Effect of adsorption geometry on the selectivity of carbonyl group hydrogenation on Pd/SiO₂

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The gas-phase acetophenone hydrogenation reaction on Pd/SiO_2 catalysts has been modelled to reveal the relationship between the adsorption geometry and the selectivity of carbonyl group hydrogenation. The mechanism of the adsorption configuration effect on the hydrogenation selectivity is discussed. The key to the hydrogenation selectivity of a ketone is related to the bonding geometry of the carbonyl group. This has been demonstrated *via* product yield, temperature effects, hydrogen-concentration effects, presorbed-oxygen effects and infrared spectroscopy. The η^1 -carbonyl ('end-on' coordination) can be hydrogenated to a hydroxy group, or be hydrogenated directly to a methylene group. The latter process can be enhanced by electron-withdrawing promoters. The η^2 -carbonyl ('side-on' coordination) tends to be hydrogenated to a hydroxy group that can be further reduced to a methylene group *via* a consecutive reaction pathway.

The mechanism of selective hydrogenation of CO to methane and/or methanol has been the subject of intensive study.^{1,2} Until recently, there has been no agreement on which reactive intermediate may lead to the production of methane and methanol. Enhanced catalytic activity for the CO hydrogenation reaction using metal supports has been reported to be a general phenomenon that can be used to increase the hydrogenation rate of carbonyl groups.³ Mechanistic studies of carbonyl-group hydrogenation may facilitate our understanding of the CO-hydrogenation reaction mechanism.⁴ We have conducted such studies and found that the pathways of the selective hydrogenation of carbonyl groups to hydroxy or methylene groups are closely related to the adsorption configurations of carbonyl groups on the surface of Pd catalysts. These results can be used to optimize catalyst design for the selective hydrogenation of carbonyl compounds.

Although the adsorbed states and the desorbed species of ketones are well defined on metal surfaces, little attention has been given to the relationship between the adsorption geometry and the reaction selectivity of the hydrogenation of carbonyl groups. Ketones have been observed to be adsorbed onto metal surfaces in η^1 (O), 'end-on', and η^2 (O,C), 'side-on' coordinations.⁴⁻¹¹ It is generally believed that η^1 species tend to be desorbed without reaction or be converted to η^2 species at elevated temperatures. The η^2 bonded species are the active intermediates in heterogeneous catalytic reactions. Ayre and Madix¹² studied reactions of atomic oxygen with ketone on Ag(111) and found that C—H bond scission can be activated by the adsorbed oxygen to produce an OH_(a) and an acetone enolate_(a) [subscript (a) indicates an adsorbed state].

Our experimental evidence shows that both the η^1 and η^2 coordinated carbonyls are active intermediates in the hydrogenation reaction of carbonyl groups. The production of hydroxy groups is largely controlled by the formation of η^2 mode carbonyls on the surface of Pd catalysts while the production of methylene groups at temperatures below 100 °C is closely related to the formation of η^1 -carbonyls that are perturbed by presorbed oxygen on the catalyst. It is surprising that an oxygen-deactivated Pd catalyst can catalyse the extensive hydrogenation reaction of carbonyls which result in the formation of a methylene group.

In this study, we used infrared spectra of acetophenone (AP) adsorption and gas-phase AP hydrogenation on Pd/SiO_2 catalysts as a model to reveal the relationships between

adsorption geometry and selectivity of the hydrogenation reaction of carbonyl groups. We chose AP rather than acetone as the model compound because the η^2 -acetone is desorbed and/or decomposed on the Pd surface at temperatures below room temperature.

Experimental

A 2.6 wt.% Pd/silica catalyst was prepared by impregnating Cab-O-Sil M-5 SiO₂ (Cabot Co., 99.8% pure) with an aqueous solution of PdCl₂. The catalyst was dried at 80 °C and calcined in flowing air at 250 °C for 5 h before the reduction treatment. Hydrogen (Sun-Fu Gas Co., 99.99% pure) and nitrogen (Sun-Fu Gas Co., 99.999% pure) were further purified by passing through a deoxo purifier. AP (Jassen, 99 + % pure) was degassed with multiple freeze-pump-thaw cycles. Oxygen was used without any further purification.

AP hydrogenation was carried out in a fixed-bed reactor system at atmospheric pressure and has been described in detail elsewhere.¹³ Samples of 10-20 mg Pd/SiO₂ were reduced in flowing H₂ at 320 °C for 10 h. The temperature was ramped from room temperature to a desired reduction temperature at a rate of 10 °C min⁻¹. The average particle size of the supported Pd after this treatment, estimated by X-ray line broadening, is ca. 160 Å. The conversion of the AP hydrogenation reaction was typically kept below 10% to avoid heatand mass-transfer effects. The AP-H2-N2 feed streams were passed over the catalysts for 30 min before a sample was taken for analysis. The gas-flow rates were measured using an MKS 1259 flow controller. AP was introduced into the reactor system via a calibrated 0.5 cm³ syringe pump and was vaporized in the preheated reactor inlet line. The catalysts were purged with H_2-N_2 for 30 min between each AP- H_2-N_2 exposure to maintain the catalytic activity.14

For reactions on oxygen-predosed Pd catalysts, the oxygen was dosed into the Pd catalyst system at the reaction temperature by injecting the oxygen into the flowing helium (100 ml min⁻¹) through a port located upstream of the reactor with a gas-tight Hamilton 1010 syringe. The injection port was similar to that used in gas chromatography. The oxygen-predosed catalysts were purged with helium between each $AP-H_2-N_2$ exposure. The flowing system of the reactor was heated with heating belts to avoid condensation of the

J. Chem. Soc., Faraday Trans., 1996, 92(9), 1595–1601 1595

samples. The products were analysed by gas chromatography (Shimadzu GC-8A) with a 6 ft[†] FFAP column. Product concentrations were determined using a Shimadzu CR-6A integrator by comparing the peak areas with those for a standard mixture.

The IR spectra were recorded on a Digilab FTS-40 FTIR spectrometer with a resolution of 2 cm⁻¹ and 256 scans at the temperatures described in the manuscript. All spectra reported here were corrected by subtracting the adsorption of the blank catalyst disk and ZnSe windows. The spectral intensity of the gas-phase samples was indistinguishable from the background noise under the pressure used (<0.1 Torr of AP). The IR cell used was a standard design that permitted the evacuation and heating of the sample under static conditions. The 20 mm diameter sample disk was made of approximately 30 mg catalyst pressed at 5000 psi,[‡] oxidized *in situ* in 760 Torr at 250 °C for 2 h, reduced in 600 Torr H₂ at 320 °C for 10 h and evacuated in 3×10^{-5} Torr in a glass vacuum system for 30 min at 350 °C. The H₂ gas was refreshed twice during the reduction treatment.

Results

AP hydrogenation reaction

The products of the AP hydrogenation reaction on Pd/SiO₂ include 1-phenylethan-1-ol, ethylbenzene, 1-cyclohexylethan-1-ol, acetylcyclohexane and ethylcyclohexane.¹⁵ The reduction of the phenyl group of AP to a cyclohexyl group can be inhibited by reducing the hydrogen partial pressure in the reactant stream. The hydrogen partial pressure used in this study is controlled at a level which avoids the reduction of the phenyl group, which would complicate understanding of the procedure. Ethylbenzene (EB) and 1-phenylethan-1-ol (PE) are the only products from Pd/SiO₂ catalysts under the reaction conditions reported in this paper. The production of EB increased with increasing numbers of oxidation-reduction treatment cycles of the catalyst. The initial oxidationreduction treatment cycles of the catalyst were performed repeatedly until the catalytic behaviour of the Pd catalysts was stabilized. Oxygen adsorption on Pd metal can induce a change of the surface reconstruction of a Pd crystal.¹⁶ Both Pd redistribution and sintering induced by the oxidation and reduction cycles have been reported.¹⁷ The formation and decomposition of palladium silicide during the oxidation and reduction cycles of Pd/SiO₂ have also been reported.¹⁸ The effect of repeated oxidation-reduction cycles of the Pd catalyst on the AP hydrogenation reaction may be the result of a gradual surface conditioning process caused by the oxidation and reduction pretreatment.

Fig. 1 shows production-rate variations of PE and EB vs. the conversion of AP at 70 °C on a reduced Pd catalyst and on an oxidized Pd catalyst at 30 °C (without reduction treatment). The conversion of AP was controlled by varying the flow rate of reactants (100–300 ml min⁻¹), the surface concentration of reactants and the amount of catalyst used in the reactions (3–20 mg). The production rate of EB increases with increasing conversion on a reduced Pd catalyst. This is a typical behaviour for consecutive reactions in which the selectivity towards the final product increases with increasing conversion. PE is the reactive intermediate for the production of EB from the hydrogenation reaction of AP. The consecutive reaction characteristics of AP hydrogenation have been reported by Aramendia and *et al.*¹⁹

The product distribution at low AP conversion is interesting. Extrapolation to zero AP conversion gives a non-zero intercept for EB on a reduced Pd catalyst. Moreover, the extrapolated value of the product percentage for EB to zero



Fig. 1 Plot of the variations of EB product (%) vs. the conversion of AP hydrogenation: (•) at 30 °C on an oxygen-calcined 2.6 wt.% Pd/SiO₂ catalyst (without reduction treatment) and (\bigcirc) at 70 °C on a reduced 2.6 wt.% Pd/SiO₂ catalyst. Partial pressures of AP and H₂ are 0.5 and 3.8 Torr, respectively; flow rate of AP-H₂-N₂ was 100 ml min⁻¹; total pressure 760 Torr; EB production (%) = (EB/all products) × 100%.

conversion of AP on an oxidized Pd catalyst is over 90%. For a consecutive reaction, the selectivity towards EB, the final product of a series reaction, should approach zero for nearzero conversion of AP.

Although many complicated factors may affect the relative rate of PE and EB formation, the positive intercept of EB formation from an extrapolation-to-zero conversion of AP on a Pd catalyst confirms that EB can be produced directly from AP. EB and PE are formed via mixed pathways of consecutive and parallel reactions. A parallel reaction pathway for the acetone hydrogenation reaction to produce propane and isopropanol has also been reported.^{20,21} The extrapolated value of the selectivity for EB to zero conversion of AP determined on a reduced Pd catalyst may or may not be distinguishable from zero. This will be discussed further below.

The effect of the amount of the predosed oxygen on the selectivity of the AP hydrogenation reaction is shown in Fig. 2. The yield of EB increases with increasing oxygen concentra-



Fig. 2 Effect of predosed oxygen on the selectivity of the hydrogenation of AP at 70 °C. Flow rate of AP- H_2 - N_2 was 100 ml min⁻¹. Partial pressures of AP and H_2 were 0.5 Torr; total pressure is 760 Torr.

^{† 1} ft = 0.3048 m. ‡ 1 psi ≈ 6.894757 × 10³ Pa.

tion on the Pd catalyst. The selectivity towards EB is almost 100% when the reaction is catalysed by an oxygen-calcined Pd catalyst.

The effect of reaction temperature on the selectivity of the AP hydrogenation reaction is shown in Fig. 3. The overall reaction conversion passes through a maximum with increased reaction temperatures. A similar phenomenon has also been observed in other hydrogenation reaction systems.²² The decrease of the overall reaction rate at 70-180 °C is not due to the poisoning of the catalytic surface by any cracking products of AP. No irreversible catalyst deactivation occurs when successive measurements are made with increased and/or decreased reaction temperatures. The 'volcano' shape of the plot of conversion vs. temperature can be explained by the overlap of two opposite influences of temperature, as suggested by a referee of this paper. At low temperatures the positive influence of temperature in the kinetic constants increases the reaction rate. At high temperatures the decrease in the concentration of the adsorbed species prevails and the reaction rate declines. The water formed in the hydrogenation reaction may also influence the conversion by changing the mass-transport limitations of the adsorption of reactants as well as the desorption of products.

The product distribution (%) towards PE, defined as the amount of PE produced as a percentage of the total products (PE + EB), *i.e.* $100 \times PE/(EB + PE)$, maximized at around 100 °C. PE decreases gradually with increasing EB at reaction temperatures higher or lower than 100 °C. This phenomenon cannot be explained by a simple consecutive reaction mechanism. For reaction in series

then

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

 $k_2/k_1 \propto \exp(E_1 - E_2)/RT$

The production of C, the final product, would increase with increasing reaction temperature if $E_1 > E_2$; decrease with increasing temperature if $E_1 < E_2$; or not be influenced by reaction temperature if $E_1 = E_2$.²³ However, the temperature effect on the behaviour of the EB selectivity variation shown in Fig. 3 cannot be explained satisfactorily by the above mechanisms.

The hydrogenation rate of PE to EB on a Pd surface increases rapidly when reaction temperature is > 100 °C (data not shown here). The increasing EB selectivity in the AP



Fig. 3 Temperature effect on the product distribution of the AP hydrogenation reaction on Pd/SiO_2 : (\odot) EB, (\blacksquare) PE, (\bigcirc) conversion = $(AP_{in} - AP_{oul})/AP_{in}$. Partial pressures of AP and H₂ were 0.5 and 3.8 Torr, respectively, flow rate of $AP-H_2-N_2$ is 100 ml min⁻¹; total pressure is 760 Torr.

hydrogenation reaction at temperatures >100 °C can be explained by a series reaction mechanism in which PE is the intermediate for EB production. However, the selectivity variations of PE and EB at low temperature are interesting. IR experiments demonstrated that the transformation of PE to EB on the Pd surface at room temperature is slow (see below) suggesting that the hydrogenation reaction pathway is not favoured for PE on the Pd catalyst at low reaction temperatures. The formation of PE and EB from AP on a Pd catalyst at low temperatures must be controlled by mixed reaction mechanisms of series and parallel pathways.

More hydrogen is required for the EB production than for PE production. The extent of surface hydrogen concentration may be attributed to the selectivity variation of the AP hydrogenation reaction. However, evidence shows that the surface hydrogen concentration cannot be solely responsible for the selectivity variation of the AP hydrogenation reaction on a Pd catalyst at low reaction temperatures. A similar trend of the PE and EB selectivity variation vs. temperature is observed when the hydrogen partial pressure in the reactant stream rises from 3.8 Torr to almost 760 Torr, except that the conversion of AP is higher and some phenyl groups of AP, PE and EB are reduced to cyclohexyl groups.¹⁵ Fig. 4 shows the hydrogen partial pressure effect on the AP hydrogenation reaction. The PE and EB distribution was unchanged when the hydrogen partial pressure was varied between 1.9 and 26.6 Torr. This result also suggests that the selectivity of AP hydrogenation to EB and PE is insensitive to a change in hydrogen partial pressure within a certain range. We do not intend to discuss the near-zero order for hydrogen observed in this experiment. The quantity of hydrogen used in the reaction system is much larger than the stoichiometric quantity of hydrogen required to react with all the AP. The reaction under investigation is a composite reaction, involving a number of stages, and experiments with high hydrogen concentration do not yield reliable order information.

Fig. 1 and 2 show that oxygen has a significant influence on the reaction selectivity of PE and EB. The strong oxygen adatom overlayer effect on the adsorption configurations of carbonyl groups on metal surfaces has been reported previously.^{5,9} Selectivity towards PE or EB of the AP hydrogenation is significantly changed by the addition of acid or alkali promoters.²⁴ The adsorption configurations of carbonyl groups on the single-crystal metal surfaces are also affected by



Fig. 4 Hydrogen partial pressure effect on the product distribution of the AP hydrogenation reaction on Pd/SiO₂ at 30 °C: (\bigcirc) EB, (\bigcirc) PE, (\bigcirc) conversion = (AP_{in} - AP_{out})/AP_{in}. Partial pressures of AP 0.15 Torr; flow rate of AP-H₂-N₂ 100 ml min⁻¹; total pressure 760 Torr.

J. Chem. Soc., Faraday Trans., 1996, Vol. 92 1597

the surface acidity.⁵ The selectivity of AP hydrogenation to PE or EB is likely to correlate with the adsorption configurations of the reactants. To understand the adsorption behaviour of AP on Pd surfaces, IR experiments were used to probe the adsorption geometry of AP.

FTIR study

(a)

The IR spectra of AP adsorption on a Pd/SiO₂ catalyst shown in Fig. 5 reveal two different kinds of adsorption configurations, *i.e.* η^1 (O) and η^2 (O,C) configurations, at AP pressure <0.1 Torr. The IR bands of the η^2 species are shadowed by the IR bands of the η^1 species adsorbed on the SiO₂ surface when the pressure of AP is >0.1 Torr. A detailed description of adsorption-desorption behaviour of η^{1} - and η^2 -AP on Pd/SiO₂ catalysts studied by FTIR and temperature-programmed desorption techniques is addressed elsewhere.²⁵ The assignments of the IR bands of AP on Pd/SiO₂ catalysts were made by comparison with the liquid phase AP spectrum (see Table 1). AP is initially coordinated to Pd/SiO₂ in the η^1 configuration. The spectra of η^1 -AP con-

0.2

absorbance (arb. units) b 1800 1700 1600 1500 1400 1300 wavenumber/cm⁻ (b) 0.01 x5а absorbance (arb. units) MMMMM C C 3200 3100 3000 2900 2800 2700 wavenumber/cm-1

Fig. 5 (a), IR spectra of 0.05 Torr AP adsorption: a, on reduced Pd/SiO₂ at room temperature for 4 min; b, for 1 h at 70 °C after a; c, on Pd/SiO₂ presorbed with 30 Torr of O₂ at room temperature for 1 min, followed by evacuation to 10^{-4} Torr; d, for 1 h at 70 °C after c. (b), IR spectra of v(CH) modes part of (a).

J. Chem. Soc., Faraday Trans., 1996, Vol. 92 1598

Table 1 Vibrational mode assignments of acetophenone on Pd/SiO₂

assignment	liquid AP	η^1 -AP	η^2 -AP
v(C ₆ H ₅)	3086		
	3061	a	3077
	3032		
v(CH ₃)	3004		
	2969		2982 ^b
	2926		
v(CO)	1686	1674	1388°
v(C=C)	1598	1598	1598
	1582	1580	
	1448	1450	1450
$\delta_{a}(CH_{a})$	1428		
δ _s (CH ₃)	1358	1366	đ

^{*a*} Very weak broad hump between 3100 and 2950 cm⁻¹. ^{*b*} Weak broad hump. ^{*c*} From ref. 26. ^{*d*} Not resolved from 1388 cm⁻¹ peak.

sisted of IR bands at 1366, 1450, 1580, 1598 and 1674 cm⁻¹ [Fig. 5(a), spectrum a] and a weak unresolved broad band at $3110-2900 \text{ cm}^{-1}$ [Fig. 5(b)]. The band at 1366 cm⁻¹ is assigned to the $\delta_s(CH_3)$ mode. The bands at 1450, 1580 and 1600 cm^{-1} are due to the v(C=C) modes of the AP phenyl group. The broad band at $3110-2900 \text{ cm}^{-1}$ consists of the v(CH) of AP phenyl and methyl groups. The band at 1674 cm^{-1} is due to the v(CO) mode of the η^1 configuration of the adsorbed AP on the Pd/SiO₂ surface.

A new band at 1388 cm⁻¹ develops gradually with decreasing intensity of the band at 1674 cm⁻¹ at elevated temperatures. The band at 3077 cm^{-1} , which originated from the mode of the v(CH) phenyl group, is resolved from the broad IR adsorption feature at elevated temperatures [Fig. 5(b), spectrum b]. The new band at 1388 cm⁻¹ is assigned as the v(CO) stretch of the η^2 -AP. The vibrational frequency of the v(CO) modes shifts from 1674 and 1388 cm⁻¹ to 1640 and 1359 cm⁻¹ when an isotope-labelled AP ($C_6H_5^{13}COCH_3$) is adsorbed onto the Pd/SiO₂ surfaces. The IR spectrum of $C_6H_5COCD_3$ on Pd/SiO₂ surfaces (not shown in this paper) is approximately the same as the IR spectra of AP except that the 1366 cm^{-1} band is not seen. These results suggest that the 1388 cm⁻¹ band is from the vibrational mode of v(CO) and is not from any kind of vibrational mode of the CH₃ group.

It is surprising that such a strong IR band is observed for the v(CO) stretch of the η^2 -AP which is polarized nearly parallel to the surface. Anton $et al.^5$ have provided an explanation for this phenomenon by considering the point-group symmetry of the adsorbed species and the dynamic dipole moment induced by the variation of the electron population of the π^*_{CO} orbital of η^2 -carbonyls. The band of the $\nu(CO)$ stretch of the η^2 -acetone on Ru and Rh single-crystalline metal surfaces is also the dominant band of the electron energy-loss spectra of the η^2 -acetone at frequencies >1000 cm^{-1} ^{4,5} Comparable effects on the other adsorption systems with similar parallel modes have also been observed.²⁶⁻²⁸ The intensity of the 1388 cm⁻¹ band is maximized at 70 °C for 1 h as shown in Fig. 5(a), spectrum b. Further increase in temperature causes a decomposition and/or desorption of the η^2 -AP. The formation of η^2 species at 70 °C on an oxygen predosed Pd/SiO₂ catalyst (Fig. 5d) is significantly less than that on a reduced Pd/SiO_2 surface. The stabilization of the η^1 -carbonyl on metal surfaces by the oxygen overlayer may be responsible for the high EB productivity of the AP hydrogenation reaction catalysed by an oxygen-perturbed Pd catalyst.

The reactivity of η^{1} - and η^{2} -AP towards hydrogenation is shown in the IR spectra in Fig. 6(a) and (b). Fig. 6, spectra a-c show the hydrogenation of η^1 -AP at room temperature on an oxidized Pd/SiO₂ catalyst. The intensity of the v(CO) mode of the η^1 species decreases rapidly when 30 Torr of hydrogen is added to the IR cell. The water band at 1620 cm⁻¹ is attrib-





Fig. 6 (a), IR spectra of the reaction of η 1- and η 2-AP with hydrogenation: a, for 3 min; b, 30 Torr of H₂ at room temperature for 4 min after a; c, evacuated to 10^{-3} Torr and kept in vacuum for 10 h after b; d, following adsorption of AP at 50 °C and 0.05 Torr for 1 h, H₂ at 50 °C and 30 Torr for 4 min after c; e, evacuated to 10^{-3} Torr and held in vacuum at 50 °C for 10 h after d. (b), IR spectra of v(CH) modes part of (a).

uted to the water produced from the EB formation reaction and/or from the reaction between hydrogen and the surface oxygen. The IR bands belonging to the vibration modes of EB and/or PE are weak but clear at 1455, 1496 and 1600 cm⁻¹



Fig. 7 IR spectra of 0.1 Torr PE on Pd/SiO_2 : a, room temperature with 100 Torr of hydrogen for 3 min; b, evacuated to 10^{-3} Torr after a; c, heated to $70 \,^{\circ}$ C for 1 h after b

[v(C=C) modes of the phenyl group]. The bands belonging to the vibrational modes of v(CH) stretching are located at 2880, 2943, 2975, 3034 and 3072 cm⁻¹. Note that the IR spectrum of the v(C=C) modes and the v(CH) stretching modes for EB and PE overlap. The only IR bands between 1300 and 3100 cm⁻¹ that can be used to distinguish the adsorbed EB and PE on Pd/SiO₂ catalysts are the PE $\delta_s(CH_3)$ band at *ca.* 1366 cm⁻¹ and the broad $\eta^2(CO)$ band of PE (or AP) at 1388 cm⁻¹. The adsorbed PE on the Pd surface will convert to AP when there is no hydrogen in the adsorption system (See Fig. 6f and Fig. 7).

There are some weak bands which originated from the v(C=C) modes at 1455, 1495 and 1600 cm⁻¹ and a tiny v(CO) band at 1674 cm⁻¹ appearing on the IR spectrum after the evacuation of hydrogen from the adsorbed η^{1} -AP oxidized Pd/SiO₂ reaction system (Fig. 6c). This result suggests that the major surface product of η^{1} -AP hydrogenation under the effect of oxygen is EB. If PE were the major product of the η^{1} -AP hydrogenation reaction, the vibrational bands of adsorbed AP would dominate the IR spectra after the evacuation of hydrogen from the reaction system (see Fig. 7).

Fig. 6d-f show the hydrogenation of the adsorbed AP when η^{1} - and η^{2} -carbonyls coexist on the surface. The IR bands belonging to the PE and/or EB vibration modes appear at



Fig. 8 IR spectra of 0.2 Torr of PE on SiO₂ (without Pd): a, room temperature for 3 min; b, heated to 70 °C for 1 h after a; c, cooled to room temperature; and d, evacuated to 10^{-2} Torr

Fig. 7 demonstrates the IR spectra of PE adsorption onto the Pd/SiO₂ surface. 10 Torr of hydrogen was dosed into the IR cell together with 0.1 Torr of PE to prevent the rapid conversion of PE to AP (Fig. 7a). The weak bands at 1455, 1495 and 1600 cm⁻¹ are assigned to the v(C=C) modes of PE. The band at 2965 cm⁻¹ is due to the vibration of the v(CH) stretch mode. The broad band at 1350-1440 cm⁻¹ is from the $\delta_{s}(CH_{3})$ and the η^{2} -(CO) vibrational modes. The PEhydrogen species are stable on the Pd/SiO₂ surface for tens of minutes at room temperature. This result suggests that the conversion of PE to EB is slow on Pd surfaces at low temperatures. The adsorbed PE converts to a mixture of adsorbed η^1 - and η^2 -AP when the coexistent hydrogen gas is evacuated from the system (Fig. 7b and c). The spectra of PE on pure SiO_2 (without Pd) are shown in Fig. 8. No reaction was observed for PE on SiO₂.

Discussion

The IR results suggest that both the adsorbed η^{1} - and η^{2} carbonyls are active in hydrogenation reactions. The η^{1} carbonyl is the precursor of the η^2 -carbonyl. The effects of presorbed oxygen (Fig. 1 and 2), temperature (Fig. 3) and hydrogen partial pressure (Fig. 4) on the selectivity of hydrogenation of AP together with the IR results reveal the relationship between the configurations of the adsorbed AP and reaction selectivity. The selectivity toward EB increases with increasing oxygen coverage on the Pd/SiO2. The IR results show that the η^1 -AP is stabilized on oxygen-dosed Pd/SiO₂ surfaces. A sharp increase in the selectivity toward PE is observed at 70 °C. This temperature coincides with the temperature at which the concentration of the η^2 -AP is maximized. These results suggest that the η^2 -carbonyls can be hydrogenated to produce hydroxy-group-containing compounds. The hydroxy group can be further reduced to give a methylene group. The η^1 -carbonyl can be hydrogenated to a hydroxy group or be hydrogenated directly to a methylene group. The electron-withdrawing promoters, such as oxygen, would enhance the direct methylene-group-formation pathway. Since the interaction of η^1 -carbonyl with the metal was weaker than the interaction of η^2 -carbonyl with the metal, the reactivity of η^1 -carbonyl was expected to be lower than the reactivity of η^2 -carbonyl.

It has been suggested that metals that are weakly basic in the Lewis sense tend to favour coordination with carbonyl groups in an η^2 configuration.⁵ If this is true, then the production of hydroxy groups from the catalytic hydrogenation of carbonyl groups would be favoured on such metals. There is extensive support for the model proposed above. Consider, for example, that the selectivity of the hydrogenation of carbonyl groups to hydroxy groups increases on a Pd catalyst when the catalyst is promoted by NaOH,²⁴ and on Ru catalyst when the catalyst is promoted by alkali metals.²⁹ The hydrogenation of acetone at temperatures above room temperature on most of the supported metal catalysts produces isopropanol with almost 100% selectivity.³ Some propane was formed when the hydrogenation of acetone was catalysed by Pt films, Pt foils or Pt powders at low reaction temperatures.³⁰ It has been reported that η^{1} -acetone tends to be adsorbed on well defined, close-packed defect-free regions of Pt surfaces at low temperatures.^{8,31} It is more likely that there are more close-packed defect-free regions on the surfaces of Pt film, foil or powder than on the surfaces of supported Pt catalysts. Therefore the selectivity of acetone hydrogenation shifts towards propane when Pt film, foil or powder is used as the catalyst. The value of the selectivity for EB (Fig. 1) conversion of AP on an oxidized Pd catalyst extrapolated to zero is over 90%. This result further supports the theory that an η^{1} carbonyl can be reduced directly to a methylene group. Thus, the production of PE and EB from the hydrogenation of AP is controlled by mixed pathways of parallel reaction and consecutive reaction.

The extrapolated value of the selectivity for EB to zero conversion of AP determined on a reduced Pd catalyst may or may not be distinguishable from zero. This result is consistent with the model above for the AP hydrogenation reaction. The frequency of the v(CO) mode of η^2 -AP is more than 300 cm⁻¹ less than the frequency of the v(CO) mode of the liquid-phase AP. Thus it is clear that the bond order of the η^2 -carbonyl group is significantly reduced. The decrease in the carbonyl CO bond order of the η^2 -carbonyls can activate the reactivity of η^2 -carbonyls more than that of η^1 -carbonyls. Therefore the reaction rate of the hydrogenation of an η^2 -carbonyl would be expected to be faster than that of an η^1 -carbonyl. Moreover, the η^1 -carbonyl on the Pd surface can be stabilized by an oxygen adlayer. Thus the production of PE on a reduced Pd catalyst is greater than the production of PE on oxygenperturbed Pd catalysts. The hydrogen required for EB production is twice that required for PE production. The η^{1} - and η^2 -carbonyls are competing for surface hydrogen to produce EB and PE during the hydrogenation of AP. The η^2 -carbonyl would be a stronger surface-hydrogen competitor because of its higher reactivity. Thus the EB production would be further lowered when the conversion is minimal and/or the surface hydrogen concentration is starved.

The adsorbate configuration that exhibits a stronger interaction (i.e. η^2 -AP) with the surface produces minimal bond scission, but the weakly interacting species (η^{1} -AP) undergoes scission of the C=O bond. This behaviour is unexpected, but explainable. The reduction of AP to EB may be considered as the reverse of Wacker-type oxidation (i.e. the oxidation of propene to acetone) that Pd complexes are known to catalyse.^{32,33} In a standard set of experiments propene is oxidized by oxygen in 5 min at 20 °C to give a 90% yield of acetone with a Wacker-type oxidation process.³⁴ The hydrogenation of some carbonyl compounds can involve the enol rather than the keto form of the compounds.35 The effect of the AP aromatic ring may cause the equilibrium to shift more markedly to the enol form than for other ketones. The aromatic ring of the AP that is adsorbed in the η^1 configuration can facilitate the formation of an ethylene-like double-bond intermediate. conjugate to the aromatic ring through an enolization process, This enolization process can be enhanced by the adsorbed oxygen. Ayre and Madix¹² found that atomic oxygen facilitates the formation of acetone enolate when oxygen and acetone coexist on the metal surface. The active complex, which may not be observable on the IR spectrum owing to the very short lifetime of the active complex, is either converted to an η^2 configuration, or hydrogenized to produce an ethyl group of EB by a mechanism analogous to a reverse Wackertype oxidation process. The positive effect of presorbed oxygen on the selectivity of AP hydrogenation to EB strongly supports the above model.

The π character of the C=O group is lost when the η^1 carbonyl is converted to an η^2 configuration. The formation tendency of the ethylene-like double-bond intermediate is inhibited when AP is adsorbed in an η^2 configuration. The reverse Wacker-type oxidation process is the less favoured.

Aramendia et al. refuted the role of the enol form in the AP hydrogenation reaction.¹⁹ This does not contradict the model proposed here. The reaction conditions selected by Aramendia et al. indicate that a consecutive reaction was the major pathway, suggesting that the η^2 adsorption configuration of AP is favoured when the reaction proceeds. As we stated in the above model, the enolation process is inhibited when AP is adsorbed in an η^2 configuration. One would not expect to observe any effect from an enol form involved in the reaction.

The other type of oxidation process that Pd complexes are known to catalyse is the allylic oxidation reaction.^{36,37} The intermediates in this case are not $\eta^{1}(O)$ species, but are typically bound to the metal centre of their π systems. However, a mechanism analogous to a reverse allylic oxidation process cannot proceed via an aliphatic ketone (e.g. acetone) hydrogenation reaction. The particle-size dependence of the selectivity of acetone hydrogenation on Pt group metals cannot be explained via the inverse allylic oxidation mechanism.³

Temperature effects on the activity of the AP hydrogenation reaction are also interesting. The overall rate of the reaction passes through a maximum with increasing temperatures. The change in selectivity of the AP hydrogenation associated with the change of reaction temperature may be explained as a result of the starving of the hydrogen concentration on the surface of the catalyst at higher reaction temperatures. The hydrogen required for EB production is twice that required for PE production. Coincidentally, the EB selectivity fell at ca. 70 °C. However, the hydrogen starvation assumption is inconsistent with the data reported here. First, the selectivity of AP hydrogenation to EB and PE is insensitive to a change in hydrogen partial pressure within a certain range (1.9-26.6 Torr), indicating that the change in the selectivity of AP hydrogenation cannot be explained by the effect of surfacehydrogen concentration variations alone. Secondly, the conversion of AP hydrogenation at reaction temperatures of 50 and 70 °C is controlled at a similar level, but a sharp increase in the selectivity toward PE at 70 °C is observed. This result also suggests that the change of the hydrogen concentration at the catalyst surface is not solely responsible for the change in reaction selectivity. A 20-80% yield of EB (depending on the promoter added in the system) from liquid-phase AP hydrogenation under mild reaction conditions has been reported.24 Under these conditions the EB yield can be higher than under gas-phase AP hydrogenation reaction conditions. The hydrogen concentration on the surface of the catalyst under liquidphase reaction conditions would be lower than under gas-phase reaction conditions. However, the product of the AP hydrogenation reaction is not shifted toward PE as expected by the hydrogen starvation model.

Conclusions

The adsorption configuration of carbonyl groups on the surface of catalysts is an important factor in controlling the selectivity of the hydrogenation of carbonyl groups to hydroxy or methylene groups. The η^1 -carbonyl can be converted to an η^2 -carbonyl during annealing of the adlayer, be hydrogenated to a hydroxy group or be hydrogenated to a methylene group via a pathway similar to a reverse Wackertype oxidation process. Oxygen can inhibit the conversion of η^1 -carbonyl to η^2 -carbonyl but it can promote the transformation of an η^1 -carbonyl to a methylene group. η^2 -Carbonyl tends to be hydrogenated to a hydroxy group. The hydroxy group can be further reduced to give a methylene group via a consecutive reaction pathway.

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