with no hydrogen-reduction, the performance of the prepared catalyst was always constant. In steam reforming of naphthalene, there has been no report on catalysts exhibiting such a high stability performance. The prepared catalyst was considered to have high practical utility for the biomass-gasification process.

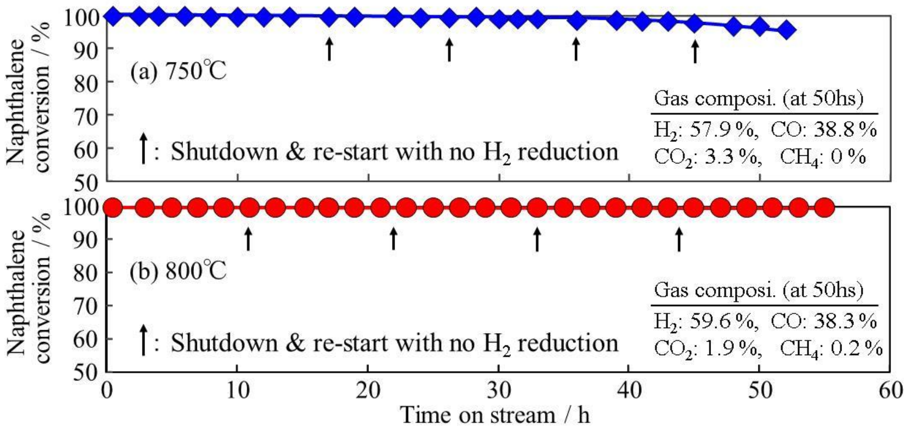

Figure 2. Naphthalene reforming property of the Ni/Al_2O_3 structured catalyst.

Fig.3 represents the XPS spectra of Ni_{2P} for the structured catalysts prepared with different plating times. Such difference in plating time clearly affected the electronic state of nickel component. In the nickel plating process, the anodic oxidation of the reducing agent ($NaBH_4$) was progressed on the Pd nuclei and nickel component was gradually deposited on it. At 30min-plating time, nickel has an oxidative state, which means the electron defect condition and a strong interaction between nickel and palladium components. According to the reference[2], such strong interaction formed a special facet surface on the deposited Ni particles, which is one of the reasons for indicating high performance and tolerance to coke deposition.

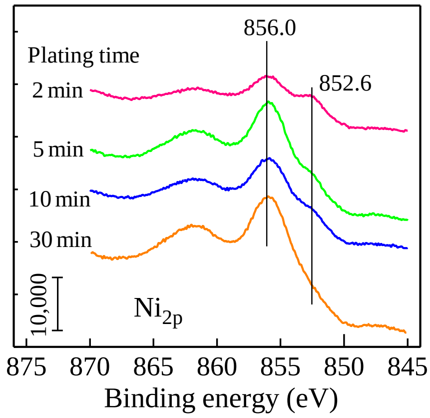

Figure 3. XPS spectra of Ni2p for Ni/Al_2O_3 structured catalyst during the nickel plating.

Furthermore, it was thought that a more high performance reforming catalyst could be prepared by optimizing the electroless plating conditions and adding the second component to this structured catalyst.

4. Conclusions

The structured Ni/Al_2O_3 catalyst prepared by electroless plating exhibited a high activity and long lifetime for steam reforming of naphthalene, which means that it can be used as a catalyst for biomass gasification system. The strong tolerance to coke deposition of this catalyst was brought by the interaction between nickel and palladium components, which was optimized by changing the plating time.

References

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