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## Catalysis Communications



### Short Communication

# Conversion of biomass-derived butanal into gasoline-range branched hydrocarbon over Pd-supported catalysts

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#### ARTICLE INFO

Article history: Received 4 August 2011 Received in revised form 19 September 2011 Accepted 19 September 2011 Available online 28 September 2011

Keywords: Biomass-derived butanal Heterogeneous catalysis C–C coupling Hydrodeoxygenation Pd-supported catalysts

1. Introduction

#### ABSTRACT

For production of gasoline-range branched hydrocarbon from butanal, Pd catalysts supported on different metal oxides were applied. Among the prepared catalysts, Pd/ZrO<sub>2</sub> showed the complete butanal conversion with the formation of  $C_7$ -to- $C_9$  branched hydrocarbon (75% yield). Additionally, the ratios of O/C and straight-chain to branched hydrocarbon (*n*-*C/br*-C) were found to be 0.005 and 0.17, respectively. This indicates that an adequate combination of Pd dispersion and amphoteric ZrO<sub>2</sub> character promoted hydrodeoxygenation, C–C coupling and isomerization reactions. Consequently, both Pd dispersion and acid–base properties of supports are suggested to play a pivotal role in producing gasoline-range hydrocarbon at a high yield.

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In recent years, an efficient pathway to convert renewable biomass sources into fuels and chemicals has been studied in the field of catalysis, because the development of such a catalytic process is a stringent challenge due to complexity of the major biomass components with higher oxygen functionalities [1]. Particularly, the practically feasible approach is required to simultaneously achieve lower O/C and higher H/C ratios close to those of conventional fossil fuels. However, this ultimate goal cannot be accomplished only using direct fermentation into bio-alcohols, because the product yield and the energy ratio (defined as (heating value of alcohol + other fuel or power export)/(fossil fuels input – process co-products)) are not satisfactory, and the O/C ratios of alcohols (0.5 for ethanol and 0.25 for butanol) are still far from that of current gasoline. Indirect fermentation was hence suggested to afford about 50% improved yield of alcohols than direct fermentation [2,3]. This process consists of three steps, such as anaerobic fermentation to carboxylic acids, their condensation to esters and subsequent hydrogenolysis to alcohols. However, since this strategy is also targeted at bioalcohols, additional endeavor to decrease the O/C ratio would be necessary.

In this work, a series of C–C coupling and hydrodeoxygenation reactions in a single catalytic system has been conducted for producing gasoline-range hydrocarbon from butyraldehyde (butanal). Typically, butyric acid, produced through anaerobic digestion of sugars [4,5], is catalytically converted into butanal which is further used as a raw material for self-aldol condensation to 2-ethylhexanal (O/C and H/C ratios of 0.125 and 2, respectively) and subsequent hydrodeoxygenation reactions. This is in accordance with the recent focus of study on C–C coupling (ketonization and aldol condensation) [6–8] for the purpose of converting biomass-derived oxygenated compounds into fuel-grade hydrocarbon. When our strategy would be successful, liquid products obtained are comprised of a majority of hydrocarbon with 4–12 carbon atoms per molecule as well as little oxygenate compounds, and, in turn, their O/C and H/C ratios become close to those of current liquid fuels including gasoline. Here, it should be emphasized that the formation of branched (*br*-C), rather than straight-chain (n-C), hydrocarbon is desired, due to their high research octane number.

Since the catalytic reduction of butyric acid to butanal was well documented in previous reports [9,10], our effort has mainly been devoted to demonstrating the one-pot conversion of butanal via aldol compounds into fuel-grade products. Pd was hence chosen as an active metal, because Pd catalysts are commonly used for condensation/coupling reactions [7,11,12], and also promote the hydrogenation of oxygenated compounds [13,14]. The other issue in catalyst development is to find an appropriate support for the desired conversion, because acidic/basic properties of supports would dominantly govern the catalytic activity and product distribution in the aldol condensation reaction [15,16]. Additionally, balancing the contributions given by metal and support would be crucial in controlling the relative rates of C–C coupling and C–O cleavage. Thus, six supports with different acidities (or basicities), such as CeO<sub>2</sub>, MgO, MgZrO<sub>3</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>– Al<sub>2</sub>O<sub>3</sub>, were utilized for Pd loading.



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#### 2. Experimental

#### 2.1. Catalyst preparation

Pd-supported catalysts with the nominal Pd loading of 0.1 wt.% were prepared via an incipient wetness impregnation method with an amount of aqueous Pd(II) nitrate hydrate solution onto CeO<sub>2</sub> (Sigma-Aldrich; BET area =  $42 \text{ m}^2/\text{g}$ ), MgO (Sigma-Aldrich; BET area =  $57 \text{ m}^2/\text{g}$ ), MgZrO<sub>3</sub> (Sigma-Aldrich; BET area =  $45 \text{ m}^2/\text{g}$ ), ZrO<sub>2</sub> (Sigma-Aldrich; BET area =  $30 \text{ m}^2/\text{g}$ ), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich; BET area =  $124 \text{ m}^2/\text{g}$ ). The prepared catalysts were then dried at 393 K overnight and calcined in air at 773 K for 2 h.

#### 2.2. Catalyst characterization

In order to measure the Pd loading in the prepared Pd-supported catalysts, the elemental analysis (EA) was carried out using a Varian 710–ES. Also, Pd dispersion was determined by CO chemisorption at 323 K using a BEL-CAT instrument (BEL Japan, Inc.) equipped with a thermal conductivity detector (TCD), where the stoichiometry factor between Pd and adsorbed CO is assumed to be 0.6 on the basis of previous reports [17,18]. Typically, the prepared catalyst (ca. 0.1 g) was reduced in H<sub>2</sub> at 623 K for 1 h and then purged in He at 623 K for 30 min. After cooling to 323 K, a pulse chemisorption was started.

CO<sub>2</sub> and NH<sub>3</sub> temperature-programmed desorption (TPD) experiments were carried out using the same instrument as above. In a typical experiment, about 50 mg of prepared catalyst was loaded and reduced in H<sub>2</sub> at 623 K for 1 h. The reactor was then purged in He at 623 K for 30 min and cooled to 313 K for CO<sub>2</sub> adsorption or to 473 K for NH<sub>3</sub> adsorption. After exposure of the reduced catalyst to a flow of 5.98% CO<sub>2</sub>/He or 5% NH<sub>3</sub>/He (50 ml/min) for 1 h, residual gases was removed by purging pure He for 1 h at 313 K for CO<sub>2</sub> or at 473 K for NH<sub>3</sub>. TPD profiles were then obtained by ramping the temperature at a heating rate of 5 K/min under pure He (50 ml/min) to 1073 K for CO<sub>2</sub>-TPD or to 1173 K for NH<sub>3</sub>-TPD. The quantitative amount of adsorbed CO<sub>2</sub> or NH<sub>3</sub> was measured by comparison of desorption peak areas with the calibration value calculated from a pulse of a known volume (sampling  $loop = 500 \mu l$ ) of the studied gas. This procedure was repeated 5–10 times until the calibration value falls within 2% error. This procedure was provided by BEL Japan, Inc., which was stated in the previous work reported by Bravo-Suárez et al. [19].

#### 2.3. Activity test

The catalytic reaction to convert butanal into fuel-grade compounds was conducted in a stainless steel reactor (10 mm i.d. and 120 mm length), where the calcined catalyst (2.54 mL in all cases) was loaded in the middle. Prior to the activity test, the catalyst was reduced in a flow of H<sub>2</sub> at 623 K for 2 h. The reaction system was pressurized to 10 bar with H<sub>2</sub> or N<sub>2</sub> and stabilized for 1 h at 673 K. This reduction is inevitable prior to the supply of the reactant for the reaction, though Pd sintering takes place in a certain degree (the decrease of Pd dispersion was observed to be 3–4% in our work). Then, the reactant was fed to the catalyst bed using an HPLC pump, where the molar ratio of  $H_2$  or  $N_2$  and reactant was 6. In order to maintain the reactant to be a vapor phase, the flow line between the pump and reactor inlet was kept constant at 473 K. In all activity tests, the liquid hourly space velocity (LHSV) and gas hourly space velocity (GHSV) were fixed at 1.2 and 2049  $h^{-1}$ , respectively. During the catalytic run, gaseous product was periodically analyzed using an online GC equipped with TCD and FID installed with Carboxen 1000 and HP-PLOT/Al<sub>2</sub>O<sub>3</sub> columns, respectively. Finally, liquid product collected in the separator was analyzed using a GC equipped with FID and MS installed with HP-5 capillary column. The conversion of butanal was determined by the difference of butanal concentration between reactor inlet and outlet, while the selectivity and yield for a given carbon species (i) were calculated as follows:

 $= \frac{(R_{i-\text{outlet}} \times N_i)}{(R_{\text{butanal-reacted}} \times N_{\text{butanal}}) \times 100}$ Carbon yield (%) =  $(R_{i-\text{outlet}} \times N_i)/(R_{\text{butanal-inlet}} \times N_{\text{butanal}}) \times 100$ O/C(mol/mo) and H/C(mol/mol)

$$= \sum (R_{i-\text{outlet}} \times M_{i,0 \text{ or } H}) / \sum (R_{i-\text{outlet}} \times N_i)$$
  
$$n - C/br - C(\text{mol}/\text{mol}) = \sum (n - R_{i-\text{outlet}} \times N_i) / \sum (br - R_{i-\text{outlet}} \times N_i),$$

where *R*, *N* and *M* represent the molar flow rate, the carbon number of a given species (*i*), and the oxygen or hydrogen number of a given sepecies (*i*), respectively. In the case of  $n-R_{i-oulet}$  and  $br-R_{i-outlet}$ , both oxygenated hydrocarbon and hydrocarbon are included. All catalytic data shown in this study were obtained at the reation period of 4 h, becuase the conversion of butanal and the carbon selectivities of carbon species obtained over all Pd-supported catalysts were almost unchanged up to the reaction period of 10 h. This implies that Pdsupported catalysts are durable for the convesion of butanal into fuel-grade compounds.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

Based on the Pd loading measured by ICP analysis (wt.%) and the CO uptake by CO chemisorption ( $\mu$ mol/g<sub>cat</sub>), the Pd dispersion (%) was calculated (Table 1): as a result, it decreased in the order of Pd/CeO<sub>2</sub>>Pd/Al<sub>2</sub>O<sub>3</sub>>Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>>Pd/ZrO<sub>2</sub>>Pd/MgZrO<sub>3</sub>  $\approx$  Pd/MgO (from 44.7% to 11.7%). In consideration of both the Pd loading and the BET area of the supports, the Pd dispersion of Pd-supported catalysts except Pd/CeO<sub>2</sub> appeared to be fairly reasonable. In the case of Pd/CeO<sub>2</sub>, an over-estimation of Pd dispersion is possible due to the formation of surface carbonate species on CeO<sub>2</sub> [20] and/or the reduction of surface Ce<sup>4+</sup> into Ce<sup>3+</sup> by hydrogen spillover taking place at the interface of the metal and the support [7,21].

Based on the results reported previously [7,22-25], NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD profiles shown in Fig. 1 were divided into three and two distinct regions, respectively: in the case of former profiles, weak and strong NH<sub>3</sub> adsorption sites were separated at 800 K [22,23], while the latter profiles represented weak (340-500 K), medium (500-700 K) and strong (above 700 K) CO<sub>2</sub> adsorption sites [7,24,25]. A quantitative number of acid and base sites are summarized in Table 1, where the unit is µmol/g<sub>cat</sub>. As a result, Pd catalysts supported on MgZrO<sub>3</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> showed the surface acidity, whereas those on CeO<sub>2</sub>, MgO, MgZrO<sub>3</sub> and ZrO<sub>2</sub> exhibited the basic property. Particularly, the addition of ZrO<sub>2</sub> into MgO increased the total amount of acid sites to 163 µmol/g<sub>cat</sub>, and decreased the total amount of base sites from 519 to  $422 \,\mu mol/g_{cat}$ . In the case of Pd/ZrO<sub>2</sub> catalyst, the total amounts of acid base sites were found to be 198 and 273  $\mu$ mol/g<sub>cat</sub>, respectively, where the strong NH<sub>3</sub> and CO<sub>2</sub> adsorption sites were 117 and 0 µmol/g<sub>cat</sub>, respectively. Furthermore, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts mainly contained acid sites, even if the former showed a weak basic character. It should be noted here that Pd/ZrO<sub>2</sub> and Pd/MgZrO<sub>3</sub> catalysts contained both surface acidity and basicity. This implies that the amphoteric property of the two catalysts lead to higher activities on dehydration, isomerization and aldol condensation reactions by acid and/or base sites.

#### 3.2. Catalytic activity of Pd-supported catalysts

Table 2 summarizes the reaction results obtained over Pd-supported catalysts at 673 K, 10 bar  $H_2$ , and 1.2  $h^{-1}$  LHSV. Pd/CeO<sub>2</sub> catalyst totally converted butanal into gas-phase products including CO and C<sub>4</sub>- (C<sub>3</sub>H<sub>8</sub>, and C<sub>3</sub>H<sub>6</sub>), due to promoted C-C cleavage (i.e.,

Table 1
Quantification of metal (CO), acid (NH <sub>3</sub> ) and base sites (CO <sub>2</sub> ) of Pd-supported catalysts.

Catalyst Pd loading (wt.%)	Pd loading	CO uptake	Pd dispersion <sup>a</sup>	TPD-NH <sub>3</sub> ( $\mu mol/g_{cat}$ )		TPD-CO <sub>2</sub> (µmol/g <sub>cat</sub> )			Total acid sites/total
	(µmol/g <sub>cat</sub> )	(%)	800 K>T	800 K <t< th=""><th>500 K&gt;T</th><th>500<t<700 k<="" th=""><th>700 K<t< th=""><th>base sites</th></t<></th></t<700></th></t<>	500 K>T	500 <t<700 k<="" th=""><th>700 K<t< th=""><th>base sites</th></t<></th></t<700>	700 K <t< th=""><th>base sites</th></t<>	base sites	
Pd/CeO <sub>2</sub>	0.09	2.26 <sup>b</sup>	44.7 <sup>b</sup>	0	0	92	32	170	0/294
Pd/MgO	0.08	0.55	12.3	0	0	67	182	270	0/519
Pd/MgZrO <sub>3</sub>	0.09	0.60	11.7	69	94	185	120	117	163/422
Pd/ZrO <sub>2</sub>	0.11	1.05	16.8	81	117	205	68	0	198/273
$Pd/Al_2O_3$	0.09	2.24	44.1	228	182	32	0	0	410/32
Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	0.10	1.45	25.7	327	152	0	0	0	479/0

<sup>a</sup> The Pd dispersion is determined on the basis of the assumption that the stoichiometry factor between Pd and adsorbed CO is 0.6 [17,18].

<sup>b</sup> The CO uptake and Pd dispersion for Pd/CeO<sub>2</sub> are over-estimated because of CO chemisorption on reduced sites of CeO<sub>2</sub> [7,20,21].

decarbonylation into CO and  $C_3H_8$ ) by highly dispersed Pd particles (Table 2a). This result is in accordance with Huber and coworkers' report wherein the higher reactivity in the decarbonylation of aldehyde compounds was observed over metal sites [26]. In contrast, other catalysts produced liquid hydrocarbon, *n*-C and *br*-C, in addition to the above gases (Table 2b and c). Pd/MgO and Pd/MgZrO<sub>3</sub> catalysts, which are highly basic and have a low Pd dispersion of ca. 6%,



Fig. 1. CO<sub>2</sub>-TPD (a) and NH<sub>3</sub>-TPD (b) profiles of Pd-supported catalysts.

exhibited the lower conversions of 74% and 77%, respectively, and the relatively higher yields toward CO. Also, these catalysts mainly yielded butanol, indicating that the hydrogenation by Pd site is more dominant than C–C coupling by acid or base sites. In the case of Pd/ZrO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts with medium-tohigh Pd dispersion as well as acid sites, the complete conversion with higher yields of liquid products than 70% was obtained. The formation of O-free hydrocarbon was also favorable, and the carbon number in liquid products ranged from 4 to 12, which is very close to that of gasoline. Among the catalysts tested in this work, the lowest *n*-C/*br*-C and O/C ratios of 0.17 and 0.005, respectively, were obtained with Pd/ZrO<sub>2</sub> (75% yield) mainly consisted of 3-methylhexane and 2-methylheptane (Table 2c).

#### 3.3. Proposed reaction pathway

For in-depth understanding of the above results, our work was then focused on describing the reaction network depicted in Fig. 2, which was based on the results presented in Table 2. Although the primary reaction would be the self-aldol condensation of butanal on acid and base sites [8], the condensed product, 2-ethyl-3-hydroxyhexanal, was not detected in liquid products. Instead, 2ethylhexenal and 4-heptanone were formed by dehydration on acid sites, and a couple of C-C cleavage and dehydrogenation on Pd metal sites, respectively. Accordingly, the rapid consumption of 2ethyl-3-hydroxyhexanal prevented the reverse aldol reaction, resulting in a high conversion of butanal. However, water produced in the conversion to 2-ethylhexenal led to disproportionation (cannizaro reaction) of butanal into butyric acid (oxidation of butanal) and butanol (reduction of butanal) [27,28], which further underwent not only self-ketonization of butyric acid to produce 4-heptanone [29] but inter-esterification between butyric acid and butanol to produce butyl butyrate [30]. The hydrogenation of 4-heptanone and the decarbonylation/dehydration of 2-ethyl-3-hydroxyhexanal then yielded 3heptene via 4-heptanol, followed by hydrogenation to heptane and further isomerization to 3-methylhexane taking place on acid sites. On the other hand, 2-ethylhexenal was hydrogenated into 2-ethylhexenol and 2-ethylhexanal competitively on Pd metal sites. Meanwhile, the C-C cleavage of 2-ethylhexenal into ethane and hexanal could occur slightly. Hexanal was then hydrogenated into hexanol or coupled with butyric acid to yield 4-nonanone that was converted to nonane, 4-octene, 2-methylheptane and 2-methyloctane, analogous with 4-heptanone. In the case of 2-ethylhexanal, the C-C cleavage occurred to form heptane which is further isomerized to 3methylhexane. Finally, 2-ethylhexanol, the hydrogenated product of 2-ethylhexanal, underwent esterification to 2-ethylhexyl butyrate.

As represented in Table 3, the experiments were conducted over unsupported  $ZrO_2$  under  $H_2$  and over  $Pd/ZrO_2$  under  $N_2$  in order to explicitly understand the contributions of Pd and  $ZrO_2$ , where the Pd content was 0.1 wt.%, the LHSV 1.2 h<sup>-1</sup>, the N<sub>2</sub>/butanal or H<sub>2</sub>/butanal ratio 6 and the pressure 10 bar. Over  $ZrO_2$  under H<sub>2</sub>, 2ethylhexananl, 2-ethylhexenal and 2-ethylhexene were mainly

#### Table 2

Product distributions of overall compounds (a), oxygenated hydrocarbon (b) and O-free hydrocarbon (c) obtained by the conversion of butanal over Pd-supported catalysts.

Catalyst	Conv. (%)	Gas-phase carbon selectivity (%)					Liquid-phase carbon selectivity (%)					
						Oxygenated hydrocarbon			Hydro	Hydrocarbon		
		CO	CO <sub>2</sub>	C <sub>4</sub>	C <sub>4</sub>	C <sub>4+</sub>	C <sub>8-</sub>	C <sub>8</sub>	C <sub>8+</sub>	C <sub>8-</sub>	C <sub>8</sub>	C <sub>8+</sub>
Pd/CeO <sub>2</sub>	100	20.4	2.2	73.9	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pd/MgO	74	17.0	1.8	16.0	0.1	0.0	19.7	7.7	16.3	5.1	0.0	0.0
Pd/MgZrO <sub>3</sub>	77	11.1	0.5	16.2	0.0	0.0	26.4	0.0	8.8	15.7	3.7	0.0
Pd/ZrO <sub>2</sub>	100	4.4	0.6	3.4	0.4	0.6	2.8	0.0	0.3	60.3	19.3	5.2
$Pd/Al_2O_3$	100	7.4	1.8	2.0	0.5	0.4	27.4	11.6	0.0	39.8	6.7	0.0
$Pd/SiO_2\text{-}Al_2O_3$	100	1.5	0.3	2.6	14.7	9.6	5.8	13.5	0.0	14.6	28.4	7.1
(b)												
Catalyst	Carbon yie	ld of oxygena	ted compo	ounds (%)								
	Butanol	4-he	ptanone	Butyl butyrate 2-et		thylhexanal 2-ethylhexenal			2-ethyl hexylbutyrate			
Pd/CeO <sub>2</sub>												
Pd/MgO	16.9	2.8		3.8		1.7			2.0		16.3	
Pd/MgZrO <sub>3</sub>	24.4	2.0									8.8	
Pd/ZrO <sub>2</sub>	0.4	2.4									0.3	
$Pd/Al_2O_3$	7.1	20.3				5.8			5.9			
$Pd/SiO_2\text{-}Al_2O_3$	1.2	4.6						1	3.5			
(c)												
Catalysts	Carbon yield of O-free compounds (%)											
	3-heptene	4-octene		Nonane 3-methylhe:		ylhexane	ne 2-ethylhexene		e 2-methylheptane		2-methyloctane	
Pd/CeO <sub>2</sub>												
Pd/MgO					5.1							
Pd/MgZrO <sub>3</sub>					15.7		3.7					
Pd/ZrO <sub>2</sub>	4.2	2.4		3.2	56.1				16.9		2.0	
$Pd/Al_2O_3$	1.8				38.0		2.3		4.4			
Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1.9			7.1	12.7		14.2		14.2			



Fig. 2. Reaction network on the conversion of butanal over Pd-supported catalysts. The asterisk represents reaction intermediates undetected in product effluents.

#### Table 3

Product distributions of oxygenated hydrocarbon (a) and O-free hydrocarbon (b) obtained by the conversion of butanal over Pd/ZrO<sub>2</sub> under N<sub>2</sub> and over unsupported ZrO<sub>2</sub> under H<sub>2</sub>.

Catalyst	Conversion (%)	Carbon yield of oxygenated compounds (%)										
		Butanol	Butanol 4-heptanone		butyrate	2-ethylhexanal	2-ethylhexenal	4-nonanone	2-ethyl hexylbutyrate			
Pd/ZrO2ª	98	7.0	41.8	6.8		10.9	0.0	2.4	0.0			
ZrO <sub>2</sub> <sup>b</sup>	98	0.0	0.0	1.6		25.2	11.8	6.1	2.8			
(b)												
Catalysts	Carbon yield of O-free compounds (%)											
	3-heptene	4-00	ctene	Nonane	3-meth	ylhexane	2-ethylhexene	2-methylheptane	2-methylocta			
Pd/ZrO2ª	20.0	0.0		0.0	0.0		0.0	0.0	0.0			
ZrO <sub>2</sub> <sup>b</sup>	14.0	0.0		0.0	0.0		31.3	0.0	0.0			

<sup>a</sup> Reaction condition: 673 K, 1.2 h<sup>-1</sup> LHSV, 6 N<sub>2</sub>/butanal, 10 bar N<sub>2</sub>.

<sup>b</sup> Reaction condition: 673 K, 1.2 h<sup>-1</sup> LHSV, 6 H<sub>2</sub>/butanal, 10 bar H<sub>2</sub>.

produced, resulting from the self-aldol condensation of butanal into 2-ethyl-3-hydroxyhexanal and its subsequent dehydration. This means that ZrO<sub>2</sub> support with acid and base sites plays a significant role on C-C coupling and oxygen removal through dehydration. On the other hand, the experiment over  $Pd/ZrO_2$  in the absence of  $H_2$ yielded the oxygenated hydrocarbon with ca. 68.9% carbon yield (mainly, 4-heptanone and 2-ethylhexanal) but the O-free hydrocarbon with 20.0% carbon yield (only 3-heptene). Since 3-heptene is formed through decarbonylation of 2-ethyl-3-hydroxyhexanal and subsequent dehydration (explained above), it was confirmed that Pd promoted the decarbonylation reaction to cleave the bond between the carbonyl carbon and its nearest carbon. Additionally, the carbon yield of oxygenated hydrocarbon was remarkably higher under N<sub>2</sub> than under H<sub>2</sub> over Pd/ZrO<sub>2</sub> catalyst, indicating that the hydrodeoxygenation reaction occurs vigorously Pd/ZrO<sub>2</sub> sites because Pd activates H<sub>2</sub> molecules.

A number of reactions described above could be divided into three classes: Class I) coupling reactions, including aldol condensation, ketonization and esterification on acid or base sites; Class II) hydrogenation, dehydrogenation and C–C cleavage on metal sites; and Class III) isomerization and dehydration on acid sites. The results obtained over Pd/ZrO<sub>2</sub> strongly suggest that Pd promotes the Class II reaction while the Class I and III reactions occurs on ZrO<sub>2</sub> support. Thus, the bifunctionality of catalyst is considered to be essential for effective reduction of O/C ratio in butanal-derived liquid compounds.

#### 3.4. Quality of liquid products obtained over Pd-supported catalysts

In order to utilize biofuels as a transportation fuel, lower ratios of O/C and *n*-C/*br*-C were required because of lower CO<sub>2</sub> emission and higher octane number. Thus, the modified version of van Krevelen diagram (Fig. 3) was utilized to visualize the fuel quality of liquid products reported herein. The O/C and *n*-C/*b*r-C ratios were decreased in the order of Pd/MgO>Pd/MgZrO<sub>3</sub>>Pd/ZrO<sub>2</sub> (from 0.168 to 0.005 in the former ratio and from 0.93 to 0.17 in the latter). Such a trend is caused by a higher acid density leading to the pronounced Class III reaction, along with the progress of Classes I and II reactions. This is in the same line with the decrease of both ratios between Pd/Al<sub>2</sub>O<sub>3</sub> (less acidic) and Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (more acidic), where the O/C and *n*-C/br-C ratios were 0.066 and 0.52 on the former catalyst, and 0.036 and 0.27 on the latter, respectively. However, the two catalysts exhibited the higher ratios than Pd/ZrO<sub>2</sub>, indicating that both base and acid sites are essential to obtain lower O/C and n-C/br-C ratios. This was confirmed by the result that the O/C ratio was lower over  $ZrO_2$ , which is well known to retain an amphoteric character [31,32], under N<sub>2</sub> (0.127), compared to that over basic Pd/MgO under H<sub>2</sub> (0.168). On the other hand, the effect of Pd loading was evident in terms of the O/C ratio due to the occurrence of hydrodeoxygenation reactions; however, the *n*-C/*b*r-C ratio was much higher over  $Pd/ZrO_2$  (6.18) than over  $ZrO_2$  (2.19) under  $N_2$  atmosphere. This is due to the production of linear compounds through decarbonylation of coupled products (e.g., 2-ethylhexenal) on metal sites.

#### 4. Conclusions

Among the prepared Pd-supported catalysts, the outstanding yield of C<sub>7</sub>-to-C<sub>9</sub> branched hydrocarbon from butanal could be achieved over Pd/ZrO<sub>2</sub> through a series of Classes I (C-C coupling on acid or base sites), II (hydrogenation, dehydrogenation and C-C cleavage on metal sites) and III (isomerization and dehydration on acid sites) reactions. In detail, ZrO<sub>2</sub> support exhibited the amphoteric property such as acidity and basicity, thus leading to higher activities on C-C coupling, dehydration and isomerization reactions, while Pd with the medium-to-high dispersion promoted the hydrodeoxygenation reaction to obtain the higher hydrocarbon yield. Therefore, a deliberate tuning of Pd dispersion and acidic-basic support property is obviously necessary in maximizing the yield of O-free hydrocarbon with the lower *n*-C/*b*r-C derived from butanal. Consequently, the present finding will enable biomass-derived liquid products to be improved up to a conventional gasoline fuel, thus offering new possibility for converting cellulosic biomass into several types of hydrocarbon fuels.



**Fig. 3.** Modified van Krevelen diagram of liquid products obtained over Pd-supported catalysts. Red and blue circles indicate the supply of  $H_2$  and  $N_2$ , respectively, for the conversion of butanal. The *n*-C/*br*-C ratio of butanal is arbitrarily assumed to be 10.

#### Acknowledgement

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2009-C1AAA001-0093293).

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