Selective hydrogenation of 1,3-butadiene on Pd–Cu bimetallic catalysts

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Abstract: The γ-Al_2O_3 supported Pd–Cu catalysts were investigated in the selective hydrogenation of 1,3-butadiene. The catalysts were characterized by SEM, TEM, XPS, TPR, CO pulse titration, and FTIR of adsorbed CO; the catalytic study was performed in a fixed-bed reactor; and the adsorption properties were studied by DFT calculations. By the addition of Cu, Pd active sites were isolated, and the particle sizes were reduced. DFT calculations predicted that the Pd–Cu alloy should be more selective to produce 1-butene, which was verified by the reactor tests.

Keywords: PdCu catalyst, selective hydrogenation, DFT calculation.

1. Introduction

The low-carbon olefins (C2–C4) are important raw materials for the synthesis of polymers. However, the olefin stream from the cracking unit contains trace amount of alkynes and dienes, which seriously degrade the quality of polymers. Therefore, it is important to remove the alkynes/dienes by the effective hydrogenation treatment. Pd-based bimetal catalysts exhibit high performance in the hydrogenation of alkynes and dienes. Previous report[1] showed that the modification of Pd by Ni was effective in the enhancement of activity and selectivity; while the modification by another non-precious metal Cu has not been studied systematically. In the current research, a series of Pd–Cu catalysts were investigated by various characterizations such as SEM, TEM, XPS, TPR, CO pulse titration, and FTIR of adsorbed CO; the catalysts were then tested in a fixed-bed reactor; density functional theory (DFT) calculations were performed on Pd(111) and Pd_1Cu_3(111) surfaces to understand the adsorption properties of the Pd–Cu system theoretically.

2. Experimental and theoretical methods

The γ-Al_2O_3 supported catalysts were synthesized by incipient wetness impregnation. The Pd loading on the Pd-based catalysts were fixed at 0.91 wt%, while the Pd–Cu molar ratios of 1:1, 1:3, 1:5, and 1:8 were chosen for the bimetallic catalysts. The impregnated samples were dried at 353 K overnight and was calcined at 563 K in air for 2 h. The Cu/Al_2O_3 with a loading of 1.63 wt% was also prepared using the same method for comparison. The catalysts were characterized by SEM, TEM, XPS, TPR, CO pulse titration, and FTIR of adsorbed CO.

The hydrogenation of 1,3-butadiene was performed in a fixed-bed reactor to evaluate the catalytic performance of the bimetallic Pd–Cu catalysts. Prior to reaction, the catalysts were reduced at 400 ^{o}C in pure hydrogen. The reactant stream contained a mixture of H_2/1,3-butadiene/N_2 with a ratio of 1:2:38 The outlet products were analyzed with a gas chromatograph.

The adsorption energies of 1,3-butadiene, butenes, butane, hydrogen and CO were calculated on Pd(111), Cu(111) and Pd_1Cu_3(111) surfaces by subtracting the energies of the bare slab and of the free molecule from the total energy of the slab plus the adsorbed molecule.

3. Results and discussion

The average particle sizes and the active sites of the prepared catalysts are presented in Table 1. By the addition of Cu, the average particle sizes of Pd-based catalysts are reduced, and the active sites on the bimetallic catalysts are generally higher than the monometallic catalysts, indicating higher dispersions on the bimetallic catalysts. The temperature peak shifts in TPR spectra and the energy shifts in XPS spectra demonstrate the formation of Pd–Cu bimetallic particles. By observing the CO-adsorbed catalysts using FTIR, the changes in CO frequencies imply the isolation of Pd active sites by Cu modification.

The conversions of 1,3-butadiene with increasing temperature are shown in Figure 1(a). PdCu11/γ-Al_2O_3 shows similar activity with Pd/γ-Al_2O_3, while PdCu13/γ-Al_2O_3, PdCu15/γ-Al_2O_3 and PdCu18/γ-Al_2O_3 show slightly lower activity than Pd/γ-Al_2O_3. Although more active sites are identified on PdCu13/γ-Al_2O_3, PdCu15/γ-Al_2O_3 and PdCu18/γ-Al_2O_3, the FTIR spectra of CO imply that the adsorption are dominant on Pd top sites, indicating the well-isolated Pd atoms by Cu. On the contrary, Pd/γ-Al_2O_3 and PdCu11/γ-Al_2O_3 exhibit less active sites, and both top and bridge sites are found in the CO spectra. Because the isolation of Pd would result in significantly lower amount of Pd hydrides, which contributes to the hydrogenation activity[2], the more isolated Pd sites and the existence of less Pd hydrides on the bimetallic catalysts contributes the slightly lower activity.

The total butene selectivity and the 1-butene selectivity are presented in Figure 1(b) and (c). The bimetallic catalysts are shown to be more selective to total butenes than the Pd monometallic catalyst. As the conversion approaches 100%, PdCu13/γ-Al_2O_3 shows uniquely high selectivity, which contributes to the suppression of butane formation. PdCu13/γ-Al_2O_3 shows the highest selectivity to 1-butene below the 1,3-butadiene conversion of 90%; when the conversion goes above 90%, 1-butene eventually isomerizes to 2-buene. The extraordinary selectivity on PdCu13/γ-Al_2O_3 could be explained by DFT calculations that the adsorption energy of 1-butene on $Pd_1Cu_3(111)$ is significantly lower than that on Pd(111).

4. Conclusions

Hydrogenation of 1,3-butadiene has been studied over Pd–Cu bimetallic catalysts. The characterization results verify the formation of Pd–Cu bimetallic particles; the bimetallic catalysts are found to possess higher dispersion of metal particles and more isolated Pd active sites than the monometallic catalyst. The catalytic test results show that the activity of Pd–Cu bimetallic catalysts are slightly lower than the Pd monometallic catalyst, while the selectivities to total butenes and 1-butene are enhanced on the bimetallic catalysts. The excellent selectivity could be explained by DFT calculations that the adsorption energy of 1-butene on $Pd_1Cu_3(111)$ is significantly lower than that on Pd(111). Among the investigated catalysts, PdCu13/γ-Al_2O_3 shows unique selectivity to total butenes and 1-butene.

Table 1. The result of TEM &CO Pulse Titration.

Catalyst	Average Particle Size (nm)	Lattice distance (nm)	CO adsorption amount (mmol/g·cat)
Pd/Al_2O_3	10-80	0.2174	0.03329
1:1 PdCu/Al_2O_3	9-15	0.1953	0.02284
1:3 PdCu/Al_2O_3	5.4680	0.2081	0.02086
1:5 PdCu/Al_2O_3	4.6566	0.2072	0.04030
1:8 PdCu/Al_2O_3	-	-	0.04863
Cu/Al_2O_3	5.0090	0.2014	-

Table 2. The lowest adsorption Energy of different molecules on the Pd(111), Cu(111) and $Pd_1Cu_3(111)$ surfaces in DFT.

E_a(ev)	Pd(111)	Cu(111)	Pd1Cu3(111)
H	-2.7775	-2.5608	-2.3106
CO	-1.3174	-0.4676	-0.6835
C_4H_6	-0.5649	-0.4020	-0.4506
1-C_4H_8	-0.5325	-0.3481	-0.4105
trans-2-C_4H_8	-0.3104	-0.2409	-0.2459
cis-2-C_4H_8	-0.4066	-0.3659	-0.3707
iso-C_4H_8	-0.6207	-0.0935	-0.2968

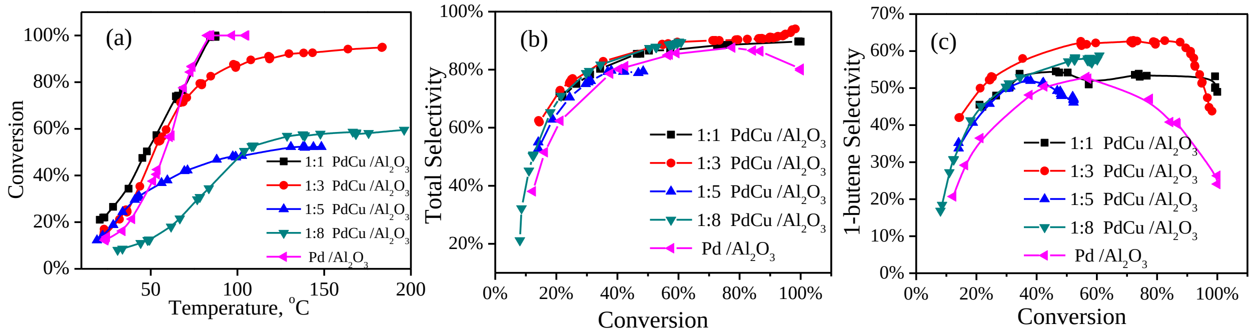

Figure 1. The results of hydrogenation reaction: (a) conversion rate of 1,3-butadiene over different catalysts; (b) selectivity of all of the produced butenes. (c) selectivity of 1-butene

References

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