Factors Affecting the Hydrogen Reduction Kinetics of CsHSO₄

V. G. Ponomareva and G. V. Lavrova

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630128 Russia

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Abstract—The hydrogen reduction of $CsHSO_4$, including in the presence of catalysts, is studied. The main factors affecting the rate of the process are determined. A possible reaction mechanism through the surface hydrated phase is discussed. Experiments show that the compound is more stable in hydrogen without any trace of moisture, including in the presence of a platinum catalyst.

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INTRODUCTION

The family of superprotonic salts $M_xH_y(AO_4)_z$ (M = Cs, Rb, K, NH₄; A = S, Se, P, As), which display high proton conductivity (10⁻²–10⁻³ S/cm) in a temperature range of 130 to 250°C, is of interest owing to the possibility of its use in medium temperature fuel elements (FEs) [1–7]. It is required in this case that a compound be stable under hydrogen reduction conditions. In the very first work [6] devoted to a new type of medium temperature FC (called a solid acid FC), CsHSO₄ was used as an electrolyte. According to [6], when a salt is hydrogen reduced on a Pt/C anode, hydrogen sulfide is emitted:

$$2C_{s}HSO_{4} + 4H_{2} = H_{2}S + Cs_{2}SO_{4} + 4H_{2}O.$$
 (1)

In a complete reaction, the CsHSO₄ weight loss should be ~22.6%. Indeed, subsequent thermogravimetric analyses showed that the reaction proceeded but very slowly without catalysts: after 10 h in a hydrogen flow at a temperature of 160°C, the CsHSO₄ loss was ~0.03 wt % [8, 9].

According to [8, 9], catalysts such as Ir, Pt, Pd, and WC efficiently accelerate the reaction of hydrogen sulfide formation: when CsHSO₄ is kept with a platinum catalyst at a temperature of 160°C (35 wt %), the loss amounts to 6.8 wt % of the salt [8], while a CsHSO₄ – Pt/C (3 : 1) system kept for 48 h at 150°C results in a loss of ~12.7 wt % [9].

The formation of Cs_2SO_4 is supported by x-ray phase analysis data. However, study [9] does not describe the experimental conditions: sample moisture, the partial pressure of water vapor, and the size of catalyst particles, which can substantially affect the reaction. The specific surface area of the catalyst (the size of granules and agglomerates), porosity, and presence of active centers are of great importance as well.

Our studies [10] show that a $CsHSO_4 + Pt (200:3)$ mixture kept in hydrogen at 160°C for 7 h leads to a loss

of only 0.4 wt % of CsHSO₄. Reaction (1) is also observed when Pt, Pt/C, and Pt/Rh are used as anodes; at the same time, the compound CsHSO₄ is chemically stable in the presence of SnO₂, Ni, and Pd [10, 11].

The FC process of H_2S emission on platinum and its effect on adsorptive and electrochemical anode characteristics may depend on relative moisture, time, and the value of the current passed, which requires a separate study.

Thermodynamic calculations [12] show that reaction (1) is an energetically advantageous process. According to the authors' estimation, even with an air pressure of 10 Pa, the inhibition of reaction (1) will require the conditions $p_{\rm H_2O} \cdot p_{\rm H_2S}^{1/4} > 10^4 - 10^6$ MPa, which cannot be achieved in the course of the experiment. However, a low reaction rate in the absence of catalysts appears to be determined by a high energy barrier at the elementary stages through which it proceeds. In particular, the reaction includes the stages of H_2 absorption, dissociation, a charge transfer reaction (forming and breaking of hydrogen bonds, breaking of S-O and Cs-O bonds), ion and water diffusion, and water and H₂S desorption. Thus, it seems relevant to study the parameters affecting the kinetics of reaction (1) in order to control it and find its inhibition mechanisms.

This work is aimed at studying CsHSO₄ reduction in hydrogen and the dynamics of H₂S emission both under the conditions of FC operation and in a catalyst + electrolyte mixture with an extended contact surface. The type of catalyst was varied (Pt, Pd, Ni), as well as the amount of catalyst with respect to CsHSO₄ (with CsHSO₄-metal contact surface), the concentration of acid centers, the temperature (160–190°C), the water vapor pressure in hydrogen (67–2900 Pa), and the residual moisture content in the sample.



Fig. 1. Dependence of the degree of CsHSO₄ conversion on the time of hydrogen flow to the CsHSO₄ + catalyst mixture (80 : 1): (1) Pt, (2) Pd, (3) Ni ($p_{H_2O} \sim 2900$ Pa, $T = 160^{\circ}$ C).

EXPERIMENTAL

Single crystals of cesium hydrosulfate were obtained by isothermal evaporation from aqueous solutions containing equimolar amounts of Cs_2SO_4 (chemically pure) and H_2SO_4 at room temperature. Platinum and palladium black were obtained by the formic acid reduction of $H_2[PtCl_6]$ aqueous solutions and palladium chloride with subsequent multiple water washings. According to x-ray phase analysis and electron microscopy data, the size of catalyst particles did not exceed 20 nm. Hydrogen used for reduction was either obtained by electrolysis and then saturated with water vapors in a saturator at 25°C or supplied from a hydrogen cylinder. The rate of hydrogen flow to the system was 0.05 ml/s.

In order to determine the amount of H_2S emitted in the process of salt reduction, reverse iodometric titration [13] was applied. According to this method, emitted hydrogen sulfide is passed through a zinc sulfide solution (buffered with sodium acetate) that absorbs H_2S and forms ZnS by the reaction

$$\operatorname{ZnCl}_2 + \operatorname{H}_2 S \longrightarrow \operatorname{ZnS}^{\uparrow} + 2\operatorname{HCl}.$$
 (2)

An excess amount of iodine aqueous solution, HCl (1 : 1), and starch were added to the solution containing ZnS. This blue solution was then titrated with sodium thiosulfate until it became colorless according to the reactions

$$I_2 + ZnS \longrightarrow ZnI_2 + S\uparrow,$$
 (3)

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6.$$
(4)

The minimum amount of hydrogen sulfide calculated by the above method is $10-15 \mu g$, which corresponds to a loss of 0.008-0.009 wt % in CsHSO₄ reduction. The method is intended for a direct determination of hydrogen sulfide in gas mixtures. Despite its labori-

ousness, it is not complicated and is quite precise (error is $\sim 2\%$).

RESULTS AND DISCUSSION

When CsHSO₄ was thermally kept for a long time in hydrogen without a catalyst (more than 24 h), the weight loss of CsHSO₄ was no more than 0.004%, which is consistent with the data of [8, 9]. The amount of H₂S emitted on a platinum anode under the conditions of FC operation (at CsHSO₄/Pt interface) in a hydrogen flow for 24 h at 160°C corresponded to the weight loss of CsHSO₄ of ~0.001%. These values are much smaller than the detection limit of the reverse titration method. Therefore, to increase the amount of H₂S emitted, the CsHSO₄ –metal contact surface was enlarged through changing the ratio of components: at the ratio of CsHSO₄ : Pt = 80 : 1 and the size of Pt, Pd, and Ni particles of ~20 nm, the contact surface was increased by several orders of magnitude.

In [14], it is shown that the exchange current density in the H₂, M/ CsHSO₄ electrode reaction in hydrogen increases in the sequence Ni \longrightarrow Pt \longrightarrow Pd, exchange currents being enhanced by an order of magnitude when passing from one metal to another. This work presents studies of the kinetics of reaction (1) in the presence of these metals. Figure 1 shows that Pt significantly catalyzes reaction (1), Pd is substantially less active as a catalyst, and Ni hardly affects the reaction rate. The smaller catalytic activity of Pd compared to Pt along with its high electrochemical activity makes it a promising material for anodes in FC, which was observed in [11].

The results obtained differ from the data in [8], which can be due to a number of factors, in particular, differences in the size of the specific surface area, the number of active centers on the catalyst surface, and sample prehistory and also different experimental conditions.

It is known that the salt : catalyst ratio can substantially affect the reaction kinetics. Apparently, a catalyst affects the reaction solely on the contact surface with the salt; thus, the maximum contact surface should be observed when the surface ratio is 1 : 1. Under normal conditions, it is hardly possible to grind CsHSO₄ particles to less than 1 μ m. With regard to the density of the catalyst and cesium hydrosulfate and also the particle size of catalysts used (platinum and palladium), it is possible to estimate that the above surface ratio can be achieved only when the salt : catalyst weight ratio is ~8 : 1 in the case of Pt and 15 : 1 in the case of Pd.

Figure 2 shows the dependence of CsHSO₄ conversion in a CsHSO₄ + Pt mixture at different ratios at a temperature of $T = 160^{\circ}$ C. It is seen that the dependence is nearly linear, and if the ratio is multiplied by 4, the amount of emitted hydrogen sulfide increases ~32-fold.

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Fig. 2. Dependence of the degree of CsHSO₄ conversion on the ratio CsHSO₄ : Pt in the mixture ($T = 160^{\circ}$ C, the time of hydrogen flow 4 h, $p_{H_2O} \sim 67$ Pa).

With a temperature increase from 160 to 190°C, the salt reduction reaction accelerates ~1.5-fold (Fig. 3), which corresponds to the activation energy of reaction (1) with the catalyst of ~50–60 kJ/mole. Note that this activation energy value is typical of a dehydration reaction of some crystalline hydrates [15].

The reaction performed in a hydrogen atmosphere with different degrees of moisture shows that an increase in the relative moisture of hydrogen speeds up cesium hydrosulfate reduction in the presence of the catalyst (Fig. 4). This effect is most vividly demonstrated by the mixture of salt and palladium rather than platinum. However, even in moist hydrogen, the degree of CsHSO₄ conversion does not exceed 3.5% at the ratio of CsHSO₄ : Pt = 80 : 1. The rate of reaction (1) decreases with time at lower moisture levels, while at higher moisture content the dependence of salt conversion is almost linear.

The effect of moisture can be associated both with better adhesion of the catalyst to electrolyte and with the formation of new catalytically active centers, probably of an acid-base type. Moreover, water is likely to participate in the reaction of sulfur reduction. For instance, adsorption of water molecules on the CsHSO₄ surface can lead to the formation of either CsHSO₄ · nH₂O crystalline hydrates with a lower energy of Cs–O and S–O bonds or hydrated microlayers in which the salt dissociates into ions, which accelerates sulfur reduction. It is known that the surface properties of MHSO₄ (M = Cs, Rb, NH₄) hydrosulfates vary considerably from bulk ones. In particular, phase transitions on the surface occur at much lower temperatures [16].

This poses a question: Will the reaction proceed if water adsorbed on the $CsHSO_4$ surface is removed to the maximum possible extent? For this purpose, the salt



Fig. 3. Dependences of the degree of CsHSO₄ conversion on the time of hydrogen flow at T = 160 (1), 190°C (2); CsHSO₄ : Pt = 80 : 1, $p_{H_2O} \sim 67$ Pa.



Fig. 4. Dependences of the degree of CsHSO₄ conversion in (a) CsHSO₄ + Pt = 80 : 1 and (b) CsHSO₄ + Pd = 80 : 1 on the time of hydrogen flow at water vapor partial pressures in hydrogen of (1) 2900 and (2) 67 Pa; $T = 160^{\circ}$ C.



Fig. 5. Dependences of the degree of CsHSO₄ conversion for samples with different acidity: (1) CsHSO₄ + H_2SO_4 (6 : 1); (2) CsHSO₄; pressure of ~2900 Pa (without a catalyst).

was preliminarily kept in a residual vacuum of $\sim 10^4$ Pa at 160°C for 2 h, then mixed with the catalyst (Pt, Pd) in a 4 : 1 ratio, pressed into a loose pellet (relative density of ~40%), and kept again under ~ 10^4 Pa at 160°C. Then hydrogen $(p_{\rm H_2} \sim (53-93) \times 10^3 \text{ Pa})$ was supplied to the cell, and it was kept at 160°C. During the first 2 h, no weight loss was recorded, and after the next 6 h, the degree of CsHSO₄ conversion did not exceed 1%. When CsHSO₄ was kept without any catalyst and also in a mixture with palladium in a 4 : 1 ratio, no weight loss was observed under similar conditions. Contrary to the data in [8], the formation of cesium sulfate, according to x-ray phase analysis, was not proved in our case. Hence, it is possible to conclude that the presence of adsorbed water is essential for the CsHSO₄ reduction reaction to proceed, and when it is absent, the reaction rate is extremely low. However, considering thermodynamic data, an increase in the partial pressure of water vapor should inhibit reaction (1). Therefore, the authors of [6] tested FC in an atmosphere with 30 mol % H₂O. In this case, the effect of the kinetics of the reaction (its mechanism) on the degree of conversion is more substantial than its thermodynamics.

Acidification of CsHSO₄ with a small amount of sulfuric acid also accelerates reaction (1). In this case, the degree of CsHSO₄ conversion increases even without any catalyst (Fig. 5), which indicates that the reaction proceeds faster in hydrated layers, apparently, with the participation of acid centers. However, it should be noted that, in this case, it is not excluded that an increase in the amount of hydrogen sulfide emitted is due to the direct reduction of sulfuric acid.

Thus, it is possible to suppose that the hydrogen reduction of cesium hydrosulfate occurs in hydrated salt layers on the crystal surface rather than in the solid phase of CsHSO₄. The presence of water first of all provides the breaking of the Cs–O bond, which is one of the elementary acts of this multistage reaction. Hydrogen adsorption by cesium hydrosulfate seems to be negligible. The presence of the catalyst accelerates the adsorption and dissociation of hydrogen, facilitates charge transfer, and reduces the formation energy of intermediate reaction products. Nevertheless, without any trace of moisture, cesium hydrosulfate can remain stable for a long time in a hydrogen reducing atmosphere even in the presence of catalysts.

CONCLUSIONS

The hydrogen reduction of CsHSO₄ both with and without catalysts (Pt, Pd, Ni) is studied. It is shown that the reaction proceeds extremely slowly without a catalyst. Catalytic activity increases in the sequence Ni \longrightarrow Pd \longrightarrow Pt. Palladium catalytic activity rises substantially with increasing relative moisture.

The factors affecting the degree of $CsHSO_4$ reduction are determined. The degree of conversion increases with increasing amount of a catalyst in its mixture with the salt, with rising temperature, with increasing relative moisture or moisture content in $CsHSO_4$, and with increasing concentration of active acid centers on the electrolyte surface. The latter two factors are close to the action of a platinum catalyst in their nature and significance.

Without any trace of moisture in hydrogen and on the salt crystal surface, cesium hydrosulfate reduction does not occur, and even in the presence of catalysts (salt : catalyst = 4 : 1), the reaction rate is extremely low.

The relatively low catalytic activity of palladium in the cesium hydrosulfate reduction reaction along with its high electrochemical activity makes it a promising electrode material for medium temperature FEs.

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