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Highly Dispersed Rhodium/Polyphosphine Metal Catalysts: Catalytic Activity for Ethylene Hydrogenation

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Rhodium metal catalysts dispersed on polyphosphine supports were employed in the hydrogenation of ethylene. The reaction was studied in a flow reactor at 395 K and 1 atm. Turnover numbers ranged between 5.8×10^{-3} and 145×10^{-3} (molecules/sec surface atom) depending on phosphorus content. Reaction orders for olefin and hydrogen were about 0.0 and 1.0, respectively.

Correlations between specific activity N and phosphorus content for various samples are reported and suggest the existence of a strong phosphorus rhodium interaction which controls the catalytic activity. This was confirmed by chemisorption measurements and activation energy data. Typical activation energy values were 5 kcal/mol for phosphinated samples and 12 kcal/mol for nonphosphinated ones.

INTRODUCTION

In the preceding paper (*1*) we reported on the synthesis and characterization of some rhodium catalysts dispersed on styrene-divinylbenzene copolymers containing pendant phosphine groups. We observed that the obtainable metal particle dimensions are determined mostly by the number of phosphines present on the support. The phosphines control the growth of the metal particle through strong coordinative interactions. The relatively well-defined nature of the interaction between the support and the metallic surface makes these catalysts rather unusual. Hence, in this paper we wish to report their reactivity in the hydrogenation of ethylene with the aim of investigating the influence of the phosphine groups on the overall activity.

EXPERIMENTAL

The catalysts reported throughout this study have been described and characterized in the preceding paper. Hereafter, catalyst numbers will refer to Table 1 of the preceding paper for the sake of simplicity.

Kinetic studies were conducted in a flow microreactor made from an 8-mm-i.d. Pyrex glass tube immersed in a fluidized sand bath heated by an external oven. A small glass tube containing an Fe–Ko thermocouple was placed in the middle of the catalyst bed. No increase in the catalyst temperature was observed during the reaction. The unit was operated at a total pressure of 1 atm. The catalyst charges were small, usually 0.3 g or less, and the analyses of the exit gas were carried out with a Hewlett–Packard 5700 A gas chromatograph equipped with a thermal conductivity detector and with a HP 3927 electronic digital integrator. The reaction mixture was separated at 323 K in a 2-m-long 0.125-in.-diameter column packed with Porapak N. High space velocities of 2500–6000 h^{-1} were used to keep ethylene conversion less than 7–8% to approximate differential conditions.

A variety of tests including altering the particle size, altering the flow rate at constant space velocity, and diluting the catalyst with the support (*2*), confirmed the absence of diffusional limitations.

A standard pretreatment was used for all catalysts: samples were heated (4 K/min) in flowing H_2 to 395 K and left at this temperature for 3 h before cooling under flowing H_2

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to the chosen reaction temperature. Then the reactant gas mixture was flowed over the catalyst for 30 min prior to sampling products for analysis. If the analyses of consecutive runs were not reproduced, runs were continued until a stationary state of the catalyst was obtained (usually 1 h).

A previously described flow system (*3*) was used to measure the accessible rhodium area by oxygen–hydrogen titration (*4*).

Ethylene (99.95%) was used as received. Research purity hydrogen, helium, and argon were purified by passing through an Oxy-trap (Alltech) and a Molecur Sieve Trap at 78 K.

RESULTS AND DISCUSSION

The hydrogenation of ethylene was carried out at 393 K using, as standard conditions, a reactant mixture of ethylene and hydrogen at partial pressures of 0.18 atm and 0.29 atm, respectively. The rates of hydrogenation (r) (expressed as moles of ethane per hour per g · atom of metal) are reported in Table 1. All catalysts maintained a stable activity for as long as 40 h on stream and no change in the metal dispersion was found at the end. These catalysts showed excellent reproducibility even when discharged and reused after a certain time, provided that the same pretreatment conditions were used. For example, rhodium-9, under the conditions reported in Table 1 and depending on whether it was freshly prepared or reused after two weeks or six months, gave the following r values: 0.31, 0.30, and 0.33, respectively.

TABLE 1

Kinetic Data for Ethylene Hydrogenation

Catalyst	r at 395 K (mol/h · g atom of Rh)	x	y	E (kcal/mol)
Rh-1	0.35	0.01	1.0	5.7 ± 0.3
Rh-2	0.19	0.04	1.0	5.0 ± 0.3
Rh-3	0.32	0.0	0.98	5.1 ± 0.3
Rh-4	0.35	0.0	0.91	5.1 ± 0.2
Rh-5	0.20	0.01	0.97	5.3 ± 0.3
Rh-6	0.20	0.04	0.96	4.5 ± 0.4
Rh-7	0.41	0.02	0.92	5.6 ± 0.3
Rh-8	0.58	0.04	0.99	4.8 ± 0.3
Rh-9	0.32	0.05	0.96	5.1 ± 0.3
Rh-10	1.40	0.01	0.92	4.7 ± 0.2
Rh-11	1.47	0.03	0.93	5.4 ± 0.3
Rh-12	1.37	0.0	0.96	5.2 ± 0.3
Rh-13	1.26	0.02	0.94	6.1 ± 0.3
Rh-14	2.55	0.02	0.94	12.3 ± 0.5
Rh-15	1.50	0.0	0.96	12.1 ± 0.6
Rh-16	79.4	0.0	1.0	12.8 ± 0.6

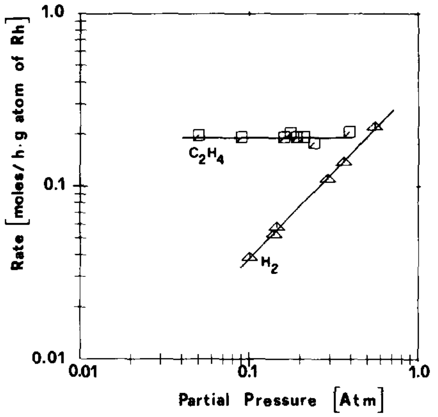

FIG. 1. Dependence of the rate of ethylene hydrogenation on the partial pressure of olefin and hydrogen for Rh-2.

The dependence of the rate of hydrogenation on the partial pressures of ethylene and hydrogen was determined by the slope of log–log plots of the rate against the reactant partial pressure. Examples of these data are shown in Figs. 1 and 2 for samples Rh-2 and Rh-15. The rate of ethane formation can be described according to the usual empirical equation

$$r = kp_E^x \cdot p_{H_2}^y$$

The values of the exponents x and y, calculated by least squares fitting of the experimental points, are reported in Table 1. For all catalysts, the exponents x and y were found ranging from 0.0 to 0.05 and from 0.9 to 1.0, respectively. These results are in good agreement with the values usually found for the hydrogenation of ethylene at low temperature with group VIII transition metal catalysts (*5*) and suggest that the acti-

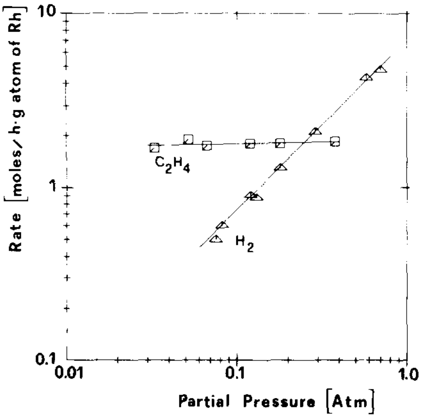

FIG. 2. Dependence of the rate of ethylene hydrogenation on the partial pressures of olefin and hydrogen for Rh-15.

TABLE 2

Turnover Number for Ethylene Hydrogenation as a Function of Dispersion Parameters

Catalyst	$P_{exp}{}^{s\,a}$	$Rh_s(\%)^b$	P/Rh_s	$N \cdot 10^3$ at 395 K (molecules/s · surf. atom)
Rh-1	0.90	0.9	5.8	10.7
Rh-2	0.93	9.2	2.3	5.8
Rh-3	0.88	0.5	10.7	10.1
Rh-4	0.82	1.3	4.3	11.9
Rh-5	0.95	0.5	8.4	6.0
Rh-6	0.89	0.9	4.5	6.3
Rh-7	0.87	1.7	2.3	13.1
Rh-8	0.66	3.3	1.2	24.7
Rh-9	0.81	2.4	2.3	11.1
Rh-10	0.71	0.4	4.6	55.9
Rh-11	0.68	0.7	2.4	60.0
Rh-12	0.53	1.1	1.6	72.2
Rh-13	0.35	1.7	0.9	100
Rh-14	0.49	0.5	—	145
Rh-15	0.30	2.0	—	139
Rh-16	0.82	1.7	—	2690

[a] $P_{exp}{}^s$ = Percentage of exposed rhodium calculated from SAXS particle size distribution function (see Table 2, Ref. (*1*)).

[b] $Rh_s(\%)$ = Weight percent of Rh exposed.

vation of hydrogen is the slow step in this process. The presence of the phosphine groups in catalysts Rh-1–Rh-13 does not appear to influence the mechanism of the hydrogenation reaction. In fact, as Table 1 clearly shows, the same reaction orders apply also to Rh-14 and Rh-15, which do not contain phosphines, and to Rh-16, for which a conventional silica support was employed.

The reaction rate *r* calculated in the individual catalysts for the total Rh content can be rearranged, on the basis of dispersion data reported in the previous paper, in terms of specific activity *N* for superficial Rh atoms (Table 2). This conversion, besides the general advantage of correlating the observed activity with the fraction of exposed metal atoms which are actually responsible for the catalysis, is particularly appropriate in our case, since the presence of phosphine surrounding the metal particle is expected to influence the general chemical reactivity of these catalysts.

A better understanding of this correlation can be gained from Fig. 3, where the turnover number *N* has been plotted versus the weight percent of Rh exposed ($Rh_s\%$) for three series of catalysts having different phosphorus contents. As the number of active sites increases, an increasing trend for the specific activity is clearly discernible for P 0.5% and, to a lesser extent, for P 1.2%. When the phosphorus content is sufficiently high (P 1.7%), the activity is practically constant independent of the weight

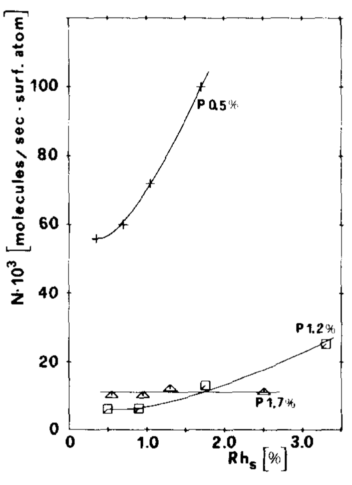

FIG. 3. Correlation between turnover number and weight percent of Rh exposed for three series of catalysts.

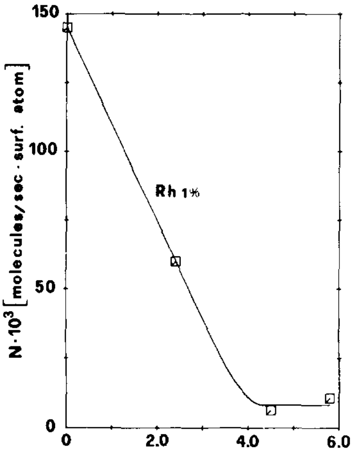

FIG. 4. Relationship between turnover number and phosphorus/rhodium (surface) ratio for catalysts with the same metal loading.

percent of Rh exposed. The saturation effect on the catalytic activity due to the presence of phosphines is more evident in Fig. 4, where N is plotted against the P/Rh_s ratio for a constant percentage of metal.

All these data indicate that the already observed strong interaction between the phosphine groups and the surface Rh atoms, which is the key parameter in determining the particle size dimensions, has also a fundamental role in the control of the catalytic activity. In fact, the number of metal active sites available for hydrogen activation is statistically lower because of the coordination of the phosphines on the metal surface. Further evidence for the role of phosphorus arises from the activity of the two catalysts (Rh-14 and Rh-15) supported on styrene-divinylbenzene only. The calculated turnover numbers are 145×10^{-3} and 139×10^{-3}, respectively. Since the two samples differ significantly in metal content and dispersion ($P_{exp}{}^{s}$), the very close values found for their catalytic activities confirm the already known (*6*) lack of sensitivity of this hydrogenation reaction to physical factors. Therefore, the drop in activity which takes place upon doping the support surface with increasing amounts of phosphorus is to be ascribed mostly to chemical factors.

The percentage exposed and the specific surface calculated from X-ray analyses form a reliable description of the physical state of the metallic particles, which does not take into account the chemical factors which influence the catalytic activity.

An attempt was made to measure the number of active sites actually available in our catalysts through chemisorption data. The relatively low thermal stability (*1*) of our supports prevented the use of high temperature treatment which is generally required, prior to chemisorption experiments, to produce an initially clean metal surface. To ascertain whether a cleaning procedure at temperatures below 445 K was sufficient to yield reliable chemisorption data, we calibrated the method by carrying out two sets of experiments at 413 K and 623 K with the reported Rh/SiO_2 catalyst (Rh-16). Since direct chemisorption of hydrogen is inadequate for the assessment of dispersion of Rh in dispersed samples because of multiple chemisorption observed by several authors (*7*), an oxygen–hydrogen titration was chosen. The hydrogen uptakes relative to the two different temperatures of cleaning treatment were 252 and 259 ml STP/g metal, respectively. From these values the corresponding surface areas could be calculated, according to the stoichiometry reported by Yao *et al.* (*8*), as being 233 and 240 m^2/g. The arbitrary choice of a O_2/Rh = 1.5 stoichiometry does not affect the meaning of our data, because the difference introduced by using a different stoichiometry does not exceed 25% (*9*). Moreover, our aim is to compare the different behaviors of the individual catalysts toward chemisorption, rather than measuring the absolute value of the surface area for which X-ray data are available.

The agreement between the two chemisorption data at different temperatures and the corresponding surface area compared with that derived from X-ray analyses, confirms the reliability of the method even for

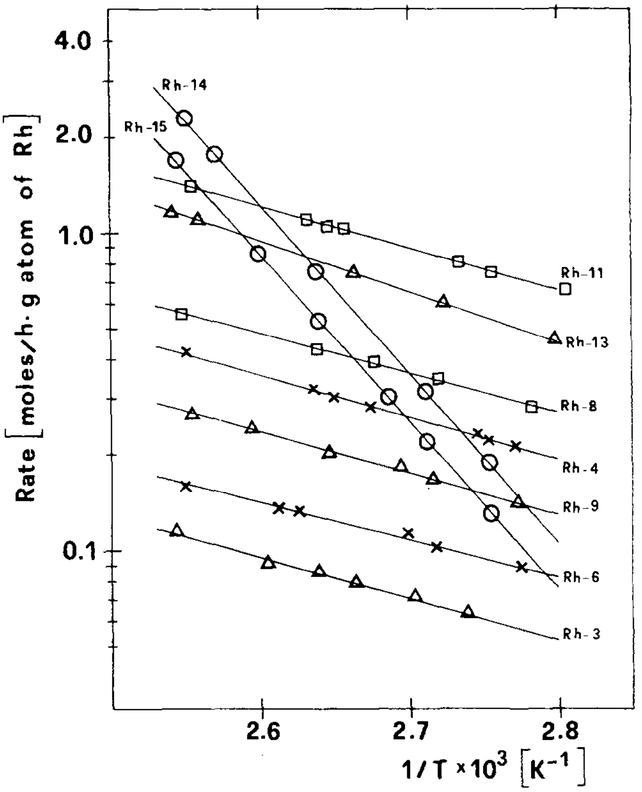

FIG. 5. Arrhenius plots for polymer supported rhodium catalysts. Some samples have been omitted for the sake of clarity.

low temperature pretreatment and makes it suitable for the investigation of our polymer supported catalysts. The hydrogen uptake for all the phosphinated catalysts under the same experimental conditions is practically negligible even for the samples with high metal content and high dispersion (for example, Rh-2 : Rh% = 9.9, $P_{\exp}{}^{s}$ = 0.93). These results again account for the strong interaction between the phosphine groups and the metal surface and confirm the inability of hydrogen at room temperature to displace a phosphine coordinated to a group VIII transition metal.

Conversely, chemisorption data for catalysts Rh-14 and Rh-15 were 68.2 and 33.5 ml STP/g metal, corresponding to surface areas of 63 and 31 m^2/gr.

The discrepancy between these data and those derived from SAXS and WAXS (*1*) accounts for the large difference in specific activity between Rh-14 and Rh-15 compared to the already mentioned Rh/SiO$_2$ catalyst. Even if direct evidence is lacking, we can speculate, as suggested by other authors (*10*), that part at the active sites in Rh-14 and Rh-15 are hidden because of interaction with the phenyl rings of the polymer support.

In Table I we have reported the apparent activation energy *E* values calculated from Arrhenius plots, which are reported in Fig. 5. As it appears, two classes of catalysts can be envisaged: a first one constituted by Rh-14 and Rh-15 with *E* values of about 12 Kcal/mol and a second one including all the others with *E* around 4–6 Kcal/mol. The former values fall in the range of 10–15 Kcal/mol and are the most commonly found activation energy for the ethylene hydrogenation reaction catalyzed by group VIII supported metals (*11*). They differ significantly from the latter, which are very similar to the values reported by Jarrell and Gates for polymer-bound rhodium cluster catalysts (*12*).

The most evident parameter which differentiates these two classes of catalysts is the presence of phosphine groups. Kinetic experiments indicate that the activation of H_2 is the slow step of the reaction and hence the calculated E refers to this specific step. From the point of view of coordination chemistry, this can be formally considered as an oxidative addition reaction, which is generally favored by the presence on the metal center of soft donor ligands, capable of increasing the electron density of the metal (*13*). We argue that the difference in the activation energy between the two groups of catalysts relies on the different chemical natures of the active sites, that is, in one case, the simultaneous presence on the same active metal center of both phosphine and hydrogen. The apparent discrepancy between this argument and the previously observed inhibition effect of the phosphine groups on the specific activity can be explained as follows: in a certain number of surface sites, due to the specific morphology of the metal particles (corners, edges, etc.), the presence of the phosphine does not completely saturate the coordination sphere of the metal; on these vacancies hydrogen can bind. Of course, the probability of such a situation is relatively low, as is demonstrated by the chemisorption results.

In conclusion, the use of phosphine groups as links between metal and support has proved successful in controlling the growth and the physical properties of the metal particles (*1*). On the other hand, the present work has also demonstrated that such a use constitutes a severe limit to the achievement of high catalytic activities in the hydrogenation of ethylene. However, despite the results in this test reaction, the unusual nature of the active sites in this class of catalysts seems to justify further expectations from the study of their activity and selectivity in other hydrogenation reactions (dienes, carbon monoxide, etc.), which are currently underway.

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