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Selective Hydrogenation of 1-Hexyne Using Pd-Cu and Pd-W Supported on Alumina Catalysts

Paisan Insorn, Katawut Suriyaphaparkorn, Boonyarach Kitiyanan*

The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
boonyarach.k@chula.ac.th

Vinyl acetylene and 1-butyne are by products in mixed C4 separation processes and they must be eliminated due to their high flammability. However, C4 acetylene can be upgraded to higher value hydrocarbons such as 1,3-butadiene and 1-butene by using selective hydrogenation. In this study, 1-hexyne is selected to be used as a model acetylene compound for liquid phase hydrogenation. Pd catalyst has been successfully utilized in hydrogenation process and several studies have shown that using bimetallic catalyst can greatly improve the activity, selectivity and stability of the catalyst. In this research, the activity and selectivity of Pd-Cu/$Al_2O_3$and Pd-W/Al_2O_3catalysts with Pd/Cu and Pd/W ratios of 0.25, 0.5, 1.0, 1.5 and 2.0 are investigated for the liquid phase hydrogenation of 1-hexyne under 1.5 bar and 40 °C. Catalytic performances of the Pd-W/Al_2O_3 in selective hydrogenation of 1-hexyne are found to be better has the Pd-Cu/Al_2O_3. Moreover, Pd-W/Al_2O_3 catalyst (at Pd to W ratio of 1) shows the optimum activity and selectivity for selective 1-hexyne hydrogenation.

1. Introduction

In typically petrochemical processes, C4 hydrocarbons are produced by naphtha cracking. Several C4 hydrocarbon compounds are then separated and utilized in many applications. Vinyl acetylene is one of the lowest value compounds in C4 Hydrocarbons. Usually, it has to be burnt away due to safety reasons. However, it can be upgraded to higher value compounds by using selective hydrogenation process. In this study, 1-hexyne is selected to be used as a model acetylene compound for liquid phase hydrogenation. Many reports have shown that palladium supported catalysts give a high catalytic performance in the partial hydrogenation reactions of alkynes and dienes to olefins (Alves *et al.,* 2011 and 2012; Ardiaca *et al.,* 2001). Using bimetallic catalyst is an efficient way to improve the catalytic performances of catalysts (Batista *et al.,* 2001; Furlong *et al.,* 1994; Sarkany, 1997; Lederhos *et al.,* 2011). In this research, the activity and selectivity of Pd-Cu/Al_2O_3 and Pd-W/Al_2O_3 catalysts with Pd/Cu and Pd/W ratios of 0.25, 0.5, 1.0, 1.5 and 2.0 are investigated for the liquid phase hydrogenation of 1-hexyne. The mild temperature and pressure, 40 °C and 1.5 bar, were considered for reaction condition because these conditions will be the similar to those utilized in vinyl acetylene hydrogenation to avoid the chance of vinyl acetylene explosion if it is heated or pressurized at high pressure (Ikegami, 1963).

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2. Experimental

2.1 Materials

2.1.1 Chemicals

1-Hexyne 97%, alumina (α-Al_2O_3), palladium nitrate dihydrate ($N_2O_6Pd.2H_2O$), copper (II) nitrate ($(Cu(NO_3)_2.3H_2O)$ and phosphotungstic acid solution ($H_3PO_4.12WO_3$) were obtained from Aldrich and the solvent, n-heptane, 95% (AR grade) was purchased from Fisher Chemical. Hydrogen (99% purity) was obtained from Thai Industrial Gas.

2.1.2 Equipment

The experimental system consists of 4 main parts: a 1/4” O.D.x7” long stainless steel packed bed reactor equipped with furnace and temperature controller, a sample reservoir made by 6.5 cm ID x 7.4cm height stainless steel, a hydrogen gas supply cylinder, and a peristaltic pump as shown in Figure1.

2.2 Catalyst preparation

The Pd-Cu/Al_2O_3 catalysts were prepared at Pd/Cu atomic ratios of 0.25, 0.5, 1.0, 1.5 and 2.0. Alumina was first impregnated with corresponding amount of palladium ($N_2O_6Pd.2H_2O$) aqueous solution, then dried at 110 °C overnight and subsequently calcined at 500 °C for 1 h. Then the second metal copper (II) nitrate ($Cu(NO_3)_2.3H_2O$) aqueous solution was deposited on the calcined Pd/Al_2O_3 catalysts and then these catalysts were dried at 110 °C overnight and calcined again at 500 °C for 3 h. The Pd-W/Al_2O_3 catalysts were prepared on similar manner except aqueous solution prepared from $H_3PO_4.12WO_3$ was used instead of the copper nitrate solution.

2.3 Catalytic experiment

A 0.5 g of catalysts was packed in the reactor without grinding. The packed catalysts were *in-situ* treated at 150 °C for 12 h by H_2 gas prior to reaction. 1-Hexyne and n-heptane, the reactant and solvent, were mixed and filled into the sample reservoir. Liquid mixture in the system was circulated by using peristaltic pump. Subsequently constant pressure of H_2 gas was applied to the system and then the flow of liquid mixture was switched to pass through the fixed bed reactor. The liquid was analyzed for its composition for every hour by a gas chromatography, HP5890 II plus, equipped with flame ionization detector (FID) and GS-alumina capillary column.

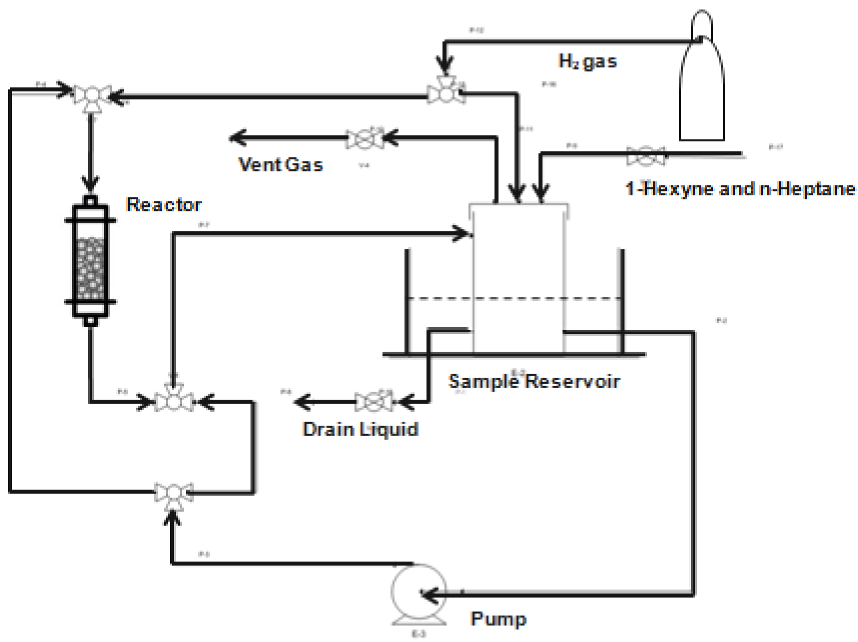

Figure1: The process flow diagram of 1-hexyne selective hydrogenation reaction

2.3.1 Catalytic evaluations

Catalytic reaction tests were carried out in a stainless steel packed bed reactor system under 1.5 bar and 40 °C. Throughout the reaction, the temperature and pressure were controlled at the desired values. After GC analysis, the conversion and selectivity were calculated.

The selectivity of 1-hexene and n-hexane can be written as followed;

$$\text{1-Hexene selectivity} = \frac{(moles\ of\ 1{-}Hexene_{final} - moles\ of\ 1{-}Hexene_{initial})}{moles\ of\ 1{-}Hexyne\ converted} \times 100 \qquad (1)$$

$$\text{n-Hexane selectivity} = \frac{(moles\ of\ 1{-}Hexane_{final} - moles\ of\ 1{-}Hexane_{initial})}{moles\ of\ 1{-}Hexyne\ converted} \times 100 \qquad (2)$$

3. Results and discussion

3.1 Catalytic Characterization

3.1.1 H_2 Chemisorption

The H_2 chemisoprtion results of Pd-Cu and Pd-W supported on alumina catalysts are reported in term of chemisorbed hydrogen mole/total Pd mole, H/Pd as shown in Figure 2. In case of Pd-Cu catalysts, when adding low amount of Cu, the H/Pd ratio slightly changed possibly due to Pd at the surface of metal cluster was not much diluted by the added Cu. At the amount of Cu higher than 0.18 wt%, Pd/Cu ratio less than 1.0, the H/Pd ratio dramatically decreases. It suggests that Pd at the surface of metal cluster is covered by Cu when using Pd/Cu less than 1.0. Moreover, it can be seen that, among the tested Pd-Cu/Al_2O_3 catalysts, the Pd-Cu catalyst with Pd/Cu ratio of 2.0 showed the highest H/Pd which can be implied that Pd-Cu catalyst with Pd/Cu ratio of 2.0 might has the highest amount of Pd at surface. In case of Pd-W catalysts, it can be seen that slightly increasing of W loading resulted in the increasing of H/Pd_t ratio because adding of W may enhance the dispersion of Pd catalysts or W may act as the catalyst. At the amount of W increase up to 1.02 wt% (at Pd to W ratio 0.5), the H/Pd ratio dramatically decreases. It suggests that Pd at the surface of metal cluster is covered by W when adding second metal up to 1.02 wt%. Conversely, the addition of the amount of W up to 2.02 wt%, the H/Pd ratio increases again possibly due to the result of hydrogen spill over. It is interesting to note that this result is not observed in Pd-Cu catalyst.

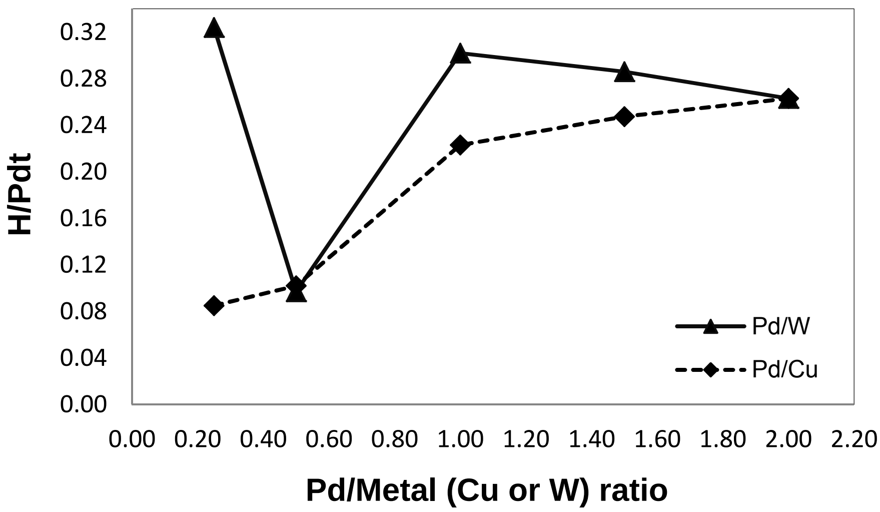

Figure2: H_2 chemisorption results of Pd-Cu/$Al_2O_3$and Pd-W/Al_2O_3catalysts with various Pd/Cu and Pd/W ratios

3.2 Catalytic Activity Measurement

3.2.1 Pd-Cu supported on alumina catalysts

The activity and selectivity of Pd-Cu/Al_2O_3 catalysts with various Pd/Cu atomic ratios were investigated for the selective hydrogenation of 1-hexyne at 1.5 bar and 40 °C. Figure 3 shows the catalytic activity of 1-hexyne hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios. It was found that Pd-Cu/Al_2O_3 (ratio 2.0) gave the highest activity among the Pd-Cu catalysts. This could be explained by the fact that, even though Cu can catalyze hydrogenation reaction, it has lower active than Pd (Sarkany, 1997) and Pd-Cu/Al_2O_3 (ratio 2.0) has the highest amount of Pd at the surface of metal cluster which indicated by H_2 chemisorption results. In addition, the activity of Pd-Cu/Al_2O_3 was decreased by increasing the amount of Cu loading because Pd at the surface of the metal cluster is diluted by Cu which is lower active than Pd catalyst as confirmed by H_2 chemisorption results.

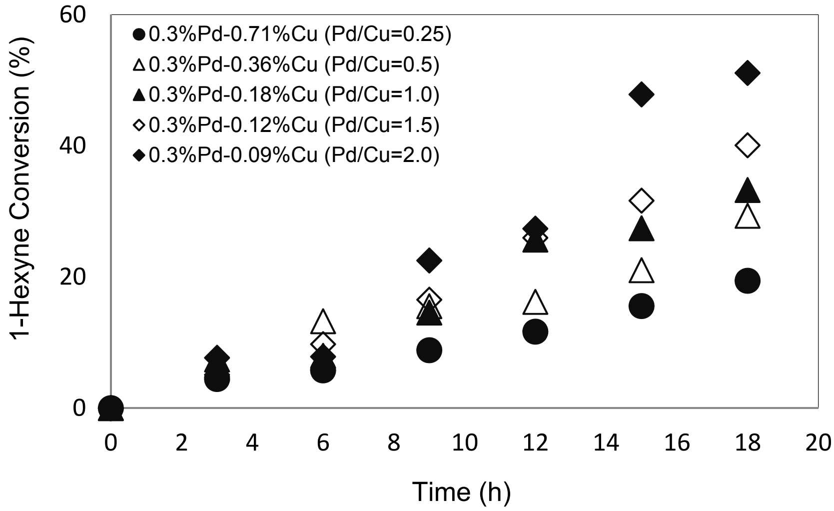

Figure 3: Catalytic activity of 1-hexyne hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios at 1.5 bar H_2 and 40 °C

The 1-hexene selectivity of Pd-Cu supported on alumina catalysts is shown in Figure 4. It can be seen that Pd-Cu/Al_2O_3 (ratio 2.0) catalyst slightly higher than the others. Furthermore, increasing amount of Cu loading causes the decreasing of the 1-hexene selectivity. As expected, selectivity of n-hexane is also increased as shown in Figure 5.

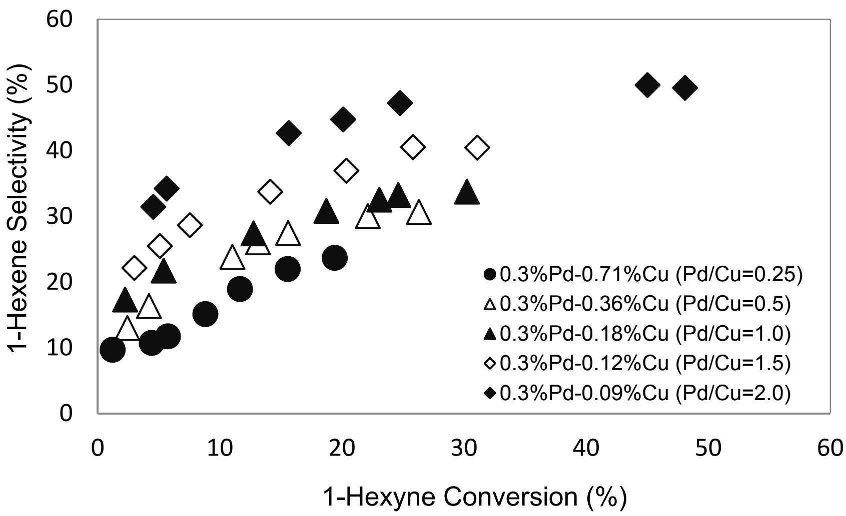

Figure 4: 1-Hexene selectivity of 1-hexyne hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios at 1.5 bar H_2 and 40 °C

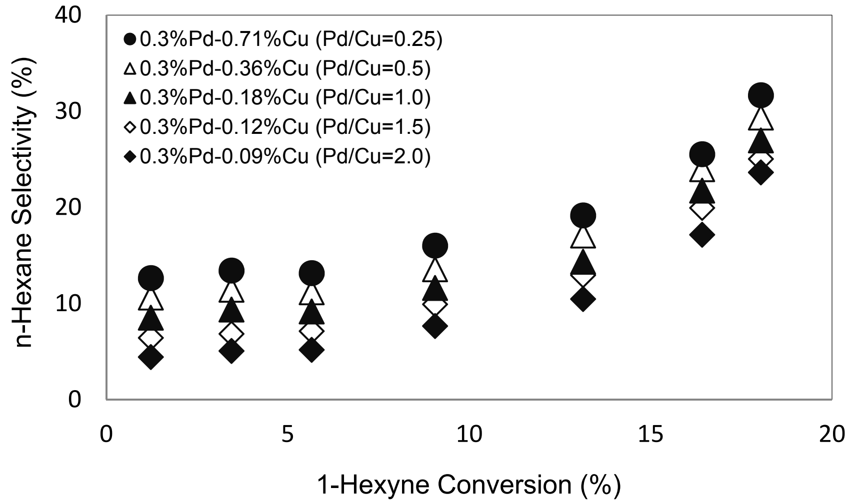

Figure 5: n-Hexane selectivity of 1-hexyne hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios at 1.5 bar H_2 and 40 °C

3.2.2 Pd-W supported on Alumina Catalysts

The catalytic performances of Pd-W in range of 0.25, 0.5, 1.0, 1.5 and 2.0 Pd/W atomic ratios were studied in the selective hydrogenation of 1-hexyne at 1.5 bar and 40 °C. Figure 6 shows the catalytic activity of 1-hexyne hydrogenation using Pd-W/Al_2O_3 at various Pd/W ratios. It was found that Pd-W/Al_2O_3 (ratio 0.25) gave the highest activity >Pd-W/Al_2O_3 (ratio 1.0)>Pd-W/Al_2O_3 (ratio 1.5)>Pd-W/Al_2O_3 (ratio 2.0)>Pd-W/Al_2O_3 (ratio 0.5) respectively. It should be noted that the high amount of hydrogen chemisorptions is also observed for Pd-W/Al_2O_3 (ratio 0.25) catalyst. For the selectivity, it can be observed that Pd-W/Al_2O_3 (ratio 1.0) shows the highest selectivity among the Pd-W/Al_2O_3 catalysts. At other Pd-W ratios, increasing or decreasing of the W loading slightly changes the 1-Hexene selectivity. Moreover, all ratios of Pd-W/Al_2O_3 catalysts provide higher 1-hexyne conversion than Pd-Cu/Al_2O_3 catalysts and more importantly the selectivity toward 1-hexene is also higher. As noticed, the selectivity of 1-hexene is more than 90% for Pd/W ratio 1 at the conversion of 1-hexyne of 100%.

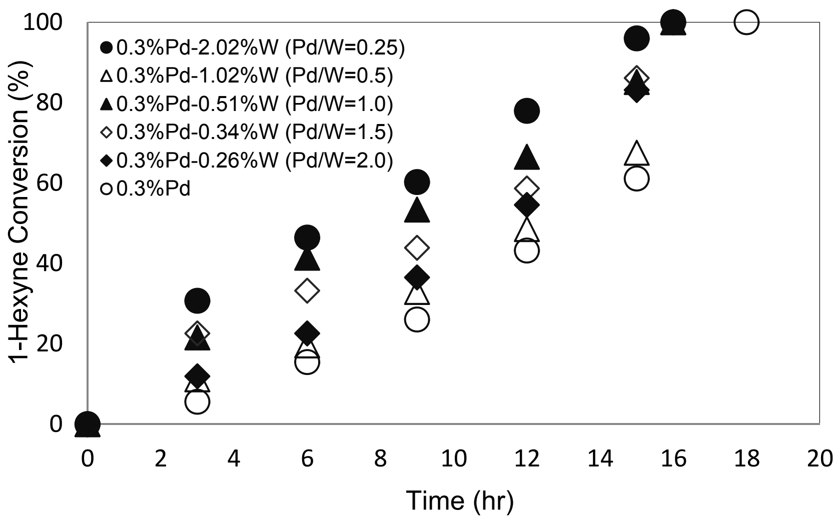

Figure 6: Catalytic activity of 1-hexyne hydrogenation using Pd-W/Al_2O_3 at various Pd/W ratios at 1.5 bar H_2 and 40 °C

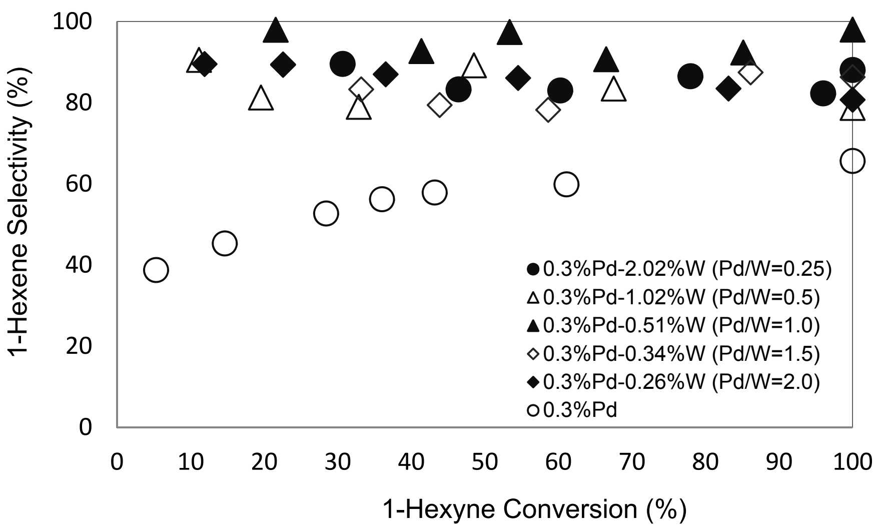

Figure 7: 1-Hexene selectivity of 1-hexyne hydrogenation using Pd-W/Al_2O_3 at various Pd/W ratios at 1.5 bar H_2 and 40 °C

4. Conclusion

The Pd-Cu and Pd-W supported on alumina catalysts were investigated for the liquid phase hydrogenation of 1-hexyne under 1.5 bar and 40°C. Pd-W/Al_2O_3 catalysts show better catalytic performances than Pd-Cu/Al_2O_3 catalysts. The Pd-W/Al_2O_3 at atomic ratio 1.0 can provide more than 90% selectivity of 1-hexene at the 100% 1-hexyne conversion.

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