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CHARACTERIZATION OF SUPPORTED PLATINUM BY A PROBE REACTION

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A probe reaction is proposed to measure the number of active hydrogen atoms on platinum supported catalysts. Adsorbed hydrogen is titrated by ethylene pulses. The reaction product, ethane, desorbs quantitatively and can be measured directly by gas chromatography. This determination yields the total number of active hydrogen atoms per Pt atom (NAH). The method was tested on a set of Pt/Al_2O_3 catalysts. The results show that NAH can exceed several times the number of metal atoms on the catalyst and increases with the time of catalyst treatment with hydrogen at high temperature. The 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 conventional methods.

1. Introduction

Numerous attempts have been made to relate the catalytic activity for olefin hydrogenation with the percentage of exposed metal on Pt/Al_2O_3 catalysts [1–18]. As a new approach to the problem, distinct from the chemisorption techniques mentioned in the papers cited above, the ethylene hydrogenation is proposed in this work as a probe reaction to count the number of active hydrogen atoms on the catalyst surface. The reaction is carried out *by pulses* of ethylene, *at room temperature*, on the catalyst saturated with hydrogen. The reaction product, ethane, is quantitatively desorbed and measured. Conversely ethylene adsorbed is then titrated with hydrogen pulses.

Previously Bond and Sermon [19] did propose 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 3 ways. First, the operation at 373 K decreases 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.

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Third, the large amount of olefin passing on 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 quantities of olefin that are sent sequentially to the surface. The Augustine and Warner method [22,23], which is more alike to that proposed here, since it uses the butene hydrogenation by pulse, at room temperature, is discussed below.

2. Experimental

CATALYSTS

The catalysts were prepared by the incipient wetness impregnation method. After the impregnation they were dried in air at 380 K in a rotating evaporator. The main characteristics and pretreatments of supports are summarized in table 1.

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) were used as carrier gases, and purified by passing them through alumina traps at 298 K. The alumina trap was dried in situ at 570 K. Hydrogen (Linde UHP, > 99.999%) or H_2 produced by an Elhygen generator were used for

Table 1
Characteristics and pretreatments of catalysts

Catalyst	wt% Pt	Support	Impregnation complex	Support pretreatment
1	0.28	γ-Al_2O_3	$(NH_4)_2PtCl_4$	NH_3 gas flow at room temperature on dried catalyst.
2	0.53	γ-Al_2O_3	H_2PtCl_6	Support suspended in a HCl solution before impregnation.
3	0.57	γ-Al_2O_3	H_2PtCl_6	none
4	0.42	η-Al_2O_3	$(NH_4)_2PtCl_4$	NH_3 gas flow at room temperature on dried catalyst.
5	0.47	γ-Al_2O_3	H_2PtCl_6	Dry support
6	0.52	η-Al_2O_3	H_2PtCl_6	Dry support

Support Surface areas: 160 m^2/g for γ-Al_2O_3; 155 m^2/g for η-Al_2O_3

the catalyst treatments. 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 HC

The experiments were carried out in a stainless steel apparatus designed to work either by pulses or continuous flow. The reactor used was a U-shaped Vycor tube, 6 mm O.D. The switching of gases was done 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 stainless steel U tube, 1/8″ O.D., filled in the middle with 20 cm of Chromosorb 102. When argon was used as carrier gas, the trap was cooled to 195 K and to 77 K when helium was used. The trapped gases were then injected to an online gas chromatograph, with a column of Chromosorb 102 kept at 303 K. A loop of 0.202 cm^3 (0.185 cm^3, NTP) was used as calibrated volume for the gas pulses.

The reactor was charged with 250 or 500 mg of catalyst, dried for 2 h at 390 K in Ar, heated up to 673 K (10 K/min) in carrier gas and then treated in H_2 through the desired time (10 min, 1 h, 5 h, overnight, etc.). The catalyst was cooled down to room temperature in hydrogen and then swept with carrier gas for 15 min. From this point on the measurements followed three successive pulse titrations. The notation used is defined in table 2.

Table 2

Sequence of titrations and notation: Subscript (a) means adsorbed, and the equations are descriptive only, not stoichiometric

Pt_t: total amount of platinum in sample, μmol
Step 1: First titration $H_{(a)} + C_2H_4 \text{- - - -} C_2H_6 + C_2H_{4(a)}$
E_1: 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.
$HN1$: stoichiometric ratio of adsorbed hydrogen titrated in step 1; $HN1 = 2E_1/Pt_t$. For Pt/Al_2O_3 catalysts, $HN1$ is also called NAH: number of active hydrogen atoms (see text).
Step 2: Second titration $C_2H_{4(a)} + H_2 \text{- - - -} C_2H_6 + H_{(a)}$
E_2: amount of ethane *formed* in the titration by H_2 of ethylene adsorbed at the end of step 1, μmol.
HT: amount of H_2 *consumed* in the second titration.
$HC(1)$: amount of H_2 *adsorbed* in the second titration; $HC = HT - E_2$, μmol.
H/Pt: stoichiometric ratio of hydrogen adsorbed at the end of the second titration: $H/Pt = 2HC/Pt_t$.
Step 3: Third titration $H_{(a)} + C_2H_4 \text{- - - -} C_2H_6 + C_2H_{4(a)}$
E_3: amount of ethane *formed* in the titration by ethylene of hydrogen adsorbed at the end of the second titration, μmol.
$HN2$: stoichiometric ratio of hydrogen adsorbed at the end of the second titration; $HN2 = 2E_3/Pt_t$.

Step 1: Hydrogen adsorbed on the catalyst was titrated with ethylene pulses until the amount of ethane formed was negligible (E_1, total amount of ethane produced). The first ethylene pulses produced most of the ethane in the titration. The stoichiometric ratio of adsorbed hydrogen titrated in this step is called $HN1$.

$$HN1 = 2(E_1)/\mathrm{Pt}_t.$$

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, $HC(1)$, is given by the difference between the amount of hydrogen consumed, HT, and the amount of ethane formed in the titration; that is:

$$HC(1) = HT - E_2.$$

Step 3: Hydrogen chemisorbed from step 2 was titrated with ethylene to give $HN2$, which is defined by the same relationship used for $HN1$.

Steps 2 and 3 has been frequently repeated 2 or 3 times to verify results reproducibility.

The amount of hydrogen chemisorbed by pulse, $HC(2)$, was measured by the following way: The catalyst treated with hydrogen at 670 K was cooled at room temperature in an Ar stream. Then it was heated again up to 670 K at a rate of 10 K/min. After this temperature was reached, the furnace was turned off, the inert gas stream was bypassed and the reactor confined overnight, by a four way valve. After that the reactor was reconnected to the gas stream and subjected to another TPD. After cooling down the catalyst to 298 K, pulses of 8.25 μmol of hydrogen were sent on the catalyst until constant peak area.

In some cases the catalyst remains, after the reduction, in a highly metastable state; in these conditions neither $HC(1)$ nor $HC(2)$ give reproducible results. The catalyst must be annealed by successive OT-HT cycles, as indicated by Menon [24], before to proceed with the measurements.

STUDIES OF CATALYTIC ACTIVITY

Initial rates of ethylene hydrogenation were measured in the reaction system modified to carry out flow reactions. The reactor was loaded with 10 mg of fresh Pt catalyst mixed with 190 mg of Vycor glass. The catalyst was dried in situ at 390–395 K in a N_2 stream (40 ml/min) for 2 h, heated up at 670 K and then reduced in a H_2 stream at this temperature for 10 min. Next, the reactor was cooled down to the reaction temperature, 273 K, in a N_2 or Ar 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 up to 670 K in a N_2 or Ar stream and subjected to one of the following treatments: (I) Catalyst reduction in a H_2 stream at 670 K for 1 h. (II) Exposure to an oxygen stream for 1 h at 670 K and then reduction in a H_2 stream at 670 K for 1 h. After H_2 treatment, the catalyst was cooled down 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.

3. Results

Table 3 shows the values E_2, $HC(1)$ and $HC(2)$ for a set of catalysts. The HC figures reported are average values after several determinations. It is observed that $HC(1)$ and $HC(2)$ values are very similar.

After the alumina supported catalysts were reduced at high temperature (670 K, in this work), posterior treatments by ethylene, hydrogen or oxygen titrations at room temperature did not change significantly the value of $HC(1)$, provided that the reactor temperature did not reach sintering temperatures. For instance, catalyst 3 titrated repeatedly with ethylene and hydrogen, including TPD of hydrogen up to 720 K, showed only a drop of the $HC(1)$, value from 8.6 to 7.1 μmol.

Table 4 shows the effect of the treatment time in a H_2 stream on the initial activity for ethylene hydrogenation measured in a flow reactor at 273 K. The effect of reduction time was studied for catalysts 5 and 6 following treatments I and II described above. The activity decreased steadily during the reaction. The initial points of the curves follow the deactivation law $N = N_0 e^{-\alpha t}$ [25]. The initial activity was then calculated for $t = 0$. Values of turnover frequency were

Table 3
Hydrogen titrations (step 2)

Catalyst	wt% Pt	HT μmol	E_2 μmol	$HC(1)$ μmol	$HC(2)$ 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	N.D.	1.1	2.7
4	0.42	5.9	2.2	3.7	3.3	0.7	2.7
5	0.47	4.3	1.5	2.7	2.8	0.9	2.8

N.D. This value was not determined.

(a): Catalyst 3 after six days of use. A large amount of ethylene and hydrogen titrations, temperature programmed desorptions (TPD) and re-reductions were performed on catalyst 3. The presence of oxygen and temperatures higher than 720 K were avoided through this lapse.

Table 4
Effect of the H_2 reduction time at 670 K on the initial catalytic activity for ethylene hydrogenation

Catalyst	Treatment	Reduction time (h)	H/Pt	*HN*1	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]	–

Reaction conditions

Ethylene partial pressure = 7.33 kPa.
Hydrogen partial pressure = 51.33 kPa.
Nitrogen partial pressure = 42.66 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*1 was taken as the measure of the number of active sites.

[c] Initial conversion = 100%

calculated twice, taking *HC* and NH1 as the measure of the number of active sites.

4. Discussion

THE *HC* DETERMINATION

Table 3 shows that on Pt/Al_2O_3 catalysts the hydrogen chemisorption values determined by titration with ethylene *HC*(1) agrees very well with those directly determined by hydrogen adsorption on clean catalysts, *HC*(2). Thus, we can talk about $HC = HC(1) = HC(2)$.

THE RATIO HT/E2

Tables 3 shows that this ratio, i.e. the ratio between the total hydrogen amount necessary to produce ethane from the adsorbed ethylene and 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:

$$3H_2(g) + C_2H_4(s) = C_2H_6(g) + 4H(s).$$

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

SOURCES OF ERROR

The hydrogen loss and the ethylene self-hydrogenation were explored as sources of error in the *HN*'s and *HC* determinations.

The E_1 values 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 always cooled in H_2.

To evaluate the effect of ethylene self-hydrogenation, a sample of clean catalyst was saturated with ethylene. The reaction products were trapped in liquid nitrogen for 1 h. The analysis showed only traces of ethane, which indicates that the ethylene self-hydrogenation is negligible at room temperature. This fact has already been pointed out by Sermon and Bond at 370 K [26].

The high reproducibility and consistency of *HC*(1) and *HC*(2) (table 3) and that of the last column of table 4 shows that any other source of error can be considered as negligible.

THE NUMBER OF ACTIVE HYDROGEN ATOMS, NAH, AND THE NATURE OF THE ACTIVE SITES

In a work of 1-butene hydrogenation by pulses at room temperature over catalysts of platinum supported on porous glass, Agustine and Warner [22] adopted the criterion of simple action for the hydrogen atoms. Agustine et al. [23] recently found much higher values of NAH than those obtained in this work. Twenty four successive pulses of 1-butene corresponding to a total conversion, of 10.7 mol for 1.1 mol of total Pt in the reactor, as shown in fig. 3 of ref. [23]. The conversion started to fall from the twentyfifth pulse, but they 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. These are: 1M (surface atoms), 2M (edge) and 3M (corner). 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 Pt type which is able to completely hydrogenate the olefin is the 3M type, and that the hydrogen migration between the different types does not take place. This last conclusion was based on their results and those from Tsuchiya et al. [27]. From these hypotheses and the results of the present work, it is very difficult to explain how 1.1 μmol of total platinum containing only 0.163 mol of 3M sites can hydrogenate 0.446 μmol of olefin per pulse.

The complexity of the surface structure of the alumina, the high disperse state of the metal, the possibility of metal support interactions, and the lack of enough spectroscopic information about adsorbed hydrogen states are compelling reasons for considering any model with extreme caution.

THE NUMBER OF ACTIVE HYDROGEN

On the studied Pt/Al_2O_3 catalysts the $HN1$ value reaches a maximum fixed value. After about 5 h of treatment in 670 K, the $HN1$ value agrees between the experimental error with that obtained after an overnight treatment. The question that arises is the physical meaning of the here called Number of Active Hydrogen (NAH). The results of the flow reaction measurements (last two columns of table 3) show that the catalytically significant quantity is the $HN1$ and not the H/Pt ratio calculated from HC. The fact that on Pt/Al_2O_3 there are several atoms of active hydrogen per metal atom show that the alumina is playing an important role on their generation. It is clear that for alumina supported catalysts, the *Number of Active Hydrogen Atoms*, NAH, is given by $HN1$.

5. Conclusions

The use of probe reactions is a simple and useful tool to study the active surface of catalysts. The ethylene hydrogenation by pulses upon Pt/Al_2O_3 revealed some interesting features of these catalysts and the reaction itself. The catalyst activity increases with the catalyst reduction time at high temperature. A measure of that activity is obtained by titration with ethylene pulses of the active hydrogen at room temperature (NAH). Catalytic activity in ethylene hydrogenation is proportional to NAH values and not to the H/Pt ratio calculated from hydrogen chemisorption. Moreover, NAH values greater than 2 suggest coparticipation of the support. Finally, the value of the ratio HT/E_2 of about 3 indicates that one ethylene molecule actively adsorbed involves 4 hydrogen sites.

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