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STRUCTURAL ASPECTS OF THE LINDLAR CATALYST FOR SELECTIVE HYDROGENATION

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Unsupported intermetallic phases of palladium and lead, formed by reduction possess attractive catalytic properties for selective hydrogenation. The significance of the ease of reduction of divalent lead in Lindlar (supported) catalysts is also discussed.

1. Introduction

The catalyst introduced by Lindlar in 1952 [1,2] for the selective hydrogenation of hydrocarbons with multiple unsaturated carbon-carbon bonds (alkynes or dienes) either in the gas phase or in solution consists essentially of palladium metal deliberately contaminated with lead, and often, but not exclusively [3,5] supported on calcium carbonate. Though widely used and well proven its mode of action remains enigmatic. The very nature of the active phase is not clear, and much scope exists both for a renewed attempt to clarify the structural aspects of the catalyst and to explore new variants based on the suspected synergy of palladium and lead for selective catalytic hydrogenation. Palczewska et al. [4] found that the catalyst containing Pd_3Pb, among other phases, exhibits even greater selectivity than the commercial Lindlar catalyst. Jenkins [5] reported that the adsorption of divalent ions of lead on the palladium is a *sine quo non* for selectivity, whereas Wovkulich et al. [6] conclude that the function of lead is merely to facilitate rearrangement of the surface of palladium. We here report on the performance and structural aspects of supported and unsupported palladium catalysts to which have been added appropriate amounts of lead, for the hydrogenation of an acetylene.

The structural investigations are based predominantly on X-ray powder diffractometry. Tests of catalytic activity and selectivity were carried out on a separate apparatus.

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2. Experimental

A conventional flow reactor was used to test the performance of the hydrogenation catalyst. More details will be given elsewhere [7]. Briefly, research grade H_2 was passed in a flow reactor (45 ml min^{-1} at 675 Torr) along with acetylene (5 ml min^{-1} at 75 Torr) through a flow system at room temperature (20 ° C), the catalyst being mounted on a porous glass plate. The acetylene was stringently purified beforehand as described in ref. [8]. The gas stream leaving the reactor was analyzed gas chomatographically. X-ray diffractograms were collected using a Siemens Diffractometer (D 500), Ni-filtered CuK_α radiation being used.

Silica gel (60–120 mesh, BDH Laboratory Reagents) was loaded with a H_2PdCl_4 by the standard incipient wetness method. After calcination in flowing oxygen at 500 ° C for 3 hours, the sample was converted into PdO/SiO_2 The catalyst was then divided into 3 parts. The first one was investigated as prepared (A), the second (B) was reduced and impregnated exactly as in the Lindlar procedure, the third one (C) was impregnated by lead acetate before reduction. Catalyst D was commercial PdO (from BDH) reduced 2 hours in a stream of H_2 at 300 ° C. The impregnation of this catalyst by lead acetate gave catalyst E, catalyst F was made from E by 2 hours annealing in hydrogen at 300 ° C. Catalyst G-N were prepared by grinding in agate mortar appropriate ratios of PdO and $Pb(OH)_2CO_3$ followed by subsequent annealing in a stream of H_2 at 300 ° C.

The amount of each alloy phase was calculated from the known content of lead and from the intensities of the (111) peaks of Pd, Pd-Pb and Pd_3Pb. Lattice parameters were calculated from extrapolation to $\theta = 90°$ of the linear functions of the parameters obtained from positions of particular peak on $\cos^2\theta$. The dispersion D of each phase was calculated from equation:

$$D = \frac{5d^2 \cdot n_s \cdot 100\%}{d^3 \cdot n_v} = \frac{928}{d}$$

where d is mean crystallite dimension in Å, obtained from Scherrer equation applied to half maximum width of (111) peak, n_s is the surface density of metal atoms ($n_s = 0.126$ at. Å^{-1}, assuming equal contributions of {100}, {110} and {111} planes in the surface) and n_v is the volume density of the atoms. The equation was evaluated on assuming the cubic shape of crystallites, in which five-sixths of the surface is catalytically active.

3. Results

First we consider the supported catalysts (A, B and C). Then we focus on the Pd-Pb alloy powders.

3.1. SiO_2 SUPPORTED CATALYSTS

Figure 1 reflects the salient structural features. There are no significant differences between palladium catalyst (A) and the Lindlar-like prepared one (B), apart from minor changes in mean crystallite size (60 Å and 80 Å respectively). Each of these samples is essentially pure Pd ($a_0 = 3.895$ Å), whereas catalyst C, impregnated before PdO reduction is obviously no longer pure Pd as $a_0 = 3.988$ Å, a figure close to the lattice parameter 4.013 Å reported for Pd_3Pb [9]. This phase is almost certainly a disordered alloy in view of the absence of superstructure peaks ((100), (110) and (210)).

3.2. Pd-Pb ALLOYS

The phase composition of Pd-Pb alloys, and other parameters deduced from XRD analysis are contained in table 1. Figure 2 summarizes the results of our measurements of catalytic performance.

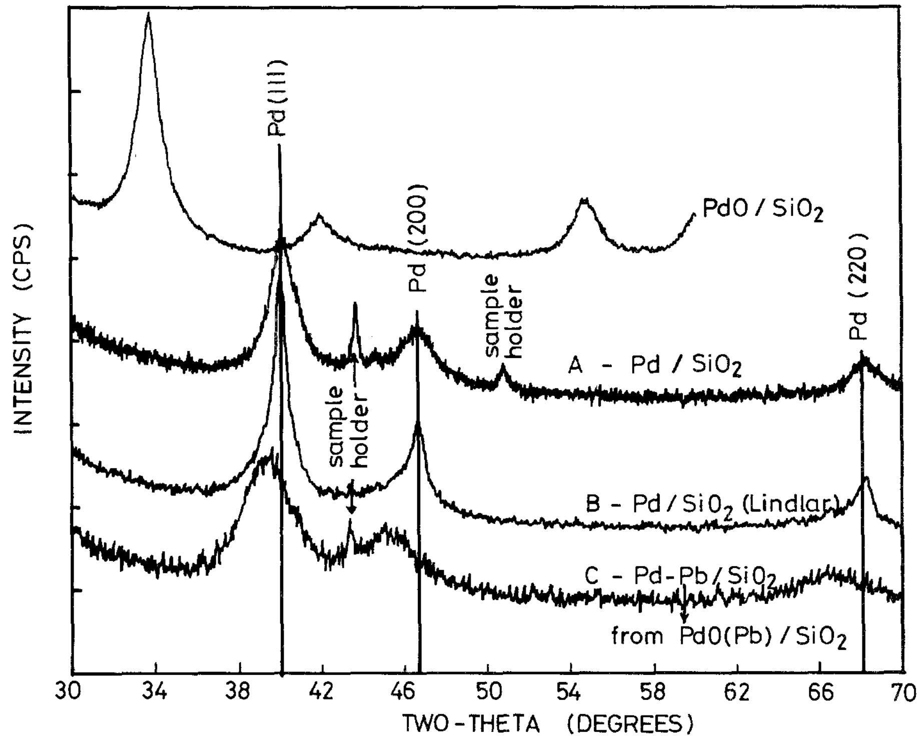

Fig. 1. The fragments of pattern of PdO/SiO_2 and of catalysts A, B and C. The shift towards low angles of the (111), (200) and (220) peaks of catalyst C with respect to that of A and B is apparent.

4. Discussion

From section 3.1 it is apparent that Pb^{2+} compounds may be reduced when they are mixed with PdO so that reduction of the precursor of the Lindlar catalyst, which is composed of Pb^{2+} (for example $Pb_2(OH)_2CO_3$) and PdO layer covering the surface of bulk Pd crystallites, also takes place readily. Evidently the reduced Lindlar catalyst is composed of a layer of either a palladium-lead alloy or intermetallic compound below which there remains the essentially unchanged palladium. (The importance of preoxidation, in air, of palladium catalyst in the course of obtaining good Lindlar catalyst was reported by Mallat et al. [3].) This surface layer is probably too thin to be visible in X-ray diffraction, resulting in the identity of the pattern of samples A and B.

So far as the Pd-Pb alloys are concerned, the activity and selectivity remain constant with lead contents from ~ 0.02 to ~ 0.17, despite the fact that the bulk composition changed considerably (fig. 2). Usually, catalytic parameters are very

Table 1
Results of XRD investigations

Catalyst	Lead content (%)	Phase composition (%)	Phase population (%)	Phase lattice constant (Å)	Phase crystal size (Å)	Mean sample dispersion (%)
D	0.0	Pd	100	3.887	250	3.71
E		Pd	100	3.887	255	3.64
F		Pd	100	3.885	265	3.50
G	1.1	Pd	99.3	3.886	250	371
		Pd_3Pb	0.7	4.04	280	
H	4.7	Pd	87	3.887	150	5.50
		Pd_3Pb	13	4.036	330	
J	10.2	Pd	60	3.893	150	4.83
		Pd-Pb	4	3.945	350	
		Pd_3Pb	36	4.039	330	
K	15.3	Pd	23	3.89	290	2.71
		Pd-Pb	26	3.939	245	
		Pd_3Pb	51	4.038	480	
L	20.2	Pd	9	3.89	295	2.39
		Pd-Pb	17	3.936	215	
		Pd_3Pb	14	4.037	500	
M	24.9	Pd_3Pb	93	4.036	730	1.27
		Pd_5Pb_3	3		720	
N	31.5	Pd_3Pb	48	4.04	540	1.87
		Pd_5Pb_3	52		460	

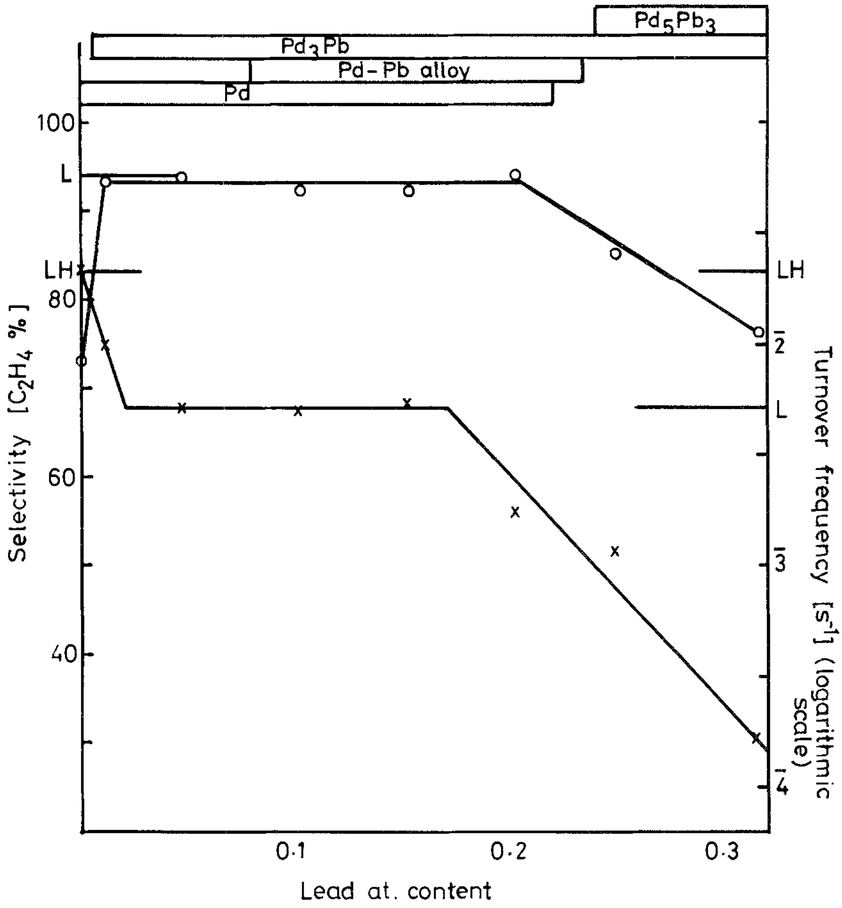

Fig. 2. Catalytic selectivity and activity (expressed in terms of log of turnover number) as a function of lead content. $S = r_{C_2H_4} \cdot (r_{C_2H_4} + r_{C_2H_6})^{-1}$, where r_n is the rate of formation of n. L- the results for the Lindlar like prepared catalyst E, LH- for this catalyst annealed at 300 °C (F). The phase composition at a given content of lead is also indicated.

sensitive to even minor changes of the surface. We conclude that the surfaces of all phases present in this system (Pd, Pd-Pb, Pd_3Pb) are essentially the same irrespective of their bulk composition since it would be unlikely for the catalytic performances of three different surfaces to be the same. We conclude that the surface composition of the Lindlar catalyst (E) as deduced from its selectivity and activity (see fig. 2) is closely similar to the composition of the surfaces of catalysts G to K inclusive. In this study neither the stoichiometry of surface phases nor the eventual order of surface Pb atoms was established but it seems indisputable that the surfaces are composed of zero-valent Pd and Pb atoms, as Pb^{2+} would be reduced together with the surface PdO.

Finally, the stability of the Lindlar surface phase is kinetically controlled. When the Lindlar catalyst is heated (to say 300 °C, e.g. sample F, fig. 2) the lead dissolves in the bulk, so that the resulting surface is akin to that of pure palladium and also to its catalytic properties.

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