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Hydrogen production via catalytic reforming of the bio-oil model compounds: Acetic acid, phenol and hydroxyacetone

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ABSTRACT

Catalytic reforming of three typical bio-oil model compounds, phenol, acetic acid and hydroxyacetone, has been carried out over a Ni/nano-Al_2O_3 catalyst. Al_2O_3, in the form of nano-rods of length approximately 40 nm, was selected as the catalyst support. The catalyst showed superior performance in terms of activity and stability. The conversions for phenol, acetic acid and hydroxyacetone reached 84.2%, 98.2% and 98.7%, respectively, at the reaction temperature of 700 °C. The corresponding hydrogen yields were 69%, 87% and 97.2%. The catalyst maintained its high reactivity for more than 10 h in the catalytic reforming of three model compounds. The influences of steam to carbon ratio, catalyst loading and Ni content in the catalyst on the reforming performance were also investigated. In addition, the possible decomposition pathways for phenol, acetic acid and hydroxyacetone are proposed.

Introduction

Hydrogen is not only a widely used chemical raw material, but is also important as a clean fuel. It is used in fuel cells and internal combustion engines. Meanwhile, because of the urgent demand for clean energy production, more and more attention is being paid to hydrogen generation from renewable and CO_2-neutral biomass. An interesting and widely studied method is the catalytic reforming of bio-oil, which is produced by the fast pyrolysis of biomass. Due to the easy transportability of bio-oil, it is possible to make the process of hydrogen production by catalytic reforming of bio-oil a more economical and more large-scale process [1–3].

Bio-oil is a mixture of hundreds of components, including low and high molecular weight oxygenated compounds, such as carboxylic acids, aldehydes, ketones, alcohols and phenols [4,5]. This complicated composition led to the steam reforming of crude bio-oil or its fraction often facing severe catalyst deactivation [6]. Therefore, it's necessary to study the individual reforming behavior of the different chemical families in bio-oil. Phenols, acids and ketones are three major chemical families in bio-oil. A comprehensive study of bio-oil

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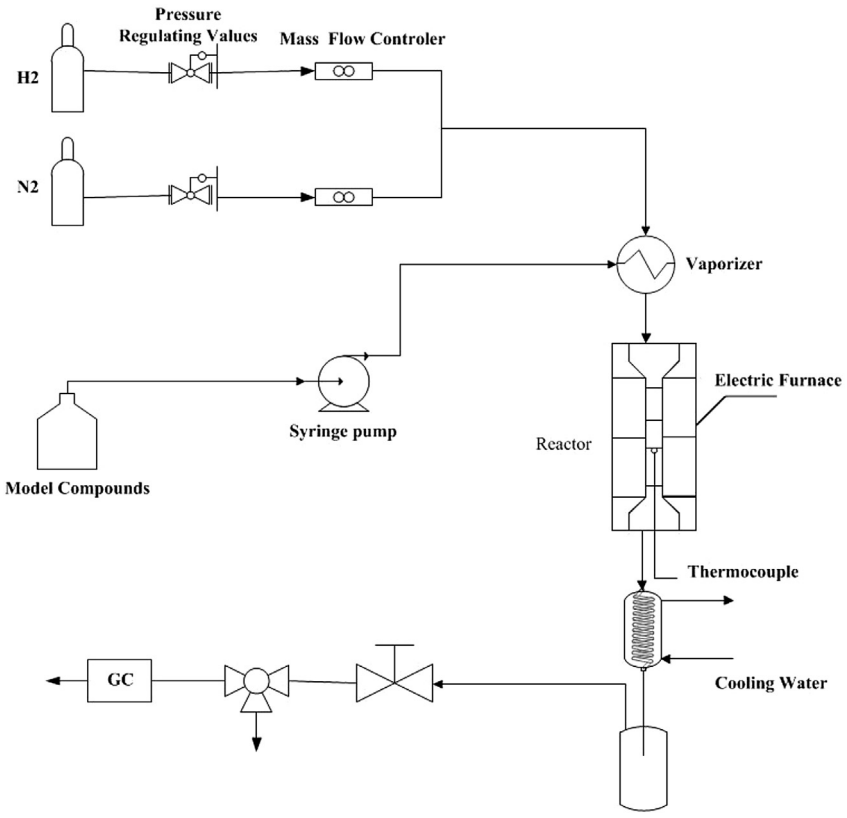

Fig. 1 – Scheme of the experimental system.

from different biomass residues showed phenols, acids and ketones had the proportions of up to about 30 wt%, 19 wt% and 21 wt%, respectively [7]. Therefore, acetic acid (HOAc), phenol and hydroxyacetone are often used as typical model compounds for each group in studies of catalytic steam reforming [8,9].

Nickel-based catalysts have been widely used for reforming of bio-oil, due to their high activity in the decomposition of oxygenated compounds [10–13]. Wang et al. studied HOAc steam reforming over commercial Ni-based catalysts; a mechanism for the combination of thermal decomposition and the steam-reforming reaction was proposed [11]. Bimbela et al. investigated the influence of catalyst reduction time, reaction temperature, catalyst weight/HOAc flow rate ratio and the nickel content on the reaction performance of HOAc reforming over Ni–Al co-precipitated catalysts [14]. Thaicharoensutcharittham et al. compared the catalytic performance of Ni-based catalysts supported on different metal oxides, such as Al_2O_3, Ce_{1-x}–Zr_xO_2, and MgO. They observed that Ce_{1-x}–Zr_xO_2 exhibited high activity and stability for HOAc steam reforming [15]. Phenols are more difficult to be converted than acetic acid, so noble metals are often adopted for its reforming. Rioche et al. found that Rh was more active than Pt and Pd in the catalytic reforming of phenol [16]. Polychronopoulou et al. carried out a series of experiments on the catalytic reforming of phenol over Rh- and Fe-based catalysts

Table 1 – Physical properties of 15%Ni/nano-Al_2O_3 and 15%Ni/γ-Al_2O_3 catalysts.

Catalyst		Reactant	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
Fresh	Ni/γ-Al_2O_3	/	133.7	0.35	10.5
	Ni/nano-Al_2O_3	/	125.3	0.44	14.1
Spent	Ni/γ-Al_2O_3[a]	HOAc	102.5	0.67	20.1
	Ni/nano-Al_2O_3[a]	HOAc	100.4	0.71	25.5
	Ni/nano-Al_2O_3[b]	HOAc	112.7	0.80	28.4
	Ni/nano-Al_2O_3[b]	Hydroxyacetone	106.4	0.72	26.9
	Ni/nano-Al_2O_3[b]	Phenol	95.6	0.59	24.8

[a] Reforming condition: $T = 500$ °C, $p = 1$ atm, S/C = 1, WHSV = 6 h^{-1}, 1 g catalyst.
[b] Reforming condition: $T = 700$ °C, $p = 1$ atm, S/C = 9.2, WHSV = 3 h^{-1}, 1 g catalyst.