Utilization of carbon dioxide is one of the most significant subjects in environmental technologies. A common idea is reducing carbon dioxide to carbon monoxide or methane, which are valuable in industry. Though it is rather easy technically, the problem is how hydrogen can be supplied more cheaply. Supplying pure gaseous hydrogen is easiest but most costly. One solution is to supply hydrogen in the form of hydrocarbons. Even if the reactions work, some remaining questions need to be answered. The first is if the dehydrogenation products from the hydrocarbons used are valuable in industry. The second is how the products will be separated. This study may give an answer to both the questions. A cyclic operation experiment of catalytic cyclohexane dehydrogenation and carbon dioxide hydrogenation was carried out successfully using LaNi5 particles as a catalyst and as a hydrogen reservoir. Five kinds of LaNi5 particles ranging from 10 to 725 μm in mean diameter were used. After a 30-minute activation of LaNi5 using hydrogen at 673 K, carbon dioxide and cyclohexane flowed through the LaNi5 particles bed for each 30 minutes at 673 K alternatively. The cycle was repeated four times. When cyclohexane was fed, cyclohexene, benzene and hydrogen were detected as products. Cyclohexane conversion increased with decrease in the mean diameter of LaNi5, i.e., with increase in external surface area per unit mass of alloy. When carbon dioxide was fed, carbon monoxide formed. Hydrogen also was detected in the outlet gas. Carbon monoxide yield also increased with decrease in the mean diameter of LaNi5.

1 Introduction

Membrane separation reactors are promising reaction device because of the following advantages compared with conventional reactors as follows.

(1) Reduced downstream separation load [1]
(2) Improved conversion for equilibrium-limited reactions [1]
(3) Direct heat exchange when the reaction at one side is exothermic and another is endothermic [2]

As their potential industrial importance increases, a lot of studies of membrane separation reactors have begun to appear in increasing numbers. At the viewpoint of the roles of the membrane material, membrane separation reactors are classified into the following three categories.

Category 1: Selective (semi-selective) permeation material
Category 2: Selective (semi-selective) permeating material and catalyst for the one side reaction.
Category 3: Selective (semi-selective) permeating material and catalyst for the both side reactions.

If we restrict the field of membrane reactors to hydrogen permeation one, still a huge number of studies have been reported. Though papers belonging to the categories 1 [3] and 2 [4] are easily found, those to the category 3 are rare. If the membrane material has all the three functions, it is very convenient. For the time being, as a hydrogen-permeating membrane, palladium is the best-known one because of its hydrogen permeating function and hydrogenation/dehydrogenation activity [5]. The problem is that palladium is very expensive and endangered as natural resource. Meanwhile, we carried out an experimental study for screening appropriate catalysts for the following reaction [6].

cyclohexane + CO2 \rightarrow \text{cyclohexene} + \text{CO} + \text{H}_2\text{O} \quad (1)

The purpose of this previous study is to utilize carbon dioxide as an oxidizing agent. The corresponding product expected is carbon monoxide, which is a rather versatile chemical raw material. When we think of more efficient ways to carry out the reaction (1), breaking down the reaction as follows is an interesting one.

cyclohexane \rightarrow \text{cyclohexene} + \text{H}_2 \quad (2)
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3)
Combining the consideration of searching better membrane materials with the idea of the divided reaction, we tried to choose an appropriate material for the membrane. Onoe et al. [7-9] studied and reported catalytic hydrogenation of carbon monoxide on rare earth-nickel type hydrogen storage alloys extensively. Since the surface of rare earth-nickel type hydrogen storage alloys segregates a nickel phase and a La$_2$O$_3$ phase [10], they are expected to have also dehydrogenation activity. Besides it is known the alloys allow hydrogen to permeate selectively. Therefore it seems very promising to choose LaNi$_5$ as a membrane material. Before a membrane reactor is designed and fabricated, a cycle operation experiment was carried out (Fig. 1) as a preliminary work, which allowed us to know if the material LaNi$_5$ works as we expected.

Figure 1. Schematic diagram of membrane reactor (left) and cycle operation of fixed-bed reactor (right).

In this study, an experimental investigation was conducted to see if the material LaNi$_5$ is applicable to a membrane reactor in which the membrane material have all the three functions, i.e., permeation, and the activities for reactions at the both side. One is hydrogenation of carbon dioxide, another dehydrogenation of cyclohexane.

2 Experimental

Figure 2 shows an experimental setup used in this study for cyclic operation of catalytic
cyclohexane dehydrogenation and carbon dioxide hydrogenation. This consisted of a reactor (a Pyrex tube of 10mm internal diameter) and feed gas regulation system. LaNi₅ particles used in this study were prepared as follows. LaNi₅ purchased from Japan Metals & Chemicals Co. Ltd. was crushed and sieved to obtain four sieved fractions, whose average diameters were 29, 51, 94 and 725 μm. Particles of 10 μm diameter were obtained by disintegrating the particles of 51 μm diameter with 20 cycles of hydrogen adsorption/desorption. The average diameter of the disintegrated particles was determined by SEM photograph inspection.

One gram of LaNi₅ particles was packed into the reactor, and was pretreated with hydrogen (50 cm³-NTP/min) at 673 K for 30 min. A cyclic operation was started with hydrogenation of carbon dioxide. Carbon dioxide (30 cm³-NTP/min) diluted with argon (200 cm³-NTP/min) flowed through the packed bed to form carbon monoxide at 673 K for 30 min. The stage of carbon dioxide hydrogenation was followed by a stage of cyclohexane dehydrogenation. In the stage of cyclohexane dehydrogenation, cyclohexane (4 cm³-NTP/min) diluted with argon (296 cm³-NTP/min) flowed through the bed to form cyclohexane and benzene at 673 K for 30 min. The first cycle consisted of those two stages described above, i.e., carbon dioxide hydrogenation and cyclohexane dehydrogenation. The reactant gas was sampled by a gas syringe, and was analyzed by a gas chromatograph.

3 Results and Discussion

Figures 3 shows the results of the cycle experiment (time course data) for 29 μm LaNi₅. It includes the yield of carbon monoxide, the yield of benzene+cyclohexene, and hydrogen concentration in the exit gas. Figure 4 shows the effect of the particle size on the carbon monoxide yield and the hydrogen concentration in the exit gas.
Carbon dioxide yielded carbon monoxide at CO2 period (Fig. 3(a)). Cyclohexane yielded benzene and cyclohexene at CA period (Fig. 3(b)). As shown in Fig. 3(c), hydrogen evolution was also observed regardless of the feed gas, though the concentration at CA period is higher than that at CO2 period. These results obviously mean that hydrogen yielded from cyclohexane dehydrogenation was absorbed by LaNi5 at CA period and desorbed at CO2 period, where part of hydrogen was consumed to reduce carbon dioxide at LaNi5 surface.

In Fig. 4, the carbon monoxide yield and the hydrogen concentration in the exit gas are approximately proportional to the reciprocal of the particle size, or the specific external surface area of LaNi5 particles. This implies that mass transfer rate of external surface and/or reaction rate at external surface is the rate-determining step.

Figure 5 shows a schematic picture of the CO2 and CA periods. At CO2 period, carbon dioxide yields carbon monoxide at the surface consuming hydrogen in LaNi5. Part of the absorbed hydrogen is simply desorbed. At CA period, cyclohexane yields benzene and cyclohexene to form hydrogen at the surface. Part of the hydrogen is absorbed by LaNi5, the rest goes to bulk flow.
4 Conclusions

LaNi₅ was found to be a promising membrane material for membrane separation catalytic reactor because the alloy had all the three functions required, i.e., hydrogen permeation, and the activities for reactions at the both side.

References