n n

Phenol hydrogenation over palladium supported on magnesia: Relationship between catalyst structure and performance

N. Mahata,^a K. V. Raghavan,^a V. Vishwanathan,^{*a} C. Park^b and M. A. Keane^{*c}

- ^a Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad—500 007, India
- ^b Department of Chemical Engineering, University of Leeds, Leeds, UK LS2 9JT
- ^c Department of Chemical & Materials Engineering, University of Kentucky, Lexington KY 40506 0046, USA. E-mail: makeane@engr.uky.edu

Received 4th January 2001, Accepted 2nd May 2001 First published as an Advance Article on the web 1st June 2001

A series of magnesia-supported palladium catalysts (Pd loading in the range 0.5-7.0 wt.%) has been prepared by impregnation from aqueous solutions of PdCl₂, Pd(NH₃)₄Cl₂ and Pd(CH₃COO)₂ and characterised by X-ray diffraction (XRD), CO chemisorption and high resolution transmission electron microscopy (HRTEM). The gas-phase hydrogenation of phenol was employed as a model reaction to probe the dependence of catalytic activity/selectivity on changes in Pd particle size and surface acid-base properties. The catalyst prepared from the acetate precursor exhibited the greatest Pd dispersion when compared with the chloride and amine precursors. The surface mobility of the metal chloride resulted in larger Pd particles from the Cl-containing precursors while the presence of residual Cl in the activated catalysts lowered the hydrogenation rate and was responsible for a decline in activity with time-on-stream. The effects of varying such process variables as temperature, hydrogen/phenol mol ratio and inlet molar phenol feed rate are presented and discussed while the question of structure sensitivity is addressed. The reaction exhibited a negative dependence on phenol partial pressure up to 503 K but a positive dependence was evident at higher temperatures. The order of the reaction with respect to hydrogen remained positive and was close to unity at 563 K; an apparent activation energy of 63 kJ mol⁻¹ was recorded. The effect of doping the support with calcium and fluoride has shown that modifications to the acid-base properties of magnesia can be used to control catalytic activity/selectivity.

Introduction

The synthesis of cyclohexanone is of commercial significance in the manufacture of caprolactam, a monomer used in the synthesis of Nylon-6. Cyclohexanone production, on an industrial scale, typically involves either the oxidation of cyclohexane or the hydrogenation of phenol.¹ The former route requires high temperatures and pressures and generates appreciable by-products that lower the product yield and complicate the recovery/separation steps. In the hydrogenation of phenol, cyclohexanone can be generated in a one- or two-step process. In the latter case, phenol is first hydrogenated to cyclohexanol which is then dehydrogenated, in the second step, to cyclohexanone. The replacement of a two-step process by a single-step (phenol \rightarrow cyclohexanone) hydrogenation is economically more advantageous in terms of capital costs and energy savings.² Based on the literature to date, Pd catalysts have shown the most promise in promoting the selective hydrogenation to cyclohexanone.³⁻¹¹ Alumina-supported Pd catalysts, though used extensively in hydrogenation processes, have a low resistance to deactivation by coke deposition.¹² Basic Group I and II oxides can, however, serve as promoters by modifying acidic supports to increase the coke resistance. While magnesia as a catalyst support suffers from the decided drawback of possessing a low surface area and poor mechanical strength,³ it exhibits some interesting support effects in terms of its ability to stabilize the supported metal.¹³ The acid-base properties of magnesia can impact on the nature of the reactant/catalyst interactions and govern the ultimate

product composition; by modifying the acid-base functions of MgO, catalytic activity/selectivity can be controlled. The interplay between surface acidity/basicity is accepted as having a bearing on cyclohexanone selectivity from phenol^{3,14,15} but the optimum surface requirements are far from established.

It is known that calcination at high temperatures and the addition of alkali/alkaline earth metals can induce significant changes in the physico-chemical and catalytic properties of alumina.¹⁶ The possibility of using promoters to modify Pd/MgO and generate a highly selective phenol hydrogenation catalyst has yet to be studied in a comprehensive The role of metal fashion. loading has been considered^{3,7,9,17-19} but no conclusive correlation between Pd dispersion/metal surface area/crystallite size and hydrogenation activity/selectivity has yet been presented for Pd/MgO. In this paper, such a correlation is proposed and the influence of (a) the nature of the Pd catalyst precursor and (b) the incorporation of calcium and fluoride additives on the overall catalytic performance is reported.

Experimental

Catalyst preparation and activation

Magnesia-supported palladium, where the palladium loading was in the range 0.5–7.0 wt.%, was prepared by impregnating a commercial magnesia (Harshaw MG-0601, surface area = $48 \text{ m}^2 \text{ g}^{-1}$ and pore volume = 1.03 cm³ g⁻¹) with

known concentrations of acidified (with HCl, pH 3) aqueous solutions of $PdCl_2 \cdot xH_2O$. Palladium acetate $(Pd(CH_3COO)_2)$ and tetraamine palladium(II) chloride $(Pd(NH_3)_4Cl_2)$ were also used as palladium sources to prepare 1 wt.% Pd/MgO catalysts. The Pd(CH₃COO)₂ was dissolved in acetonitrile while the Pd(NH₃)₄Cl solution was prepared by dissolving PdCl₂ in conc. NH₄OH solution (pH 9) at 348 K with appropriate dilution in deionised water. The magnesia support was also modified by impregnation with solutions of calcium nitrate and ammonium fluoride to deliver a 1 wt.% loading prior to the addition of palladium. The catalysts were dried overnight at 393 K, calcined in air at 723 K for 5 h and reduced at 723 K for 3 h in flowing dry hydrogen (0.26 mol h⁻¹).

Catalyst characterisation

XRD analysis of the calcined samples was conducted using a Philips PW 1140 diffractometer with Ni filtered Cu-K α radiation ($\lambda = 1.54$ Å). The residual chlorine content in the calcined/reduced catalysts derived from PdCl₂ and (Pd(NH₃)₄Cl₂) precursors was determined potentiometrically. A known weight (*ca.* 0.2 g) of the activated samples was heated under reflux in deionised water for 24 h. The water extract was filtered and the chlorine content was measured using a Metrohm (Model 278) Autotitrator (AgNO₃ titrant, combined Ag electrode).

Carbon monoxide chemisorption measurements were performed at 298 K using a conventional volumetric apparatus²⁰ where the catalyst was activated in situ, as above. The irreversible uptake of CO was measured using a dual isotherm technique, *i.e.* after determination of the first isotherm, the samples were evacuated at 298 K for 30 min and a second isotherm was obtained. The difference between the two isotherms accounts for the amount of CO irreversibly held (CO_{irr}) on the surface of the catalyst. The ratio CO_{irr}/Pd, i.e. the ratio of surface Pd atoms available for CO adsorption to the total number of Pd atoms, is used in this paper as a measure of palladium dispersion. Infrared analysis²¹ revealed that CO adsorption, under these conditions, was predominantly via a linear single point attachment. The intensity of the band at ca. 1800 cm⁻¹ attributed to a bridged mode of adsorption was insignificant when compared with the band at 2070 cm⁻¹ that is characteristic of a linear mode of adsorption. A CO_{irr}/Pd = 1 stoichiometry was accordingly taken as a reasonable estimate in determining Pd dispersion. The metal surface area (S, m^2 (g Pd)⁻¹) was calculated from CO uptake using the relationship²²

$S = CO_{irr}/1.27 \times 10^{19} \times metal content$

where 1.27×10^{19} (atoms m⁻²) corresponds to the number of surface Pd atoms per unit area of polycrystalline metal surface. The Pd crystallite size (*d*, nm) was calculated from the estimated surface area according to²²

$$d = 6 \times 10^3 / \rho S$$

where ρ is the density of palladium metal, *i.e.* 12.02 g cm⁻³. HRTEM analysis was carried out using a Philips CM200 FAGTEM microscope operated at an accelerating voltage of 200 kV. The specimens were prepared by ultrasonic dispersion in butan-2-ol, evaporating a drop of the resultant suspension onto a holey carbon support grid. The particle size distribution profiles presented in this study are based on a measurement of over 500 individual particles.

Surface acidity was probed by ammonia adsorption at room temperature. In a typical experiment, *ca.* 0.2 g of the activated catalyst was degassed for 3 h at 473 K to a pressure of 1×10^{-5} Torr and cooled to ambient temperature. The ammonia adsorption isotherm was measured by allowing ammonia from the storage bulb to come in contact with the catalyst and equilibrate. From the pressure and volume

change, the amount of ammonia adsorbed per unit weight of catalyst was calculated. After the first adsorption isotherm, the catalyst was evacuated for 1 h at the same temperature and the second isotherm was measured. The parallel isotherms were extrapolated to zero pressure and the difference in amount adsorbed was taken as the chemisorbed ammonia content.

Catalytic reactor system

The gas-phase phenol hydrogenation was carried out in a fixed-bed continuous flow tubular reactor (2.2 cm id \times 20 cm) over the temperature range $473 \leq T/K \leq 563$ and at atmospheric pressure. The catalyst precursor (particle diameter = $1400-1800 \mu m$) was calcined/reduced in situ (as above) and a mixture of phenol in cyclohexane (1:2 weight ratio) was fed to the catalyst bed (ca. 0.5 g) at a fixed rate via a calibrated motorized syringe. Hydrogen served as both reductant and carrier gas where the hydrogen/phenol inlet mol ratio was varied from 2 to 11 and the weight hourly space velocity (WHSV) from 0.02 to 0.054 mol h^{-1} g⁻¹. The partial pressures of both reactants were adjusted by dilution with nitrogen: hydrogen, 0.18-0.88 atm; phenol, 0.06-0.12 atm. Passage of phenol/H₂ through an empty reactor or over the MgO support alone did not result in any detectable conversion. The liquid products were collected periodically and analysed by gas chromatography (FID) using a packed column (Carbowax 20M on Chromosorb W). The overall conversion of phenol $(C_{\rm P})$ as a percentage is given by

$$C_{\rm P} = \frac{[{\rm C_6H_5OH}]_{\rm in} - [{\rm C_6H_5OH}]_{\rm out}}{[{\rm C_6H_5OH}]_{\rm in}} \times 100$$

while process selectivity (as a percentage) in terms of cyclohexanone formation ($S_{C=0}$) can be represented by

$$S_{\rm C=O} = \frac{[C_6 H_{10} O]_{\rm out}}{[C_6 H_5 OH]_{\rm in} - [C_6 H_5 OH]_{\rm out}} \times 100$$

Reactivity is also discussed in this paper in terms of product yield (Y) where, in the case of cyclohexanone

$$Y = \frac{[C_6 H_{10} O]_{out}}{[C_6 H_5 OH]_{in}} \times 100$$

Results and discussion

The XRD patterns of calcined Pd/MgO with varying Pd content are shown in Fig. 1. The diffractograms are characterized by strong signals due to the presence of a crystalline MgO phase. There was no evidence of any brucite (Mg(OH)₂), characteristic peak at $2\theta = 38^{\circ}$, in the calcined samples. With an increase in Pd content beyond 1 wt.%, the two PdO peaks at inter spacing values of d = 2.644 and 1.671 Å exhibited a



Fig. 1 XRD patterns for Pd/MgO samples of varying Pd loading (A = 1, B = 2, C = 3, D = 5 and E = 7 wt.%) after calcination in air at 723 K for 3 h: (\bullet) denotes the MgO phase; PdCl₂ precursor.

marked increase in intensity as noted elsewhere²³ for higher Pd loadings. There was no detectable PdO signal where Pd loading was less than 1 wt.% but this can be attributed to particle sizes less than the resolution limit (ca. 3 nm) of the diffractometer. The influence of the Pd precursor salts on Pd particle size/dispersion and phenol hydrogenation activity is shown in Table 1. The degree of Pd dispersion or number of exposed Pd atoms was determined from the irreversible CO uptake capacity of each catalyst, a technique that has been applied elsewhere^{9,24,25} and shown to yield reliable values. The Pd catalyst prepared from the acetate precursor realised the highest metal dispersion when compared with the chloride and amine precursors. This enhancement of metal dispersion may be attributed to the larger size of the counter anion²⁶ which serves to space the Pd(II) component apart more effectively, thereby limiting agglomeration during calcination to give smaller PdO crystallites and a subsequent greater dispersion of the metallic Pd component after reduction. The $Pd(NH_3)_4Cl_2$ precursor is known^{27,28} to undergo an 'autoreduction' and the lower dispersion can be linked to the inherent high surface mobility. Moreover, it is well established²⁹ that larger metal particles are typically generated from a chloride precursor due to crystallite growth involving volatile metal chloride. The Pd particle size distribution, derived from HRTEM analysis, is illustrated by the histograms given in Fig. 2; the surface weighted average particle diameters are

included in Table 1. Each catalyst exhibited a similar size distribution but there is a greater presence of particles >6 nm in the case of those activated samples derived from chlorinecontaining precursors. It is instructive to note that the Pd crystallite diameters determined by HRTEM were consistently greater than the values extracted from CO chemisorption. This discrepancy suggests that, despite the IR evidence, there must be some deviation from an exclusive 1:1 CO: Pd stoichiometry on these supported catalysts. Any surface stoichiometry will be dependent on metal loading and the assignment of one particular value is at best a convenient approximation. Moreover, CO has been shown to interact directly with MgO.³⁰ Dorling and Moss,³¹ in a study of CO chemisorption on Pt/SiO₂ likewise concluded an exposed Pt/CO adsorption ratio of one from IR analysis but found that this was not strictly the case and the surface stoichiometry was dependent on the nature of the exposed Pt faces. Smith et al.³² have also recorded lower (Ni) particle (on SiO_2) diameters from CO chemisorption when compared with TEM analysis. Indeed, there are many instances in the literature where the dimensions of supported metal particles that are measured differ depending on the nature of the analytical technique,³³⁻³⁵ an inconsistency that continues to bedevil heterogeneous catalysis research. It is, however, usually the case that each characterisation tool delivers the same trends for a family of metal catalysts. The latter holds in this study where

Table 1 Effect of palladium precursor on Pd particle size/dispersion (from CO chemisorption and HRTEM analysis) and phenol hydrogenationactivity over 1 wt.% Pd/MgO: T = 503 K, WHSV = 0.027 mol h⁻¹ (g cat)⁻¹; hydrogen/phenol = 5.4

		Crystallite diameter d/nm			
Precursor	Dispersion CO _{irr} /Pd	From CO _{irr}	From HRTEM	Activity/ 10^{-6} mol s ⁻¹ g ⁻¹	
$\begin{array}{c} Pd(CH_{3}COO)_{2} \\ PdCl_{2} \\ Pd(NH_{3})_{4}Cl_{2} \end{array}$	0.56 0.51 0.37	2.0 2.2 3.0	6.2 7.1 7.6	6.8 3.9 4.6	



Fig. 2 Palladium particle size distribution in the activated 1 wt.% Pd/MgO catalysts derived from Pd(CH₃COO)₂ (solid bars), PdCl₂ (open bars) and Pd(NH₃)₄Cl₂ (cross-hatched bars) precursors. Inset: Pd particle size distribution in the activated 7 wt.% Pd/MgO catalyst derived from PdCl₂.



Fig. 3 HRTEM of the activated 1 wt.% Pd/MgO catalysts derived from the (a) PdCl₂, (b) Pd(NH₃)₄Cl₂ and (c) Pd(CH₃COO)₂ precursors.

the order of increasing particle size was the same for both techniques. The HRTEM images, shown in Fig. 3, of the 1 wt.% Pd/MgO catalyst illustrates the nature of the Pd metal dispersion. Selected area electron diffraction analysis revealed that the Pd metal particles are crystalline and the lattice structure is in evidence in Fig. 3; the crystallinity of the MgO support is also apparent.

The palladium catalyst derived from the acetate precursor delivered the highest hydrogenation activities (Table 1) when compared with the chloride-derived samples. There was an appreciable residual chlorine associated with the activated $Pd(NH_3)_4Cl_2$ (3.9 × 10⁻⁵ mol (g cat)⁻¹) and $PdCl_2$ (3.6 × 10⁻⁵ mol (g cat)⁻¹) samples as determined potentiometrically from the water extracts after heating the samples under reflux. A subsequent STEM/energy dispersive X-ray (EDX) elemental mapping of the refluxed solid did not reveal even trace quantities of chlorine on the surface, *i.e.* the reflux treatment was fully effective in extracting the entire chlorine component from the activated catalysts. Halogens are known to act as strong poisons of transition metal catalysts^{35–37} and the presence of this electron-withdrawing residual chlorine may induce electronic perturbations in the supported Pd sites. The latter effect can impact on CO interaction(s) and may well have a bearing on the recorded CO_{irr} values. We have shown elsewhere²⁶ that the d-character of supported Pd governs, to a great extent, phenol hydrogenation activity. Moreover, a surface contamination by chlorine can disrupt the dissociative adsorption of hydrogen³⁸ and limit the reactivity of the chlorine-containing precursors surface hydrogen. The exhibited a marked loss of activity with time-on-stream as shown in Fig. 4. The presence of chlorine on catalyst surfaces is known to promote carbon deposition as demonstrated elsewhere.^{39–41} Any carbon deposits that are formed can occlude the active sites from incoming phenol with a consequent timedependent decline in conversion.

The relationship between Pd loading and the ultimate dispersion, size and surface area of the supported metal phase is presented in Fig. 5. We have adopted the Pd dispersion/size values derived from CO chemisorption that, although they differ from the values extracted from the HRTEM analysis, better represent the nature of the catalytically active surface in terms of adsorption/reactant activation. The use of TEM (even at high resolution) to determine metal particle sizes requires a deal of judgment where insufficient contrast in the image can hamper an accurate analysis, particularly for diameters of 1 nm and less. The inferred Pd particle size varied in the range 1.9 to 6.9 nm which represents a decrease in dispersion from 0.59 to 0.16. The dispersion decreased markedly as the Pd loading was increased from 1% to 3 wt.%, above which it was less dependent on Pd content; metal area (g cat)⁻¹ increased over this range of Pd loading. The results



Fig. 4 Effect of the nature of the palladium precursor on the time dependent phenol hydrogenation activity over 1 wt.% Pd/MgO. Palladium source: $A = Pd(CH_3COO)_2$; $B = Pd(NH_3)_4Cl_2$; $C = PdCl_2$; T = 503 K; WHSV = 0.027 mol h⁻¹ (g cat)⁻¹; hydrogen/phenol = 5.4.

indicate that there was no appreciable additional agglomeration of metal crystallites in the Pd-rich samples during activation. This is supported by XRD analysis where, on the basis of line broadening, there was no significant increase in PdO (calcined samples) or Pd (calcined/reduced samples) size. The greater particle size for the highest Pd-loaded sample is apparent from the representative HRTEM image shown in Fig. 6 where again metal lattice structure is evident. All the activated samples derived from the PdCl₂ precursor retained an appreciable chlorine content with a Pd/Cl mol ratio of up to 0.96. The histogram given in the inset to Fig. 2 reveals the broad (and possibly) bimodal distribution of Pd particle diameters.



Fig. 5 Effect of Pd loading on the dispersion (\bigcirc), metal area (\times) and crystallite size (\bigcirc) of activated Pd/MgO: PdCl₂ precursor.



The Pd crystallite sizes fall within the so-called mithohedrical region wherein catalytic reactivity can show a critical dependence on morphology.42 The influence of Pd loading on phenol conversion and product selectivity is shown in Fig. 7. Cyclohexanone and cyclohexanol were the only products detected and there was no evidence of the formation of cyclohexene-1-ol as a reactive intermediate or of a hydrodehydroxylation as observed in the case of supported Ni catalysts.¹⁹ The conversion of phenol increased with increasing metal loading while the cyclohexanone selectivity declined from almost 100% to <80% at a Pd content >3 wt.%. The yield of both products increased with an increase in conversion but at Pd loadings in excess of 3 wt.%, the increase in cyclohexanone yield was marginal (45% to 50%). The yield of cyclohexanol, on the other hand, was far more sensitive to Pd content and increased proportionally with an increase in Pd loading, i.e. as the overall conversion was raised. The latter effect is diagnostic of a stepwise reaction with cyclohexanone as the partially and cyclohexanol as the fully hydrogenated product. The turnover frequency (TOF, number of molecules of phenol converted per second per exposed Pd atom) was essentially invariant with particle size (>ca. 2 nm) which is indicative of structure insensitivity as noted by Galvagno et

Pd loading / wt.%

 $S_{C=0}$

 s_{c}

6

– OH

8

2716 *Phys. Chem. Chem. Phys.*, 2001, **3**, 2712–2719

2

100

80

60

40

20

ō

Conversion/selectivity (%)

View Article Online

 $al.^9$ There was, however, a discernible drop in TOF where the average Pd particle diameter was less than *ca.* 2 nm and this can be attributed to an electron deficiency at the Pd sites. It has been shown elsewhere⁴³ that Pd particles <3 nm have a tendency to remain electron deficient. There are many instances in the literature⁴² where reactivity is strongly influenced by the electron density of small supported metal particles. The presence of residual surface Cl may serve to further displace electron density from the Pd crystallites and inhibit reactant(s) activation.

The response of activity/selectivity to alterations in the hydrogen/phenol molar ratio is illustrated in Fig. 8. The degree of conversion was very sensitive to the hydrogen content of the feed and a five-fold increase is recorded in Fig. 8. This increase in activity was again accompanied by a higher degree of complete hydrogenation to cyclohexanol. While cyclohexanone was the sole product at hydrogen/phenol <5, cyclohexanol was increasingly favoured as the hydrogen content in the feed was increased. An increase in the inlet phenol molar feed rate at a constant hydrogen/phenol ratio (5.4) lowered conversion and shifted cyclohexanone selectivity to higher values (Fig. 9). The influence of reaction temperature is shown in Fig. 10 where it is evident that phenol conversion passed through a maximum (T_{max}) at ca. 503 K while cyclohexanone selectivity $(S_{C=0})$ was largely temperature invariant over the range 473-563 K. A drop in activity with increasing

*S*_{C = 0}

 C_{p}

*S*_{С – ОН}

10

100

80

60

40

20

0

0

5.5

0

2

T = 503 K; WHSV = 0.027 mol h⁻¹ (g cat)⁻¹

4

Conversion / selectivity (%)



11.3

WHSV x 10⁻⁶/mol s⁻¹ (g cat)⁻¹

15.0

7.5



6

Fig. 8 Effect of inlet hydrogen/phenol mole ratio on initial phenol

conversion (C_P) and selectivity in terms of cyclohexanone $(S_{C=0})$ and

cyclohexanol (S_{C-OH}) over 1 wt.% Pd/MgO: PdCl₂ precursor;

Mole ratio (H/Phenol)

8







Fig. 10 Effect of reaction temperature on initial phenol conversion (C_p) and selectivity in terms of cyclohexanone $(S_{C=0})$ over 1 wt.% Pd/MgO: PdCl₂ precursor; WHSV = 0.027 mol h⁻¹ (g cat)⁻¹; hydrogen/phenol = 5.4.

temperature has been noted elsewhere^{3,8,9,44,45} and attributed to thermodynamic limitations.^{3,45} The activity maximum shown in Fig. 10 could be traversed from either the high or low temperature side without any loss of activity which, in effect, negates catalyst deactivation as a possible source of the $T_{\rm max}$. The contribution of thermodynamic limitations was considered by estimating the pertinent gas-phase equilibrium reaction constants using the NIST database.⁴⁶ The calculated gas-phase equilibrium conversion does show a marked temperature dependence with complete conversion at T = 443 K and a continual drop thereafter to trace conversions at 573 K.⁴⁶ The catalytic and gas-phase equilibrium systems diverge significantly in terms of reaction selectivity. Under equilibrium conditions,⁴⁷ cyclohexanol is the predominant product at lower temperatures but cyclohexanone is increasingly preferred as the reaction temperature is raised. The observed temperature effects in our catalytic system can be attributed to surface phenomena, as concluded by Galvagno et al.9 Given the observed link between conversion and selectivity for the range of reaction conditions studied (see Fig. 8-10), it is clear that hydrogenation occurs stepwise with cyclohexanone as a reactive intermediate. A non-planar mode of phenol interaction with the basic MgO support has been proposed³ through the hydroxy function as opposed to a co-planar surface arrangement that appears to predominate on acidic $(e.g. Al_2O_3)$ supports involving a strong interaction with the aromatic nucleus. The former should favour a stepwise addition of hydrogen and a high cyclohexanone selectivity⁴⁷ as observed in this study. The maintenance of a constant $S_{C=0}$ value at elevated temperatures suggests that the mode of adsorption is not temperature sensitive.

The effect on rate of altering the partial pressure of phenol $(P_{\rm P})$ and hydrogen $(P_{\rm H})$ was also considered and the results are presented in Fig. 11. Variations in reactant(s) partial pressure had no effect on reaction selectivity. The rate of hydrogenation $(R, \text{ mol s}^{-1} \text{ (g cat)}^{-1})$ can be expressed in terms of partial pressures using the power law

$R = k(P_{\rm P})^{x}(P_{\rm H})^{y}$

where x and y are the reaction orders with respect to phenol and hydrogen, respectively. The values of x and y determined from the linear relationships (as plotted in Fig. 11) at four representative temperatures and the corresponding apparent rate constants (k) are given in Table 2. At the lowest temperatures, the reaction order with respect to phenol was negative but became positive and increased in magnitude at higher temperatures. The negative value (-0.5) at 473 K is indicative of an appreciable inhibition of rate with increasing phenol



Fig. 11 Effect of varying the partial pressure of phenol (P_p) and hydrogen (P_H) on initial reaction rate over 1 wt.% Pd/MgO: PdCl₂ precursor; T = 503 K.

concentration which suggests a strong adsorption of phenol on the catalyst. Indeed, Xu et al.48 have shown by temperature programmed desorption that phenol interacts strongly with magnesia. The switch to positive x values and increase in magnitude at elevated temperatures reflect a decrease in surface coverage and is consistent with the observed drop in conversion shown in Fig. 10. Chen et al.¹⁴ have likewise reported a negative dependence of rate on phenol concentration. The order of the reaction (y) with respect to hydrogen remained positive and was close to unity at 563 K. The temperature dependence of the rate constants yields an apparent activation energy (E_a) of 63 kJ mol⁻¹ which is the same as that quoted by Galvagno et al.9 for a closely related Pd/MgO system. In the only other directly comparable kinetic study, Gonzalez-Velasco *et al.*⁴⁹ have reported the appreciably lower value of 38 kJ mol⁻¹ for reaction over Pd/CaO–Al₂O₃.

The strength of phenol adsorption and subsequent hydrogenation activity/selectivity is known to be dependent on the acid-base properties of the support.^{3,14,15} The stronger the interaction of phenol with the surface the greater is the likelihood of complete hydrogenation to cyclohexanol. The addition of alkali or alkaline earth metals can modify, through electronic effects, catalytic performance.^{50,51} The effect of two additives (Ca and F) is illustrated in Table 3 where doping with calcium decreased $S_{C=0}$ but conversion was unaltered while the addition of fluoride did not affect selectivity but lowered activity. Addition of a basic oxide promoter has been shown to result in an electron transfer from the oxide to the supported metal, thereby increasing the electron density of the metal site^{26,52} which can, in turn, impact on conversion and/or selectivity. In this study, the presence of Ca had no effect on Pd dispersion/crystallite size and any alteration to the electronic properties of the metal phase, insofar as they influence hydrogenation activity, were negligible. The decrease in S_{C=0} over the Pd/Ca-MgO must be due to the availability of more basic sites on magnesia which increase the fraction of strongly bound phenol (as a surface phenolate¹⁵), favouring complete hydrogenation. The incorporation of fluoride in the

Table 2 Kinetic data for phenol hydrogenation over 1 wt.% Pd/MgO: $PdCl_2$ precursor

Reaction order			
T/\mathbf{K}	phenol (x)	hydrogen (y)	$k/\text{mol s}^{-1}$ (g cat) ⁻¹ atm ^{-(x+y)}
473 503 533 563	-0.53 -0.33 0.17 0.46	0.42 0.50 0.69 0.85	$3.7 \times 10^{-7} 7.3 \times 10^{-7} 2.5 \times 10^{-6} 3.8 \times 10^{-6} $

Table 3 Effect of additives on Pd size/dispersion and the degree of phenol conversion/hydrogenation selectivity: $Pd(CH_3COO)_2$ precursor; T = 503 K; WHSV = 0.027 mol h⁻¹ (g cat)⁻¹; hydrogen/phenol = 5.4

Catalyst	Dispersion CO _{irr} /Pd	d/nm from CO _{irr}	Conversion (%)	Selectivity (%)	
				S _{C=0}	S_{C-OH}
Pd/MgO	0.56	2.0	90	80	20
Pd/Ca-MgO	0.55	2.1	90	60	40
Pd/F-MgO	0.36	3.1	54	80	20

support served to induce Pd crystallite growth (Table 3) which is in keeping with our observations regarding the chlorinecontaining Pd precursors. The lower phenol conversion over Pd/F–MgO can likewise be attributed to a less effective activation of reactants on the surface. Based on ammonia chemisorption data, the acid site concentration was raised from 7 to 18 mol (g cat)⁻¹ due to the incorporation of F onto the support. Phenol conversion over this catalyst was characterized by a decided decline in activity with time-on-stream, as shown in Fig. 12, while the parent Pd/MgO and Ca-doped samples both delivered appreciably more stable conversions. Loss of activity in the case of Pd/F–MgO can be ascribed to coke formation on the acidic sites.

Conclusion

The gas-phase hydrogenation of phenol over Pd/MgO can be classified as a structure insensitive reaction where the inferred Pd crystallite size falls within the range 3-7 nm. At lower particle sizes there is a decided drop in TOF which we attribute to an electron deficiency of the Pd sites that translates into a less effective surface activation of the reactants. Palladium dispersion/particle size is dependent on both the nature of the Pd precursor and Pd loading: chlorine-containing precursors yield larger Pd particles while dispersion decreases with increasing Pd content. Palladium particle sizes measured by CO chemisorption are lower than those obtained from HRTEM analysis but the trends are the same. The calcined samples are characterized by crystalline PdO and MgO phases with no evidence of surface Mg(OH)₂; crystallinity of the MgO support is also evident from HRTEM analysis. The Pd/MgO catalysts derived from PdCl₂ and Pd(NH₃)₄Cl₂ retained an appreciable residual surface chlorine content after activation which served to lower the hydrogenation rate and induce a loss of activity with time-on-stream; Pd/MgO prepared from Pd(CH₃COO)₂ delivered a higher and more stable phenol conversion. The reaction orders with respect to phenol and hydrogen suggest that the rate-controlling step is a surface reaction between strongly bound phenol and weakly adsorbed hydrogen. An increase in reaction temperature



Fig. 12 Time-on-stream activity profiles for the conversion of phenol over Pd/MgO (\odot), Pd/Ca–MgO (\times) and Pd/F–MgO (\blacksquare): T = 503 K; WHSV = 0.027 mol h⁻¹ (g cat)⁻¹; hydrogen/phenol = 5.4.

induced a desorption of surface phenol and an accompanying decrease in reaction rate. The hydrogenation of phenol occurs stepwise where cyclohexanone and cyclohexanol are the partially and fully hydrogenated products, respectively; alterations to such process variables as Pd loading, H_2 /phenol mol fraction and inlet phenol molar feed rate that serve to increase the degree of conversion favour complete hydrogenation to cyclohexanol. The incorporation of CaO into the magnesia support had no effect on conversion but decreased cyclohexanone selectivity by strengthening the phenol/catalyst interaction(s); the presence of fluoride on the support lowered activity but had no impact on selectivity.

Acknowledgements

The authors wish to thank the University Grants Commission (UGC), New Delhi, for the award of a Senior Research Fellowship to NM.

References

- 1 I. Dodgson, K. Griffin, G. Barberis, F. Piganttaro and G. Tauszik, Chem. Ind. (London), 1989, 830.
- 2 J. F. Van Peppen, W. B. Fischer and C. H. Chan, in *Catalysis in Organic Reactions*, ed. R. L. Augustine, Marcel Dekker, New York, 1980, p. 141.
- G. Neri, A. M. Visco, A. Donato, C. Milone, M. Malentacchi and G. Gubitosa, *Appl. Catal. A*, 1994, **110**, 49.
 V. Vishwanathan and S. Narayanan, J. Chem. Soc., Chem.
- 4 V. Vishwanathan and S. Narayanan, J. Chem. Soc., Chem. Commun., 1990, 78.
- 5 V. Vishwanathan, M. S. Rajasekhar, G. Sreekanth and S. Narayanan, J. Chem. Soc., Faraday Trans., 1991, 87, 3449.
- 6 S. Narayanan and R. Unnikrishnan, J. Chem. Soc., Faraday Trans., 1997, 93, 2009.
- 7 S. Narayanan and K. Krishna, Appl. Catal. A, 1996, 147, L253.
- 8 P. Claus, H. Berndt, C. Mohr, J. Radnik, E.-J. Shin and M. A. Keane, J. Catal., 2000, 192, 88.
- 9 S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, J. Chem. Technol. Biotechnol., 1991, 51, 145.
- 10 A. K. Talukdar, K. G. Bhattacharyya and S. Sivasanker, Appl. Catal. A, 1993, 96, 229.
- 11 N. Itoh and W.-C. Xu, Appl. Catal. A, 1993, 107, 83.
- 12 N. K. Nag, Catal. Lett., 1994, 24, 37.
- 13 T. E. Holt, A. D. Logan, S. Chakraborti and A. K. Datye, Appl. Catal., 1987, 34, 199.
- Y. Z. Chen, C. W. Liaw and L. I. Lee, *Appl. Catal. A*, 1999, 177, 1.
 A. K. Talkudar, K. G. Bhattacharyya and S. Sivasanker, *Appl. Catal. A*, 1993, 96, 229.
- 16 S. Narayanan, B. Prabhu Prasad and V. Vishwanathan, React. Kinet. Catal. Lett., 1992, 48, 562.
- 17 S. Narayanan and G. Sreekanth, Ind. J. Technol., 1993, 31, 507.
- 18 S. T. Srinivas, L. J. Lakshmi and P. K. Rao, Appl. Catal. A, 1994, 110, 167.
- 19 E.-J. Shin and M. A. Keane, Ind. Eng. Chem. Res., 2000, 39, 883.
- 20 N. Mahata and V. Vishwanathan, Ads. Sci. Technol., 1997, 15, 165.
- 21 N. Mahata and V. Vishwanathan, unpublished results.
- 22 J. R. Anderson, *Structure of Metallic Catalysts*, Academic Press, London, 1975, p. 296.
- 23 Y. L. Lam and M. Boudart, J. Catal., 1977, 47, 393.
- 24 M. A. Vannice, S.-Y. Wang and S. H. Moon, J. Catal., 1981, 71, 152.
- 25 S. H. Ali and J. G. Goodwin Jr., J. Catal., 1998, 176, 3.
- 26 N. Mahata and V. Vishwanathan, Ind. J. Chem. A, 1998, 37, 652.
- 27 W. Zou and R. D. Gonzalez, Catal. Lett., 1992, 12, 73.

- W. Vogel, H. Knozinger, B. T. Carville, W. M. H. Sachtler and Z. C. Chang, J. Phys. Chem. B, 1998, **102**, 1750. C. Hoang-Van, Y. Kachaya, S. J. Teichner, Y. Arnaud and J. A. 28
- 29 Dalmon, Appl. Catal., 1989, 46, 281.
- X. Lu, X. Nin, N. Wang and Q. Zhang, J. Phys. Chem. B, 2000, 30 104, 10024.
- 31 T. A. Dorling and R. L. Moss, J. Catal., 1967, 7, 378.
- J. S. Smith, P. A. Thrower and M. A. Vannice, J. Catal., 1981, 68, 32 270.
- A. R. Gonzalez-Elipe, G. Munuera and J. P. Espinos, Surf. Inter-33 *face Anal.*, 1990, **16**, 375. J. W. E. Coenen, *Appl. Catal.*, 1991, **75**, 193.
- 34
- 35
- Y. Ohtsuka, J. Mol. Catal., 1989, **54**, 225. S. Zhuang, J. Wu, X. Liu, J. Tu, M. Ji and K. Wandelt, Surf. Sci., 36 1995, 331, 42.
- 37 M. Windaw and D. P. Zhang, Catal. Today, 1996, 30, 99.
- 38 E.-J. Shin, A. Spiller, G. Tavoularis and M. A. Keane, Phys. Chem. Chem. Phys., 1999, 1, 3173. A. Chambers and R. T. K. Baker, J. Phys. Chem. B, 1997, 101, 39
- 1621.
- 40 C. F. Cullis, J. E. Manton, G. B. Thomas and H. Wilman, Acta. Crystallogr., 1959, 12, 382.

- 41 R. J. Verderone, C. L. Pieck, M. R. Sad and J. M. Parera, Appl. Catal., 1986, 21, 329.
- 42
- M. Che and C. O. Bennett, Adv. Catal., 1989, 54, 359. J. C. Vedrine, M. Dufaux, C. Naccache and B. Imelik, J. Chem. 43 Soc., Faraday Trans., 1978, 74, 440.
- N. Itoh and W.-C. Xu, Appl. Catal. A, 1993, 107, 83. 44
- S. Narayanan and G. Sreekanth, React. Kinet. Catal. Lett., 1993, 45 51, 449.
- 46 S. G. Lias, J. F. Liebman, R. D. Levin and S. A. Kafafi, NIST Standard Reference Database 25, Structure and Properties, Version 2.01, January 1994.
- E.-J. Shin and M. A. Keane, J. Catal., 1998, 173, 450. 47
- B. Xu, T. Yamaguchi and K. Tanabe, Mater. Chem. Phys., 1980, 48 19, 291.
- 49 J. R. Gonzalez-Velasco, J. I. Gutierrez-Oritz, J. A. Gonzalez-Marcos and A. Romero, *React. Kinet. Catal. Lett.*, 1986, **32**, 505. M. E. Dry, T. Shingles, L. J. Boshoff and G. J. Oosthuizen, *J.*
- 50 Catal., 1969, 15, 190.
- D. T. Wickhaman, B. W. Logdson, S. W. Cowley and C. D. 51 Butler, J. Catal., 1991, 128, 198.
- 52 J. H. Lunsford, Stud. Surf. Sci. Catal., 1991, 61, 3.