

An Evaluation of the Single Turnover (STO) Procedure as a Method for the Determination of The Active Site Densities on Dispersed Metal Catalysts

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Results have been obtained which show that the standard single turnover (STO) reaction procedure can be used to determine the surface densities of the direct and two-step alkene saturation sites on various oxide supported Pt, Pd, and Rh catalysts if the carrier gas flow rate and reactant pulse size are such that diffusion control of the reaction is avoided. Rh catalysts are more susceptible to diffusion control than are Pt and Pd species. The extent of 2-butene formation during the STO reactions over Pd and Rh indicates that the alkene isomerization is nonstoichiometric. With Pt the extent of isomerization is also influenced by flow rate and reactant pulse size but to a lesser extent. Thus, the STO reaction procedure cannot be used for the determination of isomerization site densities on any of these catalysts. This procedure has been used to determine the saturation site densities on the EuroPt-I Pt/SiO₂ and some northwestern Pt/SiO₂ catalysts. The STO reaction sequence has also been run over Pt, Pd, and Rh catalysts using each of the isomeric butenes as the reactant alkene. Over all three catalysts the same amounts of direct and two-step saturation were observed regardless of the starting alkene showing that these saturation sites are not sensitive to the geometry of the reactant olefin. With Rh a near equilibrium mixture of all three double bond isomers is formed from each of the three starting alkenes. With Pt the extent of isomerization is characteristically low regardless of the starting olefin, so the low isomerization observed during the STO reaction of 1-butene on Pt is not the result of the formation of a primary metalalkyl on a large number of isomerization sites. The STO determined reactive site densities for series of catalysts have been correlated with transition electron microscopy (TEM) measured metal particle sizes and turnover frequency (TOF) data for a number of reactions. From these results the sites on which specific reactions take place have been determined as has the site TOF for each of the active sites involved. © 1991 Academic Press, Inc.

INTRODUCTION

It is generally acknowledged that catalyst surfaces are nonuniform and composed of various types of active sites with differing reaction and adsorption characteristics. Some of the major goals of catalytic research today are involved with the determination of the quantity and types of sites present on supported metal particles and the establishment of a relationship between the structure of the catalyst particle and its reactivity. Over the years published experimental results have led to the conclusion that the various types of active sites present on

catalyst surfaces can have different reaction characteristics (1-9). Further, it has been reported that the active sites involved in alkene hydrogenations and alkane dehydrogenations are single atoms on the metal surface while those sites used for C-C bond hydrogenolysis and alkane isomerization are composed of ensembles of atoms (10, 11). Studies using well characterized metal single crystals have shown that the sites present on a number of different crystal orientations have significantly different activities for a wide range of reactions (12-18).

The LEED techniques used to determine the detailed surface morphology of metal

single crystals are, at present, not capable of obtaining comparable data for the small metal particles present in dispersed metal catalysts. However, reflection high energy electron diffraction (HREED) has been used along with transmission electron microscopy (TEM) to study the morphology of small metal particles (19).

Of all of the instrumental techniques involved in catalyst characterization, TEM is probably the most widely used in the determination of the various aspects of metal particle morphology (20–24). Of the various approaches used, weak beam electron microscopy gives the most detailed information. While this procedure has shown that the Pt particles in a dispersed metal catalyst have a very complex surface structure (24), it is still unable, at present, to provide even an approximation of the quantities of the different types of sites present. Pt NMR has been used to examine supported Pt catalysts but the only information obtained was the surface:bulk atom ratio; no distinction could be made of the different types of surface sites present on the metal particles (25).

The extent of O₂, H₂, and CO chemisorption has been utilized to determine the ratios of the crystallographic planes present on supported metal particles (26), but extension to the more coordinately unsaturated corner or edge atoms resulting from the intersection of these planes was not made. Titrating the active sites on a catalyst with increasing amounts of a sulfur containing species and following the rate of a catalytic reaction during the titration has provided information concerning the relative numbers of hydrogenation sites present and their specific reactivity (3), but the nature of the active site could not be defined.

Other approaches to the determination of site activities and densities have relied on the analysis of results obtained from parallel reactions run over a catalyst with the premise that specific types of sites will promote only a given reaction. Ledoux and co-workers (28–31) have investigated the deuteria-

tion, deuterium exchange, and isomerization of the three isomeric butenes over Pd catalysts and applied microwave spectroscopic analysis to the resulting deuterated butane and butenes. From the results of these experiments it was concluded that there are present on the surface of Pd catalysts three different types of sites; those on which saturation is the primary reaction, those on which isomerization takes place, and some which are unreactive. Mechanistic considerations led to the conclusions that the saturation sites were corner atoms, the double bond isomerizations took place on the edge atoms, and the face atoms were not involved in this reaction. Smith and co-workers (32) have determined the relative rates of isomerization and saturation, k_i/k_a , of (+)apopinene and used this ratio, along with assumptions concerning the shape of the dispersed catalyst particles, to arrive at similar conclusions. However, they have also stated that this ratio parallels the edge atom density on the supported metal crystallites (33). The primary difficulty with these and other determinations of active site densities which are based on the amount of product formed from steady state catalytic reactions (34–36) is that there is no reason to expect that the different types of sites will react at the same rate. Unless specific site rate factors are known or assumed, no definitive correlation between product composition and site densities can be made.

To overcome this limitation a single turnover (STO) reaction procedure was developed and used to characterize the active sites on the surface of dispersed Pt/CPG (controlled pore glass) catalysts (37). In this reaction sequence the catalyst is first treated with a pulse of H₂ so every surface atom on the Pt is saturated with adsorbed hydrogen. The excess hydrogen is removed from the reactor in a stream of carrier gas so the only hydrogen available for further reaction is that which is adsorbed on the metal surface. The catalyst is then treated with a pulse of 1-butene of sufficient size to react with all of the adsorbed hydrogen and the products

formed are analyzed by on-stream gas chromatography. The materials analyzed at this stage of the sequence are unreacted 1-butene, butane formed by the saturation of the butene on what has been termed direct saturation sites, and the *cis* and *trans* 2-butene formed on isomerization sites. Some hydrocarbon remains on the catalyst surface as the metalalkyl and is removed as butane by a second pulse of hydrogen to complete the STO reaction sequence. This second butane is formed on what is called the two-step saturation sites. Further, there are two types of direct hydrogenation sites, one on which the hydrogen is weakly adsorbed and another on which the hydrogen is rather strongly held. In keeping with the terminology suggested by Siegel (38), these direct saturation sites have been named the 3M_R and the 3M_I sites, respectively. The two-step hydrogenation sites are called 3MH and the isomerization sites are 2M . Other sites which absorb hydrogen but do not take part in the alkene hydrogenation reaction are called 1M (37).

Experimental results are available indicating that H_2 migration across the surface of the catalyst does not occur under the conditions used for this reaction sequence (39). This, along with other data (37) has led to the premise that under the standard STO reaction conditions each surface site on the Pt/CPG catalysts reacts only once during this reaction sequence and, thus, a 1 : 1 correlation exists between the number of molecules of each of the products formed and the number of atoms of each specific type of site on the Pt surface. For instance, the number of molecules of butane formed from the initial contact of the hydrogen saturated catalyst with the pulse of 1-butene is equal to the number of direct saturation sites present on the metal surface. With each site reacting only once during the turnover sequence the relative rates at which each type of site reacts is not important in the determination of active site densities on the metal surface. Correlation with single crystal catalytic data has shown that the STO hydrogenation

sites, both direct and two-step, are corner atoms of one type or another on the metal surface (40). This agreement with the saturation site description proposed by Ledoux (28-31) along with mechanistic considerations has led to the conclusion that the isomerization sites are probably edge atoms and the 1M sites are present on the faces of the metal crystallites (40, 41).

The STO site characterizations of a number of Pt/CPG catalysts showed that the densities of the various active sites on the catalyst depend on a number of preparation variables and pretreatment procedures (42, 43). A primary factor was the temperature and heating technique used for the hydrogen reduction of the supported salt catalyst precursor. By varying the reduction temperature it is possible to prepare series of Pt catalysts having identical metal loading but with different STO characterized active site densities. Interestingly, with the large number of catalysts so characterized to date there has been no general relationship found between the densities of the various active sites and the catalyst dispersions as determined by hydrogen chemisorption (42).

Using series of STO characterized catalysts to investigate specific reactions has provided information concerning the reactivity of the various types of sites. In the deuterium exchange on cyclopentane the extent of polydeuteration increased through the series as the number of saturation sites or corner atoms increased indicating that the polydeuterium exchange on the alkane was taking place on these coordinately unsaturated corner atoms (44). A similar approach was used to determine the specific site turnover frequency (TOF) for each of the three kinds of saturation sites involved in cyclohexene hydrogenation (45).

All of the previously reported STO data were obtained using Pt/CPG catalysts. Pt was selected initially because it has been more widely studied than the other catalytically active metals so the STO results could be more easily correlated with known activity. CPG was used as the support since this

material is most effective in removing dispersion factors from consideration, thus making the STO reaction data more reliable (46).

However, it is not completely clear whether some of the conclusions arrived at previously were as general as originally thought. Further, for practical reasons one should be able to determine the active site densities on catalysts other than Pt/CPG. This paper discusses a reevaluation of the STO procedure as applied to Pt/CPG and some modifications of the previous conclusions concerning the active sites on this material. Also presented are the extension of the STO procedure for the investigation of Pd/CPG and Rh/CPG catalysts and the use of the STO reaction sequence to determine active sites on Pt, Pd, and Rh supported on the more common supports, SiO₂, TiO₂, and Al₂O₃. The use of the three isomeric butenes in the STO procedure is also described as is a comparison of STO site density values with steady state reaction rates observed using STO characterized catalysts. The relationship between the STO site densities and the more traditional catalyst characterization and steady state reaction results is also discussed.

EXPERIMENTAL

The turnover apparatus, details of the gas purification techniques, the product analysis, and the single turnover procedure have all been described (37, 42, 47). The STO apparatus was modified by the insertion of a Matheson Model 8249 mass flow controller into the system to control the carrier gas flow rates more accurately. The CPG, SiO₂, and TiO₂ supported catalysts were prepared by the published ion exchange procedure (42, 47) using 1.25 g of H₂PtCl₆, H₂PdCl₄, or RhCl₃ and 5 g of the appropriate support material. The Rh/Al₂O₃ precursor was prepared by dissolving 0.2 g of RhCl₃ in 40 ml of acetone, filtering, and then stirring with 2 g of 60–80 mesh γ Al₂O₃ for 2 hr under N₂. The mixture was filtered, washed with cold

TABLE 1
Percentage Metal Load on Catalysts

Metal	Support			
	CPG	SiO ₂	TiO ₂	Al ₂ O ₃
Pt	3.35			
Pd	1.60	2.02		0.44, 6.06
Rh	1.21	1.85	1.39	2.29
	3.40			

acetone until the wash liquid was clear, and then dried. The Pd/Al₂O₃ precursor was prepared in the same way using a solution of 0.15 g of PdCl₂ in 4 N HCl added to a slurry of 5 g of γ Al₂O₃ in 500 ml of deionized water. The suspension was stirred for 2 hr and filtered followed by thorough washing and drying before reduction. The Pt/SiO₂ (48) catalysts were obtained from Professor J. Butt and a sample of the EuroPt-1 Pt/SiO₂ catalyst (49) was provided by Professor G. Bond. The percent metal in each of the catalysts listed in Table 1 was determined by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

The CPG was obtained from Electro-Nucleonics, Inc. (Fairfield, NJ) with a 80/120 mesh size, 115 \pm 7.3 Å mean pore diameter and a 119.5 m²/g surface area. The SiO₂ used was 80–100 mesh, 269.4 m²/g surface area, Davison Grade 56 obtained from the Davison Specialty Chemical Co. The γ Al₂O₃ was obtained from Aldrich Chemicals with a 60–80 mesh (83.2 m²/g) portion used in the catalyst preparation. The TiO₂ was an 80–100 mesh (3.6 m²/g) portion of P-25 obtained from Degussa Corporation.

The isothermal catalyst reduction procedure was that used previously (42). The *in situ* reductions were carried out by placing 4.0–7.0 mg of a supported metal salt catalyst precursor in an STO reactor tube, purging it at room temperature for 30 min in a 30 cc/min flow of oxygen-free helium, and then heating the sample to the reduction tempera-

ture under helium. After maintaining the temperature at the desired value for 10 min, the gas stream was switched to hydrogen and the sample was held at temperature under hydrogen for 2 hr. At this time the gas stream was switched to helium and the reactor purged for 30 min at the elevated temperature and then cooled to room temperature under helium. Excess reactive hydrogen was then removed by adding successive pulses of 1-butene (50) to the reactor until the butane formed was found to comprise <1 area % of the butene. A quantitative evaluation of the gc peak areas of the products from each pulse showed that no butene remained on the catalyst. This conclusion was further substantiated by the observation that no butane was formed from interaction of the catalyst with the first hydrogen pulse of the subsequent STO reaction procedure. The catalyst was then used in the STO reaction sequence. The Pd catalysts were reduced in this way at 150°C, the Rh/CPG and Rh/TiO₂ at 200°C, and the Rh/SiO₂ and Rh/Al₂O₃ at 400°C.

The room temperature rereductions of the older catalysts were run in a similar manner. A 5.0 mg sample of a catalyst which had been previously reduced in hydrogen and then stored in air for various periods of time was placed in the reactor tube and purged with helium for 30 min. Hydrogen was then passed through the reactor at 30 cc/min for 30 min and the gas stream switched to helium. After purging with helium at 30 cc/min for 2 hr the excess hydrogen was removed by 1-butene titration (50) and the catalyst used for STO determinations. Reproducibility in all of these STO reactions was determined by repeating the various procedures with separate samples of catalyst or supported salt. In all cases the reaction data were found to agree within at most $\pm 5\%$, which is the experimental error for the STO reaction procedure.

The time of reactant contact with the catalyst was determined by passing various sized pulses of 1-butene through a reactor containing a sample of an unreduced cata-

lyst and then directly into the inlet of a VG Instruments Spectrolab 200 and monitoring the partial pressure of mass 41 as a function of time with a 14-msec interval between data points. From a pressure/time plot the peak width at half height was determined and then doubled to give the contact time. In Table 2 are listed the contact times for various reactant pulse sizes run through a reactor containing CPG at different carrier gas flow rates and the contact times at various flow rates for 20- μ l pulses passing through reactors containing each of the oxide supports used.

Samples of each support material were carried through the entire catalyst preparation sequence, including the reduction step, but without the metal salt and then subjected to the STO reaction sequence. No isomerization or saturation of the 1-butene was observed with any of the supports.

Samples of a series of STO characterized Pt/CPG catalysts (42) were examined by electron microscopy by Professor G. V. Smith and D. Ostgard at Southern Illinois University using a Hitachi H500H transmission electron microscope. The dispersions (D_{EM}) were calculated from the particle size measurements taken from the electron micrographs assuming an octahedral particle shape (51).

RESULTS AND DISCUSSION

Supported Pt Catalysts

As discussed in the Introduction the STO reaction sequence has been used to determine the amounts of five different types of sites present on the surface of a number of different Pt/CPG catalysts. In order to provide a direct comparison of the active site concentrations on different catalysts the site densities are given in moles of site/mole of metal, a form similar to the moles of surface atoms/mole of metal used to define catalyst dispersion.

The previously reported STO characterizations (37, 42) of Pt/CPG catalysts have shown that these materials generally have

TABLE 2
 Reactant Pulse Contact Time with the Catalyst (sec)

Support	Pulse size (μ l)	Flow rate (cc/min)						
		30	40	50	55	60	65	70
CPG	20	7.1	5.8	4.9	4.6	4.5	4.4	4.1
	40	7.2	6.1	5.3	5.2	5.0	5.0	4.8
	60	7.3	6.5	5.9	5.7	5.6	5.6	5.5
SiO ₂	20	7.7	6.3	5.4	5.1	4.8		4.6
Al ₂ O ₃	20	7.8	7.0	6.3	6.1	5.8		5.4

high densities of the direct saturation sites with both strongly and weakly adsorbed hydrogen (3M_I and 3M_R) as well as a fairly high number of two-step saturation sites (3MH). Isomerization site (2M) densities, however, are characteristically low. The specific site densities on different catalysts varied with changes in the preparation procedures, primarily the temperature used for the hydrogen reduction of the intermediate supported salt and the mode of this reduction; using a ramped temperature change or an isothermal procedure (42). Reductions using ramped temperature changes while the supported salt is in contact with hydrogen appear to favor the production of Pt catalysts having high saturation site densities, species apparently with very irregular metal particles having a number of surface defects and adatoms. Isothermal reductions at temperatures between 200 and 250°C give catalysts with somewhat lower active site densities. Reduction temperatures lower than 200°C are not favorable for the reproducible preparation of these supported Pt catalysts. On the other hand, reductions at temperatures of 300–400°C apparently result in the smoothing of the surface and species having fewer corner atoms and, thus, lower hydrogenation site densities (42). The relatively high STO saturation site densities generally observed with Pt catalysts agree with the weak beam electron microscopy data (24) which indicates that the Pt particles on a dispersed metal catalyst have a very complex surface structure.

In order for the STO reaction sequence to provide valid site density data it is necessary that there be sufficient time for the reactants to adsorb and interact with all of the metal surface when the reactant pulses are passing through the reactor. One way of determining if this is happening is to vary the contact time of the reactant pulse with the catalyst and then see if there is any change in the amount of products formed. If the product composition remains constant it is a reasonable conclusion that the metal surface has been completely involved in the reaction and, thus, that there are no diffusion controls on the reaction sequence.

With Pt/CPG catalysts it was found that when the time the reactants were in contact with the catalyst was changed by varying the STO reactant pulse sizes from 10 to 20 μ l and the carrier gas flow rate from 30 to 40 cc/min, there was no observable change in the amounts of the various products produced (37). However, the data in Table 2 show that while this particular modification of the flow rate seems to produce a significant change in the contact time of the reactant pulse with the catalyst, it was apparently not sufficient to induce diffusion control of the reaction. Further, these contact time measurements show that the pulse size has little effect on the contact time so the larger pulse sizes must simply increase the reactant concentration in the carrier gas stream.

It was considered necessary, then, to extend the range of carrier gas flow rate and reactant pulse size used in the STO investi-

TABLE 3

Effect of Flow Rate and Reactant Pulse Size on Product Composition for STO Reactions Run over a 3.35% Pt/CPG Catalyst

Pulse size (μl)	Flow rate ^b	Product composition ^a			
		1-Butene ^c	Butane ^d	2-Butenes ^d	Butane ^f
20	30	0.356	0.280	0.074	0.122
	50	0.338	0.291	0.070	0.131
	70	0.353	0.285	0.067	0.125
40	30	1.147	0.304	0.085	0.124
	50	1.135	0.312	0.084	0.127
	70	1.150	0.289	0.094	0.127
60	30	1.945	0.302	0.121	0.122
	50	1.978	0.292	0.086	0.134
	70	1.983	0.289	0.098	0.120

^a In moles of product per mole of Pt.

^b In cc/min.

^c Unreacted starting material.

^d Formed by reaction of the 1-butene on the direct saturation (³M) sites.

^e Formed by reaction of the 1-butene on the isomerization (²M) sites.

^f Formed by reaction of the 1-butene on the two-step saturation (³MH) sites.

gation of Pt/CPG catalysts in order to determine whether any product composition changes would be observed. If this were to occur then the limits in flow rate and pulse size which provide the constant product data without diffusion control could be defined more clearly. In this study no attempt was made to distinguish between the ³M_I and ³M_R types of direct saturation sites. Instead, the total direct saturation site density will be referred to simply as ³M.

In Table 3 is shown the effect of changing reactant pulse size and carrier gas flow rate on the STO measurement of the amount of direct and two-step saturation and isomerization observed with a 3.35% Pt/CPG catalyst. The amounts of butane formed from both the direct (³M) and two-step (³M) saturation sites are within $\pm 5\%$ which is the experimental error for the STO site characterization procedure. The amount of 2-butene formed on the isomerization sites varies by about 40%, well outside the experimental error, indicating that the isomerization reaction is not stoichiometric in these reactions. The general change in iso-

mer formation with increasing reactant pulse size and decreasing reactant contact time with the catalyst is not nearly as great as observed with Pd and RH catalysts (vide infra). These changes can be rationalized either by the presence of relatively inactive isomerization sites with more of the sites reacting with the higher 1-butene concentrations present in the larger pulse sizes or by there being only a few isomerization sites present but the isomerization reaction is nonstoichiometric with more than one reaction taking place per isomerization site during the time the pulse is in contact with the catalyst. The present data do not permit a distinction between these two possibilities. It appears, then, that the previous conclusions concerning the stoichiometry of the STO reaction sequence on Pt/CPG catalysts apply only to the direct and two-step saturation sites and not to the isomerization sites.

As an example of the applicability of the STO procedure for the surface characterization of different types of dispersed Pt catalysts, samples of some of the Northwestern Pt/SiO₂ catalysts (48) were obtained from

TABLE 4
 STO Reaction Site Densities for Some Pt/SiO₂ Catalysts^a

Site	Northwestern catalysts ^{b,c}					EuroPt-1 ^d	
	81-SiO ₂ ionX-S	63-SiO ₂ ionX-S	40-SiO ₂ PtCl-S	27-SiO ₂ ionX-S	21.5-SiO ₂ ionX-L	A ^e	B ^e
%Pt	0.83	0.48	1.17	1.48	1.48	6.3	6.3
D _H ^f	0.81	0.63	0.40	0.27	0.21	0.65	0.65
³ M _I	0.210	0.184	0.145	0.051	0.029	0.101	0.104
³ M _R	0.003	0.013	0.004	0.019	0.012	0.012	0.021
³ MH	0.041	0.016	0.060	0.009	0.005	0.033	0.028
² M	0.075	0.041	0.008	0.055	0.010	0.039	0.028
¹ M	0.268	0.179	0.034	0.067	0.113	0.352	0.344
Σ Sat'n sites	0.254	0.213	0.160	0.076	0.046	0.146	0.153
D _{STO} ^g	.60	.43	.25	.20	.17	.54	.53
^h	42	49	83	39	27	27	28
ⁱ	45	41	13	34	66	65	65

^a Site densities given as mole site/mole Pt.

^b Ref. (48).

^c Rerduced in H₂ at 150°C for 1 hr.

^d Ref. (49).

^e As received.

^f Dispersion measured using hydrogen chemisorption data and a 1:1 H:Pt ratio.

^g Sum of the STO determined site densities.

^h % Sat'n sites (³M_I + ³M_R × ³MH)/D_{STO}.

ⁱ % Inactive (¹M/D_{STO}).

Professor J. Butt and a sample of the EuroPt-1 Pt/SiO₂ (49) catalyst was obtained from Professor G. Bond. The STO characterization results are listed in Table 4. The two columns under EuroPt-1 are for the STO characterizations of a sample of the as-received catalyst, which has been shown to be extensively oxidized (52), and a sample of the catalyst which had been rerduced in a stream of H₂ at 150°C for 1 hr and then stored in air for 3–4 weeks. Reduction of the as-received catalyst was accomplished by running successive STO reaction sequences over it until the product composition remained constant as is the standard practice. The listed data show that these two reduction procedures give catalysts having only slight differences between them.

The EuroPt-1 catalyst (6.3% Pt) gave results that are quite similar to those reported for a number of Pt/CPG catalysts (42). The site densities and the various product ratios

are all comparable. This is not too unexpected since all of these catalysts have relatively high Pt loadings, were prepared by ion exchange, and were reduced using similar techniques. It is interesting to note that these STO results indicate that on the EuroPt-1 catalyst only about 25% of the surface atoms are active in the hydrogenation of a double bond while about 65% of them are STO inactive.

The Northwestern catalysts represent a wider range of preparation variables. One was prepared by impregnation and the others by ion exchange on samples of wide pore silica of different particle size (48). All of these catalysts were STO characterized after rerduction in H₂ at 150° for 1 hr followed by storing in air for 3–4 weeks. These catalysts had substantially lower amounts of Pt than did the EuroPt-1 and previously characterized Pt/CPG catalysts. As indicated by the data in Table 4 there is a consid-

erable variation in the STO characteristics with these catalysts. The use of these catalysts in steady state reactions will be discussed later.

Supported Pd Catalysts

As in the preparation of the Pt/CPG catalysts used in previous STO studies (42), the intermediate CPG supported Pd salt was prepared using an ion exchange procedure and separate portions of this supported salt were reduced isothermally in a stream of flowing hydrogen at temperatures of 150, 200, 250, 300, and 400°C. The more facile reduction of Pd permitted the use of lower temperatures than could be used for Pt. These catalysts were then stored under air in a desiccator for 2–3 weeks before use in a STO evaluation. As was observed with Pt catalysts (37, 42, 47), after exposure to air, several STO reaction sequences were needed to remove the surface oxygen and/or reduce the Pd surface in order to obtain reproducible data from further sequential STO reactions. With Pt and freshly reduced Pd catalysts this usually entailed the running of 3–5 STO sequences before reproducible data could be obtained. This procedure was also sufficient for the surface reduction of Pt catalysts up to at least 1 yr old (42). With Pd catalysts, however, the older they were the more difficult it was to accomplish this surface reduction using multiple STO reaction sequences; catalysts several months old did not give reproducible data even after exposure to over 50 STO cycles. It was found, however, that with Pd catalysts up to about 6 months old, surface rereduction could be accomplished by exposure of the catalyst to a stream of hydrogen at room temperature for 30 min before use. The excess hydrogen, spillover hydrogen, and alpha- and beta-phase hydrogen were removed by first exposing the catalyst to a stream of helium for 2 hr at room temperature. The removal of any further hydrogen on or in the catalyst was accomplished by titration of the catalyst with pulses of 1-butene (50). The first pulse produced some

butane by reaction with the hydrogen on or in the Pd but subsequent pulses, at least 15 min apart, gave little, if any, butane showing that all of the spillover or interstitial hydrogen which could react with the olefin had been removed. STO reactions run after this procedure gave reproducible results.

Other samples of the supported Pd salt were reduced in the reactor by what is described in the Experimental as the *in situ* reduction procedure and then employed directly for further reactions with no contact with air. After reduction and cooling to room temperature under helium, pulses of 1-butene were introduced into the reactor to remove any excess hydrogen present on or in the catalyst. As with the rereduced older catalysts the first pulse gave some butane formation but none was produced from subsequent pulses showing, again, that all of the reactive hydrogen had been removed from the catalyst. Comparison of the STO reaction data obtained using the *in situ* reduced catalysts and 1 month, 5 month, and 1 yr old rereduced catalysts are shown in Table 5. This shows that the *in situ* reduced catalysts and the rereduced 1 month old species are essentially the same and that rereduction of Pd catalysts up to about 6 months old can regenerate the initially produced materials. With catalysts about a year old, however, this room temperature reduction was not successful. It was found necessary to rereduce such catalysts in hydrogen at higher temperatures to promote surface reduction.

Table 5 also lists the STO site densities of 1 yr old catalysts originally reduced at 250, 300, and 400°C and rereduced under hydrogen at 150°C for 2 hr followed by sweeping with helium at 150°C for 30 min and cooling under helium to room temperature. After removal of the reactive hydrogen on and in the Pd by 1-butene titration (50) the reported results were obtained. These data show that the initial reduction temperature can have a significant effect on the site densities on these catalysts as was observed with Pt species (42). However, comparison

TABLE 5
STO Site Densities for 1.6% Pd/CPG Catalysts
Reduced at Various Temperatures

Initial red'n temperature (°C)	Site densities (moles/mole Pd)		
	³ M ^a	² M ^b	³ MH ^c
150 ^d	0.365	1.190	0.189
250 ^e	0.325	0.790	0.246
300 ^e	0.257	1.019	0.167
400 ^e	0.293	1.075	0.147
150 ^f	0.321	1.149	0.197
300 ^f	0.188	1.139	0.082
400 ^f	0.085	0.876	0.054
150 ^f	0.321	1.149	0.197
150 ^g	0.320	1.208	0.193
150 ^d	0.355	1.190	0.189

^a Direct saturation sites.

^b Isomerization sites.

^c Two-step saturation sites.

^d Five month old catalyst rereduced in H₂ at room temperature.

^e One yr old catalyst rereduced in H₂ at 150°C for 30 min.

^f *In situ* reduced catalyst.

^g One month old catalyst rereduced in H₂ at room temperature.

with the data for the catalysts reduced *in situ* at 150, 300, and 400°C shows that these older rereduced catalysts are not the same as the originally produced materials. Apparently the initial exposure of Pd catalysts to air results in the formation of adsorbed oxygen and/or surface oxides which are easily reduced to regenerate the initial metal surface. Exposure to air for prolonged periods of time, however, evidently forms a more deep-seated oxide which disrupts the surface morphology and is more difficult to reduce. When reduction of the more oxidized species is affected a new metal crystallite is formed which has a morphology different from that originally present. Because of the problems associated with the use of these older catalysts the Pd catalyst data discussed below were obtained using materials reduced at 150°C by the *in situ* method or the room temperature rereduction of 1 or

5 month old catalysts initially reduced at 150°C.

Some previous STO data obtained using two Pd/CPG catalysts showed that these species behaved differently from Pt/CPG catalysts (47). The Pd catalysts had very high isomerization site densities and a relatively low number of saturation sites. There was no evidence observed for the presence of ³M_R or ³MH sites on the Pd catalysts. Since these results were so different from those observed with Pt and only of a preliminary nature, a number of Pd catalysts were evaluated by the STO procedure to determine if these differences were real or merely incorrect conclusions drawn from early, preliminary results.

Since these previous results indicated that the introduction of the second hydrogen pulse in the STO sequence run over Pd/CPG did not liberate any butane, it was concluded that Pd catalysts did not have any two step hydrogenation sites. However, in the initial phases of this present study some partially resolved peaks were detected on the side of the *trans* 2-butene gc peak which indicated that some butane was being formed but was not being detected because of the large size of the *trans* 2-butene peak. The formation of the second butane, however, could be delayed by changing the time of the introduction of the second hydrogen pulse into the reactor and, thus, improving the gc separation of this generally small butane peak from that of the more dominant *trans* 2-butene. By doing this, detection of the second butane peak became routine; so contrary to the previous conclusions, Pd catalysts have on their surfaces two-step saturation sites.

It was confirmed, however, that as previously observed, changing the time between the initial hydrogen pulse and the butene pulse does not influence the amount of butane formed from the direct saturation sites on a number of Pd/CPG catalysts. With these catalysts it was found that when the hydrogen saturated catalyst was exposed to a stream of 30-cc/min carrier gas for 30 min no decrease in initial butane formation was

TABLE 6

Effect of Flow Rate and Reactant Pulse Size on Product Composition for STO Reactions Run over a 1.6% Pd/CPG Catalyst

Pulse size (μl)	Flow rate ^b	Product composition ^a			
		1-Butene ^c	Butane ^d	2-Butenes ^d	Butane ^f
20	30	0.036	0.330	0.558	0.192
	50	0.047	0.311	0.564	0.201
	70	0.067	0.302	0.566	0.189
40	30	0.060	0.318	1.212	0.197
	50	0.080	0.307	1.204	0.196
	70	0.112	0.319	1.162	0.194
60	30	0.255	0.313	2.300	0.183
	50	0.325	0.325	2.190	0.209
	70	0.342	0.316	2.190	0.203

^a In moles of product per mole of Pd.

^b In cc/min.

^c Unreacted starting material.

^d Formed by reaction of the 1-butene on the direct saturation (³M) sites.

^e Formed by reaction of the 1-butene on the isomerization (²M) sites.

^f Formed by reaction of the 1-butene on the two-step saturation (³MH) sites.

observed nor was there any change in the amounts of any of the other products formed in the STO reaction sequence. Some Pd/Al₂O₃ and Pd/SiO₂ catalysts, however, did show the presence of reversibly adsorbed hydrogen on some direct saturation sites; which shows that some Pd catalysts do have ³M_R sites; but the determining factor in the presence or absence of these sites appears to be the nature of the material used to support the dispersed Pd crystallites.

The most obvious difference between Pt and Pd in STO behavior is in the extent of isomeric butene formation. Over Pt catalysts only a small amount of isomerization is observed while over Pd catalysts isomerization is the primary reaction. With Pd the extent of isomerization is frequently so great that the number of molecules of isomerized butenes formed exceeds the number of Pd atoms in the catalyst sample used, so this reaction cannot be stoichiometric. More than one reaction must be taking place per active site during the time the butene pulse is in contact with the catalyst.

The product compositions shown in Table 6 show that changing the pulse size from 20

to 60 μl at a carrier gas flow rate of 30 to 70 cc/min results in the formation of the same amount of butane, within experimental error, from each of the two types of saturation sites present on Pd; but the decrease observed with the 20- μl pulse does seem to indicate the possibility that diffusion control may be important with reactions run using smaller reactant pulse sizes and the faster flow rates.

The extent of isomerization, according to the data presented in Table 6, however, is influenced more by the reactant pulse size than by the flow rate with the changes observed showing the nonstoichiometry of the isomerization of 1-butene to the 2-butenes. For a given pulse size the amount of isomerization decreases only slightly with increasing flow rate. This is especially true with the smaller pulse sizes since the isomerization reaction is so facile that essentially all of the 1-butene is converted either to butane or 2-butene even at the short contact times associated with the faster flow rates (Table 2). With the increased concentration of 1-butene in the larger pulses more of a flow rate effect on the extent of isomerization is

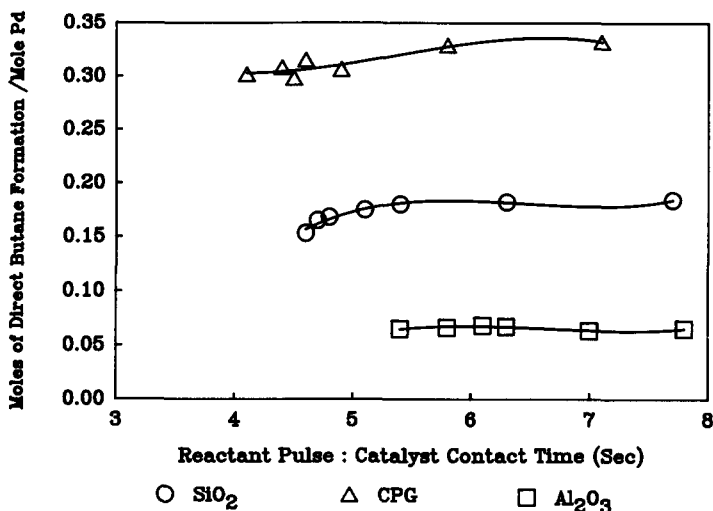


FIG. 1. Effect of reactant contact time with the catalyst on the STO measurement of the direct saturation (3M) sites on 1.6% Pd/CPG, 2.02% Pd/SiO₂, and 0.44% Pd/Al₂O₃.

found. It appears that with the 60- μ l pulses so much 1-butene is present that all of the isomerization which can take place has occurred; so the changes in flow rate do have some effect.

The results shown in Table 6 were derived from STO reactions using Pd/CPG catalysts. However, while the use of CPG as a catalyst support has some advantages (46) it is not a commonly used material in catalysis. It was considered essential, then, that the ability of the STO reaction sequence to provide active site density data for metals supported on the more common catalyst supports had to be determined. With Pd/CPG it was found that when the time the reactants were in contact with the catalyst was changed by varying reactant pulse sizes and/or carrier gas flow rate, diffusion could be observed at higher flow rates and smaller reactant pulse sizes. Fig. 1 illustrates the comparison of the direct butane formation with changing contact times (Table 2) over CPG, SiO₂, and Al₂O₃ supported Pd catalysts. The more active CPG supported catalysts show diffusion control at contact times associated with flow rates of 50 cc/min or faster. Thus, as discussed previously, the STO procedure is effective for these catalysts only at slower

flow rates. The reaction over the Pd/SiO₂ catalyst begins showing diffusion control also at flow rates greater than 50 cc/min. With the relatively inactive Pd/Al₂O₃, on the other hand, essentially no change in butane formation was observed over the range of contact times investigated. Increasing the reactant pulse size to increase the reactant concentration made no appreciable difference in these results except for the extent of observed isomerization.

Supported Rh Catalysts

The CPG supported Rh salts were prepared using an ion-exchange process with RhCl₃. Following the standard isothermal procedure, samples of this salt were reduced at various temperatures and the resulting catalysts stored in air for several weeks before STO analysis. Unlike the Pt and Pd catalysts, these Rh species showed nonreproducible results even after a large number of STO reaction sequences were run to reduce the metal surface. Room temperature hydrogen rereductions were also unsuccessful in regenerating catalysts having consistent activities and site densities. Elevated temperature rereductions could be used to obtain active species but the materials so

TABLE 7
STO Site Densities for 1.2% Rh/CPG Catalysts
Reduced *in situ*

Red'n temperature (°C)	Site densities (moles/mole Rh)			
	$^3\text{M}_I^a$	$^3\text{M}_R^b$	$^2\text{M}^c$	$^3\text{MH}^d$
200	0.098	0.033	0.473	0.036
250	0.099	0.034	0.415	0.031
300	0.076	0.022	0.445	0.031
400	0.107	0.024	0.433	0.035

^a Direct saturation sites having strongly adsorbed hydrogen.

^b Direct saturation sites having weakly adsorbed hydrogen.

^c Isomerization sites.

^d Two-step saturation sites.

produced varied with the time the original catalyst was exposed to air so this procedure could not be relied on to provide catalysts for meaningful STO characterization.

To obtain reliable and reproducible STO reaction data it was necessary to use the *in situ* reduction procedure. After reduction at the appropriate temperature in a stream of hydrogen and cooling to room temperature in helium the catalyst sample was treated with successive pulses of 1-butene to remove any spillover hydrogen which might be present (50). When no further butane formation was observed with a pulse of butene the STO reaction sequence was begun. Reproducible results were usually obtained after two or three additional turnovers.

These reductions were run on samples of the supported salt at temperatures of 200, 250, 300, and 400°C. The results of the STO characterizations run on these catalysts are listed in Table 7. Unlike Pt and Pd catalysts there does not appear to be much difference between the catalysts reduced at the different temperatures. However, like Pt catalysts (42) and some Pd catalysts, when the time between the introduction of the hydrogen pulse and the 1-butene pulse in the STO reaction sequence ("sweepoff" time) was increased the amount of initial butane for-

mation decreased; so these rhodium catalysts also have direct saturation sites on which the hydrogen is weakly adsorbed ($^3\text{M}_R$ sites) as well as those on which the hydrogen is more strongly held ($^3\text{M}_I$ sites). A plot of the product compositions observed for a series of reactions run over the same catalyst but having varying "sweepoff" times is shown in Fig. 2. There is a decrease in the formation of butane from the direct saturation sites with increasing "sweepoff" times up to 30–45 minutes; longer times had no effect so it can be concluded that all of the weakly held hydrogen was removed by this time. The amounts of isomerization and two-step saturation remain constant regardless of the amount of time elapsed between the introduction of the hydrogen pulse and the 1-butene pulse. Thus, the only reactive sites on these catalysts which have the reversibly adsorbed hydrogen are some of the direct saturation sites. The difference between the amounts of butane formed during the standard STO reaction sequence and that obtained after 45–60 minutes "sweepoff" gives the $^3\text{M}_R$ direct saturation site densities. The amount present after this prolonged "sweepoff" gives the $^3\text{M}_I$ site densities reported in Table 7.

The data in Table 8 show that these Rh catalysts are like Pd in that they promote extensive isomerization during the STO reaction sequence but not quite to the extent observed with most Pd catalysts. Increasing the 1-butene pulse size increases the amount of 2-butene formed so, as with Pd, more than one molecule of 1-butene can isomerize over each isomerization site on the Rh catalyst during the time the reactant pulse is in contact with the catalyst. As with Pd catalysts the amount of isomerization observed using the smaller pulse size is only slightly affected by the flow rate. In each of these cases only about 5% of the 1-butene remained unreacted so variations in the extent of isomerization with changes in contact time would not be noticeable. With the 40- μl pulse, though, less isomerization was observed at the faster flow rate and almost 10%

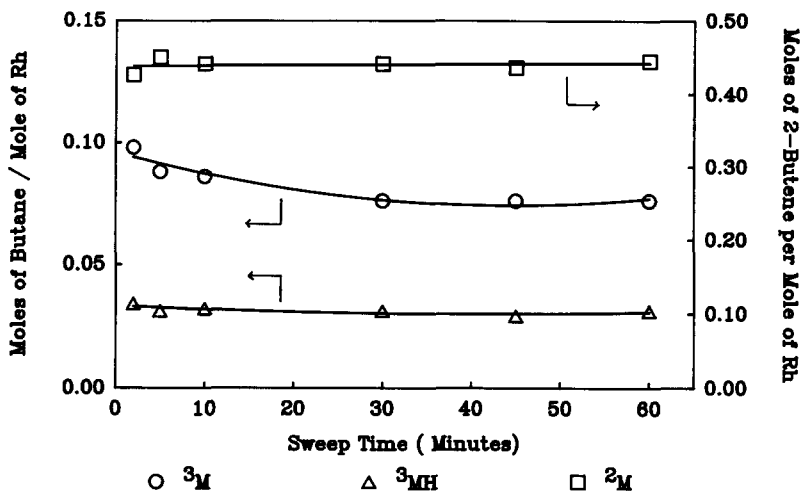


FIG. 2. Effect on product composition of the time lapse ("sweepoff" time) between the introduction of the hydrogen pulse and the 1-butene pulse in the STO reaction procedure run over a 1.2% Rh/CPG catalyst.

of the 1-butene remained unreacted so with the increased reactant concentration the flow rate had more of an effect on the amount of isomerization produced.

The data in Table 8 also show that the amount of butane formed from the direct and two-step saturation sites remains con-

stant, within experimental error, with changing reactant pulse sizes. However, increasing the flow rate results in a significant decrease in butane formation particularly from the two-step saturation sites. These results imply that Rh catalysts are more susceptible to diffusion control than is either Pt

TABLE 8

Effect of Flow Rate and Reactant Pulse Size on Product Composition for STO Reactions Run over a 1.21% Rh/CPG Catalyst

Pulse size (μ l)	Flow rate ^b	Product composition ^a			
		1-Butene ^c	Butane ^d	2-Butenes ^e	Butane ^f
20	30	0.083	0.113	0.589	0.045
	50	0.066	0.116	0.604	0.044
	70	0.094	0.095	0.612	0.029
40	30	0.510	0.120	0.983	0.047
	50	0.541	0.120	0.947	0.052
	70	0.599	0.130	0.892	0.039
60	30	1.209	0.108	1.124	0.049
	50	1.329	0.113	1.008	0.040
	70	1.356	0.115	0.985	0.034

^a In moles of product per mole of Rh.

^b In cc/min.

^c Unreacted starting material.

^d Formed by reaction of the 1-butene on the direct saturation (³M) sites.

^e Formed by reaction of the 1-butene on the isomerization (²M) sites.

^f Formed by reaction of the 1-butene on the two-step saturation (³MH) sites.

TABLE 9

Effect of Flow Rate and Reactant Pulse Size on Product Composition for STO Reactions Run over Various Supported Rhodium Catalysts

Support ^b	Pulse size (μ l)	Flow rate ^c	Product composition ^a			
			1-Butene ^d	Butane ^e	2-Butenes ^f	Butane ^g
CPG	20	15	0.056	0.250	0.652	0.080
		30	0.059	0.238	0.657	0.084
	40	15	0.115	0.246	1.464	0.090
SiO ₂	20	30	0.177	0.236	1.402	0.092
		15	0.112	0.157	0.504	0.053
	40	15	0.334	0.157	0.963	0.057
TiO ₂	20	30	0.447	0.152	0.844	0.068
		15	0.050	0.055	0.767	0.032
	40	15	0.062	0.052	0.757	0.031
Al ₂ O ₃	20	30	0.138	0.050	1.439	0.044
		15	0.194	0.052	1.384	0.040
	40	15	0.087	0.017	0.410	0.004
	20	30	0.143	0.015	0.359	0.002
		15	0.244	0.019	0.514	0.002
	40	30	0.349	0.018	0.408	0.003

^a In moles of product per mole of Rh.

^b 1.21% Rh/CPG, 1.85% Rh/SiO₂ 1.39% Rh/TiO₂, 2.29% Rh/Al₂O₃.

^c In cc/min.

^d Unreacted starting material.

^e Formed by reaction of the 1-butene on the direct saturation (³M) sites.

^f Formed by reaction of the 1-butene on the isomerization (²M) sites.

^g Formed by reaction of the 1-butene on the two-step saturation (³MH) sites.

or Pd. The results listed in Table 9, though, show that when flow rates of 15 or 30 cc/min are used, butane formation is constant regardless of the reactant pulse size; so these conditions are those which must be used for the STO reaction sequences on Rh catalysts to avoid diffusion control of product formation. Similar results were observed with supported other Rh catalysts and, as indicated by the product compositions listed in Table 9, there is no problem with using the STO procedure to investigate these species if flow rates of 15 to 30 cc/min are used. The constancy of these data for each support is well within the experimental error for the STO procedure so it can be stated that any of these sets of reaction conditions would provide acceptable STO characterization data for each of these catalysts.

It should be noted that while the STO

reaction procedure can be used with the oxide supported catalysts, attempts at extending this procedure to carbon supported catalysts all met with failure because of the ability of the carbon supports to adsorb all of the hydrocarbon in the limited reaction mixture produced by the reactant pulses. The use of repeated runs to saturate the support with hydrocarbon led to the indiscriminate release of the various components of the reaction mixture and nonreproducible analytical results.

STO Reactions Using the Isomeric *n*-Butenes

The routine use of 1-butene in the STO reaction sequence could raise some questions concerning the reliability of any extrapolation of active site data obtained using

TABLE 10
Effect of Starting Alkene on Product Composition for STO Reactions Run
over Various Catalysts

Catalyst ^b	Reactant alkene	Product composition ^a				
		1-Butene	Butane ^c	<i>cis</i> 2-Butene	<i>trans</i> 2-Butene	Butane ^d
Pt/CPG	1-Butene	0.572	0.226	0.042	0.054	0.099
	<i>cis</i> 2-Butene	0.029	0.215	0.541	0.105	0.104
	<i>trans</i> 2-Butene	0.018	0.222	0.057	0.595	0.100
Pd/CPG	1-Butene	0.123	0.355	0.308	0.690	0.185
	<i>cis</i> 2-Butene	0.042	0.335	0.407	0.698	0.185
	<i>trans</i> 2-Butene	0.037	0.345	0.245	0.858	0.180
Rh/CPG	1-Butene	0.034	0.159	0.151	0.436	0.046
	<i>cis</i> 2-Butene	0.015	0.159	0.175	0.426	0.050
	<i>trans</i> 2-Butene	0.015	0.162	0.154	0.445	0.049

^a In moles of product per mole of metal.

^b 3.35% Pt/CPG, 1.6% Pd/CPG, 3.4% Rh/CPG.

^c Formed by reaction of the alkene on the direct saturation (³M) sites.

^d Formed by reaction of the alkene on the two-step saturation (³MH) sites.

this terminal olefin to those reactions taking place on more sterically crowded materials. Further, with the extensive isomerization observed with both Pd and Rh catalysts, it can be questioned whether the butane formation from the saturation sites is influenced by the amounts of the isomeric 2-butenes present in the reactant pulse as it passes over the catalyst. To answer these questions the STO reaction sequence was run over CPG supported Pt, Pd, and Rh catalysts using 1-butene, *cis* 2-butene, and *trans* 2-butenes as the reacting alkene. The results are listed in Table 10.

The STO reactions were run using various carrier gas flow rates and reactant pulse sizes to determine the possibility of diffusion control. The data reported here have been obtained using conditions thus shown to minimize diffusion control. In all cases the carrier gas flow rate was 30 cc/min. With the Pt/CPG (4.8 mg) and the Pd/CPG (5.0 mg) 20- μ l reactant pulses were used. With the Rh/CPG (3.4 mg) 40- μ l pulses were used.

The STO data for the Pt/CPG catalysts show that the butane formation from both the direct, ³M, and two-step, ³MH, satura-

tion sites is constant regardless of the butene isomer used. Thus, these sites are not sensitive to the geometry of the alkene used in this reaction and the STO results obtained with Pt catalysts can be extrapolated for use with other systems with reasonable confidence. A similar conclusion can be arrived at with both Pd and Rh catalysts.

The data concerning the amount of each of the isomeric butenes present in the STO product mixture with these catalysts are also informative. In contrast to the extensive isomerizations observed with Pd and Rh, Pt catalysts characteristically promote only a small amount of 1-butene isomerization. Initially it was considered that on Pt the isomerization reaction was stoichiometric during the STO process while it was nonstoichiometric over Pd and Rh (37, 47). Since it was thought that these isomerization sites were edge atoms (37, 40), the apparently low isomerization site densities on Pt coupled with the observed high saturation site or corner atom densities did not fit in with any general type of crystalline shape (51, 53). In the preceding discussion it was concluded that the low isomerization ob-

served over Pt catalysts during an STO reaction sequence could be the result of either a small number of isomerization sites reacting nonstoichiometrically or a reasonable number of inactive sites with the activity of these sites increasing with an increase in the amount of 1-butene in the reactant pulse. Another reason for the small amount of observed isomerization, though, is the possibility of forming a primary metalalkyl intermediate on Pt. β -Elimination from such a species would regenerate 1-butene and the interaction with the catalyst would go unnoticed. When the *cis* and *trans* 2-butenes are used as reactant alkenes, though, such a pathway is not available.

The data in Table 10 show that while somewhat more isomerization is observed when the 2-butenes are used as reactants in the STO procedure over Pt than is the case with 1-butene, the extent of isomerization is still quite small and most of the alkene passes through the reactor unchanged. Interestingly, 1-butene is also formed from the 2-butenes under these reaction conditions. It would seem, then, that primary metalalkyl formation is not the reason for the small amount of isomerization observed with Pt catalysts in the STO procedure.

Over Rh (Table 10), the product butene isomer composition is essentially the same from each of the starting alkenes with the only difference being a small ($\sim 2\%$) excess of the starting olefin present in each case. This constancy of alkene composition regardless of the starting olefin along with the observed 1-butene: *cis* 2-butene: *trans* 2-butene ratio of 1 : 10 : 30 strongly suggests that an equilibrium of the alkenes is taking place over this Rh catalyst. Thus, isomerization over this catalyst must be particularly rapid since the reactant pulse sizes were twice that used with both Pt and Pd.

With the Pd catalyst, even though there is significant isomerization occurring (Table 10), there is a larger excess of each starting olefin present than was observed with Rh. This and the 1-butene: *cis* 2-butene: *trans* 2-butene ratio of 3 : 20 : 50 indicates that equi-

librium was not fully attained. This conclusion is further substantiated by the observation that there is more *cis* 2-butene formed from 1-butene than from the *trans* 2-butene even though the amount of *trans* 2-butene formed is the same from both 1-butene and *cis* 2-butene.

Comparison with Other Results

A direct comparison of the STO characterization data with results from steady state reactions or other, more traditional, catalyst characterization techniques is highly desirable, but it is not readily accomplished. Such comparisons cannot be made on a single catalyst. Instead, a series of STO characterized catalysts must be used so variations in reaction rate or other properties can be related to changes in one or more of the STO reactive site densities on the catalysts. Only a few of this type of comparison are available.

A series of STO characterized Pt/CPG catalysts were subjected to TEM analysis with the average particle size and size range for each of them listed in Table 11. Also listed are STO site densities and catalyst dispersions determined in various ways. The D_H values are the standard dispersions obtained using H_2 chemisorption and a 1 : 1 H : Pt stoichiometry. The D_{EM} are the dispersions calculated from the TEM determined average particle sizes and the assumption of octahedral particle shapes (51). The D_{STO} data are the dispersions based on STO site determinations combined with H_2 chemisorption data. They are the sums of the 3M , 2M , and 1M site densities for each of the catalysts. The data in Fig. 3 show that a relationship exists between the TEM measured average metal particle size on these catalysts and the STO determined saturation site densities as well as the STO dispersions which are the sum of all surface site densities. Those catalysts with the higher site densities expressed in moles of site/mole Pt are those with the smaller metal crystallites. Since a large proportion of catalytic reactions probably takes place on the

TABLE 11
 STO and TEM Data for Some Pt/CPG Catalysts

	Catalysts ^a						
	I-20/200	I-250	II-250	II-400	IV-250	IV-400	III-250
D_H^b	1.10	0.83	0.55	0.31	0.25	0.18	0.16
STO data							
$^3M_I^c$	0.186	0.150	0.099	0.038	0.049	0.003	0.040
$^3M_R^c$	0.062	0.017	0.038	0.026	0.022	0.028	0.009
$^3MH^c$	0.084	0.062	0.051	0.017	0.018	0.010	0.020
$^2M^c$	0.065	0.010	0.038	0.025	0.031	0.009	0.005
$^1M^c$	0.453	0.424	0.185	0.137	0.062	0.102	0.038
Σ Sat'n Sites	0.332	0.229	0.188	0.081	0.089	0.041	0.069
D_{STO}^d	0.85	0.66	0.41	0.24	0.18	0.15	0.11
TEM data							
Avg. Part. Size (Å)	12.4	17.7	22.6	40.1	36.8	54.4	50.3
Part. Range (Å)	4.4-22.1	7.4-36.8	7.4-58.9	11.8-139.8	13.2-102.9	14.7-132.5	5.9-265.1
D_{EM}^e	0.69	0.56	0.48	0.30	0.32	0.23	0.25

^a Ref. (42).

^b From hydrogen chemisorption assuming a 1:1 H:Pt ratio.

^c Moles site/mole Pt.

^d Sum of STO site densities.

^e From the TEM determined average particle size assuming octahedral particle shape (51).

more coordinately unsaturated corner or 3M sites (10, 11), this relationship serves to show that comparing STO determined saturation site densities with catalyst activities follows the same general pattern as the more commonly used comparisons with catalyst dispersions. However, the active site density is a more specific measure of catalyst activity than the overall surface area as determined by H_2 chemisorption since the latter measurement includes the unreactive atoms as well.

The comparison of D_H and D_{STO} for these catalysts (Table 11), as illustrated in Fig. 4, shows that the STO site density determinations provide data which are consistent with those obtained using standard techniques for measuring catalyst dispersions. The STO approach, however, has an additional advantage of not having to consider the problem of H:Pt ratios greater than one which are sometimes observed especially

with the more highly dispersed catalysts such as I-20/200 (Table 11). In the STO reaction sequence the H_2 adsorption stoichiometry is proportional to the nature of the specific sites. Based on mechanistic considerations (37) the H:Pt adsorption ratio on 3M_I and 3M_R sites is 2:1 and on all the other sites it is 1:1. Comparison of the D_H and D_{STO} for the northwestern Pt/SiO₂ catalysts (Table 4) shows a similar relationship (Fig. 4). These Pt/SiO₂ catalysts have been used for a number of studies so they are potentially the basis for the comparison of STO data with other results.

X-ray data on the 40-SiO₂, 27-SiO₂, and the 21.5-SiO₂ catalysts show that the mean metal particle size for the 40-SiO₂ material is around 2.0 nm while for the other two it is in the 4.0–5.0 nm range (54). Comparable data for the 63-SiO₂ and 81-SiO₂ catalysts are not available. As with the Pt/CPG catalysts (Table 11), there is also a general de-

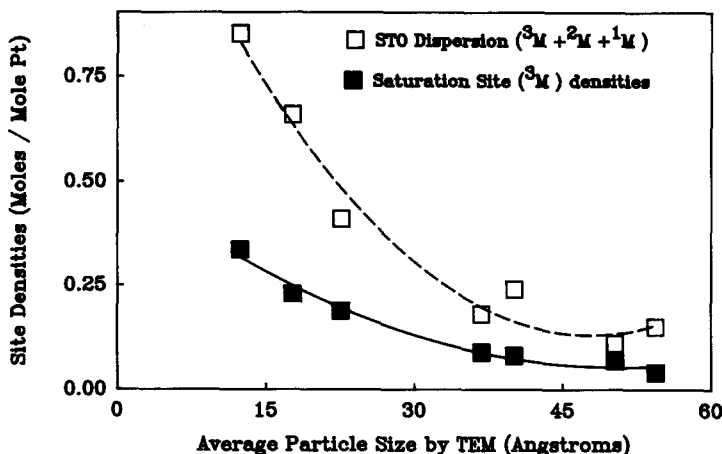


FIG. 3. Comparison of the TEM determined average metal particle size with the STO determined site densities on a series of Pt/CPG catalysts (42).

crease in saturation (3M) site densities with decreasing particle size with these Pt/SiO₂ catalysts as well. This particle size rational, however, does not extend to the EuroPt-1 catalyst which has about 75% of the metal particles 2.0 nm or less (55) but still appears, from our STO analysis, to have rather large numbers of STO inactive atoms on the surface. Apparently other effects are also operational in determining the relative "complexity" (24) of the surface of dispersed Pt catalysts. Another difference can be seen by comparing the site density data for the 40-

SiO₂ catalyst, which has a moderate dispersion but with 64% of its surface occupied by saturation sites (3M), with that of the 81-SiO₂ material. This latter species has a higher dispersion but also a lower percentage of the metal surface associated with saturation sites. It has been reported that in the deuterium exchange of cyclopentane more of the d_5 species is formed over the 40-SiO₂ catalyst than over the 81-SiO₂ (56). Since there is a higher percentage of corner atoms on the 40-SiO₂ material these results agree with our data obtained using STO characterized

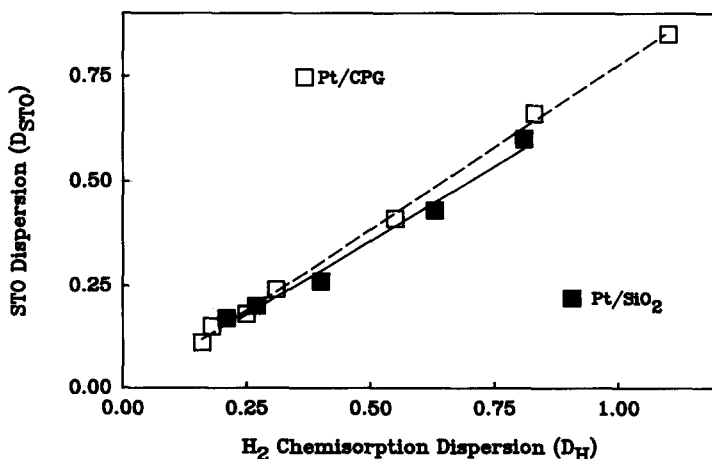


FIG. 4. Comparison of hydrogen chemisorption dispersion data and STO dispersion data for series of Pt/CPG (42) and Pt/SiO₂ (48) catalysts.

Pt/CPG catalysts which indicated that polydeuterium exchange takes place primarily over the corner atoms on the metal surface (44).

Further comparison of the STO site density values for these catalysts with published reaction data obtained using these species is hampered by the different reactivities of the various types of sites present on the catalyst surface. The use of areal turnover frequencies further complicates the comparison since the dispersion used to calculate these TOFs include nonreactive surface sites in their determination. If the overall TOF of a catalytic reaction can be considered to be the sum of the specific site TOFs then the molar TOF for a reaction taking place on the three types of corner atoms can be expressed as (45)

$$\text{Molar TOF} = A*[\text{}^3\text{M}_\text{I}] + B*[\text{}^3\text{M}_\text{R}] + C*[\text{}^3\text{MH}]. \quad (1)$$

In this equation the TOF is expressed as moles of product formed/mole of metal/unit time, the []'s are the site densities in moles of site/mole of metal, and *A*, *B*, and *C* are the specific site TOF's expressed as moles of product formed/mole of metal/unit time. The molar TOF is used instead of the usual areal TOF in order to provide a consistent relationship with the site densities which are expressed in relationship to the moles of metal present in the catalyst. When the molar TOFs are obtained for a number of reactions run under identical conditions over a series of STO characterized catalysts and the site densities of the catalysts are known, values for *A*, *B*, and *C* can be found by solving the simultaneous equations. In the hydrogenation of cyclohexene in heptane solution at 10°C over seven STO characterized Pt/CPG catalysts, the values found for *A*, *B*, and *C* were 2.1, 18.2, and 5.2 moles of alkane formed/mole of site/sec respectively (45). The most active sites, by far, are the $^3\text{M}_\text{R}$ on which the hydrogen is more weakly held even though these sites are not the most plentiful on the catalyst surface.

Extension of this approach using the mo-

TABLE 12
Comparisons of Observed and Calculated TOFs

Reaction	Catalyst	Observed TOF	Calculated TOF ^a
Cyclohexene hydrogenation ^b			
	1 ^c	0.141	0.135
<i>A</i> = 2.1	2 ^c	0.312	0.310
<i>B</i> = 18.2	3 ^c	0.354	0.328
<i>C</i> = 5.2	4 ^c	0.506	0.496
	5 ^c	0.549	0.560
	6 ^c	0.670	0.704
	7 ^c	0.891	0.889
Apopinene hydrogenation ^d			
	III-250 ^e	0.130	0.130
<i>A</i> = 1.1	IV-400 ^e	0.180	0.180
<i>B</i> = 5.7	IV-250 ^e	0.210	0.210
<i>C</i> = 1.8	II-400 ^e	0.220	0.219
<i>A</i> = 5.8	21-SiO ₂ ^f	0.387	0.414
<i>B</i> = 18.2	27-SiO ₂ ^f	0.700	0.674
<i>C</i> = 5.4	40-SiO ₂ ^f	0.977	0.973
CO oxidation ^g			
	81-SiO ₂ ^f	0.010–0.014	0.0102
<i>A</i> = 0.04	63-SiO ₂ ^f	0.008–0.009	0.0085
<i>B</i> = 0.04	40-SiO ₂ ^f	0.006–0.007	0.0064
<i>C</i> = 0.04	27-SiO ₂ ^f	0.002–0.003	0.003

^a Calculated using Eq. (1).

^b Ref. (45).

^c Site densities are listed in Ref. (45).

^d Ref. (57).

^e Site densities are listed in Table 11.

^f Site densities are listed in Table 4.

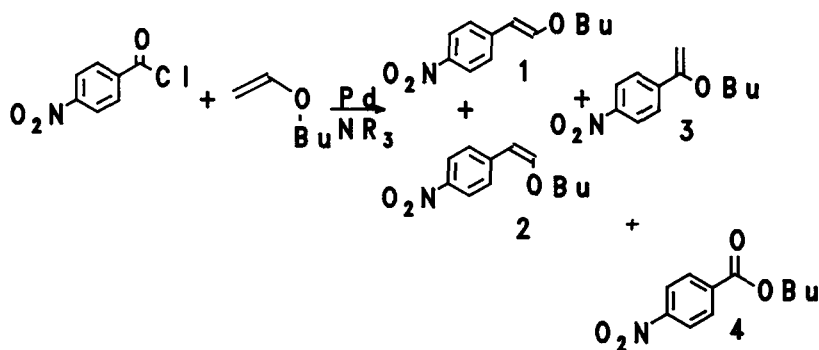
^g Ref. (59).

lar TOF data calculated from the areal TOFs reported for the hydrogenation of (+)apopinene over some of the Pt/SiO₂ catalysts listed in Table 4 (33) gave values for *A*, *B*, and *C* of 5.8, 18.2, and 5.4 moles of alkane/mole site/sec, respectively (57). When the (+)apopinene hydrogenation was run over some of the Pt/CPG catalysts listed in Table 11 values of 1.1, 5.7, and 1.8 moles of alkane/mole site/sec were found for *A*, *B*, and *C*, respectively (57). In both of these cases the $^3\text{M}_\text{R}$ sites were also the most active. In Table 12 are listed the comparisons of the experimentally obtained molar TOFs and those calculated using Eq. (1) and the *A*, *B*, and *C* values for the reaction and the site densities for the catalysts used. The correlation between these two values is excellent.

This approach can also be used for reactions other than hydrogenations. When the Heck arylation (Eq. (2)) was run over a se-

ries of STO characterized Pd/Al₂O₃ catalysts it was found that the amounts of the products, 1 and 2, formed under standard conditions was linearly related to the saturation

site densities on these catalysts (58), indicating that the reaction is taking place on the more highly coordinately unsaturated corner atoms on the Pd surface.



The oxidation of CO over several of the Northwestern Pt/SiO₂ catalysts has been reported (59). While this reaction is generally considered to be structure insensitive (60) the reported areal TOF data (59) did not provide conclusive support for this premise. If, however, the molar TOF values calculated from these areal data for the four catalysts along with the appropriate site densities (Table 11) are treated as in Eq. (1) the values of *A*, *B*, and *C* are all equal at 0.04 mole of CO₂/mole of Pt/sec. Comparison of the observed molar TOF data with the calculated TOF values is excellent (Table 12). These results indicate that not only is the oxidation taking place on the corner atoms on the catalyst surface but also that all of the different types of STO saturation sites have the same activity for this oxidation reaction. In the Pt catalyzed oxidation of secondary alcohols using O₂ in aqueous medium it was also found that all three of these active sites have essentially the same TOF values (61).

CONCLUSIONS

It has been shown that the STO reaction procedure can be used to provide surface characterization data for dispersed metal catalysts supported on the commonly used oxide supports. The only requirement is to

determine for each catalyst that diffusion factors are not involved in the reaction. This can be accomplished by changing the reactant pulse size and/or carrier gas flow rate to modify in the reactant concentration or contact time with the catalyst. Diffusion factors are minimal when the product composition remains constant with further increases in reactant contact time with the catalyst. For most STO reactions using the standard 5–10 mg of catalyst a carrier gas flow rate of 30 cc/min or lower and reactant pulse sizes of 20 μl or greater give a sufficient contact time and reactant concentration to overcome diffusion factors. Under these conditions the procedure is not under diffusion control, at least as far as saturation site reactions are concerned, and the STO procedure can be used to determine the direct and two-step saturation site densities on various CPG and oxide supported Pt, Pd, and Rh catalysts. Shorter reactant contact times associated with faster flow rates have the most significant effect on Rh catalysts. The reactions of the two-step saturation sites on Rh are particularly susceptible to diffusion control at flow rates higher than 30 cc/min.

The isomerization reactions on both Pd and Rh catalysts are nonstoichiometric with virtually none of the starting 1-butene pass-

ing through the reactor unchanged. That which is not saturated is isomerized. Contrary to previous reports, it was also found that the isomerization reaction over Pt depends on both flow rate and reactant pulse size. Thus the STO reaction procedure is not able to determine isomerization site densities with any of these catalysts.

The STO reaction sequence has also been run over Pt, Pd, and Rh catalysts using each of the isomeric butenes as the reactant alkene. Over all three catalysts the same amounts of direct and two-step saturation were observed regardless of the starting alkene showing that these saturation sites are not sensitive to the geometric environment of the reactant olefin. Thus, STO saturation site data can reasonably be extrapolated to correlations with other reactions. Over Pd and Rh extensive isomerization is observed. With Rh a near equilibrium mixture of all three isomers is formed from each of the three starting alkenes. With Pt the extent of isomerization is characteristically low regardless of the starting olefin. Because of this it can be reasoned that the low isomerization observed during the STO reaction of 1-butene on Pt is not the result of primary metalalkyl formation on a large number of isomerization sites. If this were the case then extensive *cis/trans* isomerization should occur on using the isomeric 2-butenes as reactant alkenes, something which is not observed.

A TEM investigation of a number of STO characterized Pt/CPG catalysts has shown that there is a relationship between the average metal particle size on the catalyst and the STO saturation site densities. The use of series STO characterized catalysts in a number of different types of reactions has shown that for those studied the reactions take place on the more coordinately unsaturated corner atoms on the metal surface, those which are identified in the STO reaction sequence as saturation sites. The STO site data, then, can be of considerable use in determining catalyst activity as well as in

defining the types of sites on which specific reactions take place.

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