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A tubular reactor for continuous hydrogenation of oleic acid under moderate conditions using a thin hydride layer of hydrogen Storage alloy $LaNi_{4.8}Cu_{0.2}$ as catalyst

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Abstract

The hydrogenation of oleic acid to stearic acid, over hydrogen storage intermetallic compound $LaNi_{4.8}Cu_{0.2}$ as catalyst, at 90°C and 0.5 MPa hydrogen pressure was investigated. It is found that the $LaNi_{4.8}Cu_{0.2}$ alloy has very good activity, when it is hydrided before the addition of oleic acid. The hydriding process is rather quick and is generally completed in a few minutes. Based on the results obtained, a tubular reactor for continuous operation was designed, tested and proved to work well.

Keywords: Metal hydride; Hydrogenation; Oleic acid; Catalysis; Tubular reactor

1. Introduction

Our previous research work has shown that, for hydride hydrogenation, the specific activities of hydrogen storage intermetallic compounds are generally much higher than those of the traditional industrial catalysts [1–3], and only their specific surface is much lower, hence they have not been adopted in production. In this paper, we are introducing a new scheme, where the hydrogenation reaction is completed at a lower temperature and lower hydrogen pressure over the active surface of hydrided hydrogen storage alloy as catalyst sintered on the surface of a tubular reactor.

2. Experimental procedures

2.1. Catalyst preparation

The intermetallic compounds used as catalysts were prepared by induction melting the constituent metals on a water-cooled copper boat under argon atmosphere. The small ingots obtained were pounded and crushed into powder passing through 500 mesh. Prior to the catalysis experiment, alloy powder samples were all first activated in a reactor by absorbing and desorbing hydrogen once. BET method was employed to measure surface areas based on the amount of N_2 absorbed.

2.2. Hydrogenation in reactors

Both batch reactor and continuous tubular reactor were tested.

2.2.1. Batch type reactor

Two batch experiments on the catalytic activity of intermetallic compounds were carried out in a 1 l stainless steel reactor. In the first experiment, the reactor was first filled with 30 g catalyst, evacuated and then charged with hydrogen to a pressure of 0.5 MPa at room temperature. Alloy powder was hydrided almost instantly and, then 60 g (0.318 mol) oleic acid was introduced. Hydrogenation started immediately and proceeded quickly.

In the second experiment, the reactor was filled with 30 g catalyst and 60 g oleic acid. The reactor temperature was adjusted to 90°C, a few degrees above the melting point of stearic acid (70°C). Then hydrogen at 0.5 MPa presume was introduced. As the surface of the alloy was covered with oleic acid, the powder did not come into contact with hydrogen directly. No metal hydride was formed before the liquid was agitated. When the liquid was stirred around with a electromagnetic stirrer turning at 1400 rpm, a hydrogenation reaction was observed. Hydrogen pressure and pressure drops were measured and recorded at regular

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time intervals. Each time a pressure drop was recorded, hydrogen was supplied to raise the pressure to its original value to keep the hydrogen pressure variation small. From the hydrogen pressure recorded at regular time intervals, hydrogen consumption, and hence the activity of the catalyst could be calculated:

$$\text{relative activity} = \Delta \text{mol}_{H_2}/\Delta t = k\Delta m_{H_2}/\Delta t$$

As the volume and the temperature were kept constant and the pressure variation was small, by substituting into the gas equation $\Delta PV = \Delta mRT$, we obtained

$$\text{relative activity} = \text{k}\Delta p_{H_2}/\Delta t$$

2.2.2. Tubular reactor

As shown schematically in Fig. 1, the reactor consisted of two concentric pipes 1 m in length, the inside diameters of which were 50 mm and 20 mm respectively. The inner pipe was made of compacted sintered stainless steel powder. On its outer surface a thin layer of catalyst powder (0.9–1.0 mm thick) was coated by compacting and sintering at 950°C in a hydrogen flow. The thickness of the wall was 10 mm with 21% effective porosity. The outer tube was a regular stainless steel pipe. The whole setup was immersed in a water thermostat kept at 90°C.

During testing, oleic acid was made to flow though the outer pipe and hydrogen flow though the inner. The rate of oleic acid flow in the pipe was 0.279 mg/s and the pressure of hydrogen was 0.5 MPa. While flowing, hydrogen diffused through the porous wall matrix to the catalyst layer and reacted with intermetallic compound to form metal hydride, and a small part of hydrogen entered the liquid directly. This part of hydrogen flowing into the liquid acted as a mixer for the liquid phase. Over the metal hydride, continuous hydrogenation of oleic acid was being carried out. As atomic hydrogen on the interface of catalyst was consumed by the oleic acid it was replenished by diffusion from the metal hydride with higher hydrogen content automatically, from inside.

2.2.3. Chemical analysis

The oleic acid used was chemically pure and the hydrogen used was of 99.9999% purity. The stearic acid was analyzed with infrared (IR) qualitatively and with anhydride titrimetry quantitatively. In this research work, the iodine value (IV) was determined by titration according to ASTM 01959-69. From test results, calculation can be made as follows:

$$\text{IV preservation fraction} = (\text{IV after reaction})/(\text{IVofoleicacid}) \times 100\%$$

3. Results and discussion

In the first batch experiment, 5 min were sufficient for hydriding $LaNi_{4.8}Cu_{0.2}$ into $LaNi_{4.8}Cu_{0.2}H_{4.5}$. And during subsequent hydrogenation of oleic acid the hydrogen gas pressure remained constant over the entire reaction period. This indicated that oleic acid reacted only with hydrogen from metal hydride and reacted fast. We believe that, as the volume concentration of hydrogen in $LaNi_{4.8}Cu_{0.2}H_{4.5}$ is very high, hydrogen released from the hydride is in atomic state, the metal hydride provides active hydrogen atoms to the molecule of oleic acid directly at its surface, and many steps in the traditional catalyst reaction including the dissolution of hydrogen into oleic acid and subsequent chemical adsorption of hydrogen onto the catalyst surface are all omitted, the chemical activity for hydrogenation can be very high.

From this experiment, we know also that the formation of hydride is faster than the hydrogenation of oleic acid over the hydride. Based on this phenomena, we conceived the idea of building a tubular hydrogenation reactor.

However, in the second batch experiment, hydrogen molecules must first be dissolved into the liquid phase, which is a slow step, even at high stirrer speed. As illustrated in Fig. 2, the rate of hydrogen consumption decreases linearly with time of operation. We believe that the concentration of available hydrogen in the liquid phase is approximately constant and the total reaction rate changes with the amount of oleic acid left in the reactor. This can be expressed as:

$$\text{d}[\textit{stearic acid}]/\text{d}t = -\,\text{d}[H_2]/\text{d}t = k[\textit{oleic acid}]/\text{d}t$$

It can be inferred from Fig. 2 that no metal hydride has been formed in the process. Otherwise, the experimental curve would deviate greatly from the straight line. Calcula-

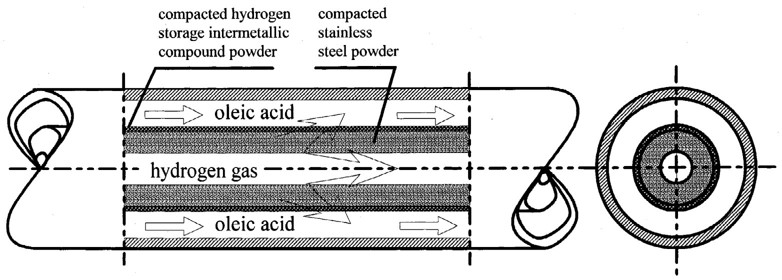

Fig. 1. Structure of the continuous tubular hydrogenation reactor.

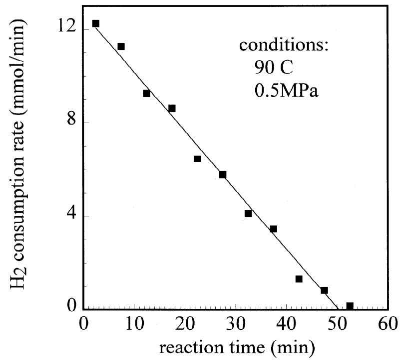

Fig. 2. The catalytic activity of $LaNi_{4.8}Cu_{0.2}$ alloy in the second series batch hydrogenation of oleic acid.

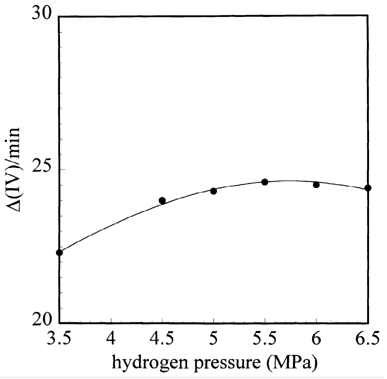

Fig. 3. The hydrogenation speed increases with hydrogen pressure slightly in the range from 3.5 to 6.5 MPa over the pressure plateau of the $LaNi_{4.8}Cu_{0.2}$ hydrogen storage alloy as catalyst.

Table 1
The experimental results of hydrogenation of oleic acid over $LaNi_{4.8}Cu_{0.2}$ alloy at 90°C and 0.5 MPa

Reactor type	Formation of metal hydride	Hydrogenation time (min.)	IV	IV preservation fraction (%)	Δ(IV)/min.
Batch	yes	4.8	0.301	0.34	18.25
Batch	no	52	0.487	0.55	1.68
Batch[a]	yes	6.5	2.541	0.21	13.49
Continuous tank[a]	yes	5.96[b]	0.378	0.43	14.69[b]
Continuous tank	yes	3.58[b]	0.405	0.45	24.3[b]

[a] Hydrogenation of 0.6 M oleic acid solution of butanol at 25°C.

[b] Calculated from 60 g oleic oil pass through the catalyst pipe.

tion confirms that the actual hydrogen consumption from the triangular area under the straight line is 0.625 mol, close to the theoretic amount of hydrogen for hydrogenation of 60 g oleic acid, 0.636 mol, and the fraction of conversion calculated is 0.9827 which is close to the experimental fraction of conversion (=1−IV preservation fraction), 0.9945.

The continuous system proved to be very efficient. As shown in Table 1, the conversion and decrease of IV per min. are all very high, compared with the industrial values, 0.86 Δ(IV)/min. in a batch reactor over Rainy nickel as catalyst at 1.4–1.6 MPa hydrogen pressure [4]. In our experiments, the reaction rate, Δ(IV)/min, increased with hydrogen pressure slightly, as shown in Fig. 3. We believe this is probably due to stronger agitation of the liquid phase due to a stronger flow of hydrogen into the oleic acid. This flow pushes the viscous stearic acid formed away from catalyst surface. On the other hand, if the agitation of hydrogen gas is too violent, the adsorption of the oleic acid molecule onto the catalyst surface will be difficult.

Adding some kind of solvent, such as butanol, lowers the melting point of stearic acid allows the reaction to be carried out at a lower temperature. This, however, leads to a lower Δ(IV)/min for the butanol solution as indicated in Table 1.

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