

Catalyst Characterization by a Probe Reaction: The Number of Active Hydrogen

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Hydrogen titration by ethylene pulses at room temperature is proposed for measuring the number of active hydrogen atoms (NAH) on metal-supported catalysts. The reaction product, ethane, desorbs quantitatively and can be measured directly by gas chromatography. On Pt/Al₂O₃ catalysts the determination of hydrogen chemisorption by titration of adsorbed ethylene with hydrogen pulses at room temperature gives values identical to those determined by direct chemisorption on clean catalysts. The method was tested on Pt/Al₂O₃ and Pt/SiO₂ catalysts. Results show that for Pt/Al₂O₃ the number of active hydrogen can exceed several times the number of metal atoms on the catalyst, and increases with the time of treatment with hydrogen at high temperature. The initial turnover rate for ethylene hydrogenation is constant when referred to NAH, but not when referred to the percentage of exposed metal atoms, as determined by hydrogen chemisorption. For Pt/SiO₂ catalysts, measurements suggest that the number of active hydrogen atoms is less than that indicated by the HC determination performed by direct adsorption of hydrogen. © 1990 Academic Press, Inc.

INTRODUCTION

Numerous attempts have been made to relate the catalytic activity for olefin hydrogenation with the fraction of exposed metal (1-18). As a new approach to the problem, distinct from the chemisorption techniques described in the papers cited above, ethylene hydrogenation is proposed as a probe reaction for counting the number of active hydrogen atoms on the catalyst surface. In this work ethylene hydrogenation is carried out using pulses of ethylene at room temperature on a catalyst saturated with hydrogen. The reaction product, ethane, is quantitatively desorbed and measured. Conversely, adsorbed ethylene is then titrated with hydrogen pulses.

Previously, Bond and Sermon (19) proposed a method of olefin titration by a flow reaction at 373 K using a low partial pressure of 1-pentene in nitrogen. This procedure differs from ours in three ways: First, the oper-

ation at 373 K reduced through desorption the amount of hydrogen to be titrated, as shown in TPD spectra (11, 20, 21). Additionally, secondary reactions may occur at 373 K (19) but not at room temperature. Third, the large amount of olefin passing over the catalyst in a flow reaction may cause the formation of carbonaceous deposits that modify the state of the catalyst. With a pulse technique this effect is minimized due to the small quantity of olefin which is sent sequentially to the surface. Our method is similar to the method developed by Augustine and Warner (22, 23) since it uses pulse-wise hydrogenation of butene.

EXPERIMENTAL

Catalysts

The catalysts were prepared by the incipient wetness impregnation method. The main characteristics and pretreatments of supports are summarized in Table 1. Aluminas and silica gel were calcined in air at 873 K

TABLE 1
Characteristics and Pretreatments of Catalysts

Catalyst	wt% Pt	Support	Impregnation complex	Support pretreatment
1	0.28	γ -Al ₂ O ₃	(NH ₄) ₂ PtCl ₄	NH ₃ gas flow at room temperature on dried catalyst
2	0.53	γ -Al ₂ O ₃	H ₂ PtCl ₆	Support suspended in a HCl solution before impregnation
3	0.57	γ -Al ₂ O ₃	H ₂ PtCl ₆	None
4	0.42	η -Al ₂ O ₃	(NH ₄) ₂ PtCl ₄	HN ₃ gas flow at room temperature on dried catalyst
5	0.47	γ -Al ₂ O ₃	H ₂ PtCl ₆	Dry support
6	0.52	η -Al ₂ O ₃	H ₂ PtCl ₆	Dry support
7	0.6	SiO ₂	H ₂ PtCl ₆	
8 ^a	0.5	Al ₂ O ₃		
9 ^b	6.3	SiO ₂		

Note. Support surface areas: 160 m²/g for γ -Al₂O₃; 155 m²/g for η -Al₂O₃; 265 m²/g for silica.

^a Sample 11 from the Committee of Reference Catalysts of the Catalysis Society of Japan.

^b EUROPT-1.

and sieved to particle sizes from 0.15 to 0.25 mm (60–80 mesh). The platinum content was determined spectrophotometrically by the stannous chloride technique (24) and X-ray fluorescence. The catalysts were all stored in glass flasks with plastic snap caps after drying.

Gases

Argon (Linde UHP, >99.999%) and helium (Linde Chromatographic, >99.9999%), purified by passing them through alumina traps, were used as carrier gases. The alumina trap was dried *in situ* at 573 K. Hydrogen (Linde UHP, >99.999%) or H₂ produced by an Elhygen generator was used for catalyst treatments and titrations. Ethylene (Linde CP, >99.5%), ethane (Matheson CP, >99.0%), and oxygen (Linde UHP, >99.99%) were used as received.

Determination of the Hydrogen Number (HN) and Hydrogen Chemisorption by Titration of Ethylene with Hydrogen (HC(E))

The experiments were carried out in a stainless steel apparatus designed to work by either pulse or continuous flow. The reactor used was a 6-mm-o.d. U-shaped Vycor

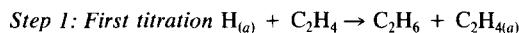
tube. Switching of gases was accomplished without mixing or access of air. The reaction products of each pulse were collected at the reactor exit in a cool trap for 8 min. The trap was a 40-cm U tube of stainless steel, $\frac{3}{8}$ -in. o.d., filled in the middle with 20 cm of Chromosorb 102. The trap was cooled to 195 K when argon was used as carrier gas and to 77 K when the carrier gas was helium. The trapped gases were then analyzed with a gas chromatograph, equipped with a column of Chromosorb 102 kept at 303 K. A loop of 0.202 cm³ (0.185 cm³, NTP) was used as a calibrated volume for the gas pulses.

The reactor was charged with 250 or 500 mg of catalyst, dried for 2 h at 393 K in Ar, heated to 673 K (10 K/min) in carrier gas, and then treated in H₂ through the desired time (10 min, 1 h, 5 h, overnight, etc.). The catalyst was cooled to room temperature and then swept for 15 min with carrier gas. From this point on, the measurements followed the next sequence (notation is defined in Table 2):

Step 1. Hydrogen adsorbed on the catalyst was titrated with ethylene pulses until the amount of ethane formed was negligible (E₁, total amount of ethane produced in this step). The first ethylene pulses produced

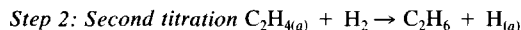
TABLE 2
Sequence of Titrations and Notation

Pt_t Total amount of platinum in sample, μmol



E₁ Amount of ethane *formed* in the titration by ethylene of adsorbed H, at room temperature, after the catalyst treatment with hydrogen at high temperature, μmol

HN Stoichiometric ratio of adsorbed hydrogen titrated in Step 1; $HN = 2E_1/Pt_t$. For Pt/Al₂O₃ catalysts, HN is also called NAH: number of active hydrogen atoms (see text).



E₂ Amount of ethane *formed* in the titration by H₂ of ethylene adsorbed at the end of Step 1, μmol

HT Amount of H₂ *consumed* in the second titration, μmol

HC(E) Amount of H₂ *adsorbed* in the second titration: $HC(E) = HT - E_2$, μmol

H/Pt Stoichiometric ratio of hydrogen adsorbed at the end of the second titration: $H/Pt = 2HC(E)/Pt_t$

Note. Subscript (a) means adsorbed, and the equations are descriptive only, not stoichiometric.

most of the ethane in the titration. The stoichiometric amount of hydrogen atoms titrated in this step per total platinum atom is called the hydrogen number (HN): $HN = 2E_1/Pt_t$.

Step 2. Following step 1, the adsorbed ethylene was titrated with pulses of hydrogen until the hydrogen peak area in successive chromatograms was constant. The amount of hydrogen chemisorbed HC(E) is given by the difference between the amount of hydrogen consumed, HT, and the amount of ethane formed in the titration, E₂; that is, $HC(E) = HT - E_2$.

The ratio of hydrogen atoms per platinum atom (H/Pt) is given by $H/Pt = 2 HC(E)/Pt_t$.

Step 3. To repeat step 2, the catalyst from step 2 was treated with ethylene pulses at room temperature until ethane was not detected.

Steps 2 and 3 were repeated two or three times to verify reproducibility of the results.

Direct Hydrogen Chemisorption (HC)

The amount of hydrogen chemisorbed on clean catalyst, HC, was measured by the method of hydrogen pulses at room temperature (4, 25, 26). The procedure was the

following: The catalyst treated with hydrogen was cooled at room temperature in an Ar stream. Then it was heated again to 673 K at a rate of 10 K/min. At this temperature the furnace was turned off and the reactor was maintained overnight in the inert gas stream. After that, the reactor was reconnected to the gas stream and subjected to another TPD. After the catalyst was cooled to 298 K, pulses of 8.25 μmol of hydrogen were sent on the catalyst until a constant peak area was measured.

In some cases the catalyst remains after the reduction in a highly metastable state; under these conditions neither HC(E) nor HC gives reproducible results. The catalyst must be annealed by successive OT-HT cycles, as indicated by Prasad et al. (26), before proceeding with the measurements.

Studies of Catalytic Activity

Initial rates for ethylene hydrogenation were measured in the reaction system fitted to carry out flow reactions. The reactor was loaded with 10 mg of Pt catalyst mixed with 190 mg of Vycor glass. The catalyst was dried *in situ* at 390–395 K in a N₂ stream (40 ml/min) for 2 h, heated to 673 K, and then reduced in a H₂ stream at this temperature

TABLE 3
Ethylene and Hydrogen Titrations over Catalysts 5, 6, and 7

E_1 (μmol)	HT (μmol)	E_2 (μmol)	HC(E) (μmol)	HN (NAH)	H/Pt	HT/ E_2
Catalyst 5 (0.47% Pt/ γ - Al_2O_3)						
11.34 ^a				2.25		
13.02 ^b	10.20	3.57	6.63	2.59	1.32	2.9
Catalyst 6 (0.52% Pt/ η - Al_2O_3)						
17.49 ^c	10.28	3.82	6.46	2.33	0.84	2.7
	11.15	3.77	7.38		0.96	3.0
	11.05	3.75	7.30		0.95	3.0
	11.15	3.74	7.31		0.95	3.0
18.07 ^c	11.34	3.62	7.72	2.35	1.00	
	10.66	3.67	6.99		0.90	
Catalyst 7 (0.6% Pt/ SiO_2)						
4.26 ^d	2.15	0.8	1.35	1.11	0.35	2.7
	2.08	0.71	1.37		0.36	2.9

^a First ethylene titration. Hydrogen reduction at 673 K for 13.5 h.

^b Second ethylene titration, after 10 min of H_2 retreatment at 298 K.

^c The same treatment as on catalyst 5, but after the reduction step in H_2 at 673 K, the catalyst was cooled down in H_2 flow instead of He and swept with carrier gas for 15 min.

^d H_2 reduction at 673 K for 10 min.

for 10 min. Next, the reactor was cooled to the reaction temperature, 273 K, in a N_2 stream. Gas samples taken during the flow experiments were analyzed using the online gas chromatograph.

At the end of the first run, the catalyst was again heated to 673 K in a N_2 stream and subjected to one of the following treatments: (I) catalyst reduction in a H_2 stream at 673 K for 1 h or (II) exposure to an oxygen stream for 1 h at 673 K and then reduction in a H_2 stream at 673 K for 1 h. After H_2 treatment, the catalyst was cooled to the reaction temperature in an inert gas stream and the reaction was again carried out. Similar procedures were followed for the last step, i.e., after 5 h of hydrogen treatment.

RESULTS

Table 3 shows the results obtained on catalysts 5, 6, and 7 as typical ones. A sample of catalyst 5, containing 10.1 μmol of Pt, was dried in a stream of carrier gas at 393 K for 2 h. It was then heated to 673 K in a H_2

stream at a heating rate of 10 K/min and kept at this temperature for 13.5 h. After this treatment, the H_2 flow was changed to He carrier gas and the catalyst was cooled to room temperature. At this temperature, the surface hydrogen was titrated with pulses of ethylene. Only ethylene and ethane were detected. A HN value of 2.25 was obtained.

In order to measure the hydrogen loss during the cooling in He flow, a source of error, the catalyst was treated with a H_2 stream for 10 min, followed by a He sweep for 10 min. The ethane produced during this ethylene titration, E_1 , which equals the HN value, increased by 15%. Right after this second ethylene titration the catalyst was titrated with pulses of hydrogen, HT. A total of 10.2 μmol of H_2 produced 3.57 μmol of ethane while 6.63 μmol of adsorbed H_2 remained on the surface, HC(E), which corresponds to a H/Pt ratio of 1.32.

Results on catalyst 6 are also shown in Table 3. This catalyst was subjected to the

TABLE 4
Dependence of HN and H/Pt Values on Hydrogen Reduction Time at 673 K

Reduction time (h)	Catalyst 7 (0.6% Pt/SiO ₂)		Catalyst 8 (0.5% Pt/Al ₂ O ₃)		Catalyst 9 (6.3% Pt/SiO ₂)	
	HN	H/Pt	HN	H/Pt	HN	H/Pt
0.25	1.10	0.37	1.2	0.83	1.85	0.91
1.00	—	—	2.6	0.84	1.86	0.90
5.00	1.17	0.35	—	—	—	—
10.00	—	—	4.3	0.73	—	—

same treatment as catalyst 5 but it was cooled in a H₂ stream instead of He after the reduction step in H₂ at 673 K was carried out. The E₁ value was 17.49 μmol C₂H₆, which corresponds to a HN value of 2.33. Three successive determinations of HT and E₂ show the high reproducibility of HC(E) obtained by ethylene titration with hydrogen pulses. A second run on a fresh sample of the same catalyst shows the reproducibility of the HC(E) values.

Table 4 shows the effect of increasing time in H₂ treatment on the HN value and the H/Pt ratio on catalysts 7 (0.5% Pt/SiO₂), 8 (0.5% Pt/Al₂O₃), and 9 (6.3% Pt/SiO₂). It is observed that for alumina-supported catalysts, HN values increase with reduction time while the H/Pt ratio—obtained from HC(E) values—remains constant and that HN values do not change with the hydrogen treatment time for silica-supported catalysts.

Table 5 shows two values of hydrogen chemisorption, HC(E) and HC, for a set of catalysts. The hydrogen chemisorption during hydrogen titration of adsorbed ethylene, HC(E), was calculated by the difference HT - E₂, and HC was measured by direct chemisorption by pulse, as described above. To ensure that the HC and HC(E) values corresponded to the same catalyst state, both were determined in the same run: First, the direct chemisorption of hydrogen, HC, was carried out on the reduced and cleaned catalyst; a titration with ethylene removed the adsorbed hydrogen and saturated the

surface with olefin; and then the procedure followed from step 2 of the sequence described in Table 2. The values of HC(E) reported are averages after several cycles of hydrogen and ethylene titrations. It is observed that both HC and HC(E) values are very similar for alumina-supported catalysts. In contrast, for the silica-supported catalysts the HC(E) value is less than HC.

After the alumina-supported catalysts were reduced at high temperature (673 K, in this work), subsequent treatments by ethylene, hydrogen, or oxygen titrations at room temperature did not significantly change the value of HC(E). For instance, catalyst 3 titrated repeatedly with ethylene and hydrogen, including TPD of hydrogen up to 723 K, showed only a drop of the HC(E) value from 8.6 to 7.1. The presence of oxygen at high temperatures was avoided to evaluate the poisoning role of carbonaceous residues.

Table 6 and Figures 1, 2, and 3 show the effect of the reduction time in a H₂ stream on the initial activity for ethylene hydrogenation measured in a flow reactor at 273 K. This effect was studied on catalysts 5, 6, and 7 using treatments I and II as described above. The activity decreased steadily during the reaction. The initial points of the curves follow the deactivation law $N = N_0 e^{-at}$ (27); the initial activity was then calculated for $t = 0$. The turnover frequencies were calculated twice, taking HC(E) and HN as measures of the number of active sites.

TABLE 5
Hydrogen Titrations (Step 2)

Catalyst	%Pt	HT (μmol)	E ₂ (μmol)	HC(E) (μmol)	HC (μmol)	H/Pt	HT/E ₂
1	0.28	7.7	2.7	5.0	4.9	1.5	2.9
2	0.53	14.3	4.9	9.4	9.4	1.4	2.9
3	0.57	13.1	4.5	8.6	8.6	1.3	2.9
3 ^a	0.57	11.3	4.2	7.1	ND	1.1	2.7
4	0.42	5.9	2.2	3.7	3.3	0.7	2.7
5	0.47	4.27	1.54	2.73	2.78	0.9	2.8
6	0.52	11.12	3.75	7.37	7.40	0.95	3.0
7	0.60	2.0	0.67	1.33	3.12	0.35 ^d	3.0
8	0.5					0.8	
9 ^b	6.3				6.0	0.75	
9 ^c					14.4	1.8	

Note. ND, not determined.

^a Catalyst 3 after 6 days of use. A large number of ethylene and hydrogen titrations, temperature-programmed desorptions (TPD), and reductions were performed on catalyst 3. The presence of oxygen and temperatures higher than 720 K were avoided throughout this period.

^b 50 mg of catalyst in hydrogen at 673 K, 10 min; 5 h in Ar at 673 K.

^c Same sample, TPD (10 K/min) up to 673 K. Confined overnight in Ar and then another TPD up to 673 K.

^d The H/Pt ratio calculated from direct hydrogen chemisorption (HC) gives a value of 0.8.

DISCUSSION

The HC Determination

Table 5 shows that on Pt/Al₂O₃ catalysts the values of chemisorbed hydrogen determined by ethylene titration with hydrogen agree very well with those directly determined by hydrogen adsorption on clean catalysts. On Pt/SiO₂, HC(E) is markedly less than HC. Catalyst 7 shows a H/Pt ratio of 0.80 when determined by direct hydrogen chemisorption; nevertheless, when ethylene left on the surface by the first set of pulses is titrated with hydrogen pulses, the corresponding H/Pt ratio is only 0.35. Similar considerations can be applied to catalyst 9 (Tables 4 and 5). The reason for the difference is that ethylene is irreversibly and inactively adsorbed on a fraction of the catalyst surface. Morrow and Sheppard (28) detected these residues spectroscopically. The high reproducibility found for the repetition step 3–step 2 cycle (Table 3) shows that this ethylene acts as a true poison and that from the very beginning only a fraction of the

catalyst surface will be active for olefin hydrogenation.

The advantage of measuring the active hydrogen by the reaction itself after the catalyst reduction at high temperature cannot be overestimated. The state of the so-called "clean surface" of a supported metal catalyst is far from known. A good example is what happened with EUROPT-1, as seen in Table 5. When the authors of this paper applied the cleaning method used by most of the laboratories participating in Part 4 of Ref. (17)—5 h at 500°C in flowing carrier—the value found for the HC determined by direct adsorption of hydrogen agreed very well with the values of Table 1 of the quoted reference, but when the catalyst was left confined overnight and then swept with carrier and heated to 673 K before cooling to room temperature, the HC value climbed to more than twice the former. This was discussed previously by Tsuchiya *et al.* in their work on platinum black (11). They found that to obtain reproducible results, they had to use a four-step

TABLE 6

Effect of the H₂ Reduction Time at 673 K on the Initial Catalytic Activity for Ethylene Hydrogenation

Catalyst	Treatment	Reduction time (h)	H/Pt	HN	Turnover ^a frequency (s ⁻¹)	Turnover ^b frequency (s ⁻¹)
5	I	0.17	0.72	0.87	7.1	5.8
		1.0	0.71	1.55	10.2	4.9
		5.0	0.71	2.05	12.1	4.1
5	II	0.17	0.75	0.84	7.1	6.3
		1.0	0.76	1.95	13.6	5.3
		5.0	0.76	2.68	^c	—
6	I	0.17	0.91	0.90	6.8	6.9
		1.0	0.86	1.80	9.5	4.5
		5.0	0.85	2.20	12.4	4.7
6	II	0.17	0.90	0.94	6.8	6.9
		1.0	0.87	2.35	14.3	5.4
		5.0	0.86	2.96	^c	—
7		0.17	0.33	1.13	7.0	2.0
		1.0	0.33	1.20	6.9	1.0
		5.0	0.33	1.20	6.9	1.0
Reaction conditions			Catalyst 5 and 6		Catalyst 7	
Ethylene partial pressure			7.33 kPa		6.40 kPa	
Hydrogen partial pressure			51.33 kPa		10.0 kPa	
Nitrogen partial pressure			42.66 kPa		84.93 kPa	
Flow of mixture = 100 cm ³ /min						
Reaction temperature = 273 K						

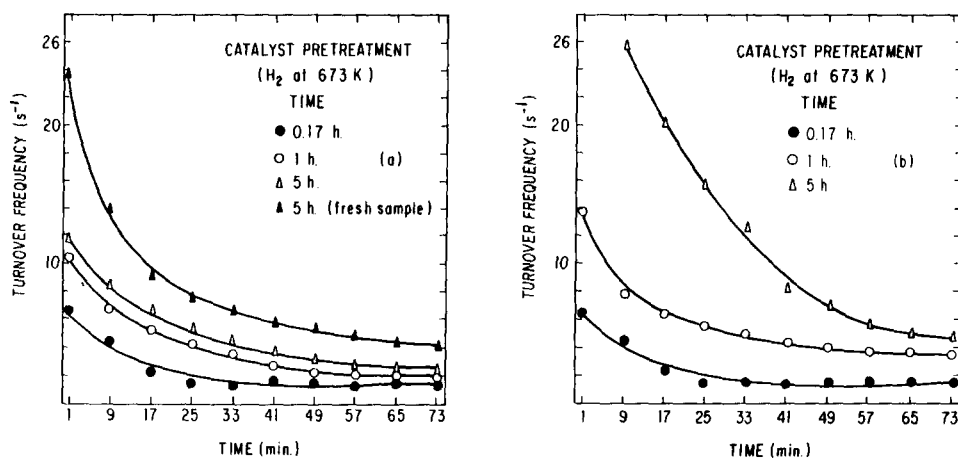
^a HC was taken as the measure of the number of active sites.^b HN was taken as the measure of the number of active sites.^c Initial conversion = 100%.

FIG. 1. Catalytic activity as a function of time for ethylene hydrogenation to ethane in a flow microreactor over catalyst 5. Reaction temperature: 273 K. (a) Treatment I. (b) Treatment II (see text).

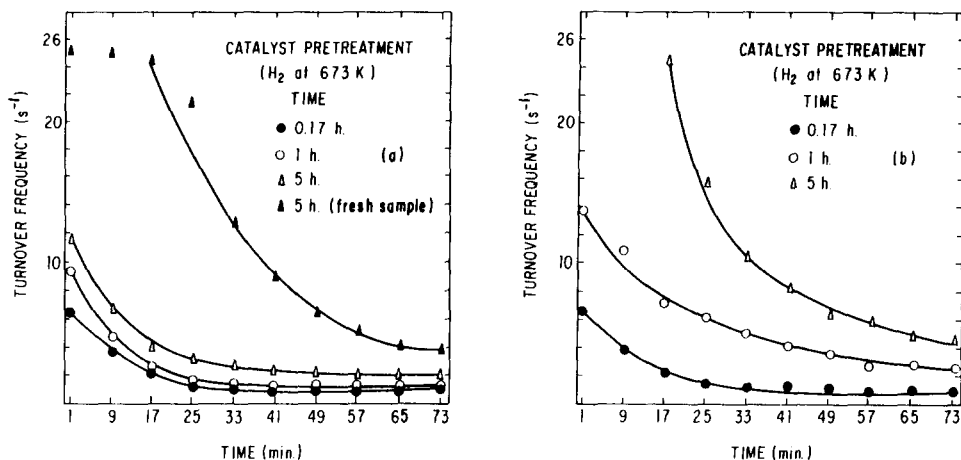


FIG. 2. Catalytic activity as a function of time for ethylene hydrogenation to ethane in a flow microreactor over catalyst 6. Reaction temperature: 273 K. (a) Treatment I. (b) Treatment II (see text).

procedure, like that used in this work; (1) using a TPD up to $500^{\circ}C$; (2) maintaining the catalyst at this temperature in a nitrogen stream for 20 min before cooling it; (3) confining the catalyst overnight at room temperature; and (4) before the next run, evacuating the catalyst to less than 10^{-5} Torr for 30 min, at room temperature.

An additional advantage in using hydrogen and ethylene titrations is that the reac-

tion product, ethane, is collected and measured quantitatively.

The HT/E_2 Ratio

Tables 3 and 5 show that this ratio, i.e., the ratio between the total hydrogen amount necessary to produce ethane from the adsorbed ethylene and that needed to saturate the surface, and the ethane produced by the ethylene actively adsorbed is constant throughout and its value is about 3, in agreement with the reaction: $3H_2(g) + C_2H_4(s) = C_2H_6(g) + 4H(s)$.

That is, one actively adsorbed ethylene molecule statistically blocks four hydrogen sites.

Sources of Error

The hydrogen loss and the ethylene self-hydrogenation were explored as sources of error in the HN and HC(E) determinations.

The amounts of ethane produced in the first ethylene titration, E_1 , were lower when the catalysts were cooled in argon than when they were cooled in hydrogen. This is an indication that a fraction of the H_2 active for the hydrogenation desorbs during the cooling in argon. To avoid this desorption, the catalysts must be cooled in H_2 .

To evaluate the effect of ethylene self-

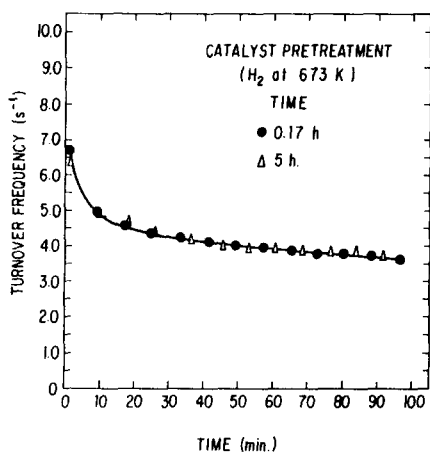


FIG. 3. Catalytic activity as a function of time for ethylene hydrogenation to ethane in a flow microreactor over catalyst 7. Reaction temperature: 273 K.

hydrogenation, a sample of clean catalyst was saturated with ethylene. The reaction showed only traces of ethane, which indicates that ethylene self-hydrogenation is negligible at room temperature. This fact has already been pointed out by Sermon and Bond for temperature of 370 K (29).

The high reproducibility and consistency of HC(E) and HC (Table 5) and that of the last column of Table 6 show that any other source of error can be considered negligible.

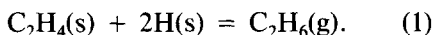
Mechanism of the Ethylene

Hydrogenation on Supported Platinum Catalysts

Ethylene hydrogenation catalyzed by platinum is a fast reaction (30–32). To obtain kinetic information it is necessary to carry out the reaction at temperatures near or below 273 K. The reaction order is 1 for hydrogen and between 0 and –0.5 for ethylene. This range can be attributed to the experimental conditions.

Recently, Soma (33) found a maximum value in the reaction rate at 203 K for increasing partial pressure of ethylene at a constant pressure of hydrogen. This suggests that a high partial pressure of ethylene should play an inhibitory role.

From analysis of the work of Horiuti and Polanyi (34), the consensus is that the reaction occurs by a Langmuir–Hinshelwood mechanism, that is, with the two chemisorbed species:

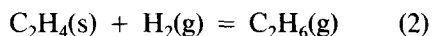


Soma measured the coverage degree of the catalyst surface by using the 2120 cm^{-1} infrared band for the reversibly adsorbed hydrogen atoms and by using the 1205 cm^{-1} band of the π complex of ethylene adsorbed on the metal (33, 35). Soma also found that the reaction ceased after evacuation of the gas phase, even in those cases in which the surface was still saturated with hydrogen and ethylene. This fact was verified by us.

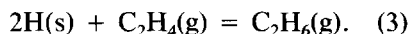
A pulse of $8.3\text{ }\mu\text{mol}$ of ethylene was injected over a charge of Pt/Al₂O₃ catalyst containing $12.5\text{ }\mu\text{mol}$ of Pt and $22.8\text{ }\mu\text{mol}$ of

reactive hydrogen atoms (HN = 1.8). The only product collected was ethane, $5.8\text{ }\mu\text{mol}$. The catalyst retained $11.2\text{ }\mu\text{mol}$ of hydrogen atoms and $2.5\text{ }\mu\text{mol}$ of ethylene. After the analysis was over (ca. 10 min) the refrigerant bath was replaced and the desorbing products from the reactor were collected during 1 h. Analysis of the trap content gave only $1.1\text{ }\mu\text{mol}$ of ethane. Immediately a new pulse of ethylene was injected on the catalyst; the products were ethylene and $1.2\text{ }\mu\text{mol}$ of ethane. The rate of desorption of hydrogen at room temperature was measured in a separate experiment. The same amount of catalyst was pretreated as the previous one and left 1 h in an argon flow of 30 ml/min. The desorbed hydrogen ($1.1\text{ }\mu\text{mol}$) was measured by resaturating the surface with hydrogen pulses. This value must be considered a lower limit of the amount of desorbed hydrogen because hydrogen pulses do not restore the totality of the adsorbed hydrogen coming from reduction. These results strongly suggest that the $1.2\text{ }\mu\text{mol}$ of ethane collected after 1 h of trapping was produced by the desorbed hydrogen coming from the gas phase.

Titration of the surface saturated in ethylene with hydrogen pulses may be described by the reaction



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Rienacker, studying the hydrogenation of butadiene on nickel film, as described by Panchenkov and Lebedev (36), concluded that the absence of a growth in the electrical resistance of the film during the course of the reaction indicates that the butadiene is not adsorbed in the presence of hydrogen, and that the reaction proceeds between the adsorbed hydrogen atoms and the molecules of butadiene approaching them from the gaseous phase.

All these facts suggest that the global re-

action occurs by coparticipation of reactions (2) and (3). The $\text{H}_2(\text{g})$ and $\text{C}_2\text{H}_4(\text{g})$ terms do not exclude the possibility that both species are in some adsorbed state before they react. The reaction occurs if adsorbed ethylene and hydrogen gas or adsorbed ethylene and hydrogen gas are present, but it stops in the absence of reactants in the gas phase. Even if the hypothesis of an Eley-Rideal mechanism is neglected, it appears that there is not a single reaction route for ethylene hydrogenation. The increase in initial activity for Pt/ Al_2O_3 catalysts with the time of treatment of hydrogen may be attributed to the increase in the number of sites on which reaction (3) occurs.

The Number of Active Hydrogen

1. *Clean catalysts.* On the Pt/ Al_2O_3 catalysts the HN value reaches a maximum fixed value. After about 5 h of treatment in hydrogen at 673 K, the HN value agrees within experimental error with that obtained after an overnight treatment. The question that arises is the physical meaning which we call the Number of Active Hydrogen (NAH). The results of the flow reaction measurements (Table 6 and Figs. 1 and 2) show that the quantity kinetically significant is HN and not the H/Pt ratio calculated from HC. For alumina-supported catalysts, the NAH is equal to HN.

The activity of Pt/ SiO_2 catalysts may be due to only a fraction of the surface platinum atoms because the greater part of them are irreversibly inhibited by the olefin from the very beginning of the reaction. The activity does not change with the time of catalyst reduction. In this case the situation is not as clear as the alumina support, but we believe that for SiO_2 -supported catalysts the NAH is represented by H/Pt measured by titration of adsorbed ethylene with hydrogen gas, HC(E), because this quantity does not change after successive cycles of ethylene-hydrogen titrations, showing that the primary inhibition is fast and fixed.

2. *Poisoned catalysts.* Leclercq and Boudart (37), studying the catalytic hydro-

genation of cyclohexene on supported platinum, found that for clean and sulfur-poisoned catalysts, only the HC values among the H_2 - O_2 adsorption and titration methods correlated well with activity on clean and poisoned catalysts. Very probably the presence of oxygen during the adsorptions and titrations modified the catalyst state. With ethylene titrations these effects are avoided because the olefin is one of the participants in the process, as proved by Leclercq *et al.* (38).

The Hydrogen Numbers and the Nature of the Active Sites

In the pulsewise hydrogenation of 1-butene at room temperature over catalysts of platinum supported on porous glass, Augustine and Warner (22) adopted the criterion of simple action for the hydrogen atoms. Augustine *et al.* (23) recently found much higher values of HN than those obtained in this work. Twenty-four successive pulses of 1-butene had total conversion, that is, $10.7 \mu\text{mol}$ for $1.1 \mu\text{mol}$ of total Pt in the reactor, as shown in Fig. 3 of Ref. (23). The conversion started to fall from the 25th pulse, but Augustine *et al.* still continued titrating large amounts of hydrogen, without hydrogen in the gas phase. They explained these results by a fast return of the hydrogen to the metal (*fast reverse spillover*). Augustine and Warner (22) classified the surface atoms as a function of the degree of coordinative unsaturation in three groups based on the structure of Pt complexes. These are: ^1M (step), ^2M (edge), and ^3M (kink). They also evaluated the proportion of each type of surface Pt atoms on the catalyst. Defining a platinum atom as the active site, they propose that the only type of Pt that is able to hydrogenate the olefin completely is the ^3M type, and that hydrogen migration between the different types does not take place. This last conclusion was based on their results and those from Tsuchiya *et al.* (39). From these hypotheses and the results of the present work, it is very difficult to explain how $1.1 \mu\text{mol}$ of total platinum containing only

0.163 μmol of ^3M sites can hydrogenate 0.446 μmol of olefin per pulse.

The complexity of the surface structure of the alumina, the highly dispersed state of the metal, the possibility of strong metal-support interaction effects, and the lack of enough spectroscopic information about adsorbed hydrogen states make it necessary to consider any model with extreme caution. Nevertheless, there is a corpus of experimental evidence that can give some clues on the matter:

—The reaction stops in the absence of ethylene or hydrogen in the gas phase because at room and lower temperatures hydrogen migration is not kinetically significant.

—TPD spectra (11, 20, 21) show that recombination and desorption of hydrogen are very low at room and lower temperatures.

—Values of HN greater than 2 in Pt/Al₂O₃ indicate that the support plays an active role, whatever the supposed stoichiometry.

—The singular conditions that are necessary to make active sites created by spillover on the support itself (i.e., high reaction temperature, long induction time) are not present in this work.

It is worth examining the possibility of reverse spillover. Suppose that all the hydrogen atoms that enhance the initial catalyst activity were spilt over during the catalyst pretreatment. If the mildest case is examined, i.e., catalyst 5 with 0.17 h of hydrogen reduction (Fig. 1a), it can be seen that it reaches the steady condition at about 25 min (turnover frequency, 2 s^{-1}). The area of the triangle defined above the line 2 s^{-1} corresponds to about 3000 μmol of ethane/ μmol of Pt. This overproduction is not possible without a source of hydrogen, keeping in mind that the titration of hydrogen with ethylene (HN = 0.87) lasts at least 1 h. Suppose now that during the flow reaction the metal atoms perform a triple function: hydrogenate ethylene, dissociate hydrogen, and, spill it over the support. This spillover hydrogen will never return to metal clusters, because the surface concentration of hydro-

gen around platinum clusters would be the greatest. Consequently reverse spillover, if it exists at room temperature in Pt/Al₂O₃ catalysts, is not kinetically significant.

We note that this work concerns catalysts in their initial state in order to study catalysts (initial activity). Our goal is the elucidation of the state of the metal and its interactions with the support. For catalysts operating at steady state, determination of the nature of the active sites is a far more complex task as suggested by Zaera and Somorjai (40) and other workers. The large decreases in activity that can be seen in Figs. 1, 2, and 3 strongly suggest that HN, HC, OT, HT, adsorption of CO, and any other method applied on clean catalysts are not the proper methods for measuring active sites in steady catalysts.

CONCLUSIONS

Probe reactions are simple and useful tools to study the active surface of catalysts. The ethylene hydrogenation by pulses on Pt/Al₂O₃ and Pt/SiO₂ revealed some interesting features of these catalysts and the reaction itself:

Pt/Al₂O₃ Catalysts

—The initial catalyst reactivity increases with the time of catalyst hydrogenation at high temperature. A measure of that reactivity is obtained by titration with ethylene pulses of the active hydrogen at room temperature (NAH). Catalyst reactivity is proportional to NAH values and not to the H/Pt ratio calculated from HC.

—NAH values greater than 2 suggest coparticipation of the support.

—A HT/E₂ ratio of about 3 indicates that one ethylene molecule actively adsorbed involves four hydrogen sites.

—The reaction does not occur at a kinetically significant rate when both olefin and hydrogen are irreversibly adsorbed. It is supposed that the global reaction takes place by coparticipation of two reactions with at least one of the reactants in the gas phase with reaction (2) (see text) the prevail-

ing one, as indicated by the zero order in ethylene. The increase in the initial catalyst reactivity may be attributed to a greater contribution of reaction (3) to the global reaction.

Pt/SiO₂ Catalysts

—The activity of Pt/SiO₂ is due to only a fraction of the surface platinum atoms because a substantial part of them are irreversibly inhibited by the olefin from the very beginning of the reaction. The NAH is probably represented by H/Pt measured by titration of adsorbed ethylene with hydrogen HC(E).

—The procedure for cleaning the catalyst surface is of great importance to the HC value determined by direct chemisorption of hydrogen. The HC value can change by a factor of 2 or more depending on the cleaning procedure.

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