Reaction Mechanism of Hydrogen Absorbers Made of Manganese Dioxide

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Previously the author found that manganese dioxide which was catalyzed with palladium or silver is an excellent hydrogen gas absorber. In order to understand the mechanism of the reaction between hydrogen gas and manganese dioxide, various oxides such as PbO_2 , RuO_2 , MnO_2 , Mn_2O_3 , Mn_3O_4 , CuO , HgO , AgO , Ag_2O were tested for hydrogen absorption. The excellent hydrogen absorption capability of MnO_2 and RuO_2 was attributed to the nature of the unique oxide system, which is reduced by accepting protons without changing the essential structure. Other oxides such as PbO_2 , HgO , CuO , etc. were far poorer in hydrogen absorption compared to RuO_2 and MnO_2 . This was attributed to the fact that the oxides are a two phase (or heterogeneous phase) oxide system in the electrochemical reduction, whereas MnO_2 and RuO_2 are one phase redox systems.

1 Introduction

Previously two types of hydrogen absorbers, both of which were made of manganese dioxide, were reported^{(1)~(4)}. One was MnO_2 which was catalyzed with palladium^{(1),(2)} and the other was MnO_2 which was catalyzed with Ag-Mn^{(3),(4)}. The purpose of this paper is to propose a probable mechanism for the hydrogen absorption reaction and provide some experimental support for this mechanism.

2 Proposed Mechanism

As we well know, oxygen gas and hydrogen gas do not react with each other unless a catalyst (*e. g.*, Pt black) is present. Similarly MnO_2 or other oxides (PbO_2 , HgO , Ag_2O , etc.) do not react with hydrogen gas without a proper catalyst such as palladium^{(1),(2)} or an Ag-Mn catalyst^{(3),(4)} which is an intimate mixture of Ag_2O (or AgO or Ag salt) and MnO_2 (or other Mn oxide or Mn salt).

An effective and practical hydrogen absorber must be composed of two essential components.

One is a catalyst and the other is an oxidant. The essential function of the catalyst seems to dissociate molecular hydrogen into atomic hydrogen. The oxidant can be any material which can react with hydrogen in a thermodynamic sense. The oxidants under consideration now, however, are metal oxides such as MnO_2 , Mn_2O_3 , PbO_2 , Ag_2O , AgO , HgO , CuO , etc. According to our experience, some oxides are good hydrogen absorbers and other oxides are not, even in the presence of the same catalyst. For example, as we will show later in Table 1, MnO_2 and RuO_2 are excellent hydrogen absorbers, but HgO , CuO , Mn_2O_3 and PbO_2 are not. What is the reason for this difference? To answer this question, the writer will propose below a mechanism based on the electrochemical behavior of these oxides.

Figure 1 shows a schematic model of a catalyzed metal oxide. Figure 2 shows the proposed mechanism. In step (a) of Fig. 2, molecular

Fig. 1 Model of catalyzed metal oxide

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Fig. 2 Proposed mechanism

hydrogen is dissociated into atomic hydrogen. The atomic hydrogen produced at the area where the catalyst and the oxide are in contact will react with Mn^{4+} ($\text{Mn}^{4+} + \text{H} \rightarrow \text{Mn}^{3+} + \text{H}^+$) and then further react with O^{2-} to form OH^- ($\text{O}^{2-} + \text{H}^+ \rightarrow \text{OH}^-$) as shown in steps (b) and (c). The Mn^{3+} sites and OH^- sites in the ionic crystal lattice of the MnO_2 are not fixed but move around, since electrons can jump between Mn sites and protons can jump from one O^{2-} site to the other as shown in step (d). Once Mn^{3+} and OH^- diffuse away from the catalyst-oxide contact area, another hydrogen atom can move into the MnO_2 lattice. Thus the reaction between Mn^{4+} and H will continue until all the Mn^{4+} ions in the lattice are converted to Mn^{3+} and all the O^{2-} sites are converted to OH^- . This reduction process of MnO_2 ($\text{MnO}_2 + \text{H} \rightarrow \text{MnOOH}$) has been thoroughly investigated previously in an electrochemical cell using KOH solution, and the mechanism has been established^{(5)~(8)}. The unique feature of MnO_2 is that the oxide is reduced without changing its essential structure and an homogeneous solid phase is maintained during the reduction. Thus the potential of the oxide decreases gradually in an S-shape fashion as the reduction proceeds as shown in Fig. 3(a). In other words, the oxide is a homogeneous solid phase redox system (or a one phase

solid redox system). RuO_2 has recently been found to be another example of a homogeneous solid phase redox system⁽⁹⁾. Other types of oxides such as HgO , PbO_2 , etc. are entirely different from MnO_2 and RuO_2 in their reduction mechanism. When they are reduced electrochemically or chemically by H_2 , a second solid phase (PbO or Pb(OH)_2 in the case of PbO_2) is produced as shown below. Because of the nature, we call this type of oxide a two phase or heterogeneous phase redox system.

When an oxide belongs to a two phase or heterogeneous phase redox system, the potential of the system remains unchanged during the entire reduction as shown in Fig. 3 (b). According to the author's experience, various oxides can be classified into two groups based on their electrochemical behavior (the shape of the potential-reduction (%) curve in the discharge). One group is a homogeneous phase system (such as MnO_2 and RuO_2) and the other is a heterogeneous phase system (such as Ag_2O , HgO , CuO , PbO_2 , etc.) These classifications and concepts were explained and discussed previously^{(7),(8)}. In the case of HgO , CuO , PbO_2 , the oxide which is in contact with the catalyst may be easily reduced, but the catalyst will soon be separated since a second phase is produced. Therefore, the hydrogen absorption reaction will not proceed continuously. The essential advantage of MnO_2 or RuO_2 as a hydrogen absorber may be that the catalyst-oxide contact is maintained since no second solid phase is produced.

To test this proposed mechanism and explanation, the hydrogen absorption rate of various oxides was measured. It was found that the proposed mechanism and the explanation seem to be correct.

3 Experimental

3.1 Preparation of test samples

The method was as follows. Each oxide listed in Table 1 was tested either with a Pd-C catalyst or an Ag-Mn catalyst. One gram of each oxide was mixed with 30 or 60 mg of the cata-

Fig. 3 Two types of discharge process of redox metal oxides

- (a): One phase solid redox system (MnO_2 , RuO_2)
 (b): Two phase solid redox system ($\text{Ag}_2\text{O-Ag}$, HgO-Hg , $\text{PbO}_2\text{-PbO}$, etc.)

Fig. 4 Apparatus for measuring hydrogen gas absorption (See Ref. (1) for operation)

A : A 10 cc beaker containing sample, B : An inverted test tube (3.5 cm in diameter, 30 cm long), C : Hydrogen gas, D : Fine plastic tubes, E : Hydrogen cylinder, F : Nitrogen cylinder, G : Vacuum, H : Oil level, I : Top of the plastic rod, J : Plastic rod, K : Vacuum pump oil in 250 ml beaker.

lyst and water (0.2–0.4 ml in a 10 ml beaker). The mixture was blended well and heated in air at 75°C for 2 hours to remove most of the added water. The dried material was crushed briefly in the 10 ml beaker and tested in a set-up shown in Fig. 4.

A simple mixture without the addition of water and the subsequent drying process was also tested. The simple mixtures were far slower in their absorption rate, although the relative rates among the oxides of the 32 mixes in Table 1 were in the same order. This means that the water treatment probably provides good contact between the oxide and the catalyst.

3.2 MnO₂

Manganese dioxide used here was the so-called electrolytic manganese dioxide which was made by electrodeposition from MnSO₄ solution (8). Battery grade manganese dioxide, *e.g.*, International Common Sample No. 1¹⁰, was used in this work. This powder material was

Fig. 5 Electrochemical reduction of RuO₂ in 9 M KOH. Sample (100 mg) mixed with carbon powder and 9 M KOH was discharged at 1.0 mA for 6 h daily in the cell described previously¹¹.

Sample : A ; RuO₂·xH₂O (E)

B ; RuO₂ (V), anhydrous oxide

composed of particles having a diameter of 1–80 μm (the average particle size was 10 μm). The surface area was about 50 m²/g, and the pore volume was about 10%. The pore size (pore diameter) was 40–50 Å and the true density was 4.3 g/ml.

3.3 RuO₂

RuO₂ is a black powder having good electrical conductivity (similar to that of a metal powder). RuO₂ is available in two forms, anhydrous and hydrated. The electrochemical characteristics of the two are different as shown in Fig. 5. To test the proposed mechanism for the hydrogen absorption process, a hydrated oxide which was approximately RuO₂·3H₂O (53% Ru) was used, because only a hydrated oxide is reduced in a homogeneous phase like MnO₂ as seen from the S-shape discharge curve (see curve A of Fig. 5).

3.4 Ag₂O and AgO

The silver oxides used in this work were reagent grade chemicals. The particle size of 90% of the material was between 1 and 2 μm in diameter.

3.5 Pd-C catalyst

The palladium catalyst was obtained from

Engelhard Industries. This material is metallic palladium dispersed on a high surface area carbon (2.5%Pd, 47.5% carbon and 50% H₂O in the composition by weight).

3.6 Ag-Mn catalyst

This Ag-Mn catalyst was prepared as follows. Five grams of Ag₂O and 5 g of MnO₂ (I. C. No. 1) were mixed with 2.0 ml of water and blended. The mixture was heated at 75°C in air for 2 h, in order to remove most of the water. The dried material was ground briefly in a glass mortar. This water treatment seems to be important to produce an active Ag-Mn catalyst. We do not know the true nature of the active center, but we know that both Mn atoms and Ag atoms have to be present in order to obtain the Pd-like activity. A mixture of MnO₂ and a AgNO₃ solution or a mixture of metallic silver powder and MnO₂ also produce a good catalyst.

3.7 Test

Figure 4 shows the set-up. The operation was described in a previous paper (1). The reading was taken only for the first 4 h, since we needed only qualitative data at this time. One gram of MnO₂ should absorb 257 ml of H₂ gas if it is reduced to MnO and 128.5 ml if it is reduced to Mn₂O₃ (or MnOOH). The test set-up contains about 50 ml of hydrogen gas, since the gas atmosphere is 80% H₂ and 20% N₂ (total of 60 ml). In the case of the Pd-catalyst, MnO₂ seems to be reduced to MnO, and in the case of the Ag-Mn catalyst, MnO₂ is reduced to MnOOH or Mn₂O₃ (3).

4 Results and Discussion

The results are summarized in Fig. 6 and Table 1. Table 1 shows the hydrogen gas absorption by one gram sample in 4 h at 23°C. The absorption value of 2 to 3 ml in 4 h is probably not a true absorption figure, rather it is the result of settling of the oil level during the first 15 to 30 min period. If we count this factor, values above 5 to 6 ml should be considered as significant absorption.

4.1 MnO₂ and RuO₂

It is clear from the results (Table 1) that Pd catalyzed MnO₂ and RuO₂ have exceptional activity for hydrogen absorption (Exp. No. 20,

Fig. 6 Hydrogen absorption by one gram sample. Then number by the curve corresponds to that in Table 1.

25, 30 in Table 1). MnO₂ alone is not capable of absorbing hydrogen, but RuO₂ alone has some capability, probably because Ru itself can be a catalyst. Ag-Mn-catalyzed MnO₂ and RuO₂ also have very high activity (Exp. No. 1, 17 in Table 1), although the activity is somewhat lower than those materials catalyzed with Pd. All other oxides (PbO₂, CuO, HgO, AgO, Ag₂O) are very poor except Ag₂O which was catalyzed with Pd.

These general results essentially support the proposed mechanism: A homogeneous phase solid redox system (MnO₂ and RuO₂) should be a better hydrogen absorber than a heterogeneous or two phase system (PbO₂, CuO, Mn₂O₃, HgO, Ag₂O, etc.).

4.2 Presence of other mechanism

As shown in experiments No. 6, 22 and 31 of Table 1, AgO(+Ag-Mn), PbO₂ (+Pd) and Mn₂O₃ (+Pd) have a fairly good hydrogen absorption capability. Since we know that these oxides are not reduced by the proton injection (or homogeneous phase reduction) mechanism, we have to conclude that there must be other mechanisms for hydrogen and metal oxide reaction. In the other mechanisms, the produced water must be removed as water vapor since H cannot stay in the solid phase. In the other mechanisms, movement of various types of vacancies and defects must be playing an important role.

4.3 Pd-catalyzed Ag₂O

As pointed out earlier, this material has un-

Table 1 Summary of the results*1

	Oxide (Oxidant)	Catalyst (or additive)	H ₂ gas absorbed*2
(1)	MnO ₂ *3	Ag-Mn (60 mg)	45.5 cc
(2)	PbO ₂	Ag-Mn (60 mg)	5.2
(3)	Ag ₂ O	Ag-Mn (60 mg)	6.0
(4)	CuO	Ag-Mn (60 mg)	3.5
(5)	HgO	Ag-Mn (60 mg)	3.0
(6)	AgO	Ag-Mn (60 mg)	9.0
(7)	PbO ₂	Ag ₂ O (30 mg)	3.2
(8)	CuO	Ag ₂ O (30 mg)	2.4
(9)	HgO	Ag ₂ O (30 mg)	2.5
(10)	PbO ₂	MnO ₂ (30 mg)	3.8
(11)	CuO	MnO ₂ (30 mg)	3.7
(12)	HgO	MnO ₂ (30 mg)	2.5
(13)	MnO ₂	Ag ₂ O (30 mg)	42.0
(14)	RuO ₂	none	9.2
(15)	RuO ₂	Ag ₂ O (30 mg)	26.0
(16)	RuO ₂	MnO ₂ (30 mg)	22.0
(17)	RuO ₂	Ag-Mn (30 mg)	24.5
(18)	MnO ₂	none	2.4
(19)	MnO ₂	Pd-C (30 mg)	13.0
(20)	MnO ₂	Pd-C (60 mg)	46.0
(21)	PbO ₂	none	2.7
(22)	PbO ₂	Pd-C (60 mg)	13.0
(23)	Ag ₂ O	none	4.0
(24)	Ag ₂ O	Pd-C (60 mg)	>60
(25)	RuO ₂	Pd-C (60 mg)	>60
(26)	none	Pd-C (60 mg)	6.5
(27)	MnO ₂ (400°C)	Ag ₂ O (30 mg)	7.0
(28)	Mn ₂ O ₃	Ag ₂ O (30 mg)	3.0
(29)	Mn ₃ O ₄	Ag ₂ O (30 mg)	3.0
(30)	MnO ₂ (400°C)	Pd-C (60 mg)	>60
(31)	Mn ₂ O ₃	Pd-C (60 mg)	9.0
(32)	Mn ₃ O ₄	Pd-C (60 mg)	6.3

*1: One gram of each oxide was mixed with the catalyst or the additive in the amount shown in the 2nd column and blended with 0.2-0.4 ml of water. Then it was dried in air for 2 h at 75°C. The dried material was crushed and tested in 80% H₂ gas (20% N₂) for absorption.

*2: H₂ gas absorbed in ml by one gram sample in 4 h at 23°C.

*3: MnO₂ is an electrolytic battery grade MnO₂ (I. C. No. 1). Mn₂O₃ and Mn₃O₄ were prepared by heating the MnO₂ at 700°C and 1000°C respectively.

usually high activity. The following two factors may account for this behavior, although we need further work to confirm these points. The first factor is the extremely small particle size of the Ag₂O sample (1-2 μ m in diameter) and the other is the possible formation of a Pd-Ag alloy which can pass atomic hydrogen very well.

5 Conclusions

Various metal oxides can be classified from the hydrogen gas absorption rate into two groups: (1) fast absorber oxides such as MnO₂, RuO₂, etc. and (2) slow absorber oxides such as PbO₂, Mn₂O₃, etc. According to our electrochemical knowledge, the first group of oxides belong to a homogeneous phase oxide group which produces an S-shaped discharge curve in electrochemical reduction and the second group belongs to a heterogeneous phase oxide which produces a flat potential upon discharge. The electrochemical reduction mechanism of the first group is essentially proton injection into the lattice, therefore it is easy to understand that hydrogen gas absorption should proceed smoothly.

Based on x-ray diffraction studies and potential measurements of MnO₂ during the discharge in KOH, the electron-proton mechanism has been well established and accepted widely in the past ten years³⁾⁻⁸⁾. Now we have direct experimental proof that the MnO₂ lattice accepts a large amount of protons (namely hydrogen).

Acknowledgement:

The writer wishes to thank Mr. R. Johnson for performing the experimental work and Mrs. H. M. Joseph for technical editing of this paper.

<E452> (Received Feb. 2, 1976)

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Hydrogen: Its Technology and Implication

米国 CRC Press 社 全5巻各巻約 200 ページ \$ 43 (船便送料共)

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