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Abstract

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On the Mechanism of the Reaction of Chemical Nickel Plating

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For controlling the process of chemical nickel plating, which has found broad practical application, elucidation of the mechanism of the reactions occurring in the reduction of metals by hypophosphite is of great importance. However, the views expressed up to the present time on the mechanism of this comparatively new process have the character of hypotheses. ($^{1-3}$) Noteworthy are the concepts concerning the possibility of reduction of nickel ions by atomic hydrogen arising on the catalytic surface during the decomposition of hypophosphite (^{4}). In work carried out in our laboratory by K. M. Gorbunova and A. A. Nikiforova (^{5}), suggestions were put forward regarding the leading role of atomic hydrogen in the processes of chemical reduction of nickel ions by hypophosphite. According to this mechanism, the process proceeds in two stages: 1) catalytic decomposition of hypophosphite by water* with formation of atomic hydrogen according to the reaction:

$$NaH_2PO_2 + H_2O \rightarrow NaH_2PO_3 + 2H; \qquad (a)$$

2) reduction of nickel ions by active hydrogen atoms adsorbed on the surface of the catalyst:

$$Ni^{2+} + 2H \rightarrow Ni + 2H^{+}. \qquad (b)$$

Along with this it is proposed that atomic hydrogen interacts with the ions $H_2PO_2^-$ and HPO_3^{2-}, leading to the formation of phosphorus, which forms with nickel, at the moment of deposition, a solid substitutional solution. The evolution of gas accompanying process (b) indicates the molization of a considerable portion (60% and more) of the atomic hydrogen formed as a result of reaction (a).

In order to clarify the origin of the hydrogen evolved, a number of investigators studied the mechanism of reaction (a), which underlies the process of chemical nickel plating. A. N. Bakh (^{6}) believed that in the decomposition of hypophosphite hydrogen is formed exclusively from water. From the investigations of Wieland and Winkler (^{7}), confirmed by Frank and Mench (^{8}), who used deuterium as an indicator, it follows that the hydrogen evolved is formed half from hydrogen bound directly to phosphorus (P—H bond), and half from the O—H group of hypophosphorous acid, or correspondingly from the water molecule, owing to the rapidly occurring exchange of hydrogen of water with hydrogen from the O—H group (P—OH bond). The data available in the literature on the mechanism of decomposition of an aqueous solution of hypophosphite do not make it possible to evaluate the role of hydrogen atoms bound in different ways to phosphorus in the process of reduction of Ni^{2+} ions.

The purpose of the present study was to elucidate the share of participation of hydrogen atoms, differently bound in the hypophosphite molecule (P—H bond or P—OH bond), in the process of chemical reduction of nickel in hypophosphite solutions. To solve the stated problem, a comparison was made of the isotopic composition of the gas evolved during decomposition of pure hypophosphite solutions with that for conditions under which, along with the decomposition reaction (a), the reaction of reduction of nickel ions (b) proceeds. The hydrogen isotope deuterium served as the indicator. The isotopic composition of the gas was determined with an MX-1302 mass spectrometer. The catalysts

* In other solvents (alcohol, dioxane) the decomposition reaction does not proceed.

for the process of hypophosphite decomposition were metallic and chemically reduced nickel.

We studied the reactions of hypophosphite decomposition and reduction of nickel ions by hypophosphite in two ways: in the first, heavy water served as the solvent and the reduction was carried out with ordinary calcium hypophosphite; in the second, dissolution was carried out in ordinary water, and heavy calcium hypophosphite with deuterium in the P—D bonds, specially synthesized from white phosphorus, calcium oxide, and heavy water (99.4% D_2) by the method described in the literature (^{9}), was used as the reducing agent. In carrying out experiments using heavy water (99.4% D_2) as the solvent, the possibility of a change in its isotopic composition due to exchange with the hydrogen atoms of hypophosphite (^{10}) and with the water of crystallization of the reagents introduced was taken into account; for this reason the latter were first dehydrated or recrystallized 2-3 times from heavy water. For the same reason, anhydrous calcium hypophosphite was used as the reducing agent, introduced into the solutions in an amount of 25 g/l; nickel was introduced in the form of $NiCO_3$, which, owing to its low solubility, could be present in the reaction vessel in large excess (100-150 g/l), making it possible to maintain strictly the conditions corresponding to the process of reduction of nickel ions. Solutions with pH 5-5.5 were used for the investigation; the temperature was maintained at about 98°. The gas was collected in a system of previously evacuated ampoules.

In accordance with the results of Frank and Mench (8), in the decomposition of a hypophosphite solution (pH 5), irrespective of the position of deuterium in the molecule, it was found that its content in the evolved gas was close to 45-50% (see Table 1). The content of D_2 in the gas evolved in the process of reduction of Ni^{2+} ions (method 1) decreases sharply in comparison with its content in the gas obtained in the process of decomposition of a hypophosphite solution free of Ni^{2+} ions (Table 1). When deuterium is introduced into the P—D bond (method 2), the ratio of D_2 and H_2 in the gas, as should be expected, is the reverse of that obtained when deuterium is introduced into the P—OD bond.

Table 1

	Solution composition	D_2, %	H_2, %	Note
1	$Ca(H_2PO_2)_2$, 25 g/l;solvent D_2O (99% D) (I)	43	57	Decomp. process
2	I + $NiCO_3$, 150 g/l	8	92	Reduction process

According to reaction (6), the hydrogen atoms taking part in the reduction of metal ions pass into the solution in the form of protons; therefore their amount in the gas should decrease. In carrying out the reaction of reduction of nickel ions under the conditions described above, a decrease was found in the content of deuterium in the gas, and hence of hydrogen bound to phosphorus through oxygen (P—OH bond) (Table 1). This makes it possible to conclude that the hydrogen of the P—OH bond is reactive with respect to the reduction of nickel ions. The hydrogen of the P—H bond does not take a noticeable part in the reduction of nickel and, becoming molecularized, is evolved as gas.

The data presented, indicating the different reactivity of the hydrogen atoms of the hypophosphite molecule in the process of reduction of nickel ions, make it possible to understand the reason for the evolution of gaseous hydrogen accompanying the deposition of metal. At the same time, the results obtained cast doubt on Gutzeit' s assumption (4) that the slowest stage of the chemical nickel-plating process is the process of reduction of nickel ions, since as evidence for this the author cites only the evolution of hydrogen in this process.

The different behavior of the hydrogen atoms of the hypophosphite molecule in reduction reactions, in particular in the reduction of diazonium salts, has been pointed out in the literature previously. However, as has been established in a number of studies (11), only the hydrogen atoms of the P—H bond, i.e., those most strongly bound to phosphorus, possess reducing action in the process indicated. The specific behavior of hydrogen atoms from the P—OH bond of hypophosphite in the reduction processes of Ni^{2+} ions was confirmed by us in studying the hydrogenation reactions of organic compounds (cyclohexene, octene-1, methylene blue) in hypophosphite solutions in heavy water (method 1) on a Ni catalyst.

Isotopic analysis of the gas evolved in the hydrogenation of unsaturated compounds on nickel showed that its deuterium content is considerably higher than in the gas collected during the chemical reduction of nickel ions ($\sim 8\%$ D_2), amounting to 32% D_2 for cyclohexene and methylene blue and 51% D_2 for octene.

When the hydrogenation reaction of the above-mentioned substances is carried out on a palladium catalyst, the deuterium content in the gas even exceeds that found in the decomposition reaction of a pure hypophosphite solution. Since in the present study the possibility of exchange of hydrogen of organic compounds for deuterium of heavy water was not taken into account and the isotopic composition of the hydrogenation products was not studied, there are no grounds for completely denying the participation of hydrogen from the P—OH bond of hypophosphite in the hydrogenation process. However, the results obtained make it possible to assert that hydrogen of the P—H bond is active in the hydrogenation process, although the degree of activity also depends on the nature of the catalyst. To elucidate the mechanism of action of the salts of organic acids introduced into solutions to increase the rate of the chemical nickel-plating process, a series of studies was carried out in which deuterium also served as an indicator. Deuterium was introduced into the calcium hypophosphite molecule by the methods described above, and into the additive molecules—to the carbon of the methyl groups. Sodium salts of acetic, succinic, and malonic acids were used as additives; for control experiments, salts of deuteroacetic and deuteromalonic acids were used.

The mechanism of action of the additives was judged from the change in the isotopic composition of the gas evolved during the decomposition of hypophosphite and the reduction of metal ions in the presence of additives in the solution. In parallel with study of the gas composition, the rate of the reduction process, the phosphorus content in the deposits, and the hypophosphite utilization coefficient were determined. When any of the listed additives is introduced into nickel-plating solutions in amounts of 10-20 g/l, the rate of the process increases (by a factor of 2-3) and the hypophosphite utilization coefficient increases (from 26-29% to 39-41%); the phosphorus content in the deposits decreases. Some authors ([12]) consider the main reason for the increase in the rate of the process in the presence of additives to be their ability to form complexes with the hypophosphite molecule, whereby the bond of the hydrogen atoms with phosphorus is weakened, their detachment is facilitated, and, accordingly, the fraction of their participation in the reduction process increases. If one assumes that the considerations expressed are correct and that the hydrogen atoms of the P—H bond in the presence of salts of organic acids in solution participate in the reduction process according to reaction (6), being converted into protons, then after reduction of nickel ions by heavy hypophosphite dissolved in H_2O, deuterium from the P—D bond should form a deuteron and pass into the water. However, even after repeated use of the same portion of H_2O for preparing solutions of heavy hypophosphite—$Ca(D_2PO_2)_2$—and carrying out in them the reaction of reduction of nickel ions both in the presence of additives and without them, no traces of deuterium were found in the gas after decomposition of the water by magnesium amalgam.

The results of experiments on the isotopic composition of the gas in the decomposition of hypophosphite solutions (method 1) showed that, if for solutions without additives the fraction of hydrogen atoms in the gas originating from the P—OH bond and

which, as was shown above, are reactive in the process of reduction of nickel ions does not exceed 42–43%, then, upon introduction into the solutions of the listed accelerators, it increases and, for example, in the case of sodium tartrate reaches, in a solution with pH 5, 48%. The isotopic composition of the gas in the decomposition of hypophosphite, however, depends to a considerable extent on the acidity of the solution (Table 2).

Table 2

Deuterium content in the gas during decomposition of hypophosphite with addition of tartaric acid on a Ni catalyst at various pH values

Solution composition	pH	D_2, %
$Ca(H_2PO_2)_2$, 25 g/lTartaric-acid Na, 20 g/lSolvent D_2O (99% D_2)	5	48
$Ca(H_2PO_2)_2$, 25 g/lTartaric-acid Na, 20 g/lSolvent D_2O (99% D_2)	4	44
$Ca(H_2PO_2)_2$, 25 g/lTartaric-acid Na, 20 g/lSolvent D_2O (99% D_2)	3.4	42

Table 3

Use of hypophosphite in the nickel-reduction reaction as a function of the pH of the solution

Solution composition	pH	Use of hypophosphite, %
$NaH_2PO_2 \cdot H_2O$, 10 g/l$NiCl_2 \cdot 6H_2O$, 25 g/lTartaric acid, 7.5 g/lGlycocol, 30 g/l	5.6	41.3
$NaH_2PO_2 \cdot H_2O$, 10 g/l$NiCl_2 \cdot 6H_2O$, 25 g/lTartaric acid, 7.5 g/lGlycocol, 30 g/l	4.5	35.5
$NaH_2PO_2 \cdot H_2O$, 10 g/l$NiCl_2 \cdot 6H_2O$, 25 g/lTartaric acid, 7.5 g/lGlycocol, 30 g/l	3.5	29.8

As is evident from the data of Table 2, the deuterium content in the gas during decomposition of hypophosphite decreases with acidification of the solution and at pH 3.4 reaches the value that is usually obtained in solutions without additives. In accordance with this, when the process of metal reduction is carried out in more acidic solutions, a decrease in the rate and a decrease in the coefficient of utilization of hypophosphite are observed (Table 3)*.

The data presented above indicate that the course of the nickel-reduction reaction is favored by all conditions that facilitate the cleavage of reactive hydrogen atoms from the P—OH bond. On this basis, the action of additives of salts of organic acids can be explained by their ability to maintain the pH value within limits that lead to acceleration of the hypophosphite decomposition process and to an increase in the fraction of reactive hydrogen atoms evolved.

The present study makes it possible to explain the reason for obtaining low values of the coefficient of utilization of hypophosphite, which is connected with the small fraction (not more than 50%) of hydrogen atoms reactive in the process of metal reduction and with their partial molization.

In conclusion, we express our gratitude to A. A. Nikiforova for valuable advice and guidance in carrying out and writing this work, and to V. A. Glazkov for performing the measurements of the isotopic composition of the gas.

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* In Table 3 use is made of results obtained in the work of A. A. Nikiforova.

Note: Figure translations are in progress. See original paper for figures.

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