JOURNAL OF CATALYSIS **146**, 608–612 (1994)

NOTE

Novel Multimetallic Hydroisomerization Catalysts

Recent work in our laboratory with supported multimetallic catalysts has resulted in the discovery of a class of catalysts with unique selectivity and activity for the hydroisomerization of 1-butene, as well as the hydrogenation of butadiene (1). Specifically, it was found that catalyst particles are composed of three metallic components, one from the third row of the Periodic Table, one from the first row of rare earths, and a platinum group metal, have higher activity and are far more selective for 1-butene isomerization than any single metal catalyst, including commercial catalysts widely used for selective hydrogenation (2, 3).

Testing thus far has been restricted to catalysts composed of the following three components: (i) a metal from the third row of the Periodic Table, particularly iron, or cobalt, (ii) a nearly equal (molar) amount of a rare earth, particularly cerium, lanthanum, or praseodymium, and (iii) about one-tenth as much of one of the noble metals, in particular palladium. Grafoil is the support used in the present study, although on silica supports similar behavior has been observed. GTA Grafoil is a high-purity (<700 ppm sulfur), high surface area (22 m^2/g) graphitic material composed primarily of graphite flakes (4–6). Before metal addition most of the sulfur is removed by a 12-h high-temperature pretreatment (1100 K) in flowing hydrogen. The advantages of using Grafoil for a support are that (i) X-ray analysis is simplified and (ii) there is no evidence of hydrogen spillover to the support modifying the measured activity or selectivity.

The catalysts are prepared using standard incipient wetness techniques. A detailed description of the preparation of Catalyst #1 (FePrPd/Grafoil) is given below. Similar techniques were used in the preparation of the other catalysts, with appropriate changes in support material, salts (in all cases nitrates were used), and metal concentrations of impregnating aqueous solutions. The Fe solution contained 0.00891 g Fe/ml, the Pr solution contained 0.0225 g Pr/ml, and the Pd solution contained 0.0017 g Pd/ml. Seven grams of ground up Grafoil were slowly added to 35 ml of the mixed aqueous solution (equal volumetric quantities of each metal solution). This procedure ensures complete and incipient wetness. Next, the catalyst was dried for 3 h in air at 100 C. The nominal atomic ratio of metal elements in the final catalyst was Fe : Ce : Pd, 1 : 1 : 0.2, and metal (Fe + Ce + Pd) represented approximately 5% by weight of the catalyst.

Chemical analysis (Galbraith Laboratories, Knoxville TN) of most elements agrees relatively well with the nominal compositions (Table 1), although the concentrations of cerium are slightly lower than expected. In any event, this small discrepancy between the nominal loading and the chemical analysis does not impact the qualitative model postulated below.

All studies were conducted with 30 mg of catalyst at just over ambient pressure using a stainless steel gas handling system, calibrated glass rotameters, and a Pyrex microreactor very similar to a system described in more detail elsewhere in the literature (7). All gases (hydrogen, nitrogen, oxygen, and reaction mix) were provided by Matheson and were ultra high purity grade. Pre-mixed reaction gas, consisting of 2% 1-butene, 18% hydrogen, and the balance helium, was used in all cases. Analysis was conducted using a gas chromatograph (Perkin–Elmer Model 8300) fitted with a 15-m packed Carbopak column (Alltech) maintained at 323 K.

Experiments were designed to determine (i) the selectivity of various alloys produced using either iron or cobalt and cerium or praseodymium and (ii) the impact of the addition of a relatively small amount of hydrogen atom generator (palladium) on the activity and selectivity of the alloys. Several control studies on single and bimetallic catalysts were conducted as well.

A comparison between Catalysts #1 (FePrPd/Grafoil) and #2 (FePr/Grafoil) serves to illustrate the general findings. The selectivity of these catalysts is shown in Fig. 1. Note for 1-butene conversions of less than 80% that the selectivity of both catalysts is consistently greater than 85%. The drop in selectivity at very high conversions is due to the impact of equilibrium. (Equilibrium conversion for the given reaction mixture is greater than 99% butane even at 473 K.) However, the reactivity of the catalysts is totally different. The activity of the catalyst without palladium (#2) is orders of magnitude lower than that of the sample with palladium (#1). Indeed, for Catalyst #2 it was impossible to measure any activity with the available system at temperatures less than 393 K. In order to obtain selectivity data over the full range of conversions it was necessary to run the system at 475 K.

0021-9517/94 $6.00

TABLE 1

Nominal and Measured Composition of Grafoil Supported Catalysts

		Nominal composition		Measured composition	
Catalyst no.	Catalytic metal	Wt% metal	Metal ratio (molar basis)	Wt% metal	Metal ratio (molar basis)
1	Fe : Pr : Pd	5	1 : 1 : 0.2	4.84	1 : 1 : 0.15
2	Fe : Pr	5	1 : 1	4.77	1 : 0.83
3	Fe : Ce : Pd	5	1 : 1 : 0.2	4.08	1 : 0.79 : 0.19
4	Fe : Ce	5	1 : 1	4.65	1 : 0.79
5	Co : Ce : Pd	5	1 : 1 : 0.2	3.74	1 : 0.93 : 0.17
6	Co : Ce	5	1 : 1	4.68	1 : 0.94
7	Pd	5		4.95	
8	Pd	0.2		0.195	

Activity differences are so great it is easiest to discuss them in terms of "temperature difference" to obtain a 50% level of conversion at approximately the same flow rate. For these two catalysts the temperature difference was more than 175 K (see Table 2).

Control studies demonstrate that the three component catalysts have the best properties due to some type of synergism. Indeed, it was demonstrated that the activity of Catalyst #1 is not due to the palladium fraction alone. A 5% Pd/Grafoil catalyst (Catalyst #7) had very high activity, but relatively poor selectivity (Fig. 1). Essentially the same selectivity was found for a Grafoil supported catalyst with only a 0.2% palladium loading. It is important to note that the selectivity difference between pure palladium and the multimetallic catalysts is more significant than Fig. 1 might suggest. For example, 85% selectivity is equivalent to a 2-butene/1-butane ratio of almost 6/1, whereas 50% selectivity is equivalent to a 1/1 ratio.

Other systems display behavior with a pattern similar to that observed for Catalysts #1 and #2. That is, for Grafoil supported samples the addition of a small amount of palladium dramatically increased the activity without impacting the selectivity. For example, Catalysts #3 and #4 (Table 1) are essentially identical to Catalysts #1 and #2, except cerium was substituted for praseodymium. Once again, the addition of palladium (#3) increased the activity dramatically, without significantly impacting the selectivity. The temperature difference for these two catalysts was about 120 K, and the selectivity was only slightly lower than Catalysts #1 and #2. Catalysts #5 and #6 were similar to Catalysts #3 and #4, respectively, except cobalt was substituted for iron. For this system the selectivity was consistently lower than that seen for Catalysts

TABLE 2

The Relative Activity of Catalysts/Gram of Catalyst

Catalyst # (composition)	Total conversion of 1-Butene (%)	Selectivity at 50% conversion (%)	Flow rate of reactants (CC/min at 50% conversion)	Reaction temperature (K)
1 (FePrPd/G)	50	90	315	298
2 (FePr/G)	50	95	10	475
3[a] (FeCePd/G)	50	85	210	298
4 (FeCe/G)	50	75	146	420
5 (CoCePd/G)	50	75	325	273
6 (CoCe/G)	50	75	44	440
7 (Pd/G)	50	50	558	273
0.5% Pd/Alumina[b] (commercial catalyst)	50	25	550	298

[a] Three nominally identical, but independently synthesized, batches were tested. Flow rates and selectivities were all within 5% of the (reported) mean values.

[b] 0.5% Pd $\frac{1}{16}$" alumina spheres from CALSICAT (Batch identification 5-92-042, E0144SDU) were crushed before testing.

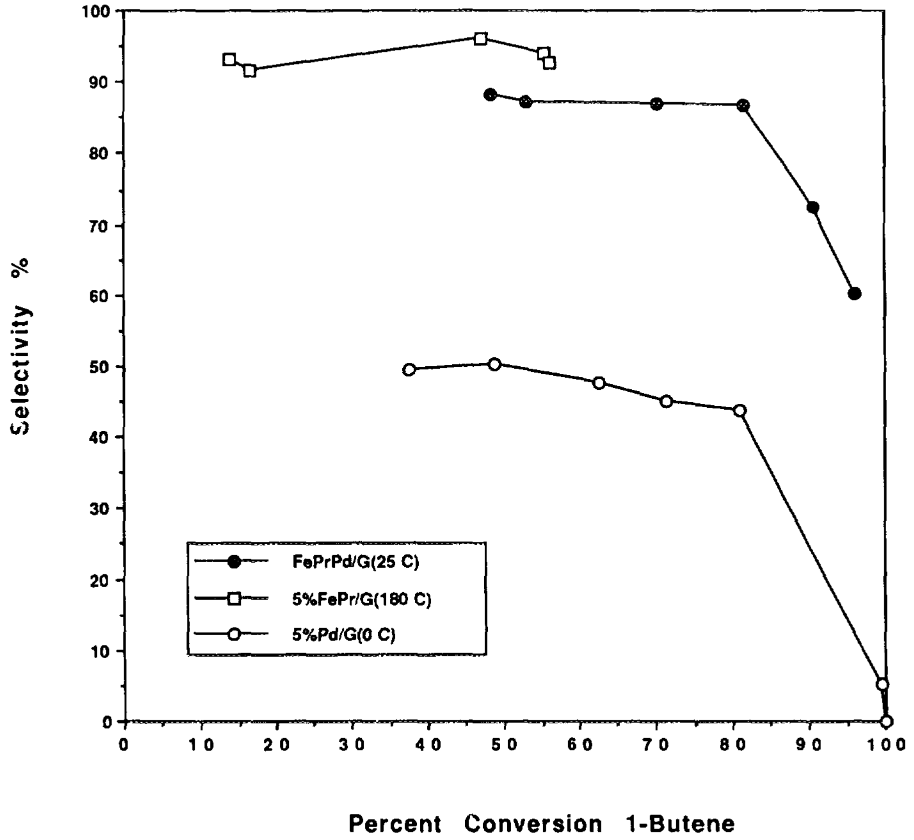

FIG. 1. Selectivity of multimetallic catalysts. The dats shown in this figure are representative of all the multimetallic systems studied. In the absence of palladium all had excellent selectivity (>75%), but very low activity (data collected at temperatures higher than 150°C). The addition of palladium only marginally changed the selectivity, while it greatly enhanced activity.

#1 and #2 (maximum selectivity approximately 75%), and the activity consistently higher. Indeed, the activation energy of this catalyst was not measured because the flow rates required to determine differential conversions at temperatures greater than 298 K were too high to achieve with our present system (maximum rate approximately 1000 ml/min). In this case the temperature difference was more than 175 C. Multimetallic catalysts of virtually identical nominal composition to all those listed in Table 1 (except 1% total metal) were also produced on silica, and very similar activity and selectivity behavior were observed (1).

Preliminary work (Fig. 2) suggests that the activities normalized for palladium content are very similar for all of those catalysts successfully studied. However, it must be noted that there is reason to believe that the activity of Catalyst #5 (per gram palladium) is still higher. This suggests, as discussed in more detail below, that the rate-determining step in all cases may relate to a process taking place on the palladium fraction of the catalyst surface.

A simple model can explain the above observations. This is discussed in terms of the contrast in behavior of Catalysts #1 and #2, but the analogy to the other systems is clear. It is postulated that most of the activity takes place on the FePr surfaces of both catalysts. However, on Catalyst #2 (no palladium) the activity is low because the catalyst cannot create hydrogen atoms, which it is understood are required for isomerization (8–11). The addition of palladium (Catalyst #1) removes this "bottleneck" to isomerization. Hydrogen is dissociated on the small section of the surface which is palladium, and "spills over" onto that part of the surface which is FeCe. This section of the surface retains its high selectivity, and thus the selectivity of the catalyst as a whole remains high. The overall activity of the catalyst might be controlled by the rate of hydrogenation generation at palladium sites.

There are many questions which must be answered before the above "working hypothesis" is proven. Implicitly the hypothesis indicates that the surface of those catalysts with palladium consist of segregated "alloy" sections and palladium metal sections. There are a number of recent studies (12–14) which demonstrate that multimetallic catalyst particles can have heterogenous surfaces with segregated sections of different compositions and

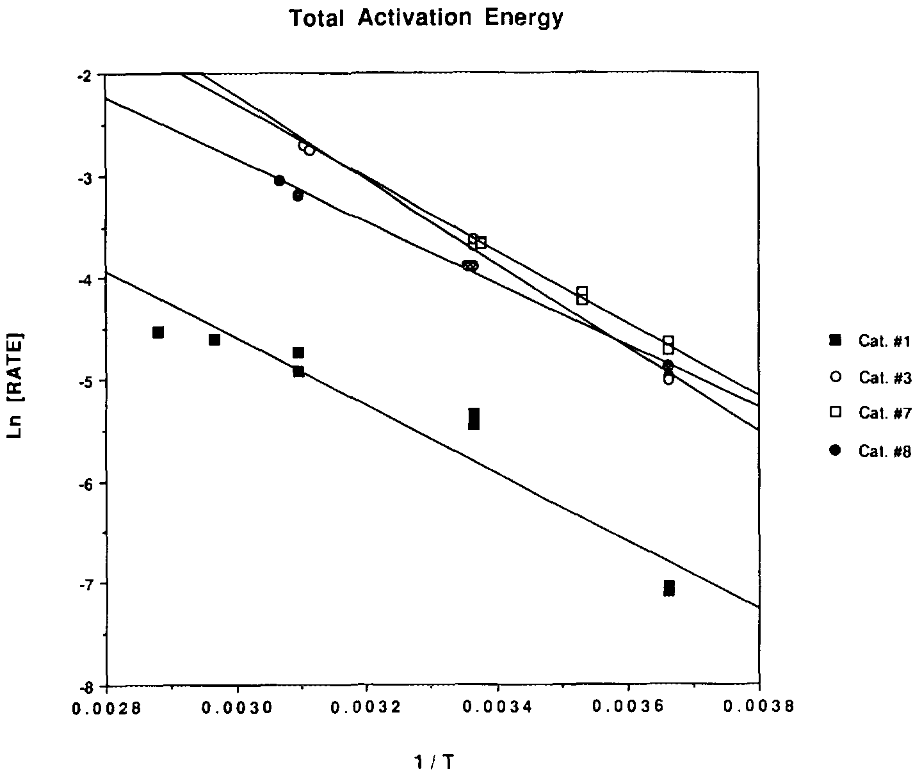

FIG. 2. Relative activity and activation energy. The rates shown are the rates of 1-butene conversion per gram of palladium in the catalyst. Data were taken in a true differential reactor (conversion <10%). Note that these rates, as well as the activation energies, are close in all cases.

structures. X-ray analysis (method discussed elsewhere (13, 15)) is consistent with this analysis. Indeed, the only additional X-ray spectral line following the addition of palladium to FeCe (Fig. 3) is that of palladium metal. Can the difference in activity be attributed to dramatic changes in dispersion following the addition of palladium? Preliminary particle size distribution data obtained from both Catalysts #1 and #2 show there is virtually no difference in the degree of dispersion. Another question is why does the segregated palladium not dominate the kinetics, or at least reduce the overall selectivity?

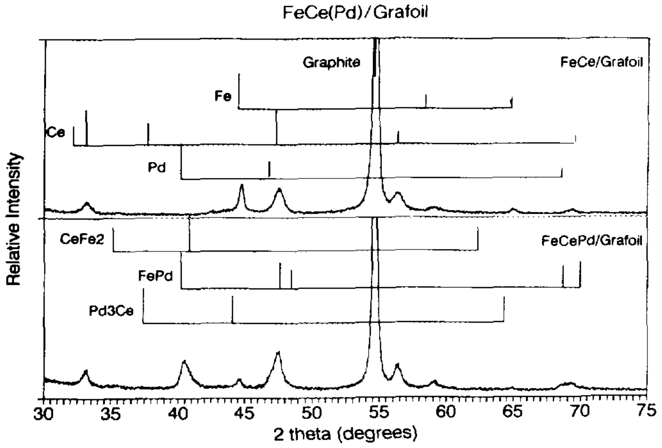

FIG. 3. X-ray analysis of Catalysts 3 and 4. The only new peak which appears after the addition of Pd (bottom frame) is a palladium metal peak.

It has long been recognized that hydrogen spillover potentially is of great value to the design of heterogeneous catalysts (16), and in fact there are many examples of catalysts which successfully utilize this phenomenon to enhance catalyst activity (17–19). If the working hypothesis outlined above is correct, the present communication concerns the use of spillover not only to enhance activity, but to significantly improve selectivity as well. It suggests there is a potential for designed selectivity without significant activity loss in hydroisomerization reactions. In fact, it has already been found that some catalysts from the multimetallic family discussed here are active for selective butadiene hydrogenation, under typical industrial conditions, at far lower temperatures than current commercial catalysts (1).

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Received June 14, 1993; revised October 19, 1993

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