

HYDROGEN SPILLOVER CATALYSIS IN PACKED BED REACTORS: KINETICS OF 1-BUTENE HYDROISOMERIZATION OVER DUAL BEDS OF PUGRAFOIL AND FeCe/GRAFOIL

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Keywords: catalysis, olefins, hydrogen spillover, carbon supports

INTRODUCTION

Recently a new family of very selective and active olefin double bond shift catalysts was discovered (1). These catalysts have potential value for increasing the octane of petroleum components both directly (β -position olefins generally have far higher octane value than α -olefins) and indirectly (improved input to alkylation units leads to higher octane product). This family of catalysts consists of one metal from the first row of the transition metals (typically iron or cobalt), one metal from the lanthanide series (typically cerium or praseodymium) and a relatively small amount of one noble metal (typically palladium). The multimetallic catalysts (e.g. Fe:Ce:Pt, 1:1:0.1) have some catalytic properties of each parent material. For example, FeCePt/Grafoil has selectivity (excellent) similar to FeCe/Grafoil, but high activity similar to that of Pt/Grafoil, a material with poor selectivity.

The following model was proposed to explain the unusual activity and selectivity of the multimetallic catalysts (1). First, the particle surfaces are 'compound'. They consist primarily of 'alloy' transition metal-lanthanide metal zones, but there are also postulated to be small zones of unalloyed noble metal. Second, each zone on the surface performs a different chemical function, and these functions add together to yield highly active and selective catalysts. Specifically, the alloy zone selectively isomerizes the 1-butene, and the noble metal zone provides hydrogen atoms via 'spillover' to allow this process to take place at a high level of activity. This model was shown to be consistent both with the known mechanism of bond shift and with information regarding hydrogen spillover.

Recent results support the above hypothesis. For example, it was shown that a physical mixture of the two components (e.g. FeCe/Grafoil and Pt/Grafoil) is as much as an order of magnitude more active than the sum of each component tested separately for 1-butene isomerization. The synergism also resulted in dramatically improved selectivity (2). It was also found that physical mixtures showed strong synergism for selective conversion of butadiene to butene (3).

These are not the first reports of physical mixtures demonstrating synergistic catalytic properties. Two models exist to explain synergism of physical mixtures. The classic model is the 'polyfunctional catalyst model' (4), and the second is the hydrogen spillover model (5). The earlier results strongly support the hydrogen spillover model. Indeed, it is difficult to identify an intermediate between 1-butene and 2-butene. Such an intermediate is required for the 'polyfunctional catalyst' model. Moreover, as discussed in earlier papers (2,3) the improvement in selectivity found in all cases and the 'limit' on synergism found in the hydroisomerization of butadiene are clearly consistent with the spillover hypothesis, but difficult to explain using any alternative model.

The present study was an attempt to test for spillover leading to synergism in segregated bed reactors. Specifically, the present work was designed to test the hypothesis that hydrogen spillover will lead to synergism in packed bed reactors with two stages, a graphite supported noble metal section and a graphite supported FeCe section. Synergism was found, but surprisingly the bed order was found to significantly impact the results.

EXPERIMENTAL

Catalyst Preparation. Two catalysts, FeCe/Grafoil and Pt/Grafoil, were prepared via the incipient wetness technique (1,6). GTA-grade Grafoil (Union Carbide) is a moderately high surface area (22 m²/gm), high purity, graphitic material (7). More detail on the catalysts is available elsewhere (1-3).

Kinetics. The bond shift in 1-butene was studied using a differential Pyrex microreactor operated at 1 atmosphere pressure (8). Reaction gas was purchased from Matheson and mixed with rotameters to yield a reaction gas with 2% butene, 18% hydrogen, and helium as balance. Analyses were done using a 6840 Hewlett Packard gas chromatograph equipped with a TC detector, a packed column containing Carbowax C/0.19% picric acid obtained from Supelco. In all studies intended for the purpose of comparing levels of activity total conversion was kept to less than 12% in order to justify the 'differential reactor' approximation.

In order to test the impact of physical mixtures on catalytic activity and selectivity physical mixtures containing different absolute amounts and different relative amounts of each material were required. In each case a section of 2 mg of Pt/Grafoil mixed with 18 mg of unloaded Grafoil was placed in the reactor. Variable amounts (zero to seventy mg) of FeCe/Grafoil were also placed in the reactor. Caution was taken to assure that the two beds were firmly in contact, but not mixed. In this configuration the reaction mixture encountered FeCe/Gr first. Beds with the components loaded in the opposite order, so that the reaction gas encountered the Pt/Gr first, were also tested. Next, all the catalyst material was reduced in flowing hydrogen at 400 C for four hours. After cooling the reaction gas mixture was added and the system allowed to stabilize.

RESULTS/DISCUSSION

In previous work (2,3) many relevant control studies were reported, including the impact of Grafoil addition on catalytic behavior (very minor), the activity of FeCe/Grafoil in the absence of any metal (extremely low at temperatures of interest) and the initial activity of noble metal only. This last 'control' was repeated in the present case as well. That is, the activity and selectivity of a bed consisting of 18 mg of Grafoil and 2 mg of Pt/Grafoil at 373 K was determined after 15 minutes or less on stream.

The next studies were designed to determine the activity and selectivity of beds with noble metal on top (first contact with feed mix) and to contrast this with the activity/selectivity of beds in which the alloy fraction is on top and the noble is on the bottom (at reactor exit).

The behavior of systems in which the noble metal is on the bottom are easy to explain. Each addition of FeCe/Grafoil resulted in a significant increase in measured activity (Figure 1). As the FeCe/Grafoil in the absence of noble metal has barely any activity at the temperatures employed, these results indicate synergism. In all likelihood hydrogen atoms generated on the noble metal surface diffuse 'upstream' and activate FeCe in the 'upper bed'.

It should be noted that the data shown in Figure 1a (except for the Pt/Grafoil only case) was collected after the catalysts had been on stream for between two and five hours. In all instances this was found to correspond to a period in which the overall activity of the bed declined relatively little (Figure 2). In most cases the activity dropped by less than 10% during this period.

Selectivity data for the case of the platinum bed on bottom is shown in Figure 1b and it is clear that the selectivity decreases as the activity synergism increases. This is different than that observed previously for well mixed beds with the same net catalyst composition (2). In those studies selectivity was found to improve with each increment of FeCe/Grafoil. A possible explanation for the surprising impact of bed segregation is that all products must pass through a bed of noble metal prior before leaving the reactor. Platinum may be a better catalyst for converting 2-butenes than 1-butene. In contrast, in a well mixed bed much of the 2-butene formed on FeCe may not encounter platinum before leaving the reactor.

Defining synergism in beds in which the noble metal is on top is more difficult. In all cases deactivation was rapid. After one hour on stream the catalysts bed had lost more than 35% of their initial activity in most cases, after two hours activity loss approached 50% and the decline in activity continued rapidly thereafter. Thus, at present no plots of activity or synergism are available.

In sum, it is clear that the present work demonstrates that synergism is found in integral bed reactors, containing segregated beds of platinum and FeCe/Grafoil. The nature of the synergism is a function of several factors, including the relative placement of the beds. In the event that the platinum is on top the overall deactivation rate is rapid. This can be fully explained by the deactivation of platinum. Apparently platinum at the bottom of a bed of FeCe is protected from deactivation and the spillover process continues for a far longer period of time. A second finding is that the overall selectivity of segregated beds is different than that of well mixed beds of the same composition. A third finding is that there appears to be a limit to the 'reach' of spillover. That is, the degree of activity enhancement per gram of FeCe appears to gradually diminish as more FeCe is added.

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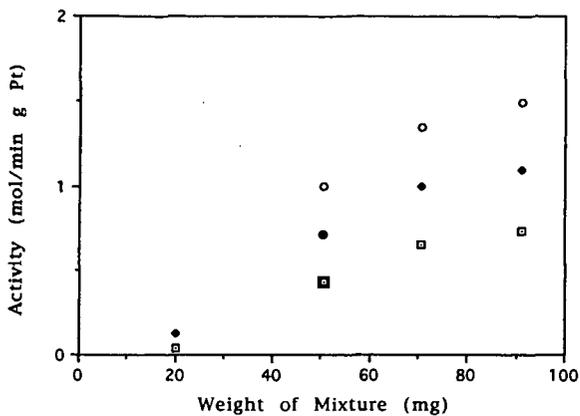


Figure 1a. Activity increase upon addition of FeCe/Grafoil
 ■ 80C • 100C ○ 120C

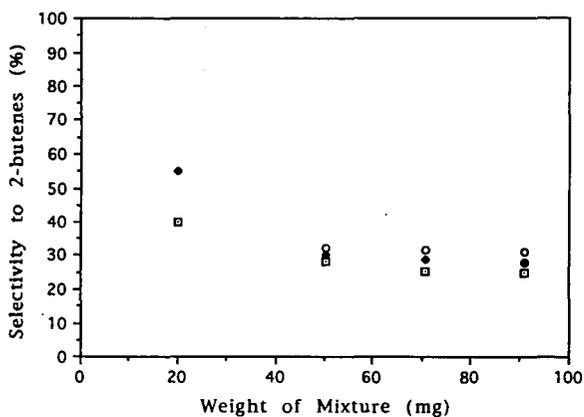


Figure 1b. Selectivity upon addition of FeCe/Grafoil
 ■ 80C • 100C ○ 120C

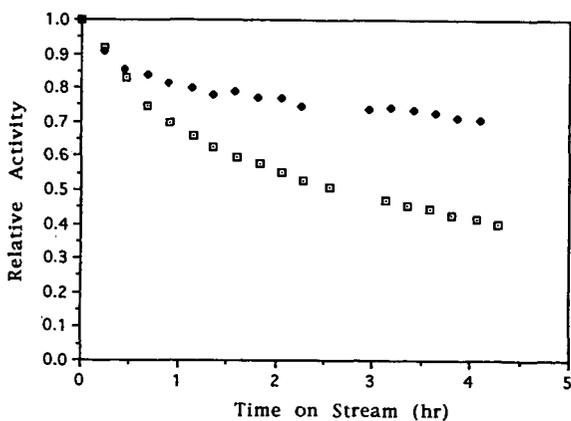


Figure 2. Impact of bed configuration on deactivation rate
 ■ Pt/Grafoil on top • Pt/Grafoil on bottom