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Supported Metal Catalysts: Preparation, Characterization, and Function

V. Activities and Selectivities of Platinum Catalysts in the Reactions of Cyclopropane, Ethene, 1,3-Butadiene, and 2-Butyne with Dihydrogen

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A correlation of the catalytic properties of three supported Pt catalysts with their physical properties, chemical composition, and adsorption properties is presented. The catalytic properties of 0.75 wt% Pt/silica, 0.89 wt% Pt/alumina, and 0.48 wt% Pt/molybdena are reported for the hydrogenolysis of cyclopropane and for the hydrogenations of ethene, 1,3-butadiene, and 2-butyne. The corresponding catalytic properties of the standard reference catalyst EUROPT-1, a 6.3 wt% Pt/silica, are reported for comparison. Pt/silica and EUROPT-1 each contained fully reduced Pt and were chloride free; their activities for structure-insensitive 1,3-butadiene and 2-butyne hydrogenations were in proportion to their respective Pt dispersions and product selectivities were identical. This intercatalyst comparison could not be extended to ethene hydrogenation because reaction over Pt/silica showed a kinetic discontinuity which is described in detail. Pt/alumina contained $Pt^{\delta+}$ which had the effect of reducing activity in each hydrogenation reaction and of altering product selectivity in 1,3-butadiene hydrogenation. A condition was found under which this support effect was reversed. Cyclopropane hydrogenolysis over all four catalysts obeyed the Bond–Newham rate equation, and the rate coefficient varied with Pt particle size indicating the reaction to be structure sensitive. Pt/molybdena, the only catalyst having a wide range of Pt particle size, behaved in contrasting and predictable ways depending upon the structure-sensitive or -insensitive nature of the reaction under study.

INTRODUCTION

This series of papers records a study in which the preparation, characterization, and evaluation of a series of catalysts has been coordinated so that measurements of activity and selectivity can be related to preparative methods and catalyst structure. This paper describes the catalytic properties of a 0.75 wt% Pt/silica, a 0.89 wt% Pt/alumina, and a 0.48 wt% Pt/molybdena. The preparation of these catalysts by impregnation, their physical and chemical characterization, and their properties in terms of ethene adsorption and CO adsorption have been described in Parts I to III (1–3). Reactions chosen for study were the hydrogenolysis of cyclopropane and the hydrogenations of ethene, 1,3-butadiene, and 2-butyne. The first, the conversion of cyclopropane to propane, is a process in which the reactants are known to exhibit comparable free energies of adsorption (4) and therefore to compete for surface sites on fairly equal terms. The second, ethene hydrogenation to ethane, is the archetypal hydrogenation in which the hydrocarbon is the more strongly adsorbed reactant. The third and fourth are reactions of diunsaturated hydrocarbons which are very strongly adsorbed and which exhibit two types of selectivity, (i) selectivity of hydrogen addition in the first step leading to the preferential formation of one of the butenes, and (ii) selectivity for butene formation as opposed to complete hydrogenation to butane. The mechanisms of these alkadiene and alkyne hydrogenations have been elucidated by D-tracer methods (5–9). The challenge in the present work is to relate the activities and selectivities observed to the known physical properties of the catalysts against the background of the published reaction mechanisms.

During this project we had available the standard reference catalyst EUROPT-1, a 6.3 wt% Pt/silica for which a detailed characterization has been published (10–13). This catalyst has been included in the study of each reaction so as to provide a benchmark that is accessible to other investigators.

EXPERIMENTAL

Catalysts

Catalysts designated Pt/silica, Pt/alumina, and Pt/molybdena were prepared for this project; their preparation

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and characterization is reported in Part I[3] (1). Briefly, Pt/silica was prepared by impregnation of H_2PtCl_6 onto M5 Cab-O-Sil silica of surface area 203 $m^2 g^{-1}$ and contained 0.75 wt% Pt. The standard reduction procedure (1) removed chlorine originally present in the precursor and provided Pt metal in the zero oxidation state (by XPS) with a large fraction of very small metal particles (≤ 0.7 nm) and minimal metal–support bonding (as judged by Pt L_3-edge EXAFS spectroscopy). Pt/alumina was prepared by impregnation of Degussa Aluminum Oxid C of 102 $m^2 g^{-1}$ surface area with the same precursor and contained 0.89 wt% Pt. After the standard reduction procedure a significant amount of chlorine (1.01 wt%) was retained which was associated with the support and not with the Pt. Again, electron microscopy showed the metal to be highly dispersed. Substantial metal–support bonding was evident from the EXAFS spectrum (coordination number of O about Pt was 0.8) and from XPS which showed the metal to be present as $Pt^{\delta+}$. Pt/molybdena was prepared by impregnation of H_2PtCl_6 onto BDH AnalaR MoO_3 of 2.1 $m^2 g^{-1}$ surface area and contained 0.48 wt% Pt. Under the standard reduction conditions the support formed the molybdenum bronze H_xMoO_3 where x was ca. 1.0 (0.9 by TGA, 1.2 by TPR, or 0.8 by XPS). Again, the Pt retained a significant $\delta+$ character in the reduced state (XPS) which is consistent with the hydrogen bronze formation. The Cl content was minimal (0.02 ± 0.02 wt%). This material contained Pt particles having a wide distribution of sizes ranging from 0.7 to 20 nm. Samples of EUROPT-1 (6.3% Pt/silica) were rereduced at 373 K for 0.5 h. This catalyst has a Pt particle size distribution ranging from 0.7 to 3.5 nm with a well-marked maximum at about 1.8 nm (11); the particles show raft-like morphology under certain conditions (14).

Platinum dispersions. The original characterization of EUROPT-1 established the Pt dispersion, based on a cubic particle model, to be 60% (11). For Pt/molybdena, the dispersion calculated by the same method is about 15%; because of the wide range of particle sizes present, this value is not sensitive to any failure to register particles below the detection limit of 0.7 nm in diameter.

The electron microscopic method is not suitable for the determination of the Pt dispersion in Pt/silica and Pt/alumina where the mean particle size is very small and the distribution is narrow and where a significant proportion of metal particles probably went undetected. The alternative is to deduce the dispersion from chemisorption measurements. In Part II (2) it was recorded that Pt/silica and Pt/alumina adsorbed 5.73×10^{18} and 6.81×10^{18} O_2 molecules $(g \cdot cat)^{-1}$ at 273 K respectively. Assuming dissociative adsorption of O_2 in each case and an adsorption stoichiometry of $O : Pt_s = 0.53 : 1.00$ as suggested by surface science experiments (17), these values correspond to a dispersion of 93% for each catalyst. This value is consistent with the model configuration for the average Pt particle in Pt/silica based on EXAFS spectroscopy (1) which was that of a 14-atom cluster having a nominal dispersion of 85%. EXAFS spectroscopy suggested an even higher value for the Pt dispersion in Pt/alumina.

Thus, values for the dispersion of the Pt active phase in EUROPT-1 and the catalysts prepared for this project fall in the sequence:

$$\begin{array}{ccccc} \text{Pt/alumina} \geq \text{Pt/silica} & > & \text{EUROPT-1} & > & \text{Pt/molybdena} \\ \text{ca. } 90\% & & 60\% & & \text{ca. } 15\% \end{array}$$

0.1 wt% Pt–ZSM-5. This catalyst was prepared for another study and full details are given elsewhere (15). ZSM-5 (99.6% SiO_2, 0.4% Al_2O_3) was converted to the caesium form and then ion exchanged using $Pt(NH_3)_4(OH)_2$. The Pt-containing precursor was reduced without calcination under one atmosphere pressure of H_2 at 573 K for 3 h.

Apparatus

Catalysts were studied at subatmospheric pressure in a glass static reactor of 200 cm^3 volume attached to a standard grease-free high vacuum system capable of achieving 1.5 mPa in the region of the reaction vessel. Chemical analysis was by gas chromatography and mass analysis was achieved using a Vacuum Generators Micromass spectrometer with electron impact ionization (20 eV). Pressure changes were measured by use of a pressure transducer with digital readout. Initial rates were determined by measurement of the initial gradients of pressure fall versus time curves. As a basis for the comparison of one catalyst with another, values of the initial rate are expressed per unit weight of Pt, i.e., R_n/Pa s^{-1} (0.10 mg Pt)$^{-1}$ and are referred to as *normalized initial rates.*

Materials

Cyclopropane and 2-butyne (Aldrich) and ethene and 1,3-butadiene (Matheson) were purified by bulb to bulb distillation before use. Dihydrogen and dideuterium (BOC) were purified before use by passage through heated Pd/Ag thimbles.

RESULTS

Cyclopropane Hydrogenolysis

Reaction of cyclopropane with dihydrogen to give propane was examined at 313 K. Reactions over Pt/alumina, Pt/silica, and EUROPT-1 show a common feature in that

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[3] These catalysts were denoted as Pt/silica(I), Pt/alumina(I), and Pt/molybdena(I) in Parts I–III where (I) denotes preparation by impregnation; this distinguished them from catalysts prepared by coprecipitation which were denoted (C). This annotation is not used in this paper because all catalysts used were prepared by the impregnation method.

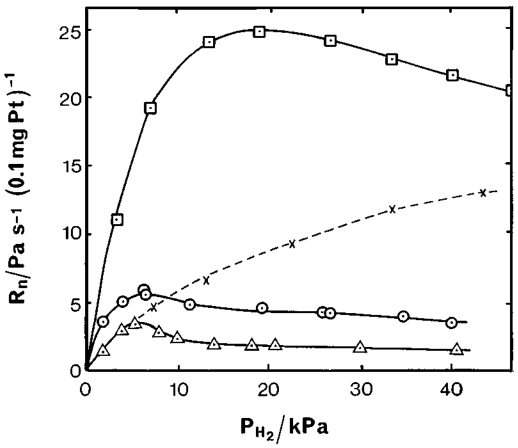

FIG. 1. Cyclopropane hydrogenolysis at 313 K. Variation of the normalized initial rate, R_n/Pa s^{-1} (0.1 mg Pt)$^{-1}$, with initial dihydrogen pressure. Initial cyclopropane pressure = 16.7 kPa throughout. Pt/silica (open circles), EUROPT-1 (triangles), Pt/alumina (squares), and Pt/molybdena (crosses, dashed curve).

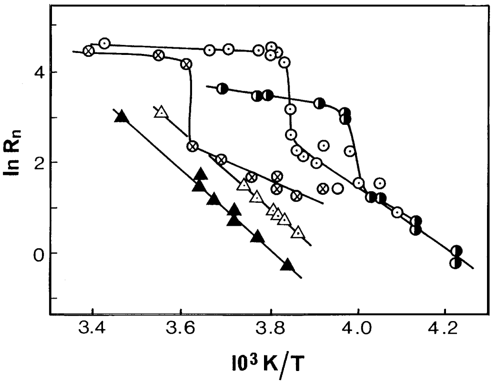

FIG. 3. Ethene hydrogenation. Variation of the normalized initial rate, R_n/Pa s^{-1} (0.1 mg Pt)$^{-1}$, with temperature for reactions catalyzed by Pt/silica (circles) and EUROPT-1 (triangles). Pt/silica samples were freshly reduced; in two cases (open circles and half-filled circles) first contact of the catalyst with ethene occurred at a temperature above the kinetic discontinuity; in one case (crossed circles) first contact occurred at a temperature below the discontinuity. Open triangles show the behavior of freshly reduced EUROPT-1, and filled triangles show the behavior after use for 2-butyne hydrogenation. Initial reactant pressures: ethene = 6.7 kPa, dihydrogen = 14.7 kPa.

all curves of normalized initial rate versus pressure exhibit a maximum (Figs. 1 and 2). This behavior has been reported before for Pt/alumina (4) and indicates that the reactants are adsorbed with comparable strengths of adsorption, so that each tends to inhibit reaction when present at a pressure sufficiently high to reduce significantly the surface concentration of the other. Pt/molybdena behaved differently. The order in hydrogen was between 0.6 and 0.7 and that in cyclopropane was zero (initial dihydrogen pressure 6.7 kPa; cyclopropane pressures 13.3–46.6 kPa). These orders are similar to those obtained in, for example, propene hydrogenation over Pt/alumina (16).

The behavior of Pt/silica was similar to that of the standard catalyst EUROPT-1, Pt/silica being the more active by a factor of about 2. The activity of Pt/alumina substantially exceeded that of Pt/silica except at high cyclopropane pressures. At high hydrogen pressures the activity of Pt/molybdena was intermediate between that of Pt/alumina and Pt/silica.

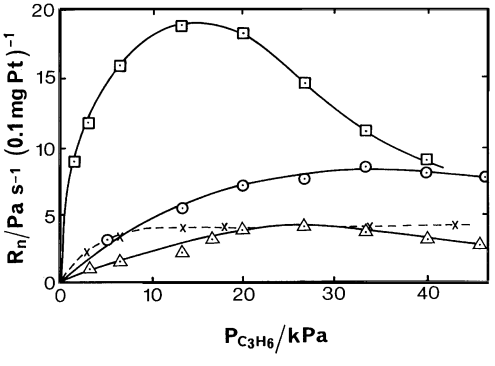

FIG. 2. Cyclopropane hydrogenolysis at 313 K. Variation of the normalized initial rate, R_n/Pa s^{-1} (0.1 mg Pt)$^{-1}$, with initial cyclopropane pressure. Initial dihydrogen pressure = 6.7 kPa throughout. Pt/silica (open circles), EUROPT-1 (triangles), Pt/alumina (squares), and Pt/molybdena (crosses, dashed curve).

Reaction of 20.0 kPa cyclopropane with 40.0 kPa dihydrogen over Pt/molybdena(D-bronze) at 293 K resulted in no appearance of deuterium in the hydrocarbons.

Ethene Hydrogenation

Ethene hydrogenation over Pt/silica at 253 K and over Pt/alumina and EUROPT-1 at 273 K was of the expected kinetic form, i.e., zero order in alkene and first order in dihydrogen. These catalysts showed reproducible activity immediately following reduction and the temperature dependencies of the initial rates are shown in Figs. 3 and 4. By contrast, the initial activity of Pt/molybdena at 288 K quickly declined from an initial high value to a lower reproducible value, whereupon the temperature dependence was measured as recorded in Fig. 4.

The temperature-dependent activity of Pt/silica showed a discontinuity (Fig. 3). The effect was reversible. For example, for the catalyst sample 1 (open circles), experiments were carried out alternately above and below the discontinuity temperature of 260 K; it was this procedure that was responsible for the scatter in the points at the lower temperatures. The discontinuity was observed irrespective of whether the first exposure of the catalyst to ethene was made at a temperature above the discontinuity temperature (half-filled circles) or below (crossed circles). No kinetic discontinuity was observed with Pt/alumina, Pt/molybdena, or EUROPT-1.

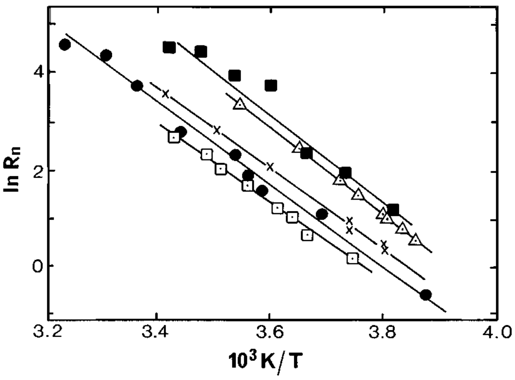

FIG. 4. Ethene hydrogenation. Variation of the normalized initial rate, R_n/Pa s^{-1} (0.1 mg Pt)$^{-1}$, with temperature over freshly reduced Pt/alumina (open squares), Pt/molybdena (crosses), and EUROPT-1 (open triangles). (Behavior over fresh Pt/silica is shown in Fig. 3. EUROPT-1 is shown in both Figs. 3 and 4.) Filled circles and squares show activity of Pt/silica and Pt/alumina, respectively, after use for 2-butyne hydrogenation. Initial reactant pressures: ethene = 6.7 kPa, dihydrogen = 14.7 kPa.

Reaction of 14.9 kPa ethene with 15.7 kPa dihydrogen over Pt/molybdena(D-bronze) at 298 K resulted in no appearance of deuterium in the hydrocarbons.

Pt/silica showed a reduced activity for ethene hydrogenation after use for 2-butyne hydrogenation and the kinetic discontinuity was no longer evident (compare open, half-filled, and crossed circles Fig. 3 and filled circles Fig. 4). EUROPT-1 showed a more modest deactivation after similar treatment (Fig. 3), and the apparent activation energy for ethene hydrogenation was not affected. Remarkably, exposure of Pt/alumina to but-2-yne/dihydrogen mixtures caused a substantial *increase* in ethene hydrogenation activity (Fig. 4), but again the apparent activation energy remained the same.

Pt/molybdena provided an activity intermediate between that of EUROPT-1 and Pt/alumina. Figures 3 and 4 show that for all catalysts except fresh Pt/silica the apparent activation energy for ethene hydrogenation was 67 ± 8 kJ mol^{-1}.

1,3-Butadiene Hydrogenation

Reactions were carried out over fresh samples of catalysts. Butene compositions (independent of conversion until 80% removal of diene) and selectivities are given in Table 1 and the temperature dependencies of the normalized rates are shown in Fig. 5. Butene isomerization and further hydrogenation occurred above 303 K over each catalyst, although overall reaction rate continued to obey the Arrhenius equation. The apparent activation energies (±5 kJ mol^{-1}) were (in kJ mol^{-1}); Pt/silica, 60; EUROPT-1, 60; Pt/alumina-1, 39; Pt/molybdena, 58.

All catalyst samples behaved reproducibly with respect to activity and product composition throughout their period of use except the second sample of Pt/alumina designated Pt/alumina-2. This catalyst was used for 20 reactions over a period of 40 h with evacuation between each experiment; the results are shown in Table 1 and Fig. 5 (filled squares). Initial activity and butene composition (reaction 3) concurred with that expected by comparison with the first sample, Pt/alumina-1. After 8 reactions the rates had not changed but the product composition had become richer in 1-butene. By reactions 18 and 19 both the activity and the butene composition were exactly as expected for Pt/silica.

2-Butyne Hydrogenation

Reactions were carried out over samples previously used for ethene hydrogenation. Table 1 shows butene compo-

TABLE 1

Butene Compositions and Selectivities for 1,3-Butadiene Hydrogenation and for 2-Butyne Hydrogenation

Hydrocarbon	Catalyst	Expt.	Temp. (K)	Butene composition (%) 1-*b*	*t*-2-*b*	*c*-2-*b*	Selectivity[a]
1,3-Butadiene	Pt/silica		273–298	79	14	7	0.68
	EUROPT-1		273–291	78	15	7	0.68
	Pt/molybdena		273–301	80	14	6	0.77
	Pt/alumina-1		273–303	65	22	13	0.60
	Pt/alumina-2	3	295	67	22	11	0.58
		7	295	75	17	8	0.62
		8	284	73	18	9	0.59
		18	306	78	15	7	0.66
		19	315	78	13	9	0.68
2-Butyne	Pt/silica		293–333	2	10	88	0.91
	EUROPT-1		293–353	1	10	89	0.90
	Pt/molybdena		328–346	1	9	90	0.90
	Pt/alumina		293–378	2	11	87	0.80

[a] Selectivity = butenes/(butenes + butane).

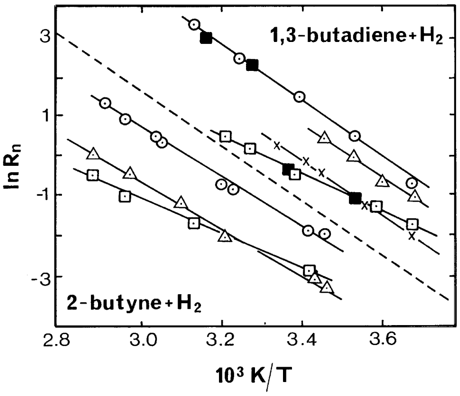

FIG. 5. 1,3-Butadiene hydrogenation and 2-butyne hydrogenation. Variation of normalized initial rate, R_n/Pa s^{-1} (0.1 mg Pt)$^{-1}$, with temperature over Pt/silica (open circles), EUROPT-1 (triangles), Pt/alumina-1 (open squares), Pt/alumina-2 (filled squares), and Pt/molybdena (crosses). Butadiene hydrogenations were conducted over fresh catalysts. Catalysts for butyne hydrogenation had previously been used for ethene hydrogenation. Initial reactant pressures: hydrocarbon = 6.7 kPa, dihydrogen = 20.0 kPa.

sitions and selectivities. The yield of the major product, *cis*-2-butene, varied by only ±2% over the indicated temperature range, but at higher temperatures butene isomerization and further hydrogenation became important. The apparent activation energies (±5 kJ mol^{-1}) were (in kJ mol^{-1}): Pt/silica, 49; Pt/alumina, 36; EUROPT-1, 48; Pt/molybdena, 50.

Exchange Reactions of Pt/Molybdena (D-Bronze)

Exposure of a 0.0298 g sample of Pt/molybdena(D-bronze) to 7.3 kPa dihydrogen at 293 K resulted in the immediate formation of HD and D_2 corresponding to the appearance of 8×10^{18} D atoms in the gas phase. This quantity of deuterium is less than 1% of that present in the bronze, but this number of D atoms exceeds by a factor of 100 the number of surface Pt atoms in the sample. When the temperature was raised to 713 K at 5 K min^{-1} further exchange occurred such that about 8% of the deuterium originally in the bronze appeared in the gas phase. At room temperature, only a very small fraction of the deuterium present in the bronze in able to equilibrate with the gas phase via hydrogen atoms adsorbed at the Pt surface.

Exposure of 0.0324 g Pt/molybdena(D-bronze) to 6.4 kPa propane at 293 K resulted in no formation of deuteriated propanes; however, exchange occurred at 473 K, which was also the threshold temperature for isotope exchange between C_3H_8 and D_2 over Pt/molybdena(H-bronze).

DISCUSSION

A. General Considerations

Catalyst activity has its origin in the physical, chemical, and electronic structure of the active phase, and it was the prime objective of this study to characterise Pt/silica, Pt/alumina, and Pt/molybdena so that their patterns of activity would be interpretable in terms of their characterization and structure. For this purpose mechanisms are not of the first importance provided the comparisons being made each involve common processes. The reactions were chosen because previous deuterium tracer studies had shown that each involves the addition of an adsorbed H-atom to an adsorbed half-hydrogenated state as the rate-determining step and, in all but the reaction of cyclopropane, that the half-hydrogenated state is in equilibrium with adsorbed reactant. Thus, in comparing catalyst activities, the constant feature is the nature of the rate-determining step, i.e., the removal of the half-hydrogenated state from its adsorption site by hydrogen atom addition.

In choosing these reactions, regard was also paid to the relative strengths of adsorption of the reactants. 1,3-Butadiene and 2-butyne are very strongly adsorbed on platinum by comparison with dihydrogen, cyclopropane is weakly adsorbed and competes on fairly equal terms with dihydrogen, and ethene occupies an intermediate position. It was considered important that this range of hydrocarbon–metal interactions should be available in order to provide a wide range of catalytic effects for interpretation.

Before detailed consideration can be given to structure/activity relationships, three matters require discussion: (i) the kinetics of cyclopropane hydrogenolysis must be modelled, (ii) the kinetic discontinuity in ethene hydrogenation over Pt/silica must be discussed, and (iii) the curious time-dependent variation of activity and selectivity afforded by Pt/alumina-2 in 1,3-butadiene hydrogenation (Fig. 5) must be interpreted.

Cyclopropane Hydrogenolysis

The rate versus pressure curves shown in Figs. 1 and 2 are examples of the classical behavior expected for a bimolecular surface reaction proceeding by a Langmuir–Hinshelwood mechanism where neither reactant is very strongly or very weakly adsorbed (18). Curves of this type may be described by

$$\text{rate} = k\theta_C\theta_H = \frac{kb_CP_Cb_HP_H}{(1 + b_CP_C + b_HP_H)^2}, \qquad [1]$$

and Bond and Newham have reported that platinum-catalyzed cyclopropane hydrogenolysis obeys this equation (4). In Eq. [1], k is the rate coefficient, θ_C and θ_H are the surface coverages of adsorbed cyclopropane and of adsorbed H, and b and P are, respectively, the adsorption coefficients and the pressures of the reactants. Figure 6 shows that the kinetic behavior of cyclopropane hydrogenolysis over Pt/silica, shown in Fig. 1, is well modeled by Eq. [1]; modeling using several variants of Eq. [1] gave much less satisfactory agreement with experiment (19). Equation [1] has been used successfully to model the kinetic behavior for

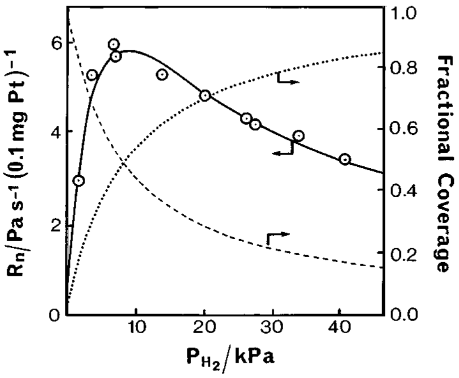

FIG. 6. Cyclopropane hydrogenolysis over Pt/silica at 313 K. Comparison of the observed dependence of initial rate, R_n, on initial dihydrogen pressure (open circles) with that calculated using Eq. [1] (continuous curve) and $k = 10.6$, $b_C = 0.31$, $b_H = 0.62$. The experimental points are those shown in Fig. 1 and the parameters are from Table 2. The dashed and dotted curves show, respectively, the calculated variations of fractional surface coverages of adsorbed cyclopropane and adsorbed H as dihydrogen pressure was varied.

the other catalysts used in this work (19); the parameters obtained are given in Table 2.

There is prima facie evidence from Table 2 that cyclopropane hydrogenolysis shows structure sensitivity. The rate constant, k, increases as mean Pt particle size decreases for the high area catalysts EUROPT-1, Pt/silica, and Pt/alumina. The validity of the high value of k for Pt/alumina is supported by observations from a separate study of cyclopropane hydrogenolysis over 0.1% Pt–ZSM-5 at 313 K (15). This catalyst, which contained very small Pt particles in the zeolite pores (dispersion >90%), showed rate versus pressure curves similar to those for Pt/alumina; the value of k was 45.8. The position of Pt/molybdena in Table 2 is interesting. If the rate of cyclopropane hydrogenolysis had been proportional simply to the available Pt surface area (structure-insensitive reaction), then the value of k should have been less than that for EUROPT-1. The observed value, $k = 27.9$, is consistent with the catalyst containing a high proportion of very small Pt particles (not inconsistent with the electron microscopy) and the structure-sensitive nature of the reaction then determines that a majority of the observed cyclopropane conversion occurs on this small proportion of the total available Pt surface. Pt/molybdena is also exceptional in that it was the only catalyst in this group to adsorb cyclopropane substantially more strongly than dihydrogen. Nevertheless, all catalysts studied showed pressure-dependent rates that obeyed the Bond–Newham equation (Eq. [1]) and hence the variation of rate coefficient with Pt particle size has become evident.

TABLE 2

Kinetic Parameters for Cyclopropane Hydrogenolysis as Described by Eq. [1]

	EUROPT-1	Pt/silica	Pt/molybdena	Pt/alumina
k	4.7	10.6	27.9	43.9
b_C	0.20	0.31	0.68	0.72
b_H	0.59	0.62	0.12	0.63

The structure sensitivity or otherwise of the Pt-catalyzed hydrogenative opening of the C_3 ring in cyclopropane and in methylcyclopropane has been much debated. Early investigations suggested the reaction to be structure insensitive (Boudart and co-workers (20)), less structure sensitive than ethane hydrogenolysis (Sinfelt and co-workers (21)), or mildly structure sensitive (Burwell and co-workers (22)). Careful measurements of the dependence of activity (turnover frequency) on the dispersion of Pt on a given support have led to the conclusion (23) that C_3 ring opening is indeed structure sensitive although the detailed behavior may depend also on catalyst preparation procedure (24, 25). Such structure sensitivity has also become evident in poisoning and deactivation studies (26, 27). Although variation of the catalyst support normally obscures activity/dispersion correlations, whether or not a reaction is structure sensitive in such circumstances should become evident when the activity parameter determined is the rate coefficient, as in the present work. To our knowledge, this is the first report of the dependence of rate coefficient for cyclopropane hydrogenolysis on Pt particle size. Evidence is accumulating that hydrogenative C_3 ring opening is also structure sensitive over Pt (28), Rh (29), and Ru (30, 31).

Kinetic Discontinuities in Catalysis

The majority of metal-catalyzed reactions exhibit rates that obey power rate laws and the Arrhenius equation so that, given rate measurements under one set of conditions, the rate under changed conditions of pressure or temperature can be determined with confidence. However, in some systems, this predictability breaks down, as for example in the Pd-catalyzed hydrogenation of ethyne (32) for which the variation of rate with temperature exhibits a discontinuity closely similar to that shown here by ethene hydrogenation over Pt/silica (Fig. 3). The kinetic discontinuity in ethyne hydrogenation is accompanied by a sudden product discontinuity in the C_4 yield (33). For each of these hydrogenations, (i) reaction with a high apparent activation energy is observed in a low-temperature region, (ii) the discontinuity appears as a sudden increase in activity as temperature is raised by a small increment, (iii) above the discontinuity reaction proceeds with a lower value of the apparent activation energy, and (iv) experimentally the discontinuity can be traversed, back and forth, reproducibly and indefinitely. In the present work, the apparent activation energy over Pt/silica above the discontinuity temperature was almost zero, possibly indicating the occurrence of a diffusion-controlled reaction. In ethyne hydrogenation over Pd, the order in ethene was negative at temperatures below the discontinuity (strong adsorption) but positive at temperatures above the discontinuity (weaker adsorption), and it was suggested, as a working hypothesis, that the discontinuity was evidence of a phase change in the ad-layer of ethyne on the Pd surface (32). Alternatively, the discontinuity might signal a temperature at which a sudden change occurs in the stability of a reaction intermediate, such as adsorbed vinylidine or vinylidyne. For present purposes it is sufficient to note that ethene hydrogenation over Pt/silica reported here provides a second example of such a kinetic discontinuity.

The Time-Dependent Behavior of Pt/Alumina-2 in 1,3-Butadiene Hydrogenation

The activity and selectivity of Pt/alumina-2 in butadiene hydrogenation changed with catalyst use (Table 1, Fig. 5) in contrast to that of Pt/alumina-1.

Deuterium-tracer studies have shown that direct hydrogenation of 1,3-butadiene to butene over Pt occurs by 1 : 2- and 1 : 4-addition giving product compositions at room temperature close to 78% 1-butene, 14% *trans*-2-butene, 8% *cis*-2-butene (5). This balance of 1 : 2- and 1 : 4-addition is modified in favor of 1 : 4-addition if conditions prevail such that the Pt-active phase adopts a $\delta+$ polarization, as for example when a sulfur-containing compound is adsorbed on the platinum surface (34). It has thereby been established that the butene yield in 1,3-butadiene hydrogenation is a sensitive indicator of site oxidation state (the test applies to all of the Group 8 metals) and it was for this reason that 1,3-butadiene hydrogenation was included as a test reaction in this investigation.

On this basis the butene distributions obtained over Pt/silica, EUROPT-1 and Pt/molybdena (Table 1) indicate that the sites active in 1,3-butadiene hydrogenation are electronically unperturbed, i.e., in the zero oxidation state. By contrast, both Pt/alumina-2 in its initial state and Pt/alumina-1 throughout its period of use provided enhanced 1 : 4-addition which is evidence for the existence of active sites containing $\mathrm{Pt}^{\delta+}$. As mentioned above, XPS demonstrated the presence of $\mathrm{Pt}^{\delta+}$ in Pt/alumina but not in Pt/silica or EUROPT-1. It is pleasing that evidence for a polarization effect in Pt/alumina first detected spectroscopically under uhv conditions is now accompanied by independent evidence of the existence of such an effect under reaction conditions.

Pt/alumina-1 and Pt/alumina-2 behaved differently in that the latter gave butene compositions that changed over the course of 20 experiments (Table 1) in the sense that would be expected if the $\delta+$ polarization of the Pt atoms at the active sites had been neutralized. This change brought both the butene composition and the normalized rate into line with that of Pt/silica for which the active phase is Pt^0 both by XPS and the 1,3-butadiene hydrogenation test.

Pt-edge EXAFS spectra of reduced evacuated Pt/alumina showed that, on average, the Pt atoms possessed 0.8 O neighbors. We speculate that, as Pt/alumina-2 was used, these Pt–O bonds underwent hydrogenolysis,

$$\text{–Pt–O–Al} + \mathrm{H_2} \rightarrow \text{–Pt–H} + \text{HO–Al–}, \qquad [2]$$

thus destroying the $\delta+$ polarization at the active sites. The analogous process and its reverse occurs as EUROPT-1 is repeatedly subjected to temperature-programmed desorption of dihydrogen and readsorption of dihydrogen on cooling (12). The failure of Pt-alumina-1 to behave similarly indicates that precise conditions for the control of this metal–support interaction have yet to be achieved.

B. Comparison of Catalytic Activities

In this section the relative catalytic activities of Pt/silica, Pt/alumina, Pt/molybdena, and EUROPT-1 are compared and the differences are interpreted.

Cyclopropane Hydrogenolysis

Variation of the normalized initial rate at 313 K is described by the Bond–Newham equation [1] and the values of the constants are recorded in Table 2.

Pt/silica and EUROPT-1. The closely similar values of b_C and b_H show that the Pt surfaces in these two catalysts are equivalent in respect of the energetics of cyclopropane adsorption. This accords with the platinum phase being Cl free and in the zero oxidation state in each case. The higher catalytic activity observed over Pt/silica (Fig. 1) is represented by the higher value of the rate coefficient k, which reflects the influence of a lager number of smaller Pt particles present per 0.1 mg of supported metal in this catalyst.

Pt/silica and Pt/alumina. Cyclopropane adsorbed much more strongly on Pt/alumina than on Pt/silica (compare values of b_C, Table 2) whereas the strength of hydrogen adsorption on the two catalysts was comparable. The initial interaction of cyclopropane with a metal atom site has been attributed to the interaction of the incipient π-system of the strained hydrocarbon ring with d-orbitals of the metal atom (4), and such an interaction is expected to be enhanced where the site exhibits $\delta+$ polarization, as in Pt/alumina. This increase in b_C of itself produces an 8% increase in rate at $P_\mathrm{C} = P_\mathrm{H} = 50$ Torr according to Eq. [1]; the considerably higher activity of Pt/alumina at these pressures is due to the higher value of the rate coefficient, which is particle size dependent. This is consistent with the evidence from EXAFS spectroscopy that, on average, Pt/alumina contained smaller Pt particles than Pt/silica (1). As the pressure of cyclopropane is increased above 26.7 kPa the term $b_\mathrm{C}P_\mathrm{C}$ in the denominator of Eq. [1] becomes dominant and the observed activities of Pt/alumina and Pt/silica become comparable.

Pt/molybdena. The value of b_{C} is close to that for Pt/alumina and unlike that for Pt/silica and EUROPT-1; this shows that a majority of the reaction occurred at Pt sites which have a $\delta+$ polarization arising from a metal–support interaction. The smallest Pt particles, which are responsible for the majority of the reaction, are also expected to be the most significantly polarized. The conclusions are: (i) that because of the structure-sensitive nature of cyclopropane hydrogenolysis, most of the observed reaction occurred over the smallest Pt particles present in the Pt/molybdena, although they contribute but a small fraction to the total Pt surface area; and (ii) that because the smallest particles are the most strongly affected by the metal–support interaction, the adsorption constants and rate coefficient are those that apply to this small fraction of the total Pt surface.

The relatively weak adsorption of hydrogen is unexpected, and it is this difference between b_{C} and b_{H} which gives the reaction the kinetic appearance of an alkene hydrogenation. Weak hydrogen adsorption may be related to the presence of a large quantity of hydrogen in the H-bronze support, but the isotope tracer experiment with the D-bronze support showed that there was no mixing of hydrogen isotopes between the support and the active phase at 313 K.

1,3-Butadiene Hydrogenation

Pt/silica, EUROPT-1, and Pt/molybdena. Apparent activation energies were identical, and hence relative activities can be compared over the range of temperature studied. Relative activities and platinum dispersions decreased in parallel:

	Pt/silica	EUROPT-1	Pt/molybdena
Relative activities	1.00	0.60	0.25
Pt dispersion	~90%	60%	~15%

This semiquantitative internal consistency indicates that reaction rate was closely proportional to Pt surface area and was not influenced by profound differences in particle size; that is, the reaction was structure insensitive.

The butene compositions (Table 1) over all three catalysts were characteristic of that expected at electronically unperturbed Pt^0 sites. This is consistent with the XPS information for Pt/silica and EUROPT-1, but at variance with that for Pt/molybdena. However, the anomaly is resolved when account is taken of the fact that, for a structure-insensitive reaction, the whole of the Pt surface is equally effective in butene formation, and that the majority of the active surface is associated with large Pt particles for which the surface atoms (being distant from the metal–support interface where the $\mathrm{Pt}^{\delta+}$ is location) are in an unperturbed zero-oxidation state.

Pt/alumina. Pt/alumina-1 exhibited a lower apparent activation energy than the other catalysts (Fig. 4), normalized initial rates were lower than expected based on the Pt dispersion, and the product composition showed enhanced 1 : 4-addition in butene formation (Table 1). This last feature is indicative of $\delta+$ polarization at the majority of sites and leads to an expectation of an enhanced strength of adsorption of the alkadiene. This strengthening of alkadiene adsorption will tend to bring about an increase in its surface coverage, a reduction in the hydrogen coverage, and thereby a lowering of reaction rate. Because the majority of the Pt particles in Pt/alumina are very small ($\leq$0.7 mm), the $\delta+$ polarization detected by XPS is a property of most if not all of the active surface; the situation is therefore the opposite of that rehearsed above for Pt/molybdena. To summarize, the lower activity of Pt/alumina-1 (by comparison with that of the similarly highly dispersed Pt/silica) is attributed to an enhanced strength of 1,3-butadiene adsorption occasioned by the presence of a metal–support interaction.

Initially, Pt/alumina-1 and Pt/alumina-2 behaved identically. However, with use the metal–support interaction in Pt/alumina-2 became ineffective (see Section A) whereupon the rates, product compositions and (as far as can be judged from the limited results) the activation energy became that expected for electronically unperturbed Pt particles having a high dispersion. The behavior of Pt/alumina-2 thus became indistinguishable from that of Pt/silica.

Ethene Hydrogenation

Pt/silica and EUROPT-1. The behavior of freshly reduced Pt/silica and the kinetic discontinuity (Fig. 3) has been considered in Section A of the Discussion. The complexity of this behavior prevents any meaningful comparison of the activities of Pt/silica and EUROPT-1 other than noting that the activity of the former was generally much higher than expected based on its higher Pt dispersion.

EUROPT-1 and Pt/molybdena. These catalysts showed closely similar, though not identical activation energies. At the midpoint of the temperature range studied the relative activities were EUROPT-1 = 1.00 and Pt/molybdena = 0.45, whereas the ratio of the Pt dispersions is 1 : 0.25. Thus Pt/molybdena is nearly twice as active as expected based on available Pt area.

Pt/alumina. Orders of reaction and the apparent activation energy over Pt/alumina were identical to those observed over EUROPT-1. The lower activity is attributed to the effect of an increased strength of adsorption, and the argument advanced above for low activity in 1,3-butadiene hydrogenation applies equally to this ethene hydrogenation.

2-Butyne Hydrogenation

2-Butyne was hydrogenated over catalyst samples previously used for ethene hydrogenation, and hence the surfaces contained hydrocarbonaceous residues derived from ethene.

Pt/silica, EUROPT-1, and Pt/molybdena. Relative activities again decreased with decreasing dispersion. In this case the relative activities of EUROPT-1 and Pt/molybdena (1.00 : 0.25) correspond exactly to their relative dispersions. By comparison, Pt/silica showed an activity 3.7 times that of EUROPT-1, whereas a factor of 1.5 would be expected based on dispersion. It was noted above that the same Pt/silica catalyst in the fresh state was particularly active for ethene hydrogenation, and that characteristic was clearly retained. All four catalysts provided the expected high selectivity for *cis*-2-butene formation; the butene composition from this reaction is not sensitive to electronic perturbation of the active surface.

Re-examination of Ethene Hydrogenation

Pt/silica and EUROPT-1 were partially deactivated for ethene hydrogenation following their use for 2-butyne hydrogenation. The former was the more extensively deactivated, which is not unexpected since it contained smaller Pt particles, and the smaller metal particles are known to be more susceptible to poisoning by hydrocarbonaceous residues (35). The Pt/silica surface in this state did not show the kinetic discontinuity and by inference did not sustain the formation of the adsorbed intermediates responsible for the discontinuity.

Remarkably, Pt/alumina was substantially *activated* toward ethene hydrogenation following use in 2-butyne hydrogenation; indeed Pt/alumina had now become the most active of the catalysts studied. We interpret this as indicating that the hydrogenation of 2-butyne (like that of 1,3-butadiene discussed above) had destroyed the metal–support interaction. There is a hint of the presence of a kinetic discontinuity of the behavior of Pt/alumina in this final state.

Brief comparison of the behaviors of Pt and Pd. Hub *et al.* have reported variations of catalytic activity with metal dispersion and partial oxidation state for 1-butene and 1-butyne hydrogenations over various Pd/aluminas (36). Alkene hydrogenation activity increased as Pd particle size diminished and as adsorption coefficient increased, which concurs with our observation of the cyclopropane reaction over Pt. 1-Butyne hydrogenation over Pd/alumina occurred more slowly when the metal was in a partially positive oxidation state, which is consistent with our observations for 1,3-butadiene and 2-butyne hydrogenations over alumina- and silica-supported Pt. In some other respects, however, the two studies diverge.

CONCLUSIONS

The objective of this continuing investigation is to relate catalyst performance to physical constitution and chemical composition, and thereby to the method of catalyst preparation. Progress achieved so far is summarized as follows.

1. Platinum particles in the zero-oxidation state supported on silica in preparations free of chloride ion exhibit activities for structure-insensitive 1,3-butadiene hydrogenation which are related only to dispersion and not to method of preparation (cf. Pt/silica and EUROPT-1). This demonstration that a catalyst prepared in-house emulates the standard reference catalyst is of importance.
2. Platinum particles in a fractionally positive oxidation state supported on alumina exhibit lower activities in 1,3-butadiene hydrogenation than similarly sized platinum particles in the zero oxidation state (cf. Pt/alumina and Pt/silica) due probably to stronger adsorption of reaction intermediates. This deficit of activity is recovered on conversion of the active phase to the zero oxidation state.
3. Cyclopropane hydrogenolysis obeyed the Bond–Newham rate equation, and variation of the rate coefficient with platinum particle size in the range of dispersion 15 to 90% demonstrated the reaction to be structure sensitive. The adsorption coefficients for cyclopropane adsorption on platinum in the zero-oxidation state were comparable (cf. Pt/silica and EUROPT-1) and were higher for adsorption on platinum in a fractionally positive oxidation state, again indicating stronger adsorption of reaction intermediates (as aforementioned with Pt/alumina and Pt/molybdena).
4. The contrast of behavior of structure-sensitive and structure-insensitive reactions over Pt/molybdena was particularly informative. In structure-sensitive cyclopropane hydrogenolysis the higher rate coefficient exhibited by reaction over smaller particles caused the majority of product to be formed over this small fraction of the total active platinum surface. For structure-insensitive 1,3-butadiene hydrogenation (the products of which are diagnostic of surface electronic state) it is inferred that the majority of product was formed at the substantial fraction of the total active surface provided by the electronically unperturbed larger particles.
5. Pt/silica showed a kinetic discontinuity in ethene hydrogenation which was not shared by EUROPT-1 with which it was otherwise equivalent. The discontinuity would therefore appear to be associated with the small platinum particle size in Pt/silica but it would be premature to attribute it directly to particle size and thereby to class the reaction as structure sensitive.
6. Matters requiring further investigation include (i) the process whereby conversion of $\mathrm{Pt}^{\delta+}$ to Pt^0 was achieved during 1,3-butadiene hydrogenation over Pt/alumina and whether it was sensitive to the presence of Cl (a study of catalysts prepared from halide-free precursors would be valuable); (ii) the unexpectedly weak adsorption of hydrogen on Pt/molybdena, as evidenced by the low value of b_{H}, which caused the general kinetics to resemble those of propene hydrogenation; and (iii) the kinetic discontinuity observed in ethene hydrogenation over Pt/silica.

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