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FACILE PREPARATION OF PLATINUM SOLS BY SODIUM BOROHYDRIDE REDUCTION AND ITS EVALUATION IN THE PHOTOSENSITIZED REDUCTION OF WATER TO HYDROGEN

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Colloidal platinum prepared from K_2PtCl_4 by $NaBH_4$ reduction in basic solution showed marked efficiency and satisfactory reproducibility in the hydrogen evolution reactions with a $Ru(bpy)_3Cl_2$/MV/EDTA model system. Examinations of electron microscopy indicated obvious relations between the activity and size of particles. Cyclodextrins as a support tend to stabilize the colloids, probably by retarding its aggregation.

Evolution of hydrogen and oxygen from water through electron transfer reactions induced by visible light involves fundamental significance relevant to conversion and storage of solar energy into chemical energy as in photosynthesis. During our work on photochemical hydrogen production by the use of synthetic ferredoxin,[1] the development of efficient and specific redox catalysts has been highly desired for quantitatively exact studies. Namely, not only the activity and stability of Pt catalysts depended largely on the methods employed,[2-6] but also the procedures seemed to be insufficient with respect to reproducibility. Actually, the relation between activity and property of Pt sols is still under considerable confusion of argument in this field.[2-3,7]

Remarkable catalytic activity of platinum hydrosols with an average diameter of 22 Å by sodium borohydride reduction has been claimed, however no detailed procedures are given.[8-9] We wish now to describe our study in detail concerning effects of alkali and supports on the synthesis of Pt sols by $NaBH_4$ reduction and their catalytic activity for H_2 generation by a well known model system consisting of $Ru(bpy)_3Cl_2$ (50 μM), methyl viologen (5mM), EDTA (50 mM) and Pt catalyst (66 μM). In a typical experiment, 20 ml of the above mixture at pH 4.7 was illuminated with a halogen lamp A or B (above 390 nm, light intensity: A, 2.5×10^{-2}; B, 8.0×10^{-2} J/cm^2.s measured with Model 65A Radiometer from Yellow Springs Instrument). The gas was periodically analyzed by glc,[1] and the rates of hydrogen formation r_{H_2} (ml/h·l solution) were calculated from the slopes by the method of least squares (the regression coefficients were over 0.99 for

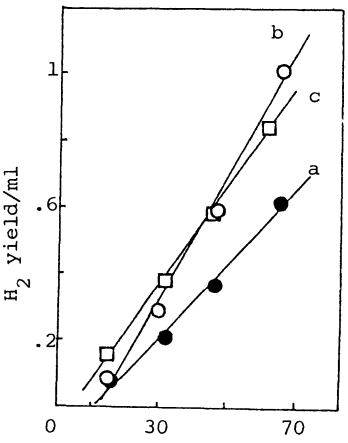


Fig.1. Influence of catalyst preparation on H_2 yield. a) 1M; b) 0.1M; c) 0.001M-NaOH

M=mol·l^{-1}

all cases). Platinum catalysts were prepared in such a way that 2ml of $NaBH_4$ solution (2-4 mM) was added dropwise to a 20 ml of K_2PtCl_4 (380 μM) in desired alkaline solution with or without supporting material at room temperature and stirred for 1h.

Effect of base in the preparation of Pt catalysts

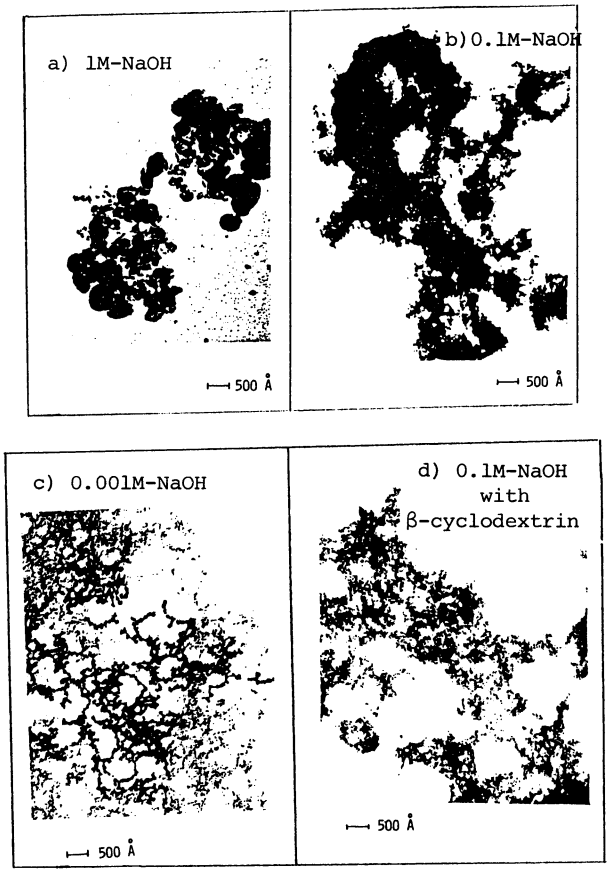
As shown in Fig. 1 where the influence of the catalyst preparation in different sodium hydroxide concentrations on hydrogen yield is illustrated, the catalytic activity is clearly affected by concentration of the alkali used, and Pt sols obtained in a 0.1M-NaOH solution exhibited the highest efficiency among them. Notably, reproducibility of the method was remarkably good (error of within 5%)[1,2] and examinations with other kinds of bases were also carried out. The results in terms of hydrogen-formation rate are summarized in Table 1. The pronounced activities of the catalysts formed in 0.1M-NaOH and 0.1M-$NaHCO_3$ solutions are obvious.

Table 1. Effect of catalyst preparation in the presence of bases on hydrogen formation rates

	r_{H_2}		particle sizes(A)
base used	1st d	30th d.	30th day
1M-NaOH	37.0	14.2(38%)*	300-500
0.1M-	57.0	37.1(65)	90-110
0.001M-	43.6	65.6(150)	10-30 & 80-100
0.05M-K_2CO_3	43.1	30.8(71)	
0.1M-$NaHCO_3$	56.6	72.0(127)	
0.1M-NH_4OH	41.5	29.2(70)	

*Numbers in parentheses indicate %activity at 30th day after preparation relative to at 1st day. Lamp A used (see text).

Fig. 2. Electron micrograph of the Pt catalyst. (30 days after preparation)



To investigate stability of these catalysts at room temperature under air, efficiency of H_2-generation was periodically checked, and the rates of H_2 production at the 30th day are given as well in Table 1. A significant decrease in activity was observed with the elapse of time for almost every catalyst tested here, however unexpected increase of the rate was recognized in the case of $NaHCO_3$ and 0.001M-NaOH.

Examination of particle sizes of the catalysts concurrently with activity determination was then performed by transmission electron microscopy, and typical examples at the 30th day of preparation are given in Fig. 2.

It is evident that the particle sizes differ largely from one another, depending upon the preparation conditions employed. And from the micrographs, the observed distributions of diameters are between 300 and 500 Å, 90 and 110 Å, and 10 and 30 Å (partly 80-100 Å by gathering the small ones) for the catalysts obtained in 1M, 0.1M and 0.001M-NaOH, respectively (see a-c in Fig. 2 and Table 1). Comparing the latter two, degree of aggregations was apparently lower in the sample of 0.001M-NaOH.

Effect of support

Another factor to be considered for stabilizing and activating the catalysts may be effect of supporting materials. Therefore, the catalysts were prepared in the presence of several kinds of supports, and their efficiency in the hydrogen formation reaction was determined. Obtained were decreased rates of hydrogen formation rather than the increased in most cases. Only β-cyclodextrin and polyphenylene derivatives showed the same extent of activity as the reference (see Table 2).

Table 2. Effect of support on H_2-generation rates[1]

	none	PVA	zeolite	α-CD	β-CD	β-CD[2]	TiO_2	Phe[3]	Phe-S[4]
r_{H_2}(1st d.)	58.9	46.4	42.3	42.4	57.0	46.7	52.6	55.8	59.6
ratios	100	79	72	72	97	79	89	95	101
r_{H_2}(30th d.)	36.0				44.5	69.8		36.9*	47.1*
(% activity)[5]	(61)				(78)	(149)		(66)	(79)

1) Prepared in 0.1M-NaOH solution. 2) Catalyst prepared in 0.001M-NaOH solution. 3) poly-phenylene 4) poly-p-phenylene sulfide 5) % activity relative to 1st day of preparation: *after 1 yr. Lamp A used.

However, although, at the 30th day of preparation, efficiency of the catalyst without any support decreased to 60% of its initial activity, the β-cyclodextrin supported catalyst maintained still 80% efficiency of the initial value.

Evidence of good homogeneity with small particles in the latter and appreciable extent of aggregations in the former was obtained from microscopic examination (d and b, respectively, in Fig. 2).

An increase in activity of β-cyclodextrin supported platinum sols was recognized in the case of 0.001M-NaOH, but the exact effect is not well understood at the moment (Table 2).[10]

Effect of catalyst concentration on the rate of hydrogen formation

A linear relation between hydrogen formation rate and amount of platinum was observed with a correlation constant of 1.3×10^5 h^{-1} in the platinum concentration range up to about 20 μM.

Table 3. Hydrogen formation rate as a function of Pt contact area

	Platinum concentration(μM)[a]								
	0.66	2.0	4.0	6.6	9.9	17	33	66	130
[colloid][b,c] (nM)	2.4	7.1	14	24	35	61	120	240	470
$S^{d,c}$ $\times10^{-4}$ (cm^2/g)	1.4	4.2	8.1	14	21	35	70	140	280
r_{H2}[e] (ml/h/l)	8.2	26	39	68	104	153	186	204	203

a) Prepared in 0.1M-$NaHCO_3$. b) Colloidal Pt concentration c) Calculated assuming an average diameter of 20 A, corresponding to a mean aggregation number of 280 Pt atoms per particle. d) Surface area e) Rateof H_2 formation with lamp B.

Assuming an average diameter of 20 Å (based on electron micrographic examination) which corresponds to a mean aggregation number of 280 atoms per particle, colloid concentration and surface area in different atomic platinum concentrations were calculated and summarized in Table 3.

A plot of hydrogen formation rate vs. surface area of the platinum catalyst gives a straight line up to 6×10^{-8}M of the colloid concentration as shown in Fig. 3.

In summary, we have shown facile and reproducible preparation of platinum hydrosols by sodium borohydride reduction, and obvious relation between hydrogen formation activity and particle size.

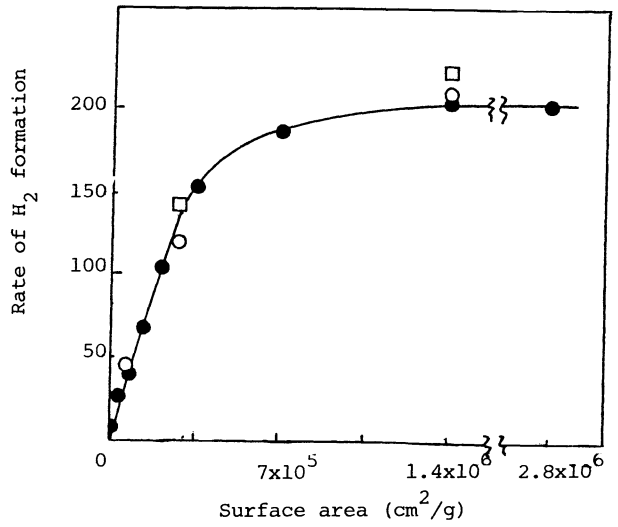


Fig. 3. The H_2-formation rate as a function of surface area of the Pt colloids[a)]

a)Catalyst prepared in 0.1M-$NaHCO_3$(●), and lamp B used. The converted rates of the NaOH preparations by multiplying 3.2 (light intensity ratio of lamp A & B) are also given (○; without support, □ ; with β-CD); calculated by assuming mean particle sizes of 400, 100 and 20 Å (based on micrographs examination) for 1M-, 0.1M- and 0.001M-NaOH preparations, respectively.

Formation of hydrogen and oxygen simultaneously at separate parts may be feasible in conjunction with the water oxidation device employing manganese dioxide catalyst that is found to be specific for oxygen generation,[11] which is now in progress.

The application of these catalysts to organic synthesis is also attractive.

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10) Catalyst preparations with diluted NaOH solution or weak base such as $NaHCO_3$ seem to be liable to produce high efficiency samples. Detailed studies toward this are in progress, and will be presented in a full paper: e.g. r_{H_2}=212(after 2 months), 204(6 months) for 0.1M-$NaHCO_3$ preparation with lamp B.
11) Y. Okuno, O. Yonemitsu, and Y. Chiba, Chem. Lett., 1983, 815.
12) At least three experiments are repeated for the main catalysts.

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