

Reaction Probe Study of the Dual Surface Structure of Graphite-Supported Fe-Rh Catalysts

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As part of a continuing effort to characterize the structure of base-metal noble-metal bimetallic catalyst particles the catalytic chemistry of graphite-supported iron-rhodium particles was tested after two different pretreatments. Specifically, the activity of the catalyst for 1-butene isomerization/hydrogenation was tested after oxidation and (i) low-temperature (375 K) hydrogen reduction and (ii) high-temperature (675 K) reduction. It was found that the catalytic chemistry of these two reduced surface states was entirely different. After the low-temperature reduction the chemistry was very much like that of rhodium. After high-temperature reduction the surface had activity similar to that of rhodium, but, like iron, selectively isomerized rather than hydrogenated the 1-butene. These results could be readily explained on the basis of an earlier model which suggests that following low-temperature reduction the surface consists of "zones" of zero-valent iron and zones of zero-valent rhodium, and after high-temperature reduction the surface is a true iron-rhodium alloy. © 1990 Academic Press, Inc.

INTRODUCTION

Recent studies of bimetallic catalysts suggest that the surface structure of some of these systems is dependent upon the prior sequence of treatments. For example, it was shown that iron-rhodium catalyst particles can have one of two different surfaces following reduction. Following oxidation at 475 K or higher and subsequent low-temperature (ca. 400 K) reduction the surface is composed of adjacent "zones" of metallic iron and metallic rhodium. Metallic iron zones were shown to predominate. In contrast, following high-temperature reduction (ca. 675 K) the surface was that of a true alloy (1, 2).

The present study was designed to determine if the two different reduced surfaces have different catalytic properties. Specifically, 1-butene hydrogenation was carried out over the catalysts after they had been treated to produce one of the two previously

found reduced surface states. This reaction was chosen for three reasons. First, this is a thoroughly studied system over single metal catalysts (3-6). These previous studies provided a standard for comparison. Second, it takes place at a high rate at relatively low temperatures. Thus reaction rates can be studied without concern for temperature-induced changes in the surface structure. Third, data concerning selectivity as well as apparent activation energies is available, thus providing two types of data for purposes of contrast/comparison.

Results of the kinetic studies clearly show that the surface formed following oxidation and then low-temperature hydrogen reduction (segregated metal state) has very different catalytic properties than that formed following oxidation and high-temperature hydrogen reduction (true alloy state). Both the apparent activation energies for 1-butene conversion and the selectivities were found to be very different. Moreover, comparisons between the activity of the two surface structures with those of pure iron and

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pure rhodium catalysts showed that the segregated metal surface behaves as if it is dominated by the small amount of rhodium metal present in the surface. In contrast, the chemistry of the true alloy surface is significantly different than that of either parent metal.

EXPERIMENTAL

Catalyst preparation. The bimetallic catalyst samples (5.4 wt% metal, 1:1 Rh to Fe ratio) used in this study were taken from the same batch of Grafoil-supported iron-rhodium used in previous studies (2). This was done as particle size and surface area were studied exhaustively in the previous work. As described in earlier work the catalysts were prepared from a cluster compound, μ -(η (cycloheptatrienyl))-tricarbonyl-iron-cyclooctadiene rhodium.

The Grafoil-supported rhodium (7) catalysts were also taken from previously prepared catalysts. Again, the catalyst had been extensively characterized in a previous studies. A new batch of Grafoil-supported iron catalyst was made up specifically for this study, using an incipient wetness technique described in detail elsewhere (8). In order to confirm that no dramatic changes in the average particle size or the particle size distribution had taken place (bimetallic and rhodium) or to measure the particle size distribution of new catalyst (iron) X-ray diffraction and transmission electron microscope (TEM) studies were performed as described below.

Catalyst characterization. The X-ray instrument used was a Rigaku Model D/Max IIIA. The following settings were used in all cases, scan rate 4° per min, time constant 0.5, 1000 counts/s. For the TEM studies a Philips Model 420 TEM was used.

Kinetics. All studies were performed at 6 atm using a fully stainless-steel gas handling system with calibrated glass rotameters and a pyrex microreactor very similar to others described in more detail elsewhere in the literature (9). Analysis of the reaction products was made using a Model P-E 8300 gas

chromatograph with a hot wire detector and utilizing an FT-1700 fused silica capillary column. The column was maintained at 263 K which permitted virtually complete separation of all component gases. Premixed cylinders containing approximately 18% hydrogen, 2% 1-butene (Matheson), with the balance being helium, were used as received to insure that the stoichiometry of the reaction mixture remained constant. The gas was checked at frequent intervals with the chromatograph to insure that it was identical in composition to that claimed and that no conversion took place either in the tank or gas handling system. Calibration of the detector system was performed using a calibration mixture obtained from Matheson. The hot wire detector response factors calculated for the various species were very close to those previously published (10).

A ten-port valve was controlled using the programming capability of the system, such that samples were taken at regular intervals. This permitted multiple samples to be taken after a 1-h equilibration period at each temperature. In fact, all data plotted below represent an average of between 4 and 10 readings. For the activity measurements flow rates, measured in every instance with a bubble flow meter, were adjusted at each temperature such that less than 10% of the 1-butene was converted. Thus, the system was run in an effectively differential fashion. Moreover, for the activity measurements data were only collected over that range of flow rates in which it was shown that the total rate of conversion was independent of the flow rate. This was done to insure that mass transfer was not influencing the observed kinetics. Not surprisingly diffusion limitations were readily overcome as the support material Grafoil has a relatively low surface area (22 m²/gm) and large pores (11-13). Furthermore, very little catalyst was needed so that the total bed depth was never greater than 3 mm. Finally, it must be noted that for the selectivity measurements the flow rates were adjusted so that various levels of conversion could be studied. The

TABLE 1
Catalyst Characterization

Catalyst	Percentage metal
Rh/Grafoil	5.1
Fe/Grafoil	5.2
FeRh ^a /Grafoil	5.4

^a The Fe : Rh atomic metal ratio in this catalyst is 1 : 1.

system was not in a differential mode for those studies, nor were mass transfer limitations considered.

RESULTS

Particle size. Three catalysts were used in this study, iron on Grafoil, rhodium on Grafoil, and a bimetallic iron-rhodium on Grafoil. The weight loadings of each sample, determined by analysis at Galbraith laboratory, are given in Table 1. The average particle size of the iron and rhodium particles determined using the Scherrer equation (14) to analyze X-ray peaks is given in Table 2. This was not done for the bimetallic particles because of uncertainty regarding the meaning of such data as the morphological model suggests that multiple crystalline zones exist within each particle (1, 2). As the X-ray results in a previous study indicated that the rhodium particles were unchanged, measures of dispersions (7) were used in calculating turnover-frequencies

(TOF) for rhodium in the present study. An earlier study had clearly shown that for Grafoil-supported iron particles, X-ray and TEM results can be used to accurately determine dispersions. Thus, in the present study iron dispersions were determined from X-ray and TEM results as described elsewhere (8).

Particle size distributions determined for iron and bimetallic catalysts are given in Fig. 1. The average particle sizes (Table 2) and the particle size distributions for the bimetallic catalyst are nearly identical to those measured in previous studies (2). This suggests that the catalysts are identical to those previously studied (as they should be) and thus other information obtained in the previous studies, such as surface areas, was used to determine dispersion.

Kinetics. The first kinetic studies were designed to contrast the behavior of the Fe-Rh catalyst following each of two different pretreatments. The first treatment was

TABLE 2
Catalyst Particle Size

Catalyst	Average particle size, Å	
	X-ray diffraction	T.E.M. ^a
Fe/Grafoil	250	240 ^b
Rh/Grafoil	100 ^c	—
Fe-Rh	—	150

^a Measure of the volume-weighted average (D_v), which is computed as discussed in Ref. (14).

^b Compares very well with a previous measure of a catalyst prepared in a similar fashion in an earlier study (Ref. (8)).

^c Compares very well with measures of the particle size of the same catalyst made in an earlier study (Ref. (7)).

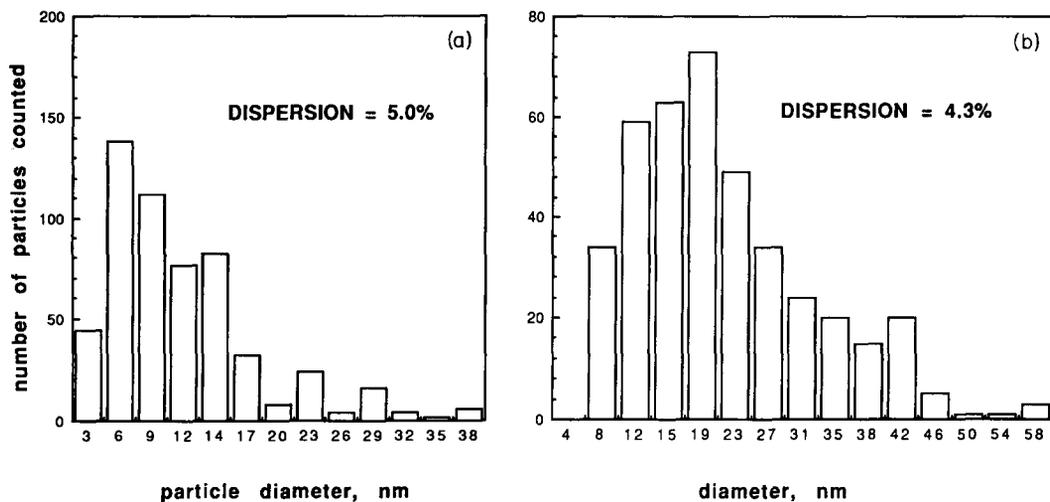


FIG. 1. Particle size distributions determined using TEM. (a) Particle size distribution (diameter) of FeRh/Grafoil catalyst. (b) Particle size distribution of Fe/Grafoil catalyst.

intended to produce particles consisting of zones of metallic iron and zones of metallic rhodium (1, 2). This so-called "segregated metals" state was produced by oxidation (525 K) and low-temperature (400 K) hydrogen reduction of the Fe–Rh catalyst. The second state, the so-called, "alloy" state, was produced simply by treating the sample at high temperature (675 K) in flowing hydrogen.

On the basis of measures of the total surface area of these catalysts and the kinetic studies carried out in the present investigation it is possible to compute the turnover frequencies at various temperatures. In fact, the Arrhenius plots (Fig. 2) from which the activation energies are determined are plotted in terms of TOFs. Comparison of activity in terms of TOFs allows for a standardized comparison between different catalysts.

Both overall activity and selectivity of the Fe–Rh catalyst were influenced by the treatment sequence. As shown in Fig. 2 below 350 K the overall activity (1-butene conversion) of the segregated metal state was always less than the activity of the alloy state. Both of these conclusions independently apply to the rate of hydrogenation

and the rate of isomerization. Moreover, the apparent activation energy of the two states is very different. Note that the activities are reported in terms of turnover frequencies. With one exception (6) in the many previous studies of this reaction the difference in the activity of various metals has only been reported qualitatively.

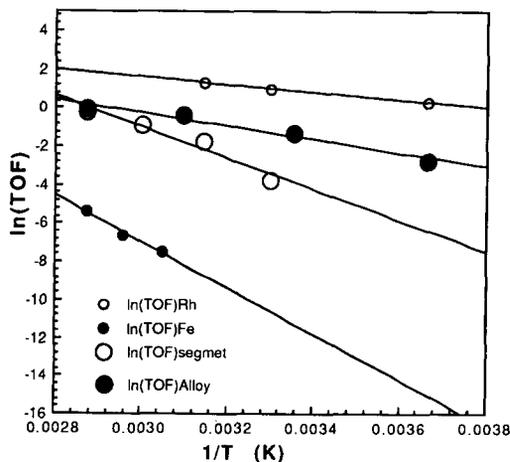


FIG. 2. Turnover frequencies (TOF) for 1-butene usage are plotted as a function of temperature for all the catalysts studied. Activation energies were also obtained from this plot.

TABLE 3
Activation Energies (kJ/mol)

Catalyst	1-Butene depletion	N-Butane formation	Isomer formation	Temperature Range, K
Fe/Grafoil	100	100	105	325–350
Rh/Grafoil	15	15	30	273–320
FeRh/Grafoil-Alloy	30	20	35	273–350
FeRh/Grafoil-Segregated	65	70	65	300–350

Activation energies for various states of the catalyst are reported in Table 3. It must be understood that only approximate activation energies are reported. For example, it is reasonable to question the validity of reporting separately the activation energies for hydrogenation and isomerization. However, it is conventional to do this for differential extents (virtually constant hydrogen and 1-butene concentrations) of this reaction (3, 15, 16). It is assumed in this work, as it has been previously, that the concentration of product species is so low that the contribution of product interactions, for example *cis*- or *trans*-hydrogenation and *cis*-*trans* isomerization, contributes negligibly to the measured concentration profile. That is, all products are assumed to form by reaction between 1-butene and hydrogen. Indeed, isomerization will occur in the absence of hydrogen, but even in the presence of very low levels of hydrogen the hydrogen-mediated isomerization process will dominate (17). Thus, as pointed out by others (4), the activation energies must be regarded with caution, but still represent valid approximations. They also serve as a basis for comparison between the various catalysts.

Figure 3 shows that the selectivity of the two states are very different. The segregated metal state produces a great deal of butane at all conversion levels. In contrast, the catalyst in the alloy state produces more isomerized products than hydrogenated products below 80% total conversion level. It is important to note in connection with the selectivity data that at equilibrium virtually

all of the 1-butene should be converted into butane. Thus, it is not surprising that at the highest conversion levels butane was found to be the only product.

It is important to note that data was obtained both with progressive increases in temperature and progressive decreases in temperature. There was virtually no difference found in the rate vs temperature curves. Furthermore, the catalyst was cycled through the two states repeatedly (alloy-segregated metal–alloy-segregated metal), and the kinetics were studied. Both the alloy and the segregated metal kinetics were unaltered by the cycling process.

In order to better understand the kinetics on the bimetallic catalyst, activity and selec-

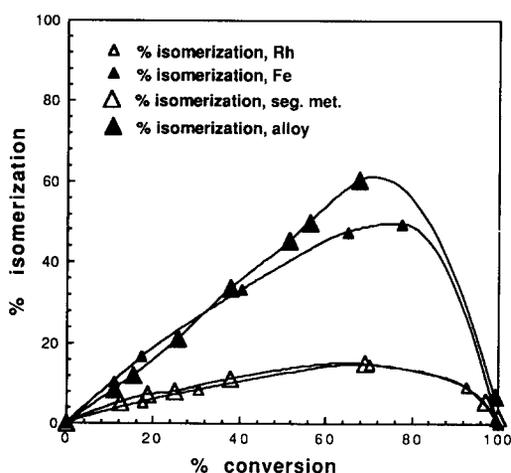


FIG. 3. Selectivity: The fractional amount of butane produced as a function of the degree of overall 1-butene conversion. Yield data were collected at 350 K.

tivity experiments were conducted with iron- and rhodium-only catalysts on the same support material. The rhodium catalyst proved to be extremely active (Fig. 2) and had a turnover frequency significantly higher than that of any other catalysts. The selectivity of the rhodium catalyst was very similar to that of the segregated metal catalyst as well (Fig. 3). The iron-only catalyst had a very low level of activity, but showed surprisingly high selectivity toward isomers, very much like the alloy state of the bimetallic catalyst.

DISCUSSION

This study clearly demonstrates that the surface chemistry of bimetallic catalysts is strongly influenced by the sequence of treatments. In particular it was demonstrated that a new model of the dynamic phase behavior of bimetallic particles, described in the Introduction and in more detail elsewhere (1, 2), can be used to successfully understand the variations in the catalytic chemistry of graphite-supported Fe/Rh particles. Alternative models of the structure of bimetallic catalysts, which indicate that there is only one reduced metal surface state (18), are not adequate to explain the changes in kinetics which take place as a function of catalyst treatment. Models which suggest that iron is unreduced after a high-temperature reduction, for example on silicon supports (19), are also inadequate to describe the observed behavior. Mossbauer, X-ray, and calorimetric studies previously conducted (1, 2, 8) all indicate that the iron in Grafoil-supported particles is fully reduced.

Kinetic studies clearly show that the bimetallic iron-rhodium system has two entirely different fully reduced active surface states. The character of each surface is best understood on the basis of a comparison with independent studies of the two parent metals.

Iron and rhodium. Single metal catalysts were studied in the present work primarily as a source for comparison with the behav-

ior of the mixed metal catalyst. It might appear that this was unnecessary as there have been numerous previous studies of these catalysts (3, 5, 6, 17, 20-24). There are two reasons that independent studies were required. First, with one exception (6), in none of the previous studies have turnover frequencies been reported. It has long been understood that TOFs permit comparisons between catalytic studies done in different laboratories. In the present study they also provide a mechanism for assessing the contribution of each element in the bimetallic surface to the overall activity. Second, previous studies clearly show that the support material, even its pretreatment, strongly influences the chemistry of the catalysts (17, 24). Carbon- or graphite-supported particles have never been studied. It is generally understood that the mechanism by which supports influence the catalytic chemistry is that of supplying hydrogen. Hydrogen originating in the form of surface hydroxyl groups apparently migrates to the metal surface. Indeed, metals on fully dehydroxylated supports will not catalyze isomerization (20) in the absence of molecular hydrogen. Unsupported metal particles never catalyze isomerization in the absence of molecular hydrogen (24). It has also been shown that the isomerization activity of alumina-supported catalyst particles can be correlated to the hydroxyl density on the support surface (17, 24, 25).

It was found that the selectivity results obtained for rhodium in the present study are similar to those already published in the literature. For example, previous studies of rhodium show that it is primarily a hydrogenation catalyst and relatively inactive for isomerization (20, 21). In contrast, previous studies of iron do not provide information regarding selectivity valid for comparison with the conditions employed in the present study (26, 27).

The activity results for both metals are in qualitative agreement with earlier studies. For example, it is known that rhodium is

very active (3). Indeed, the TOF for rhodium measured in the present study is in excellent agreement with the value of 2.0 determined at 293 K in a previous study (6). However, the previously reported activation energies for Rh/ α Al₂O₃ for both hydrogenation and isomerization are about 10 kJ/mol higher than those measured in this study (20, 21). Iron has generally been found to have little or no activity below 100°C (22, 23). In the present study, in order to obtain data over the same temperature range as that used for the other catalysts, approximately 15 times as much iron catalyst was used. Again, previous workers have ranked catalysts by activity, but on a qualitative basis. There was no means with which to quantify the differences in activity precisely. In contrast, the turnover frequencies measured in the present study make this a relatively simple task. Clearly, the activity of rhodium, normalized to a per surface atom basis, is almost three orders of magnitude higher than that of iron over the temperature range studied.

Alloy. Following reduction at 675 K in flowing hydrogen the particles are found to have a relatively low apparent activation energy for the overall conversion of 1-butene over the range of temperatures studied. Moreover, the particles in this state are excellent isomerization catalysts. That is, as shown in Fig. 3, at 348 K the products are primarily isomers for conversion levels of less than approximately 80%.

A comparison with the data obtained in this study and others for the same reaction over iron and rhodium reveals that in this state the surface chemistry of the bimetallic system resembles neither of the parent metals, but has a mix of the parents' properties. The overall turnover frequency is somewhat less than that of rhodium (Fig. 2), but much greater than that of iron. The apparent activation energy for 1-butene conversion is greater than that of rhodium, but significantly less than that of iron. The activation energy for isomerization is about equal for

rhodium. The selectivity for isomers is similar to that of iron. Thus, in terms of activity the alloy is not too unlike rhodium, but in terms of selectivity, it is very much like iron.

Altogether the data suggests that the alloy surface has unique chemical properties. This finding is consistent with the previously published suggestion that following high-temperature reduction the particles are in a true alloy state (1, 2). It was suggested that the surface is in fact composed of virtually equal quantities of iron and rhodium in the normal arrangement of an alloy.

The available information permits a limited amount of speculation regarding the cause of the observed behavior of the alloy. In the alloy arrangement it is possible that the rhodium atoms provide the ability to adsorb and dissociate hydrogen molecules, a capability missing from small iron particles over the temperature range studied (28, 29). The presence of dissociated hydrogen could dramatically increase the TOF relative to that on pure iron as it is clear that hydrogen-mediated reaction is much faster than reaction in the absence of hydrogen. However, the geometric arrangement apparently favors "iron-like" selectivity toward isomerization. Indeed, it is generally understood that the variation in selectivity observed for different metals during 1-butene hydrogenation can be traced to the geometric arrangement of the catalyst surface (3, 4, 18, 25). This simple model helps explain how each metal might contribute to the overall chemistry of the alloy. Finally, it is interesting to note that the selectivity toward isomerization of both iron and the alloy state are better than that of palladium, which is generally regarded as the best single metal 1-butene isomerization catalyst (4, 6).

Segregated metals. After oxidation at 475 K and reduction at 400 K in flowing hydrogen the catalyst was found to have an activation energy for the conversion of 1-butene to products higher than that of the metal in the alloy state, or that of either of the parent metals. It also had high activation energy for

the production of both butane and isomers. The TOF values were between those of rhodium and iron, and in fact were a little more than an order of magnitude lower than those of rhodium over most of the reported temperature range. Critical to the understanding of this material was the finding that selectivity of the material in this state was virtually identical to that of rhodium over the entire conversion range.

The above findings are consistent with the previously published model of the surface structure of bimetallic iron-rhodium particles following oxidation and subsequent low-temperature reduction (segregated metals). In that model it is suggested that the surface is composed primarily (90%) of metallic iron zones and a small amount of rhodium in metallic rhodium zones. On the basis of the low TOFs measured for pure iron and the high TOFs measured for rhodium it is clear that a small amount of rhodium in the surface would dominate the catalytic behavior for the reaction under study if the particles are in fact in the segregated metal arrangement as postulated. Indeed, the selectivity of the segregated metals supports the suggestion that the surface chemistry of the segregated metal state is dominated by the small amount of rhodium present at the surface. Once the TOFs are corrected for the fact that only about 10% of the surface (1, 2) consists of rhodium, they become reasonably close to those of rhodium.

Clearly, there are some differences between the chemistry of the particles in this state and that of the pure rhodium particles. The main differences are between the measured activation energies. The activation energies for the segregated metals is much higher than it is for pure rhodium. However, it is generally understood that the activation energies for 1-butene hydrogenation/isomerization are the least repeatable values. It has been suggested that the activation energies are strongly influenced by low levels of impurities (4). Thus, selectivities rather than activation energies are frequently compared. The selectivities totally rule out the

possibility that the iron component of the surface is participating in the activity. Possibly the electronic structure of the rhodium is modified by the close proximity of iron crystals. In turn this modifies the activation energy of the process, but not the selectivity; the selectivity of the process is most sensitive to the geometry of the reaction site.

SUMMARY

In this study it was shown that an earlier model (1, 2) of bimetallic particle surface structure can successfully explain the two distinct catalytic surfaces found to be associated with Fe-Rh/Grafoil catalyst particles. That is, following oxidation and low-temperature reduction the surface acts like it is dominated by a small amount of slightly modified rhodium metal. This would be expected on the basis of the earlier model which suggests that zones of rhodium metal (approximately 10%) and zones of iron metal make up the surface following the low-temperature reduction. Following oxidation and high-temperature reduction the catalyst surface shows behavior uncharacteristic of either parent metal. Such behavior might be expected from the true alloy surface postulated in the earlier model to be present following high-temperature reduction. Other models of base-metal/noble-metal bimetallic catalyst structure postulate only a single reduced surface structure (18, 19, 30, 31). Clearly, none of those models is consistent with the observations made in the present work.

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