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Hydrogen production by sequential cracking of biomass-derived pyrolysis oil over noble metal catalysts supported on ceria-zirconia

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Abstract

Conversion of crude pyrolysis bio-oil for H_2 production is investigated using a sequential process which alternates (i) cracking reaction steps, during which the bio-oil is converted to syngas and carbon stored on the catalyst and (ii) regeneration steps allowing to combust coke under an air flow. The performances of Pt and Rh catalysts supported on ceria-zirconia in powder form or deposited on cordierite monoliths are comparatively studied. From these data and calculated thermodynamic equilibrium, the co-existence of thermal and catalytic processes is demonstrated. A stable hydrogen productivity up to ca. 18 mmol of H_2 g^{-1} of bio-oil (∼50% H_2 in the gas stream) with a minimized methane formation (ca. 6%) is obtained with the monolith configuration. Both Pt and Rh-based catalysts allow a good control of carbon formation, the coke being fully combusted during the regeneration step. Slow deactivation phenomena and selectivity changes along time on stream, mostly observed for platinum powder samples, are related to changes in catalyst structure and to the peculiar role of oxygen stored in the zirconia-ceria support. The heat balance evaluation of the sequential cracking/regeneration cycle shows that the process could be auto-thermal, i.e., minimizing the energy input, being competitive with conventional steam-reforming process under the same operating temperature.

Keywords: Hydrogen production; Pyrolysis bio-oil; Catalytic cracking and steam reforming; Pt; Rh; Ceria-zirconia; Monolith

1. Introduction

Within the perspective of using hydrogen as a prominent energy carrier, a crucial issue is to find alternative production technologies based on other resources than fossil fuels. Besides water hydrolysis, still too energy demanding, using biomass as renewable feedstock would strongly contribute to decrease green house emissions, since the CO_2 balance is neutral in this case. From a technical point of view, biomass resources (energy crops, agricultural residues, organic, forestry, industrial or municipal wastes) can be transformed into sustainable hydrogen by thermo chemical processes like gasification and pyrolysis [1–3], or biological processes like bio-photolysis, photo-fermentation or dark fermentation [4].

Among these various strategies, a lot of interest was devoted in the last decade to bio-oils, obtained by fast pyrolysis of biomass, as intermediate feedstock [5]. Bio-oils exhibit a complex composition with more than 200 different compounds, including acids, alcohols, aldehydes, ketones as well as lignin derived oligomers emulsified with water [5,6]. Compared to other routes of biomass valorization, bio-oils offer a high flexibility in storage and transportation, which increases the economical efficiency with respect to its production and utilization [4,7].

Bio-oils can be treated directly as a crude feedstock [8] or using specific fractions. Thus, by adding water, bio-oils split up into two immiscible phases: (i) an aqueous phase containing carbohydrates-derived compounds and some light oxygenated compounds, which can be steam reformed to hydrogen and (ii) a hydrophobic phase formed mainly by aromatic and lignin derivatives [6]. Direct feeding of the crude bio-oil into a reformer reactor would avoid this primary separation processes, improving the overall energy yield. However, handling this

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crude feedstock is not straightforward, since bio-liquids are highly unstable upon heating and polymerize around 80–90 °C.

Up to now, most of the published studies have been limited to the catalytic steam reforming (SR) of oxygenated compounds such as acetic acid, hydroxy-acetaldehyde, ethanol, acetone, phenol, cresol or guaiacol among others, used as model compounds of bio-oils [9–17]. For catalytic processes, Ni-based materials have been mainly used [9,11–13], whereas only a few examples considering noble metals have been reported until now [14,15]. For the studies dedicated to SR of the water-soluble fraction of bio-oil, an hydrogen productivity close to 1.7 mmol $H_2\ g_{cat}{}^{-1}\ min^{-1}$ was reported over Ni/α-AlO_3 [6]. In the case of aqueous phase reforming of biomass-derived sugar type molecules (glucose and glycerol), a productivity close to 0.7 mmol $H_2\ g_{cat}{}^{-1}\ min^{-1}$ was reached in the presence of Pt/α-Al_2O_3 at temperatures below 265 °C [18], which is comparable to the performance achieved by enzymatic decomposition of sugars [19].

Recently, Rioche et al. [20] have reported the use of a crude bio-oil feedstock for catalytic steam reforming, using noble metal-based catalysts supported on alumina and on ceria-zirconia materials. Higher H_2 yields were obtained with ceria-zirconia supported catalysts, indicating that the support plays an important role in the catalytic activity. In all these studies, the deactivation of the catalytic systems by carbon deposition was a major drawback to be solved for any process development.

As an alternative to continuous steam reforming of oxygenated compounds aiming at a better management of carbon deposition, the sequential cracking/reforming process using fast pyrolysis crude bio-oil has been investigated in our laboratory [21]. This process alternates (i) a cracking reaction step in which the bio-oil is transformed into a gas mixture containing H_2, CH_4, C_{2+}, CO and CO_2 and (ii) a regeneration step allowing the combustion of the coke deposited during the cracking step. Ni-based catalysts have proved their good activity and stability in this sequential process [21].

In the present paper, the investigation of the sequential cracking/reforming of a crude bio-oil was continued, to get a better understanding of the complex mechanisms involved and to evaluate the impact of reactor configuration on performances. For this purpose, the specific role of the catalyst was evaluated by comparing carefully the conversion, selectivity, carbon, and oxygen balances either in the absence (thermal decomposition) or in the presence of catalysts. The thermodynamic equilibria, never reported before for crude bio-oils, were also calculated and compared to the experimental data. The impact of reactor/catalyst configuration was evaluated by testing the catalysts either as powders or supported onto a cordierite monolith. These materials were characterized before and after reaction.

Platinum and rhodium catalysts supported on ceria-zirconia materials were selected as active catalytic phases, taking into account (i) the specificity of noble metals for minimizing coke formation and (ii) the capacity of ceria-zirconia support to meet the requirements of unsteady-state redox processes [22,23]. The heat balance of the sequential cracking/regeneration cycle was calculated in order to assess the possibility to run this process in an auto-thermal way. The sequential cracking process has been compared with continous steam reforming performed on the same catalytic systems, in terms of hydrogen productivity and gaseous products distribution.

Table 1
Standard composition range of a bio-oil obtained by fast pyrolysis of beech wood residues

Compound type	Standard composition range (wt.%) [5]	Selected model compounds	Simulated composition (wt.%)[a]
Acids	15–25	Acetic acid	20
		Propanoic acid	3
		Pentanoic acid	2
Esters	1–3	Methylformate Butyrolactone	2
			1
Alcohols	2–6	Methanol	2.5
		Ethanol	1.5
		Ethylene glycol	2
Ketones	2–4	Acetone	3
		Butanone	1
Aldehydes	10–20	Acetaldehyde Pentanal	11
		Ethanedial	1
			5
Phenols and substituted aromatics	2–6	Phenol	4
		Dimethylphenol	1
		Ethylbenzene	2
		Dihydroxybenzene	3
Furfurals	2–6	Furan	6
Water	~30	Water	29

[a] Estimated values used for thermodynamic equilibrium calculation.