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ACTIVE METAL/OXIDE SYSTEMS FOR WATER DECOMPOSITION

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Several Metal/WO_3 systems (Metal = Re, Ir, Rh, Ru, Os, Pd, Pt) exhibit high hydrogen evolution activities when contacted with water vapor at 480°C. The use of WO_3 along with a metal species is necessary to bring about the high activity. X-Ray diffraction data of Rh/WO_3 systems strongly suggest that W_3O species formed by activation (reduction by H_2) is responsible for the unique property of WO_3.

When certain metals or metal oxides of lower valence states are oxidized by water, hydrogen is evolved. Utilizing this reaction, the steam-iron process[1)] has been developed, in order to produce hydrogen necessary for coal processings. However, the process still needs much improvement.[2)] Findings of materials with high water decomposing activities appear urgent for the progress of the hydrogen production process. Under this situation, Otsuka and Morikawa[3)] have proposed the use of In_2O_3 and K_2CO_3 for water decomposition. The present paper reports the high activities of several Metal/WO_3 systems (Metal = Re, Ir, Rh, Ru, Os, Pd, Pt) found by the authors.

The activity measurements were carried out using a microcatalytic pulse reactor.[4)] In each run, a sample[5)] (100 mg) placed in the reactor was evacuated for 10 min at room temperature, heated gradually in a H_2 stream (30 $cm^3 min^{-1}$) and kept at 480°C for 1 h. Then the sample was evacuated for 10 min at the same temperature and He was introduced into the reactor. Ten minutes later, the first H_2O pulse was injected and the gas produced was analyzed by gas chromatography. The conditions for the activity measurements and product analysis were as follows: reaction temperature, 480°C; H_2O pulse size, 111 μmol; pulse interval, 20 min; He flow rate, 40 $cm^3 min^{-1}$; gas chromatographic column, Porapak T (1.25 m, 140°C). The H_2O injection and the gas analysis were continued untill the sample lost its activity for water decomposition. Powder diffraction patterns of Rh/WO_3 systems in different oxidation states were taken by an X-ray diffractometer (Geiger Flex 2013, Rigaku Denki CO.).

The systems composed of WO_3 and a noble metal or rhenium exhibited high activities for hydrogen evolution. The total amounts (μmol) of hydrogen evolved during the runs were: Re/WO_3 = 648, Ir/WO_3 = 645, Rh/WO_3 = 525, Ru/WO_3 = 505, Os/WO_3 = 503, Pd/WO_3 = 494, Pt/WO_3 = 455, Fe/WO_3 = 280, Ni/WO_3 = 197, Rh/In_2O_3 = 126, Co/WO_3 = 93, Rh/CeO_2 = 40, Rh/Nb_2O_5 = 11. Other Rh/oxide systems[5] gave less than 10 μmol of hydrogen.[6] Typical behaviors of hydrogen evolution are exemplified in Fig. 1.

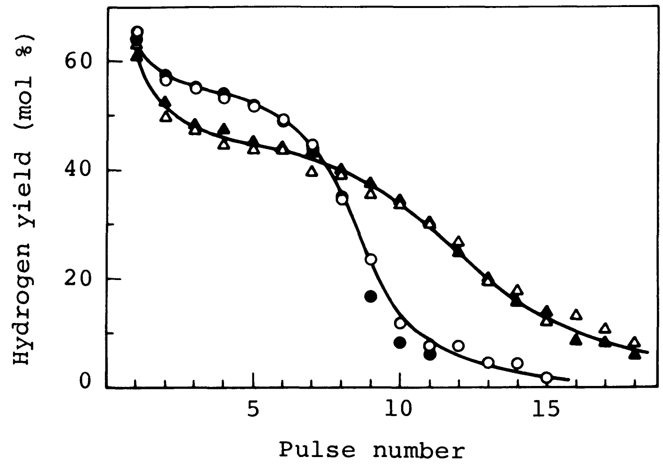

Fig. 1 Two typical behaviors of hydrogen evolution at 480°C.
○ : Rh/WO_3,
● : Pd/WO_3,
△ : Re/WO_3,
▲ : Ir/WO_3.

The results shown above indicate that an addition of metal species (Re, Ir, Rh, Os, Pd, Pt) to WO_3 is necessary to bring about the high activity, since the total amount of hydrogen evolved over WO_3 alone is only 94 μmol. These metallic additives act as promoters or catalysts for the reaction of WO_3 with hydrogen, and increase the rate of the reduction of WO_3 by the activation of molecular hydrogen.[7] Moreover, the metallic additives may act as the active site for the decomposition of water, though the details are still to be discovered.

X-Ray diffraction data for Rh/WO_3 seem to throw some lights upon the role played by WO_3. The data listed in Table 1 inform that W_3O[8] (β-W) species formed by reduction disappears upon contacting with water vapor, except for the ones formed in the samples reduced at high temperatures (>530°C). This suggested that

Table 1 Species found in Rh/WO_3 samples reduced at different temperatures and for different periods

Temp. (°C)	Time (h)	Observed species	
		After reduction	After reaction
480	1	W_3O(*m*), $W_{20}O_{58}$(*m*)	$W_{20}O_{58}$(*m*)
530	1	W(*s*), W_3O(*m*)	$W_{20}O_{58}$(*m*), WO_2(*w*), W_3O(*w*)
580	1	W(*vs*), W_3O(*w*)	W(*m*), $W_{20}O_{58}$(*m*), WO_2(*w*), W_3O(*w*)
480	0.5	$W_{20}O_{58}$(*m*), W_3O(*m*)	$W_{20}O_{58}$(*m*)
480	1	W_3O(*m*), $W_{20}O_{58}$(*m*)	$W_{20}O_{58}$(*m*)
480	2	W_3O(*m*), W(*m*)	$W_{20}O_{58}$(*m*)
480	3	W_3O(*m*), W(*m*)	$W_{20}O_{58}$(*m*)

: very strong, : strong, : medium, : weak.

the W_3O species is responsible for the rapid uptake of oxygen from water. This view is strongly supported by Fig. 2 which informs of a proportionality between

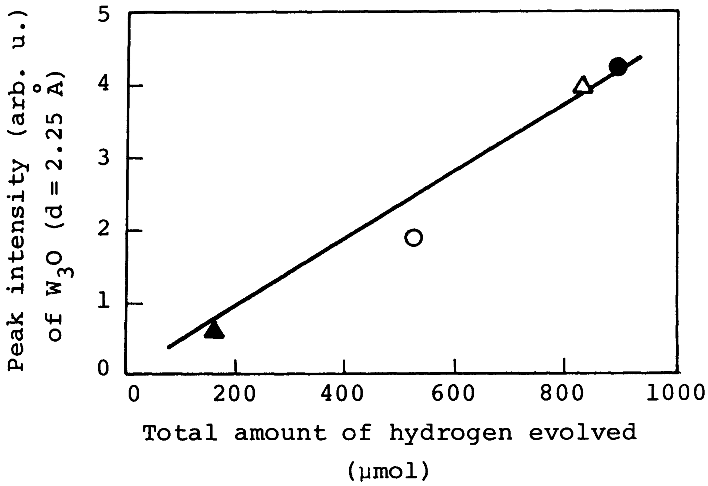

Fig. 2 Linear relation between the total amount of hydrogen evolved and the X-ray peak intensity of W_3O. Sample = Rh/WO_3 reduced at 480°C; period of reduction = 0.5 h (▲), 1 h (○), 2 h (△), 3 h (●).

the X-ray peak intensity (d = 2.25 Å) of W_3O and the total amount of hydrogen evolved. The figure shows that the activity as well as the peak intensity is similar for the samples reduced for 2 h and 3 h. This is an indication that the activation at 480°C for the period of 2 - 3 h may be sufficient for the system.

References

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4) Y. Kato, A. Igarashi, and Y. Ogino, Nippon Kagaku Kaishi, 1979, 842.
5) Samples of the type A(metal, 1 wt%)/B(oxide) were used. Here A represents Re or any one of the group VIII elements and B, La_2O_3(*b*), SnO_2(*e*), MoO_3(*d*), WO_3(*d*), V_2O_5(*d*), Sb_2O_3(*e*), ZnO(*b*), MnO_2(*c*), In_2O_3(*b*), Cr_2O_3(*b*), ZrO_2(*b*), Nd_2O_3(*c*), CeO_2(*b*), Nb_2O_5(*a*), Tb_4O_7(*a*), Pr_6O_{11}(*a*), GeO_2(*e*), HfO_2(*e*). (*a*), (*b*),--- indicates the starting materials listed below. These samples were prepared by the following procedures: i) calcination of (*a*) oxide, (*b*) hydroxide, (*c*) carbonate, (*d*) ammonium salt, or (*e*) hydroxide obtained by the hydrolysis of chloride, in a stream of N_2(or air) at 450°C for 2 h; ii) mixing of the resulting oxide (B) with an aquous solution of a compound of A (ammonium perrhenate for Re; nitrates for Rh, Fe, Co, and Ni; chlorides for Ru, Pd, and Ir; chloroplatinic acid for Pt; osmium tetroxide for Os) at room temperature; iii) drying at 100°C for 14 h; iv) calcination of the dried material in a stream of N_2(or air) at 450°C for 2 h; v) pelletizing and crushing 0.5 - 1 mm in diameter.
6) For the Rh/oxide systems, the total hydrogen evolution expressed as a fuction of $-\Delta H_f^0$ (the standard heat of formation of the most stable oxide of an element)

exhibited a maximum at $-\Delta H_f^0 = 200$ kcal mol-metal^{-1} (tungsten). This appears worth reporting, though the theoretical meaning of the relations is uncertain and open to further studies.

7) N. I. Il'chenko, Russ. Chem. Rev., 41, 47(1972).

8) "Index to the Powder Diffrction File" ed. W. F. McClune et al., JCPDS International Centre for Diffraction Data (1981) 2-1138.

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