(1 H, m, = CCHC=), 5.9-6.1 (3 H, m, =CH), 7.0-7.5 (4 H, m, Ar); GC-MS (*m/e*) 182 (M^+), 167, 152, 141, 128, 116, 91, 89, 67, 51, 41. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.54; H, 7.88.

b. **5b** (384 mg, 2 mmol) was reacted with indenylsodium (2 mmol) in THF (10 mL) in the presence of 2 mol % catalyst. Column chromatography (SiO_2, cyclohexane) of the crude mixture gave an oil from which excess indene was removed by distillation, to afford as a residue the 1-substituted indene (320 mg, 65%): NMR 1.25-1.55 (6 H, m, aliphatics), 2.3 (1 H), 2.4 (2 H), 3.15 (1 H, m, =C CH), 3.3 (2 H, m, $ArCH_2C$=), 3.75 (1 H, m, =CCHC=), 5.8 (2 H, =CH), 6.1 (1 H, m, =CH), 7.1-7.5 (4 H, Ar); GC-MS (*m/e*) 248 (M^+), 233, 220, 205, 191, 181, 165, 152, 133, 118, 115, 91, 79, 67, 51, 45. Further elution (80:20 cyclohexane/EtOAc) afforded two fractions: 30 mg (0.16 mmol) of recovered acetate **5b** and 50 mg (0.33 mmol) of alcohol **5a**.

Attempt at Isomerization of 5b. **5b** (192 mg, 1 mmol) was mixed with tetraethylammonium acetate (523 mg, 2 mmol) in THF (10 mL) in the presence of 4 mol % catalyst. After 72 h of reaction, no isomerization was detected by GC analysis. Distillation of the residue afforded 145 mg (75%) of recovered **5b**.

Reactions with PhZnCl. Phenylzinc chloride was prepared through addition of an equimolecular amount of phenylmagnesium chloride to a cooled (0 °C), stirred solution of zinc chloride in THF.

a. A reaction was carried out with 126 mg of **1** (1 mmol) and 1 mmol of a PhZnCl mixture in THF, in the presence of 2 mol % catalyst. After workup, the product was distilled to give a mixture of biphenyl and 3-phenylcyclopentene, from which this latter compound was isolated by column chromatography (44 mg, 30%): NMR 1.4-2.6 (4 H, m), 3.85 (1 H, m, CHPh), 5.7-6.0 (2 H, m, CH=), 7.2 (5 H, aromatics); GC-MS (*m/e*) 144 (M^+), 129, 125, 91, 77, 66, 51, 39.

b. A reaction performed with 192 mg (1 mmol) of **5b** and 1 mmol of PhZnCl in the presence of 2 mol % catalyst afforded, after removal of the biphenyl by distillation, the phenyl-substituted dihydrocyclopentadiene (101 mg, 48%) as an oil: NMR 1.2-1.6 (m, 6 H, aliphatics), 2.3 (m, 3 H), 3.15 (m, 1 H, CHC=), 3.68 (m, 1 H, CHPh), 5.67 (ddd, 1 H, =CH), 5.74 (ddd, *J* = 5.6, 1.6, 1.4 Hz, 1 H, =CH), 7.0-7.3 (m, 5 H, aromatics); GC-MS (*m/e*) 210 (M^+), 167, 153, 143, 128, 115, 91, 77, 67, 51, 41.

Reactions with $LiP(S)Ph_2$. Lithium thioxodiphenylphosphide (2 mmol, prepared by addition of equimolecular amount of *n*-BuLi to $HP(S)Ph_2$ in THF) was added to a mixture of **5b** (192 mg, 1 mmol) and **1** (126 mg, 1 mmol) in the presence of 2 mol % catalyst. After workup, the crude mixture was distilled (90-100 °C, 1 Torr) to give **5b** (146 mg, 76% recovery). The residue purified by column chromatography to afford 280 mg (81%) of (cyclopent-2-enyl)diphenylphosphine sulfide: NMR 2-2.25 (2 H, m, aliphatics), 2.3 (2 H, m, CH_2 C=), 4.0 (1 H, m, PCH), 5.43 (1 H, m, CH=), 5.98 (1 H, m, CH=), 7.45 (6 H, m, aromatics), 7.85 (4 H, m, aromatics); GC-MS (*m/e*) 284 (M^+), 218, 183, 152, 139, 107, 97, 77, 63, 51, 41. Anal. Calcd for $C_{17}H_{17}PS$: C, 71.80; H, 6.03; S, 11.28; P, 10.89. Found: C, 71.91; H, 5.97; S, 11.40; P, 11.15.

Reaction with Ammonium Formate. To **5b** (192 mg, 1 mmol) and ammonium formate (126 mg, 2 mmol) dissolved in dioxane (10 mL) were added $Pd(OAc)_2$ (5 mg, 0.02 mmol) and PPh_3 (26 mg, 0.1 mmol). After 12 h of stirring, water (50 mL) was added and the resulting mixture was extracted with pentane (2 × 50 mL). The pentane layer was dried, the solvent removed, and the residue purified by column chromatography (pentane as eluent) to give 3a,4,5,6,7,7a-hexahydro-(3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (72 mg, 54%).

Acknowledgment. We thank Professor H. Kagan for fruitful discussions and are grateful to the compagnie des Mêtaux Prêcieux for a loan of palladium chloride.

Registry No. **1**, 20657-21-0; **2**, 65437-13-0; **3a**, 58616-86-7; **3b**, 102935-87-5; **4**, 5019-96-5; **5a**, 19926-79-5; **5b**, 107407-81-8; **8**, 107407-83-0; dimethyl cyclopent-2-enylmalonate, 88444-66-0; *N*-(cyclopent-2-enyl)morpholine, 6284-13-5; 1-(cyclopent-2-enyl)cyclopentadiene, 5202-73-3; 2-(cyclopent-2-enyl)cyclopentadiene, 24667-77-4; 1-(cyclopenten-2-yl)indene, 107407-82-9; biphenyl, 92-52-4; 3-phenylcyclopentene, 37689-22-8; (cyclopent-2-enyl)diphenylphosphine sulfide, 107407-84-1; 3a,4,5,6,7,7a-hexahydro-(3aα,4α,7α,7aα)-4,7-methano-1*H*-indene, 2825-86-7; dicyclopentadiene, 77-73-6; sodium dimethyl molonate, 18424-76-5; morpholine, 110-91-8; cyclopentadienylsodium, 4984-82-1; indenylsodium, 23181-84-2; phenylzinc chloride, 28557-00-8; lithium thioxodiphenylphosphide, 54572-97-3; ammonium formate, 540-69-2; palladium acetate, 3375-31-3; triphenylphosphine, 603-35-0; $Pd(dba)_2$, 32005-36-0; dppe, 1663-45-2.

Heterogeneous Catalysis in Organic Chemistry. 6.[1] An Experimental Description of the Nature of the Hydrogenation Sites Present on Dispersed Pt Catalysts

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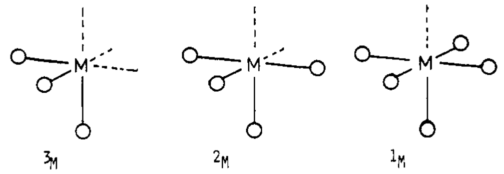
Ten Pt/controlled pore glass (CPG) catalysts having different reactive site densities as determined by single turnover (STO) characterizations were used to catalyze the dehydrogenation of cyclohexane to benzene under conditions previously used for the Pt single-crystal catalysis of this same reaction. It was found that the extent of benzene formation was related to the number of STO hydrogenation sites present on the catalyst. Since the single-crystal study showed that this dehydrogenation reaction occurred over corner atoms, it is concluded that the hydrogenation sites on the dispersed Pt catalysts are corner atoms as previously implied on mechanistic considerations.

One of the problems associated with the use of heterogeneous catalysts is the frequent lack of selectivity encountered in reactions promoted by such species. One reason for this problem is the presence on the catalyst of a number of different types of surface atoms having varying degrees of coordinative unsaturation and, thus, differing reaction characteristics.[2] In order to more fully utilize these catalytic species, it is necessary to have some understanding of the types of reactions promoted by these

Scheme I



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(1) For Part 5, see: Augustine, R. L.; Lenczyk, M. E. *J. Catal.* **1986**, *97*, 269.

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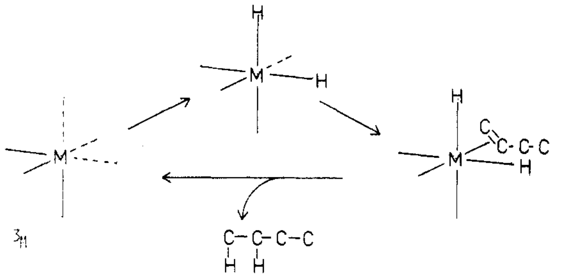
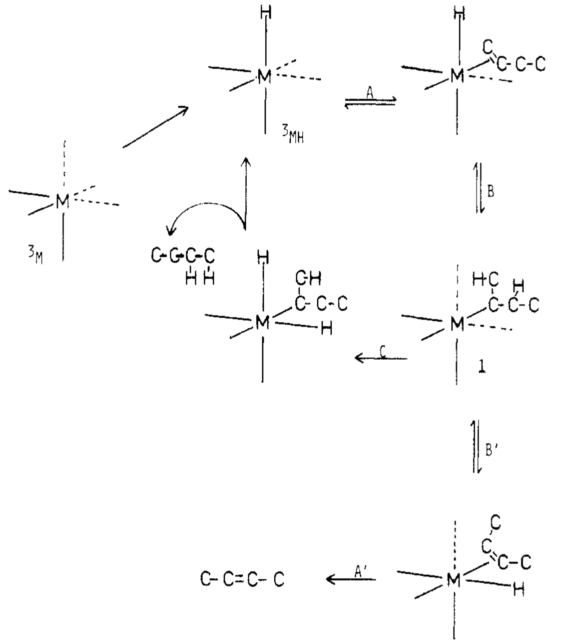
Scheme II



Scheme III

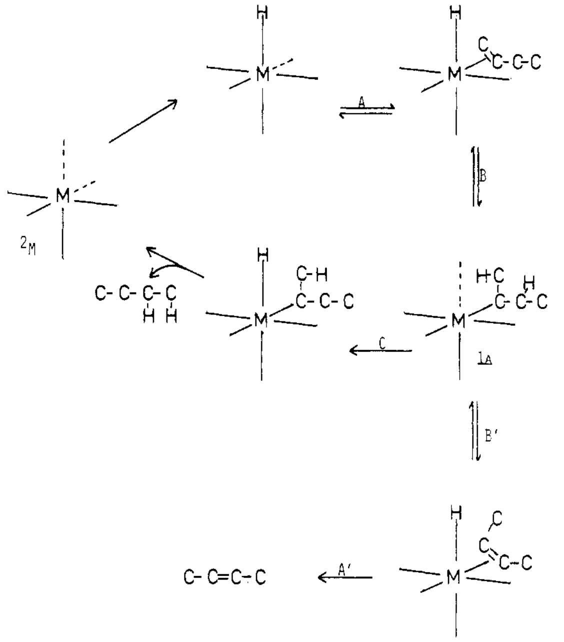


individual surface atoms.

A mechanistic comparison has been proposed[3] that relates what are thought to be reasonable reaction sequences for the hydrogenation of alkenes over corner, edge, and face atoms with those known to take place on a number of related homogeneous catalysts. In this comparison the corner, edge, and face atoms were defined as ^{3}M, ^{2}M, and ^{1}M atoms, respectively, having the coordinative unsaturation shown in Scheme I. The hydrogenation of a double bond over these ^{3}M sites is proposed to take place in two possible ways.[3,4] In Scheme II is shown the reaction sequence proceeding through the dihydride species labeled $^3MH_2$. In this sequence[3] the two hydrogens are considered to be transferred to the adsorbed alkene almost simultaneously so any metalalkyl intermediate that might be formed would be very short-lived. This sequence is based on the mechanism for alkene hydrogenation[5] taking place over $((C_6H_5)_3P)_3RhCl$ which occurs via the diphosphine species, $((C_6H_5)_3P)_2RhCl$, a material considered to be analogous to a ^{3}M site.[3]

A second alkene hydrogenation sequence was envisioned[3] as proceeding through a ^{3}MH species as shown in Scheme III. In this sequence the metalalkyl intermediate 1 would be formed with no additional hydrogen on the metal atom and further reaction to the alkane would take place only after the adsorption of an additional hydrogen molecule.

Scheme IV



This sequence differs from that shown in Scheme II primarily by the number of distinct steps involved in the saturation process. The hydrogenation depicted in Scheme II is essentially a one-step process with both hydrogens added to the double bond coming from the same dihydrogen molecule. The mechanistic proposal shown in Scheme III, which is analogous to olefin hydrogenation over $HRh(CO)(P(C_6H_5)_3)_3$,[6] involves two separate hydrogen adsorption steps with the hydrogens added to the alkene coming from two different dihydrogen molecules. In the absence of this second molecule of hydrogen step C would not take place and step B could reverse to regenerate an adsorbed alkene which could then desorb by reversal of step A. Reversal of step B could take place by abstraction of a hydrogen from either of the two α carbons so double-bond isomerization could take place via steps B′ and A′. Another reaction sequence utilizing edge or ^{2}M atoms for this two-step hydrogenation and/or isomerization has also been proposed[4] as shown in Scheme IV. Here, too, a metal alkyl intermediate, **1A**, would be involved in the two-step hydrogen–addition sequence and the isomerization reaction.

The face atom or ^{1}M sites are proposed[3,4] to adsorb either a single hydrogen or a double bond but not both together so these sites would not be expected to take part in alkene hydrogenations.

In our single turnover (STO) technique,[4,7] reactivity differences observed between catalysts are attributed to the presence of differing numbers of these various types of sites on the dispersed metal surface. In this procedure, a catalyst sample is placed in a reactor tube under a stream of He. It is then exposed to a pulse of hydrogen large enough so all surface metal atoms can adsorb as many hydrogens as needed for complete coverage. The excess hydrogen is removed in the carrier gas stream, a pulse of 1-butene is then passed over the catalyst to react with the adsorbed hydrogen, and the products are analyzed by on-stream gas chromatography. At this stage some of the 1-butene is hydrogenated to butane, some is isomerized to the *cis*- and *trans*-2-butenes, and some remains on the catalyst presumably as the half-hydrogenated state or

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Table I. Site Densities and Percent Benzene Formation

	site densities[a]								
	non heated catalyst[b]					heated catalysts			% benzene formation[c]
catalyst[b]	$^{3}\mathrm{M}$[d]	$^{2}\mathrm{M_S}$[e]	$^{2}\mathrm{M_C}$[f]	$^{1}\mathrm{M}$	*D*[g]	$^{3}\mathrm{M}$[d]	$^{2}\mathrm{M_S}$[e]	$^{2}\mathrm{M_C}$[f]	
IV-400	0.031	0.01	0.009	0.102	0.15	0.0034	0.0001	0.0295	1.0(1.0)
II-400	0.064	0.017	0.025	0.137	0.24	0.0036	0.0001	0.0692	7.2(10.4)
IV-250	0.071	0.018	0.031	0.062	0.18	0.0125	0.0067	0.099	26.2(24.3)
II-250	0.137	0.051	0.038	0.185	0.41	0.0214	0.0105	0.0818	65.4(59.3)
I-400	0.136	0.019	0.040	0.291	0.49	0.0256	0.0067	0.1022	44.6(na)[h]
IV-200	0.199	0.071	0.040	0.207	0.52	0.044	0.0221	0.117	87.8(82.3)
II-200	0.204	0.068	0.027	0.144	0.44	0.058	0.0308	0.067	99.0(99.0)
I-200	0.186	0.059	0.001	0.636	0.88	0.066	0.0354	0.044	92.3(85.1)
I-40/200	0.298	0.099	0.042	0.453	0.61	0.146	0.111	0.093	97.8(96.1)
I-250	0.167	0.062	0.010	0.424	0.66	0.158	0.099	0.229	97.1(95.7)

[a] mol/mol Pt [b] Reference 11. [c] From 1 μmol of C_6H_{12} pulses. Values in parentheses are from 2.5-μmol pulses. [d] Direct hydrogenation sites. [e] Metalalkyl sites. [f] Isomerization sites. [g] Dispersion. [h] na = not available.

metalalkyl. This species is removed as butane by reaction with a second pulse of hydrogen which completes the STO sequence. With Pt at least, it has been shown[4] that each surface site reacts only once during this sequence so the amount of butane formed initially is a measure of the number of direct hydrogenation sites on the catalyst surface. The extent of isomerization gives the number of isomerization sites and the amount of butane formed from the second hydrogen pulse determines the number of two-step hydrogenation sites present. In addition, there are sites present that adsorb hydrogen but do not take part in the hydrogenation reaction. Since there is no direct information available concerning the specific nature of these different types of sites, the reaction-based models presented above were used as working descriptions[4] with the direct hydrogenation sites termed $^{3}\mathrm{M}$, the isomerization sites called $^{2}\mathrm{M_C}$, the metalalkyl sites labeled $^{2}\mathrm{M_S}$, and the nonreactive sites named $^{1}\mathrm{M}$.

While these site descriptions seemed reasonable in light of the mechanisms shown in Schemes II and IV, it would be beneficial if some supporting evidence could be obtained concerning these site descriptions. While direct instrumental data are available to determine the surface morphology of metal single crystals,[8] such an approach is not presently applicable to dispersed metal catalysts. When metal single crystals are cleaved at various angles, the resulting materials can be shown instrumentally to have varying corner, edge, and face atom densities as illustrated by the examples shown in Figure 1.[9] The use of these different crystals in catalytic reactions has made it possible to relate product formation with specific types of sites present on the metal surface.[9,10] It should be possible, then, to apply a similar approach with STO-characterized catalysts to relate the nature of specific active sites present on dispersed metals with the instrumentally determined sites present on single-crystal catalysts.

Experimental Section

All gas purification and STO characterization procedures have already been reported.[4,7] The preparation and characterization of the catalysts used here have been described[11] and the STO site data are listed in Table I. Catalysts I are 6.9% Pt/CPG (controlled pore glass), II are 6.1% Pt/CPG, and IV are 4.4% Pt/CPG. Catalyst I-200 is material I reduced under H_2 isothermally at 200 °C, I-40/200 is I reduced in a stream of H_2 at a programmed temperature rise of 40°/min to a maximum of 200 °C.

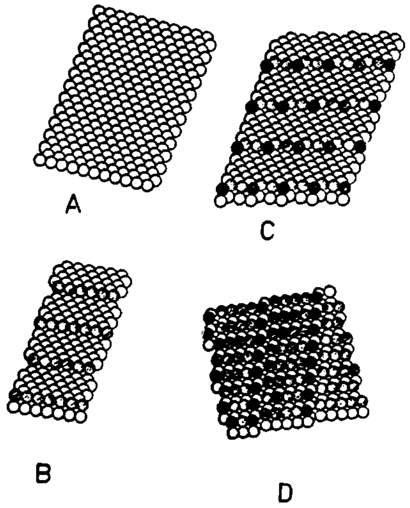

Figure 1. Representations of variously cleaved Pt single crystals. Corner atom density increases in the order A < B < C < D.

The GC separations of the aliphatic and benzene portions of the reaction mixtures were accomplished by using a 4 ft × $^{1}/_{4}$ in. column of 20% DC-200 on 80/100-mesh Chromasorb P at room temperature and a 30 mL/min He carrier gas flow rate.

The mass spectral data were obtained on a microcomputer-controlled VG Instruments Spectralab SX-200 quadrupole mass spectrometer interfaced with an on-line gas chromatograph and utilizing a 16-channel specific mass analyzer to provide digital readout and continuous recording (computer disk) of the partial pressures of the *m/e* values: 16 (CH_4), 30 (C_2H_6), 44 (C_3H_8), 57 (C_4H_9), 71 (C_5H_{11}), 82 (C_6H_{10}), 84 (C_6H_{12}), 85 (C_6H_{13}), and 78 (C_6H_6). The GC–MS system was calibrated by the injection of known volumes of cyclohexane and each of the potential reaction products. Fragmentation factors were obtained for each peak scanned for all compounds analyzed and used in correcting reaction product data after a background subtract.

The cyclohexane reactions were run in the standard STO apparatus,[7] which had been modified by the inclusion of a flask containing degassed distilled cyclohexane through which pure H_2 was bubbled and the effluent mixture passed through 8-port Carle sampling valves for introduction into the reactor. The amount of cyclohexane present in the H_2/cyclohexane pulses was determined by comparison with standard GC curves. The two sizes of pulses contained 1 and 2.5 μmol of cyclohexane in an excess of H_2.

A 15-mg portion of the catalyst was placed in the STO reactor (6-mm Pyrex tube). This corresponds to 5.31 μmol of Pt for catalysts I, 4.69 μmol for catalysts II, and 3.38 μmol for IV. The reactor was purged with O_2-free He for 30 min and then heated to 300 °C, held at the temperature for 1 h in a He flow, and cooled to ambient temperature, and an STO characterization[4,7] was run with the results listed in Table I. The catalyst, still under He, was then reheated to 300 °C for 1 h at which time a pulse of H_2/cyclohexane (1 μmol of C_6H_{12}) was passed over the catalyst

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Table II. Aliphatic Product Formation

catalyst[a]	product[b] CH_4	C_2H_6	C_3H_8	C_6H_{10}	C_6H_{14}
IV-400	1 (1)	2 (2)		2 (2)	3 (3)
II-400	1 (1)			2 (2)	2 (2)
IV-250	1 (1)			1 (2)	2 (2)
II-250	1 (1)			(1)	1 (2)
I-400	1 (1)	1 (–)	(1)	2 (3)	3 (3)
IV-200	1 (1)	1 (1)		1 (1)	1 (1)
I-40/200	2 (2)	(1)	(1)	(1)	1 (1)
I-200	1 (1)			(1)	1 (1)
II-200	3 (3)	2 (2)	2 (1)		
I-250	1 (2)		1 (2)		

[a] Reference 11. [b] Products from 1 μmol of C_6H_{12} pulses. Values in parentheses are from 2.5-μmol pulses. Scale: 1 = trace to 0.05%, 2 = 0.05–0.5%, 3 = 0.5–1%.

and the reaction mixture analyzed by GC–MS. This was followed by 3–5 additional pulses with the product composition the same for all pulses. This was followed by 3–5 of the larger pulses (2.5 μmol of C_6H_{12}). The product compositions from these reactions are listed in Tables I and II.

Results and Discussion

We have recently reported that Pt/CPG catalysts having varying site densities as determined by the STO reaction sequence could be prepared by changing the metal load and the method and temperature of reduction.[11] Thus, there was available a number of catalysts having a range of one-step hydrogenation, isomerization, and metalalkyl or two-step hydrogenation sites on their surfaces. For working purposes these sites have been labeled ^3M, ^2M_C, and ^2M_S, respectively. This series is comparable to the various Pt single crystals with different corner, edge, and face atom densities[12] that have been used in a number of specific reaction/active site correlations.[9,10] In the single-crystal investigation of cyclohexane dehydrogenation/hydrogenolysis[9] a mixture of H_2 and cyclohexane at pressures near atmospheric was passed over the variously cleaved crystals depicted in Figure 1 at 300 °C and the products formed were analyzed by mass spectrometry. Product analysis showed that benzene formation increased with an increasing corner atom density on the catalyst (A < B < C < D in Figure 1) while the extent of C–C bond hydrogenolysis was related to the terrace atom density.[9]

It was considered that a similar approach could be applied to dispersed metal catalysts by modifying the standard STO apparatus[4,7] to include a flask containing degassed cyclohexane through which H_2 could be bubbled with the resulting H_2/cyclohexane mixture passed through a sampling valve for introduction into the reactor. The products could be run through an on-line gas chromatograph to separate the unreacted cyclohexane and aliphatic reaction products from the benzene formed, and the effluent then passed into a mass spectrometer with selected ion scaning capability for the analysis of the various aliphatic components of the reaction mixture as well as verification of the amount of benzene present.

We have recently shown that heating Pt/CPG catalysts to 250–300 °C in an inert atmosphere results in a change in the STO site densities on the surface of these materials.[13] Since the cyclohexane reactions were to be run at 300 °C, the catalysts used in this work were first heated to 300 °C for 1 h in a stream of helium and then cooled to room temperature and characterized by the STO procedure. These results are shown in Table I along with the surface characterizations of these catalysts obtained prior to the heat treatment.[11]

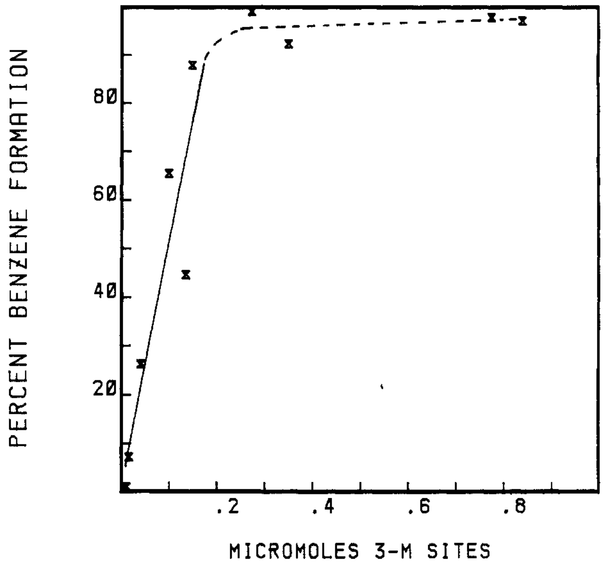

Figure 2. Relationship between the number of direct hydrogenation (^3M) sites present as determined for preheated catalysts and the extent of benzene formation from pulses containing 1 μmol of cyclohexane. The solid line is the best least-squares fit for the first six data points; the dashed line is an extrapolation.

To run the reaction a small portion of a catalyst was placed in the reactor tube of the STO apparatus. After being purged with helium, the catalyst was heated to 300 °C and held at that temperature for 1 h before the introduction of the H_2/cyclohexane pulses. Several pulses containing 1 μmol of cyclohexane each were then passed through the catalyst bed and the products analyzed by GC–MS. This was followed by exposure of the catalyst to several more pulses of H_2/cyclohexane each containing 2.5 μmol of cyclohexane. The aliphatic products obtained from these reactions are listed in Table II and the amount of benzene formed is given in Table I. Surprisingly, very little aliphatic material was formed in these reactions, only about 1–2% of the total reaction mixture. In those cases where little benzene was formed, unreacted cyclohexane was the primary material present. Because of this low conversion, no conclusions can be drawn concerning the types of active sites responsible for the formation of these hydrogenolysis products.

The formation of benzene in most cases, though, was rather extensive and showed a considerable difference from catalyst to catalyst. Since the reaction was run at 300 °C, it is appropriate to use the site densities obtained for the heated catalysts to correlate with the benzene production. The number of hydrogenation sites (^3M) present in the reactor and the percent benzene formation from the 1-μmol pulses are plotted in Figure 2. From this plot it can be seen that there is a good correlation between these two factors, with a linear relationship existing with those catalysts producing less than a 90% yield of benzene. With the other catalysts, benzene formation is almost complete. The data in Figure 3, though, show that the correlation between the catalyst dispersions and the extent of benzene formation in these reactions is rather poor. An even more random relationship exists between isomerization site (^2M_C) density and benzene formation. There is, however, a correlation between the number of metalalkyl sites (^2M_S) present and the amount of benzene formed. A plot of the ^3M + ^2M_S site sum vs. benzene formation shown in Figure 4 shows a very good correlation between these factors.

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(12) In single-crystal nomenclature, corner, edge, and face atoms are referred to, respectively, as kink, step, and terrace atoms.

(13) Augustine, R. L.; Kelly, K. P. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 3025.

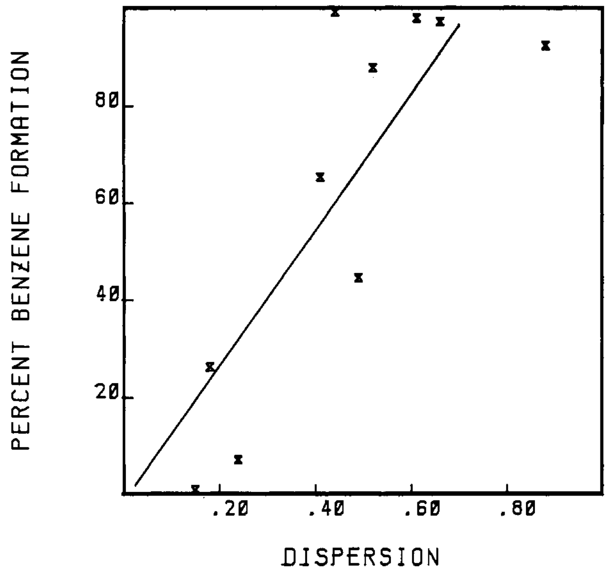

Figure 3. Relationship between the catalyst dispersions and the extent of benzene formation from pulses containing 1 μmol of cyclohexane. The line is the best least-squares fit of the data.

Similar results were obtained with the 2.5-μmol pulses.

While it seems more logical to use the site densities found for the heated catalysts in these correlations, fairly reasonable relationships also exist between the ^3M, ^2M_S, and $^3M + {}^2M_S$ site densities on the unheated catalysts (Table I) and the extent of benzene formation.

All of these comparisons suggest that cyclohexane dehydrogenation is taking place on those sites responsible for alkane formation in the STO olefin hydrogenation reaction sequence. Since it has previously been established that this dehydrogenation to benzene occurs over corner atoms on Pt single-crystal catalysts under these same reaction conditions,[9] it would appear that these STO hydrogenation sites are corner atoms and that the ^3M site designation used as a working hypothesis[4,11] is a reasonable description of this type of surface site.

These findings also indicate that the metalalkyl sites that we have previously termed[4] ^2M_S are also a type of corner atom and not an edge site as implied by the ^2M notation and the mechanistic proposal in Scheme IV. One attractive possible description of these sites is the ^3MH designation as shown in Scheme III. Why some corner or kink atoms would become $^3MH_2$ sites on adsorption of hydrogen and others ^3MH is not clear, but factors such as the types of planes intersecting to make the corner and the nature of the adjacent sites could be involved in such a distinction.

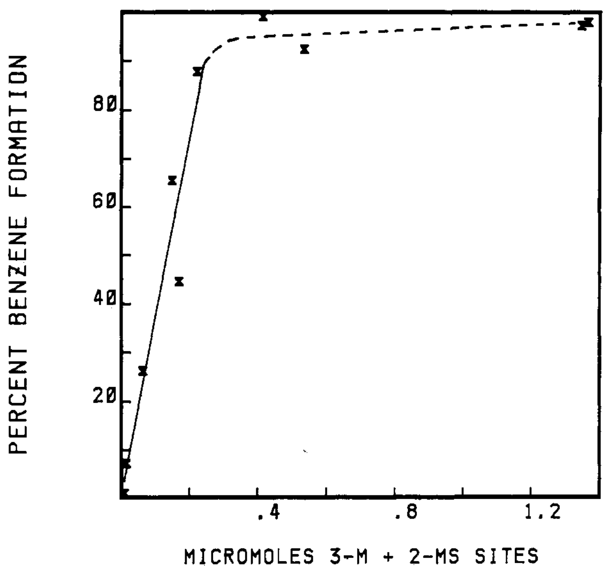

Figure 4. Relationship between the number of $^3M + {}^2M_S$ sites present as determined for preheated catalysts and the extent of benzene formation from 1-μmol pulses of cyclohexane. The solid line is the best least-squares fit for the first data points; the dashed line is an extrapolation.

Some support for the similarity between the STO hydrogenation and metalalkyl sites and their difference from the isomerization sites can come from an examination of the changes in site densities observed on heating these supported catalysts. In almost every case previously reported,[13] with all of the catalysts used here (Table I), and in a number of other catalysts that we have investigated in other contexts, heating the catalyst above 200–250 °C decreases both the direct hydrogenation and metalalkyl site densities and increases the number of isomerization sites. Further, both the hydrogenation and the metalalkyl sites are involved in the alkene saturation process, the former apparently by direct addition from a $^3MH_2$ configuration and the latter by a multistep, single H addition sequence.

Because of the correlations and mechanistic considerations presented above, future STO characterizations will still refer to the direct hydrogenation sites as ^3M but the metalalkyl sites will be designated as ^3MH. Isomerization sites, which are still considered as edge atoms with a facile reversal a part of their reaction characteristics, will still be labeled, ^2M_C.

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