

## Article

# Selective Hydrogenation of Concentrated Vinyl Acetylene Mixed C4 by Modified Pd Catalysts: Effect of Cu

Paisan Insorn<sup>1</sup> and Boonyarach Kitiyanan<sup>1,2,\*</sup>

<sup>1</sup> The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand; paisan\_i@yahoo.com

<sup>2</sup> Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand

\* Correspondence: boonyarach.k@chula.ac.th; Tel.: +66-2-218-4144

Academic Editor: Leonarda F. Liotta

Received: 19 September 2016; Accepted: 5 December 2016; Published: 9 December 2016

**Abstract:** The Pd and Pd-Cu on alumina catalysts were tested for hydrogenation of vinyl acetylene in mixed C4 in a circulating tubular reactor. The results showed that adding proper amounts of Cu improved the reaction activity, but inhibited 1,3-butadiene selectivity. Moreover, the presence of Cu retarded the carbon deposition on catalysts during the reaction. Temperature programmed oxidation (TPO), Temperature programmed reduction (TPR), H<sub>2</sub> chemisorption, and X-ray photoelectron spectroscopy (XPS) were utilized to characterize the catalysts. The characterization suggested both geometric and electronic modifications.

**Keywords:** Pd-Cu; bimetallic; vinyl acetylene; selective hydrogenation; Pd/Al<sub>2</sub>O<sub>3</sub> catalyst

## 1. Introduction

Concentrated vinyl acetylene mixed C4, containing vinyl acetylene up to 30 wt %, generated from the butadiene extraction process is continuously flared due to safety reason [1,2]. Therefore, converting vinyl acetylene in this stream by selective hydrogenation to 1,3-butadiene is not only a benefit to environmental concerns, but also to the economics of the entire C4 processes. However, the available catalysts for selective hydrogenation of a large portion of vinyl acetylene are still very limited [1,3]. Therefore, we attempted to test the catalysts for hydrogenation of vinyl acetylene in mixed C4 from a commercial butadiene extraction process. In this study we show the results from using alumina-supporting Pd-Cu catalysts and compare them to monometallic Pd catalyst.

Supporting Pd catalysts have been studied in selective hydrogenation of alkyne in both gas and liquid phases [4–8]. In particular, Pd supported on alumina (Pd/Al<sub>2</sub>O<sub>3</sub>) is utilized as a catalyst in several commercial hydrogenation processes [9–11]. Furthermore, Pd/Al<sub>2</sub>O<sub>3</sub> can be promoted or doped by other transition metals (e.g., Cu, Ag, Pb) to improve the catalytic performance. Pachulski et al. [12] investigated Ag-promoted Pd/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the incipient wetness impregnation technique on gas phase acetylene hydrogenation and observed that, by adding Ag to Pd/Al<sub>2</sub>O<sub>3</sub>, the catalytic activity was slightly reduced, but ethylene selectivity and catalytic stability are significantly improved. Kim et al. [13] studied the effect of adding Cu and Ag to Pd/Al<sub>2</sub>O<sub>3</sub> by using a surface redox and impregnation on selective hydrogenation of acetylene. They reported that, if the catalysts are prepared by the surface redox method, Cu-promoting catalysts provided the highest ethylene selectivity while Ag promoting catalysts showed the highest ethylene selectivity if the catalysts are prepared by impregnation method. Nevertheless, catalyst promoted by either Cu and Ag showed significantly drop in their activity. Lederhos et al. [14] also reported that the Pd-W

and W-Pd bimetallic catalysts can greatly improve both selectivity and conversion in the liquid phase hydrogenation of 1-heptyne.

Cu was selected to promote the Pd catalyst for vinyl acetylene hydrogenation because Cu was reported to be active and selective in the hydrogenation of alkyne hydrogenation. For example, Koeppl et al. [15] investigated the hydrogenation of unsaturated C4 including vinyl acetylene, 1-butyne and 1,3-butadiene by Cu on silica catalysts. Their results showed that the catalysts can hydrogenate only alkynes but not alkenes. Setiawan et al. [16] also reported the removal of alkynes contaminants from industrial C4 stream by using Cu on silica catalysts. Wehrli et al. [17,18] studied the hydrogenation of propyne by supported Cu catalysts and they found that the supported Cu catalysts have the high selectivity of propyne hydrogenation toward propene. Friedrich et al. [19] studied partial acetylene hydrogenation by 60:40 atomic ratio of Cu: Pd catalyst. They reported that the Cu<sub>60</sub>Pd<sub>40</sub> catalysts provide higher ethylene selectivity with less deactivation than the Pd catalyst. Furthermore, Cai et al. [20] studied the denitrification reaction of nitrate by Pd-Cu alloy nanocatalysts on alumina under a hydrogen atmosphere. It was found that adding Cu increases nitrate conversion compared to Pd monocatalyst and the Pd:Cu 50:50 provides the highest nitrate conversion.

In this work, the Pd and Pd-Cu catalysts are prepared by conventional incipient wetness impregnation method and tested for catalytic hydrogenation of vinyl acetylene in the mixed C4. The reaction conditions, including temperature and pressure of hydrogen, are set in the safety region and the reaction is conducted in liquid hexane. The catalytic performances including rate of vinyl acetylene conversion and 1,3-butadiene selectivity are then obtained. Furthermore, the catalysts are also characterized by several techniques, including X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), temperature programmed oxidation (TPO), and H<sub>2</sub>-chemisorption.

## 2. Results and Discussion

Figure 1 shows the rate of vinyl acetylene, 1,3-butadiene selectivity and yield of Pd-Cu catalysts compared to those of the Pd catalyst. As shown in Figure 1A, Pd-Cu catalysts have a relative constant rate of vinyl acetylene conversion until vinyl acetylene conversion is around 80%, beyond 80% conversion, the rate is significantly decreased similar to the case of using Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Comparing to Pd, Pd:Cu 1:1 and 3:2 catalysts exhibited the higher rate of hydrogenation while Pd:Cu 1:4, 1:2, and 2:1 exhibited the lower rate. To observe the catalysts' performance, we compare the rate of vinyl acetylene conversion of each prepared catalyst at the 70% conversion where the yield of 1,3-butadiene is the maximum (Figure 1C). The rate of vinyl acetylene conversion for Pd:Cu 1:4, 1:2, 1:1, 3:2, 2:1, and Pd catalysts are 0.032, 0.039, 0.048, 0.052, 0.040, and 0.047 (mole vinyl acetylene per gram catalyst per hour), respectively, as illustrated in Figure 1D. Obviously, a proper amount of added Cu to Pd/Al<sub>2</sub>O<sub>3</sub> catalyst improves the rate of vinyl acetylene conversion. It is interesting to note that the Pd:Cu ratio of 3:2 shows the highest reaction rate which corresponds to the highest hydrogen adsorption per Pd as obtained from hydrogen chemisorption experiments. For comparison purposes, the Cu/Al<sub>2</sub>O<sub>3</sub> catalyst was also tested and the hydrogenation did not take place.

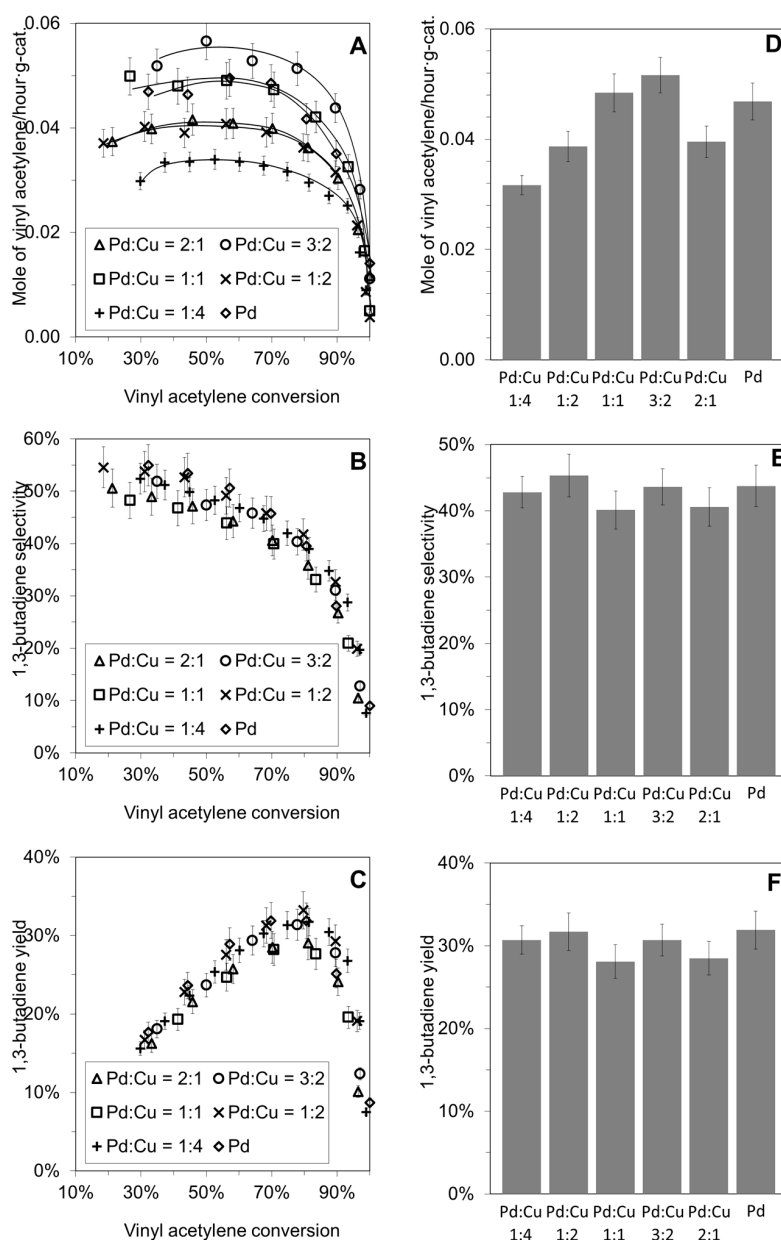
The turn-over frequency (TOF) number of vinyl acetylene on Pd is calculated based on the exposed Pd obtained from chemisorption. As shown in Figure 2, 1:4, 1:2, and 1:1 Pd:Cu catalysts exhibit TOF around 4 s<sup>-1</sup> which is higher than TOF number of Pd:Cu at ratios 3:2, 2:1, and Pd catalysts (TOF around 2.5 s<sup>-1</sup>). This suggests that Pd with more neighboring Cu is more active, possibly due to the electronic modification as hinted by the results from XPS.

In Figure 1B, the selectivity of 1,3-butadiene is gradually decreased with increasing vinyl acetylene conversion, however, the 1,3-butadiene selectivity is significantly dropped when the vinyl acetylene conversion is greater than 80%, due to further hydrogenation of 1,3-butadiene to butenes as shown in Figure S1 and S2. Interestingly, the amount of added copper does not have significant effect on 1,3-butadiene selectivity, as shown in Figure 1E.

As illustrated in Figure 1C, the yield of 1,3-butadiene for each catalyst is increased with an increase of the conversion and reached the maximum at around 70%–80% conversion. The yield is

dramatically dropped when the conversion is beyond 80%. Figure 1F shows the yield of 1,3-butadiene at 70% conversion of vinyl acetylene for different Pd:Cu atomic ratio catalysts. It can be observed that adding Cu has no effect on 1,3-butadiene yield for the tested catalyst.

Adding Cu to Pd/Al<sub>2</sub>O<sub>3</sub> catalyst can cause both positive and negative effects on the rate of vinyl acetylene hydrogenation. For the Pd:Cu ratio of 1:4 and 1:2, adding Cu to the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst significantly reduces the rate of vinyl acetylene hydrogenation per gram of catalyst, but the selectivity toward 1,3-butadiene is still comparable to the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at 70% conversion. However, as the ratio of Pd to Cu increases, until the Pd:Cu ratio of 1:1 and 3:2, the rate of vinyl acetylene hydrogenation is higher than that of monometallic Pd catalyst. However, if the Pd:Cu ratio is increased to 2:1, the rate of vinyl acetylene hydrogenation is significantly dropped, as shown in Figure 1D.



**Figure 1.** Catalytic performances: (A) reaction rate; (B) 1,3-butadiene selectivity; and (C) 1,3-butadiene yield as the function of vinyl acetylene conversion; (D) rate of vinyl acetylene at 70% vinyl acetylene conversion; (E) 1,3-butadiene selectivity at 70% vinyl acetylene conversion; and (F) 1,3-butadiene yield at 70% vinyl acetylene conversion against Pd:Cu atomic ratios.

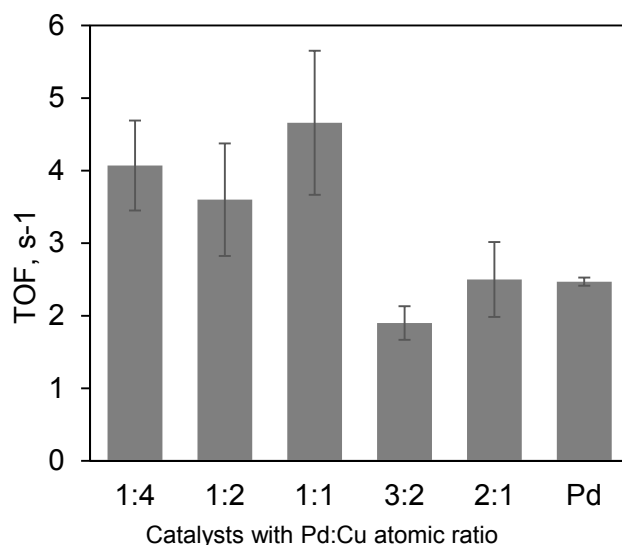


Figure 2. Turn-over frequency of Pd and Pd-Cu catalysts.

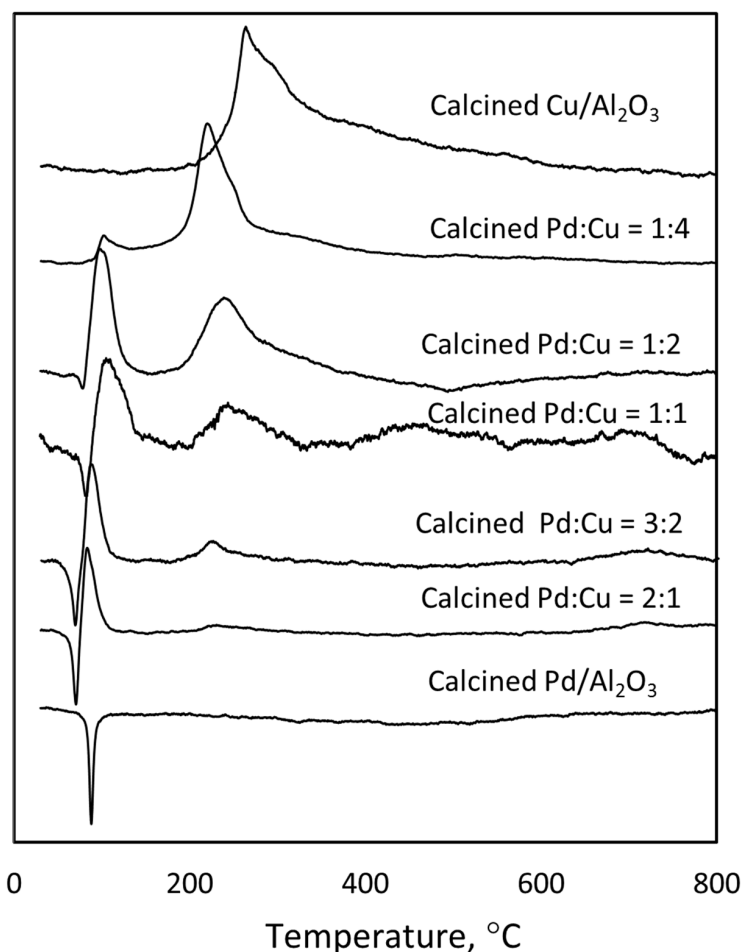
The Pd dispersion based on the results of hydrogen chemisorption on the studied catalysts are summarized in Table 1. The Pd/Al<sub>2</sub>O<sub>3</sub> catalyst has 19% dispersion while the Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts with Pd to Cu ratio less than 1 show significantly lower Pd dispersion. However, for Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts with the Pd:Cu ratio higher than 1, the catalyst shows the metal dispersion at the similar level of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, only Pd:Cu 3:2 catalyst provides about 27% dispersion which is higher than the monometallic Pd catalyst.

Table 1. Measured Pd and Cu contents and Pd dispersion of catalysts.

Properties	Pd	Pd:Cu Catalyst				
		1:4	1:2	1:1	3:2	2:1
Pd wt % <sup>1</sup>	0.352 ± 0.012	0.273 ± 0.010	0.328 ± 0.012	0.270 ± 0.009	0.288 ± 0.010	0.287 ± 0.010
Cu wt % <sup>1</sup>	-	0.612 ± 0.022	0.358 ± 0.013	0.179 ± 0.006	0.119 ± 0.004	0.096 ± 0.003
Pd Dispersion <sup>2</sup> , %	19.35 ± 0.44	7.83 ± 0.76	10.63 ± 1.53	16.35 ± 4.77	27.11 ± 1.61	15.70 ± 2.12
Actual Pd/Cu	-	0.266 ± 0.019	0.548 ± 0.039	0.902 ± 0.063	1.446 ± 0.101	1.783 ± 0.124

<sup>1</sup> by AAS; <sup>2</sup> by hydrogen chemisorption.

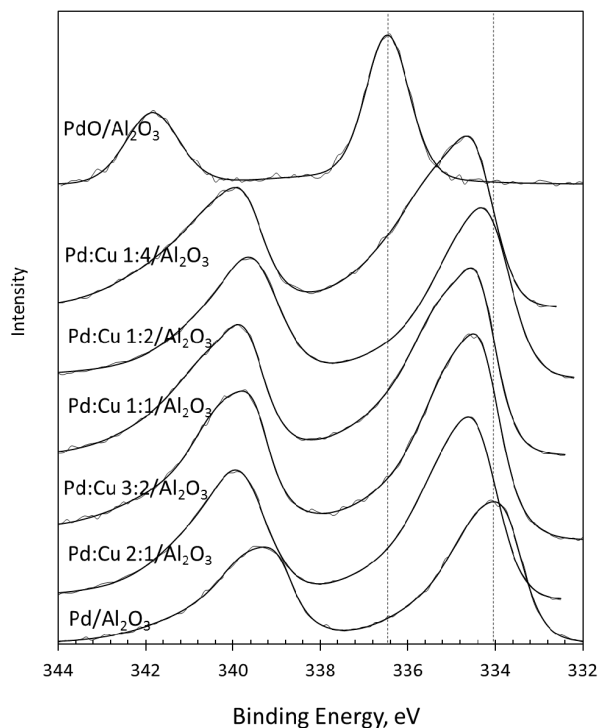
The results of temperature program reduction (TPR) of calcined catalysts are illustrated in Figure 3. For the calcined copper on alumina (calcined Cu/Al<sub>2</sub>O<sub>3</sub>), a broad positive peak which is maximum at 261 °C indicates the reduction of CuO by hydrogen. Interestingly, the TPR of calcined Pd/Al<sub>2</sub>O<sub>3</sub> has a negative peak at 88 °C possibly due to hydrogen generating from palladium hydride decomposition [21,22]. For the Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst with a high Pd:Cu ratio (Pd:Cu 2:1, 3:2, and 1:1), TPR of these catalysts shows both negative and positive peaks of Pd at around 90 °C, while the lower Pd:Cu ratio catalysts (Pd:Cu 1:2 and 1:4) show only positive TPR peaks. It is interesting to note that the negative peak at low temperature is smaller as the amount of Cu is increased in the prepared catalysts suggesting that less Pd hydride is formed. Moreover, the TPR peaks of PdO in calcined Pd-Cu/Al<sub>2</sub>O<sub>3</sub> are shifted to a higher temperature as the amount of Cu is increased. Furthermore, the reduction peaks of copper in the calcined Pd-Cu/Al<sub>2</sub>O<sub>3</sub> are at a lower temperature than the reduction peak in the calcined Cu/Al<sub>2</sub>O<sub>3</sub>. These indicate the possibility of Pd-Cu interaction in the calcined Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts as suggested in the work done by Molenbroek et al. [23].



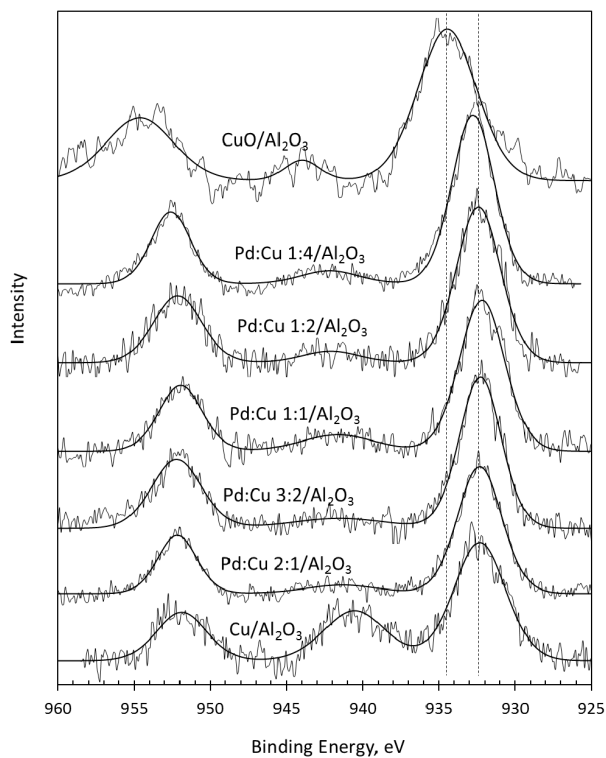
**Figure 3.** TPR profile of calcined Pd-Cu/ $\text{Al}_2\text{O}_3$  catalysts compared to calcined Pd/ $\text{Al}_2\text{O}_3$  and calcined Cu/ $\text{Al}_2\text{O}_3$ .

From the TPR results, Pd on all catalysts should be completely reduced by hydrogen at 300 °C, however, at this condition, copper may not be completely reduced to metallic Cu, particularly copper in the copper-rich catalysts (1:4, 1:2, and 1:1 Pd:Cu) may not be completely reduced. The XPS results, as shown in Figures 4 and 5, and summarized in Table 2, also suggest a similar observation. In Figure 4, the Pd 3d binding energy of reduced Pd/ $\text{Al}_2\text{O}_3$  catalyst is observed at 334.2 eV with the full width at half maximum (FWHM) of 1.97, while the calcined catalyst (PdO/ $\text{Al}_2\text{O}_3$ ) spectra shows at 336.4 eV with 1.23 FWHM. This confirmed that Pd from reduced Pd/ $\text{Al}_2\text{O}_3$  and from PdO/ $\text{Al}_2\text{O}_3$  are Pd(0) and Pd(II), respectively. The reduced Pd-Cu/ $\text{Al}_2\text{O}_3$  catalysts show the Pd 3d spectra around 334.5–334.6 eV which is 0.3–0.4 eV higher than the reduced Pd/ $\text{Al}_2\text{O}_3$  catalyst. This suggests that Pd may be electronically modified when Cu is added. In addition, Pd-Cu catalysts may contain some Pd<sup>+</sup> species as suggested by the broader Pd 3d FWHM of Pd-Cu catalysts which is around 1.98–2.43 eV. The Pd may be oxidized possibly due to the brief exposure to air during sample transfer to XPS. As shown in Figure 5, the Cu 2p<sub>3/2</sub> is observed around 932.7 eV for the all the prepared catalysts containing copper. In addition, weak Cu 2p<sub>3/2</sub> satellite peak are also observed at around 10 eV higher (B.E. about 940–945 eV) for the CuO/ $\text{Al}_2\text{O}_3$ , and copper-rich sample (1:4, 1:2, and 1:1 Pd:Cu on alumina catalyst) suggesting the presence of Cu<sup>2+</sup> [24]. Moreover, the satellite peak is also observed in reduced Cu/ $\text{Al}_2\text{O}_3$  indicating that the sample is not completely reduced, possibly due to the reduction condition and the oxidation by air when transferring the samples to XPS. For the sample with low copper loading (3:2 and 2:1 Pd:Cu on alumina catalyst), the satellite peak is not clearly observed probably due to the low copper

loading. In addition, the Pd/Cu intensity ratios of bimetallic catalysts were 10.04, 6.90, 5.15, 3.20, and 1.80 for Pd:Cu 2:1, 3:2, 1:1, 1:2, and 1:4, respectively, caused by the dilution of Pd by Cu.



**Figure 4.** X-ray photoelectron spectra of the Pd 3d of each catalyst.



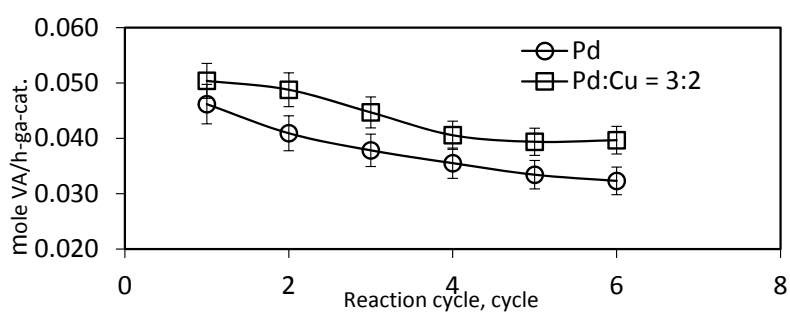
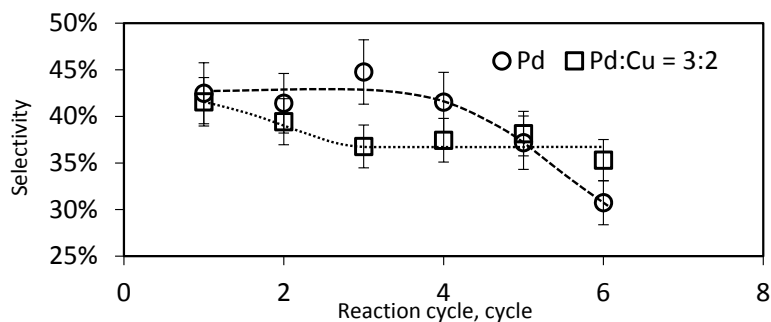
**Figure 5.** X-ray photoelectron spectra of the Cu 2p of each catalyst.

**Table 2.** The measured binding energy (eV), full width at half maximum (FWHM), and intensity ratios of Pd, Cu, and Pd-Cu on Al<sub>2</sub>O<sub>3</sub>.

Catalysts	Pd 3d <sub>5/2</sub>		Cu 2p <sub>3/2</sub>		Pd/Al	Cu/Al	Pd/Cu
	Position	FWHM	Position	FWHM			
PdO/Al <sub>2</sub> O <sub>3</sub>	336.4	1.23	-	-	0.07	-	-
Pd/Al <sub>2</sub> O <sub>3</sub>	334.2	1.97	-	-	0.09	-	-
Pd:Cu 2:1/Al <sub>2</sub> O <sub>3</sub>	334.6	1.98	932.4	3.50	0.16	0.016	10.04
Pd:Cu 3:2/Al <sub>2</sub> O <sub>3</sub>	334.6	2.04	932.3	3.21	0.02	0.003	6.90
Pd:Cu 1:1/Al <sub>2</sub> O <sub>3</sub>	334.6	2.11	932.2	3.10	0.13	0.025	5.15
Pd:Cu 1:2/Al <sub>2</sub> O <sub>3</sub>	334.5	2.43	932.3	3.43	0.09	0.028	3.20
Pd:Cu 1:4/Al <sub>2</sub> O <sub>3</sub>	334.6	2.24	932.8	3.28	0.07	0.039	1.80
Cu/Al <sub>2</sub> O <sub>3</sub>	-	-	932.3	3.75	-	0.003	-
CuO/Al <sub>2</sub> O <sub>3</sub>	-	-	934.4	4.57	-	0.016	-

The addition of Cu to Pd/Al<sub>2</sub>O<sub>3</sub> catalyst leads to both electronic and geometric modifications [25,26]. For geometric effect, Cu may induce Pd to be more exposed at the metal surface, particularly at Pd:Cu 3:2, which also has the highest Pd dispersion.

The Pd:Cu 3:2 catalyst was selected to study the effect of prolonged reaction time by refilling the system with concentrated vinyl acetylene mixed C4 without catalyst replacement for six cycles. Each reaction cycle proceeded until vinyl acetylene was completely used up, which takes about 5–7 h. The reaction rate and 1,3-butadiene selectivity as the function of reaction cycles are illustrated in Figures 6 and 7, respectively. As observed in Figure 6, the rate of reaction in case of using Pd:Cu 3:2 catalyst is decreased until four cycles, and then it is relative stable. On the other hand, Pd/Al<sub>2</sub>O<sub>3</sub> catalyst indicates the continuously decreasing reaction rate along six cycles. Interestingly, catalyst Pd/Al<sub>2</sub>O<sub>3</sub> provides higher 1,3-butadiene selectivity than Pd:Cu 3:2 catalyst as shown in Figure 7 (except cycle 6). The Pd:Cu 3:2 catalyst has potential to improve the catalyst stability for the hydrogenation of vinyl acetylene.

**Figure 6.** The vinyl acetylene reaction rate of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd:Cu 3:2 on Al<sub>2</sub>O<sub>3</sub> catalysts as the function of reaction cycles.**Figure 7.** The 1,3-butadiene selectivity of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd:Cu 3:2 on Al<sub>2</sub>O<sub>3</sub> catalysts as a function of the reaction cycles.

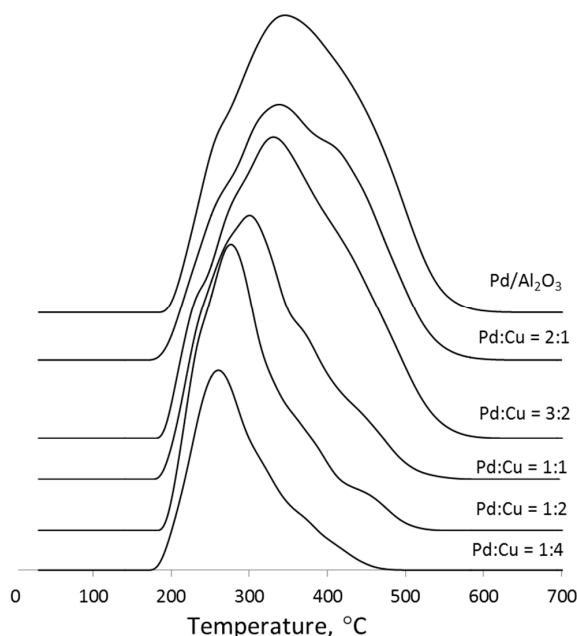


The TPO was used to characterize the deposited carbon on spent catalysts. The TPO profiles of spent catalysts are shown in Figure 8. The used Pd catalyst shows a broad TPO peak around 200 to 600 °C while the used Pd-Cu catalyst containing highest Cu (at Pd:Cu = 1:4) shows between 120 and 470 °C. The order of peak boarding are Pd/Al<sub>2</sub>O<sub>3</sub> > Pd:Cu 2:1 > Pd:Cu 3:2 > Pd:Cu 1:1 > Pd:Cu 1:2. It can be inferred that a higher Cu content reflects a lower TPO temperature.

Carbon content of spent catalysts is calculated and shown in Table 3. Among one reaction cycle, the carbon content of Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts is not significantly lower than of Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The Pd/Al<sub>2</sub>O<sub>3</sub> catalyst has carbon content 2.12 wt % while Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts have carbon content in the same magnitude, 1.79–2.62 wt %. On the other hand, among spent catalyst with six reaction cycles, Pd:Cu 3:2 catalyst produces carbon to 3.19 wt % while Pd/Al<sub>2</sub>O<sub>3</sub> catalyst shows carbon content 5.96 wt %. Therefore Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst can inhibit the polymerization of polyolefins in this system and should promote the longer catalyst life.

**Table 3.** Deposited carbon on spent catalysts performed reaction tests of one and six cycles.

Catalysts	Deposited Carbon, wt %
1 Cycle	
Pd	2.12 ± 0.08
Pd:Cu 2:1	2.43 ± 0.10
Pd:Cu 3:2	2.62 ± 0.11
Pd:Cu 1:1	2.13 ± 0.09
Pd:Cu 1:2	1.79 ± 0.07
Pd:Cu 1:4	2.45 ± 0.10
6 Cycles	
Pd	5.96 ± 0.24
Pd:Cu 3:2	3.19 ± 0.13



**Figure 8.** Temperature programmed oxidation (TPO) profiles of spent Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts.

### 3. Materials and Methods

The concentrated vinyl acetylene mixed C4 was obtained from Bangkok Synthetics Co., Ltd (Rayong, Thailand). Analytical reagent grade (AR grade) hexane was purchased from Fisher Scientific Company LLC. (Pittsburgh, PA, USA). The pelletized aluminium oxide, palladium (II) nitrate dihydrate,



and copper (II) nitrate trihydrate were purchased from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA). The high purity (HP, 99.95%) hydrogen and nitrogen gases were purchased from Linde (Thailand) Public Company Limited (Bangkok, Thailand).

Prior to experiment,  $\gamma$ - $\text{Al}_2\text{O}_3$  was pretreated at 1000 °C in a furnace for 2 h to obtain the mixed phases of alumina [27]. We also found that Pd supported on alumina, pretreated at 1000 °C, provided much less carbon deposition (three times less) than untreated  $\gamma$ - $\text{Al}_2\text{O}_3$ , while the 1,3-butadiene yield is also increased, but not significant (about 2%). Subsequently, the pretreated  $\text{Al}_2\text{O}_3$  were impregnated by palladium (II) nitrate dihydrate aqueous solution to obtain 0.3 wt % Pd loading on the alumina. The Pd-Cu/ $\text{Al}_2\text{O}_3$  catalysts were prepared by sequential impregnation; the support was first impregnated by palladium (II) nitrate dihydrate precursor, then dried at 110 °C and calcined at 500 °C for 1 h. Subsequently, the calcined Pd/ $\text{Al}_2\text{O}_3$  was further impregnated by the aqueous solution of copper (II) nitrate trihydrate. The Pd-Cu/ $\text{Al}_2\text{O}_3$  catalysts were prepared by varying Pd/Cu atomic ratios from 1:4 to 2:1. The impregnated catalysts were then dried at 110 °C for 8 h and calcined in a furnace at 500 °C for 3 h. The calcined catalysts were reduced by hydrogen at 300 °C for 1 h prior to use.

The reaction was conducted in a recirculating liquid phase through an external fixed-bed reactor (Swagelok Company, Solon, OH, USA) as described in previous work [28]. The known amount of reduced catalyst (0.5 g) was packed in 1/2 inch stainless steel tube fixed-bed reactor. Prior to reaction, the system was sufficiently purged by nitrogen to remove residue oxygen, and the catalyst was reduced in situ by flowing hydrogen at 150 °C for 8 h in order to treat Pd oxide possibly formed during the sample transfer. Subsequently, 650 mL of hexane was filled into the sample reservoir and the system was again purged by nitrogen. Then, the concentrated vinyl acetylene mixed C4 was introduced into the sample reservoir. After that, hydrogen was applied to the reservoir at 5.5 bar. The liquid mixture in the sample reservoir was continuously stirred by a magnetic stirrer and recirculated by a diaphragm pump through the fixed-bed reactor at a flow rate 700 mL/min since we have checked by varying the flow rate and found that at least 400 mL/min is required to avoid external diffusion limitation. The temperature of the fixed-bed reactor and sample reservoir was controlled by a temperature controller (OMRON Electronics Co., Ltd, Bangkok, Thailand). To quantitatively analyze for compositions, a sample was sent every 30 min for gas chromatography (HP, 5890 II Plus) (Agilent Technologies, Inc., Santa Clara, CA, USA) which was equipped with flame ionization detector (FID) and GS-alumina capillary column. The reaction rate and product selectivity were then obtained from the analysis of C4 compositions.

The reaction rate, vinyl acetylene conversion, 1,3-butadiene selectivity, and 1,3-butadiene yield were calculated as described below:

$$\text{Reaction rate} = \frac{VA_i - VA_f}{t \times W_{\text{cat}}} \quad (1)$$

$$\% \text{Vinyl acetylene conversion} = \frac{VA_i - VA_f}{VA_i} \times 100 \quad (2)$$

$$\%1,3\text{-Butadiene selectivity} = \frac{BD_f - BD_i}{VA_i - VA_f} \times 100 \quad (3)$$

$$\%1,3\text{-butadiene yield} = \% \text{Vinyl acetylene conversion} \times \%1,3\text{-Butadiene selectivity} \quad (4)$$

where:

$VA_i$  = initial mole of vinyl acetylene

$VA_f$  = final mole of vinyl acetylene

$t$  = reaction time in hour

$W_{\text{cat}}$  = catalyst weight in gram

$BD_i$  = initial mole of 1,3-butadiene

$BD_f$  = final mole of 1,3-butadiene

The amount of palladium extracted from the prepared catalysts was determined by a Varian SpectrAA 300 atomic absorption spectroscopy. The reduced catalysts (0.05–0.2 g) were digested in 3 mL of 48% hydrofluoric acid at 50 °C for 6 h. Then 1 mL of aqua regia was added and the solution was kept at 50 °C overnight. After that, it was filtered by syringe filter and diluted by deionized water.

Dispersion of palladium was determined by hydrogen chemisorption. The exposed Pd atom on the surface was calculated from the dissociative chemisorbed hydrogen. First, the reduced catalysts were packed in a quartz tube reactor and heated up to 120 °C with a ramping rate 10 °C/min, and was then kept for 30 min under a hydrogen gas flow. Subsequently, helium was flowed over the catalyst at 120 °C for 30 min. Then, the known amount of hydrogen was pulsed to the reactor containing the catalyst at the previous temperature. The surface of Pd was considered to be saturated when the pulsed hydrogen coming out with the same area of the thermal conductivity detector (TCD) signal for at least three consecutive pulses.

Temperature program reduction, TPR, was performed by heating the calcined catalysts at the rate 10 °C/min from 30–800 °C in a 10 mL/min flow rate of 5% hydrogen in argon gas. The signal of hydrogen were detected by TCD.

For temperature program oxidation, TPO, 5% oxygen in helium gas was flowed over the spent catalysts which packed in quartz tube reactor. The sample of spent catalysts was heated up from 30–900 °C with 10 °C/min ramping rate. The effluent gases (CO<sub>2</sub> and/or CO) generated from oxidation of deposited carbon compounds on the spent catalysts was passed through a methanator which converts CO/CO<sub>2</sub> to methane. The methane was detected by using a flame-ionized detector (FID). Quantification of methane was calibrated by pure methane with 100 µL pulse. Therefore, the carbon content of the spent catalysts was then determined.

The reduced catalysts were also characterized by X-ray photoelectron spectroscopy (XPS, Kratos Model Axis Ultra DLD, Manchester, UK) analyzing area 700 µm × 300 µm, using a monochromator Al K alpha X-ray source and operating at 10 mA anode HT 15 kV. The Pd 3d and Cu 2p spectra were reported with respect to the C 1s spectra (284.6 eV).

#### 4. Conclusions

The Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by incipient wetness impregnation and tested for the hydrogenation of vinyl acetylene in the waste stream from the butadiene extraction process. The results show that the adding Cu to Pd/Al<sub>2</sub>O<sub>3</sub> catalysts can increase the rate of reaction, while decreasing the amount of carbon deposited on spent catalyst. However, the 1,3-butadiene selectivity is not significantly changed. In addition, among the prepared Pd and Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts, Pd:Cu 3:2 catalyst provides the highest reaction rate possibly due to highest Pd dispersion. On the other hand, catalysts with low Pd:Cu ratios, 1:4, 1:2, and 1:1, provide higher TOF number. The stability test found that, compared to Pd catalysts, Pd:Cu 3:2 catalyst has the potential to improve the activity and selectivity for long-term application.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4344/6/12/199/s1](http://www.mdpi.com/2073-4344/6/12/199/s1), Figure S1: Possible reaction of mixed C4 hydrogenation, Figure S2: The C4 compositions as function of time of Pd:Cu 2:1/Al<sub>2</sub>O<sub>3</sub>.

**Acknowledgments:** The authors would like to thank the Royal Golden Jubilee Ph.D. Program, Thailand Research Fund (RGJ-TRF) for Ph.D. scholarship to Paisan Insorn and TRF Senior Research Scholar Grant (RTA578008) for partial financial support. We would like to thank Bangkok Synthetics Co., Ltd., Thailand for supporting chemicals and instruments.

**Author Contributions:** P.I. and B.K. designed and conducted the experiments; analyzed the data; and wrote the article.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- SK-KBR Boosting Butadiene Extraction by Converting Acetylene. Available online: <http://www.sk-kbr.com/Technologies-and-Services/License-Technologies/C4AC/C4AC.pdf> (accessed on 22 September 2015).
- Ikegami, T. Studies on explosion reaction of monovinyl acetylene gas: I. Explosion limits of monovinyl acetylene and monovinyl acetylene-air mixture. *Rev. Phys. Chem. Jpn.* **1963**, *32*, 13–29.
- Johnson-Matthey-Process-Technologies C4 Acetylene Hydrogenation. Available online: <http://www.jmprotech.com/olefins-C4-acetylene-hydrogenation-johnson-matthey> (accessed on 31 October 2016).
- Venezia, A.M.; Liotta, L.F.; Deganello, G.; Schay, Z.; Gucci, L. Characterization of Pumice-Supported Ag–Pd and Cu–Pd Bimetallic Catalysts by X-ray Photoelectron Spectroscopy and X-ray Diffraction. *J. Catal.* **1999**, *182*, 449–455. [[CrossRef](#)]
- Crespo-Quesada, M.; Dykeman, R.R.; Laurenczy, G.; Dyson, P.J.; Kiwi-Minsker, L. Supported nitrogen-modified Pd nanoparticles for the selective hydrogenation of 1-hexyne. *J. Catal.* **2011**, *279*, 66–74. [[CrossRef](#)]
- Kennedy, D.R.; Webb, G.; Jackson, S.D.; Lennon, D. Propyne hydrogenation over alumina-supported palladium and platinum catalysts. *Appl. Catal. A Gen.* **2004**, *259*, 109–120. [[CrossRef](#)]
- Ryndin, Y.A.; Stenin, M.V.; Boronin, A.I.; Bukhtiyarov, V.I.; Zaikovskii, V.I. Effect of Pd/C dispersion on its catalytic properties in acetylene and vinylacetylene hydrogenation. *Appl. Catal.* **1989**, *54*, 277–288. [[CrossRef](#)]
- Teschner, D.; Vass, E.; Hävecker, M.; Zafeirotas, S.; Schnörch, P.; Sauer, H.; Knop-Gericke, A.; Schlögl, R.; Chamam, M.; Wootsch, A.; et al. Alkyne hydrogenation over Pd catalysts: A new paradigm. *J. Catal.* **2006**, *242*, 26–37. [[CrossRef](#)]
- Axens-Headquarters (Ed.) Axens catalysts and adsorbents. In *Product Listing*; Axens-Headquarters: Malmaison, France, 2011.
- Süd-Chemie (Ed.) General catalogue Süd-Chemie catalysts. In *Catalyst Index and Contact Details*; Süd-Chemie: Munich, Germany, 2007.
- Büchle, W.; Roos, H.; Wanjek, H.; Müller, H.J. Catalyst research—One of the cornerstones of modern chemical production. *Catal. Today* **1996**, *30*, 33–39. [[CrossRef](#)]
- Pachulski, A.; Schödel, R.; Claus, P. Performance and regeneration studies of Pd–Ag/Al<sub>2</sub>O<sub>3</sub> catalysts for the selective hydrogenation of acetylene. *Appl. Catal. A Gen.* **2011**, *400*, 14–24. [[CrossRef](#)]
- Kim, S.K.; Lee, J.H.; Ahn, I.Y.; Kim, W.-J.; Moon, S.H. Performance of Cu-promoted Pd catalysts prepared by adding Cu using a surface redox method in acetylene hydrogenation. *Appl. Catal. A Gen.* **2011**, *401*, 12–19. [[CrossRef](#)]
- Lederhos, C.R.; Maccarrone, M.J.; Badano, J.M.; Torres, G.; Coloma-Pascual, F.; Yori, J.C.; Quiroga, M.E. Hept-1-yne partial hydrogenation reaction over supported Pd and W catalysts. *Appl. Catal. A Gen.* **2011**, *396*, 170–176. [[CrossRef](#)]
- Koeppel, R.A.; Wehrli, J.T.; Wainwright, M.S.; Trimm, D.L.; Cant, N.W. Selective hydrogenation of C<sub>4</sub>-alkynes over a copper on silica catalyst. *Appl. Catal. A Gen.* **1994**, *120*, 163–177. [[CrossRef](#)]
- Setiawan, I.; Cavell, K.J. Removal of unsaturated contaminants from an industrial C<sub>4</sub>-stream using Cu/SiO<sub>2</sub> catalysts: Subsequent testing of the purified stream with an alkyne sensitive catalyst system. *Appl. Catal. A Gen.* **1995**, *131*, 225–241. [[CrossRef](#)]
- Wehrli, J.T.; Thomas, D.J.; Wainwright, M.S.; Trimm, D.L.; Cant, N.W. Selective hydrogenation of propyne over an ion-exchanged copper on silica catalyst. *Appl. Catal.* **1990**, *66*, 199–208. [[CrossRef](#)]
- Wehrli, J.T.; Thomas, D.J.; Wainwright, M.S.; Trimm, D.L.; Cant, N.W. Selective hydrogenation of propyne over supported copper catalysts: Influence of support. *Appl. Catal.* **1991**, *70*, 253–262. [[CrossRef](#)]
- Friedrich, M.; Villaseca, S.; Szentmiklósi, L.; Teschner, D.; Armbrüster, M. Order-Induced Selectivity Increase of Cu<sub>60</sub>Pd<sub>40</sub> in the Semi-Hydrogenation of Acetylene. *Materials* **2013**, *6*, 2958–2977. [[CrossRef](#)]
- Cai, F.; Yang, L.; Shan, S.; Mott, D.; Chen, B.; Luo, J.; Zhong, C.-J. Preparation of PdCu Alloy Nanocatalysts for Nitrate Hydrogenation and Carbon Monoxide Oxidation. *Catalysts* **2016**, *6*, 96. [[CrossRef](#)]
- Zhang, Q.; Li, J.; Liu, X.; Zhu, Q. Synergetic effect of Pd and Ag dispersed on Al<sub>2</sub>O<sub>3</sub> in the selective hydrogenation of acetylene. *Appl. Catal. A Gen.* **2000**, *197*, 221–228. [[CrossRef](#)]
- Grosso, E.; Agostini, G.; Piovano, A.; Muddada, N.B.; Leofanti, G.; Pellegrini, R.; Portale, G.; Longo, A.; Lamberti, C. Effect of reduction in liquid phase on the properties and the catalytic activity of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. *J. Catal.* **2012**, *287*, 44–54. [[CrossRef](#)]

23. Molenbroek, A.M.; Haukka, S.; Clausen, B.S. Alloying in Cu/Pd Nanoparticle Catalysts. *J. Phys. Chem. B* **1998**, *102*, 10680–10689. [[CrossRef](#)]
24. Figueiredo, R.T.; Andrade, H.M.C.; Fierro, J.L.G. The Role of the Coprecipitation Sequence of Salt Precursors on the Genesis of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> Catalysts: Synthesis, Characterization and Activity for Low Temperature Shift Reaction. *Braz. J. Chem. Eng.* **1998**, *15*. [[CrossRef](#)]
25. Guczi, L.; Schay, Z.; Stefler, G.; Liotta, L.F.; Deganello, G.; Venezia, A.M. Pumice-Supported Cu-Pd Catalysts: Influence of Copper on the Activity and Selectivity of Palladium in the Hydrogenation of Phenylacetylene and But-1-ene. *J. Catal.* **1999**, *182*, 456–462. [[CrossRef](#)]
26. Kim, W.-J.; Moon, S.H. Modified Pd catalysts for the selective hydrogenation of acetylene. *Catal. Today* **2012**, *185*, 2–16. [[CrossRef](#)]
27. Komeili, S.; Ravanchi, M.T.; Taeb, A. The influence of alumina phases on the performance of the Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalyst in tail-end selective hydrogenation of acetylene. *Appl. Catal. A Gen.* **2015**, *502*, 287–296. [[CrossRef](#)]
28. Insorn, P.; Kitiyanan, B. Selective hydrogenation of mixed C4 containing high vinyl acetylene by Mn-Pd, Ni-Pd and Ag-Pd on Al<sub>2</sub>O<sub>3</sub> catalysts. *Catal. Today* **2015**, *256*, 223–230. [[CrossRef](#)]



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).