



Steam reforming of tar derived from lignin over pompom-like potassium-promoted iron-based catalysts formed on calcined scallop shell



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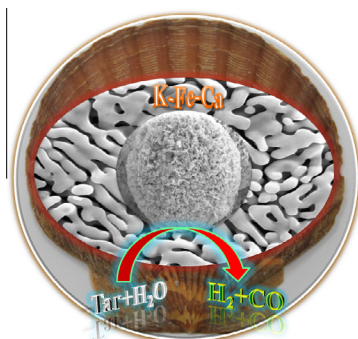
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HIGHLIGHTS

- Pompom-like K-promoted iron-based catalysts were prepared on calcined shell.
- A mechanism for the formation of pompom-like microspheres was proposed.
- An excellent catalytic activity were exhibited for the steam reforming of tar.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to understand the improvement effect of potassium (K) on the catalytic activity of iron-loaded calcined scallop shell (CS) for the steam reforming tar derived from biomass, various K precursors were applied for the catalyst preparation. It is found that pompom-like iron-based particles with a mesoporous structure were easily formed on the surface of calcined scallop shell (CS) when K_2CO_3 was used as K precursor while no such kind of microsphere was formed when other kinds of K precursors such as KOH and KNO_3 were applied. The optimum K-loading amount for the preparation of this catalyst was investigated. Based on the experimental results obtained, a mechanism for the formation of these microspheres was proposed. This pompom-like potassium-promoted iron-based catalyst showed a better catalytic activity and reusability for the steam reforming of tar derived from lignin.

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1. Introduction

Hydrogen production by the gasification of biomass instead of fossil fuel is considered a potentially attractive and alternative

resource to meet the future demands of a hydrogen economy, mainly as the feedstock for fuel cells (Huber et al., 2006; Piatkowski et al., 2011; Trane et al., 2012; Yin, 2012). However, due to a large amount of tar being generated during the gasification process, and the unreformed tar condensing at low temperatures, plugging and corrosion of pipelines can result. It is expected that the tar produced can be completely captured and simultaneously also converted to useful gases such as H_2 , CO and CH_4 in the

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gasification process. Catalytic steam reforming of tar is one of the effective methods for transformation of tar and has been widely investigated (Acharya et al., 2010; Di Felice et al., 2010; Han and Kim, 2008; Li et al., 2009a,b). Various natural mineral catalysts, such as dolomite and olivine, and manufactured catalysts such as Ni, Co, Fe and some noble metals supported on common materials such as Al_2O_3 , MgO, CaO and SiO_2 have been developed for this purpose (Delgado et al., 1997; Di Felice et al., 2011; Li et al., 2009a,b; Sutton et al., 2001; Park et al., 2010; Zhang et al., 2011). In order to promote the conversion efficiency and coking resistance, bimetallic and tri-metallic catalysts were synthesized by addition of other transition metals or rare earth metals such as Pt, Rh, La, or Ce to the above catalysts (Asadullah et al., 2001; Bona et al., 2008; Constantinou and Efstathiou, 2011; Nishikawa et al., 2008; Polychronopoulou and Efstathiou, 2006; Rapagná et al., 2002). In the previous study, Fe-based catalyst was supported on calcined scallop shell (CS) and used for the steam reforming of tar derived from biomass. It was found that the transfer of a small amount of potassium from the biomass to the catalysts promoted the catalytic activity of the original catalyst (Guan et al., 2012). Also, when a small amount of K was doped on CS or Fe-loaded CS using KNO_3 as K-precursor for the steam reforming of tar derived from dealkaline lignin, it was found that hydrogen production rate was greatly increased (Guan et al., 2013). Alkali and alkaline earth elements have been identified to have good catalytic effects on the pyrolysis of biomass (Wang et al., 2010). Several studies also indicated that K plays a key role in the formation of active sites for the surface carbon gasification reaction (Devoldere and Froment, 1999; Hirano, 1986; Jiang et al., 2012; Li et al., 2010; Li and Shanks, 2011; Mckee, 1983; Shekha et al., 2004). In order to investigate in details the effects of K on the catalytic performance for the steam reforming of tar, K-doped Fe-based catalysts were supported on the CS using different K precursors in this study. Interestingly, it was found that pompom-like microspheres with a mesoporous structure were formed on the surface of CS if potassium carbonate (K_2CO_3) was used as the K-precursor. To the best of our knowledge, this is the first report on the preparation of such mesoporous spheres for Fe-based materials via a facile method without any templates. Furthermore, when it was applied for the steam reforming of tar derived from lignin, excellent catalytic activities were observed for the production of H_2 .

2. Methods

2.1. Materials and catalyst preparation

In this study, the catalyst support, i.e., CS, was prepared by calcinations of dried scallop shell chips (Aomori, Japan) with an average size of approximately $4 \times 4 \times 2 \text{ mm}^3$ in air at 800°C for 2 h. 0.2–5 wt% K-doped 2 wt% Fe-based pompom-like catalyst particles were supported on CS by the incipient wetness impregnation method using a mixed aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (WAKO, Japan) and K_2CO_3 (Wako, Japan). After impregnation and aging for approximately 2 h, the slurry was dried overnight at 80°C . Finally, the supported catalysts were calcined in air at 650°C for 3 h before storage and further use. As a reference, KNO_3 (Wako, Japan) and KOH (Wako, Japan) were also used as K precursors. Powders of dealkaline lignin (Tokyo Chemistry Industry Co., Ltd., Japan, pH 4.12) with minor alkaline elements, and alkaline lignin (Kanto Chemical, Japan, pH 9.3) with approximately 0.53 wt% of Na and 0.015 wt% of K were pressed, crushed and sieved to 0.5–1 mm particle size before used.

2.2. Characterization of catalyst

The morphology and elemental mapping of as-prepared catalyst were characterized with a scanning electron microscope (SEM,

SU6600, Hitachi) equipped with energy dispersive spectrometer (EDS). The crystal structure of as-prepared catalyst was determined by X-ray diffraction (XRD 610, Shimadzu, Japan). The radiation used was $\text{CuK}\alpha$ and the operating potential was 30 kV, current 30 mA, and the scanning rate $4^\circ/\text{min}$.

2.3. Catalytic steam reforming experiment

Catalytic steam reforming of tar derived from lignin was performed in a fixed bed reactor with an inner diameter of 19 mm, which was precisely described in our previous study (Guan et al., 2012). 0.3 g of lignin and 4.5 g of catalyst were located separately into the reactor with quartz wool, and the reaction was performed at a stable temperature with a heating rate of $25^\circ\text{C}/\text{min}$. Steam was generated by bubbling of 90°C water ($p_{\text{H}_2\text{O}} = 70 \text{ kPa}$) with $50 \text{ cm}^3/\text{min}$ of Ar gas flow. The tar, derived from the steam pyrolysis of lignin placed on the catalyst, was carried by the Ar gas into the catalyst layer, and reformed with steam over the catalyst. The gases produced were passed through two cold traps and a filter, and collected in a gas bag. The reaction time for all experiments was fixed at 2 h. The gases produced were analyzed using a gas chromatograph (Agilent 7890A GC system).

3. Results and discussion

3.1. Catalyst characterization

During the experiments, it was found that pompom-like particle (Fig. S-1(b) and (c)) was easy to be formed on the surface of 2 wt% Fe-based CS when the loading amount of K was between 0.2 and 2.1 wt% in the case of K_2CO_3 as the precursor. If the loading amount was too high or too low, no pompom-like particle was obtained (Fig. S-1(a) and (d)). As shown in Fig. S-1, one can see that uniform particles with a size of approximately $10 \mu\text{m}$ and a microporous structure were formed on the surface of CS in the case of the loading amount of 0.5 and 1.5 wt% K. For this kind of particle, if the surface morphology was enlarged, it is obvious that the sphere was mainly composed of nanorods as well as nanosheets (Fig. S-2(a)–iv and (b)–iv). With the increase in the concentration of K, the sphere size remained almost unchanged but the porous structure changed to some extent. However, when the K concentration increased higher, pompom-like particle disappeared (Fig. S-1(d)). It is possible that the vigorous hydrolysis of K_2CO_3 in the solution hindered the formation of the sphere particles. Such porous pompom-like morphology is expected to have an advantage if utilized for the adsorption and decomposition of biomass tar. EDS analysis results indicated that the main composition of the pompom-like sphere was Fe element but K element spread over almost the entire CS support (Fig. S-3 in electronic annex of this paper). In the XRD patterns (Fig. S-4 in electronic annex of this paper), similar to iron supported CS, the crystallographic phases of iron oxide and $\text{Ca}_2\text{Fe}_2\text{O}_5$ in K-doped Fe-based catalyst were observed. $\text{Ca}_2\text{Fe}_2\text{O}_5$ may be formed at the interfaces of the pompom-like spheres and CS due to the liberation of Ca^{2+} ions into the alkaline solution, which might play a beneficial role towards providing adhesion and support of the spheres on the surface of CS. However, it is found that the peak strength of $\text{Ca}_2\text{Fe}_2\text{O}_5$ in the product decreased (Fig. S-5 in electronic annex of this paper) with the increase in K concentration as K_2CO_3 used as precursor, and compared with other K precursors, the peak strength of $\text{Ca}_2\text{Fe}_2\text{O}_5$ in the case of K_2CO_3 showed the highest (Fig. S-6 in electronic annex of this paper). On the other hand, as shown in Fig. S-7 (in electronic annex of this paper), when only K or Fe was supported on CS or KNO_3 or KOH was used to replace K_2CO_3 as the K-precursor, no pompom-like sphere was found to be formed on CS. Similarly, if

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