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Pt/SiO_2

III. Activity and Selectivity for Some Hydrogenation Reactions

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The activities and selectivities of the series of Pt/SiO_2 catalysts described in Parts I [Uchijima, T., Hermann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* 50, 111 (1977)] and II [Sashital, S., Cohen, J. B., Burwell, R. L., Jr., and Butt, J. B., *J. Catal.* 50, 111 (1977)] have been determined for the hydrogenation of cyclopropane, methylcyclopropane, and propene. All three reactions are found to be mildly structure sensitive under the conditions of investigation, with variations in the turnover numbers by a factor of about 3 over the range of metal exposure. Activation energies were essentially the same for the three reactions and in all cases were independent of the percentage of Pt exposed. On this basis, a simple geometric correlation is shown to provide a reasonable explanation of the data, except where significant strain exists within the metal crystallites. It is also shown that an excellent correlation of activity vs metal vibrational amplitude is obtained for these catalysts.

INTRODUCTION

The hydrogenation of various cyclopropane compounds has been employed from time to time as a convenient probe reaction for evaluating the catalytic properties of supported metals, particularly platinum. Ethylene hydrogenation has also been employed for this purpose. In both cases the hydrogenation may be run under mild conditions where deactivation is minimized and only primary hydrogenation products are found (*3*, *4*). In addition, for a compound such as methylcyclopropane a distribution between iso- and *n*-butane is obtained so that selectivity as well as activity factors may be investigated (*5*, *6*).

Bond and Newham (*5*) have proposed that the mechanism of cyclopropane hydrogenation involves the reaction of a single adsorbed cyclopropane molecule with an adsorbed hydrogen atom as the rate-limiting step. Cyclopropane chemisorption results from bonding of delocalized ring electrons and *d* orbitals of a single metal surface atom. Since a single atom is involved, the reaction should thus provide a good means for correlation between measurements of metal percentage exposed via hydrogen chemisorption or hydrogen–oxygen titration and experimentally determined catalyst activities. Much the same can also be said concerning olefin hydrogenation (*7*).

The objectives of the present research were to obtain precise information on the activity and selectivity of the series of Pt/SiO_2 catalysts described and characterized in Parts I (*1*) and II (*2*) of this series for the hydrogenation of cyclopropane, methylcyclopropane, and propene. A summary of some pertinent prior results for these reactions on supported platinum

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TABLE 1

Hydrogenation of Cyclopropane, Methylcyclopropane, and Ethylene on Supported Platinum

Catalyst	E (J/kmol × 10^{-6})	P_{H_2} (Torr)	P_{HC} (Torr)	N at 0°C (sec^{-1})	S at 0°C (iC_4/nC_4)	Reference
(a) Cyclopropane						
1.96% Pt/Al_2O_3	33.5–37.7	46	10	0.16	—	*(8)*
4.3% Pt/SiO_2	33.5–37.7	46	10	0.07	—	*(8)*
5% Pt/pumice	37.7 ± 4.2	10–400	40	—	—	*(5)*
Pt metal	51.1	—	—	0.104	—	*(9)*
Pt film (D_2)	46.0 ± 2.1	100	10	—	—	*(10)*
0.6–4.8% Pt/Al_2O_3	—	720	3.8	0.0028	—	*(11)*
(b) Methylcyclopropane						
5% Pt/pumice	35.2 (iC_4) 42.3 (nC_4)	10–400	40	—	22	*(5)*
Pt film (D_2)	—	100	10	—	26	*(10)*
0.5% Pt/SiO_2	—	50	10	0.038	20	*(12)*
0.5% Pt/SiO_2 with 95% Al_2O_3 diluent	—	50	10	0.047	5.0	*(12)*
0.5% Pt/SiO_2 with 95% SiO_2/Al_2O_3	—	50	10	0.416	0	*(12)*
0.3–4.8% Pt/Al_2O_3	—	720	3.8	0.013–0.021[a]	7.0[a]	*(11)*
0.3–3.0% $Pt/(SiO_2Al_2O_3)$	—	720	3.8	0.050–0.167[a]	7.0[a]	*(11)*
(c) Ethylene						
0.05% Pt/SiO_2	38.1 ± 2.1	152	23	0.011[b]	—	*(13)*
0.5% Pt/SiO_2	37.3 ± 0.8	152	23	0.17[c]	—	*(13)*
2.45% Pt/SiO_2	44.0	152	23	0.018[d]	—	(7)

[a] Values at 24°C.

[b] Computed from measured value at 24°C to temperature of −50°C with given activation energy.

[c] Value at −50°C.

[d] Corrected by Schlatter and Boudart *(13)* to their conditions of P_{H_2} and P_{HC} and computed here at −50°C from given activation energy.

is given in Table 1. Propene hydrogenation has not been investigated in this manner previously, so information on ethylene, which should be roughly analogous, is presented in the table. The turnover numbers (N) for the cyclopropanes given in Table 1[2] are those reported in the original references and represent a wide range of conditions with respect to hydrogen and hydrocarbon partial pressures. Direct comparison of such results may be misleading in the absence of kinetic correlations, as will be discussed later. All the results given are for catalysts pretreated in hydrogen at temperatures greater than 300°C, as it has been indicated elsewhere that this is important in determining the activity levels of the supported Pt *(1, 7)*.

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[2] Nomenclature: E, activation energy, joules per mole; D, percentage of metal exposed; D_{CO}, percentage of metal exposed as measured by CO chemisorption; D_h, percentage of metal exposed as measured by H_2 chemisorption; D_t, percentage of metal exposed as measured by H_2–O_2 titration; N, turnover number, molecules reacted per surface metal atom-second; n, number of fcc unit cells; P_{H_2}, hydrogen partial pressure, Torr; P_{HC}, hydrocarbon partial pressure, Torr; S, selectivity in MCP hydrogenation, isobutane/n-butane; $(\mu^2)^{\frac{1}{2}}$ mean square amplitude of vibration.

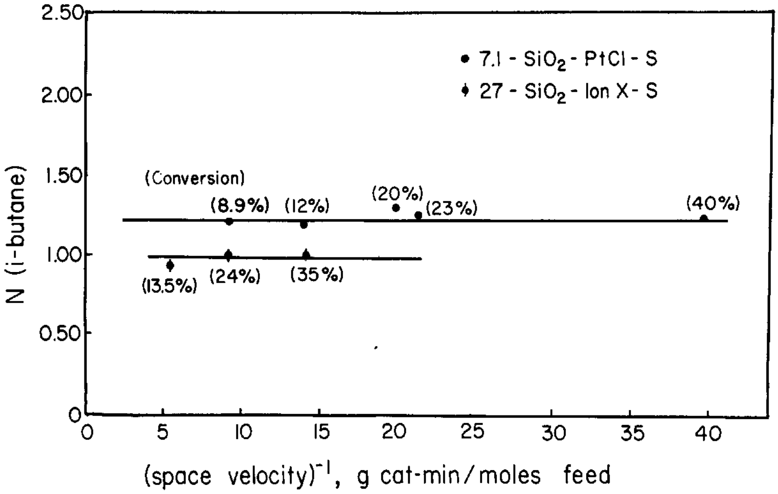

FIG. 1. Turnover number for methylcyclopropane hydrogenation to isobutane (0°C) as a function of conversion.

EXPERIMENTAL

Turnover numbers were determined in a differential reactor flow system designed to operate under conditions such that all intra- and interphase transport gradients were absent (*14*). Reactant conversion levels were generally kept smaller than 10% to approximate differential conditions. In the case of the cyclopropanes it was found that the kinetics were essentially zero order in hydrocarbon; in this case low conversion restrictions are not necessary, as demonstrated in Fig. 1 for methylcyclopropane hydrogenation at 37°C.

Reagents. Hydrogen (Linde ultrahigh purity grade; 99.999% minimum purity, 3 ppm maximum H_2O) was further purified by passing it successively through an Englehard Deoxo unit Model 10-2500, a room temperature Drierite trap, and a silica gel trap (Davison Grade 62) at liquid nitrogen temperature. A final trap containing Cr^{2+}/SiO_2 was used to indicate the possible presence of oxygen contamination in the purified hydrogen.

In experimentation with cyclopropane (Union Carbide Corp.; 99.0% minimum purity) purification was accomplished by passage through a Na/Al_2O_3 trap and a 4-H molecular sieve trap (25°C) to remove olefins and water. The procedure for methylcyclopropane (K and K Co.; 98% minimum purity) was similar except a more efficient trap for olefins prepared by exchange of $Cu(NH_3)_4^{2+}$, and Grade 62 silica (*15*) was used in place of the Na/Al_2O_3. It was found that a major impurity in the methylcyclopropane was 1-butene; in order further to ensure the absence of this olefin, the hydrogen/hydrocarbon feed mixture was passed through a Pt/Filtros silica catalyst bed at 25°C, catalyst and conditions highly selective for olefin hydrogenation, prior to passage over the test catalyst sample.

The propene (Phillips polymerization grade; 99.0% minimum purity) was deoxygenated by passage through a Na/Al_2O_3 trap; the remaining impurity was ~0.5% propane.

Reaction mixture. The reactant gas stream was prepared by passage of the purified hydrogen stream through a bed of 15-cm^3 40- to 60-mesh Filtros silica saturated with the hydrocarbon under study. For cyclopropane and methylcyclopropane the saturator temperatures were −78 and −50°C, respectively, resulting in a 14:1 hydrogen to hydrocarbon ratio. For propene the saturator temperature was −97°C, giving a 19:1 ratio. Hydrogen flow rates were determined with a Brooks mass flowmeter, Model 5810.

Reactor. The reactor was a 0.4-cm-i.d. glass tube, filled with 0.05 to 0.40 g of catalyst held in place by two small plugs of calcined glass wool. A temperature equilibration coil 1 m in length was placed upstream of the reactor, and the reactor effluent was sampled through a 1-cm^3 sampling loop, Carle Model 5518, into the gas chromatograph (G. C.). Feed could also be sampled by use of a bypass around the reactor to the sampling valve. Inlet coil, reactor, and sampling valve were all immersed in the same constant-temperature bath, with temperatures in the various experiments ranging from −70 to 40°C.

Analysis. G.C. analysis was carried out for all three reactions using a 0.25-in.-diameter by 4-m column packed with 25% dimethylsulfolane on 60/80 mesh Chromosorb P, with Linde ultrahigh purity helium (minimum purity 99.999%, 3 ppm maximum H_2O) at 50 cm^3/min as the carrier gas. Column temperature was 0°C, and thermal conductivity (T.C.) detector was at 65°C with a filament current of 250 mA.

Catalyst pretreatment. As documented by Dorling *et al.* (*7*) for ethylene hydrogenation, differing pretreatment procedures for Pt/SiO_2 can result in catalysts of differing apparent activities. In addition, it is shown in Part I (*1*) for this series of catalysts that the reduction of stored samples is a matter quite different than for fresh samples. Accordingly, the same general pretreatment procedure, reduction in hydrogen at elevated temperatures, was employed for all three reactions, and literature comparisons are restricted to catalysts pretreated at high temperature in hydrogen. Typical reduction conditions consisted of heating the catalyst in flowing hydrogen from room temperature over a period of 2 hr to a final temperature of 350°C for the cyclopropane experiments and 470°C for propene and maintaining this condition for 1 hr. The catalyst was then cooled to room temperature in flowing hydrogen. High-temperature reduction seems required for attaining reproducible activity levels on an aged catalyst; the difference in final reduction temperature for the cyclopropane vs propene experiments is not significant, since any final reduction temperature in the range of 300 to 500°C for the time indicated yielded constant, reproducible activity levels. In addition, it was verified that the high-temperature reduction in hydrogen used for the kinetics experiments did not change the metal percentage exposed.

Catalyst 40-SiO_2-PtCl-L was treated in oxygen at 300°C for 30 min, reduced in hydrogen at 315°C for 1 hr, and heated to 450°C for 1 hr in helium, which was the reduction procedure used in the measurements of metal percentage exposed (*1*). A turnover number of 0.151 sec^{-1} for cyclopropane hydrogenation at 0°C was obtained following this treatment vs 0.163 sec^{-1} for the standard procedure.

Details of the differences in the behavior of this series of catalysts, classified as to high- and low-temperature treatment, mode of preparation, and halide content will be discussed elsewhere.

Operation. After reduction and cooling the catalyst was isolated from the system so that the hydrocarbon reactant could be adsorbed on the Filtros feed saturator. Finally, hydrogen was reintroduced through the trap, the resulting saturated feed mixture was passed through the reactor, and feed and effluent were sampled periodically for G.C. analysis. Saturator capacity was sufficient for 3 to 5 hr of operation, permitting several individual activity determinations for each run. In the experiments with cyclopropane, the activity of the catalyst declined from 10 to 15% in approximately linear fashion over a period of about 1 hr, and initial activity levels were determined by extrapolation to zero time. Typical behavior is shown in Fig. 2. The reduction procedure was always able to return cata-

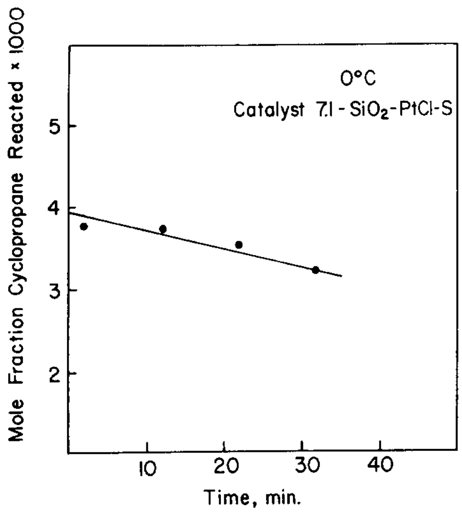

FIG. 2. Typical change in activity as observed for cyclopropane hydrogenation.

lyst activity to its initial level, so the same as well as different samples could be used for measurements at a given condition. No deactivation was observed in the experiments with methylcyclopropane or propene.

The reproducibility of turnover number measurements was excellent in general. Sample results for the methylcyclopropane hydrogenation are given in Table 2; comparable reproducibilities were obtained for the other reactions.

TABLE 2

Typical Catalyst Activity Reproducibility[a]

Run	$N(iC_4)$ (sec^{-1})	$N(nC_4)$ (sec^{-1})
1	0.157	0.0111
2	0.121	0.0071
3	0.130	0.0078
4	0.156	0.0097
5	0.126	0.0080
6	0.103	0.0069
7	0.145	0.0081
8	0.121	0.0073
Average	0.132 ± 0.015[b]	0.0083 ± 0.0011[b]

[a] Methylcyclopropane, 0°C, H/HC = 14/1; catalyst 27-SiO_2-IonX-S [catalyst nomenclature as described in Part I (*1*)].

[b] ± limits computed from $(\sum_1^n |N_{\mathrm{Avg}} - N_i|)/n$, with n = number of experiments.

RESULTS

The activities of the series of catalysts for cyclopropane and methylcyclopropane hydrogenation in terms of total turnover number are shown in Fig. 3 for the series of experiments run at 0°C. Corresponding data for propene hydrogenation at −57°C are given in Fig. 4.

The cyclopropane reactions are structure

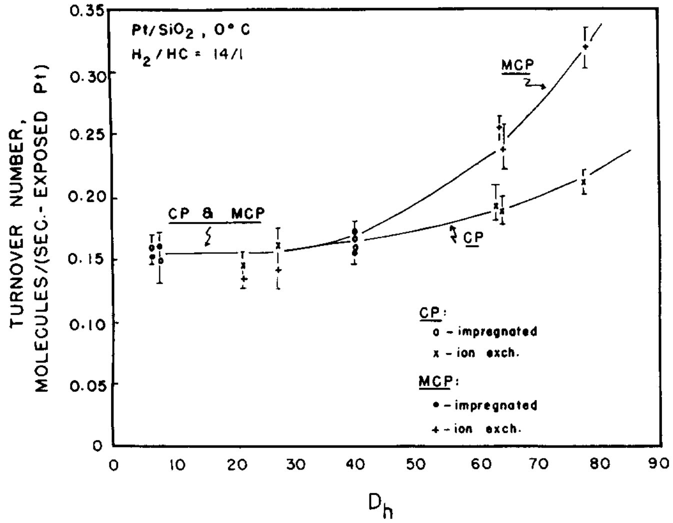

FIG. 3. Total turnover numbers for cyclopropane and methylcyclopropane hydrogenation at 0°C vs percentage of Pt atoms exposed.

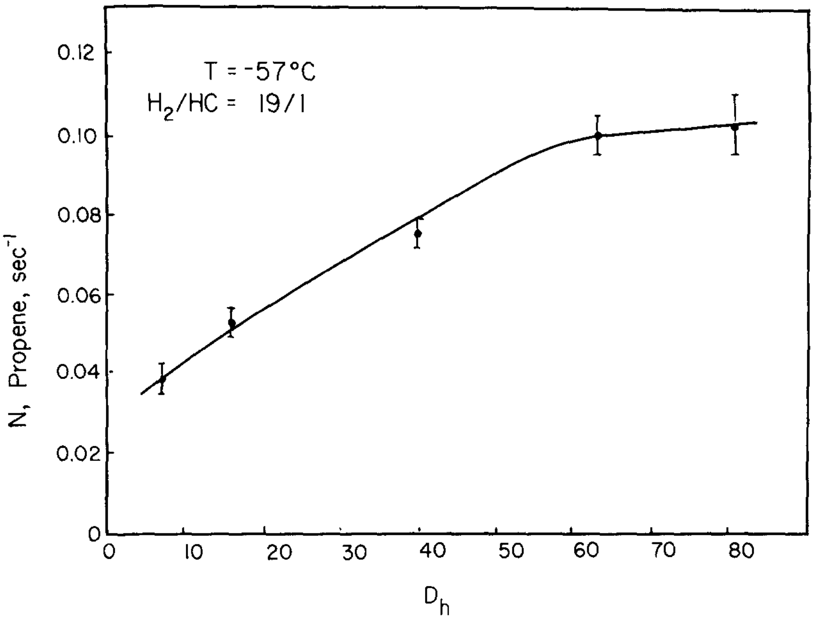

FIG. 4. Turnover number for propene hydrogenation at −57°C vs percentage of Pt atoms exposed.

insensitive for values of the percentage of exposed metal, D_h, below about 50; however, the turnover numbers increase at higher D_h. The total change in activity is not large, at maximum by about a factor of 2, but the changes are clearly beyond the range of experimental uncertainty so these reactions are moderately structure sensitive. Propene hydrogenation offers an interesting result by way of contrast, since

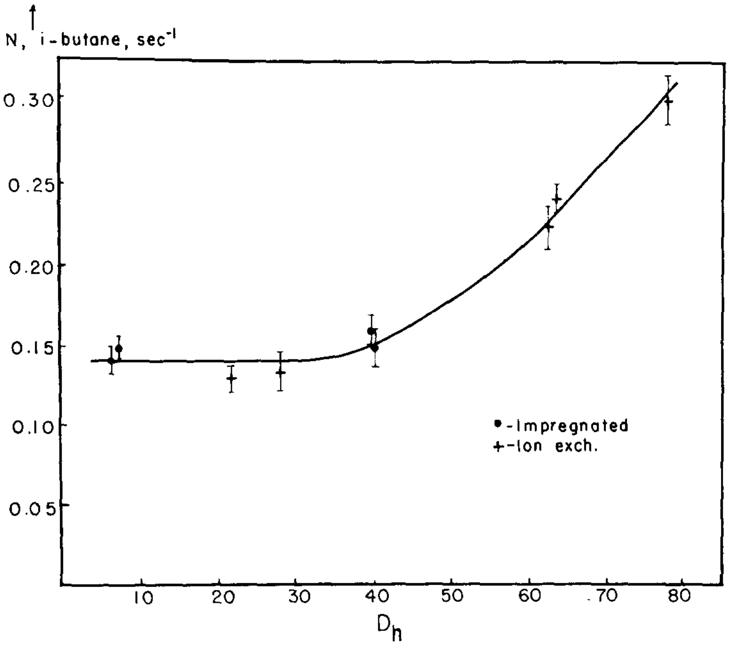

FIG. 5. Turnover number for isobutane formation at 0°C vs percentage of Pt atoms exposed.

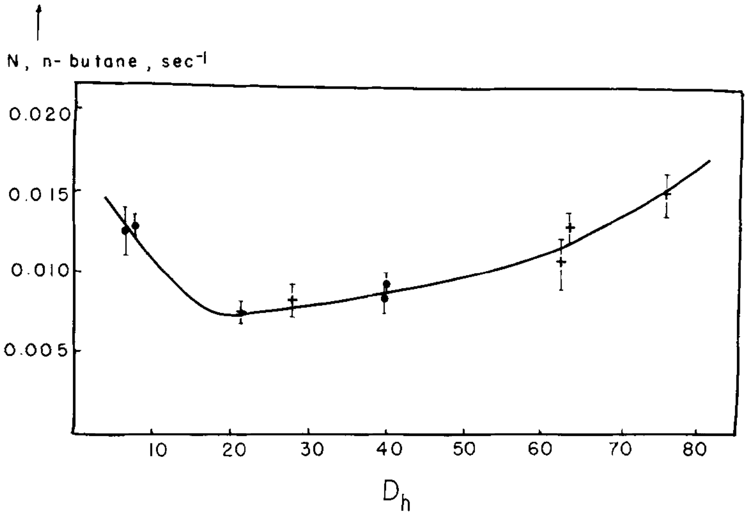

FIG. 6. Turnover number for normal butane formation at 0°C vs percentage of Pt atoms exposed.

the major variation in turnover number occurs at lower D_h where the cyclopropanes were constant.

Selectivity behavior in the methylcyclopropane hydrogenation at 0°C is shown in Figs. 5 and 6. The parallelism between the predominate reaction, isobutane formation, and the total turnover number (cf.

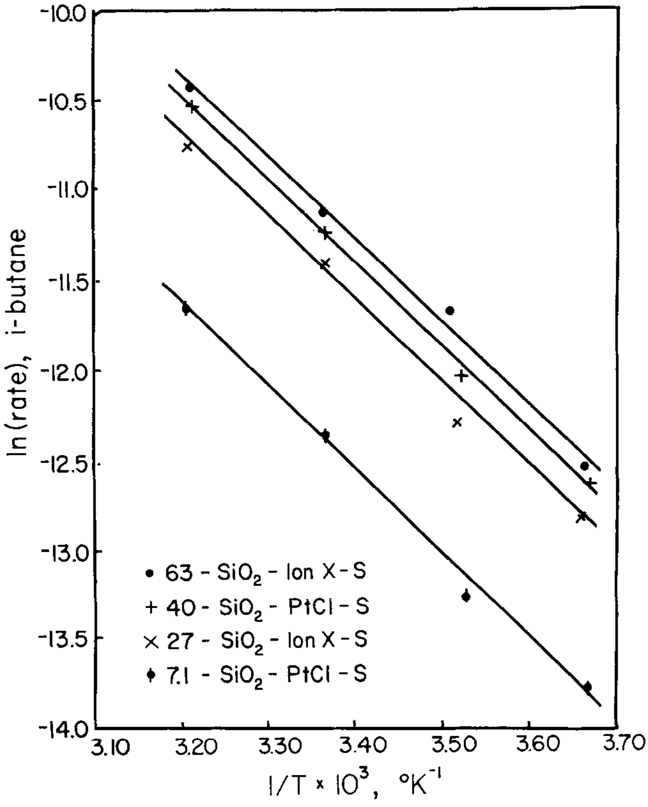

FIG. 7. Arrhenius correlation, methylcyclopropane to isobutane.

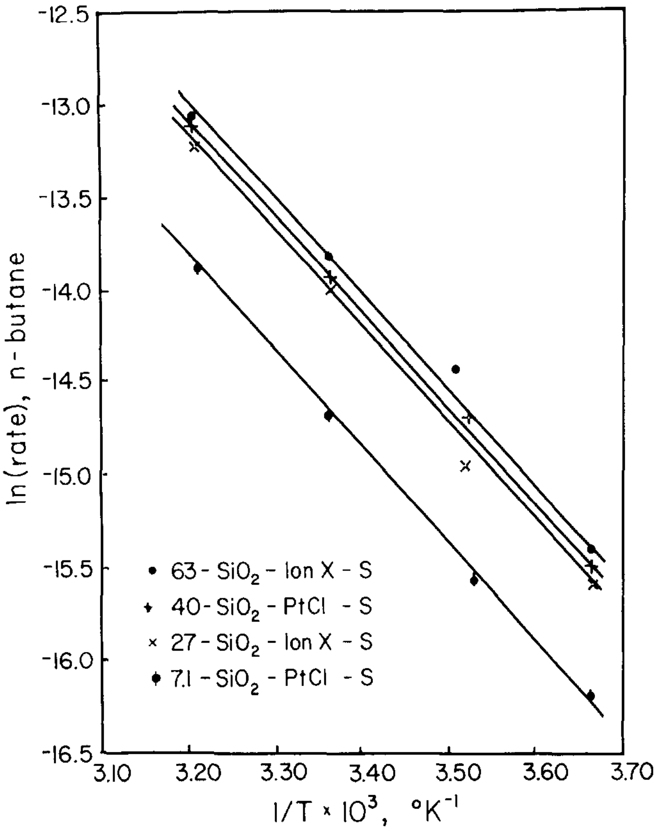

FIG. 8. Arrhenius correlation, methylcyclopropane to *n*-butane.

Fig. 3) is apparent. Activity with respect to *n*-butane formation is seen to pass through a minimum as a function of D_h.

The activity and selectivity patterns illustrated in Figs. 3–6 are, interestingly, insensitive to temperature variation in the experimentally accessible range for all three reactions. As an example, the methylcyclopropane data are reported in Figs. 7 and 8. The lines on these figures are placed in somewhat arbitrary fashion to illustrate that a reasonable representation of temperature behavior can be provided by parallel Arrhenius plots. Individual best-fit correlations were also determined from the data on all these reactions; the results are given in Table 3. For propene only one catalyst, 40-SiO$_2$-PtCl-L, was investigated for high-temperature pretreatment conditions. Experiments with room-temperature pretreatment conditions, however, indi-

TABLE 3

Individual Activation Energy Results[a]

Catalyst	E(J/kmol × 10^{-6})	
1. Cyclopropane (−10 to 21°C)		
7.1-SiO$_2$-PtCl-S	40.2 ± 3.8	
40-SiO$_2$-PtCl-S	37.3 ± 3.3	
81-SiO$_2$-IonX-S	41.9 ± 7.1	
2. Methylcyclopropane (0 to 38.5°C)		
	E(iC$_4$)	E(nC$_4$)
7.1-SiO$_2$-PtCl-S	39.6 ± 2.3	43.4 ± 2.1
27-SiO$_2$-IonX-S	38.0 ± 2.9	43.7 ± 2.9
40-SiO$_2$-PtCl-S	36.5 ± 2.5	41.7 ± 3.8
63-SiO$_2$-IonX-S	39.0 ± 2.9	46.0 ± 4.2
3. Propene (−68 to −44.5°C)		
40-SiO$_2$-PtCl-L	43.5 ± 3.3	

[a] Lines plotted in Figs. 7 and 8 correspond to the following activation energies (J/kmol × 10^{-6}): Fig. 7, 38.7; Fig. 8, 44.2.

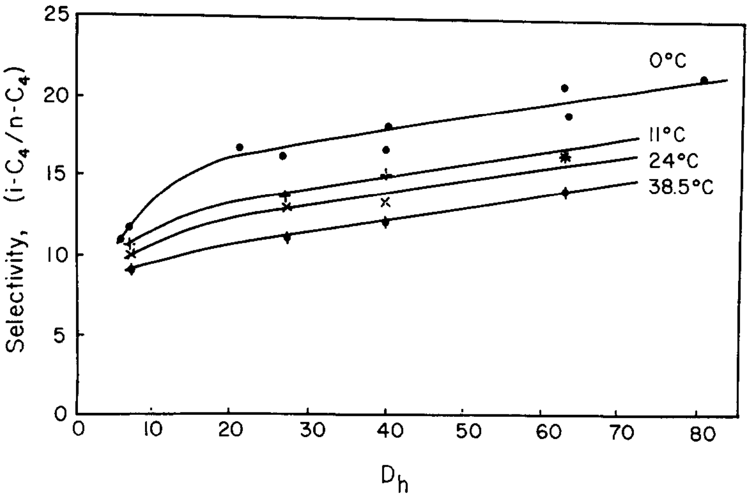

FIG. 9. Selectivity variations with temperature and percentage of Pt atoms exposed in methylcyclopropane hydrogenation.

cated that the activation energy for this reaction is also independent of the percentage exposure of Pt.

Selectivity in the hydrogenation of methylcyclopropane is shown in Fig. 9. With the exception of 7.1-SiO_2-PtCl and 6.3-SiO_2-PtCl, the ratio of iso to normal products is nearly independent of percentage exposed, while the ratio of activation energies for the two reactions indicates decreasing selectivity for isobutane formation with increasing temperature.

DISCUSSION

The results described in the previous section appear reasonable in terms of available literature data. The activation energies for cyclopropane and methylcyclopropane hydrogenation, including the differences between isobutane and *n*-butane formation, are in agreement with the prior results of Bond and Newham (*5*) and Boudart *et al.* (*8*) detailed in Table 1. The activation energy for propene hydrogenation is somewhat higher than reported by Schlatter and Boudart (*13*) for ethylene hydrogenation but is in excellent agreement with that determined by Dorling *et al.* (*7*) for a catalyst of slightly higher percentage exposed.

Turnover numbers are more difficult to compare in absolute magnitude because they will depend on conditions of reactant partial pressure even if other factors such as temperature and pretreatment procedure result in identical catalysts. Kinetic correlation is required to reduce data to common experimental conditions, a procedure which is always somewhat risky. However, there does appear to be sufficient information available to attempt some comparisons of absolute magnitudes of turnover number.

Boudart *et al.* (*8*) report a turnover number for cyclopropane hydrogenation at 0°C on a Pt/SiO_2 catalyst of $D_t = 17$ of 0.073 sec^{-1}. This catalyst had been pretreated for 12 hr in H_2 at 500°C. We ran a similar experiment for a catalyst of about the same percentage exposed (21.5-SiO_2-IonX-L), pretreated in hydrogen at 450°C for 12 hr; the measured turnover number was 0.089 sec^{-1}. In view of literature evidence that order is fractional or near zero with respect to cyclopropane at this temperature (*5*, *11*), these two numbers should be directly comparable.

One other direct comparison is afforded by literature data, this for selectivity ratios (iC_4/nC_4) in methylcyclopropane hydrogenation.[3] Schlatter and Boudart (*12*) report a value of 20 at 0°C for two Pt/SiO_2 catalysts of $D_t = 58$ and 61, respectively. Our value at 0°C for 63-SiO_2-IonX-S is 19.0. A somewhat more indirect comparison of activity and selectivity in methylcyclopropane hydrogenation is afforded by the results of Bond and Newham (*5*) indicating a selectivity of approximately 22 at 0°C on a Pt/pumice catalyst (*D* not available). The selectivity for isobutane formation is in accord with what is understood concerning the influence of steric and electronic factors on the hydrogenation of substituted cyclopropanes on transition metals (*6, 16*). Alkyl substitution leads to hydrogenation of the 2, 3 bond; for example the reaction of $(C_2H_4\text{-}PtCl_2)_2$ with n-C_6H_{13}-cyclo-C_3H_5 gives a metallocyclobutane derived from insertion in this bond (*17*). Roth and others (*18, 19*) have shown that phenyl substitution generally leads to the hydrogenation of the 1,2 bond with both Pt/SiO_2 and $(Rh(CO)_2Cl)_2$. The insertion reaction with $(C_2H_4\text{-}PtCl_2)_2$ is not so clear-cut. For R = H, o-NO_2, insertion occurs in the 2,3 bond of R-C_6H_4-cyclo-C_3H_5; for R = p-Me insertion occurs in the 1, 2 bond (*17*).

The rate of hydrogenation of methylcyclopropane was reported to be a factor of 1.6 greater than that of cyclopropane by Bond and Newham over the entire temperature range (0–200°C) they investigated. This is in accordance with our results for catalysts of $D_h > 50$, given the very similar activation energies for the two reactions. Schlatter and Boudart (*12*) report a turnover number for methylcyclopropane at 0°C of 0.04 sec^{-1}, of which a direct comparison with present results is beclouded by kinetic uncertainties. If the reaction is zero order in methylcyclopropane as our present results indicate, this rate is a factor of about 4 lower than those reported here; however, if the order is 0.6 as quoted by Compagnon *et al.* (*11*) for cyclopropane the comparison becomes 0.10 sec^{-1} vs 0.15 sec^{-1}.

TABLE 4

Some Comparisons of Turnover Number and Selectivity

Reference	Catalyst	N (sec^{-1})	
1. Cyclopropane, 0°C; direct comparison			
8	Pt/SiO_2 (D_t = 17)	0.073^a	
This work	21.5-SiO_2-IonX-L	0.089^a	
8	Pt/Al_2O_3	$0.16^{a,b}$	
11	Pt/Al_2O_3	$0.016^{a,b}$	0.029^c
2. Methylcyclopropane, 0°C; direct comparison			
12	Pt/SiO_2 (D_t = 58, 61)	0.04^a	0.10^d
This work	63-SiO_2-IonX-S	0.15	
3. Methylcyclopropane, 24°C; indirect comparison			
11	Pt/Al_2O_3 (D_t > 50)	0.019^b	0.09^d
This work	40-SiO_2-PtCl-S	0.61	
4. Methylcyclopropane, 0°C; direct comparison			
		$S(iC_4/nC_4)$	
12	Pt/SiO_2 (D_t = 58, 61)	20	
This work	63-SiO_2-IonX-S	19	
5. Methylcyclopropane, 24°C; indirect comparison			
		$S(iC_4/nC_4)$	
11	Pt/Al_2O_3 (D_t > 50)	6.5^b	
This work	40-SiO_2-PtCl-S	13.3	
6. Propene, −50°C; comparison with ethylene[e]			
		N (sec^{-1})	
13	Pt/SiO_2 (D_t = 61)	0.17	
13	Pt/SiO_2 (D_t = 26)	0.011	
7	Pt/SiO_2 (D_{CO} = 65)[f]	0.018	
This work	63-PtSiO_2-IonX-S	0.044	
This work	7.1-SiO_2-PtCl-S	0.017	

[a] Corrected to conditions of this work assuming zero-order kinetics with respect to cyclopropane or methylcyclopropane.

[b] Taken to be independent of dispersion in references (*8*) and (*11*).

[c] Adjusted to conditions of reference (*8*) assuming 0.6-order kinetics with respect to cyclopropane.

[d] Adjusted to conditions of this work assuming 0.6-order kinetics with respect to methylcyclopropane.

[e] Adjusted to conditions of reference (*13*) assuming first-order kinetics in hydrogen, zero-order in hydrocarbon, and activation energies as reported by individual groups.

[f] D_{CO} estimated from CO adsorption data and reaction rate reported at −80°C.

Additional results concerning activity and selectivity for cyclopropane and methylcyclopropane hydrogenation are given by Compagnon *et al.* (*11*) for a series of Pt/Al_2O_3 catalysts of $D_t > 50$ (crystallite diameters reported in the range of 1.0–3.0 nm). They report selectivities of 6.0 to 7.5 for this series at 24°C; our measured value at 24°C is 13.3 for 63-SiO_2-IonX-S. Similar discrepancies appear in comparison of turn-

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[3] Comparison of selectivities is simpler than comparison of turnover numbers, since kinetic dependencies should hopefully divide out in the ratio.

over numbers which are well beyond the range of uncertainty that might be involved in kinetic correlations. A summary of comparisons between present and previous results is given in Table 4. With the exception of the uncertainty in comparison of turnover numbers for methylcyclopropane hydrogenation noted above, our results are quite consistent with those of Boudart and co-workers. It is possible that the activity and selectivity results of Compagnon *et al.* (*11*), which appear to be much lower than expected, are due to differing support interactions, but it is doubtful that such an effect would be as large as an order of magnitude.

A comparison of present results for propene hydrogenation with literature data on ethylene hydrogenation is also given in Table 4. As indicated, these values for turnover number are adjusted to the conditions of Schlatter and Boudart (*13*), following the kinetic correlation reported by them. The results for propene hydrogenation are quite in line with expectations based on results for ethylene hydrogenation from the reports of Dorling *et al.* (*7*) and for the low D_t catalyst of Schlatter and Boudart. The reported turnover number for their high D_t catalyst seems anomalously high.

For all three reactions in this series of catalysts there is no difference in activity or selectivity between ion-exchanged and impregnated catalysts of similar D_h as long as high-temperature pretreatment in hydrogen is employed for both. A similar conclusion has also recently been reported by Brunelle *et al.* (*20*) for the hydrogenolysis and isomerization of *n*-pentane on a comparable series of Pt/SiO_2 catalysts.

Although the region of D_h where structure sensitivity appears is different for the cyclopropanes and propene, the trend is the same overall with decreasing activity as D_h decreases. The fact that the activation energy of these reactions is independent of the percentage of metal exposed while the overall activities vary suggests an activity compensation [Type B in the nomenclature of Boudart (*21*)] in which variations in activity are due to variations in preexponential factor. Entropic contributions to the rate are included in this factor, thus it might be possible to offer a simple geometric interpretation of these results. If it is postulated that edge and corner atoms on the exposed crystallite are more active than surface atoms, then there should be a correlation between their concentration and the enhanced activity of very small crystallites (*22*, *23*). In this work the crystallites were modelled as isodimensional cubes with five sides exposed,[4] and the edge/corner statistics were obtained directly from the fcc unit cell of Pt. The average length of this is 3.92 Å, so the crystallite sizes can be related to a multiple of the unit cell length. For example, catalyst 81-SiO_2-IonX-S, which has a crystallite size of about 1.1 nm, corresponds to an isodimensional crystallite of three unit cells in each direction. The statistics given below are based on n isodimensional fcc unit cells with ⟨100⟩ planes exposed (*24*):

$$\frac{\text{Corner + Edge Atoms}}{\text{Total Surface Atoms}} = \frac{8n}{10n^2 - 2n + 1}. \tag{1}$$

In Fig. 10 are plotted the measured turnover numbers for propene and cyclopropane hydrogenation and for methylcyclopropane hydrogenation to isobutane. It is clear that the nature of structure sensitivity for the cyclopropanes differs from that for propene. While enhanced activity seems to be reasonably correlated with the hypothesis of more active edge and corner sites in all cases, no simple geometric explanation would suffice to explain the continuing decrease in propene hydrogenation activity for larger crystallites.

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[4] Variations from this geometry are suggested by the results presented in Part II (*2*) for these catalysts, but differences between various geometric models are not particularly significant in this sort of analysis (*20*).

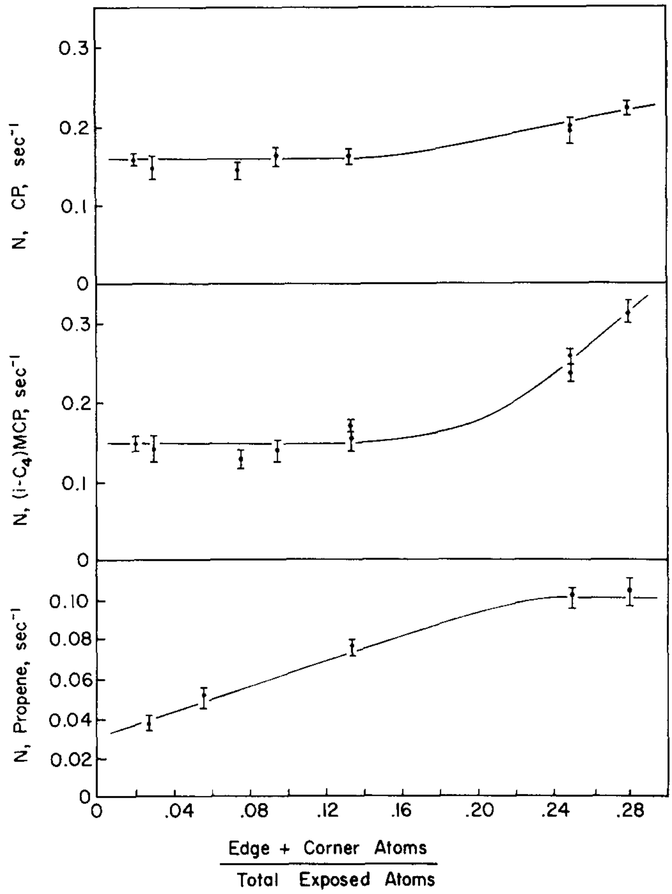

Fig. 10. Correlation of cyclopropane, methylcyclopropane (to isobutane) and propene data in terms of surface site statistics.

Turnover numbers vs edge/corner statistics for methylcyclopropane hydrogenation to *n*-butane are given in Fig. 11. The correlation is similar to that for isobutane product except for catalysts 7.1-SiO_2-PtCl-S and 6.3-SiO_2-PtCl-L. The large de-

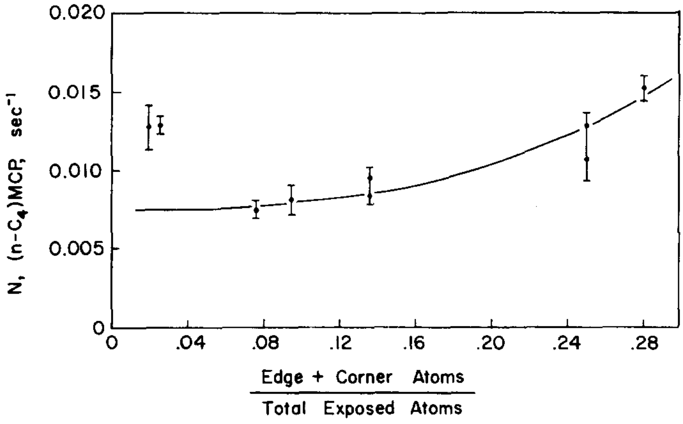

Fig. 11. Correlation of methylcyclopropane (to *n*-butane) data in terms of surface site statistics.

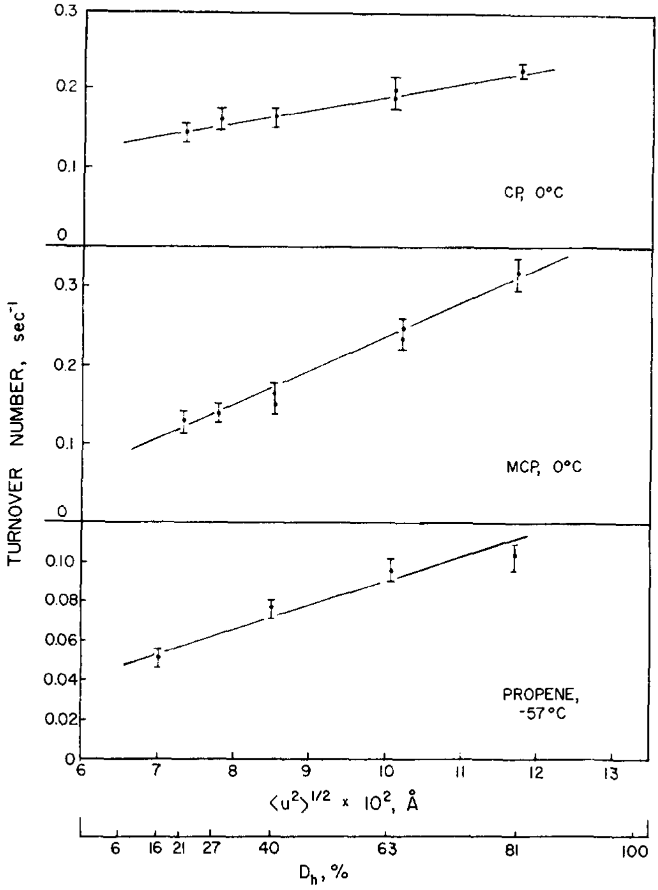

FIG. 12. Correlation of overall turnover numbers with mean-square vibrational amplitude.

crease in isobutane selectivity for these two catalysts is not due to a decrease in the rate of isobutane formation but rather to increased rates of *n*-butane formation. The only respect in which these two catalysts differ from others is in the ratio of crystallite to pore size; average dimensions of the crystallites for these two samples are 12.8 and 14.9 nm, while the pore diameter of Davison Grade 62 silica is 14.0 nm, so the crystallites are comparable in size to the pore diameter of the support.

In Part II (*2*), it is shown that a linear correlation exists between the percentage exposed and log of the mean-square amplitudes of vibration. This permits estimation of amplitudes for catalysts of $D_h > 40\%$, which were not measured experimentally. Although the X-ray measurements were conducted for catalysts in which the platinum was covered with oxygen, the good agreement between D_x and D_h and the inclusion of platinum metal values for the limits of the amplitude correlation (*25*, *26*) indicate that the $(\mu^2)^{\frac{1}{2}}$ values may pertain also to the platinum as employed under reaction conditions. Interestingly enough, there appears to be a good correlation between $(\mu^2)^{\frac{1}{2}}$ and the measured turnover numbers. This is shown in Fig. 12 for the three reactions. The lowest percentage exposed catalysts, where crystallite and pore dimension are of the same magnitude, have been omitted since their behavior is in some respects different from the other members of the series. Reasons for this will be discussed elsewhere.

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