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A pressure–temperature swing process for the methanation of carbon oxides using fluorinated hydriding alloys

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Abstract

A catalytic reaction process called the Pressure–Temperature Swing Process (P–T Swing Process) was developed in this laboratory for recovering carbon oxides by using fluorinated hydriding alloys. The process is based on the extreme reactivity of the monatomic hydrogen stored in the crystalline structure of the fluorinated metal hydride which exhibits high affinity with hydrogen and a strong resistance against impurities. The hydrogenation of carbon oxides takes place near the surface of the fluoride layer and produces methane and water while molecular hydrogen leaves the fluoride layer to the gas phase as the temperature and pressure is increased. The aim of this paper is to demonstrate the validity of the proposed process through experimental studies on 1000 ppm, 5% and 8% CO_2-containing H_2 gas mixtures during temperature switching between 2 isothermal conditions at 30 °C and 150 °C. The adsorbed CO_2 is found to be converted easily to CH_4 and water by the P–T swing process. The roles of the fluoride layer during hydriding and dehydriding reactions are as yet unknown and should be subjected to further detailed studies.

Keywords: Pressure–temperature swing process; Carbon oxide; Fluoride

1. Introduction

Metal hydrides have long been expected to be applicable for the separation and purification of low-grade hydrogen, and as catalysts. Many experimental studies have been performed in the past and these were extensively reviewed by Sandrock [1].

Durability of ordinary metal hydrides has been known to be poor against impurities such as water vapor, air, CO, CO_2, H_2S and others, mostly due to the high sensitivity of the surface [1]. Among 5 major shortcomings of the conventional hydriding alloys [2], the surface sensitivity must be the most important property to be improved.

The fluorinated hydriding alloys invented by this laboratory in 1991 [3] have been proved experimentally to exhibit strong resistivity against air and water [4–7] and impurities [8]. After then the fluorinated hydriding alloys have been found to function as excellent catalysts for the methanation of carbon monoxide and carbon dioxide to produce methane [9,10]. As the durability of the fluorinated surface during methanation reaction has been proved experimentally, a methanation process called the P–T Swing Process is proposed here with a series of experimental illustrations. Properties and characteristics of the fluorinated hydriding alloys are described in detail by Liu [11,12].

2. Principles of the P–T swing process

The proposed P–T Swing Process (Fig. 1) is composed of 4 processes, i.e.: (1) isothermal process at lower temperature and pressure for absorbing hydrogen molecules in the metal lattice as monatomic hydrogen and for adsorbing carbon oxides at the surface (1.2 in Fig. 1), (2) temperature upgrading process for methanation (2.3 in Fig. 1), (3) isothermal process at higher temperature for releasing the reaction products from the reactor system, (3.4 in Fig. 1), and (4) cooling process for the preceding absorption/adsorption process, (4.1 in Fig. 1). The following terms are given for individual processes for the sake of simplicity: (1) AB/AD Process for process 1.2, (2) Methanation Process for process 2.3, (3) Product Recovery Process for process 3.4, and (4) Recovery Process for process 4.1.

Hydrogen absorption by hydriding reaction and carbon oxides adsorption are performed during the AB/AD Process. After reaching the equilibrium conditions at T_L, the bed temperature is upgraded to T_H during the Methanation Process where the atomic hydrogen is released from the

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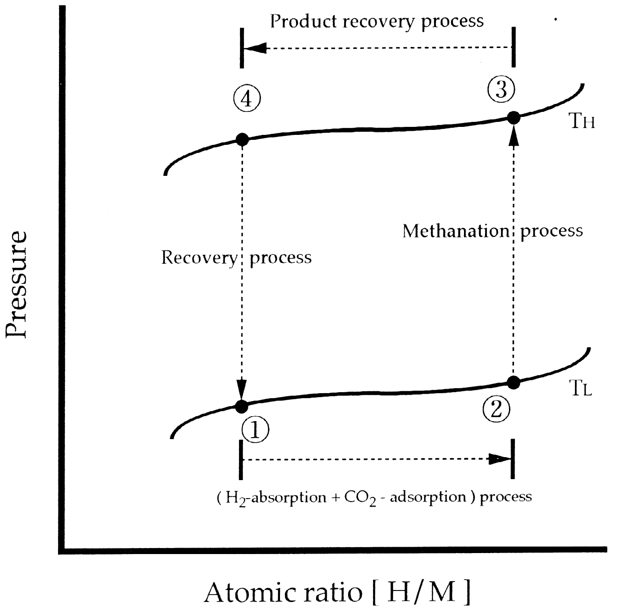

Fig. 1. Schematic diagram of the 4 processes in the P–T Swing Process.

bed to the fluorinated surface layer and reacts with carbon oxides to form methane and water. Along with the isotherm at T_H, the products and the non-reacted hydrogen and carbon oxides are released from the reactor to the outer space during the Product Recovery Process. Before the non-reacted gases are fed to the next reactor connected in series, the reaction products methane and water are recovered by conventional separation and condensation procedures. While the bed is cooled down in the Recovery Process to the lower temperature, T_L, the new feed gas is introduced to the reactor for the next AB/AD Process. These processes are illustrated in Fig. 2.

These 4 processes are operated in a cyclic manner by connecting at least 2 reactors in series until all carbon oxides in the reactor system are converted to CH_4 and water. The number of reactors to be connected depends on the concentration of carbon oxides in the gas mixture, and also on the overall surface area of the adsorption bed, i.e., the total surface area of the fluorinated metal hydride particles.

The reactions of CO_2 and CO at the surface are shown in Eq. (1) and Eq. (2).

In the case of the CO_2/H_2 gas mixture:

$$8H_{\text{in metal lattice}} + CO_{2\ \text{on fluorinated surface layer}} \rightarrow CH_{4\ \text{in gas phase}} + 2H_2O_{\text{coexisting in liquid and vapor phases}} \quad (1)$$

In the case of the CO/H_2 gas mixture:

$$6H_{\text{in metal lattice}} + CO_{\text{on fluorinated surface layer}} \rightarrow CH_{4\ \text{in gas phase}} + H_2O_{\text{coexisting in liquid and vapor phases}} \quad (2)$$

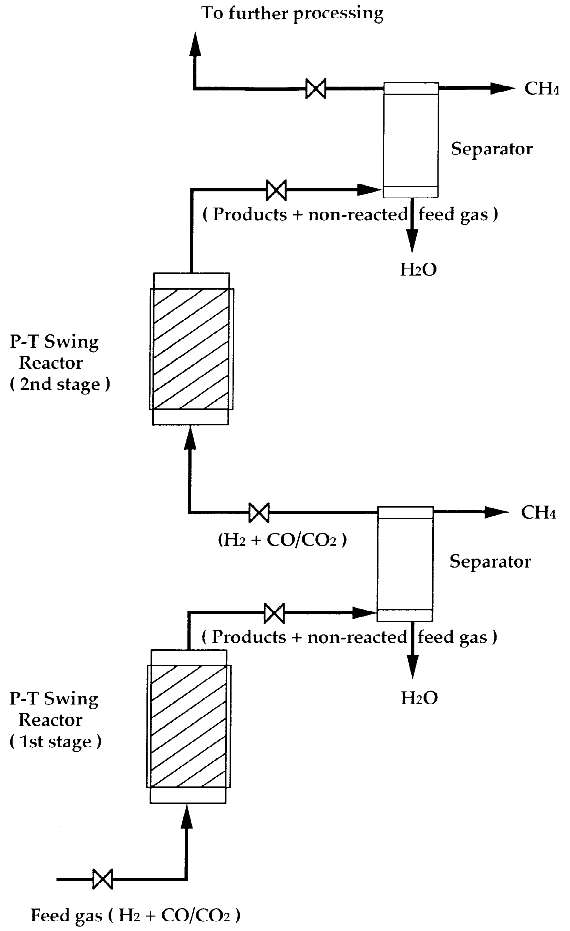

Fig. 2. Flow diagram illustrating the P–T Swing Process.

Adsorbed molecules such as CO and CO_2, and the unsaturated hydrocarbons are easily hydrogenated to form saturated hydrocarbons by extremely reactive atomic hydrogen before it leaves the surface as molecular hydrogen.

3. Experimental apparatus and procedures

The experimental apparatus is basically the same as a Sievert-type unit. The gas was introduced to a reactor system which contains 20 g of the fluorinated $LaNi_{4.7}Al_{0.3}$ along the absorption isotherm at 30 °C ($=T_L$ in Fig. 3). During this process H_2 gas is absorbed as atomic hydrogen in the crystalline lattice to form hydride and CO_2 is adsorbed on the surface (AB/AD Process).

Then the system is heated up to 150 °C ($=T_H$ in Fig. 3) until it reaches the equilibrium condition (Methanation Process). At this point, a small amount of gas sample was taken for gas chromatographic analysis where the pressure–composition relation turns to the desorption isotherm at 150 °C. These 2 processes were repeated in a cyclic manner from 3 times up to 20 times.

The total amount and concentration of the gas mixture introduced in each experiment was calculated from P–V–T

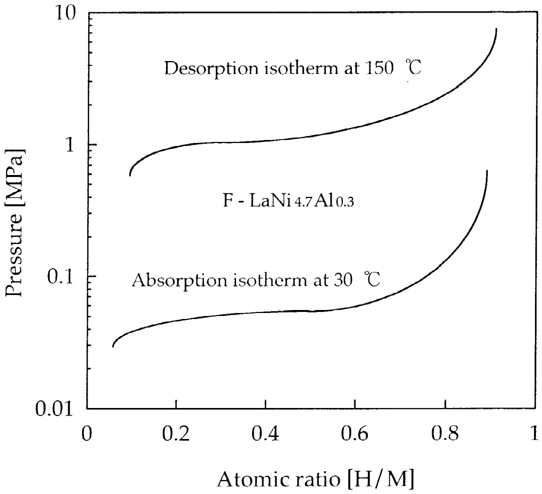

Fig. 3. Absorption and desorption isotherms of the fluorinated $LaNi_{4.7}Al_{0.3}$.

relations for gas phase and P–C–T relations for metal hydrides where the equilibrium adsorption pressure of CO_2 and the vapor pressure of water were thought to be negligible.

Data obtained by the gas chromatographic analysis was used for evaluating the ratio of CO_2 to CH_4 (designated the CO_2/CH_4 ratio) since the number of moles of CO_2 consumed is equal to that of CH_4 generated.

4. Experimental results

Methanation reaction by the P–T Swing Process was confirmed by performing experiments for 3 different CO_2-containing gases where the temperature and pressure were shifted in the ranges 303–423 K and 0.05–2.1 MPa, respectively.

4.1. Case 1

H_2 gas with 1000 ppm CO_2 was introduced in the reactor system. Then the CH_4 produced after 3 cyclic operations was analyzed by a gas chromatograph and the results are given in Fig. 4 as the CO_2/CH_4 ratio. After 3 cycles, no CO_2 was detected in the gas sample where the CO_2 in the feed gas was completely converted to CH_4. The durations of the AB/AD Process and the Methanation Process were 15 min each.

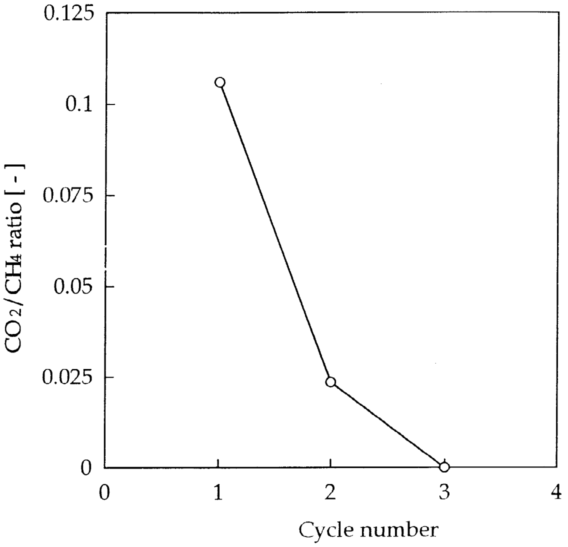

Fig. 4. The CO2/CH4 ratio during 3 P–T swings for the 1000 ppm CO2-containing hydrogen (Case 1).

4.2. Case 2

Hydrogen gas containing 5% CO_2 was subjected to the P–T Swing Process more than 20 times. The CO_2/CH_4 ratio is plotted as a function of the cycle numbers in Fig. 5. Water produced during the Methanation Process covers the particle surface as a liquid in equilibrium with its saturated gas phase and is supposed to slow the hydriding and dehydriding kinetics during these 2 processes. The time intervals required for the AB/AD and Methanation Processes are largely dependent on the heat-transmission characteristics of the reactor system (mostly of the thermal conductivity of the fluorinated hydride bed).

4.3. Case 3

Pure H_2 gas was introduced first and then CO_2 gas was introduced to the reactor system after reaching the equilibrium condition at 30 °C. These P–T Swing Processes were repeated 3 times. In this experiment, the CO_2 concentration was calculated to be about 8% as the gas was

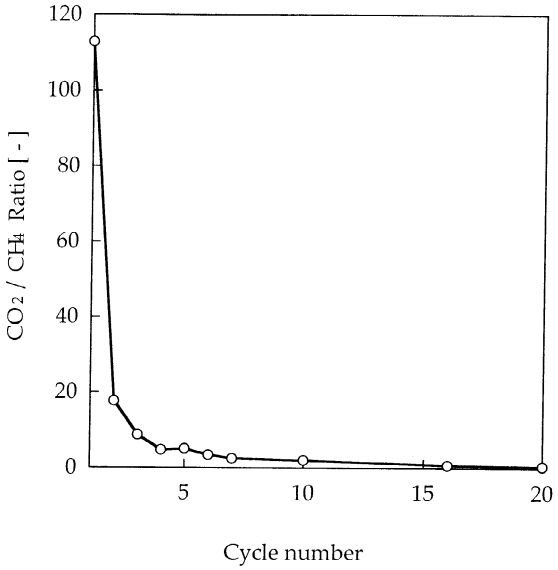

Fig. 5. The CO2/CH4 ratio during 20 P–T swings for the 5% CO2-containing hydrogen (Case 2).

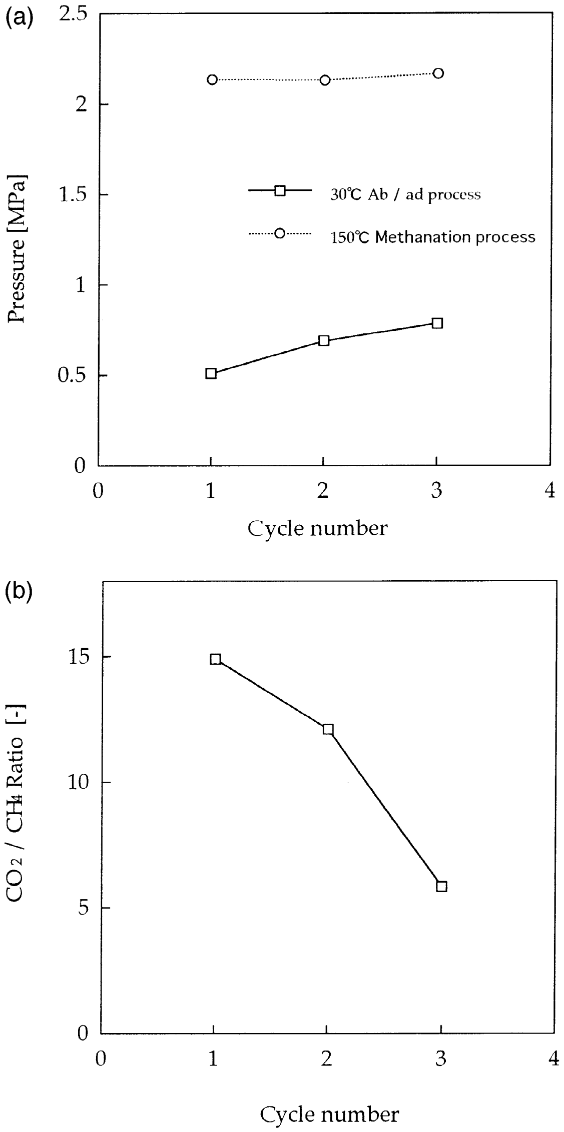

Fig. 6. (a) System pressure changes during 3 P–T swings at isothermal conditions of 30 °C and 150 °C (Case 3). (b) The CO2/CH4 ratio during 3 P–T swings (Case 3).

introduced in the reactor at 30 °C. Pressure changes during the process are given in Fig. 6a, and the CO_2/CH_4 ratio is shown in Fig. 6b. As the Methanation Process was repeated, the system pressure at 30 °C was increased during consecutive cycles.

For all experiments, no trace of by-products were detected through a mass spectrometric analysis other than CO_2, H_2, CH_4 and water. It is reasonable to consider that the reaction simply follows Eq. (1).

5. Discussion

In each experiment, the CO_2 concentration of the feed gas increases in the gas phase after the AB/AD Process due to the comparatively larger amount of H_2 being taken into the fluorinated hydride bed by hydrogenation. A simple material balance calculation indicates that the CO_2 concentration in the gas phase tends to increase from 1000 ppm to 9400 ppm in Case 1, and from 5% to 8.95% in Case 2.

A decrease of the CO_2/CH_4 ratio during cyclic operation is a clear sign of CH_4 formation at each cycle. From these results one can estimate that the CH_4 produced at the surface leaves instantly from the surface to the gas phase and that the CO_2 remaining in the gas phase is adsorbed simultaneously in place of CH_4 at the surface.

Although the water produced was neither detrimental for H_2 uptake nor poisonous against the fluorinated metal hydrides, it was the only rate-limiting factor in the proposed P–T Swing Process since it resulted in an increase of the system pressure.

The pressure increase at 30 °C (Fig. 6a) after 3 preceding processes is explained by the accumulation of liquid water in the compressed region which covers the fluorinated hydride particle surfaces. It acts as a barrier for the hydrogen uptake at the interface between the gas and particle surface. Due to this reason, the hydrogen gas released in the Methanation Process is returned only with difficulty to the bed at the next AB/AD Process, and, as a result, the partial pressure of hydrogen in the gas phase is increased after repeating the cycle.

On the other hand, little pressure changes were observed in experiments at 150 °C (see Fig. 6a) under system pressures between 2.2 and 2.4 MPa, and the water produced was compressed, the saturated vapor pressure being only 0.476 MPa at 150 °C.

From the above observations it is suggested that the produced water should be removed such that after completion of the Methanation Process at $T_H = 150$ °C, the reactor bed is maintained at the same temperature during the Product Recovery Process and then the system pressure is lowered while the temperature is kept at 150 °C so that the water exists as a superheated vapor in the course of the Recovery Process.

This was achieved by transferring all gas phase materials, including the non-reacted and/or the surplus H_2 and CO_2, to another reactor at lower pressure and higher temperature conditions. Water vapor and methane can be separated by an ordinary condensation technique during the transfer procedure between two reactors.

6. Conclusions

Fluorinated hydride alloys are applicable as methanation catalysts without being influenced by carbon oxides and by products such as methane and water.

Carbon dioxide is successfully converted to methane by the proposed P–T Swing Process. The P–T Swing Process is considered applicable as an industrial process for both the production of methane from carbon oxides and for the separation/purification of low-grade hydrogen.

Formation of liquid water can be avoided in the AB/AD Process by keeping it in the superheated vapor state under moderately high-temperature conditions. From a technical viewpoint, however, the water and methane produced are easily separated by a conventional condensation technique in non-reacted gases where the products are transferred to the next reactor.

It is important to prepare the fluorinated hydriding alloy particles with higher specific surface areas in order to recover carbon oxide molecules efficiently. The efficiency of the proposed process depends on the specific surface area of the fluorinated hydride particle.

Acknowledgments

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