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Supported Metal Catalysts from Cation Exchange Resins

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Pt- and Pd-containing resins were prepared by ion exchanging the metal ammine cation into a macroporous, sulfonated styrene–divinylbenzene copolymer. The metal ammines were reduced to give metal crystallites distributed in the resin matrix. Radial profiles of Pt and Pd in spherical resin beads (determined with an electron microprobe) varied between the extremes of uniformity throughout the bead and restriction to a peripheral shell. Crystallites formed by reduction in hydrogen were found by electron microscopy to have sizes narrowly distributed about 2 nm. Metal complexes reduced instead by hydrazine solutions formed many of the small crystallites in addition to a few large crystallites and polycrystalline particles (10–250 nm) in the macropores. The supported metals were catalytically active at 328°K for oxidation of ethanol, which proceeded by a complex reaction network involving direct oxidation to give CO_2 and parallel successive oxidations to give acetaldehyde, acetic acid, and ethyl acetate.

INTRODUCTION

Metal catalysts used in chemical processing are often maintained in a high degree of dispersion on the surface of a high-area solid, typically carbon or a metal oxide such as alumina or silica. In many instances, the chemical as well as the physical nature of the support is important. Metal-support interactions, for example, influence aging of a catalyst, in particular the rate of loss of exposed metal surface. The support may also play a direct catalytic role, as does the acidic alumina in bifunctional reforming catalysts.

Although supported metal catalysts have found many applications, with numerous metals having been investigated, there is only a narrow literature concerning supports (*1*). We may speculate that many little-investigated solids will find catalytic application. A broad class of such solids is organic polymers, which can be tailored with relative ease to give a wide range of desired physical and chemical properties.

Organic matrices have been used as supports for metal catalysts prepared, for example, by drying colloidal metal held in a swollen gel of polyvinyl alcohol (*2*). The metal particles were irregularly shaped and larger than those usually applied on inorganic supports (5–50 nm compared to about 1–5 nm). Rhodium and iridium complexes chelated in phosphine-substituted styrene–divinylbenzene resins have been prepared and reduced to give hydrogenation catalysts (*3, 4*). A strong base ion-exchange resin was impregnated with

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$AgNO_3$ and then reduced to give a silver-containing bifunctional catalyst (*5*). Strong acid ion-exchange resins were similarly impregnated and reduced to give palladium-containing bifunctional catalysts (*6*). Alternatively, bifunctional catalysts have been prepared by ion exchange of Pt- and Pd-complexes into cation-exchange resins followed by reduction to give deposited metal (*7–10*). The metals catalyze a number of typical reactions like H_2–D_2 exchange, and they show interesting selectivity differences from metals supported on carbon or metal oxides, as exemplified by data for alkyne hydrogenation (*7*).

The method of preparation involving ion exchange, due to Haag and Whitehurst, offers the prospect of applicability to many ion exchangers and metal ions, and since the unreduced metal ions are atomically dispersed, the reduced metal might be expected to be highly dispersed as well (*7*). The present research was undertaken to provide a preliminary characterization of this class of catalysts. The investigation focused on the metal in a series of catalysts prepared by ion exchanging complex metal cations into sulfonated styrene–divinylbenzene resin.

EXPERIMENTAL

Catalysts were prepared from beads of Amberlyst 15 (Rohm and Haas), a macroporous, sulfonated styrene–divinylbenzene copolymer, which has a rigid pore structure with average pore diameters of 20–60 nm (*11*). The 20–50 mesh size fraction of the ion-exchange resin was washed with water, then methanol, cycled between the H^+ and Na^+ forms, washed again with water, and dried in air. In a typical preparation, the Na^+ form resin* was contacted with an aqueous solution of one of the following compounds: $Pt(NH_3)_4Cl_2$, $Pd(NH_3)_4Cl_2$, $NiCl_2$ in excess NH_4OH, and $AgNO_3$ in excess NH_4OH. The transition metal ions were almost quantitatively ion exchanged into the resin as evidenced by their removal from the solution phase, indicated by color changes of nickel solutions and by qualitative tests with $Na(C_6H_5)_4B$ and $(C_6H_5)_4AsCl$ for Pt and Pd cations and anions, respectively. Back exchange could be effected by treatment with excess HCl solution.

Two catalysts were prepared from beads of macroporous styrene–divinylbenzene copolymer (XAD-2, Rohm and Haas) by introduction of sodium phosphinate groups (*12*) followed by contacting with aqueous $Pd(NH_3)_4Cl_2$.

Beads containing transition metal were washed with water, then ethanol, and dried in air. After vacuum drying at 380°K, the metals were reduced to the zero-valent state in flowing hydrogen. Alternatively, metals were reduced with aqueous solutions of basified hydrazine; Pd samples were also reduced with aqueous ethyl formate, which failed to reduce Pt. Details of reduction procedures are given in Table 1. In general, the metals were more difficult to reduce in the resin than in aqueous solution.

Analysis of several digested samples by atomic absorption confirmed that there were negligible losses of metal to solutions during ion exchange, washing, and reduction.

Radial profiles of Pt, Pd, Na, P, S, Cl, and C in catalysts were determined from traverses of sectioned beads with the ARL EMX/SM electron microprobe at Chevron Research Co. Samples were prepared by potting in 50 wt% Cu-loaded bakelite inside 0.95-cm brass rings. They were ground to expose nearly the maximum bead cross-sections, finished with 1-μm diamond, and rinsed with pure xylene and then *n*-hexane (no aqueous solutions were used). A thin evaporated carbon coating was applied to give good surface conductance. Analyses were done for three or four beads of each of the samples indicated in the right-hand column of Table 1. Microprobe conditions were the following: 10 kV accelerating voltage; 50 nA sample current (on brass); 1-μm beam; 3.33 μm/sec scan

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* The H^+ form resin was inappropriate because in its presence the Pd complex underwent hydrolysis and the Pt complex was not reduced by hydrazine.

TABLE 1. CATALYST PREPARATION CONDITIONS AND METAL CRYSTALLITE SIZES AND RADIAL DISTRIBUTIONS

Sample number	Metal	Wt. % Metal	Reducing agent	Wt. % reducing agent in aqueous solution	Concentration of NaOH in reducing solution, M	Reduction temperature, °K	10^{-3} x Reduction time, sec
1	Pt	3.3	$N_2H_5^+$[a]	—	0.4	353	7.2
2	Pt	5.8	N_2H_4	40	0.05	373	22
3	Pt	1.2	N_2H_4	28	0.05	365	7.2
4	Pt	3.5	N_2H_4	30	0.05	364	5.4
5	Pt	0.4	N_2H_4	32	0.05	365	5.4
6	Pt	0.1	N_2H_4	32	0.05	365	5.4
7	Pt	1.4	H_2	—	—	473	27
8	Pt	1.5	H_2	—	—	503	18
9	Pd	<1[c]	N_2H_4	25	—	323	3.6
10	Pd	2.0	N_2H_4	27	0.4	323	7.2
11	Pd	<1	$N_2H_5^+$[b]	—	—	353	7.2
12	Pd	1.1	ethyl formate	50	—	325	3.6
13	Pd	1.1	N_2H_4	30	—	323	3.6
14	Pd	1.1	ethyl formate	50	2.4[d]	323	3.6
15	Pd	4.3	ethyl formate	50	—	323	3.6
16	Pd	1.8	ethyl formate	50	—	323	3.6
17	Pd	0.5	N_2H_4	32	0.05	323	2.2
18	Pd	0.1	N_2H_4	32	0.05	323	2.2
19	Pd	2.0	ethyl formate	50	—	323	2.2
20	Pd	2.0	N_2H_4	40	0.07	323	2.2
21	Pd	2.0	H_2	—	—	423	22
22[e]	Pd	1.0	N_2H_4	22	—	323	2.2
23	Pd	2.0	N_2H_4	40	—	286[f]	5.4
24[e]	Pd	0.5	H_2	—	—	423	14
25	Ag	<2	N_2H_4	32	—	321	2.2
26	Ag	2	H_2	—	—	473	18
27	Ni	3.5	H_2	—	—	503	27

Notes:

[a] Reduction did not occur until NaOH was added.

[b] Substantial Pd black formed in the external solution.

[c] Substantial decomposition of Pd ammine occurred during ion exchange.

[d] Na^+ concentration was 2.4M, but solution was initially buffered at pH=3; final pH was 6-8.

rate. $K\alpha_1$ x-ray lines were used, except for Pd ($L\alpha_1$) and Pt ($M\alpha_1$).

Dimensions of metal crystallites were determined by x-ray diffraction line broadening. A General Electric XRD x-ray diffractometer equipped with an SPG spectrogoniometer and a nickel filter was used with unresolved Cu$K\alpha$ radiation.

Electron micrographs were obtained by Nielson (*13*) with a transmission electron microscope. Catalyst beads were mounted in epoxy resin, microtomed, examined at 33,000–71,000×, and photographically enlarged to 264,000–572,000×.

The catalytic oxidation of ethanol was carried out in a stirred 500-ml flask held in a constant-temperature bath. Beads of the supported metal catalyst were sus-

Dimension of small crystallites from electron micrographs ± 1 standard deviation, nm	Range of dimensions of large particles from electron micrographs, nm	Dimension of crystallites from x-ray diffraction, nm	Outer fraction of bead radius containing 90 % of metal as determined from electron microprobe data
—	—	13	0.38
—	—	32	—
2.1 ± 0.7	16-250	28	0.64
1.9 ± 0.5	20-200	30	—
1.8 ± 0.4	17-140	11	—
—	—	—	—
1.7 ± 0.3	—	<4	0.27
—	—	<4	—
—	—	—	—
—	—	11	0.55
—	—	13	—
—	—	9.8	—
—	—	16	—
—	—	8.8	—
—	—	18	—
—	—	10	0.31
—	—	—	—
—	—	—	—
—	—	9.8	0.40
2.2 ± 0.6	6-24	16	0.32
1.9 ± 0.2	—	4	0.35
—	—	<4	0.13
—	—	21	0.38
—	—	—	0.12
—	—	<4	—
—	—	<4	—
—	—	<4	—

[e] In these preparations the resin was sodium polystyrenephosphinate. Metal contents were determined from electron microprobe data.

[f] Initially at 279°K; upon gradual heating reduction occurred rapidly at 285°K.

pended in absolute ethanol and brought to the reaction temperature of 328°K under a nitrogen blanket. Oxygen was then sparged into the reactant at about 1 ml/sec, flowing out of the reactor through a water condenser, through which small amounts of volatile reaction products were continually lost. Samples of the liquid reactant and effluent gas were taken periodically and analyzed by gas chromatography.

RESULTS

Distribution of Metal in Beads

Electron microprobe analysis of sectioned beads gave radial distributions of metal exemplified by the results of Figs. 1 and 2; data are summarized in Table 1. Sulfonate groups and unreduced Pt were distributed uniformly throughout Amberlyst beads. The Pt distribution was un-

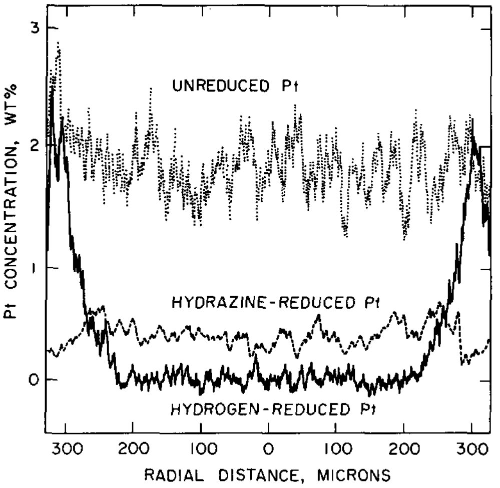

FIG. 1. Radial profiles of Pt in polystyrenesulfonate resin beads as determined from electron microprobe analysis. Unreduced catalyst, 2.5 wt% Pt in sample; hydrogen-reduced catalyst, sample 7; hydrazine-reduced catalyst, sample 3.

affected by reduction with hydrazine, but catalysts reduced with hydrogen contained Pt in a peripheral shell (Fig. 1).

Solution-reduced Ag catalysts similarly had uniformly distributed metal, and catalysts reduced in hydrogen had peripheral shells; a shell was also found in hydrogen-reduced Ni catalyst.

Unreduced Pd catalysts had metal concentrated near the periphery, and the profile remained unchanged on reduction with hydrogen, hydrazine, or ethyl formate (Fig. 2A).*

Phosphinate groups introduced into XAD-2 resin were concentrated near bead peripheries, and the Pd in these samples showed the same profile (Fig. 2B).

The Pd contents of catalysts calculated from integrated profiles were within 10% of the values expected from the preparations. Variations in Pd content from bead to bead were less than 20%.

The Pt contents calculated from integrated profiles of four catalysts were all less than the values expected from the preparations, occasionally being as little as half the expected values. The discrepancy is unresolved; it may be just an indication of variations in Pt content from bead to bead; the microprobe data show these were as much as 100%.

Crystallite Sizes

Estimates of crystallite size of metal in the reduced catalysts were obtained from the equation of Scherrer (*14*). The pure diffraction line broadening was obtained from the observed x-ray line broadening by application of the correction for instrument contributions according to the convolution analysis of Klug and Alexander (*15*). Since the resin was amorphous, the line breadths could always be determined for the most intense reflections, those for the (111) plane. Values of the volume-average metal crystallite dimension determined from data for the (111) plane were considered to be characteristic although they were consistently slightly larger than those determined from data for the (200) and (311) planes.

All of the catalysts prepared by hydrogen reduction were amorphous to x-rays, indicating the absence of metal crystallites with dimensions greater than about 4 nm. Catalysts reduced in aqueous hydrazine or ethyl formate all contained some metal crystallites larger than 4 nm (Table 1), and the results of Figs. 3 and 4 show a pattern of an increasing average dimension of such crystallites with increasing metal content of the catalyst. Average dimensions ranged from about 10 to 30 nm. Of the crystallites observable with x-ray diffraction, the Pd crystallites were consistently smaller than the Pt crystallites at a particular metal content (Figs. 3 and 4), and the Pd crystallites formed by ethyl formate reduction were smaller than those formed by hydrazine reduction (Fig. 4); a 30% increase in Pd crystallite size was observed when hydrazine reduction temperature was decreased from 323 to 284°K (Table 1).

A number of catalysts were examined by electron microscopy, and representative

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* *An exceptional profile was observed when a* modified reduction procedure was followed—$N_2H_5^+$ form resin was contacted with $Pd(NH_3)_4Cl_2$ (Table 1). An external shell of Pd was formed, as found by Haag and Whitehurst (*8*).

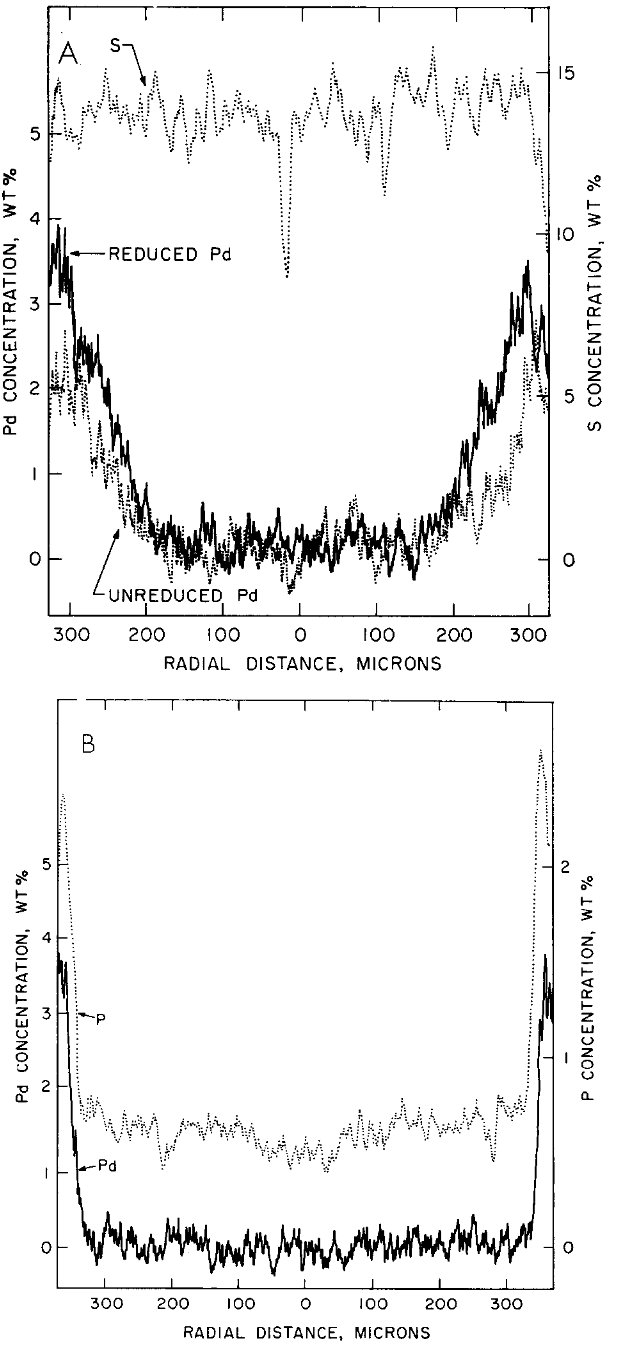

FIG. 2. Radial profiles in catalysts containing Pd as determined from electron microprobe analysis. (A) Unreduced polystyrenesulfonate resin (1.0 wt% Pd in sample) and reduced polystyrenesulfonate resin (sample 21). (B) Reduced polystyrenephosphinate resin (sample 24).

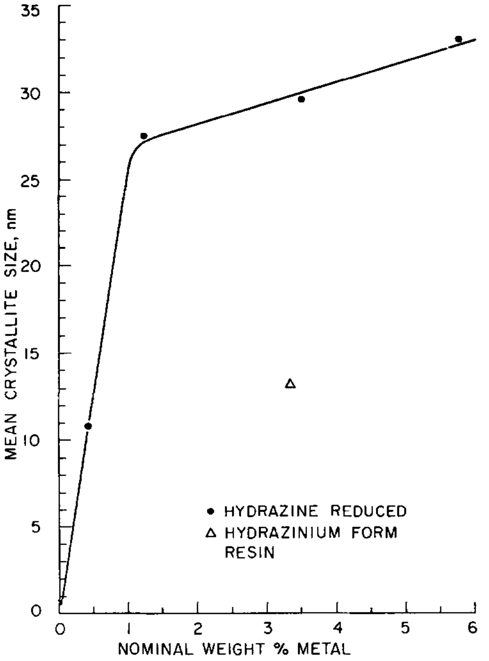

FIG. 3. Mean dimensions of Pt crystallites in solution-reduced catalysts as determined from x-ray diffraction line broadening.

micrographs are shown in Figs. 5 and 6. All catalysts contained many metal crystallites too small to be detected by x-ray diffraction. A typical dimension of these crystallites is 2 nm; the precise dimensions determined from electron micrographs (Table 1) show that they are nearly uniform in size. These small crystallites were the only ones observed in the hydrogen-reduced catalysts, and they greatly outnumbered the larger crystallites in solution-reduced catalysts, as exemplified by Fig. 6. The results thus show a strongly bimodal crystallite size distribution for the solution-reduced catalysts, and the electron micrographs indicate that the largest metal particles (with dimensions as great as 250 nm) were agglomerates of crystallites that the x-ray data show were smaller than 30 nm.

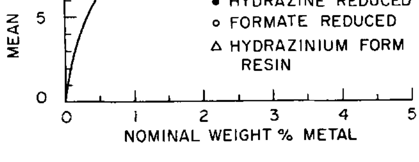

FIG. 4. Mean dimensions of Pd crystallites in solution-reduced catalysts as determined from x-ray diffraction line broadening.

Ethanol Oxidation

The hydrogen-reduced catalysts, which contained no metal crystallites larger than about 2 nm, catalyzed the partial oxidation of ethanol to a detectable degree only after an induction period of the order of 10^4 sec (Fig. 7A).* No induction period was observed for the solution-reduced catalysts. The solution-reduced catalysts of relatively low metal content and the polystyrenephosphinate catalysts were relatively active initially and underwent rapid deactivation.

The hydrogen-reduced and solution-reduced catalysts showed significant selectivity differences, as the latter catalyzed formation of much larger amounts of partial oxidation products at a particular conversion of ethanol (Table 2).

Intrinsic kinetics of ethanol oxidation were not observed. From mass transport rates estimated by standard methods, it was concluded that mass transport of the sparingly soluble oxygen through the liquid reactant significantly influenced the rate (*12*).

The resins containing reduced Pt and Pd all catalyzed the oxidation of ethanol to give CO_2, water, acetaldehyde, acetic acid, and ethyl acetate; no other products were detected. Typical conversion data are

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* The induction period was also observed for a catalyst sample recontacted with hydrogen in the reactor prior to oxygen flow; this result demonstrates that the induction period was not associated with reduction of the surface which might perhaps have been oxidized during transfer to the reactor.

FIG. 5. Electron micrograph of hydrogen-reduced Pt catalyst. Sample 7; 290,000×.

TABLE 2
CATALYST SELECTIVITIES IN ETHANOL OXIDATION

Sample no.	Metal	wt% Metal	Reaction temperature (°K)	Time for 2% conversion of ethanol (min)	Selectivity at 2% conversion[a]	Selectivity at 5% conversion[a]
4	Pt	3.5	328	170	4.5	1.8
4	Pt	3.5	308	320	12	5.8
5	Pt	0.4	328	390	0.9	0.7
7	Pt	1.4	328	470	0.2	0.2
16	Pd	1.8	328	210	6.2	4.0
16	Pd	1.8	308	480	5.3	2.8
17	Pd	0.5	328	450	2.9	0.6
21	Pd	2.0	328	575	0.2	0.3

[a] Selectivity is defined as moles of (acetaldehyde + acetic acid + ethyl acetate)/(moles of water not accounted for in formation of these intermediates).

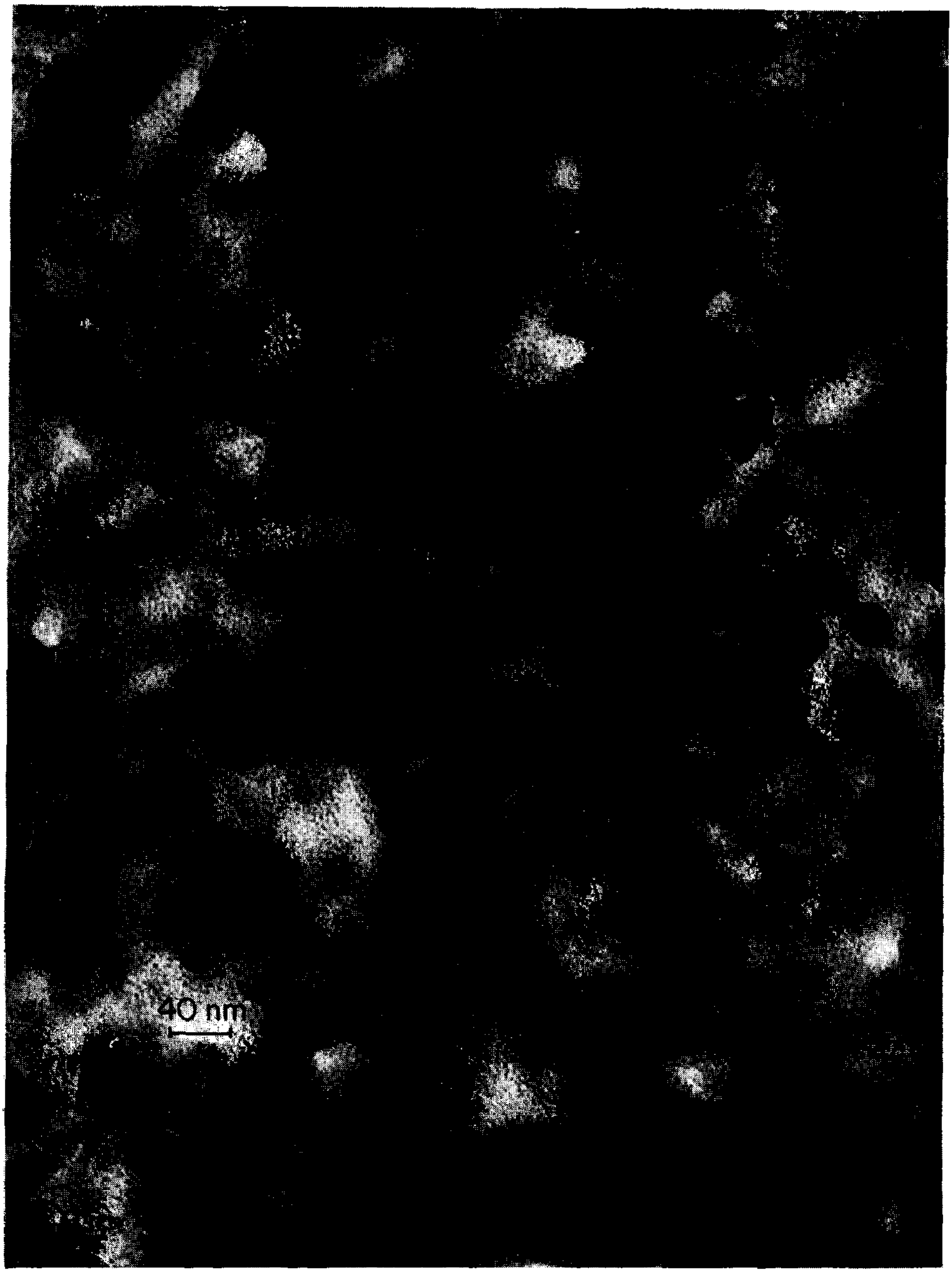

Fig. 6. Electron micrograph of Pd catalyst reduced in hydrazine solution. Sample 20; 205,000×.

shown in Fig. 7. Analysis of off gases showed that CO_2 was produced from the beginning, demonstrating that complete oxidation of ethanol was a primary reaction. Concentrations of acetaldehyde and ethyl acetate passed through maxima, demonstrating that these products underwent further oxidation. The data are not sufficient to establish the complete reaction network.

Surface Contamination

A hydrogen chemisorption experiment designed to give a measure of the surface

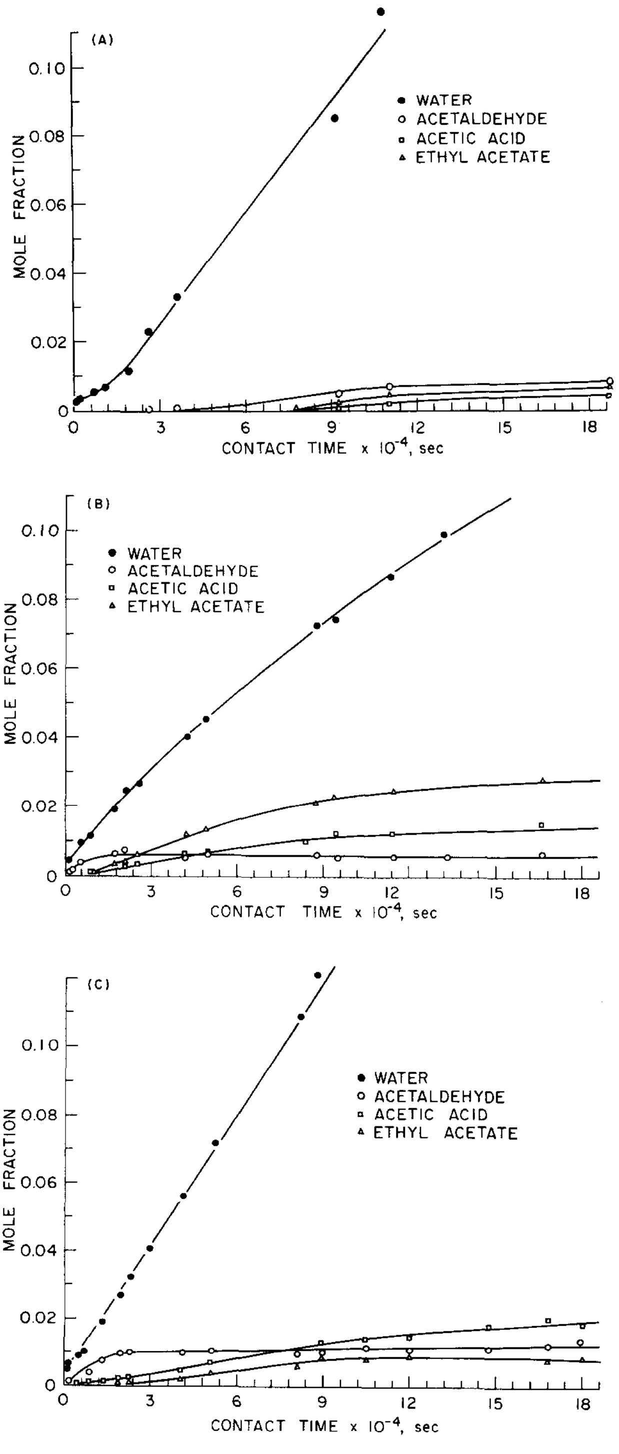

FIG. 7. Conversion of ethanol at 328°K. (A) Catalyst sample 7, 1.4 wt% Pt, reduced in hydrogen; (B) catalyst sample 4, 3.5 wt% Pt, reduced in hydrazine; (C) catalyst sample 16, 1.8 wt% Pd, reduced in ethyl formate. The latter two catalysts contain approximately equal numbers of metal atoms per unit volume.

area of a Pt catalyst failed because attempts to clean the Pt surface by outgassing at 480°K were unsuccessful (*12*). A brown liquid was continually collected in the liquid nitrogen trap. The liquid was apparently a product of resin decomposition, and its presence suggests that the metal surface was contaminated and that clean surfaces of metals in the styrene–divinylbenzene resin may be difficult to prepare. The ethanol conversion data for the hydrogen-reduced catalysts are consistent with the suggestion that a carbonaceous residue was present on the metal surface; initial rates of CO_2 formation were high and rates of water formation low.

Discussion

The distribution of metal in a solution-reduced catalyst was generally the same as that in the unreduced catalyst (Figs. 1 and 2). The peripheral shells observed in hydrogen-reduced Pt and Ni catalysts are inferred to have resulted from migration of the complex metal ions during the drying preceding reduction. We conclude that, in general, the reduction process had no effect on the radial distribution of metal.

The distributions of unreduced metal appear to be related to the stabilities of the metal ammine cations (*16*). Stable complexes of Pt and Ag gave uniform distributions, and the less stable complexes of Pd and Ni gave shells. We infer that during the ion-exchange process the relatively unstable Pd and Ni complexes diffused into a resin bead and reacted rapidly with exchange sites encountered near the periphery to give relatively stable bound complexes; these might have incorporated water molecules in the hydration spheres of sulfonate groups as neutral ligands replacing NH_3 (*17*). The more stable Pt and Ag complexes might have simply been ion exchanged into the resin, attaining a uniform, equilibrium distribution in a bead. The hydrated metal complexes could have migrated with water when the beads were dried.

The uniform distribution of very small crystallites shown in Figs. 5 and 6 (each consisting of roughly 300 atoms) is evidence that the metal in the resin matrix was relatively immobile during reduction. The occurrence of much larger crystallites (some containing as many as 10^8 atoms) in the solution-reduced, but not the hydrogen-reduced, catalysts demonstrates that the metal was reduced in the macropore liquid, where it was evidently highly mobile, and even agglomerates of crystallites were formed.

The latter conclusion suggests that the large crystallites were formed in the macropores in a reduction process similar to that which occurs in solution. Turkevich *et al.* studied the formation of colloidal Au by reduction of solutions of chlorauric acid with sodium citrate (*18*, *19*) and the formation of colloidal Pd by reduction of solutions of chloropalladous acid with sodium formate and sodium citrate (*20*). The following qualitative results confirm the similarity between reduction in the macropores and the reductions observed by Turkevich: For each process, the mean crystallite size increased with increasing cation concentration; it was dependent on the nature of the reducing agent and the rate of reduction as influenced by temperature; and the rate of reduction increased rapidly after an induction period, suggesting the process was autocatalytic.

The preparation methods described here appear to be applicable to most metals of catalytic interest and may even be suitable for preparation of alloys. The results may point the way toward broadly applicable methods of preparing very small crystallites of supported metals having narrow size distributions; such preparations would be useful in allowing precise determination of effects of crystallite size on catalyst performance. Some unanswered questions about the sizes of the crystallites have to do with the dimensions and density of the polymer matrix and the nature and density of the attached functional groups.

The catalytic nature of the Pt and Pd crystallites is defined in only a preliminary way by the present results. At a given metal content, the Pd catalyst was slightly less active and more selective than Pt for partial oxidation (Figs. 7B and C). In this respect and in the character of the reaction network, the results for ethanol oxidation are similar to results of Kemball and Patterson (*21*) and Hall *et al.* (*22, 23*) for Pt- and Pd-catalyzed oxidation of ethylene. The strong dependence of catalyst selectivity on reduction conditions (Table 2) is ascribed to differences in the compositions of the metal surfaces. The induction period observed for the hydrogen-reduced catalysts was perhaps required for removal of surface contaminants by oxidation.

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