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CATALYTIC PROPERTIES OF THE PLATINUM AND PALLADIUM BLACKS OBTAINED FROM VAPORIZED METALS AS REVEALED IN THE HYDROGENATION OF 4-METHYLCYCLOHEXANONE IN ETHANOL

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The platinum and palladium blacks obtained from vaporized metals have been found to catalyze the acetal formation efficiently in the hydrogenation of 4-methylcyclohexanone in ethanol. The catalytic properties of these blacks are compared with those of various blacks prepared by chemical procedures.

Previously it has been reported that in the hydrogenation of 4-methylcyclohexanone (**1**) in ethanol prereduced and well washed Adams platinum oxide$^{1)}$ catalyzes the formation of the corresponding diethyl acetal (**2**), and 1-ethoxy-4-methylcyclohexane (**3**) is produced as a hydrogenation product, together with methylcyclohexane (**4**) and 4-methylcyclohexanol (**5**).$^{2)}$ The acetal formation also occurred rapidly over prereduced palladium hydroxide and in this case **3** was formed in a high selectivity of 97%.$^{2)}$ A platinum black prepared by repeatedly reducing platinum(II) hydroxide with hydrogen in water followed by washing with water catalyzed the acetal formation more efficiently and gave a higher yield of **3** than the prereduced and washed Adams catalyst.$^{3)}$ On the other hand, no acetal was formed over prereduced but not washed Adams platinum oxide. It appears that the reaction greatly depends on the alkaline or acidic impurities associated with catalyst preparations. In usual procedures, however, it would be rather difficult to remove the impurities completely without losing high catalytic activities.

Recently, fine transition metal particles have been prepared from vaporized metals produced by a plasma hydrogen gas-molten metal reaction under an arc melting condition.$^{4)}$ The platinum and palladium blacks thus prepared (denoted as Pt(NRIM) and Pd(NRIM), respectively)$^{5)}$ cannot contain any alkaline as well as acidic impurities as would be obvious from their method of preparation. Therefore, we have been interested in their catalytic behaviors in the hydrogenation of **1** in ethanol. Thus, **1** was hydrogenated in ethanol at 25°C and atmospheric pressure over these blacks as catalysts and the results were compared with those obtained by use of various platinum blacks and a palladium black prepared by usual chemical procedures.

Table 1 summarizes the methods of preparation of the catalysts investigated as well as the results on the hydrogenation of **1**. The sodium contents of the catalysts are also included in the last column of Table 1. Fig. 1 shows the amount of acetal **2** formed as a function of the extent of hydrogenation.

Table 1. Hydrogenation of 4-Methylcyclohexanone in Ethanol over Platinum and Palladium Blacks of Various Methods of Preparation[a)]

No.	Catalyst	Reducing agent	Medium for reduction	Acetal formation[b)]	10^4k[c)]	Hydrogenation product[d)]					Na content
					mol $min^{-1}gcat^{-1}$	Selectivity/mol%			Cis/trans ratio		ppm
						3	**4**	**5**	**3**	**5**	
1	Pt(Loew)[e)]	CH_2O	NaOH-H_2O, washed with AcOH, H_2O	Moderate	1.3	20.2	16.1	63.7	3.6	1.4	200
2	Pt(Adams)[f)]	H_2	EtOH, not washed	No	2.6	0.0	4.6	95.4	-	0.38	g)
3	Pt(Adams)[f)]	H_2	H_2O, washed	Moderate	3.0	5.5	20.4	74.1	2.4	1.3	93
4	Pt(Adams)[f)]	H_2	AcOH, H_2O, washed	Moderate	1.3	16.4	13.8	69.8	3.9	1.4	71
5	Pt(Brown)[h)]	$NaBH_4$	H_2O, washed	No	1.2	0.0	0.0	100	-	0.40	178
6	Pt/Pt$(OH)_2$[i)]	H_2	H_2O/neutral[j)]	No	0.13	0.0	6.5	93.5	-	0.94	425
7	No.6 + HCl[k)]	-	-	Very fast	16.3	30.6	17.8	51.6	2.6	1.5	-
8	No.6 + NaOH[l)]	-	-	No	5.1	0.0	0.0	100	-	0.68	-
9	Pt/Pt$(OH)_2$[m)]	H_2	H_2O/acidic[n)]	Very fast	1.0	36.9	14.0	49.1	4.8	1.6	154
10	Pt/$H_2Pt(OH)_6$[o)]	CH_2O	H_2O, washed	Fast	2.5	29.0	18.6	52.4	3.7	1.4	30
11	Pt/$H_2Pt(OH)_6$[p)]	H_2	H_2O/neutral[j)]	Fast	1.5	28.1	20.6	51.3	3.8	1.3	165
12	Pt(NRIM)[q)]	-	-	Very fast	2.8	27.2	15.8	57.0	2.8	1.5	-
13	Pd/Pd$(OH)_2$	H_2	H_2O/acidic[n)]	Very fast	1.9	98.8	0.0	1.2	13.6	1.4	-
14	Pd(NRIM)[q)]	-	-	Very fast	0.52	98.0	0.0	2.0	14.7	2.1	-

a) 4-Methylcyclohexanone (0.03 ml) was hydrogenated in 2 ml of EtOH at 25 °C and atmospheric pressure over 5-10 mg of catalyst which had been shaken with H_2 for 10 min before the addition of substrate. b) See also Fig. 1. c) Average rate from 0 to ca. 50% hydrogenation. d) **3**: 1-ethoxy-4-methylcyclohexane; **4**: methylcyclohexane; **5**: 4-methylcyclohexanol. e) O. Loew, Ber., 23, 289 (1890). f) R. Adams and V. Voorhees, J. Am. Chem. Soc., 44, 1683 (1922). In this preparation H_2PtCl_6 was fused with $NaNO_3$ at 400-450 °C. g) According to Keenan et al. (Ref. 1), Adams platinum oxide contains 1.8-2.2% of sodium. h) H. C. Brown and C. A. Brown, J. Am. Chem. Soc., 84, 1494 (1962). i) Precipitated from $PtCl_2$ with $NaHCO_3$ at the pH of 7.8-8.0. j) The water was almost neutral during hydrogen reduction of Pt hydroxide or oxide. k) 0.13 µl of conc. HCl was added to 6 mg of platinum. l) 0.21 mg of NaOH was added to 6 mg of platinum. m) Precipitated from $PtCl_2$ with NaOH at the pH below 7.6. n) The water became acidic during hydrogen reduction, but the reduction followed by washing was repeated until the water became no more acidic. o) L. Wöhler, Z. Anorg. Chem., 40, 434 (1904). Cf. also Ref. 1. p) Heated at 300 °C for 1 h before reduction. q) Obtained from vaporized metal at the National Research Institute for Metals (Ref. 4).

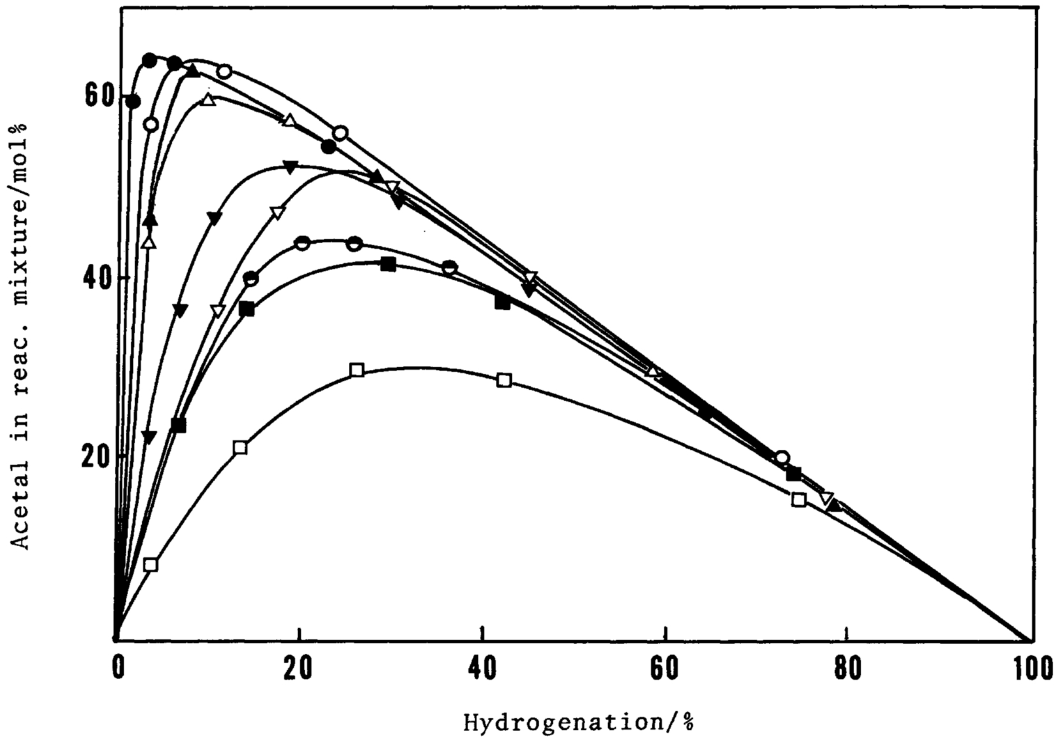

Fig. 1. The amount of acetal formed in hydrogenation of 4-methylcyclohexanone in ethanol as a function of the extent of hydrogenation. ●, Pd(NRIM)(No.14); ○, Pt(NRIM)(No.12); ▲, Pt/Pt(OH)$_2$+ HCl(No.7); △, Pt/Pt(OH)$_2$(No.9); ▼, Pt/H$_2$Pt(OH)$_6$(No.11); ▽, Pt/H$_2$Pt(OH)$_6$(No.10); ⊖, Pt(Loew)(No.1); ■, Pt(Adams)(No.4); □, Pt(Adams)(No.3). For the numbers in parentheses, see Table 1.

As seen from Fig. 1, both Pt(NRIM) and Pd(NRIM) are highly active catalysts for the acetal formation. In particular, Pt(NRIM) is the most active for the reaction of the platinum blacks investigated. Among the platinum blacks prepared by usual chemical procedures, only the platinum obtained by reduction of Pt(OH)$_2$ which was precipitated from PtCl$_2$ with NaOH at the pH below 7.6 (No.9) showed a comparative or slightly inferior activity. In this preparation, the water in which the hydroxide was reduced became strongly acidic, although the reduction followed by washing was repeated until the water became no more acidic.[3] The platinum prepared by reduction of H$_2$Pt(OH)$_6$[6] with formaldehyde (No.10) and the platinum prepared by hydrogen reduction of the oxide obtained by heating H$_2$Pt(OH)$_6$ at 300 °C for 1 h (No.11) were both fairly active for the acetal formation. Usually **3** is formed in 27-29% yields over the catalysts which are active for the acetal formation. A higher yield of **3** with No.9 platinum appears to reflect slightly acidic character of the catalyst because the yield is further increased by addition of hydrochloric acid.[7] No acetal was formed over prereduced but not washed Adams catalyst (No.2), the platinum obtained by NaBH$_4$ reduction of H$_2$PtCl$_6$[8](No.5), and the platinum obtained from Pt(OH)$_2$ which was precipitated from PtCl$_2$ with NaHCO$_3$ at the pH of 7.8-8.0 (No.6)(the water used as the reduction medium didn't become acidic.). Prereduced (in water or in acetic acid) and washed Adams platinum oxide (No.3 and No.4) and the platinum black of Loew[9](washed with AcOH) (No.1) showed moderate activities and gave lesser yields of **3**. Hydrogenation of **1** over No.6 catalyst was extremely slow as shown in Table 1, but the addition of a trace amount of HCl or NaOH (No.7 and No.8) greatly promoted the hydrogenation. Since in t-BuOH the hydrogenation proceeded in a rate of 3.0×10^{-4} mol $min^{-1}gcat^{-1}$ over the same catalyst, the extremely small rate in ethanol is probably due to a strong solvation of ethanol or hemiacetal formation.[10] It is noted that the characteristic properties of Pt(NRIM) are almost fully reproduced in the hydrogenation with No.6 catalyst added by a trace amount of HCl (No.7) and are completely lost with No.6 platinum which contains 425 ppm of sodium, although the nature of the sodium is not obvious. As described previously,[2] the acetal formation is associated with the adsorbed hydrogen, probably in an ionized state. The above results suggest that a strongly ionized species of hydrogen[11] may be responsible for the acetal formation.

The cis/trans isomer ratio of **5** formed is also very sensitive to alkaline impurities. The catalysts which gave no acetal afforded the trans isomer in greater amounts than the cis isomer, while over the catalysts which were active for the acetal formation the cis isomer was formed in excess amounts. The hydrogenolysis to give **4** appears less sensitive to alkaline impurities since the hydrogenolysis occurred even over the catalysts which gave no acetal (Nos.2 and 6), while no hydrogenolysis occurred over No.5 and No.8 catalysts.

Pd(NRIM) and the palladium black obtained by reduction of $Pd(OH)_2$ (No.13) showed very similar properties and, in accord with the previous results,[2] gave **3** of high cis/trans ratios in very high yields.

The crystallite size of Pt(NRIM) as determined by an X-ray diffraction analysis is 41.8 nm which is far larger than those of the other platinum blacks listed in Table 1 (7-9.5 nm). The surface area of Pt(NRIM) is only 2.7 m^2g^{-1} which may also be much smaller than those of the other catalysts (17.7 m^2g^{-1} for a catalyst with the crystallite size of 9 nm). Thus, it appears that the catalytic activity of Pt(NRIM) is considerably greater than those of the usual platinum blacks on the basis of unit surface area.

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