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Hydrogenation of Ethylene on Supported Platinum

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The rate of hydrogenation of ethylene on Pt/SiO_2 catalysts has been studied between 207 and 371°K. Referred to unit surface area of the metal, our data are in excellent agreement with those of others on films of evaporated platinum. Contamination of the metal by a poison that desorbs from the support during reduction of the catalyst at about 700°K could be removed by a short oxidation at 600°K. When this accidental contamination was taken into account, no beneficial effect resulting from mixing Pt/SiO_2 with $\eta - Al_2O_3$ could be observed in the present work. In particular, there was no evidence in our work for spillover of hydrogen from the metal to the alumina with enhanced rates of hydrogenation of ethylene adsorbed on the alumina.

INTRODUCTION

Several reactions on supported transition metals have recently been reported where neither the nature of the support nor the particle size of the metal between one and ten nm exerted any appreciable effect on the rate of reaction referred to unit surface area of the metal (*1*). The latest studies to report such a negative result are those of Platteeuw *et al.*, who have investigated nickel, palladium, and platinum supported on silica, alumina, silica–alumina, and silica–magnesia for the hydrogenation of benzene as well as the isomerization and dehydrocyclization of hexanes (*2*, *3*). In all cases, no effect of support or particle size could be found.

Thus, it beomes imperative to scrutinize reports where differences in activity of a metal have been found for a given reaction as a result of changes in support or particle size. Explanations of such effects may involve the need for certain surface structures (*4*) or electronic interactions between metal and support (*5*, *6*).

A third possible explanation was first proposed by Khoobiar *et al.* to account for certain results obtained during a study of the dehydrogenation of cyclohexane on Pt/Al_2O_3 (*7*). These authors imagined that an important part of the reaction took place not on the platinum surface, but elsewhere, as a result of migration of hydrogen atoms away from the metal surface. In a companion study, Khoobiar attempted to prove this *spillover* of hydrogen atoms by mixing Pt/Al_2O_3 and WO_3 and watching the appearance of blue H_xWO_3 in a flow of molecular hydrogen at room temperature (*8*). However, it was subsequently shown that this reduction of WO_3 did not take place except in the presence of water (*9*). Besides, the reasons put forward by Khoobiar *et al.* to explain their catalytic results in the dehydrogenation of cyclohexane were later shown to be suspect as a result of a needed correction in their calculation of heat and mass transfer (*10*).

The merit of Khoobiar *et al.* has been to focus attention on the phenomenon of spillover, the reality of which cannot be questioned (*11*). *The question that remains is whether this migration of atomic hydrogen away from a metal onto the support can produce substantial catalytic effects on the support.* An affirmative answer to this question was given by Sinfelt and Lucchesi whose data are presented on the left-hand side of Fig. 1 (*12*). In their work, Sinfelt and Lucchesi showed that mixtures of

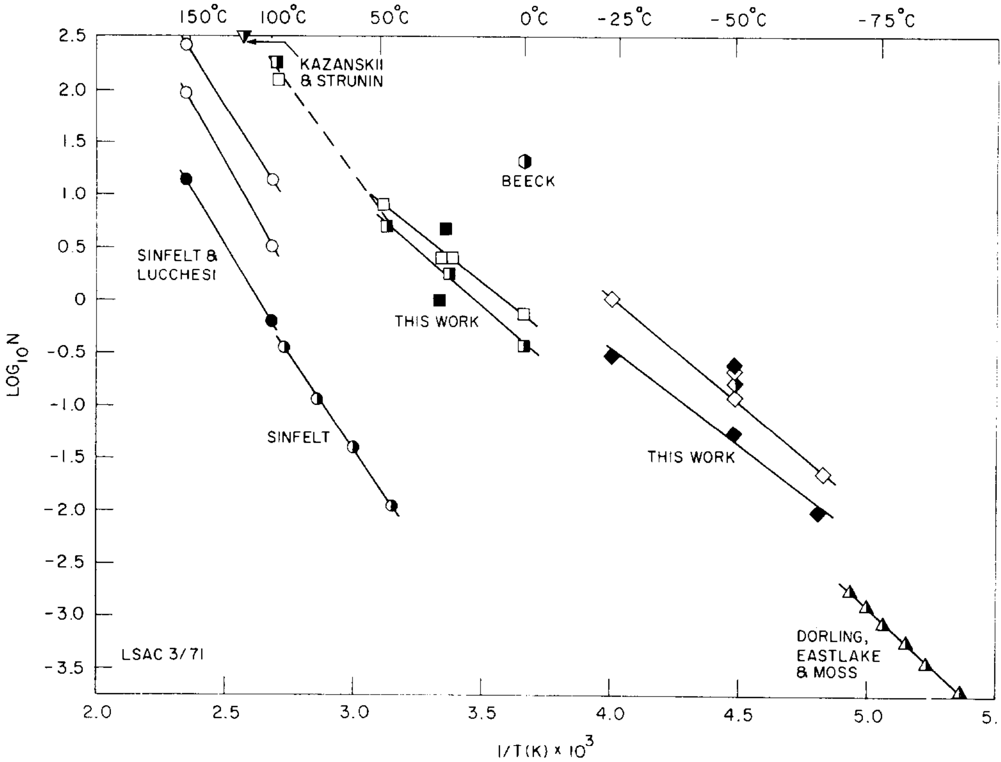

FIG. 1. Collected data for ethylene hydrogenation over platinum: All values were corrected to the conditions of our work (23 Torr C_2H_4, 152 Torr H_2) using a zero-order dependence for ethylene and first-order for hydrogen. Individual experimental conditions and activation energies were as follows: Kazanskii and Strunin—Pt wire, 26 Torr C_2H_4, 116 Torr H_2, E = 10 kcal mole^{-1}; Beeck—evaporated Pt film, 41 Torr C_2H_4, 41 Torr H_2, E = 10.7 kcal mole^{-1}; Dorling, Eastlake, and Moss—2.45% Pt/SiO_2, 19 Torr C_2H_4, 741 Torr H_2, E = 10.5 kcal mole^{-1}; Sinfelt and Lucchesi—0.05% Pt/SiO_2, our conditions, E = 17–20 kcal mole^{-1}; Sinfelt—0.05% Pt/SiO_2, our conditions, E = 16 kcal mole^{-1}; this work (25°C)—0.05% Pt/SiO_2, $E = 9.1 \pm 0.5$ kcal mole^{-1}; this work (−50°C)—0.5% Pt/SiO_2, $E = 8.9 \pm 0.2$ kcal mole^{-1}. The half-filled points represent platinum catalysts (supported or unsupported) used without dilution; open points denote mixtures with alumina; solid points denote mixtures with silica. The one open and two solid points in our work that lie above the Arrhenius lines for the alumina mixtures represent activities measured after a 300°C air dose.

Pt/SiO_2 and Al_2O_3 were much more active than mixtures of Pt/SiO_2 and SiO_2 for the hydrogenation of ethylene. As can be seen in Fig. 1, the rate, as expressed by a turnover number of the platinum atoms, is increased tenfold by mixing the same Pt/SiO_2 catalyst with Al_2O_3 instead of SiO_2. This suggests that alumina catalyzes the hydrogenation of ethylene if it is mixed with a Pt/SiO_2 catalyst although the activity of Al_2O_3 alone is nil under the same conditions. A similar result has recently been reported by Sancier who studied the hydrogenation of benzene in a pulse reactor on Pd/Al_2O_3 diluted with increasing amounts of Al_2O_3 (*13*). In this case, dilution increased the percentage hydrogenation per milligram of palladium by a factor approaching three at the highest dilution.

The explanation favored by Sinfelt and Lucchesi on the one hand and by Sancier on the other hand is one that is based on hydrogen spillover from Pt or Pd onto Al_2O_3 where the atomic hydrogen hydrogenates adsorbed ethylene or benzene, respectively. The present work was undertaken in order to verify the unchallenged observations of Sinfelt and Lucchesi, with the original hope of confirming, extending and explaining the very large effect reported by them.

All the available data from which it was possible to extract a turnover number *N*, i.e., the number of molecules of ethylene converted per surface platinum atom per second under standard conditions, are collected in Fig. 1. The standard conditions chosen were those of Sinfelt and Lucchesi: 23 Torr of C_2H_4 and 152 Torr of H_2. To obtain *N* at our standard conditions, it was assumed, following the work of others *(14)*, that the rate was zero order in ethylene and first order in hydrogen. The validity of the zero order in ethylene assumption will be taken up later. The dispersion of a very dilute Pt/SiO_2 catalyst (0.05 wt % Pt) of Sinfelt and Lucchesi was assumed to be identical to a sample made following exactly their procedure and provided us by Dr. J. H. Sinfelt. The same remark applies to the data of Sinfelt also shown on Fig. 1 and obtained with the same catalyst *(15)*. The data of Dorling *et al.* *(16)* were referred to unit surface area of Pt, and to obtain *N* we used the average surface site density of $1.2 \times 10^{15} cm^{-2}$. The same value was used for the other data when needed.

TABLE 1
Ethylene Hydrogenation on an Evaporated Film of Platinum by Courtesy of W. Ritchie, Shell Development Company

	Run I	Run II
system volume, cm^3	380	380
C_2H_4 pressure, Torr	40	42
H_2 pressure, Torr	40	42
temperature, °C	0	0
film weight, mg	15.8	16.3
H_2 adsorption, 10^{16} molecules/mg	1.73	1.90
$t_{1/2}$, min	1.73	1.75

For the data of Kazanskii and Strunin *(17)*, it was assumed that the catalytic area was equal to the geometric area of their Pt wire. Finally, the value of *N* for a film of evaporated platinum was obtained from unpublished data of the late Otto Beeck and his collaborators (Table 1).

Experimental

The reaction was studied in a Pyrex batch recirculation system (Fig. 2). The reactor was 30 mm in diam and about 15 mm high with a medium grade fritted disc to support the catalyst in the amount

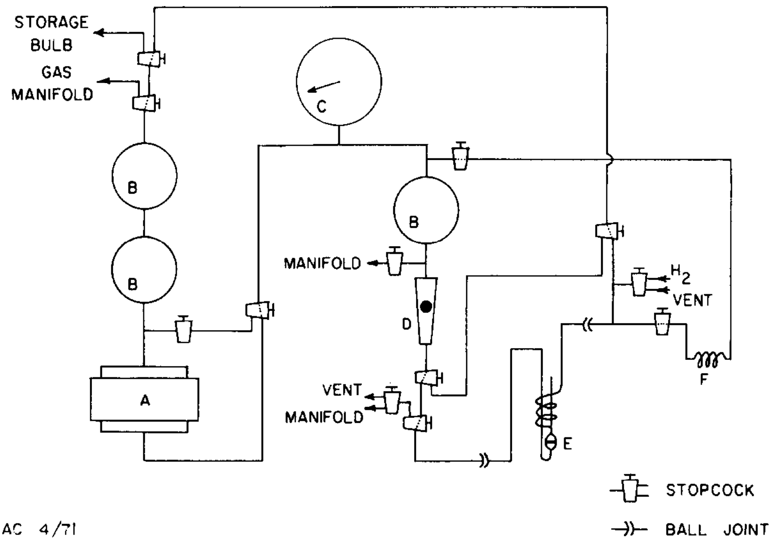

Fig. 2. Recirculation system for kinetic studies: A—bellows pump for circulating reactants; B—surge bulbs (two one-liter, one half-liter); C—Bourdon-type pressure gauge; D—flowmeter; E—catalyst chamber; F—sampling coil for chromatographic analysis of gas mixture. The dotted lines indicate stopcock positions during a reaction.

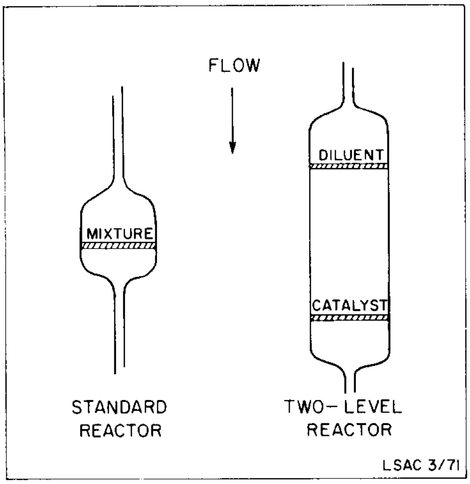

FIG. 3. Reactors for studying mixtures: The two-level reactor eliminates the possibility of surface migration of intermediates between catalyst and diluent.

of about 0.5 g. Some experiments required a reactor with two fritted discs so that the catalyst mixture components could be separated (Fig. 3). When the two-level reactor was used, the diluent was always placed on the top (upstream) level. The temperature was measured with a thermocouple inserted into a well extending through the reactor wall to a point just above the center of the fritted disc. A glass coil above the reactor served to preheat or precool the reaction gases. The gases were recirculated over the catalyst by a Teflon bellows pump (*18*). The pump was driven by compressed nitrogen rather than air to avoid any possibility of contamination resulting from the diffusion of oxygen through the bellows. A flow rate of 500 cm^3/min was used in a system of 2.55 l total volume, and 23 cm^3 samples were withdrawn at approximately 8 min intervals for chromatographic analysis.

The ethylene, Phillips research grade (99.96%) with a trace of ethane, was subjected to several freeze–pump–thaw cycles before being used. The hydrogen was diffused through a palladium thimble while the helium (99.995%) was passed through a glass coil at −195°C before use.

The catalyst used in most of this work and provided by Dr. H. A. Benesi was 60/200 mesh 0.5% Pt/SiO_2 prepared according to the method of Benesi *et al.* (*19*). It was reduced at 400°C in hydrogen and stored in air prior to use. The standard pretreatment for this catalyst involved a 1 hr evacuation at 150°C after which hydrogen flowing at approximately 100 cm^3/min was started through the reactor while the temperature was raised to 400°C. After 4 hr at 400°C, the sample was cooled in flowing hydrogen to the reaction temperature and evacuated for 10 min just prior to admitting the reactant mixture. The platinum surface area was determined according to the method of Benson and Boudart (*20*): the dispersion (ratio of surface to total platinum atoms) was 0.61 both before and after the above pretreatment. Another catalyst, also provided by Dr. H. A. Benesi, was similar to the one described above but contained 2.5% Pt on SiO_2. Its dispersion was determined to be 0.58. It was pretreated as the other catalyst.

A third catalyst, provided by Dr. J. H. Sinfelt, duplicated that used by Sinfelt and Lucchesi (*12*). It was 0.05% Pt/SiO_2 prepared by impregnation of Davison silica gel with a solution of H_2PtCl_6 followed by calcination in air at 538°C; our pretreatment of 3 hr at 500°C in flowing hydrogen also duplicated theirs. The dispersion measured after the reduction was 0.26. The catalyst was in powder form; so before use, it was pressed at 10,000 psi and crushed to 48/200 mesh. It was not reduced prior to an experiment.

The diluents were all used as 48/100 mesh (150–300 μm) particles. The alumina was the η form prepared by calcination of Davison β-alumina trihydrate for 4 hr at 593°C; it was supplied by Esso Research and Engineering Company with a reported surface area of 296 m^2g^{-1}. The Davison silica gel was Grade 40, initially 6/12 mesh, and its surface area was believed to be about 400 m^2g^{-1}. The Cabosil, Cabot Corporation's HS-5, was pressed at 10,000 psi and then crushed to the desired particle size. Cabot reported its surface area to be 325 ± 25 m^2g^{-1}. The components of a mixture were blended by shaking in the reactor until the catalyst particles appeared to be uniformly distributed in the diluent.

In cases where air was used to treat the sample between runs, the procedure went as follows: right after the first run hydrogen was started over the catalyst as the temperature was raised to 300°C; after 30 min, the reactor was evacuated for 10 min and vented to the room for 30 sec; following another 10 min evacuation, the hydrogen was restarted, and after 30 min at 300°C, the reactor was cooled for the next run.

Each run with the 0.5% Pt/SiO_2 used 25 mg of catalyst; the standard amount of diluent was 475 mg. In order to duplicate the work of Sinfelt and Lucchesi as closely as possible, we used 50 mg of 0.05% Pt/SiO_2 per run and 450 mg of silica or alumina in mixtures with the low platinum content catalyst. The reactant gas contained 23 Torr (0.03 atm) ethylene, 152 Torr (0.20 atm) hydrogen, and 585 Torr (0.77 atm) helium, again duplicating Sinfelt and Lucchesi. In what follows, these partial pressures will be referred to as *standard conditions*. While the catalyst was being cooled for a run, the reactants were circulated through the system (bypassing the catalyst) to provide a uniform composition. A 52 vol % ethylene glycol in water solution was cooled to a viscous mass to provide a —50°C bath for the reactor and precooling coil. The temperature remained constant during the course of an hour's run, but from run to run the bath temperature drifted by as much as 2°C. The data in Table 2 were corrected where necessary for the effect of a reaction temperature differ-

TABLE 2

TURNOVER NUMBERS FOR ETHYLENE HYDROGENATION UNDER STANDARD CONDITIONS

	Turnover number at −50°C (sec^{-1})[a]						
	0.5% Pt/SiO_2	0.5% Pt/SiO_2 + Al_2O_3		0.5% Pt/SiO_2 + silica gel		0.5% Pt/SiO_2 + Cabosil	
Treatment		mixed	separate	mixed	separate	mixed	separate
Standard (H_2 flow 4 hr at 400°C)	0.17	0.15	0.13	0.069	0.03	0.061	0.052
H_2 flow at 25°C or below following reaction	0.17	0.13	0.11		0.03	0.063	0.056
H_2 flow at 400°C following reaction				0.050			
air dose at 25°C following reaction							0.077
air dose at 300°C following reaction	0.15	0.19		0.23	0.15		0.16
second air dose at 300°C		0.22		0.25	0.19		
H_2 flow over fresh sample at 25°C	0.22			0.25			
H_2 flow 4 hr at 450°C following reaction	0.17						
air dose at 300°C following reaction	0.16						

	Turnover number at 25°C (sec^{-1})		
	0.05% Pt/SiO_2	0.05% Pt/SiO_2 + Al_2O_3 mixed	0.05% Pt/SiO_2 + silica gel mixed
Standard (H_2 flow 3 hr at 500°C)	1.95	2.86	0.94
air dose at 300°C following reaction			4.92

[a] Uncertainty in the reported values is not more than ±10%.

ent from —50°C; the value used for the activation energy was 9 kcal $mole^{-1}$.

The reaction was followed by periodic analysis of gas samples in a Varian-Aerograph A-90-P chromatograph equipped with a silica gel column. Only hydrogen, ethane, and ethylene were detected. The reaction rate was taken as the initial slope of the plot of product concentration vs time. Conditions were such that all the catalyst mixtures gave convenient levels of conversion; the highest measured was about 10% (approximately 1% per pass), and the usual value was less than 5%. The plots of ethane concentration vs time were always linear; so determination of the initial slope was very simple.

RESULTS

Although no detailed study of the kinetics was attempted, the results shown on Fig. 4 indicate zero order with respect to ethylene up to a high conversion with the 0.5% Pt/SiO_2 catalyst at 0°C and at our standard conditions. Under our conditions, the negative one-half order with respect to ethylene reported by others (*14*) clearly does not apply.

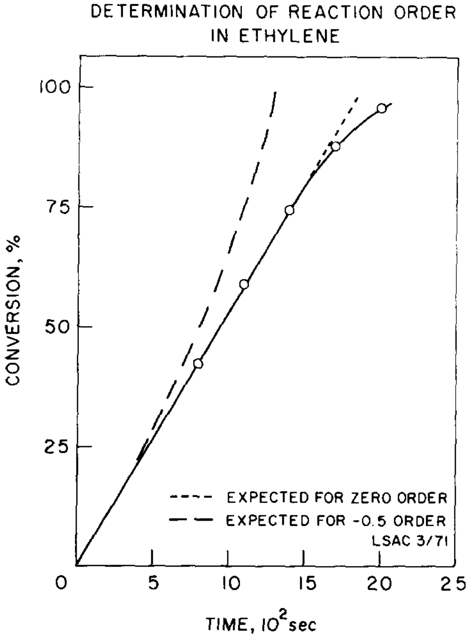

FIG. 4. A kinetic run for ethylene hydrogenation up to high conversions: 0.5% Pt/SiO_2; 0°C; standard conditions.

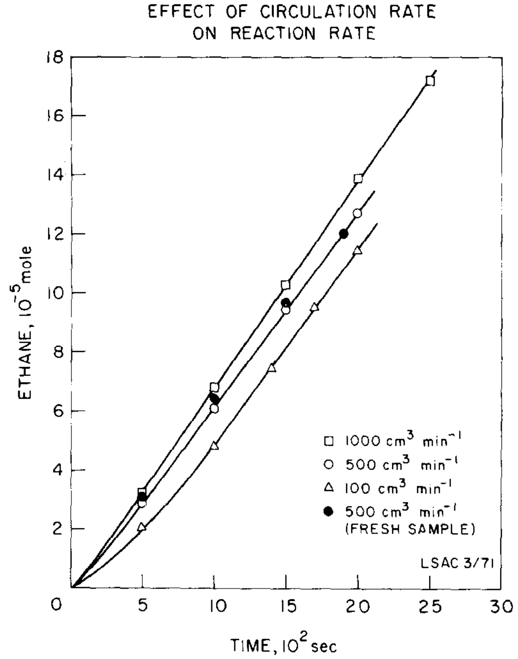

FIG. 5. Reproducibility of runs at —50°C and effect of gas flow rate.

Normally, there was no measurable deactivation between runs, and the reproducibility from run to run was excellent. These points, together with the lack of dependence of the rate of reaction on flow rate, are illustrated by the data shown on Fig. 5. These data were obtained on a single sample of 0.5% Pt/SiO_2. Hydrogen was passed over the catalyst at —50°C between runs. The reaction rate (slope of the linear portion of the curve) was independent of the flow rate. Since the latter was varied over a tenfold range, external heat and mass transfer appear to be unimportant problems in our system. These data also show that the simple low-temperature hydrogen purge was adequate to maintain the activity of the catalyst, and the filled circles show the degree of reproducibility between like samples. The shift of the curves to the right with decreasing flow rate reflects the time lag involved in the sampling technique when the gas flow was small compared to the total system volume.

Another result indicates quite clearly the absence of both internal and external heat and mass transfer limitation at low temperatures. The values of the turnover number at —50°C under standard conditions were 0.17 and 0.18 sec^{-1} for the 0.5% Pt and 2.5% Pt catalysts on silica gel. The absence of any significant change in N as the amount of metal was increased fivefold is a convincing test of the lack of influence of transport phenomena under these conditions (*21*).

Both the 0.5% and the 0.05% Pt/SiO_2 catalysts showed similar behavior for the hydrogenation of ethylene. Let us first present the data obtained with the 0.5% Pt/SiO_2 catalyst.

The initial experiments, using the standard pretreatment for each catalyst mixture, appeared to support the idea of an enhanced hydrogenation activity when alumina was in contact with the catalyst. This is shown in Table 2; the mixtures with Al_2O_3 gave turnover numbers about two and one-half times those of mixtures with silica. As diluents, Davison and Cabosil silica gels did not differ significantly from one another, and they are not distinguished in this discussion. Quite unexpectedly, the alumina-plus-catalyst system gave nearly the same turnover number when the components were separated in the tall reactor with two fritted glass supports as when they were mixed. This observation prompted us to undertake a more detailed study of the mixtures containing the 0.5% Pt/SiO_2 catalyst.

The rate for the catalyst alone was slightly greater than that for the catalyst mixed with alumina; thus it became clear that silica gel was not inert as originally anticipated. In general, the activities of the various samples could be retained by flushing the reactor between runs with hydrogen at room temperature or below, although the samples involving alumina dropped slightly (<20%) from their initial activities. A high temperature (400°C) treatment with hydrogen was somewhat less effective than the room temperature regeneration. Evidently the silica, and to a lesser extent the alumina, contaminated the platinum surface. Hydrogen, even at 400°C, was not capable of removing the contaminants from the metal. Oxygen, however, when administered as a dose of air at 300°C, cleaned the catalyst to the extent that its activity in some cases even surpassed that of a fresh, unmixed sample. The particularly favorable cases were those in which the catalyst and diluent were well-mixed; if no diluent was present or if it was separated from the catalyst, the activity after the air treatment rose only to that of the fresh, unmixed catalyst. Exposure to air at room temperature was relatively ineffective in removing contaminants, but the contamination could be avoided altogether by omitting the initial high-temperature pretreatment of the fresh mixture. Even the unmixed catalyst gave a 30% higher activity when pretreated in hydrogen at room temperature rather than at 400°C.

Let us now introduce the results obtained with the 0.05% Pt/SiO_2 catalyst. The turnover number for the catalyst alone was midway between that for a mixture with silica and that for a mixture with alumina; so, in this case the alumina did enhance the catalyst's activity somewhat. However, an air dose at 300°C raised the activity of the silica mixture considerably beyond that of the alumina mixture. It appears, then, that the presence of small amounts of contaminants was responsible for the observed activity differences in mixtures with the 0.05% catalyst, too.

The temperature dependence of the activities of several samples was determined for comparison with the work of other authors. The values obtained for the activation energies are shown in the caption of Fig. 1; the average of about 9 kcal $mole^{-1}$ is in agreement with the bulk of reported data for ethylene hydrogenation. It must be noted that above 50°C, with the 0.05% Pt/SiO_2 catalyst, the slope of the Arrhenius line in Fig. 1 appears to increase. This is due to the fact that the temperature of the catalyst, as indicated by the reading of the thermocouple just above the catalyst, went up by about 10°C immediately after introduction of the reactants into the system. The true temperature of the catalyst must have been higher than that indicated by the thermocouple. The value of N at 100°C is, therefore, too high because of heat transfer limitation. Even then, no beneficial effect of mixing the catalyst with alumina could be detected.

In order to check whether the air treatment of the supported catalysts at 300°C could affect their dispersion, a standard platinum titration *(20)* was obtained on the 2.5% Pt/SiO_2 catalyst both prior to and after exposure to oxygen at 160 Torr during 20 min at 300°C, with reduction at 300°C in flowing hydrogen during 2 hr after the exposure to oxygen. The metal surface area was the same within experimental error before and after the oxygen treatment.

DISCUSSION

First, we shall discuss the data obtained in the present study. Then these data will be related to those of other investigators.

As we look first at the information of Table 2 pertaining to the 0.5% Pt/SiO_2 catalyst, we recognize two sets of data. In the first set we have values of N at —50°C ranging between 0.13 and 0.25 sec^{-1}. These will be referred to as *high* values of the activity. In a second set we have all *low* values of the activity, below 0.13 sec^{-1} and as low as 0.03 sec^{-1}. Our first concern is to explain the reason for the existence of the two sets of values.

The initial experiments done in this investigation gave results similar to those of Sinfelt and Lucchesi *(12)*. Thus, a mixture of the platinum–silica catalyst with alumina gave a *high* value of N (0.15 sec^{-1}) whereas a mixture of the same catalyst with silica gel gave a *low* value of N (0.061–0.069 sec^{-1}). This is only a slightly more than twofold difference in activity as compared to a tenfold difference recorded by Sinfelt and Lucchesi, but we worked at —50°C and they worked above 100°C. However, subsequent experiments indicated that spillover of active hydrogen from the platinum to the diluent could not explain our early results.

Rather, it became clear that surface contamination was responsible for the *low* values of N while the *high* values of N appear to characterize the behavior of clean platinum. In particular, the poisons responsible for low values of N were apparently neither reaction products nor impurities in the reactant gases. If such were the case, the catalyst activity would decrease as the reaction proceeded, but no deactivation occurred during the course of any run (see Fig. 5). Thus the contaminants must have been deposited on the platinum prior to the start of the reaction, i.e., during the pretreatment. Palladium-diffused hydrogen used for the pretreatment is an unlikely source of impurities. Thus, the contaminants must have been added to the system along with the diluents, that is, as adsorbed species on the silica or alumina. Since no special precautions were taken to keep the silica and alumina from contacting air during storage, it is certainly conceivable that various hydrocarbons in the air were adsorbed on the diluents and retained there until being transferred to the platinum during the pretreatment. It should be noted that the amounts of contaminants required to account for the low values of N are quite small. In particular 25 mg of 0.5% Pt/SiO_2 used in a run contains only about 0.4 μmole of surface platinum. On the other hand, assuming a site density of 10^{15} cm^{-2} for the diluents, one finds that the 475 mg mixed with the catalyst possesses nearly 3000 μmole of adsorption sites. A very small fraction of these, if covered with potential contaminants, would suffice to poison a large fraction of the platinum surface.

The process by which the contaminants were transported is probably a simple desorption from the diluent as the temperature is raised, followed by transfer through the gas phase to the platinum surface where readsorption takes place. Because gas-phase transport is involved, it is not surprising that the intimacy of contact between catalyst and diluent had little effect on the measured activity. If anything, the separated solids gave slightly poorer results than the corresponding mixtures, most probably because the desorbing contaminants passed through the entire catalyst bed when the diluent was above the catalyst in the two-level reactor. The stronger deleterious effect of silica as compared to alumina could be the result of the fact that alumina adsorbs hydrocarbons more strongly than does silica; so when heated the silica loses its contaminants to the platinum more easily than does alumina.

This concept of contaminants desorbing from the diluents to poison platinum can readily explain the separation between low and high values of N as a result of the various pretreatments and conditions summarized in Table 2.

Thus one dose of air at 300°C is sufficient to raise the activity of all catalysts plus diluents (mixed or separate) with a low activity so that the turnover number goes from a low value to a high value. The same dose of air at 300°C does not change the high value of N observed for the catalyst taken alone. A dose of air at 25°C is not enough to burn off the contaminant (see column to the extreme right in Table 2). Reduction of the catalyst at 25°C, alone or mixed with silica gel, is enough to produce a high value of the activity. Presumably, the contaminant cannot desorb from the diluent at that low temperature of pretreatment, although it will cut the activity by a factor from four to eight if the pretreatment takes place at a high temperature at which the poison desorbs from the surface of the diluent.

The same concept accounts for the data of Table 2 pertaining to the 0.05% Pt/SiO_2 catalyst. However, as seen in Fig. 1, the maximum activity of this catalyst is still lower than that expected from clean platinum by extrapolation of the low temperature data obtained with the 0.5% Pt/SiO_2 catalyst. This may be due to the fact that a single air dose is not sufficient in the case of the more dilute catalyst to burn off the poison contributed by a proportionately higher amount of nonmetallic adsorbent. Similar observations concerning smaller values of the turnover number of supported platinum catalyst containing less than 0.1% of metal might well be explained in this fashion (*22*).

Before comparing our data to those of others, we wish to note that the uncertainity in the reported values of N is small enough that a further dissection of the set of high N values for the 0.5% Pt/SiO_2 catalyst into two subsets of high values appears entirely justified. Thus, there are values of N in Table 2 corresponding to what appears to be a "normal" uncontaminated platinum surface grouped around 0.17 sec^{-1} in one subset and some values grouped around 0.23 sec^{-1} in another subset. The higher values in the second subset are all pertaining to cases where the surface of the metal might have been reconstructed (roughened up) by air treatment and where this reconstruction was not erased by subsequent pretreatments. Although the effect appears real, its magnitude is small as compared to that due to contamination. It is discussed more fully elsewhere (*23*). At any rate, the effect of oxygen treatment on activity cannot be ascribed to a change in dispersion, as shown by the results presented in the previous section.

After attributing the low N values to contaminants desorbed from the nonmetallic parts of the catalyst system, let us now compare our high values to those of others (Fig. 1 and Table 3). To obtain the tem-

TABLE 3
ACTIVITY OF PLATINUM CATALYSTS FOR THE HYDROGENATION OF ETHYLENE

Author	Temperature (K) Required for $N = 1\ sec^{-1}$ at 23 Torr C_2H_4, 152 Torr H_2	Reference
Beeck (Pt film)	236	Table 1
This work (0.5% Pt/SiO_2 + SiO_2 after air doses)	239	Fig. 1
Dorling, Eastlake, and Moss (2.45% Pt/SiO_2)	268	(*16*)
Kazanskii and Strunin (Pt wire)	269	(*17*)
This work (0.05% Pt/SiO_2 + SiO_2 after air dose)	270	Fig. 1
Sinfelt and Lucchesi (0.05% Pt/SiO_2)	335	(*12*)
Sinfelt (0.05% Pt/SiO_2)	384	(*15*)

perature at which the standard turnover number is one per second, we used, when necessary, the values of the activation energies shown in the caption of Fig. 1. Our results with Pt/SiO_2 are in good agreement with those of Dorling *et al.* (*16*) from whose work we selected the data pertaining to the catalyst most like ours and one which did not exhibit any of the various artifacts mentioned in their paper. Our results with the 0.5% Pt/SiO_2 catalyst are in striking agreement with those of Beeck *et al.*, who used a platinum evaporated film. Thus, after getting rid of accidental contamination brought by support material, we have apparently succeeded in measuring the activity of an uncontaminated surface. The results of Kazanskii and Strunin must be assessed in the light of a "carbiding" pretreatment given by these authors to their platinum wire; the activity of their metal is inferior to that of our more active catalyst and similar to that found on our 0.05% catalyst.

The only severe discrepancy then is between our work on the 0.05% Pt/SiO_2 catalyst and that of Sinfelt using a similar sample; at the same temperature and partial pressures our activity is nearly three orders of magnitude higher than that reported by Sinfelt.

The discrepancy in rate is not the only anomaly in the work of Sinfelt. Whereas typical activation energies range from 8 to 11 kcal $mole^{-1}$, his value is 16 kcal $mole^{-1}$. Finally his reaction order in hydrogen does not agree with the majority of literature reports. The hydrogen order is generally observed to be near unity, but Sinfelt measured 0.5. The evidence seems to be, then, that his surface was badly contaminated and not representative of a clean platinum catalyst. Sinfelt reported that his activity "can vary markedly over an extended series of measurements and is also sensitive to the length of time that the catalyst is reduced" (*15*).

Since the data of Sinfelt and Lucchesi (*12*) for the 0.05% Pt/SiO_2 catalyst mixed with SiO_2 are right in line with those of Sinfelt for the 0.05% Pt/SiO_2 catalyst alone, it appears that contamination of the metal was very much the same in both investigations. Apparently, alumina succeeded in scavenging some of the contaminant, but even the most active of the mixtures of Sinfelt and Lucchesi is still more than two orders of magnitude less active than our platinum and that of Beeck.

That alumina can act as a scavenger for contaminants is shown by the following special experiment. In the two-level reactor of Fig. 3, the usual quantity of silica gel was placed on the upper level while the usual mixture of 0.5% Pt/SiO_2 catalyst with alumina was positioned on the lower level. Under these conditions at −50°C and under standard conditions the turnover number was 0.13 sec^{-1} whereas, as shown in Table 2, the value was only 0.03 sec^{-1} when silica gel was on the upper level with only the undiluted catalyst on the lower level.

It is of course possible that the particular samples of catalyst used by Sinfelt and Lucchesi did in fact exhibit the effects of spillover, because they were so badly contaminated. Maybe the carbonaceous contaminant—if it was carbon—succeeded in bridging the platinum and silica interface for the transport of atomic hydrogen as suggested by us for the case of carbon supported platinum (*24*).

CONCLUSION

Although the phenomenon of hydrogen spillover (surface diffusion of dissociated hydrogen from a metal across a metal-support interface) has been observed very clearly in a number of noncatalytic situations (*11*), there is no evidence in the present investigation of the catalytic effect of spillover in the case of ethylene hydrogenation on supported platinum.

Rather, there appears to be a common problem of contamination of platinum by carbonaceous residues that can be removed by a short oxidation at 300°C. This method was already used in the case of carbon supported platinum (*4*, *24*). Cleaning by oxidation may be a general precaution to be taken in all investigations with platinum, as indicated in the present work. Reports of catalytic effect of spillover and diluent effects must be accompanied with a demonstration that the rate of the reaction under study per unit surface of the active metal is indeed higher in the presence of diluents than that of the *clean* metal alone. Otherwise artifacts of the kind demonstrated in this paper may be present.

Finally, it is quite encouraging to note once more that supported metals, if managed with care, are yielding catalytic rates comparable, if not identical within experimental error, to those obtained with evaporated metal films. In the case of the hydrogenation of ethylene, this point was first made by Schuit and van Reijen (*25*). It is illustrated quantitatively in the present investigation.

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REFERENCES

1. Boudart, M., *Advan. Catal. Relat. Subj.* **20**, 153 (1969).

2. Aben, P. C., Platteeuw, J. C., and Stouthamer, B., *Rec. Trav. Chim. Pays-Bas* **89**, 449 (1970).

3. Dautzenberg, F. M., and Platteeuw, J. C., *J. Catal.* **19**, 41 (1970).

4. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).

5. Figueras, F., Mencier, B., de Mourgues, L., Naccache, C., and Trambouze, Y., *J. Catal.* **19**, 315 (1970).

6. Schwab, G.-M., Block, J., and Schultze, D., *Angew. Chem.* **71**, 101 (1959).

7. Khoobiar, S., Peck, R. E., and Reitzer, B. J., *Proc. Int. Congr. Catal. 3rd,* 338 (1965).

8. Khoobiar, S., *J. Phys. Chem.* **68**, 411 (1964).

9. Benson, J. E., Kohn, H. W., and Boudart, M., *J. Catal.* **5**, 307 (1966).

10. Chambers, R. P., and Boudart, M., *J. Catal.* **6**, 141 (1966).

11. Boudart, M., Vannice, M. A., and Benson, J. E., *Z. Phys. Chemie Neue Folge* **64**, 171 (1969).

12. Sinfelt, J. H., and Lucchesi, P. J., *J. Amer. Chem. Soc.* **85**, 3365 (1963).

13. Sancier, K. M., *J. Catal.* **20**, 106 (1971).

14. Horiuti, J., and Miyahara, K., *Hydrogenation of Ethylene on Metallic Catalysts* NSRDS-NBS 13 (1968).

15. Sinfelt, J. H., *J. Phys. Chem.* **68**, 856 (1964).

16. Dorling, T. A., Eastlake, M. J., and Moss, R. L., *J. Catal.* **14**, 23 (1969).

17. Kazanskii, V. B., and Strunin, V. P., *Kinet. Katal.* **1**, 553 (1960).

18. Bernard, J. R., and Teichner, S. J., *Bull. Soc. Chim. Fr.* **1969**, 3798.

19. Benesi, H. A., Curtis, R. M., and Studer, H. P., *J. Catal.* **10**, 328 (1968).

20. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).

21. Koros, R. M., and Nowak, E. J., *Chem. Eng. Sci.* **22**, 470 (1967).

22. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6**, 92 (1966).

23. Schlatter, J. C., *Ph. D. dissertation,* Stanford (1971).

24. Boudart, M., Aldag, A. W., and Vannice, M. A., *J. Catal.* **18**, 46 (1970).

25. Schuit, G. C. A., and van Reijen, L. L., *Advan. Catal. Relat. Subj.* **10**, 242 (1958).