JOURNAL OF CATALYSIS **79**, 493–496 (1983)

Hydrogen from Water by Reduced Cerium Oxide

A metal or a partially reduced metal oxide decomposes water thus producing hydrogen at moderate temperatures. The production of hydrogen applying the solid-gas reaction has recently been studied and developed (*1–6*). The authors have demonstrated a two-step hydrogen production from water by a reduction (step 1) and oxidation (step 2) cycle of metal oxides (*3, 5, 6*). There are many metal oxides which are allowed to thermodynamically produce hydrogen by the two-step cycle. However, only a few metal oxides are applicable to the two-step process on the basis of kinetic requirement (*7*). Among those metal oxides CeO_2 has been suggested to be one of the potential compounds for the production of hydrogen by the cycle (*7*).

In this note we will describe a fundamental behavior of the CeO_2 in its reduction by hydrogen and carbon monoxide and in the oxidation by water and carbon dioxide. It is believed that CeO_2 works as an oxidation catalyst by its redox mechanism (*8, 9*). The oxidation–reduction behavior of CeO_2 may be worthy of a further study in connection with its role in catalysis. The effects of solid additives on the rates of reduction and oxidation of the oxide will also be described briefly.

The CeO_2 used was a reagent-grade powder (purity >99.9%) obtained from the Wako Pure Chemical Co. The BET surface area of the fresh CeO_2 was 18.8 $m^2\ g^{-1}$. The reduction (step 1) and oxidation (step 2) of the oxide were carried out using a conventional mercury-free gas-circulation apparatus of ca. 334 cm^3 volume, capable of achieving a vacuum to 1.3×10^{-4} Pa. Before each experiment of step 1, the sample oxide was calcined in an atmosphere of oxygen (ca. 1.3×10^4 Pa) at 873K and degassed in a vacuum for 2 hr at the same temperature. The water formed during step 1 was always condensed at 77K in a U-shaped trap placed in the gas circulation line. After CeO_2 had been reduced by hydrogen or carbon monoxide to a certain extent, the gases in the reaction system were pumped out; reoxidation of the reduced oxide (step 2) was then initiated by adding and circulating water vapor (2.1×10^3 Pa was kept constant during step 2) or carbon dioxide (2.13×10^4 Pa, initial pressure).

Open circles in Fig. 1 show an example of the kinetic curves of the consumption of hydrogen by the reduction of CeO_2 at 873K and that of subsequent formation of hydrogen from water accompanying the reoxidation of the reduced oxide at 573K. The kinetic curves for the reduction at 873K and oxidation at 673K by carbon monoxide and carbon dioxide, respectively, are also indicated in the figure by solid triangles. The results in the figure indicate that the oxidation by water in step 2 is much easier than that by carbon dioxide. The apparent activation energies of the reduction by hydrogen and carbon monoxide obtained from the Arrhenius plot of the rates at temperatures 773–973K were 156 and 112 kJ mol^{-1}, respectively; the rates of reactions were measured at 3.1%-degree of reduction of CeO_2 under the pressures of the reductants of $1.23 \pm 0.03 \times 10^{-4}$ Pa. These observations may be explained by the differences in enthalpy or in Gibbs-energy changes between reactions 1 and 2,

$$xH_2 + CeO_2 \rightleftharpoons xH_2O + CeO_{2-x}, \quad (1)$$

$$xCO + CeO_2 \rightleftharpoons xCO_2 + CeO_{2-x}, \quad (2)$$

i.e., the enthalpy change of the forward reaction of 1 is greater than that of 2, but this

0021-9517/83/020493-04$03.00/0

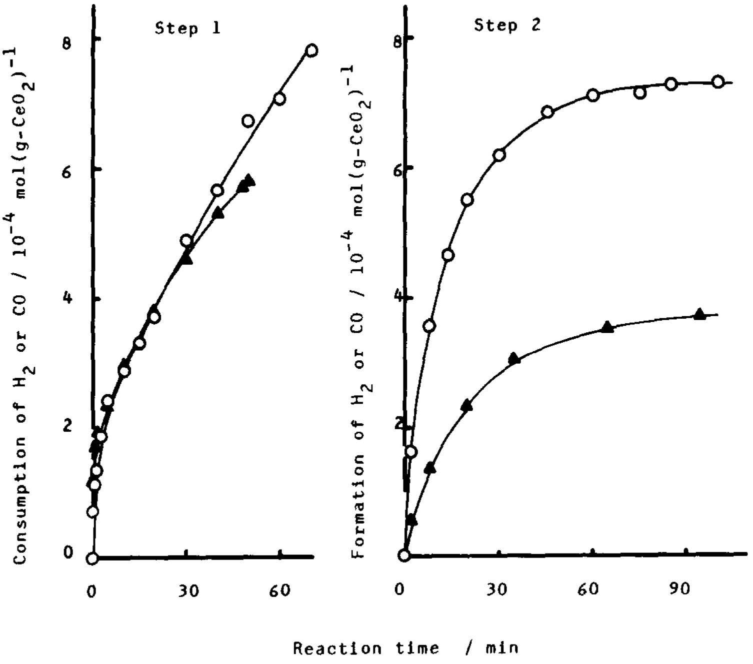

FIG. 1. Examples of kinetic curves for reduction and oxidation of cerium oxide. Step 1 was carried out at 873K under the initial pressure of 1.36 × 10^{-4} Pa of the reductants (○, H_2; ▲, CO). Step 2 at 573K for H_2O decomposition (○) and at 673K for CO_2 decomposition (▲).

is reversed for the backward reactions. As can be seen in the figure the recoveries in the amounts of hydrogen and carbon monoxide in step 2 are not complete compared to the quantities consumed in step 1. However, almost 100% recovery was observed for both cases when the temperature had been raised above 773K.

The reduction by hydrogen at 873K and reoxidation by water at 573K were repeated for seven cycles. The kinetic curves obtained for the cycles showed that the progress of the reaction is reproducible even after six cycles. The surface area of the sample decreased from 18.8 (fresh sample) to 14.1, 11.7, and 10.0 m^2 g^{-1} after first, second, and third reduction, respectively. The decrease in the surface area, however, did not reduce the rates of reduction and oxidation of the sample. Although it is difficult to explain this observation at the moment, the active sites which initiate or promote the reactions might not be uniformly formed on the surface.

The details of the thermodynamic and structural properties of CeO_y (y = 1.50–2.00) have been reported (*10, 11*). The system of the CeO_y displays a fluorite dioxide (CeO_2) and a hexagonal A-type sesquioxide ($CeO_{1.50}$) and some intermediate rhombohedral ($CeO_{1.71}$ or $CeO_{1.78}$; ι and ζ phases, respectively), triclinic ($CeO_{1.82}$; δ phase), or f.c. cubic ($CeO_{1.83}$; α′ phase) phases (*11*). In any intermediate oxides the metal ions occupy crystallographically equivalent positions regardless of charge. In addition, there is only a very small shift in position of the cations from one structure to another. When the oxide is oxidized or reduced all the change in the ionic position is virtually in the oxygen itself. Hence the structures of the reduced CeO_2 may be looked upon crudely as fluorite structures with anion vacancies. Under the experimental conditions applied in the present work, y in CeO_y was between 1.85 and 2.00. In this range, the inintial rate of hydrogen production from water at 573K was propor-

TABLE 1

Enhancing Effects of Additives on the Two-Step Hydrogen Production from Water

Additive	Weight % (mol%)	Rate in step 1 at 823K (10^{-8} mol s^{-1} g^{-1})	Rate in step 2 at 298K (10^{-8} mol s^{-1} g^{-1})	Time needed for 50% recovery in step 2 at 473K (min)
None	—	1.75	0.26	36
Pd	1.7	3.21	281	<2
Pt	1.9	2.30	323	<2
NiO	(2.0)[a]	3.86	175	<2
NiO	2.0	3.11	3.08	6
CuO	(2.0)[a]	3.01	10.7	<2
CuO	2.1	2.16	6.86	<2
SiO_2	2.1	3.91	n[b]	31
MgO	(2.0)[a]	2.29	n[b]	120
Al_2O_3	(2.0)[a]	1.55	n[b]	120

[a] The additives were added to CeO_2 in the form of their nitrates from aqueous solution. The nitrates were decomposed to the oxides during the pretreatment.

[b] The experiment was not carried out.

tional to the concentration of the anion vacancies created in step 1 at least at the initial stage of the reaction in step 2.

The effects of various additives on the rates of reduction and oxidation using hydrogen and water, respectively, were measured. The results are summarized in Table 1. Before each experiment the admixture of additive and CeO_2 was thoroughly ground in a mortar with a pestle. After a quick reduction of the added NiO and CuO at the very early stage (<2 min) in step 1, a steady reduction of CeO_2 was followed. The rates of the steady reduction shown in the third column were evaluated from the slopes of the kinetic curves at 2.5%-degree of reduction of CeO_2. All the samples reduced to 5.0%-degree of reduction of CeO_2 were subjected to the experiments in step 2. Marked enhancing-effects of Pt, Pd, Ni, and Cu were observed in step 2. Very fast hydrogen formation occurred in the presence of these metals even at room temperature. The enhanced rates at 473K were too fast to be measured accurately. Therefore, the results at 473K are demonstrated by the length of time needed for 50% recovery to CeO_2 in the fifth column of the table. The presence of these remarkable promoting effects of the additives indicates that neither diffusion process, such as oxygen ions, anion vacancies, reactants or products diffusions, can be a rate-determining step of the oxidation. The additives may exert catalytic effects by splitting HO–H bonds or spilling over some activated species, probably OH or O atoms, onto the surface of the reduced CeO_2. In the case of MgO and Al_2O_3, however, negative effects were observed in step 2. In addition, it is obvious from the table that some additives such as SiO_2, Pt, Ni, and Cu also promote the reaction in step 1, though the effect is insignificant compared to that in step 2. Further studies are necessary to give clear pictures of these observations.

REFERENCES

1. Tarman, P. B., *Proc. Synth. Pipeline Gas Symp.* **8,** 129 (1976).
2. Tarman, P. B., *Appl. Cryogenic Technol.* **7,** 22 (1978).
3. Otsuka, K., Takizawa, Y., Shibuya, S., and Morikawa, A., *Chem. Lett.* **1981,** 347.
4. Otsuka, K., Yasui, T., and Morikawa, A., *J. Catal.* **72,** 392 (1981).

5. Otsuka, K., Yasui, T., and Morikawa, A., *Bull. Chem. Soc. Japan* **55,** 1758 (1982).
6. Otsuka, K., Takizawa, Y., and Morikawa, A., *Fuel Process. Technol.* **6,** 215 (1982).
7. Otsuka, K., Murakoshi, S., and Morikawa, A., *Fuel Process. Technol.*, in press.
8. Minachev, Kh. M., Kondratiev, D. A., and Antoshin, G. V., *Kinet. Katal.* **8,** 131 (1967).
9. Hattori, T., Inoko, J., and Murakami, Y., *J. Catal.* **42,** 60 (1976).
10. Bevan, D. J. M., and Kordis, J., *J. Inorg. Chem. Nucl. Chem.* **26,** 1509 (1964).
11. Brauer, G., "Progress in the Science and Technology of the Rare Earth" (L. Eyring, Ed.), Vol. II, p. 312. Pergamon, Oxford, 1966.

Kiyoshi Otsuka
Masaharu Hatano
Akira Morikawa

Department of Chemical Engineering
Tokyo Institute of Technology
Ookayama, Meguro-ku,
Tokyo 152, Japan

Received August 2, 1982; revised October 7, 1982