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Support Effects in Ethene Hydrogenation Catalyzed by Platinum

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The reaction of ethene with deuterium has been catalyzed at 20°C by platinum supported on titania, magnesia, alumina, silica, and silica–alumina. Product compositions, which have been analyzed by Kemball's method, show that the likelihood of ethene desorption from the various catalysts increased in the sequence Pt/silica ≈ Pt/alumina ≈ Pt/silica–alumina < Pt/magnesia < Pt/titania. The behavior of adsorbed ethyl groups at these platinum surfaces was little influenced by the nature of the support. Silica, alumina, and silica–alumina behave as inert supports under the conditions used, whereas titania and magnesia interact with platinum in a manner that appears to cause a reduction in the strength of ethene adsorption. For Pt/titania, this is attributed to the effects of partial reduction of the titania at elevated temperatures; for Pt/magnesia, the effect may result from the preferential development of low-index planes at the surface of the platinum crystallites.

INTRODUCTION

In catalysis by supported metals the major role of the support is to provide a large surface area on which the metal may be retained in a highly dispersed state. However, the support may not be inert; on occasion it may supply hydrogen atoms to, or accept hydrogen atoms from, the active metal component (*1*), and in principle it may influence the electronic and geometric structure of the metal particles, especially if these are very small. In the present paper the influence of a range of supports on the ethene–deuterium reaction has been examined. This reaction was chosen because it is one of the very few formally simple catalyzed reactions for which the product composition is amenable to quantitative assessment.

EXPERIMENTAL

Supports used were "Aerosil" silica (Bush, Beech, and Bailey), alumina (Ketjen CK 300), 25% silica–alumina (Crossfield), magnesia (Analar), and "Cab-O-Ti" titania (Cabot). Catalysts were prepared by impregnation of these supports with solutions containing the required amounts of H_2PtCl_6. After evaporation to dryness and overnight drying at 150°C, the impregnated materials were reduced in a flow of hydrogen and nitrogen at 150°C. Catalysts prepared in this way contained 0.1% Pt by weight; a 12% Pt/silica was also prepared. After evacuation, these catalysts were pretreated at 300°C with 200 Torr oxygen for 1 h, evacuated to $<10^{-5}$ Torr, exposed to 200 Torr deuterium for 1 h, evacuated again, and allowed to cool to room temperature in fresh deuterium. This procedure was adopted in view of our previous work on ethene hydrogenation (*2*) which indicated that anomalous kinetic behavior, attribut-

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able to the presence of carbonaceous residues, could thus be avoided. The Pt/titania, which was originally off-white, went blue-grey at 300°C in hydrogen, and reverted to off-white when treated in oxygen at 300°C; in the absence of the platinum these color changes did not occur.

A 6.4% Pt/silica reference catalyst (EUROPT-1) prepared for the Council of Europe Study Group on Catalysis by Johnson, Matthey and Company was also examined. This catalyst, which was supplied in the reduced state, was activated by heating in flowing hydrogen at 700 or 1000°C.

Ethene (British Oxygen) was thoroughly degassed before use. Deuterium (Matheson) was either purified by passage through a heated Pd–Ag alloy thimble (work with EUROPT-1) or was maintained at 76 K to minimize admission of traces of water to the reactor.

Reactions were performed in a Pyrex static rector (200 ml) connected to a conventional high vacuum system capable of attaining 10^{-7} Torr. In studies of the 0.1 and 12% Pt-catalysts the initial pressures of ethene and deuterium were each 100 Torr; the gases were mixed before admission to the reactor. In studies with EUROPT-1 the initial pressures of ethene and of deuterium were 10 and 20 Torr, respectively; ethene was admitted before deuterium.

Samples removed from the reactor were separated into ethene and ethane fractions by glc and the mass sepctra were obtained at 16 eV. The magnitudes of the ion currents were corrected for the presence of ^{13}C and for fragmentation. The problem of calculating parent ion currents for the isotopically distinguishable ethanes is well known; the method adopted by Bond *et al.* (*3*), including the procedure described in the appendix of their paper, was used throughout. Calculated distributions of deuterium in the products have been obtained by use of the method initially described by Kemball (*4*) and subsequently revised by Kemball and Wells (*5*).

RESULTS

Reactions of ethene with deuterium were examined as a function of conversion over each catalyst and as a function of reactant pressures and temperature over 12%

TABLE 1

Product Distributions Obtained from Reactions of Ethene with Deuterium at 20°C, and Calculated Distributions (Conversion = 15 ± 2%)[a]

Catalyst	Calculation	Products (%)										
		C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4	C_2H_6	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$	$C_2H_2D_4$	C_2HD_5	C_2D_6
0.1% Pt/titania		11.1	1.2	0.0	0.0	2.6	17.2	59.9	5.3	2.0	0.7	0.0
	A	11.5	1.4	0.1	0.0	1.4	17.8	57.2	9.3	1.2	0.1	0.0
0.1% Pt/magnesia		10.7	3.9	0.0	0.0	3.6	24.7	40.3	9.2	4.3	2.5	0.8
	B	10.7	3.0	0.6	0.1	3.1	24.6	40.7	14.8	4.4	0.9	0.1
0.1% Pt/alumina		4.8	1.1	0.0	0.0	7.0	26.0	41.7	10.4	5.3	2.3	1.4
	C	4.8	1.1	0.2	0.0	5.0	28.0	43.3	13.5	3.4	0.6	0.1
0.1% Pt/silica		3.3	0.4	0.0	0.0	4.9	27.9	43.3	11.4	4.4	2.9	1.5
0.1% Pt/silica[b]		2.6	0.5	0.0	0.0	3.5	27.6	42.6	13.0	5.2	2.9	2.1
	D	2.9	0.7	0.1	0.0	5.0	28.1	44.0	14.6	3.8	0.7	0.1
0.1% Pt/silica-alumina		3.8	1.2	0.0	0.0	3.1	24.3	44.8	12.7	5.1	3.4	1.6
6.4% Pt/silica[c]		3.1	1.6	1.6	0.0	0.4	22.2	51.0	12.3	4.8	2.1	0.9
	E	2.6	0.4	0.1	0.0	2.9	25.5	54.1	12.0	2.1	0.3	0.0
6.4% Pt/silica[d]		2.2	0.5	0.0	0.0	9.2	16.5	57.1	8.6	3.6	1.5	0.8

[a] For reactant pressures, see text.

[b] Catalyst admixed with equal weight of Ketjen CK 300 alumina.

[c] EUROPT-1 pretreated at 700°C.

[d] EUROPT-1 pretreated at 1000°C.

Pt/silica. Product compositions for reactions at room temperature were substantially independent of conversion because the rates of formation of deuteriated ethenes and of HD and H_2 were both very slow. The ethene exchange increased only slowly with increasing temperature; thus, over the range 23 to 200°C the yield of C_2H_3D at 20% conversion increased only from 2.5 to 5.7%.

Typical product compositions obtained from reactions at 20°C and 15% conversion over a range of catalysts are shown in Table 1 together with a set of calculated distributions. The most striking feature of these results is that the rate of exchange of H for D in ethene (*expressed relative to the rate of formation of ethane*) was faster over Pt/titania and over Pt/magnesia than over Pt/alumina and Pt/silica. The behavior of 0.1% Pt/silica–alumina closely resembled that of 0.1% Pt/silica and the behavior of the latter was not modified when it was mixed with an equal quantity of Ketjen CK 300 alumina.

We considered it prudent to establish whether the product distribution from the ethene–deuterium reaction was influenced by platinum particle size. For this purpose samples of EUROPT-1 were treated in flowing hydrogen at 700°C for 3 h or at 1000°C for 6 h and then examined as ethene hydrogenation catalysts at 20°C. Electron microscopy showed that catalysts so treated at 700°C possessed a narrow platinum particle size distribution centered at about 15 to 20 Å (virtually identical to that of the catalyst as received), whereas catalyst pretreated at 1000°C had sintered and possessed a wide platinum particle size distribution centered at about 55 Å. The support was not modified by the high temperature treatment. Sintered and unsintered catalyst gave closely similar product distributions (Table 1) from which we conclude that the products and the balance between ethene exchange and hydrogenation are not influenced by platinum particle size under these conditions.

DISCUSSION

The characteristics of these ethene–deuterium reactions concur with previous reports of the platinum-catalyzed reaction (*2*, *3*, *6*). Bond observed a slightly faster rate of exchange in ethene over Pt/alumina than over Pt/silica (*6*), with which we agree. We now probe the support effect further in order to interpret the variations in the product distributions contained in Table 1.

It is generally accepted that metal-catalyzed ethene hydrogenation occurs via the formation of adsorbed ethene and adsorbed ethyl (*4*). Supposing these to be the only reactive hydrocarbon entities, then six isotopically distinguishable ethenes and twelve isotopically distinguishable ethyls may be formed in the ethene–deuterium reaction as a result of the molecular interconversions shown in Fig. 1. We suppose that ethene molecules experience on average a p^*% chance of acquiring a H or D atom to become adsorbed ethyl groups, and a $(100 - p^*)$% chance of undergoing desorption, whereas adsorbed ethyls experience an r^*% chance of losing an H or D atom to reform adsorbed ethene and a $(100 - r^*)$% chance of conversion to ethane. An isotope effect is allowed for in the loss of an H or D atom from the various isotopically distinguishable ethyls. Thus, a product composition can be calculated (*5*), via the solution of 18 simultaneous equations (one for each isotopically distinguishable adsorbed hydrocarbon species), for given values of p^*, r^*, and the isotopic compositions of the "hydrogen" atom added in each step. Table 1 contains the results of five such calculations lettered A to E; the chances of ethene desorption and of ethyl hydrogenation used in these calculations are shown in Table 2.

The calculations reveal that for the 0.1% loaded catalysts there is a sixfold change in the chance of ethene desorption on passing from Pt/titania to Pt/silica, whereas the chance of ethyl hydrogenation to ethane

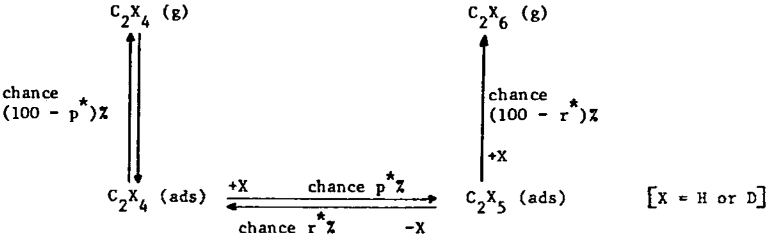

FIG. 1. Proposed processes in ethene hydrogenation, and definitions of p^* and r^*.

varies by a factor of only 1.4. Furthermore, the calculations show that the extent of formation of deuteriated ethenes is not, of itself, an accurate measure of the chance of ethene desorption. Thus, the extents of exchange in ethene over Pt/titania and over Pt/magnesia appear similar in Table 1, but the chances of ethene desorption from these platinum surfaces are seen in Table 2 to be different. Contrariwise, the small difference in the extents of exchange in ethene over Pt/alumina and Pt/silica might be thought to be significant from Table 1, but this is not supported by the calculations recorded in Table 2. Clearly, in every case, the behavior of the catalyst is reflected in the *total* product composition, which arises from the characteristic behavior of both the adsorbed ethene molecules and the adsorbed ethyl groups.

The sixfold variation in the chance of ethene desorption must be due either to changes in the strength of ethene adsorption or to changes in the availability of hydrogen for the conversion of adsorbed ethyl. If the latter were the case, the change in hydrogen availability should cause a parallel change in the fate of adsorbed ethyl (since the sources of hydrogen in the two addition steps are the same—see footnote, Table 2) and no such parallelism of behavior is observed. Thus we conclude that the support influences, either directly or indirectly, the strength of ethene chemisorption to platinum. Morever, since unsupported Pt and Pt/silica behave similarly (*6, 7*), we further conclude that silica behaves as a relatively inert support and that the effect of titania and of magnesia is such as to diminish the strength of adsorption of ethene on the small supported platinum crystallites. The effect of the support thus diminishes in the sequence:

$$TiO_2 > MgO > Al_2O_3 \simeq SiO_2 \simeq SiO_2\text{–}Al_2O_3$$

This support effect must reside either in an electronic interaction between support and metal, or in a variation in the geometry of metal particles such that the types of site available for ethene adsorption vary with the support used. However, any geometrical effect cannot be attributed simply to a variation in particle size in the region 15 to 60 Å, which is often deemed critical for particle size effects (*8*), because similar product compositions were obtained using

TABLE 2

Calculated Behavior of Adsorbed Ethene and Adsorbed Ethyl during Ethene Hydrogenation Catalyzed by Platinum

Calculation[a]	Chance of ethene desorption $(100 - p^*)\%$	Chance of ethyl hydrogenation to ethane $(100 - r^*)\%$
A (cf. Pt/titania)	40	67
B (cf. Pt/magnesia)	20	47
C (cf. Pt/alumina)	11	53
D (cf. 0.1% Pt/silica)	6.7	53
E (cf. 6.4% Pt/silica)	10	67

[a] In the language of Ref. (*5*), for example: Calc. A: $p = 1.5$, $r_H = 0.217$, $r_D = 0.059$, $q = 5.0$, $s = 7.0$ ($r = 0.50$); Calc. B: $p = 4.0$, $r_H = 0.506$, $r_D = 0.137$, $q = 3.0$, $s = 3.0$ ($r = 1.14$); Calc. D: $p = 14.0$, $r_H = 0.378$, $r_D = 0.102$, $q = 2.0$, $s = 3.0$ ($r = 0.88$). N.B. $q \approx s$, hence adsorbed ethene and ethyl probably acquire D- and H-atoms from the same source.

the sintered and unsintered 6.4% Pt/silica (Table 1). We now consider interpretations in terms of electronic and geometrical effects.

Tauster *et al.* (*9*) have shown recently that exposure of Pt/titania to hydrogen at 500°C results in the reduction of TiO_2 to lower oxides together with electron donation from low oxidation states of titanium to platinum. For iridium catalysts (*10*) this reduction and support–metal interaction was evident after hydrogen treatment at 350°C. No such reduction of the support was reported for Pt/silica or for Pt/alumina. In the present work, the 0.1% Pt-catalysts were heated to 300°C in hydrogen regularly (see Experimental). Thus, in view of our observed color changes (see Experimental) and the findings of Tauster *et al.* we conclude that some reduction of the surface of the support in our Pt/titania occurred and that this was accompanied by electron donation from the reduced support to the platinum crystallites, thus weakening ethene chemisorption. It is known that exposure of Pt/alumina to hydrogen at 500°C causes some reduction of the support and the formation of a platinum–aluminum alloy (*11*). In the present work alumina behaved as an inert support from which we conclude that no significant reduction occurred at 300°C.

There is no previous report of ethene hydrogenation catalyzed by Pt/magnesia. Since magnesium, like aluminium, is a main group element, we might expect that any reduction of a magnesia support in the presence of hydrogen at elevated temperatures would follow the mechanism proposed for Pt/alumina rather than that for Pt/titania. However, whether such platinum–magnesium interactions can be so induced awaits further investigation. There exists a possibility that the proposed weakened adsorption of ethene on Pt/magnesia might be due to a geometrical effect. Studies of the infrared spectra of carbon monoxide chemisorbed on various faces of copper single crystals, Cu/silica, Cu/alumina, and Cu/magnesia, have shown that adsorption on Cu/magnesia is consistent with an abundance of close-packed low-index planes of copper, whereas that on Cu/silica and Cu/alumina is consistent with the existence of copper crystallites having high-index facets (*12*). If such distinctions apply to our variously supported platinum catalysts, then relatively strong adsorption of ethene on Pt/silica and Pt/alumina is consistent with bonding of ethene at sites of relatively low coordination number, whereas weaker adsorption of ethene on Pt/magnesia is as expected for bonding of ethene at sites of relatively high coordination number.

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