

Novel Dual Bed Reactors: Utilization of Hydrogen Spillover in Reactor Design

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Introduction

Traditionally, the goals of increasing activity, selectivity, and of supported metal catalysts have been accomplished by discovering, or designing, a single catalyst with the best combination of properties. Recent work indicates that physical mixtures of two different catalysts may achieve these goals better than any single-catalyst system for hydroisomerization reactions [Lu et al., 1994; Chang et al., 1996; Chang and Phillips, 1997; Weigle and Phillips, 2004]. Phillips and co-workers demonstrated that physical mixtures of a noble metal catalyst and a bimetallic catalyst exhibited increased activity, selectivity, and stability toward the isomerization of 1-butene the selective hydrogenation of 1,3-butadiene. They attributed the dramatic increases in activity, selectivity, and stability of the physical mixtures, relative to each component independently, to hydrogen spillover.

Two novel reactor configurations were tested to validate the spillover hypothesis and to investigate the length over which hydrogen spillover occurs. In both reactors, a carbon-supported noble metal catalyst and bimetallic catalyst were segregated into distinct zones within the reactor. The only contact between the two catalysts was at the interface between the two zones. In the first reactor, referred to as the dual-feed reactor, the 1-butene was fed directly into the bimetallic zone and never contacted the noble metal. The noble metal was exposed only to hydrogen. Therefore, any 1-butene conversion had to occur within the bimetallic zone. Since the bimetallic catalyst by itself shows no activity at the temperatures studied, any conversion would be evidence of hydrogen spillover. The second reactor was a simple U-tube and was designed to test the limits of hydrogen spillover. Initially, 2.5mg of the noble metal catalyst was loaded into the U-tube reactor and its activity measured. Bimetallic catalyst was then added incrementally, upstream of the noble metal catalyst. The activity and selectivity of the bed were measured after each incremental addition. A similar procedure was followed for the dual-feed reactor.

Results and Discussion

The experiments with the dual-feed reactor provide convincing evidence of hydrogen spillover. Two control studies were conducted with this reactor. When the Pd/Grafoil was the only catalyst in the reactor, or when blank Grafoil was loaded in the place of the FeCe/Grafoil catalyst, no conversion was detected, indicating that very little 1-butene back-diffuses to the noble metal catalyst. Virtually no conversion occurs when only bimetallic catalyst was loaded into the reactor, showing that the bimetallic catalyst by itself has no activity at the temperatures tested. However, as seen in Figure 1, when the bimetallic catalyst was loaded into the zone above the noble metal catalyst, activities as high as 0.25 molC₄H₈/min-gPd were measured. In light of the control studies, this reaction must be occurring on the bimetallic surface. However, since the bimetallic catalyst alone is

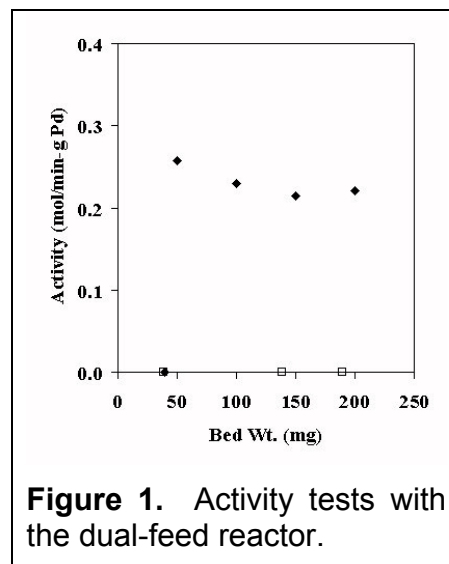


Figure 1. Activity tests with the dual-feed reactor.

essentially inactive at these temperatures, some activation process must be occurring in order to exhibit this activity. Our hypothesis is that molecular hydrogen adsorbs and dissociates on the noble metal surface. It then diffuses across the support surface (spills over) to the bimetallic catalyst and activates it.

Results from the U-tube reactor also show evidence of hydrogen spillover activating the bimetallic catalyst, as seen in Figure 2. When only the Pd/Grafoil and blank Grafoil are present in the bed, the activity is only 0.26 molC₄H₈/min-gPd at 40°C. A control study reveals that this activity does not change as blank support is added to the bed. However, addition of FeCe/Grafoil to the reactor results in activity increases. The activity increased with each addition of bimetallic catalyst. An activity of 0.44 molC₄H₈/min-gPd was measured in the 90mg bed when FeCe/Grafoil was added, and an activity of 0.78 molC₄H₈/min-gPd was measured when FePr/Grafoil was added. These activities resulted with the bimetallic catalyst *upstream* of the noble metal catalyst, indicating hydrogen spillover can occur against significant convective fluxes. This suggests spillover occurs at the support surface. A semi-quantitative mathematical model describes these results [Weigle et al., 2004]. The model predicts the activity trends observed in the experiments, however the parameters are not known to a great enough certainty to achieve quantitative accuracy. The results also suggest a new strategy for designing catalytic reactors.

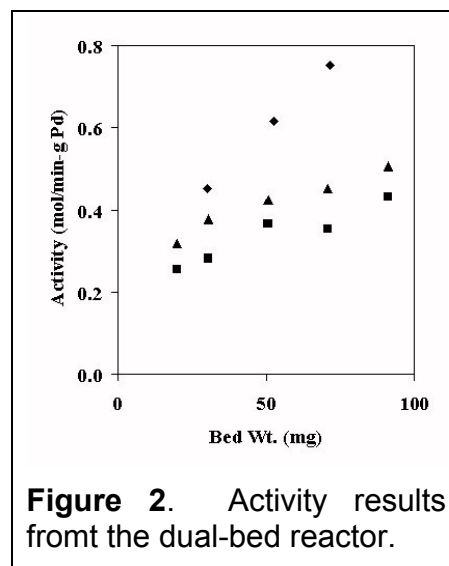


Figure 2. Activity results from the dual-bed reactor.

References

- Chang, H., J. Phillips, and R. Heck, "Catalytic Synergism in Physical Mixtures," *Langmuir* **12**, 2756-2761 (1996).
- Chang, H., and J. Phillips, "Catalytic Synergism in Physical Mixtures of Supported Iron-Cerium and Supported Noble Metal for Hydroisomerization of 1,3-Butadiene," *Langmuir* **13**, 477-482 (1997).
- Lu, W. C., H. Chang, and J. Phillips, "Novel Multimetallic Hydroisomerization Catalysts" *J. Catal.* **146**, 608-612 (1994).
- Weigle, J. C., and J. Phillips, "Novel Dual Bed Reactors: Utilization of Hydrogen Spillover in Reactor Design," *Langmuir*, **20**, 1189-1193 (2004).
- Weigle, J. C., Zea, H. R., and J. Phillips, "Modeling Hydrogen Spillover in Dual-Bed Catalytic Reactors," *AIChE J.*, **50**, 821-828 (2004).