Transformation of the Cluster $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$ into $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$ upon Impregnation onto Inorganic Supports

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The impregnation of organic solutions of $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$ onto inorganic supports used for catalysis or chromatography has been shown to produce $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$, depending upon the nature of the support, its pre-treatment, and the solvent used; these observations are relevant to the preparation of cluster-derived catalysts.

Molecular clusters of the transition metals continue to attract increasing interest, *inter alia* as precursors of new highly dispersed heterogeneous catalysts.[1,2] Ideally, it is hoped that the metallic particles obtained from careful decomposition of the cluster impregnated onto an inorganic support will be of better controlled size and composition (in mixed-metal systems) than conventional catalysts. It is usually assumed that the first step in the preparation of the cluster-derived catalyst, *i.e.* the impregnation of an organic solution of the cluster onto an inorganic support, does not drastically modify the *core* structure of the cluster, although there are spectroscopic indications in the literature to the contrary.[3] We present here a definitive example of cluster framework modification upon chemisorption.

We have observed that simple impregnation of an organic solution of the *triangulo*-$Pt_3(\mu\text{-}CO)_3(PPh_3)_4$ cluster[4] (abbreviated Pt_3) can result in its transformation on the support into the pentanuclear $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$ cluster[5] (abbreviated Pt_5). Such dramatic structural and nuclearity changes will of course have an influence on the particle size and are relevant to the use of platinum-containing clusters for *e.g.* the catalytic reforming of hydrocarbons.[6]

We have verified that in a typical impregnation in which an organic solution of the Pt_3 cluster is agitated with the inorganic support and the solvent is then evaporated under reduced pressure, the same results were obtained as during a column chromatography of pure Pt_3 (using the same solvent and support).† We then carried out a series of chromatographic experiments differing from each other in the nature of the support and the solvent. The quantity of Pt_3 cluster used in each experiment was constant (0.2 g). The eluted solution was evaporated (room temp., reduced pressure), and the solid obtained was weighed and identified by its fingerprint i.r. spectrum in the ν(CO) region.[4,5] Various inorganic supports which are typically used for chromatography or for catalyst preparation were investigated[2] (see Table 1). Different treatments were applied to the supports before use in order to evaluate the influence of such pre-treatment on their reactivity (see Table 1). The solvents used were toluene, dichloromethane, and tetrahydrofuran (THF), in all of which the Pt_3 cluster is perfectly stable. In all the experiments except expt. 2 in toluene, we found that the Pt_3 cluster is partly or totally transformed upon adsorption of its organic solution onto the support. The transformation products, separated and isolated by chromatography, are the Pt_5 cluster and a complex, X, so far unidentified [with ν(CO) KBr: 1980 br.s and 1770 br.m cm^{-1}]. An important and variable fraction of the starting cluster is transformed into species which remain on the column and cannot be further eluted.

The factors which influence these transformations are (i) the nature of the support, (ii) its pre-treatment, and (iii) the solvent.

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† All operations were carried out under purified nitrogen and the solvents distilled before use.

Table 1. Yields (%)[a] of products isolated from the transformation of $Pt_3(CO)_3(PPh_3)_4$ upon impregnation.

			In toluene			In CH_2Cl_2			In THF		
Expt.	Support[b]	Pretreatment[c]	Pt_3	Pt_5	X[d](g)	Pt_3	Pt_5	X[d](g)	Pt_3	Pt_5	X[d](g)
1	MgO	A	55	0	0	65	0	0	75	0	0
2	MgO	C	95	0	0						
3	TiO_2	A	0	traces	0.045	10	50	0	0	0	0.070
4	$Al_2O_3 - 1$	A	0	0	0	0	0	0	30	0	0
5	$Al_2O_3 - 1$	C	30	0	0	35	0	0			
6	Al_2O_3-C	A	0	35	0.040	15	45	0	25	35	0
7	Kieselgel	A	0	40	0	0	30	0	35	0	0
8	Kieselgel	B	15	20	0	10	25	0	35	0	0
9	Kieselgel	C	25	5	0	10	25	0			
10	Kieselgel	D	30	15	0	traces	45	0			
11	Aerosil	A	10	52	0	0	40	0	10	15	0

[a] % Yield based on platinum; Pt_3 is $Pt_3(CO)_3(PPh_3)_4$, Pt_5 is $Pt_5(CO)_6(PPh_3)_4$. [b] The supports are the following: MgO (Magnesium Oxide RP Prolabo), TiO_2 (P-25 Degussa), $Al_2O_3 - 1$ (Aluminoxid 90 neutral Merck 1077), Al_2O_3-C (Degussa), Kieselgel (Kieselgel 60 Merck 9385), Aerosil 200 (Degussa). [c] Pre-treatment A = degassed at 10^{-2} mmHg, 20 °C, 24 h; B = A, then washed with Et_2O; C = A, then washed with THF; D = degassed at 10^{-2} mmHg, 180 °C, 5 h. [d] Quantity expressed in g since yields cannot be calculated (the quantity of Pt_3 used is always 0.2 g).

The acid/base properties of the support play a determining role; acidic supports always transform Pt_3 to a large extent (expt. 3, 4, 6, 7). Washing the support, before impregnation of the cluster, with a hydrophilic solvent such as Et_2O or THF (expt. 5, 8, 9) significantly decreases the transformation of Pt_3 into Pt_5 (expt. 8, 9 *vs.* 7), or, in toluene, limits the irreversible retention on the support (expt. 2 *vs.* 1). These solvents will both remove some water from the support (evidence for this can be obtained by freezing out at −20 °C this water from the solvent used to wash the column) and decrease the number of Lewis-acid sites, which accounts for the lower reactivity observed. For comparison, thermal treatment of the support at 180 °C leads to a lower Pt_3 transformation than degassing at room temperature (expt. 10). Complete dehydroxylation of such supports is known to be very difficult.[7] The interactions of a carbonyl cluster with an inorganic support can be followed by chemical transformations such as (i) nucleophilic attack of a surface-OH group on a co-ordinated CO, leading to a metal-hydride and CO_2 (the classical base reaction[8]), (ii) oxidative-addition of a surface OH group on a metal centre or across a metal–metal bond, (iii) deco-ordination of a basic ligand *via* interaction with the Lewis sites of the support, or (iv) protonation of the cluster *via* the Brönsted acidity of the support.[2]

In our case, we have verified in a separate experiment that (i) is not responsible for the observations made in toluene in expt. 1. Thus, a toluene or THF solution of Pt_3 does not react at room temp. with water, nor with KOH pellets. On the other hand, Pt_3 in THF solution reacts with 48% aqueous HBF_4 to give Pt_5, indicating that (iv) could well occur on the support. This is consistent with our observations (expt. 6, 7).

How the metallic core of Pt_3 is fragmented to give Pt_5 eventually cannot yet be stated. Our observations emphasize the possible occurrence of dramatic structural modifications at the early stage of the preparation of a cluster-derived catalyst and also that column chromatography is often not an 'innocent' separation technique.

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