JOURNAL OF CATALYSIS **80**, 358–368 (1983)

A Facile Technique for the Surface Characterization of Dispersed Metal Catalysts

ROBERT L. AUGUSTINE[1] AND ROBERT W. WARNER

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079

Received August 31, 1982; revised December 3, 1982

The product compositions obtained from a single-turnover olefin hydrogenation process were used to determine the relative number of the different types of active sites present on a series of Pt/CPG (Controlled Pore Glass) catalysts. It was shown that during this procedure each site reacted only once per turnover sequence so the product compositions could be related directly to the densities of the various types of sites present. The amount of alkane formed was related to the number of ^3M sites present while the extent of isomerization occurring and the amount of stable half-hydrogenated species present indicated the density of ^3MH and/or ^2M sites. The ^1M sites present were determined by subtracting from the total amount of hydrogen required to saturate the metal surface that which was present on the ^3M and ^2M sites.

One of the more important problems associated with the efficient use of dispersed metal catalysts is the lack of selectivity which can occur in reactions run over such species. It can be assumed that this lack of selectivity is due to the presence on the catalyst surface of a number of different types of active sites, each with its own adsorption and reaction characteristics. To date most of the success achieved in the development of selective catalytic processes has been the result of trial-and-error efforts, an approach made necessary by the general lack of detailed information concerning the nature of the surface of practical, dispersed metal catalysts, and the adsorption and reaction characteristics of the different types of active sites present on such catalysts. Support for the assumption that the different types of sites can have differing reaction properties comes from the fact that atoms located on terraces, steps, and kinks of metal single crystals have been shown to have different adsorption capabilities and also to promote different reactions on the same substrate (*1*). While the arrangement of the surface atoms on these single crystals can be determined directly by use of the proper instrumentation, there is at present, no comparable method available for the direct surface characterization of the metal crystallites present in a supported metal catalyst.

Over the past several years, though, a number of attempts have been made to describe the different types of active sites which could be present on the surface of these metal crystallites. One of these descriptions was based on the number of atoms neighboring each different type of surface atom (active site) which are present on the various idealized crystals possible with fcc, bcc, and hcp crystal lattices (*2*). A mathematical analysis was used to calculate the number of each of the different kinds of surface atoms present on varying sizes of each crystalline arrangement. In this way the effect of particle size change on the relative proportion of each type of site present could be predicted. Presumably, then, if an appropriate reaction were run over a series of similar catalysts having different metal particle sizes, the change in product composition over this series should provide some evidence of the types of products formed on specific kinds of active sites. Whether the metal crystallites

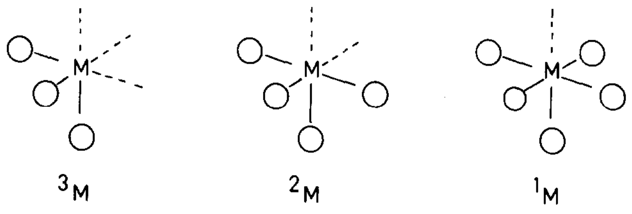
---

[1] Author to whom correspondence should be addressed.

0021-9517/83 $3.00

present in such catalysts have these idealized crystal shapes is, however, open to question. Further, there is no assurance that all of the catalysts of such a series would have the metal particles present in the same general shapes. It is quite possible that a high-dispersion catalyst could have one type of metal particle present while other shapes will be present in catalysts of lower dispersions, thus invalidating any such direct mathematical correlation.

In the other descriptions the active sites on the catalyst were looked on as surface complexes having different degrees of coordinative unsaturation. The reactions occurring at these sites were related to those taking place on comparable catalytically active homogeneous complexes with known reaction characteristics (*3, 4*). Siegel *et al.* (*4*) have defined those surface atoms which are capable of adsorbing three additional ligands (reacting atoms or molecules) as ^3M sites. A ^2M site is one on which two distinct species can be adsorbed while a site on which only a single moiety can adsorb is classed as ^1M.

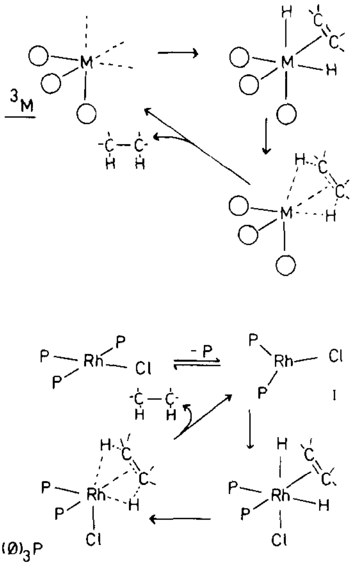


The ^3M sites are effectively corner or kink atoms, ^2M are edge or step atoms, and ^1M are plane, face, or terrace atoms. In an olefin hydrogenation the reaction characteristics of the ^3M sites were considered to be analogous to those observed with $(\phi_3P)_2RhCl$ (**I**), the catalytically active species formed from $(\phi_3P)_3RhCl$ (*5*). As shown in Scheme 1 both **I** and ^3M sites can adsorb two hydrogens and an olefin at the same time. Transfer of the two hydrogens to the double bond leads directly to alkane formation. In the classic Horiuti–Polanyi (*6*) mechanism for the hydrogenation of an olefin (Scheme 2) a reaction occurring at a ^3M site involves the transfer of two adsorbed hydrogens

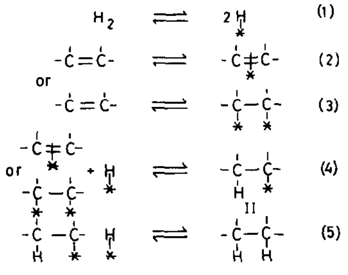
$$\begin{array}{c}H\\|\\*\end{array}$$

to the double bond with no reversal of intermediate half-hydrogenated state (**II**) formation (step (4)). Thus, no double-bond isomerization is taking place on these sites.

It was also proposed (*4*) that some ^3M sites would be converted to ^3MH species which would have reaction characteristics similar to those of $(\phi_3P)_2Rh(CO)H$ (**III**) (*7*) as shown in Scheme 3. Transfer of hydrogen to the adsorbed (complexed) double



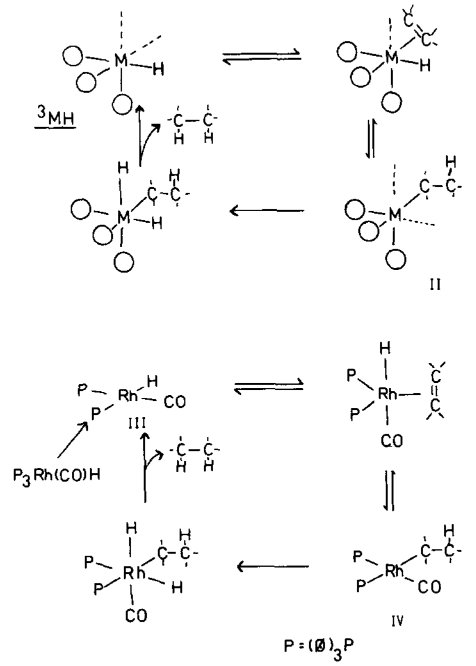
Scheme 1



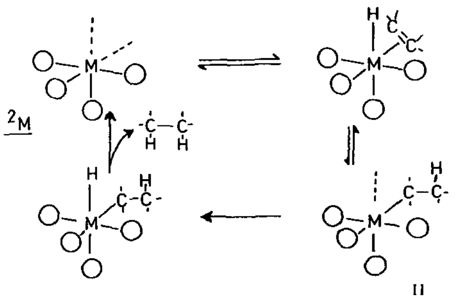
SCHEME 2

bond leads to the formation of a metalalkyl (**IV**) or half-hydrogenated state (**II**). Reversal of the hydrogen transfer step and subsequent desorption (steps (4), (3), and (2) in Scheme 2) can lead to the formation of isomeric olefins. In the absence of such reversal, further addition of hydrogen to **II** or **IV** followed by a hydrogen transfer to the alkyl group leads to alkane formation (step (5), Scheme 2). While the isotopic distribution observed in isomeric olefins formed on deuteration of alkenes was readily accounted for by utilization of ^{3}MH (D) sites for this process (*4*), it is also possible that some isomerization could be taking place on ^{2}MH sites as depicted in Scheme 4. The primary difference between this process and isomerization taking place on a ^{3}MH site (Scheme 3) is the necessity in the ^{2}MH sequence of having the dissociative adsorption of H_2 take place using two metal atoms. This would presumably occur via a bridged adsorption between neighboring atoms. Since the partial temperature-programmed desorption/olefin hydrogenation studies of Tsuchiya *et al.* (*8, 9*) indicate that intersite surface migration of hydrogen does not readily take place, such a bridged adsorption–dissociation procedure must also be postulated for the adsorption of hydrogen on ^{1}M sites. The ready adsorption of hydrogen on such sites is an essential prerequisite for the utilization of hydrogen adsorption data in the determination of metal surface areas. It must be recognized, though, that under normal reaction conditions isomerizations taking place on ^{2}M sites could have little influence on isotopic distribution patterns if either the number of such sites present was rather small or the reactions taking place on ^{3}MH sites occurred so readily as to dominate the product composition.

In any event it would seem, that a strong case has been established for the presence on a catalyst of surface complexes based on ^{3}M, ^{2}M, and ^{1}M coordinative unsaturation. Thus, one should be able to determine the quantity of each of the types of sites present on a catalyst by an analysis of the products obtained during an olefin hydrogenation. Unfortunately, such an approach is



SCHEME 3



SCHEME 4

not as straightforward as it might seem because all types of sites will not necessarily react at the same rate. Thus, even examination of the products formed at low conversion will not provide any definitive data concerning the site densities on a catalyst. It is always possible that one type of site could be so reactive that even though it might be present in minor amounts it could dominate the entire reaction output. In order to use the product composition as a viable means of determining the relative quantities of the different types of sites present on a catalyst (i.e., as a surface characterization probe), something different from the common procedures used in the study of catalytic reactions must be used. What is needed is a method by which all rate differences between the various reactive sites are eliminated. One such approach is the "time-lapse" procedure developed for the study of catalytic reactions in a detailed stepwise manner, one turnover at a time (*10*). In an olefin hydrogenation this technique involves first the saturation of the catalyst surface with hydrogen and removing the excess in a carrier gas stream. A pulse of olefin is then introduced and the products from the resulting, essentially stoichiometric, reaction are analyzed with an on-stream gas chromatograph. If it can be shown that during this single-turnover sequence each site reacted only once, the nature of the products obtained will have a direct bearing on the quantity and types of reactive sites present on the catalyst surface. The following is a presentation of our preliminary efforts at such a surface characterization.

EXPERIMENTAL METHODS

The hydrogen used was commercial grade purified by passage through, successively, an Englehard Deoxo unit, a Drierite trap, a Matheson model 450 gas purifier, and a Matheson model 6183 high-purity filter. The helium and nitrogen were Zero Grade, 99.9995% pure, and were further treated by passage through a 30 × 0.8-cm column of Redox (Fisher Scientific), two 30 × 0.8-cm columns of indicating oxy-trap (Altech Associates), a model 450 gas purifier, and a model 6183 filter. From the specifications provided for these oxygen traps it was estimated that the oxygen level in these carrier gases was considerably less than 1 ppm on passage through the reactor. The 1-butene was 99.0% pure and was passed through a 50 × 0.4-cm column of alumina, a model 450 purifier, and a model 6183 filter before use. The apparatus used was described previously (*10*).

The preparation of the catalysts and properties of the Controlled Pore Glass (CPG) support have also been described (*10*). Pt-A is 4.9% Pt/CPG; Pt-B and Pt-C are 4.3% Pt/CPG. Pt-B and Pt-C were prepared from the same batch of CPG-supported platinum complex but were reduced by hydrogen at different temperatures: Pt-B at 150°C and Pt-C at 200°C. Pt-A, was prepared by the hydrogen reduction of a different batch of CPG-supported complex at 200°C. After reduction, the catalysts were stored in screw-capped bottles under air for at least 3–4 weeks before use and were then used in this study without further treatment.

For the single-turnover studies a 4- to 5-mg portion of a Pt/CPG catalyst was placed in a reactor tube and flushed for 1–2 hr with O_2-free He. A 10-μl pulse of H_2 in a stream of O_2-free He was introduced to saturate the catalyst. This was followed after an appropriate time by a 10-μl pulse of 1-butene and the product composition was determined by an on-line gas chromatograph. A portion of the olefin remained on the catalyst at this point but it could be removed as butene by the introduction of another 10-μl H_2 pulse. The single-turnover sequence, thus was the introduction of three pulses of reactants into the reactor: H_2–olefin–H_2. After three to four such turnovers the product composition reached constant values for all succeeding sequences. All definitive results were obtained after this point was reached. All product composition data were corrected for the relative response factor of each component of the reaction mixture as determined by calibration of the detector response with known quantities of the pure materials.

To determine the amount of hydrogen needed to totally saturate these catalysts 5.0-mg samples of Pt-A or Pt-B or 4.0-mg portions of Pt-C, were placed in a reactor tube and swept at room temperature for 15–19 hr by a 30 cm^3/min stream of O_2-free N_2. After this was done several 10-μl pulses of H_2 were introduced into the system and the amount of H_2 adsorbed was determined by the gas chromatographic analysis of the effluent. Several samples of each catalyst were so treated and the quantity of H_2 adsorbed with each catalyst was reproducible to within ±10%. The average value was used for the surface characterizations and is given as H_2 adsorbed per milligram of catalyst in Table 2.

RESULTS AND DISCUSSION

The reaction to be used as a probe for any single-turnover surface characterization must be well understood mechanistically, have reaction paths available which are unique for the type of site involved, and, in order to provide a generality to the technique, be catalyzed by a variety of different metal catalysts. The olefin hydrogenation is such a reaction. It has been extensively studied (*11*) and is quite thoroughly understood mechanistically. It takes place readily over almost all of the common metallic catalysts (*12*) as well as homogeneous catalysts (*13*). Further, as the previous discussion points out, the different types of sites present on a metal surface interact in different, but distinguishable ways, with the reactants (*4*). 1-Butene was selected as the appropriate olefin for this type of study not only because its use is compatible with a room-temperature, vapor-phase reaction but also because both the saturation and isomerization reactions could readily be detected with it as the substrate.

In the time-lapse, single-turnover technique (*10*) a small sample of the catalyst was first exposed to a pulse of hydrogen of sufficient size that all of the surface metal atoms were saturated with adsorbed hydrogen. The excess was removed in the carrier gas stream and a pulse of 1-butene, again of sufficient size to react with all of the adsorbed hydrogen, was then passed over the catalyst and the products obtained were analyzed by an on-stream gas chromatograph. Quantitative analysis of the products obtained at this stage showed that not all of the olefin pulse could be accounted for; some olefin remained on the catalyst. Introduction of another hydrogen pulse resulted in the removal of this material as butane. The amount of butane formed at this stage in addition to the butane, *cis*- and *trans*-2-butene, and unreacted 1-butene detected originally accounted for all of the initial olefin pulse. A turnover sequence was, therefore, composed of three pulses, H_2–olefin–H_2, with this sequence repeatable as often as desired. Generally, after three or four turnovers the product compositions reached constant values and all definitive data were taken after this point was reached. Data obtained were reproducible to within ±3% for successive runs on the same catalyst sample and ±5% for runs on different portions of the same catalyst.

If the time between the introduction of the initial hydrogen pulse and the olefin pulse were lengthened the amount of butane formed at this stage would decrease, presumably because of the loss of some reversibly adsorbed hydrogen by sweep-off with the carrier gas. As seen by the data in Fig. 1 the extent of this sweep-off varied from catalyst to catalyst. For short sweep-off times the changing of the carrier gas flow from 30 to 50 cm^3/min had little effect on the product composition. Within the time span investigated for each catalyst this sweep-off had no effect on the extent to which isomerization took place or on the amount of butane formed on reaction with the second hydrogen pulse of the turnover sequence. Extrapolation of these curves gave the amount of initial butane formation at zero sweep-off time.

In order to ensure the viability of this single-turnover technique for a surface characterization study, it was necessary to determine whether the various sites present on the catalyst were reacting only once during each turnover sequence. To establish this the contact time of the 1-butene with the hydrogen-pretreated catalyst was varied over a wide range both by changing the size of the olefin pulse as well as the carrier gas flow rate at short sweep-off times. It was reasoned that if the sites could react more than once increasing the contact time would result in an increase in the products formed at those sites. It was found, though, that in every instance the absolute amounts of the butane and isomerized olefins formed initially and the butane formed by the second hydrogen pulse remained constant. There was essentially no variation observed in the product composition with changing flow rate and the only modification noted with a change in the 1-butene pulse size was the amount of this material going through the reactor unchanged. It would appear, then, that each active site was reacting only once per turnover, and, thus, the compositions of the product mixtures obtained were directly related to the quantities of the different types of sites present on each of the platinum catalysts studied.

One further complication could be the possible migration of surface-adsorbed hydrogen from one type of site to another but the temperature-programmed desorption (TDP) studies of Tsuchiya *et al.* (*8*, *9*) have shown that such migration does not readily take place, at least on a platinum surface. The product compositions obtained with the catalysts used in this study are listed in Table 1.

As pictured in Scheme 1 the ^3M sites are considered (*4*) to have reaction characteristics analogous to $(\phi_3P)_2RhCl$ (**I**) (*5*) with both entities being capable of adsorbing (complexing with) two hydrogens and a double bond. Since hydrogenations of olefins over **I** take place without double-bond isomerization (*5*) and the deuteration of terminal alkenes gives only the 1,2-dideuterated product (*14*) either the two hydrogens (deuteriums) are transferred almost simultaneously to the double bond or the reversal of the formation of the intermediate metal-alkyl (**IV**) does not take place readily. In either case, transfer of the two hydrogens on the $^3MH_2$ site to the olefin should take place to give only the alkane. The ^3M sites, then, in the present study should give butane directly in the first stage of the turnover sequence so the amount of butane

TABLE 1

Product Compositions from Single-Turnover Reaction Sequences[a]

Catalyst	Sweep-off time (min)	Initial butane (%)	2-Butenes (%)	Butane from half-hydrogenated state	1-Butene (%)
Pt-A[b]	0	23 (0.019)	4 (0.003)	9 (0.007)	65
	30	14 (0.012)	4 (0.003)	9 (0.007)	73
Pt-B[b]	0	62 (0.052)	4 (0.003)	29 (0.024)	5
	30	57 (0.047)	4 (0.003)	29 (0.024)	10
Pt-C[c]	0	55 (0.057)	4 (0.004)	26 (0.027)	15
	30	30 (0.031)	4 (0.004)	26 (0.027)	40

[a] Ten-microliter pulses of reactants at 20°C. Numbers in parentheses are micromoles per milligram of catalyst.

[b] Five-milligram portion of catalyst used.

[c] Four-milligram portion of catalyst used.

formed on reaction of the pulse of 1-butene with the hydrogen-saturated catalyst is a direct measure of the number of ^3M sites present. The sweep-off results depicted in Fig. 1 show, however, that some of the hydrogen on these sites could be relatively easily removed by the carrier gas stream. This hydrogen could be replaced easily, though, by merely adding an additional pulse of hydrogen which returns the catalyst to its initial saturated state. Product composition was influenced only by the length of time between the last hydrogen pulse and the introduction of the olefin. Sweeping the hydrogen off and then replacing it had no effect on the products obtained. Since this hydrogen removal was indicated only by a decrease in the initial butane formation, this reversibly adsorbed hydrogen must be present only on ^3M sites. Further, examination of Fig. 1 shows that only a portion of the hydrogen used for initial butane formation could be readily removed in this way. It appears, then, that there are two types of ^3M sites present; one on which the hydrogen is reversibly adsorbed which can be termed ^3M_R, and another having irreversibly adsorbed hydrogen, the ^3M_I. This irreversibility is, however, a misnomer since this hydrogen could also be removed, but at a much slower rate. Complete removal of the ad-

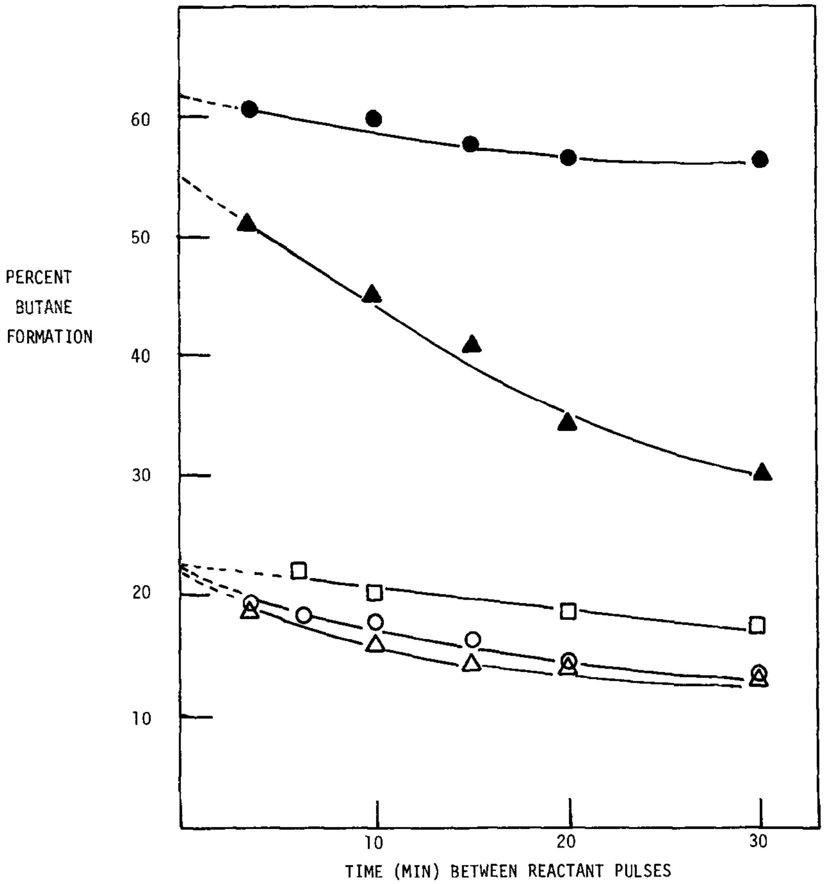


FIG. 1. Extent of hydrogen sweep-off before olefin pulse is introduced in the single-turnover reaction sequence. Amount of butane formed after 1-butene pulse is introduced: □, Pt-A, 15 cm^3/min carrier gas flow; ○, Pt-A, 30 cm^3/min carrier gas flow; △, Pt-A, 50 cm^3/min carrier gas flow; ●, Pt-B, 30 cm^3/min carrier gas flow; ▲, Pt-C, 30 cm^3/min carrier gas flow.

sorbed hydrogen at room temperature required exposure to a 30 cm^3/min carrier gas stream for from 12 to 18 hr. As seen from Fig. 1 the reversibly adsorbed hydrogen could be removed in this way in only about 30 min.

The amount of butane formed with a zero sweep-off time (Table 1) gives a measure of the total number of ^3M sites present on the catalyst. The number of ^3M_I sites can be found from the amount of butane formed after the reversibly adsorbed hydrogen had been removed. We have chosen a 30-min sweep-off time to accomplish this. The number of ^3M_R sites is obviously the difference between these two numbers.

^3MH or ^2M sites, because they adsorb only one hydrogen along with the olefin, do not promote alkane formation directly. Instead, as shown in Scheme 3, (*4*), and Scheme 4 a half-hydrogenated state, **II**, is formed on transfer of the hydrogen to the double bond. This step can then reverse by transferring the hydrogen back to the metal and regenerating an olefin with isomerization a possible outcome. The amount of *cis*- and *trans*-2-butene formed in the turnover sequence is a measure of the extent to which this type of site is present. It is possible, though, that reversal of this hydrogen transfer could regenerate the 1-butene. How much of this might be taking place is, however, not determinable at this time. It is also possible that some of the isomerized olefin formed on contact of the leading edge of the olefin pulse with the catalyst could desorb and be saturated on an $^3MH_2$ site further along the catalyst plug. We do not feel that this is a very important consideration because of the constancy in the amount of isomerized products produced regardless of the contact time of the olefin pulse with the catalyst. The 1-butene regeneration, though, is a critical factor so the estimate of the number of ^3MH or ^2M isomerization sites must be recognized as probably being a low value.

There is also the possibility that the half-hydrogenated species, **II**, formed on some ^3MH or ^2M sites might be a reasonably stable species and, instead of regenerating an olefin, this moiety could simply remain as such until another hydrogen becomes available to the site. This hydrogen can then be transferred to the half-hydrogenated state to give the alkane (Scheme 3). The butane formed after the introduction of the second hydrogen pulse in the turnover sequence is probably produced by such a process. An alternative explanation for the formation of butane at this stage is that it is merely the result of the saturation of olefin molecules from the end of the pulse which have been adsorbed on ^3M sites vacated by a reaction taking place at the beginning of the pulse. If this were the case, though, varying the olefin pulse size and contact time with the catalyst would be expected to change the amount of olefin so adsorbed and, thus, the amount of butane produced by the second hydrogen pulse. This is not what is observed. Further, the introduction of a second olefin pulse prior to the final hydrogen treatment had no effect on the product composition.

It appears, then, that there are at least two types of sites present on these catalysts on which the adsorbed olefin reacts with one hydrogen at a time; one which promotes isomerization and one on which the half-hydrogenated state is a relatively stable entity. The ratio of these sites is different for each of the catalysts studied here so the difference cannot be simply statistical, i.e., that a certain percentage of the half-hydrogenated state reverses under the conditions used. It could be that one of these types is a ^3MH site and the other a ^2MH, but it is not possible at this time to distinguish between these two entities. Instead, these two types of sites have been labeled ^2M_C for those promoting isomerization and ^2M_S for those on which the half-hydrogenated state is reasonably stable (*15*) and, for clarity in presentation and to distinguish them from the ^3M saturation sites both of these types are classified in the rest of this discussion as ^2M sites.

From the product distributions and sweep-off results listed in Table 1 amounts of the different ^3M and ^2M sites present on each of the catalysts can be determined. A more complete surface characterization, though, should also include the number of ^1M sites present as well. Since these sites are not involved in any of the reactions occurring during an olefin hydrogenation but do adsorb hydrogen, the number of such sites must be determined from hydrogen adsorption data. If one subtracts from the total amount of hydrogen adsorbed on the catalyst that which is present on the ^3M and ^2M sites the remainder should be adsorbed on ^1M sites in a 1 : 1 ratio. All that is needed then along with the product distributions already discussed is the determination of the amount of hydrogen required to saturate the catalyst surface. This was readily accomplished by simply passing measured pulses of hydrogen over the catalyst and determining the amount not adsorbed by gas chromatographic analysis of the effluent gas (*16*). The obtaining of reproducible data can be a problem, however, since if anything is adsorbed on the catalyst before exposure to the hydrogen anomalous results can be obtained. It is necessary to clean the catalyst surface before such adsorption data are obtained. One of the standard ways of accomplishing this is to heat the catalyst at elevated temperatures first under hydrogen and then under nitrogen for a period of several hours followed by cooling in a nitrogen stream prior to exposure to the hydrogen. While in our hands such a procedure gave good results with silica-supported catalysts, with these CPG-supported species the results were erratic in most instances. It appeared that with the CPG-supported catalysts the heat treatment might be having an effect on the catalyst morphology. If this were true then the species which was being treated with hydrogen could be different from that on which the turnover analyses were run. It was found, however, that exposure of these catalysts to an oxygen-free helium or nitrogen gas stream for 15–19 hr gave a clean surface on which hydrogen adsorption was reproducible both with the same sample and different samples of the same catalyst to within ±10%. It was also established that this treatment had no effect on the product compositions of the turnover reactions or on the sweep-off of the reversibly adsorbed hydrogen. The amounts of hydrogen required to saturate the surfaces of the catalysts under consideration are listed in Table 2.

In order to determine the number of ^1M sites from the turnover composition and hydrogen adsorption data it was first necessary to ascertain the extent to which the hydrogens were adsorbed on the ^3M and ^2M sites. One could either have the coordinative unsaturation at each site fully satisfied by hydrogens or only that amount of hydrogen needed for further reaction is adsorbed on each site and some of the coordinative unsaturation remains available for olefin adsorption. In the former situation olefin adsorption could only take place by the displacement of some of the hydrogens. When the hydrogen-saturated catalyst was exposed to a pulse of 1-butene no displaced hydrogen was observed in the effluent gas stream so it appears that each ^3M saturation site will adsorb two hydrogen atoms while

TABLE 2

Surface Site Characterization Data[a]

	Catalyst		
	Pt-A	Pt-B	Pt-C
Total ^3M	0.019 (23.2)	0.052 (27.5)	0.057 (47.5)
^3M_R	0.006 (7.4)	0.005 (2.6)	0.026 (21.7)
^3M_I	0.012 (14.8)	0.047 (24.8)	0.031 (25.8)
Total ^2M	0.010 (12.3)	0.027 (14.2)	0.031 (25.8)
^2M_C	0.003 (3.7)	0.003 (1.6)	0.004 (3.3)
^2M_S	0.007 (8.6)	0.024 (12.6)	0.027 (22.5)
^1M	0.052 (64.4)	0.110 (58.1)	0.032 (26.7)
Total sites	0.081	0.189	0.120
Pt content	0.25	0.22	0.22
H_2 adsorbed	0.050	0.120	0.088
Dispersion[b]	0.32	0.86	0.55

[a] Micromoles per miligram of catalyst. Numbers in parentheses are percentage of total sites.

[b] Total sites/Pt content.

each ^{2}M and ^{1}M site will adsorb only one (*17*). The total hydrogen adsorbed is represented by

$$H_T = 2\ {}^3M + {}^2M + {}^1M$$

and thus

$${}^1M = H_T - 2\ {}^3M - {}^2M.$$

The site distributions for each of the catalysts studied here are given in Table 2.

This technique not only gives the relative amounts of each type of site present on the catalyst surface but it also provides a direct measure of total number of atoms on the surface of the metal crystallites. From this the dispersion or ratio of the number of surface atoms to the total number of metal atoms can be directly determined. The dispersions for the catalysts used in this study (Table 2) in conjunction with the site densities can provide some interesting conjecture regarding the general nature of the metal particles present in each catalyst. It is usually thought that the higher the dispersion the more active the catalyst. In the present study it is true that Pt-A, with the lowest dispersion, is also the least active catalyst for the production of butane. It has the least number of ^{3}M sites. But this parallel between dispersion and activity does not always hold. Pt-B has a very high dispersion while that for Pt-C is only moderate. Yet, Pt-C is, by far, the most active catalyst used in this study. It is readily seen from the data in Table 2 that this increased activity is caused by the presence of more ^{3}M sites than on Pt-B or Pt-A. The higher dispersion found for Pt-B is the result of there being present on this catalyst almost 60% of ^{1}M sites, face or terrace atoms which apparently adsorb hydrogen but do little else in an olefin hydrogenation. The Pt-C, on the other hand, has only about 25% of such sites but almost 50% of the alkane-producing ^{3}M sites. These results tend to indicate that the metal particles present in the Pt-B catalyst possibly have a somewhat two-dimensional raft-like shape since only this kind of arrangement can account for the high dispersion of this catalyst along with the large number of face atoms apparently present. Pt-C, however, probably has more spherically shaped metal particles. This difference, in itself, is quite interesting since both Pt-B and Pt-C were obtained from the same batch of CPG-supported platinum complex, Pt-B was prepared by hydrogen reduction at 150°C, only 50°C lower than the temperature used for the reduction of Pt-C. Further work is under way to verify both the presumptions made here concerning the shapes of these metal particles as well as the relationship between reduction temperature and metal particle shape. If the present statements are found to be correct it will show that this proposed method for surface characterization is, indeed, a viable one and that a great deal of information concerning the morphology of the metal crystallites in a dispersed metal catalyst can easily be obtained in this way. Studies involved with the extension of this procedure to the surface analysis of other metal/support combinations are also currently being undertaken.

ACKNOWLEDGMENTS

We thank the Ameron Corporation for their support of this work and Johnson Matthey, Inc., for supplying the chloroplatinic acid used for the catalyst preparation through their Platinum Group Metals Loan Program.

REFERENCES

1. Somorjai, G. A., *Catal. Rev.* **7,** 87 (1972); **18,** 173 (1978); *in* "Advances in Catalysis and Related Subjects," Vol. 26, p. 1. Academic Press, New York/London, 1977. Smith, C. E., Biberian, J. P., and Somorjai, G. A., *J. Catal.* **57,** 426 (1979).
2. Van Hardeveld, R., and Hartog, F., *Surf. Sci.* **15,** 189 (1969).
3. Augustine, R. L., and Van Peppen, J. F., *Ann. N.Y. Acad. Sci.* **172**(9), 244 (1970).
4. Siegel, S., Outlaw, J., Jr., and Garti, J., *J. Catal.* **52,** 102 (1978).
5. Osborn, J. A., Jardine, F. H., Young, S. F., and Wilkinson, G., *J. Chem. Soc. A,* 1711 (1966).
6. Horiuti, I., and Polanyi, M., *Trans. Faraday Soc.* **30,** 1164 (1934).
7. O'Connor, C., and Wilkinson, G., *J. Chem. Soc. A,* 2665 (1968); Evans, D., Osborn, J. A., and Wilkinson, G., *J. Chem. Soc. A,* 3133 (1968);

Yagupsky, M., and Wilkinson, G., *J. Chem. Soc. A*, 941 (1970).

8. Tsuchiya, S., Amenomiya, Y., and Cvetanovic, R. J., *J. Catal.* **19,** 245 (1970).

9. Tsuchiya, S., Nakamura, M., and Yoshioka, N., *Bull. Chem. Soc. Japan* **51,** 981 (1978).

10. Augustine, R. L., and Warner, R. W., *J. Org. Chem.* **46,** 2614 (1981).

11. See, for instance, Burwell, R. L., Jr., *Catal. Rev.* **7,** 25 (1972); and Siegel, S., *in* "Advances in Catalysis and Related Subjects," Vol. 16, p. 123. Academic Press, New York/London, 1966.

12. Augustine, R. L., "Catalytic Hydrogenation, Techniques and Applications in Organic Synthesis." Dekker, New York, 1965.

13. James, B. R., "Homogeneous Hydrogenation." Wiley, New York, 1973.

14. Morandi, J. R., and Jensen, H. B., *J. Org. Chem.* **34,** 1889 (1969).

15. These labels were chosen to avoid confusion with the ^3M_I and ^3MH definitions previously presented. The ^2M_C is for sites on which the olefin is changed (isomerized) and the ^2M_S is for sites associated with a stable half-hydrogenated state.

16. Freel, J., *J. Catal.* **25,** 139 (1972).

17. Since the number of ^2M_C sites determined by this method is probably a low value, those ^2M_C sites not determinable at this time will be accounted for as ^1M sites.