Reduction of Supported and Unsupported Palladium Oxide Catalysts using Methane

Characterization of Active Oxides

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Palladium oxide and TiO₂-supported palladium oxide, prepared by the deposition–precipitation technique were reduced using CH₄ at temperatures greater than 300 °C. Other oxides, such as PtO₂, PtO_x/TiO₂, Co₃O₄/TiO₂ and Fe₂O₃ were also used. These oxides showed varying degrees of reduction. During reduction, CH₄ was oxidised and the reaction products (CO, CO₂, H₂O_(g) and H₂) were identified by gas chromatography. The results indicate that CH₄ is capable of causing deep-level redox reactions in the bulk by diffusing through the catalyst surface. Palladium and platinum oxides were found to be suitable materials for such reduction treatments. The most active catalysts were characterized by diffuse reflectance spectroscopy (DRS), elemental analysis, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Formation of Pd with different oxidation states was noted on the surface of the reduced catalyst. Unlike Pd-based catalysts, PtO₂/TiO₂ samples showed a stabilisation of Ti³⁺ on the catalyst surface.

Reduction of supported noble metals, is an important step involved in catalytic reactions. Generally during catalytic reaction studies, it is assumed that a complete reduction of the metal oxide precursor is achieved.¹ Using ultrahigh vacuum techniques on single-crystal and model catalysts, several workers have identified quantitatively the oxidation state of the metal resulting from the reduction treatment.²⁻⁷ It is reported that when various transition metal oxides were reacted with CH₄ at temperatures in the range 700-900 °C, the metals in the oxides were reduced to lower oxidation states.⁸ Using CH₄, metal oxides such as Fe₂O₃, MnO₂, SnO₂, V₂O₄, Cu₂O, Mn₃O₄, BaO₂, Co₃O₄, PbO etc. can be reduced. The aim of our study was to reduce supported or unsupported oxide catalysts using CH4 at moderate temperatures (300-600 °C) and to study the reduction process in a systematic way. Some of the catalysts employed in this study, notably supported palladium oxide, were found to be active for oxidative dimerisation of methane9 under flow conditions and at temperatures as low as 315 °C. Therefore in the present study we used a small batch reactor and avoided ethane formation by extending the contact time. This ensures maximum reduction of the metal oxide. The CO, CO₂, H₂O and H₂ produced during the reaction were monitored. The resulting catalysts were subjected to XPS measurements to estimate the degree of metal reduction and the formation of intermetallic species. These catalysts were also studied by diffuse reflectance spectroscopy (DRS) and transmission electron microscopy (TEM).

Experimental

Palladium oxide catalysts supported on TiO₂ were prepared by the deposition-precipitation procedure previously reported from this laboratory with minor modifications.^{10,11} Since palladium exists in more than one oxidation state in a fresh catalyst, as shown later in this paper, these catalysts will be designated as PdO_x/TiO_2 throughout this study. The preparation of PdO_x/TiO_2 was carried out as follows: required amounts of $PdCl_2 \cdot 2H_2O$ were dissolved in 150 cm³ of 0.1 mol dm⁻³ HCl. TiO₂ (P25 Degussa) was added to the solution. NaOH (0.1 mol dm⁻³) was slowly added over a period of 6-7 h (stirring at 70 °C) and the pH was raised to 10.6. The suspension was then allowed to evaporate to dryness at 90 °C. This powder was heated to 170 °C for 18 h and was held at 370 °C for the same period of time in air. Residual Cl⁻ ions were eliminated by dialysing for 4 days. After dialysis the material was dried and stored. Co₂O₃ on TiO₂ was prepared using CoCl₂ · 6H₂O and the hydrolysis was allowed to proceed until pH 6.6. Other details for these preparations are similar to those for the PdO_x/TiO_2 case. The PtO_x/TiO_2 catalysts used were obtained by DC sputtering of Pt on TiO_2 powder, as recently reported from this laboratory.¹² Pt dispersion (up to 50%) has been obtained by using this technique. The oxidation states for Pt on TiO₂ are a function of sputtering time and are reflected on three different states: i.e., Pt⁰, Pt^{II} and Pt^{IV}. The fluctuating electron densities of these three states would favourably influence the catalytic activity of these materials.9,12

Reactions were carried out in quartz cells of 20 cm³ in volume, typically containing 18 cm³ Ar and 2 cm³ CH₄ with 100 mg catalyst. Prior to reaction, the samples in the cell were heated up to the chosen temperature in a stream of Ar to eliminate physisorbed gases and moisture. The cell has been designed to allow a flow of gas through the cell and to enable the samples to be withdrawn periodically for analysis. The above was used as a batch reactor by closing the inlet and outlet valves after the catalyst pretreatment. Periodic gas analysis was carried out using a gas chromatograph with a thermal conductivity detector (TCD) in He carrier gas. For CO analysis, a molecular sieve 5 Å column, and for CO_2 , CH_4 and $H_2O(g)$ a Carbosieve or Porapak column, were used. Hydrogen detection was achieved using a Gow Mac TCD equipped with a molecular sieve 5 Å column and Ar carrier gas.

Diffuse reflectance spectroscopy (DRS) was carried out using a Perkin-Elmer-Hitachi Model 340, equipped with an integrating sphere. Electron microscopy (TEM) was carried out with a Phillips/300S instrument. The limit of resolution for such an instrument is 2 Å.

Carbon analysis was carried out by means of a Perkin-Elmer model 240 elemental analysis unit, provided with a 240 DS data processing unit. The limit of resolution of this instrument was 10^{-7} mol C in a 20 mg sample.

Photoelectron spectroscopy (XPS) was carried out using a Leybold Heraeus instrument, Mg K $\alpha_{1,2}$ line at 1253.6 eV.† The base pressure of the spectrometer was 10^{-10} Torr[‡] and during the measurements 2×10^{-8} Torr. The analysed area was 1.5 cm². For the spectrometer calibration, the Au $4f_{7/2}$ peak at 84.0 eV (Mg $K\alpha_{1,2}$) was used.^{13,14} All the XPS measurements were carried out in situ by the following method. After inserting the samples in the high-vacuum system they were annealed for 1 h at 300 °C under a slow Ar stream in a separate cell attached to the main analysis chamber of the XPS unit. The sample could be transferred between the pretreatment cell and the analysis chamber by means of a vacuum-sealed transfer stick. All samples were pretreated for 1 h at 10⁻⁸ Torr and 300 °C to remove physisorbed gases and moisture and only then were they transferred to the highvacuum chamber. Therefore, any contamination of the catalyst surface after gas treatment is excluded.

Results and Discussion

Reduction of TiO₂-supported Palladium Oxide using Methane

A 4.4% Pd containing TiO₂-supported palladium oxide catalyst was used for the reduction with methane. All the percentage values of Pd and other metals reported here are based on the total reducible metal content in the sample. During the reaction CO, CO₂, H₂ and H₂O were formed as products. Simultaneously, the palladium oxide was also reduced. In 4 h 16 μ mol CH₄ was consumed from the gas phase, while 15 µmol CO₂ and 1 µmol CO were evolved. Analysis of the fresh catalyst revealed the presence of 0.12% carbon impurity. After the pre-treatment this value came down to 0.06% and did not change further on reaction with CH_4 . 26 µmol H₂ was also evolved over 4 h. Consumption of 16 µmol CH₄ should give rise to 32 µmol H₂, stoichiometrically. However, part of this H₂ was converted to H₂O. During the runs $H_2O(g)$ was also detected as a product. Its quantitative determination was not possible owing to condensation and absorption taking place on the catalyst surface and the walls of the reactor. Since we find oxygenated products (like CO, CO_2 and H_2O , it is clear that the lattice oxygen of the noble metal oxide is intervening in the reaction. The total amount of O_2 available from palladium oxide was 21 µmol or 0.5 cm³. As 16 µmol CH₄ was consumed, leaving behind nearly 26 μ mol H₂, it was evident that although the system was in a net reducing atmosphere, only a partial reduction of palladium oxide had taken place. The removal of oxygen from a noble metal oxide proceeds under much less demanding conditions than it does from TiO2.15 Moreover, CH4 oxidation involving lattice oxygen has previously been reported by Kaliaguine et al.,¹⁶ Aika and Lundsford¹⁷ and Arai et al.,¹⁸ for a variety of systems.

The 4.4% PdO_x/TiO_2 catalyst after reduction could be reoxidised in air by calcining at 400 °C. This helps the powder to regain its original initial brown appearance from the black (Pd⁰) colour attained at the end of the reduction. Such reoxidised samples were used again for reduction experiments and it was observed that after three such cycles they consumed *ca*. 20% less CH₄ for the reduction process. The catalyst sample did not show any increase in C content after the reaction. In fact, several catalyst samples after the reaction registered a net decrease in the C level showing that during reduction, a part of the chemisorbed or physisorbed impurities (notably CO_2 and CO_3^{-}) were removed. This happens mostly during Ar pretreatment.

Other Oxides

As a reference material pure PdO sample was used and allowed to react with CH₄ but the amount of CH₄ consumed was *ca.* 25% less than that for the corresponding amounts of PdO_x in 4.4% PdO_x/TiO₂. 5% Co₃O₄/TiO₂ and Fe₂O₃ were also tried as oxides for reduction with CH₄. After 6 h 15.2 µmol (0.361 cm³) CH₄ was consumed, producing 15.3 µmol (0.365 cm³) CO₂ and 0.97 µmol (0.023 cm³) H₂ but no CO. Interestingly enough Fe₂O₃ (Alpha-Ventron, 99.99%) produced 7.8 µmol (0.185 cm³) CO₂ with a trace of CO, but no H₂ and it consumed 16 µmol (0.380 cm³) CH₄ over a period of 19 h. This reaction takes place at 398 °C with the formation of black, highly magnetic Fe₃O₄ particles. H₂ has been shown to reduce Fe₂O₃ and Fe₂O₃ supported on Al₂O₃ or SiO₂, above 400 °C.^{19,20}

Oxygen-containing products formed in the overall reaction are indicative of the reduction process occurring on the palladium oxide surface.

$$3MO + CH_4 \rightarrow CO + 2H_2O + 3M$$
; M = Pd, for example

(1)

$$CO + H_2O \rightleftharpoons CO_2 + H_2; \quad \Delta G^\circ = -9.8 \text{ kcal mol}^{-1} \quad (2)$$

Combining eqn. 1 and 2,

$$3MO + CH_4 \rightarrow CO_2 + H_2O + H_2 + 3M \tag{3}$$

A proportion of the oxygen atoms will be taken away from the oxide surface according to the following reactions:

$$CH_4 + 4PdO \rightarrow CO_2 + 2H_2O + 4Pd$$
 (4)

$$2CH_4 + 6PdO \rightarrow 2CO + 4H_2O + 6Pd \tag{5}$$

CO and H_2 produced in the reaction could also cause metal reduction, for example,

$$CO + MO \rightarrow CO_2 + M$$
; $M = Pd$ or other metals (6)

Eqn. 3-6 account for the reduction observed when the PdO_x/TiO_2 catalysts lose lattice oxygen. It is surprising, as seen later in this study, that PdO_x/TiO_2 was not fully reduced at 368 °C in the presence of the hydrogen generated during the reaction. In the presence of hydrogen, noble metal oxides are usually reduced at even lower temperatures. From this behaviour it is inferred that the Pd ions interact strongly with the support.

Characterization of the Catalyst Surface by Reflectance Spectroscopy

Fig. 1 shows the diffuse reflectance spectra (DRS) for TiO₂ loaded with different amounts of PdO_x on TiO₂. The absorption increases when the loading increases up to 7%. The inflection in the curves at around 400 nm is due to a band gap for TiO₂ of 3.2 eV. The absorbance up to 900 nm is due to the PdO loading. Trace 1 refers to TiO₂. Curves 2–5 show TiO₂ with PdO loadings of 1, 2, 4 and 7%, respectively, on TiO₂. Taking 0.50 Å for the radius of Pd²⁺ and 1.40 Å for $O^{2^-,21}$ then 0.1 g TiO₂ with 55 m² g⁻¹ BET surface area would require 4.85 × 10¹⁹ molecules of PdO on the surface in order to form a homogeneous layer. If we assume a monolayer, 4.4% PdO would cover only 45% of the available surface. However, TEM (transmission electron microscopy) pictures (as seen in Fig. 2, later) show that PdO is not uni-

^{† 1} eV ≈ 1.602 × 10^{-19} J.

 $[\]ddagger 1 \text{ Torr} \approx 101 \ 325/760 \text{ Pa.}$

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Fig. 1 Diffuse reflectance spectra (DRS) for (1) TiO₂; (2) 1% PdO_x/TiO₂; (3) 2% PdO_x/TiO₂; (4) 4% PdO_x/TiO₂; (5) 7% PdO_x/TiO₂

formly present as a monolayer but is deposited in individual particles, thus exposing a larger fraction of the available TiO_2 surface.

Electron Microscopy and XPS Measurements

Fig. 2(a) and (b) present the results of TEM studies on PdO_x/TiO_2 catalysts. 1, 4 and 7% PdO_x/TiO_2 were studied. PdO_x clusters were observed having sizes of 20 ± 5 Å. The size distribution of the particles was determined by counting particles which exhibited high contrast against the support. From 1% up to 7% PdO_x loading, they occupied most of the available surface on TiO₂. Fig. 2(a) shows a 4% PdO_x/TiO_2 catalyst before reaction. Fig. 2(b) shows the transmission electron microscope image of a reduced sample of 4% PdO_x/TiO_2 in CH₄ atmosphere at 400 °C. The agglomeration and reduction of PdO_x to Pd^0 particles takes place on the support surface owing to the mobility of noble metal oxide on TiO₂ at this temperature (400 °C). The metal oxide particles seem to agglomerate to form larger particles of 50 ± 10 Å, as shown in Fig. 2(b). After reoxidation in air for 10 h at 400 °C, PdO particles similar to those of a fresh sample were again obtained. Concomitantly, the catalyst changes from black to brown. The black colour of the reduced catalyst [sample shown in Fig. 2(b)] arises from partial reduction of the Pd oxide during the reaction, to Pd metal. This aspect will be examined in Fig. 3-5.

X-Ray photoelectron spectroscopy (XPS) measurements were carried out in the Pd 3d region (Pd $3d_{5/2}$, Pd $3d_{3/2}$) on a 4.4% PdO_x/TiO₂ freshly prepared sample and the results are shown in Fig. 3. For the evaluation of the XPS spectra the values shown in Table 1^{13,14} were used. In Fig. 3, (a) represents the XPS spectrum of fresh 4.4% PdO_x/TiO₂. This spectrum consists of 90% PdO^{II} and 10% Pd^{II}Cl as shown by the two Gaussian doublets (c) and (d). Addition of the deconvoluted (c) and (d) curves is shown in (b). (See also Table 2, later.) The curve thus obtained fits the experimental curve (a) to >96% accuracy.

In Fig. 3, the XPS spectrum for the Pd 3d region (Pd $3d_{5/2}$, Pd $3d_{3/2}$) of the 4.4% PdO_x/TiO₂ freshly prepared catalyst was referenced as follows. The spectra shown in Fig. 3-5





Fig. 2. Electron microscope image of (a) freshly prepared 4% PdO_x/TiO₂, (b) 4% PdO_x/TiO₂ reacted at 400 °C in CH₄, magnification 600 000

Table 1 Typical XPS reference values for Pd 3d_{5/2}

Pd species	E _b /eV
Pd ^o metallic	334.9
PdO, Pd ^{II}	336.1
PdO_2 , Pd^{IV}	337.6
K ₂ PdCl ₆	339.9

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Fig. 3 (a) XPS spectrum of the Pd 3d region for a 4.4% PdO_x/TiO_2 freshly prepared material, (b) addition of deconvoluted (c) and (d) curves, (c) Gaussian-generated $PdO^{II} 3d_{5/2}-3d_{3/2}$ doublet, (d) Gaussian-generated $Pd^{II}Cl 3d_{5/2}-3d_{3/2}$ doublet

present experimental data for which the binding energies (E_b) were not corrected for electrostatic charging of the catalysts during the measurements. In order to obtain true binding energies, pure TiO₂(P25) and several Pd/TiO₂ samples of similar dispersions were measured using the same sets of parameters. The degree of dispersion was checked by TEM.

Data analysis for the XPS spectra shown was carried out as follows: The relevant peaks were identified, satellite peaks were subtracted. Smoothing of the experimental curves was performed by polynomial fitting. Shirley-type background was then subtracted from the relevant peaks and peak integration was carried out using the relative sensitivity factors and the transmission function of the spectrometer. In the second stage, the deconvolution was carried out taking into account the peak positions. The electrostatic charging of the sample was determined using standard literature values²²⁻²⁵ before assessing the chemical oxidation states of Pd. By means of Gaussian-Lorentzian fitting routines we have determined the chemical states. The appropriate Gaussian-Lorentzian character was chosen for p-, d- or f-like XPS signals for each element. Care was taken to maintain peak widths within reasonable limits. Finally, the chemical states were determined with respect to the electrostatic charging of the sample by measuring peak distances to C 1s, Ti 2p and



Fig. 4 (a) Experimental XPS spectrum of the PdO region for a 4.4% PdO_x/TiO₂ sample treated for 1 h with He at 368 °C; (b) addition of deconvoluted curves (c), (d) and (e); (c) doublet-generated curve of electron-rich Pd species; (d) Pd⁰ doublet-generated curve; (e) PdO^{II} doublet generated curve



Fig. 5 (a) Experimental PdO₂/TiO₂ XPS spectrum for a 4.0% PdO₂/TiO₂ sample treated with CH₄ for 1 h at 368 °C; (b) addition of deconvoluted curves (c), (d) and (e); (c) doublet-generated curve of electron-rich Pd species; (d) Pd^o doublet generated curve; (e) PdOⁿ doublet generated curve

O 1s signals. The amounts of the different oxidation states are reported in Table 2. The curve analysis for Pd/TiO₂ samples turned out to be much more complicated than in the case of Pd on other supports such as SiO_2 .²⁻⁷ The observed peak shift was much higher than any anharmonicity correction may reasonably account for. It may be possible that Pd-Ti interactions (as it was observed for Pt_3Ti^{\dagger})²⁶ are causing weak peak shifts (below 0.5 eV). The $E_{\rm b}$ values observed for PdO and Pd^{II}Cl reported in Fig. 3 at 340 and 343 eV do not correspond to the typical reference values for Pd $3d_{5/2}$ as shown in Table 1. These values have been corrected as stated in the two preceding paragraphs. Therefore, to calculate the correct amount of Pd in each oxidation state reported in Table 2, we have used the standard $E_{\rm b}$ shown in Table 1 after charge correction. The charging effect is dependent on the actual sample measured in each case. This correction does not affect the accuracy of the determination of peak position which is accurate to ± 0.1 eV. The $E_{\rm b}$ values of metallic Pd or Pd on various supports and the influence of the Pd dispersions have been reported in several studies.²⁻⁷

The Pd electron-rich species shown in Table 2 turns out to be a low-energy contribution to the Pd-XPS signal not characterised until now. It cannot be ascribed to a 'dispersion shift' or 'relaxation shift'²⁷ where E_b shifts to higher values. The energy shift to the low E_b side of the peak was of the

 \dagger Several Pt₃Ti phases have been reported in ref. 26. The authors have not found a reference that unambiguously identifies Pd₃Ti species.

order of -0.9 eV. This is unusual and indicative of an electron-rich minority phase of Pd present on TiO₂. We cannot at present describe further this species. These Pd-Ti interactions therefore contribute, as seen in the case of other supported noble metals,^{22,23} to the peak broadenings observed in Fig. 3–5.

The Pd and TiO_2 regions of the XPS spectrum were also investigated with other X-ray wavelengths to make sure that no Auger signals were hidden under the Pd signals or under the positions of the shifted species.

By performing XPS, a quantitative evaluation of the surface concentrations for Pd, Ti, O, F, Cl, Na and C was carried out for the sample shown in Fig. 4. The results are given in Table 3. Residual chlorine (as $Pd-Cl_x$) was responsible for the species $Pd^{II}Cl$ shown in Table 2, since $PdCl_2 \cdot 2H_2O$ was employed in the sample preparation.

Fig. 4 shows the XPS spectrum (a) for a 4.4% PdO_x/TiO_2 sample treated in a flowing He atmosphere at 368 °C for 1 h. Curve (b) shows the addition of the deconvoluted curves (c), (d) and (e). The deconvolution was carried out as mentioned before, by fitting a Gaussian distribution for each of the three doublets present, in such a way that at the E_b used they should add to the convoluted spectrum (b). In this way the deconvoluted curves were fitted to the equivalent experimental curve (a). It is important to note here that Table 1 shows reference values and that the spectra in Fig. 4 represent the original curves without charge correction as reported in Table 2. Curve (c) for the electron-rich Pd species of the catalyst makes up 28.5% of the XPS signal. Curve (d) shows the

Table 2	Amount of P	d species pre	sent in various	s catalysts
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catalyst	Pd, electron-rich (%)	Pd ⁰ (%)	PdO ^{II} (%)	Pd ^{II} Cl (%)
4.4% PdO _x /TiO ₂ fresh	_		90.2	9.8
4.4% PdO $\sqrt{7}$ /TiO $\sqrt{2}$, He, 368 °C	28.5	41.5	29.9	
4.4% PdO_x/TiO_2 , CH_4 , 368 °C	32.2	35.8	32.0	—

 Table 3
 Surface concentration (atom %) in various catalysts

element	4.4% PdO_x/TiO_2 , fresh	4.4% PdO _x /TiO ₂ , CH ₄ , 368 °C	4.4% PdO_x/TiO_2 , He, 368 °C
Pd	2.0	3.4	1.5
Ti	17.6	17.4	16.9
0	62.7	60.7	62.1
F	1.7	1.5	0.7
Cl	0.8	0.9	1.0
Na	2.5	2.6	2.6
С	12.5	13.3	15.1

Pd⁰ doublet comprising 41.5% of the reacted species. Curve (e) with 29.9% of the area represents the PdO^{II} present. Arrows on these traces mark the uncorrected maxima for electron-rich Pd, Pd⁰ and PdO^{II} as Pd $3d_{5/2}$, Pd $3d_{5/2}$ ox' and Pd $3d_{5/2}$ ox'', respectively.

Fig. 5 shows the XPS spectrum (a) for a 4.4% PdO_x/TiO₂ sample reacted for 1 h with CH₄ at 368 °C. Curves (b), (c), (d) and (e) have the same meaning as for Fig. 4. The only difference is that for electron-rich Pd, Pd⁰ and PdO^{II} the areas are: 32.2, 35.8 and 32.0%, respectively. The differences in the percentages reported in Table 2 for He- and CH₄-treated catalysts at 368 °C are significant. The statistics carried out on the different samples are sufficient to support this statement experimentally.

The He and CH_4 treatments have been shown to induce a distinct reduction of the metal oxides under study. Small metal clusters (as in our case) show a smaller peak asymmetry, but a more pronounced line broadening was noticed when compared with macroscopic samples.^{22,27,28} From the XPS data it is evident that the heat treatment with He was enough to cause partial reduction of the surface palladium oxide particles. On further treatment with CH₄, the concentration of Pd⁰ decreased by *ca*. 5.7%. Consequently, the level of electron-rich Pd and PdO^{II} concentrations increased by 3.7 and 2.0%, respectively. This may be explained by the fact that, unlike He which is an inert gas, CH₄ can cause deeplevel redox reactions in the bulk by diffusing through the surface. Such exothermic reactions perturb the oxidation

state of the Pd ions on the surface. This may also facilitate the migration of Pd and O atoms from deeper levels.

Fe₂O₃ was examined using XPS techniques before and after reaction with CH₄ gas at 400 °C. After reaction, the Fe $2p_{3/2}$ signal was only slightly shifted by 0.06 eV from 711.06 to 711.00 eV. The reacted material was black and magnetic. From the small shift observed by XPS it seems that the reactive surface of these oxides retains close to the initial degree of oxidation.²² XPS experiments were also carried out on Co₃O₄ before and after reaction, as for Fe₂O₃. The shift in the peak (0.7 eV) revealed lower oxidation states after the reaction. The surface reduction observed by XPS was small for PdO powders, but high for supported catalysts such as PdO/TiO₂.

XPS measurements were carried out on a Pt loaded TiO₂ catalyst as well. These platinum-based catalysts were treated with CH₄ in a manner similar to that carried out for PdO_x/TiO₂ catalysts. In Fig. 6, a pronounced peak broadening in the case of Pt/TiO₂ as compared to the Pd/TiO₂ material is observed. The peak broadening (in the Pt/TiO₂ case) was ca. 1.3–1.4 eV for the Ti $2p_{3/2}$ signal and ca. 0.6–1.0 eV for the oxygen signal. Comparable values were found by referencing to pure TiO₂ (P25). Because peak broadening was observed for both Ti and O (and not for the other elements present), it is reasonable to think that at least two TiO species exist with oxidation states Ti⁴⁺ and Ti^{3+.29,30}. The existence of two different oxidation states reflects a valence change from Ti⁴⁺ to Ti³⁺ and this has been reported when



Fig. 6 XPS spectrum for Pt/TiO₂ and Pd/TiO₂ in the 2p region. For other details see text

the DC sputtering technique was used for catalyst prep-aration.¹² The XPS spectrum in Fig. 6 makes this clear. The Ti 2p signal was shifted towards lower binding energies for Pt-loaded TiO₂ samples. This indicates the presence of ca. 40% Ti^{3+} and 60% Ti^{4+} . In the case of Pt/TiO₂ samples, a stabilization of Ti³⁺ on the catalyst surface by metal-support interactions^{31,32} has taken place. This effect was not found for PdO_x/TiO_2 prepared by precipitation techniques.

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Conclusions

This study shows palladium oxide (supported or unsupported) to be reduced by CH_4 at T > 300 °C. Thermal treatment in an inert gas such as He also causes a significant degree of reduction. Other oxides amenable to reduction by CH₄ were Co₃O₄, platinum oxides and to a lesser extent Fe_2O_3 . Fe_2O_3 is known to be less efficient in this type of reaction. The low degree of reduction, as well as the small amount of gas evolved, reflects this behaviour.

XPS measurements have shown the existence of Pd⁰, Pd^{II} and electron-rich Pd species on a reduced catalyst. A stabilization of Ti³⁺ on the catalyst surface indicating metalsupport interactions for Pt/TiO₂ was also noted. This was not observed for Pd/TiO_2 . There is further scope in this area for a detailed study of several other metals and catalystsupported materials to understand their reduction behaviour in the presence of CH_{4} .

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