



Characterization and catalytic performance of hydrotalcite-derived Ni-Cu alloy nanoparticles catalysts for steam reforming of 1-methylnaphthalene

Dalin Li^{a,*}, Miaomiao Lu^a, Kosuke Aragaki^b, Mitsuru Koike^b, Yoshinao Nakagawa^b, Keiichi Tomishige^{b,*}

^a National Engineering Research Center of Chemical Fertilizer Catalyst (NERC-CFC), School of Chemical Engineering, Fuzhou University, Gongye Road No.523, Fuzhou 350002, Fujian, PR China

^b Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

ARTICLE INFO

Article history:

Received 26 November 2015

Received in revised form 22 March 2016

Accepted 24 March 2016

Available online 26 March 2016

Keywords:

Gasification

Tar

Steam reforming

Hydrotalcite-like compounds

Nickel-copper alloy

ABSTRACT

Supported Ni-Cu alloy nanoparticles prepared from Ni-Cu-Mg-Al hydrotalcite-like compounds (HTLcs) with Cu/Ni = 0.25 have been shown to be an active catalyst for the steam reforming of tar derived from the biomass pyrolysis. In the present work, Ni-Cu alloy catalysts with wider compositions of Cu/Ni were characterized and their performances were evaluated in the steam reforming of 1-methylnaphthalene (1-MN), which has lower reactivity than the biomass tar, in order to make the effect of Cu/Ni much clearer. The characterizations with XRD, STEM-EDX, H₂ chemisorption, and FIIR of CO adsorption suggest that the obtained Ni-Cu alloy nanoparticles had uniform composition in the range of Cu/Ni = 0.1–1; the particle size was decreased with the increase of Cu/Ni ratio (ca. 5–7 nm), and Cu tended to be enriched on the particle surface. The HTLcs-derived Ni-Cu alloy catalysts showed a volcano-type dependence of activity on the alloy composition; the highest reforming activity and lower yields of byproducts including benzene, naphthalene, and coke were obtained at Cu/Ni = 0.25. The kinetic study indicates that 1-MN was strongly adsorbed on both the Ni and Ni-Cu catalysts; in contrast, the adsorption of steam was promoted by the alloying of Ni with Cu even in the presence of strongly adsorbed 1-MN. The property of stronger adsorption of steam can be connected to higher reforming activity and lower coke deposition through the dissociative adsorption of steam to supply more adsorbed oxygen species, which enhance the gasification of carbonaceous species.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Gasification is one of the most important technologies for clean and high efficient utilization of solid carbon resources such as coal, petroleum coke, and biomass [1,2]. Gasification is a thermal chemical conversion process producing a fuel gas rich in hydrogen and carbon monoxide. The product gas or synthesis gas (CO + H₂) has great application potentials for electricity generation, hydrogen production, and synthesis of chemicals and liquid fuels. However, the raw product gas from the gasifier contains many contaminants. Particularly, the presence of tar by-product is highly undesired. Tar is a complex mixture of organic compounds,

including monocyclic and polycyclic aromatic hydrocarbons as well as other oxygen-containing hydrocarbons, e.g., benzene, toluene, naphthalene, phenol, etc. [2]. Tar can condense in the gasifier pipe outlets and in particulate filters leading to blockages and filter clogging. It causes further downstream problems and clogs fuel lines and injectors in internal combustion engines. Moreover, tar would cause serious coke deposition on the downstream catalyst if the synthesis gas is used for the production of liquid fuels and chemicals. Therefore, considerable efforts have been devoted to the development of effective methods for tar removal. Among the different methods, the catalytic steam reforming of tar seems to be very promising, since it can convert tar into useful gaseous products, not only improving the synthesis gas quality and overall energy efficiency, but also avoiding the need for the collection and disposal of tar as well as tar pollution [3,4].

Supported metal catalysts including Ni, Co, Fe, and noble metals such as Rh have been widely studied for the steam reforming

* Corresponding authors.

E-mail addresses: dalinli@fzu.edu.cn (D. Li), tomi@erec.che.tohoku.ac.jp (K. Tomishige).

of tar and its model compounds, e.g., benzene, toluene, phenol, naphthalene, and 1-methylnaphthalene (1-MN) [5–12]. Owing to its relatively low cost and high activity, the Ni catalyst has attracted much attention. However, the main problem of Ni catalyst is the deactivation caused by the coke deposition and agglomeration of Ni metal particles. Alloying Ni with other transition metals (Pt, Rh, Pd, Ru, Fe, Co) [6,13–18] has been applied to improve the catalyst activity, stability, and coke resistance. Particularly, alloying Ni with non-precious metals such as Fe [6,14–17] and Co [18] appears attractive, which exhibits better performance than the corresponding monometallic catalysts. Typically, the alloy catalysts were prepared by the impregnation method. However, this method usually gave large metal particles and weak interaction between metal particles and support. Moreover, it may cause large inhomogeneity in the composition of the alloy particles, leading to the formation of alloy particles with different structures such as *fcc* alloy, *bcc* alloy, and/or intermetallic compounds [14,18,19]. Since the catalytic performance of alloy particles are greatly dependent on their structure, composition, and particle size, the preparation of uniform alloy nanoparticles catalyst is critical for the catalytic performance.

Utilization of hydrotalcite-like compounds (HTLcs) as precursor offers a feasible route for the controlled preparation of alloy catalysts [20–22]. HTLcs, also known as layer double hydroxides (LDHs), are a class of anionic clays that consist of positively charged two-dimensional brucite-like sheets in which a fraction of the divalent cations are isomorphously substituted by trivalent cations, together with charge-compensating anions and water in the inter-layer [23]. Owing to their versatility in chemical composition and uniform distribution of cations in the brucite layers, HTLcs have been widely used as precursors of metal catalysts [24–26]. By incorporating Ni²⁺ and Fe³⁺ into the Mg–Al HTLcs, followed by calcination and reduction treatments, we have successfully prepared a well dispersed Ni–Fe alloy catalyst with single phase and rather uniform composition [20,21]. The HTLcs-derived uniform Ni–Fe alloy catalyst showed superior performance for the steam reforming of biomass tar than the Ni–Fe/ α -Al₂O₃ catalyst prepared by the conventional impregnation method in terms of activity, stability, coke resistance and regenerability, demonstrating the advantage of using HTLcs as precursor for tuning the alloy structure and catalytic performance.

Recently, we explored this strategy to prepare a uniform Ni–Cu alloy catalyst from Ni–Cu–Mg–Al HTLcs [27], and the uniform Ni–Cu alloy nanoparticles obtained at Cu/Ni = 0.25 showed high performance in the steam reforming of tar from the biomass pyrolysis. The performance was comparable or even higher than that of HTLcs-derived Ni–Fe alloy catalyst [21]. Therefore, it is important to investigate the structural property and catalytic performance of the HTLcs-derived Ni–Cu alloy catalysts in details. However, regarding the comparison of various Ni–Cu catalysts with different compositions in terms of the catalytic performance, the tar from the biomass pyrolysis is not suitable because of its high reactivity, which makes the performance difference smaller [27]. In order to make the difference clearer, the model substrate with lower reactivity was used in the present work. In the previous reports [10–12], 1-methylnaphthalene (1-MN) has been used as model compound of tar, which is a representative poly-aromatic component of tar and is among the most difficult to convert. The effects of alloy compositions and reaction parameters including Cu/Ni ratio, contact time, reactant partial pressure, and time on stream were investigated and the catalysts before and after reaction were characterized by various techniques. In particular, the utilization of 1-MN enabled the kinetic study, although the kinetic study is difficult in the case of biomass tar due to the mixture of various compounds [27]. The kinetic study can give the information on the adsorption strength of the substrates and their coverage. Based on these results, the

relationship between the alloy structure and catalytic performance was discussed; in particular, the kinetic study made the role of Cu clearer.

2. Experimental

2.1. Catalyst preparation

All the chemicals used in this work were of analytical grade (Wako Pure Chemical Industries). Ni–Cu–Mg–Al HTLcs were synthesized by co-precipitation method as reported previously [27]. In brief, a 100 mL aqueous solution of mixed nitrates (Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Mg(NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O) was dropwise added to 100 mL aqueous solution of Na₂CO₃ under vigorously stirring. The pH of the solution was adjusted with an aqueous solution of NaOH (2 M) and kept constant at 10 ± 0.5. The solid product thus obtained was recovered by filtration followed by washing and drying at 383 K. Ni–Cu/Mg/Al samples were obtained by calcination at 1073 K for 5 h in air to decompose the HTLcs precursor. The molar ratio of (Ni + Cu + Mg)/Al was kept at 3, and the Ni content was fixed at 12.0 wt% as a weight percentage in the calcined sample, whereas the Cu content varied from 1.3 to 13.0 wt% to obtain a molar ratio of Cu/Ni between 0.1 and 1.0. For comparison, two monometallic catalysts, i.e., Ni/Mg/Al and Cu/Mg/Al with 12.0 wt% metal content were also prepared by a similar procedure described above. The detailed chemical compositions of the samples are listed in Table S1 (Supplementary material).

2.2. Catalytic reaction

Steam reforming of 1-MN was conducted in a fixed-bed flow reactor. A quartz tube (inner diameter 4 mm) was used as the reactor. The reaction temperature was monitored with a thermocouple located at the catalyst bed outlet. The catalyst was pre-reduced with a H₂/N₂ (30/30 mL min⁻¹) gas flow at 1073 K for 0.5 h. After the reduction treatment, the reactor was purged with N₂, and the temperature was increased to 1123 K. Subsequently, both steam and 1-MN were introduced to the catalyst bed, which were supplied by two syringe pumps, respectively, followed by vaporization in a heating chamber at 673 K with N₂ as the carrier gas. The effluent gas passed through an iced water condenser loaded with mesitylene to trap 1-MN, naphthalene, toluene, benzene, and other liquid products. The sample of gaseous products was taken by a syringe and analyzed by gas chromatograph (GC). The H₂ concentration was determined by TCD-GC (Molecular sieve 13×), and the concentrations of CO, CH₄, and CO₂ were measured by FID-GC (Gaskuropack 54) equipped with a methanator. The total flow rate of the gaseous products was measured by a bubble flow meter. To determine the concentrations of 1-MN, naphthalene, toluene, and benzene, the trapped solution was analyzed by FID-GC (InertCap 5MS/Sil) using *n*-heptane as an internal standard. After reaction, supplies of 1-MN and steam were stopped, and oxygen was introduced to the catalyst to combust deposited coke on the catalyst. The amount of coke was determined based on the amount of CO₂ and CO formed during the combustion by FID-GC. The carbon balance of residual 1-MN and products (CO, CO₂, C₆H₆, C₁₀H₈, and coke) with respect to the fed 1-MN was 100 ± 5%, which is acceptable within the experimental error. The 1-MN conversion, carbon-based yields, and product selectivities were calculated by the following equations, where the molecular formula represents the amount of each component.

$$1\text{-MN conversion}(\%) = ([1\text{-MN}]_{\text{in}} - [1\text{-MN}]_{\text{out}}) / [1\text{-MN}]_{\text{in}} \times 100\%$$

(1)

Download English Version:

<https://daneshyari.com/en/article/6499127>

Download Persian Version:

<https://daneshyari.com/article/6499127>

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