Catalytic removal of oxygen from biomass-derived syngas

Qiangu Yan [a], Caixia Wan [a], Jason Street [a], David W. Yan [b], Jun Han [a,c], Fei Yu [a,*]

[a] Department of Agricultural & Biological Engineering, Mississippi State University, Mississippi, MS, USA
[b] The Mississippi School for Mathematics and Science, 1100 College St, Columbus, MS, USA
[c] Hubei Key Laboratory of Coal Conversion and New Materials, Wuhan University of Science and Technology, Wuhan 430081, PR China

HIGHLIGHTS

- O_2 in bio-syngas was selectively removed by the Pt, Pd, and Cu catalysts.
- O_2 was completely converted by the Pt and Pd catalysts at lower temperatures.
- The Pd catalyst was most active on O_2 conversion at low temperature (<75 °C).
- The Cu catalyst was most sensitive to gas hourly space velocity (GHSV).
- CO_2 and moisture in bio-syngas reduced O_2 conversion by all catalysts.

ARTICLE INFO

ABSTRACT

Selective oxygen (O_2) removal from wood-derived syngas was investigated over three types of ceria-modified alumina supported metal catalysts (i.e., Pt, Pd, and Cu). Complete O_2 removal was observed with the Pt and Pd catalysts at a lower temperature than with the Cu catalyst. Gas hourly space velocity (GHSV) was another critical parameter affecting O_2 removal, substantially reducing O_2 conversion by all three catalysts at 4000 h^{-1} or above. The Cu catalyst appeared to be most sensitive to GHSV. Among three catalysts, the Pd catalyst had the best performance on O_2 removal. In addition to reaction conditions, CO_2 and water vapor in the syngas also influenced O_2 removal, both of which had adverse effects on O_2 conversion. Stability tests indicated that both Pt and Pd catalysts were quite stable over a 300 h testing period while the Cu catalyst was deactivated after 50 h and regenerated by elevating reaction temperature.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass-derived fuels are becoming more popular due to national security and environmental issues associated with the use of fossil fuels. Currently, biomass gasification followed by catalytic conversion has been considered one of the best developed and technically proven technologies for converting biomass to biofuels (Demirbas, 2009; Haro et al., 2013; Woolcock and Brown, 2013). Raw syngas obtained from biomass gasification is primarily comprised of CO and H_2. This gas also contains impurities, such as tars, NH_3, H_2S, and O_2, which can poison Fischer–Tropsch synthesis (FTS) catalysts and thus reduce syngas conversion efficiency (Leibold et al., 2008; Street et al., 2012). Therefore, these impurities must be removed before biomass-derived syngas (bio-syngas) can be used as a feedstock gas for catalytic conversion. Among syngas impurities, O_2 has been found to be one of the most toxic compounds to FTS catalysts, especially iron and cobalt-based catalysts

(Bartholomew, 2012). O_2 can temporarily or permanently deactivate an FT catalyst even at a trace level. Frequent regeneration of FT catalysts not only increases the difficulty of operation but also significantly increases the associated costs (Stelmachowski and Nowicki, 2003). As raw bio-syngas generally contains a significant amount of O_2 (~1%), efficient O_2 removal is particularly important for its downstream FTS process (Yan and Yu, 2012; Yan et al., 2013).

The primary O_2-removal techniques include catalytic oxidation, adsorption/absorption, and combustion (Seshan and Sharma, 1993; Wang et al., 2004). The most efficient and widely used method for O_2 removal is catalytic oxidation, especially when H_2 and/or CO exist in the gas stream. The oxidation catalysts must be highly active to reduce the O_2 level in the syngas to less than 10 ppm before going through the FTS process (Wang et al., 2004). Transitional metal catalysts, including both precious and non-precious metals, have been extensively studied for catalytic O_2 removal (Seshan and Sharma, 1993). A large variety of support materials (e.g., CeO_2, Al_2O_3, and SiO_2) with different redox, acidic and basic properties have been investigated as the O_2-removal catalyst supports.

---

* Corresponding author. Tel.: +1 662 325 0206; fax: +1 662 325 3853.
  E-mail address: fyu@abe.msstate.edu (F. Yu).

Table 1
Physical property of the catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Metal dispersion
γ-Al_2O_3	252	0.95	10.5	–
CeO_2/γ-Al_2O_3	193	0.73	8.2	–
$Pt/CeO_2/Al_2O_3$	185	0.50	7.5	90.3%
$Pd/CeO_2/Al_2O_3$	187	0.49	7.2	87.6%
$Cu/CeO_2/Al_2O_3$	129	0.31	4.7	13.2%

Ceria supports and its modified supports are typically superior to other supports as they can act as O_2 buffers and are capable to feed the metal with O_2 under O_2-deficient conditions (Wang et al., 2004).

Currently, catalytic O_2 removal has been studied mostly for combustible gases, such as H_2 and CO (Seshan and Sharma, 1993) but rarely for syngas (Wang et al., 2004). There are no research efforts reported for O_2 removal from bio-syngas. Efficient conversion of bio-syngas is closely dependent on its impurity levels. Since FTS catalysts are highly sensitive to the O_2 level in the syngas, it is particularly important to remove O_2 while minimizing H_2 and CO consumption. Therefore, we aimed to develop a catalytic process for selective O_2 removal from the bio-syngas by ceria modified alumina supported metal-based catalysts. The effects of catalytic reaction conditions and feed gas composition on O_2 conversion were investigated. Performance of different metal catalysts was also compared.

2. Methods

2.1. Catalyst preparation

Active metal/CeO_2/Al_2O_3 catalysts were prepared through the stepwise impregnation method. γ-Alumina (75 g) was first impregnated with 15 ml 2.5% $Ce(NO_3)_3 \cdot 6H_2O$ solution, and then dried at 120 °C overnight followed by calcinating at 550 °C for 6 h. Ten grams of the above prepared ceria modified γ-Alumina (CeO_2/Al_2O_3) support were impregnated with 5 ml 4.2% H_2PtCl_6, 4.1% $Pd(NO3)_2 \cdot 2H_2O$, and 31% $Cu (NO_3)_2 \cdot 3H_2O$ solutions, respectively, to obtain 1% $Pt/CeO_2/Al_2O_3$, 1% $Pd/CeO_2/Al_2O_3$ and 8% $Cu/CeO_2/Al_2O_3$. The Pt and Pd catalysts were dried at room temperature overnight followed by calcining at 550 °C for 3 h, while the Cu catalyst was dried at 120 °C overnight followed by calcining at 550 °C for 6 h.

2.2. Characterization of the catalysts

The surface areas and pore volume/sizes were measured via N_2 adsorption/desorption using a surface area analyzer (Autosorb-1C, Quantachrome). Samples were prepared by degassing at 300 °C overnight. Data were analyzed using the Brunauer–Emmett–Teller (BET) theory. Metal dispersion of both Pt and Pd catalysts was determined via H_2 chemisorption using a surface area analyzer (Autosorb-1C, Quantachrome). The catalyst ($\sim$1.0 g) was reduced in a quartz tube (I.D.=10 mm) under a H_2 flow with 15 ml/min at 300 °C for 2 h and then cooled to 30 °C for the H_2 chemisorption measurement. The dispersion of the Cu catalyst was measured

Table 2
Syngas composition monitored throughout the gasification process.

Time (min.)	CO (%)	CO_2 (%)	CH_4 (%)	H_2 (%)	O_2 (%)
0	0	0	0	0	21
20	0	0	0	0	21
40	10	11.5	0.4	4.2	3.8
60	15.2	11.8	1.1	7.3	1.7
80	20.7	11.8	1.9	15	0.95
100	22.5	11.8	2.5	17.8	0.50
120	21.8	12.8	2.9	18.7	0.47
140	21.6	13.2	2.8	19.2	0.47
160	22.1	13.1	2.6	19.1	0.45
180	23.6	12.7	2.8	20.1	0.46
200	21.6	14.1	3.5	19.4	0.43
220	21.9	13.1	2.7	19.2	0.41
240	23.5	12.1	2.3	18.8	0.42
260	23.9	12.3	2.5	18.7	0.43
280	23.1	12.7	2.4	19.1	0.40
300	22.9	12.7	2.4	18.9	0.38
320	22.7	13.7	2.9	19.5	0.40
340	22.7	12.8	2.5	19	0.37
360	22.6	12.1	2.3	19	0.38
380	22.5	12.9	2.6	19.3	0.36
400	22	13.4	3	19.6	0.38
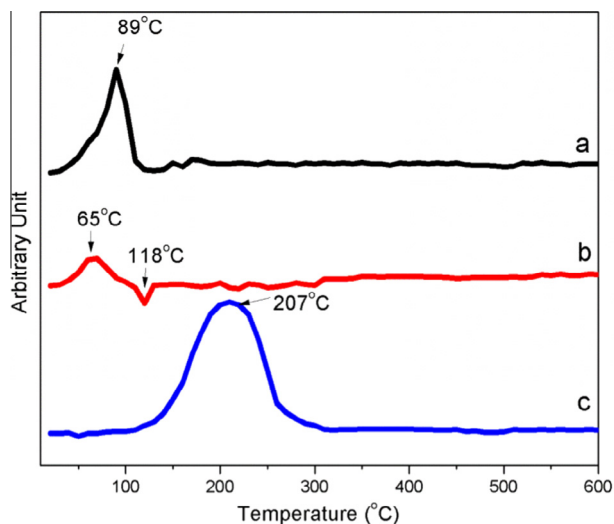
Fig. 1. TPR profiles of the Pd (a), Pd (b), and Cu (c) catalysts.
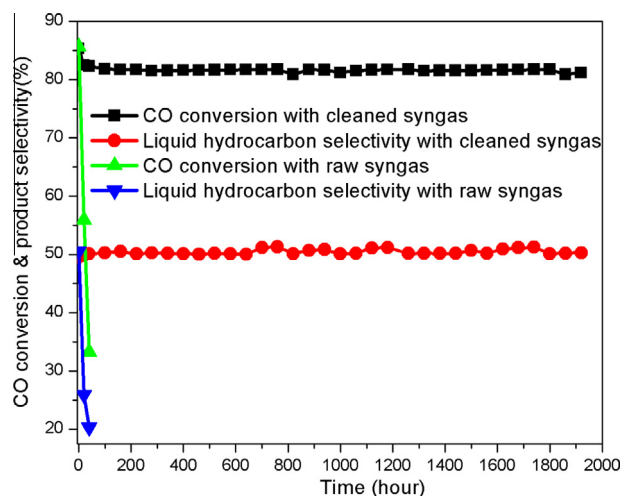
Fig. 2. Influence of oxygen on syngas conversion.