Clusius' Separation Column as a Reactor to Produce Highly Concentrated Hydrogen

Kozo Hirota, Kazuo Aizawa, and Tsuneyuki Nishizawa

Chiba Institute of Technology, Tsudanuma, Narashino-City 275, Japan

Dedicated to Professor Dr. G.-M. Schwab on his 80th Birthday

A Clusius' separation column of hot wall catalytic activity was applied as a reactor to produce highly concentrated hydrogen. Satisfactory results are obtained in the decomposition of hydrogen sulfide and the conversion of carbon monoxide with water.

Forty years ago, a powerful separation column, based on thermal diffusion and thermal convection, was invented by Clusius [1]. One of the present authors (K.H.) got the idea to use the column as a reactor with hot wall catalytic activity. This idea resulted from the expectation that some reactions would proceed to completion if one of the products would be separated in the column automatically. Due to thermal diffusion such an effect will occur if the molecular weight of one product differs much from those of the other products and the starting gas.

The above idea was found to work in the decomposition of methane and the polymerization of acetylene and ethylene [2]. It is the intent of this paper to present two new and interesting examples.

(A) Decomposition of hydrogen sulfide
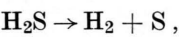
$$H_2S \rightarrow H_2 + S,$$

(B) Conversion of carbon monoxide

$$CO + H_2O \rightarrow CO_2 + H_2.$$
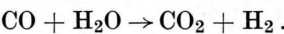
Reaction (A) $H_2S \rightarrow H_2 + S$

When a usual reactor is used, the equilibrium concentration of hydrogen at 500 °C is <1%. In order to test the separation method, three columns made of pyrex glass and equipped with quartz pipe heaters and water jacket coolers were used (Table 1). The surface of the hot wall was coated with catalysts such as sulfides of chromium, cobalt, nickel or iron.

The column was filled with a batch of hydrogen sulfide under 1 atm. Shortly after the experiment was begun, due to heating the pressure increased to a maximum value of ca. 1.5 atm. The hydrogen

Correspondence to: Kozo Hirota, 1532-246 Nagasakucho Chiba-City 281, Japan.

concentration as observed at the top of the column is plotted vs. time in Figs. 1 and 2. After 4 hrs, the stationary state was nearly reached. The activity of the catalysts in column C, at a wall temperature of 500 °C, increased in the order: chromic sulfide > cobalt sulfide > nickel sulfide > iron sulfide. The catalytic activity did not decrease during a 35 to 45 hrs operation.

Table 1. Dimensions of the thermal diffusion columns (length of the pipe heater = 100 cm; length of the column = 128 cm).

Column	Hot wall diameter (mm)	Heater	Cold wall diameter (mm)	Wall distance (mm)	Total volume (ml)
A	12	Fe-Cr ribbon	24	6	500
B	12	Fe-Cr ribbon	32	10	870
C	12	Fe-Cr wire	24	6	500
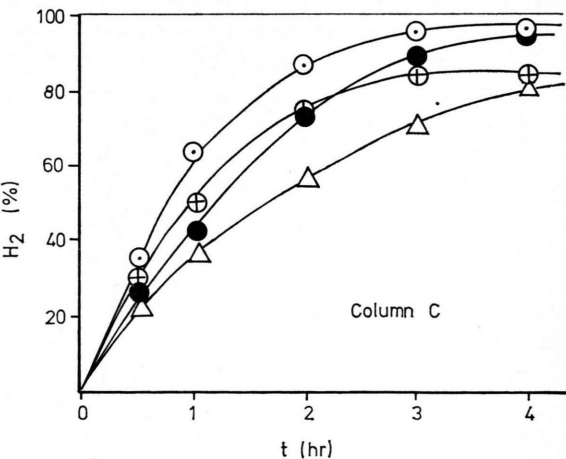
Fig. 1. Hydrogen concentration at the top of Column C vs. time. $T = 500$ °C. Catalyst: ⊙ Cr_2S_3, ● NiS, ⊕ CoS, △ FeS.

Fig. 2. Hydrogen concentration at the top of the Column vs. time. Column A: ⊙ 500 °C, ⊕ 450 °C, ● 400 °C; Column B: △ 500 °C.

The other product is elementary sulfur, which condenses on the cold wall in a half melting state and flows down slowly.

The distribution of hydrogen along the column height is shown in Figure 3. If hydrogen would be withdrawn from the top, while hydrogen sulfide is fed slowly and continuously at the bottom, all hydrogen sulfide could be decomposed into hydrogen and elementary sulfur [3].

Reaction (B) $H_2O + CO \rightarrow H_2 + CO_2$
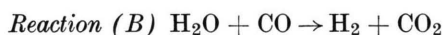
It is known that at 250—350 °C and with an active catalyst the reaction B proceeds easily to the equilibrium state, which still contains CO. An inert gas as nitrogen remains in the product. For a test of the column method a stainless steel column was constructed (see Figure 4). The hot wall of the column was coated with a carbon filament impregnated with Cr_2O_3-CuO-ZnO (1:1:2 by metal weight). In order to absorb carbon dioxide and to supply water vapor a reservoir of sodium hydroxide solution was situated at the bottom of the column.

To begin with, the accumulation rate of hydrogen at the top of the column was investigated. From the linearity of the plot of $\ln(1 - (H_2)_t/(H_2)_\infty)$, see Fig. 5, the rate can be expressed by

$$(H_2)_t = (H_2)_\infty [1 - \exp(-kt)], \qquad (1)$$

where $(H_2)_t$ and $(H_2)_\infty$ are the hydrogen concentrations at times t and ∞, respectively. The constant k was dependent on the hot wall temperature T_h, the starting gas pressure P_2 and the
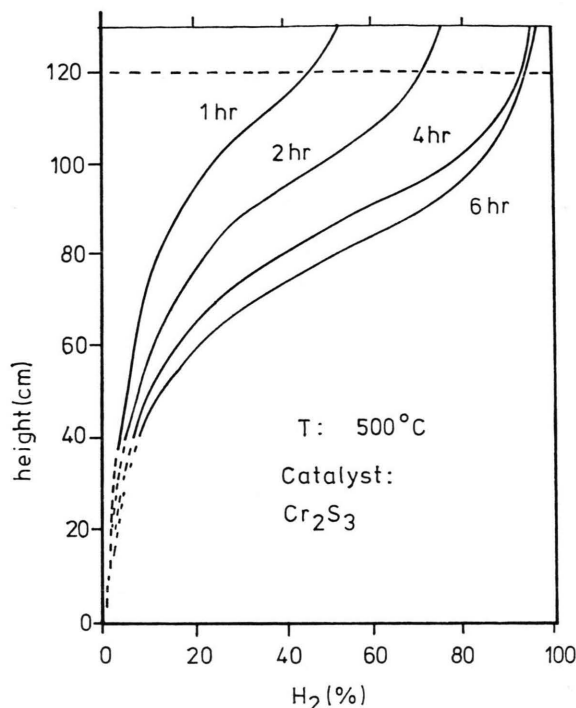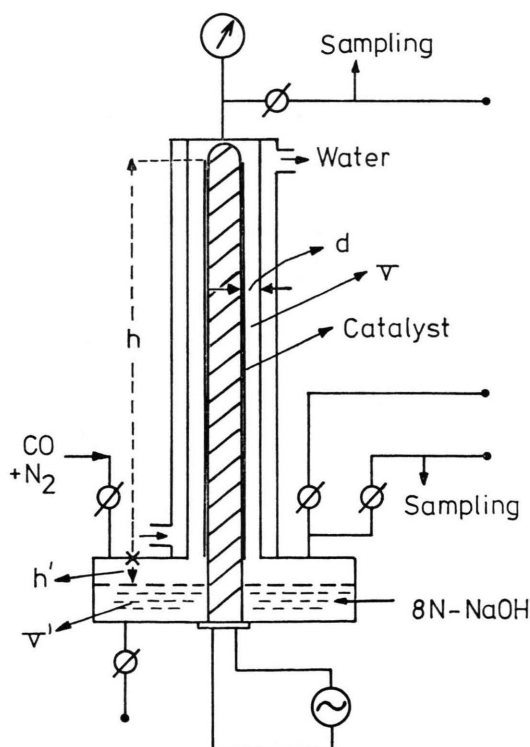

Fig. 3. Distribution of hydrogen in Column A.

Fig. 4. Apparatus for Reaction B, $h = 100$ cm, $h' = 2$ cm, $d = 6.5$ mm, $V = 500$ ml, $V' = 1600$ ml.
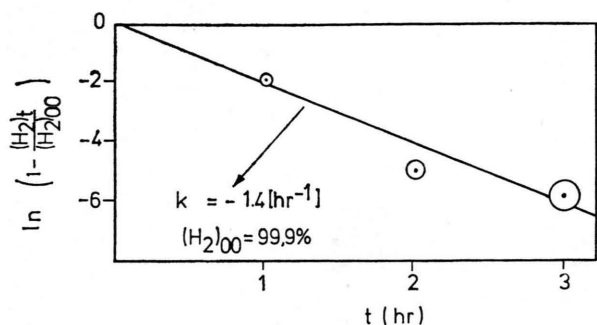
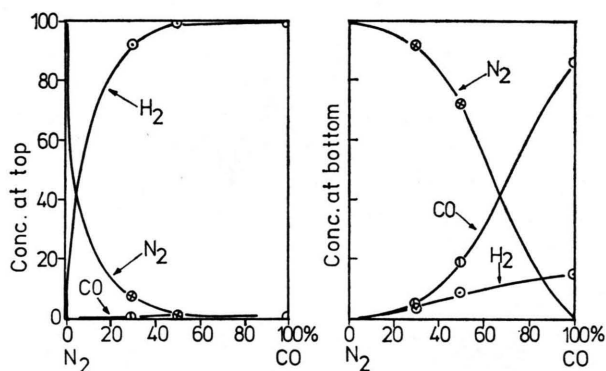Fig. 5. Accumulation rate of hydrogen to check Equation (1). CO 100%, 1 atm, $T_h \cdot 300\,°C$.

Table 2. Dependence of k on T_h.

Temp. (°C)	250	300	350
k (hr^{-1})	0.77	(ca. 1), (ca. 2), 2.0	3.7

nitrogen concentration in the starting gas C_n. The dependence of k on T_h is shown in Table 2, where the k values in brackets correspond to starting gases $CO/N_2 = 3:7$ and $5:5$, respectively. From these data, the apparent activation energy for enrichment is estimated to be 10 ± 10 kcal.

Highly concentrated hydrogen can be easily obtained with $C_n \approx 100\%$ and $P_s = 2$ atm. The concentration reached 99% at $250\,°C$ and nearly 100% at $300-350\,°C$. Noteworthy points of the extended experiments, which will be published elsewhere [4], are as follows:

i) The hydrogen concentration at the top of the column decreases with increasing nitrogen concentration in the starting gas, but it reaches 80% even if the starting gas contains 30% CO and 70% N_2 at $P_s = 2$ atm and $T_h = 300\,°C$ (see Figure 6).

ii) High P_s is found to be more favorable at $300\,°C$, i.e. if P_s is 1 atm, the ratio H_2/CO becomes 30 and if P_s is 2 atm this ratio becomes 300. This is due to the accelerated rate of carbon monoxide removal from the reacting system.

Fig. 6. Concentration of the components after 3 hrs vs. CO% in the starting gas.

[1] K. Clusius and G. Dickel, Naturwiss. **26**, 546 (1938); Z. Phys. Chem. **44**, 397 (1939).
[2] K. Hirota, Bull. Chem. Soc. Japan **16**, 274 (1941).
[3] T. Nishizawa, Y. Tanaka, and K. Hirota, Nippon Kagaku Kaishi **1977**, 929.
[4] To be published, Nippon Kagaku Kaishi.