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The properties of platinum or palladium supported on β-aluminium trifluoride or magnesium difluoride: catalysts for the hydrodechlorination of 1,1-dichlorotetrafluoroethane

Heinz Berndt,[a] Hamid Bozorg Zadeh,[b] Erhard Kemnitz,*[b] Mahmood Nickkho-Amiry,[c] Martina Pohl,[a] Tomaž Skapin[d] and John M. Winfield[c]

[a]*Institute of Applied Chemistry e.V., D-12489 Berlin, Germany*
[b]*Institute of Inorganic Chemistry, Humboldt University, D-12489 Berlin, Germany. E-mail: erhard.kemnitz@chemie.hu-berlin.de*
[c]*Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ*
[d]*Institute "Jožef Stefan", 1000 Ljubljana, Slovenia*

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Palladium or platinum supported on β-aluminium(III) fluoride or magnesium fluoride are effective catalysts for the conversion of the ozone-depleting compound, CCl_2FCF_3, to the environmentally acceptable refrigerant, CH_2FCF_3 (HFC-134a). The gas phase hydrodechlorination reaction has been studied in the temperature range 373–773 K under steady flow conditions, under which the fluorides were shown not to catalyse any isomerization or dismutation reaction that would lead to unwanted by-products. Increased catalytic activity was found for both metals with increasing metal content of the catalysts. The temperature dependencies revealed higher yields with increased temperature. The selectivity to the desired product, CH_2FCF_3, is significantly higher in the case of Pd on both supports and is slightly higher for β-AlF_3 than for MgF_2. The results of temperature programmed reduction (TPR) of the catalyst precursors and hydrogen chemisorption and transmission electron microscopy (TEM) studies on the catalysts are discussed in relation to the surface hydrolysis of the support materials, for which evidence has been obtained from [^{36}Cl] measurements. It is proposed that water desorbed from the hexagonal channels of β-AlF_3 has an influence on the metal dispersions of the catalysts.

Introduction

Selective hydrogenolysis of chlorofluorocarbons (CFCs) is an important reaction because it represents an HF-free route for conversion of CFCs into hydrofluorocarbons (HFCs), the favoured replacements for the ozone depleting CFCs.[1–14] Hydrodechlorination of dichlorodifluoromethane (CFC-12) to give, selectively, difluoromethane (HFC-32) according to eqn. (1), using supported palladium,

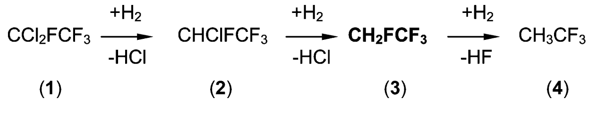
$$CCl_2F_2 + 2H_2 \rightarrow CH_2F_2 + 2HCl \qquad (1)$$

platinum or other noble metals, has been particularly well studied.[4,5,8,10,11,13] In particular, an extensive series of papers has described the behaviour of Pd supported on activated carbon in some detail and a conceptual process for selective hydrodechlorination of CCl_2F_2 has been developed.[10,11,15]

Oxidic support materials, including alumina,[2,4,8,11,12,16-19] silica,[6,17] zirconia and titania,[8,11,17] ZnO,[7,16] MgO[9,17,19] and Mg–Cr hydrotalcite,[20] have been used for hydrodechlorination catalysts in order to investigate possible relationships between catalytic activity and support acidity. Fluorination of the support occurs to some extent during the hydrodechlorination, as selectivity to formation of the desired hydrofluorocarbon is seldom 100%, and this has been suggested as a cause of catalyst deactivation.[4,7,8,17,18] In contrast, fluorination of the MgO support during hydrodechlorination has been claimed recently to result in a superior catalyst.[19] Fluoride supports, which should interact with hydrogen halides to a smaller extent than do oxides, have also received some attention. The use of Al,[4,8,13,17,18] Ti and Zr[8] and Mg fluorides[21] has been reported, as has the behaviour of a deliberately, partially fluorinated support, alumina treated with aqueous HF.[18]

We became interested in catalytic hydrodechlorination through the design of a scheme to convert unwanted stocks of the CFC solvent, 1,1,2-trichlorotrifluoroethane (CFC-113) to 1,1,1,2-tetrafluoroethane (HFC-134a), the most widely used CFC-alternative refrigerant. The first two steps involve isomerization of CCl_2FCClF_2 to CCl_3CF_3 and dismutation of the latter to give CCl_2FCF_3 as one of the products. These are achieved using β-aluminium trifluoride or fluorinated γ-alumina as heterogeneous catalysts.[22] It was logical therefore to consider these materials as potential supports for the noble metal catalysts required for the hydrodechlorination of CCl_2FCF_3 to CH_2FCF_3. The hydrodechlorination steps are summarised in Scheme 1.

d'Itri *et al.*[12] have described the hydrodechlorination of compound **1** in the presence of Pd supported on γ-alumina. They found a zero reaction order in H_2 at high H_2 partial pressure and the formation of compounds **2**, **3** and **4** as products. The selectivity towards the desired CH_2FCF_3 (**3**) was 85%. In a later study,[18] γ-alumina, fluorinated to different extents, and AlF_3 were used as supports for Pd; all catalysts exhibited rapid and significant decrease in activity with **1** as reactant. Somorjai *et al.* investigated the kinetics of Scheme 1 on Pd(111), Pd(100), and a Pd foil at atmospheric pressure. All possible products (**2**–**4**) were observed, selectivities being



Scheme 1 Hydrodechlorination steps for the conversion of CCl_2FCF_3 to CH_3CF_3.

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independent of the conversion and of the structure of the palladium surface used.[23] Experiments with D_2 and $CHClFCF_3$ (**2**) over Pd on carbon and Pd black catalysts indicated that the irreversible adsorption of CFC was the rate-determining step.[24] The support was found to have no influence on the reaction.[25] Employing Pd(111) surfaces as catalysts, Zhou *et al.*, established a linear free energy relationship for the rate of dechlorination in an attempt to probe the nature of the transition state to C–Cl bond cleavage. They found that the intrinsic dechlorination barrier remained unchanged as the degree of fluorination in the reacting molecule was varied.[26]

Thomson *et al.* have claimed that addition of zinc oxide to γ-alumina supported palladium results in enhanced conversion of the reactant **1** and higher selectivity to dechlorinated products[16] indicating, in contrast to the findings of Ribeiro *et al.*,[25] that the support does influence the activity of the catalyst.

It is evident from the summary given above that the role of the support, if any, in Pd catalysts for Scheme 1 needs clarification. At a basic level, the criteria for a satisfactory support are that it should: (i) be chemically inert towards HCl and/or HF, both of which can be formed during hydrodehalogenation (Scheme 1), (ii) not catalyze any dismutation and/or isomerization reactions of CFCs and (iii) not catalyze dehydrofluorination of the desired reaction product, *i.e.* $CH_2FCF_3 \rightarrow CHFCF_2 + HF$.

We here report the synthesis, characterization and testing of platinum and palladium catalysts using MgF_2 and β-AlF_3 as supports in the reaction sequence (Scheme 1) making comparisons with Pd/carbon as the benchmark.

Experimental

Catalyst preparation

Magnesium fluoride and β-aluminium trifluoride were prepared according to the literature.[27,28] Their BET areas were 20.7 and 30.0 $m^2\ g^{-1}$ respectively. Active carbon (Darco, Fa. Aldrich) with a BET area of 600 $m^2\ g^{-1}$ was washed thoroughly to remove traces of metal oxides from the synthesis process using concentrated HCl followed by prolonged washing with de-ionized water. The support was impregnated with a 60% solution of $PdCl_2$ (Chempur, 99.99%) in 36% aqueous HCl or 40% aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Chempur) followed by drying at 393 K for 2 h. These precursors were activated by reduction at 523 K in a N_2/H_2 gas stream for 2 h and then stored in a closed container. Immediately before use, the preactivated catalysts were again treated in the reactor at 623 K in a N_2/H_2 gas stream for at least 30 min. Analytical data for the metal contents quoted in Table 1 were determined from the impregnated precursors after drying at 393 K but before activation, whereas the BET data refer to the activated (reduced) catalysts. Chlorine was determined in selected cases by oxidative Schöniger decomposition[29] followed by potentiometric titration with $AgNO_3$.

Catalyst characterization

Catalyst characterization was carried out by means of XRD, BET, temperature-programmed reduction (TPR), physi- and chemisorption using static adsorption and pulse chemisorption, respectively, transmission electron microscopy (TEM) and [^{36}Cl] studies with anhydrous HCl.

XRD characterization was performed using XRD 7 Seiffert FPM (Cu-Kα) equipment. Specific surface areas, S_{BET}, Table 1, were determined by means of dinitrogen physisorption measured with ASAP 3000 equipment (Micromeritics). Samples were pretreated by evacuation at 593 K for 2 h. Palladium surface areas were determined with an Autosorb-1C equipment (Quantachrome) applying the established 'back sorption technique' to eliminate the hydrogen absorption in the palladium bulk (β-Pd hydride formation).[30,31] Precursor samples (0.1 to 0.2 g) were reductively activated in a flow of 5 vol.% H_2/Ar by heating from room temperature to 623 K with a heating rate of 10 K min^{-1} and an isothermal hold for 30 min.

Table 1 Catalysts studied

Catalyst	Metal content/wt%	$S_{BET}{}^a/m^2\ g^{-1}$
1Pt/β-AlF_3	0.85	30.3
3Pt/β-AlF_3	2.55	n.d.[b]
7.5Pt/β-AlF_3	6.38	32.4
10Pt/β-AlF_3	8.5	27.8
1Pt/MgF_2	0.85	20.5
3Pt/MgF_2	2.55	n.d.
7.5Pt/MgF_2	6.38	24.0
10Pt/MgF_2	8.5	17.8
1Pd/β-AlF_3	1[c]	29.8
3Pd/β-AlF_3	3	17.8
7.5Pd/β-AlF_3	7.5	30.0
10Pd/β-AlF_3	10	27.5
1Pd/MgF_2	1	20.2
3Pd/MgF_2	3	20.5
7.5Pd/MgF_2	7.5	27.0
10Pd/MgF_2	10	18.2

[a] S_{BET} values, MgF_2 = 20.7 $m^2\ g^{-1}$, β-AlF_3 = 30.0 $m^2\ g^{-1}$. [b] n.d. = not determined. [c] Values for the Pd catalysts are nominal and based on the stoichiometries used.

Temperature-programmed reduction (TPR) of the supported platinum and palladium precursors was studied by means of TPR (AMI-1 equipment, Altamira/Zeton) using the parameters, sample mass 0.1 g, gas composition 5 vol.% H_2/Ar, flow rate 30 $cm^3\ min^{-1}$, heating rate 10 K min^{-1}. Water vapour or HCl desorbed or formed during the TPR experiments were removed by molecular sieve 4A before the gas entered the thermal conductivity detector (TCD). The peak area of the hydrogen consumption plot was calibrated by argon pulses into the TPR H_2/Ar gas flow.

Pulse chemisorption measurements were carried out with the AMI-1 equipment used for the TPR studies. After reductive activiation by a TPR run up to 623 K and 30 min reduction in a flow (30 $cm^3\ min^{-1}$) of 5 vol.% H_2/Ar, the samples were eluted by an Ar flow (50 $cm^3\ min^{-1}$) at 623 K for 1 h and allowed to cool to 273 K for chemisorption measurements on Pt and 353 K on Pd, respectively. Pulses (100 μL) of 20 vol.% H_2/Ar were added to the Ar flow until the metal surface was saturated with hydrogen, that means constant H_2 peaks were observed by the TCD.

TEM investigations were carried out with an electron microscope (CM20 Philips, LaB_6), equipped with an EDX detector, PV9900, for qualitative analysis. Samples were prepared by dispersing the catalysts directly on Lacey-carbon-coated grids, mesh 300.

The interaction of anhydrous hydrogen chloride with the catalysts and the support materials was investigated by the following method. A precisely measured aliquot (0.10 mmol) of $H^{36}Cl$, determined from a measured pressure (5333 Pa) contained in a calibrated bulb (48.5 cm^3), was transferred *in vacuo* to a silica flask fitted with a Pyrex/PTFE stop-cock (J. Young). The flask contained a weighed sample of catalyst (usually *ca.* 0.5 g) that had been freshly heated under dynamic vacuum at 473 K overnight. The mixture was allowed to react at 623 K for 18 h. The $H^{36}Cl$ was removed by distillation and absorbed in aqueous NaOH (*ca.* 2.5 mmol, 5 cm^3) and the solution made up to 100 cm^3. To the ampoule containing the solid was added distilled H_2O (25 cm^3), the mixture was shaken several times for 2 min periods and the solid allowed to settle overnight. The major part of the solution (20 cm^3) was removed using a syringe and made up to 100 cm^3. This solution and one derived from an identical aliquot of $H^{36}Cl$ that served as a standard were diluted according to the following regime. In

Table 2 Interaction of $H^{36}Cl$ (0.10 mmol) with support materials at 623 K for 18 h

Solid	Mass/g	$[^{36}Cl]$ Count rate/count min^{-1}			Radio-chemical balance (%)	$[^{36}Cl]$ Retained by solid[a]	
		Initial HCl	Final HCl	Extracted from solid			
γ-Alumina	0.0506	26205	18324	5971	92.8	0.300[b]	0.228[c]
F-Alumina	0.6030	26205	24284	1995	100	0.073	0.076
β-AlF_3	0.5370	26205	24061	1441	97.3	0.082	0.055
MgF_2	0.5683	20394	14262	5330	96.1	0.300	0.261
MgF_2	0.6488	20394	13569	6125	96.6	0.335	0.300
Carbon	0.5428	20394	10321	9711	98.2	0.494	0.476

[a]Relative error < ±3%. [b]Data in this column determined from the count rate of the $H^{36}Cl$ recovered. [c]Data in this column determined from the count rate of aqueous $^{36}Cl^-$ extracted from the solid.

Table 3 Interaction of $H^{36}Cl$ (0.10 mmol) with the catalysts at 623 K for 18 h

Catalyst[a]	Mass/g	$[^{36}Cl]$ Count rate/count min^{-1}			Radio-chemical balance (%)	$[^{36}Cl]$ Retained by solid[b]	
		Initial HCl	Final HCl	Extracted from solid			
7.5Pd/β-AlF_3	0.5000	26205	22957	2511	97.2	0.124[c]	0.096[d]
7.5Pt/β-AlF_3	0.5000	26205	23404	2493	98.8	0.106	0.095
3Pd/β-AlF_3[e]	0.1840	20394	19538	618	98.8	0.041	0.030
7.5Pd/MgF_2	0.4700	20394	13861	6741	101	0.320	0.330
7.5Pt/MgF_2	0.5000	20394	10040	10886	102.6	0.508	0.534
3Pd/MgF_2[e]	0.2890	20394	15306	5026	100	0.249	0.246
10Pd/carbon	0.3563	20394	11344	9109	100	0.443	0.447
10Pt/carbon	0.5252	20394	13831	5265	93.6	0.321	0.258
10Pd/carbon[e]	0.2545	20394	17009	2696	96.6	0.165	0.132
10Pt/carbon[e]	0.2319	20394	15070	4393	94.4	0.261	0.215

[a]Descriptions as in Table 1. [b]Relative error ≤ ±4%. [c]Data in this column determined from the count rate of the $H^{36}Cl$ recovered. [d]Data in this column determined from the count rate of aqueous $^{36}Cl^-$ extracted from the solid. [e]Used catalysts.

both cases the solution, prepared as described above, was designated 1; 5 cm^3 of 1 were made up to 50 cm^3 giving solution 2; 8 cm^3 of 2 were made up to 25 cm^3 giving solution 3; 10 cm^3 of 3 were made up to 25 cm^3 giving solution 4; 12 cm^3 of 4 were made up to 25 cm^3 giving solution 5. An aliquot (1 cm^3) of each solution was counted after the addition of a scintillator (Ecoscient™ A, 9 cm^3) using a liquid scintillation counter (LKB 1214). Count rates were determined for each solution from replicate determinations after background subtraction. Radiochemical balances were normally ⩾95%, although separation difficulties encountered with γ-alumina and the carbon-based materials resulted in some radioactivity loss. Radiochemical data are summarised in Tables 2 and 3.

Catalytic tests

The hydrodechlorination of CCl_2FCF_3 with dihydrogen was carried out in a fixed bed micro-reactor connected on-line to a gas chromatograph. A catalyst sample (*ca.* 0.7 g) was placed in the reactor and a gas stream comprising CCl_2FCF_3 and H_2 with N_2 as the carrier was passed over the catalyst. Prior to GC sampling, the product mixture was scrubbed with aqueous KOH solution to remove HCl/HF formed during the reaction. The product mixture was analysed quantitatively using a capillary gas chromatograph (HP 5890, Hewlett Packard, column Pona, 50 m, 0.5 μm polydimethylsiloxane). Catalytic tests were carried out using different temperatures, contact times and feedstock ratios.

Results and discussion

Catalysts, their composition and specific surface area

Four different catalyst systems were used in this study derived from palladium and platinum on MgF_2 and β-AlF_3 supports. The characteristic data of all samples prepared are summarized in Table 1. With increasing metal loading, a slight decrease of the specific surface area, S_{BET}, of the catalysts was sometimes observed. However, this did not exceed a 10% deviation from the surface area of the corresponding support. Under the reaction conditions used for hydrodechlorination, neither β-AlF_3 nor MgF_2 were catalytically active towards dismutation/isomerization of CCl_2FCF_3, in accordance with previous observations.[22]

Temperature programmed reduction (TPR) of the precursors

The main aim of the TPR studies was to determine the temperature necessary to achieve complete reduction of the supported platinum(IV) and palladium(II) precursors. In addition, the TPR profiles reflected interactions between the metal precursor species and the support. The reduction of H_2PtCl_6 supported on β-AlF_3 and MgF_2 respectively is compared in Fig. 1. Reduction was complete at 523 K in the case of 10Pt/MgF_2 (curve b) and was almost so for 10Pt/β-AlF_3 (curve a). Measured hydrogen consumptions corresponded to the reduction of Pt^{IV} to Pt^0. This temperature was normally used for reductive activation of the precursors before the characterization of the metal surface of the catalysts and catalytic testing.

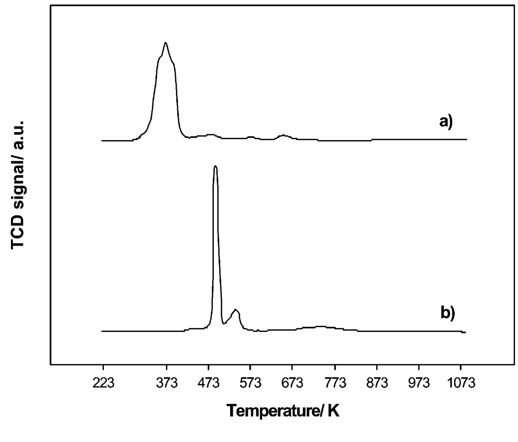

Fig. 1 TPR profiles of, (a) 10Pt/β-AlF_3 and (b) 10Pt/MgF_2.

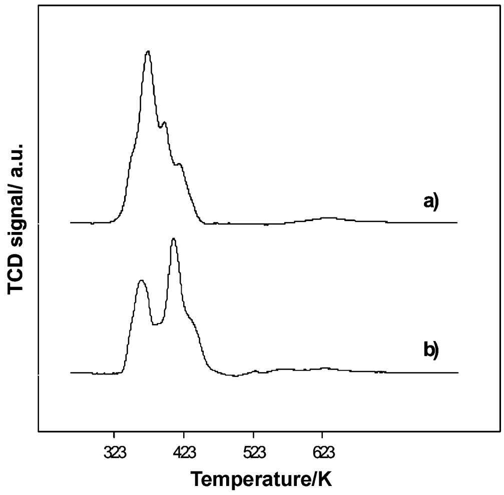

Fig. 2 TPR profiles of $7.5Pd/MgF_2$, (a) without pretreatment, (b) dried *in situ* before TPR run.

There was a significant difference in the maximum main peak temperature for $10Pt/\beta\text{-}AlF_3$ compared with $10Pt/MgF_2$. Pure $\beta\text{-}AlF_3$ did not show any evidence for hydrogen consumption. On $\beta\text{-}AlF_3$, $[PtCl_6]^{2-}$ was reduced completely by *ca.* 363 K. Complete loss of chlorine due to hydrolysis to the easily reducible $Pt(OH)_4$ or PtO_2 during the impregnation of the support and drying of the precursor sample could be excluded by analysis of the chlorine content, which corresponded to a Pt : Cl ratio of *ca.* 1 : 6. Small reduction peaks observed at higher temperatures could reflect the presence of partially fluorinated Pt species.

The reduction of the platinum precursor on the MgF_2 support required a higher temperature (>100 K) than for Pt^{IV} supported on $\beta\text{-}AlF_3$ (Fig. 1). A peak at *ca.* 740 K indicated the presence of a species whose reduction was difficult. In order to avoid sintering of platinum particles, the samples for catalytic testing were reduced only at 623 K.

A portion of the palladium precursor on $\beta\text{-}AlF_3$ was reduced at room temperature during the initial phase of the TPR procedure. Furthermore, the plots obtained were a superimposition of the reduction of the remainder of Pd^{II} and the decomposition of β-palladium hydride in the palladium particles previously formed. Because such profiles cannot be deconvoluted unambiguously, no interpretation is included here. Reduction of Pd/MgF_2 precursor samples was observed above *ca.* 323 K, illustrated for $7.5Pd/MgF_2$ in Fig. 2, curve a. A TPR performed with a $7.5Pd/MgF_2$ sample dried *in situ* by evacuation at 393 K for 1 h (Fig. 2, curve b), indicated that a change in pre-treatment influenced the pathway of the reduction. It also had an effect on the palladium metal dispersion as shown below. Hydrogen consumption for reduction of the palladium precursor on both supports was essentially complete by *ca.* 473 K. However, for catalytic testing and chemisorption measurements, a reduction temperature of 623 K was chosen to guarantee complete reduction.

Hydration and hydroxylation of the support surface: interactions with $H^{36}Cl$

Although both $\beta\text{-}AlF_3$ and MgF_2 are regarded as kinetically inert with respect to hydrolysis, surface hydration and hydroxylation of the support during the aqueous impregnation method used to prepare the catalyst precursors cannot be discounted completely. We have shown recently that during heating of $\beta\text{-}AlF_3$ *in vacuo*, water is desorbed slowly from the hexagonal channels of the hexagonal tungsten bronze structure and we have interpreted the subsequent behaviour of anhydrous hydrogen chloride and $H^{36}Cl$ towards $\beta\text{-}AlF_3$ in terms of the existence of surface $Al\text{-}OH_2$ and Al-OH groups.[32] IR spectroscopic and thermogravimetric examinations of MgF_2 have indicated that its surface is hydroxylated to some extent,[33] the OH surface density being estimated as 3–4 OH groups nm^{-2}.[34]

In the present work we wished to determine whether there was evidence for surface hydroxyl groups on the surfaces of unused and used catalysts. $[^{36}Cl]$ measurements of $H^{36}Cl$ interaction at $\beta\text{-}AlF_3$, presumed to occur *via* hydrated surface sites, is readily observed at ambient temperatures and mass spectrometric measurements indicate the desorption of H_2O and HCl is rapid above *ca.* 373 K.[32] The fraction of $[^{36}Cl]$ activity permanently retained, due to the replacement of surface Al–OH by Al–Cl groups, estimated as *ca.* 10%, was, however, too small to quantify precisely by direct Geiger-Müller monitoring of the surface.[32] We have therefore examined the behaviour of supports and catalysts towards anhydrous $H^{36}Cl$ under conditions (623 K for 18 h) that would favour the conversion of M–OH to M–Cl, M = Al or Mg. The radiochemical data, obtained before and after exposure, have been given in the experimental section (Tables 2 and 3. Data for the $[^{36}Cl]$ atom uptakes (atom nm^{-2}) are given for several support materials in Table 4 and for various Pd and Pt catalysts, supported on $\beta\text{-}AlF_3$, MgF_2 or carbon, in Table 5.

Chlorination of γ-alumina by HCl has been studied previously by using neutron activation analysis combined with measurements of $[^{36}Cl]$ count rates from $H^{36}Cl$ before and after reaction.[35] Chlorination of γ-alumina that had been calcined at 523 K, using HCl at 293 K, resulted in Cl atom surface densities in the range 4.4–5.0 nm^{-2}. Calcination at 373 K followed by chlorination gave a value of 9 atom nm^{-2}. The $[^{36}Cl]$ uptake value of 2.86 atom nm^{-2} (Table 4) is therefore not unreasonable.

The data obtained for $\beta\text{-}AlF_3$ are entirely consistent with the results of the room temperature direct monitoring experiments described previously.[32] It is suggested that retention of $[^{36}Cl]$ is the result of reactions between HCl and surface hydroxyl groups that have a basic character. The behaviour is very

Table 4 Uptake of $[^{36}Cl]$ (atom nm^{-2}) by support materials

Solid	Mass/g	Average retention/ mmol g^{-1a}	BET area/ $m^2\ g^{-1}$	$[^{36}Cl]$ Uptake/ atom nm^{-2}
γ-Alumina	0.0506	0.522	110	2.86
F-γ-Alumina	0.6030	0.012	80	0.89
$\beta\text{-}AlF_3$	0.5370	0.013	30.7	0.255
MgF_2	0.5683	0.049	20.7	1.42
MgF_2	0.6488	0.049	20.7	1.42
Carbon	0.5428	0.089	600	0.09

[a]Relative error ± 4%.

Table 5 Uptake of $[^{36}Cl]$ (atom nm^{-2}) by supported Pd and Pt catalysts

Catalyst	Mass/g	Average retention/ mmol g^{-1a}	BET area/ $m^2\ g^{-1}$	$[^{36}Cl]$ Uptake/ atom nm^{-2}
$7.5Pd/\beta\text{-}AlF_3$	0.5000	0.022	30.0	0.44
$7.5Pt/\beta\text{-}AlF_3$	0.5000	0.020	32.4	0.37
$3Pd/\beta\text{-}AlF_3$[b]	0.1840	0.019	17.8	0.64
$7.5Pd/MgF_2$	0.4700	0.069	27.0	1.54
$7.5Pt/MgF_2$	0.5000	0.104	24.0	2.61
$3Pd/MgF_2$[b]	0.2890	0.086	20.5	2.53
10Pd/carbon	0.3563	0.125	392	0.192
10Pt/carbon	0.5252	0.055	431	0.077
10Pd/carbon[b]	0.2545	0.058	[c]	[c]
10Pt/carbon[b]	0.2319	0.103	[c]	[c]

[a]Relative error ±5%. [b]Used catalyst. [c]Not determined.

Table 6 Pulse chemisorption of H_2 over Pt catalysts at 273 K

Sample	H_2 chemisorption/μmol g_{cat}^{-1}	Pt_s/Pt_t × 100[a](%)	Pt surface area [a]/m^2 g^{-1}
$1Pt/MgF_2$	1.0	4.6	0.10
$3Pt/MgF_2$	2.8	4.4	0.27
$7.5Pt/MgF_2$	9.2	5.6	0.88
$10Pt/MgF_2$	8.4	3.8	0.81
$10Pt/MgF_2$[b]	7.8	3.6	0.75
1Pt/β-AlF_3	10.4	48.2	1.00
3Pt/β-AlF_3	17.3	27.0	1.66
7.5Pt/β-AlF_3	20.0	12.5	1.92
10Pt/β-AlF_3	14.8	6.8	1.42
10Pt/β-AlF_3[b]	1.6	0.7	0.15

[a] Pt_s = no. surface atoms, Pt_t = total no. Pt atoms; based on a stoichiometry $Pt_s:H = 1$ and 1.25×10^{15} Pt atoms cm^{-2}. [b] Precursor sample calcined at 673 K for 1 h in air before reduction.

similar to that of γ-alumina that has been fluorinated at ambient temperature by sulfur tetrafluoride (F-γ-alumina in Tables 2 and 4). In both cases, the extent of the interaction is small but it is measurable. The [^{36}Cl] retention values obtained from two samples of MgF_2 examined are greater and indicate that the surface of MgF_2 becomes hydroxylated to some extent when it is manipulated without the rigid exclusion of moisture. The Cl atom surface density estimated correlates reasonably well with a previous estimate of surface hydroxyl density for this compound.[34] It is concluded that hydroxylation of a metal fluoride surface must always be considered as a possibility even when the fluoride is not normally considered to be very susceptible to hydrolysis. The surface Cl atom density of the carbon sample used, although minimal, is consistent with the known ability of this material to interact with acids such as HCl.

The behaviour of unused Pd and Pt catalysts supported on β-AlF_3, towards $H^{36}Cl$ was almost identical. In both cases, the fraction of [^{36}Cl] retained was greater than that by β-AlF_3 alone (Tables 5 and 4). The aqueous impregnation method used to prepare the catalysts had little effect on BET area but it is considered that the increased [^{36}Cl] uptakes were the result of increased hydroxylation of the β-AlF_3 support. Retention of [^{36}Cl] by the used Pd catalyst examined was similar to that of the fresh catalyst sample (Table 5) although the Pd loadings were different. Retention of [^{36}Cl] by Pd and Pt supported on MgF_2 was also greater than by the support material alone, particularly in the Pt case (Table 5). As for β-AlF_3, it is considered that this is the result of additional hydroxylation of the MgF_2 surface occurring during the aqueous impregnation step. The behaviour of the used Pd/MgF_2 sample examined was similar. From a comparison between the β-AlF_3 and the MgF_2 samples, it might be concluded that surface hydroxylation is relatively more important when MgF_2 is used as a support.

Data obtained from Pd and Pt supported on carbon did not follow the simple pattern found for the two other supports. Here the interpretation is less obvious, since relatively large changes in BET area were found after impregnation (Table 5). The retention data per unit mass followed the order Pd/C > C alone >Pt/C for unused materials but Pt/C > C alone >Pd/C for used catalysts. These orders are not explicable solely in terms of HCl—support interactions and direct interactions with Pt could be a factor.

Hydrogen chemisorption

Platinum catalysts. Results of pulse chemisorption experiments on platinum catalysts of different loadings are shown in Table 6. The degree of hydrogen chemisorption was usually significantly smaller for Pt supported on MgF_2, consistent with the smaller specific surface area, S_{BET}, of MgF_2 compared with β-AlF_3 (Table 1). Platinum dispersions and surface areas were calculated using the stoichiometry ratio $Pt_s:H = 1$ which is frequently used for the evaluation of pulse chemisorption measurements.[36] While the platinum dispersion on MgF_2 was largely independent of the Pt content, that on β-AlF_3 decreased with increasing loading as expected.

Calcination of the precursor at 673 K before reduction had a significant effect on the subsequent chemisorption behaviour for 10Pt/β-AlF_3 and resulted in far lower chemisorption and hence Pt dispersion (Table 6). However, the effect of calcination on 10Pt/MgF_2 was barely significant. As was shown above, both surfaces become hydroxlyated to an extent during impregnation, the effect being greater for MgF_2. However, β-AlF_3 contains water, coordinated to surface Lewis acid sites and located in the hexagonal channels.[32] The marked effect of prior calcination in the β-AlF_3 case suggests that this water, rather than surface hydroxyl groups, has an important role in the reduction process $Pt^{IV} \rightarrow Pt^0$ on the surface, possibly resulting in a higher extent of hydrolysis of the Pt–Cl bonds and, thus different sintering behaviour during reduction.

Palladium catalysts. Results of the pulse chemisorption of H_2 on palladium catalysts are shown in Table 7 In order to avoid β-palladium hydride formation, a temperature of 353 K was chosen for the pulse chemisorption measurements. Because the stoichiometry of the hydrogen layer formed at this temperature is not well verified in the literature, only the different amounts of chemisorbed hydrogen are given and no palladium dispersions or surface areas were calculated.

Hydrogen chemisorption was observed to occur on Pd/β-AlF_3 samples to greater extents than on the analogous

Table 7 Chemisorption of H_2 on Pd catalysts at 353 K. All precursor samples were reduced at 623 K in H_2-flow prior to chemisorption but additional pretreatments prior to reduction are indicated

Sample	Precursor pretreatment prior to reduction	Pulse H_2 chemisorption/μmol g_{cat}^{-1}	Static H_2 chemisorption/μmol g_{cat}^{-1}
$1Pd/MgF_2$		0.1	
$3Pd/MgF_2$		1.0	
$7.5Pd/MgF_2$ (B)[a]		5.0 (4.5)[b]	
$7.5Pd/MgF_2$ (C)[a]	1 h, vacuum, 393 K	21.2	
$7.5Pd/MgF_2$ (D)[a]	1 h, vacuum, 393 K		38.2 (38.7)[b]
$10Pd/MgF_2$		10.5	
$10Pd/MgF_2$	1 h, air calcined, 673 K	4.9	
1Pd/β-AlF_3		2.1	
3Pd/β-AlF_3		6.1	
7.5Pd/β-AlF_3		21.7	
7.5Pd/β-AlF_3 (A)[a]	1 h, vacuum, 393 K		29.4 (29.4)[b]
10Pd/β-AlF_3		23.1	
10Pd/β-AlF_3	1 h, air calcined, 673 K	18.2	

[a] Examined also by TEM; letters correspond to those in Table 8. [b] Second measurement.

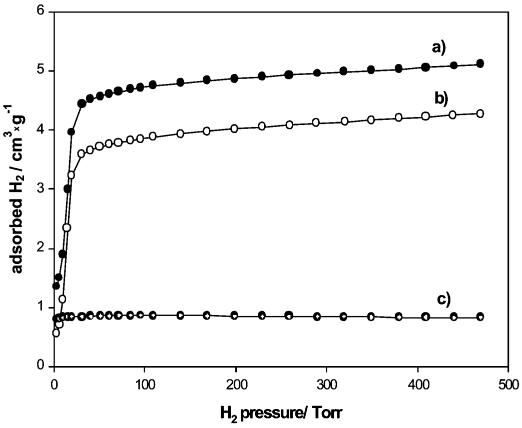

Fig. 3 Static H_2 adsorption on 7.5Pd/MgF_2, (a) 'combined isotherm', (b) 'weak isotherm', and (c) 'strong isotherm'.

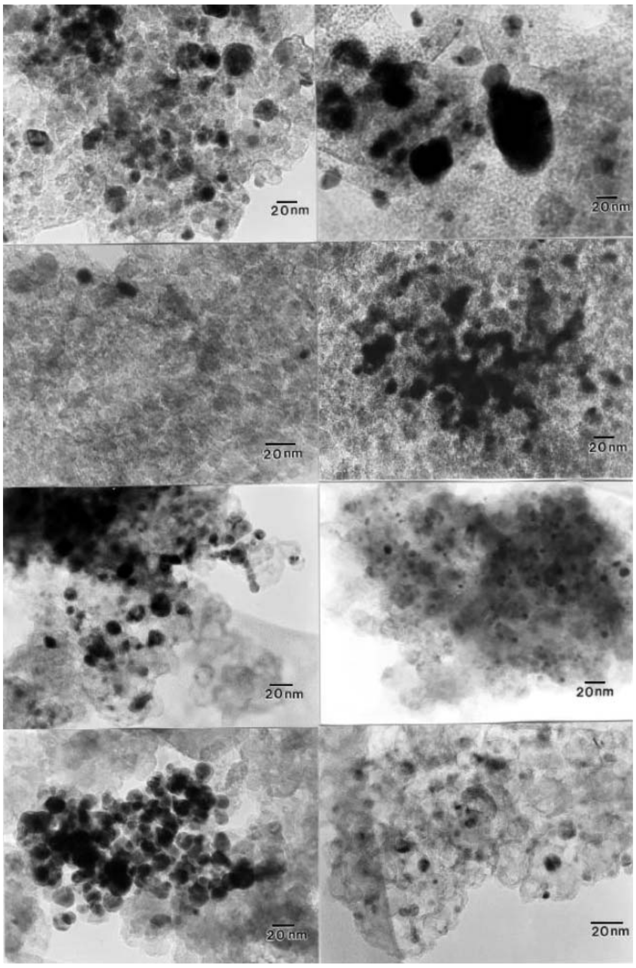

Fig. 4 TEM micrographs of (in descending order) 7.5Pd/β-AlF_3 sample (A) and 7.5Pd/MgF_2, samples (B), (C) and (D). For pre-treatment details see Tables 7 and 8. In each case two different characteristic regions of the sample are shown.

Pd/MgF_2. Calcination of the precursors prior to reduction had a measurable effect, a reduction in both cases (Table 7). Interestingly, heating the 7.5Pd/MgF_2 precursor at 393 K *in vacuo* prior to reduction resulted in an approximately fourfold increase in H_2 uptake (Table 7). This would not have been predicted from the air calcination data. It was shown above (Fig. 2) that pumping *in situ* prior to a TPR experiment resulted in a change in the reduction profile.

Two palladium samples, (A) and (D) in Table 7, were examined also by H_2 chemisorption under static conditions at room temperature using the 'back sorption technique'.[30,31] The adsorption isotherms obtained from 7.5Pd/MgF_2 (D) are shown in Fig. 3. The so-called 'combined isotherm' (a) reflected the sum of the irreversible chemisorption on the Pd surface, the absorption into the Pd particles (β-Pd-H) and the reversible adsorption on palladium and support. The so-called 'weak isotherm' (b), obtained after recording the combined isotherm and evacuation of the sample, reflected repeated reversible adsorption and β-Pd hydride formation. The difference between both isotherms resulted in the so-called 'strong isotherm' (c), yielding the hydrogen volume chemisorbed in the monolayer by extrapolation to $p = 0$. Estimation of the average particle size from these data is more reliable than a calculation based on H_2 pulse chemisorption, because saturation at static conditions, *i.e.* $Pd_s : H = 1$ is more likely to be achieved. The values, 13 and 10 nm, for Pd and Pt respectively, are compared with those estimated from TEM examination in Table 8.

Micrographs from the four samples examined are shown in Fig. 4.

The agreement between TEM observations and H_2 chemisorption measurements was satisfactory, since the most frequent particle size values can be correlated with the H_2 chemisorption values. For example, a slightly higher dispersion was indicated for sample (D) compared with sample (A). In the latter, 7.5Pd/β-AlF_3, there was evidence for larger particles; probably these were plate shaped and therefore, the hydrogen chemisorption would not be lowered drastically as would have been the case for spherical particles. In sample (B), 7.5Pd/MgF_2, for which no pre-treatment had been undertaken, a significant fraction of Pd existed as fused particles, dominating the H_2 chemisorption observed. The generally more uniform dispersions found for samples (C) and (D), 7.5Pd/MgF_2 pre-treated *in vacuo* before reduction, together with the observations reported above, leads us to conclude tentatively that the reduction process is influenced markedly by the degree of hydroxylation of the MgF_2 support.

Catalytic results. Results of catalytic testing are presented in Figs. 5 and 6, showing the product distribution obtained *versus* reaction temperature after *ca.* 2 h time on stream, using fresh samples at each temperature. The influence of the Pt and Pd content of MgF_2 based catalysts is demonstrated in Fig 5(a) and 5(b) respectively. The Pd/MgF_2 samples used were not subjected to pre-treatment prior to reduction. Comparing both figures, indicates that, for both metals, the degree of conversion increased with increasing metal loading, although even with

Table 8 TEM observation of Pd catalyst samples after H_2 chemisorption measurements

Sample[a]	Pre-treatment and reduction conditions	Most common particle size/nm	Other information	Average particle size[b]/nm
7.5Pd/β-AlF_3 (A)	393 K vacuum 1 h reduction at 693 K	10–30	Some larger particles; probably plates	13
7.5Pd/MgF_2 (B)	None reduction at 693 K	10–20	'Fused' particles and vacant support surface	
7.5Pd/MgF_2 (C)	393 K vacuum 1 h reduction at 693 K	10–30	Some particles <10 nm	
7.5Pd/MgF_2 (D)	393 K vacuum 1 h reduction at 693 K	10–20	Some particles <5 nm	10

[a] Letters correspond to those in Table 7. [b] Determined from H_2 chemisorption under static conditions (Table 7), assuming $Pd_s : H = 1$, 1.27×10^{15} Pd atoms cm^{-2} and Pd = 7.5 wt%.

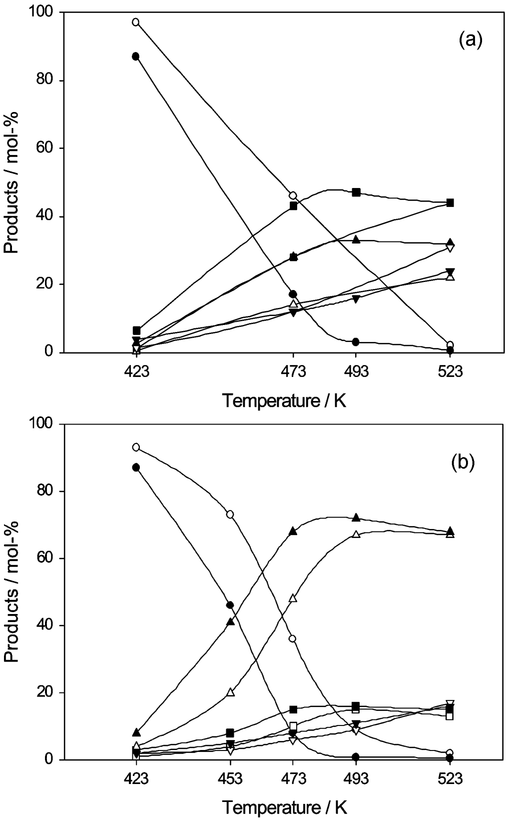

Fig. 5 Products formed, (a) on Pt/MgF_2 catalysts and (b), on Pd/MgF_2 catalysts depending on the reaction temperature. 3Pt/ or 3Pd/MgF_2, hollow symbols; 7.5Pt/ or Pd/MgF_2, filled symbols; ●, CCl_2FCF_3; ■, $CHClFCF_3$; ▲, CH_2FCF_3; ▼, CH_3CF_3.

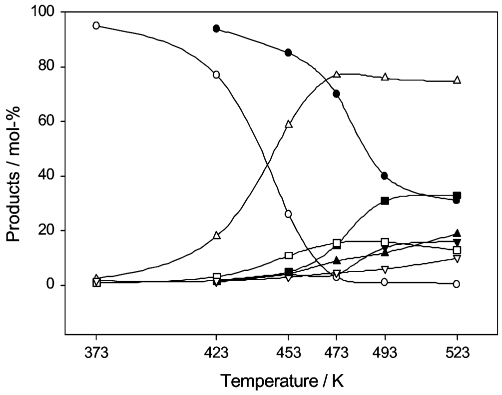

Fig. 6 Products formed on 7.5Pd/β-AlF_3 (hollow symbols) and 7.5Pt/β-AlF_3, (filled symbols) depending on the reaction temperature. ●, CCl_2FCF_3; ■, $CHClFCF_3$; ▲, CH_2FCF_3; ▼, CH_3CF_3.

lower metal contents good yields could be obtained at slightly higher reaction temperatures. However the metals differed remarkably in their selectivity. The Pt/MgF_2 catalysts are less selective but the Pd/MgF_2 catalysts exhibit very high selectivity towards the desired product, CH_2FCF_3 (**3**, HFC-134a). The major product using Pt/MgF_2 catalysts was the unwanted intermediate compound $CHClFCF_3$ (**2**, HCFC-124) even at higher temperatures.

Catalytic properties of 7.5Pt/β-AlF_3 and 7.5Pd/β-AlF_3 are compared in Fig. 6. The catalyst 7.5Pd/β-AlF_3 was the more reactive and had far higher selectivity towards CH_2FCF_3 (**3**). Moreover, its conversion of CCl_2FCF_3 (**1**) was slightly higher, 97 as opposed to 92% at 473 K (Table 9) than with 7.5Pd/MgF_2. The selectivity of the catalyst, as measured by the product distributions of **2**, **3** and **4** was slightly better for 7.5Pd/β-AlF_3, 16 : 79 : 5 (Table 9) than in the case of 7.5Pd/MgF_2, 16 : 74 : 9. The conversion data can be correlated qualitatively with the larger hydrogen uptakes exhibited by the Pd catalysts (Tables 6 and 7). More particularly this could be a result of the far greater H_2 chemisorption by Pd supported on β-AlF_3 compared with Pd on untreated MgF_2 (Table 7), although there is no numerical correlation. It is tentatively suggested that the magnitude of the pool of available hydrogen on the catalyst is one of the factors that determines the outcome of the hydrogenolysis. The conversion and the selectivity did not depend on the contact time, which was varied between 0.3 and 1 s without any significant change in the conversion and product distribution.

Table 9 Selected data for the conversion of CCl_2FCF_3 and the selectivity of products obtained under steady flow conditions (t_r = 1 s, 473 K, feed ratio, n_{H2}/n_{CFC} = 10)

		Selectivity		
Catalyst[a]	Conversion (%)	CF_3CHClF	CF_3CH_2F	CF_3CH_3
Pt/MgF_2	83	52	34	14
Pd/MgF_2	92	16	74	9
Pt/β-AlF_3	30	50	30	23
Pd/β-AlF_3	97	16	79	5
Pt/carbon	70	11	57	26
Pd/carbon	90	7	79	9

[a] Nominal metal loading of the catalysts = 7.5%.

Although the curves in Figs. 5 and 6 seem to indicate a consecutive reaction path, **1** → **2** → **3** → **4**, this was inconsistent with the independence of the selectivity on the contact time. For a consecutive reaction path, a decrease in the first intermediate product $CHClFCF_3$, **2**, and an increase in **3** and **4** would have been expected but the product distribution was always constant. Even when starting with $CHClFCF_3$ (**2**) only low degrees of conversion were obtained under otherwise similar reaction conditions. No reaction was observed using CH_2FCF_3 (**3**) as reactant. This is a further argument for concurrent rather than consecutive reaction paths. The conclusion is in agreement with the findings of others who have described similar behaviour using other catalysts and have discussed a carbene mechanism,[12,23,24,26] similar to that discussed in some detail for the hydrodechlorination of CCl_2F_2.[10,11,14] An aspect which requires further study is the reason for the slightly greater extent to which 'overhydrogenolysis' leading to the formation of **4**, was observed using 7.5Pd/MgF_2 compared with 7.5Pd/βAlF_3 (9 *vs.* 5%, Table 9).

Catalyst deactivation and regeneration. In a representative reaction, a sample of a 3Pd/β-AlF_3 catalyst showed constant catalytic activity during the first 2 h time on stream at 493 K but was deactivated over the next 32 h of use. The conversion, which was *ca.* 75% during the first 2 h, decreased to 15% after *ca.* 8 h, then remained constant over the remaining period. The original activity of the sample was restored by H_2 flow at 623 K for 2 h. Deactivation could be the result, either of deposition on the metal surface of organic (polymeric) residues and/or a change of the valence state of Pd. The carbon content, determined by elemental analysis of the deactivated sample, was low (0.23%) and for this reason it is considered that the loss in activity was not the result of Pd coverage. An alternative suggestion is based on the evolution of hydrogen chloride, and possibly hydrogen fluoride, during the hydrodechlorination. Some of the hydrogen halide evolved will interact with surface hydroxyl groups, particularly important when MgF_2 is the support, or surface H_2O, important when β-AlF_3 is used. Whatever the exact mechanism, new acid sites will be created. We assume that highly dispersed palladium can be oxidised partially by protons in a similar way to that known for Ag and

Cu dispersed on acid zeolites. Thus, TPR of Ag^+/HY[37] and unpublished work on TPD of reduced Cu^{2+}/HY revealed desorption of dihydrogen formed by redox reactions between the metals and H^+. This type of process is perhaps more problematic in the present work but at least the surface of the small Pd particles could acquire a positive charge in this way. Reductive treatment in the absence of hydrogen halides could regenerate the uncharged palladium surface.

Comparisons among support materials. It has been demonstrated in this work that palladium supported on MgF_2 or β-AlF_3, can be used as catalysts to convert 1,1-dichlorotetrafluoroethane (CFC-114a) into 1,1,1,2-tetrafluoroethane (HFC-134a) *via* a hydrodechlorination reaction. Their behaviour in terms of activity and selectivity are very similar to the Pd/carbon catalysts used as a benchmark (Table 9). One obvious advantage of the widely used carbon[10,11,15] and γ-alumina[2,4,8,11,12,16-19] materials is their large surface areas on which the catalytically active metals, Pt and Pd, can be dispersed as small particles. In contrast, MgF_2 (20.7 m^2 g^{-1}) and β-AlF_3 (30 m^2 g^{-1}) have significantly lower surface areas; surprisingly, however, this does not result in lower catalytic activity. Both Pd on MgF_2 and Pd on β-AlF_3 have the same or even slightly higher conversion and better selectivity toward CH_2FCF_3 compared with Pd on carbon under the conditions used (Table 9). Provided well dispersed metals can be prepared, the specific surface area of the support is not an important characteristic. Adequate dispersions were achieved in most of the samples studied here and the possible explanations for this can be addressed by considering the nature of the support surfaces and their role during the formation of the catalyst precursors. The two metal fluorides used here as supports provide an interesting comparison. A conventional support such as γ-alumina exhibits predominantly Brϕnsted surface sites, whereas on β-AlF_3 surfaces exclusively Lewis acid sites are found;[38] MgF_2 has weak but detectable Lewis surface sites.[33,39] In both cases, interactions with the Lewis base, water are plausible; they will be important for β-AlF_3 but relatively unimportant for MgF_2. Additionally, slow desorption of water from the hexagonal channels of β-AlF_3 will occur during the latter stage of the reduction of the metal cations.[32] The [^{36}Cl] study indicates that the fluoride surfaces are both hydroxylated to some extent, the hydroxyl surface density being significantly greater for MgF_2 (Table 4). The balance between surface hydration, dominant on β-AlF_3, and surface hydroxylation, relatively more important on MgF_2, is a possible way of explaining the different behaviour of β-AlF_3 compared with MgF_2 during the reduction of the precursors. The differences in the reduction characteristics of the Pt or Pd salts on the two fluorides, as indicated by their TPR behaviour will be reflected in the H_2 sorption behaviour described above. The amount of adsorbed H_2 is greater on Pd/β-AlF_3 than on Pd/MgF_2 and reduction of Pd^{II} on β-AlF_3 occurs at temperatures significantly lower compared with MgF_2. The same pattern was found for the analogous platinum systems (Fig. 1). It is well known that oxygen-containing Pt and Pd surface species can be reduced more easily than fully chlorinated species such as $[PtCl_6]^{2-}$ and $PdCl_2$. Although there was no evidence that complete hydrolysis occurred on β-AlF_3 during impregnation, a partial thermohydrolysis of the Pt–Cl and Pd–Cl bonds to give $M(Cl,O)_x$ surface species during the course of H_2-reduction is likely. In the MgF_2 case, interactions between Pt(Pd)–Cl species and surface hydroxyl groups that have basic character can be envisioned as an alternative to surface water. It appears that both types of reaction can result in well-dispersed metal particles on the surface after reduction

The effect of precursor pre-treatment prior to reduction, although only briefly explored, provides supporting evidence for the role of surface water on the β-AlF_3 support. Calcination in air of a Pt/β-AlF_3 precursor resulted in a lower Pt dispersion but had almost no effect for Pt/MgF_2 (Table 6). For the Pd analogues however, H_2 uptakes, and by implication, metal dispersions, were reduced on calcined samples (Table 7). However, a mild pretreatment, 393 K *in vacuo* for 1 h, had a beneficial effect on the uniformity of particle distribution in the Pd/MgF_2 case (Table 8), suggesting that the degree of hydroxylation had increased. The hypothesis that the degree of metal dispersion on β-AlF_3 is influenced by surface water also accounts for the observation that, whereas the dispersion of Pt on MgF_2 was largely independent of the $[PtCl_6]^{2-}$ loading, it decreased markedly as the loading on β-AlF_3 was increased (Table 6).

Comparing the catalytic activity and selectivity of the metal fluoride supported catalysts with charcoal as the support (Table 9) indicates that Pd/β-AlF_3 is the best catalyst system of those studied here. It has an excellent selectivity towards CH_2FCF_3, although Pd/MgF_2 and Pd/carbon are almost as good. Carbon has Lewis acid sites and this seems to be the common factor. A large surface area, though undoubtedly beneficial, is not the only important factor.

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