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ADJUSTING THE HYDROGEN-CARBON MONOXIDE RATIO IN SYNTHESIS GAS BY POLYSTYRENE-COPPER ALUMINATE COMPLEX

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The molar ratio of hydrogen to carbon monoxide in synthesis gas, which has the initial molar ratio of 1.25 and is saturated with water, is adjusted to a desired value by the selective separation of carbon monoxide by the absorbent composed of polystyrene, cuprous chloride, aluminum chloride, and toluene.

Synthesis gas, prepared by the steam reforming of petroleum and natural gas or the water gas reaction of coal, is an important starting material for the production of many kinds of chemicals in industry. These processes, however, do not directly provide gas suitable for the industrial application. For example, the molar ratio of hydrogen to carbon monoxide in the synthesis gas appropriate for the syntheses of hydrocarbons by the Fischer-Tropsch reaction is around 2, although that in a typical water gas is 1.25.1) Thus, the adjustment of the hydrogen-carbon monoxide ratio is required for effective usage of synthesis gas. In addition, synthesis gas is saturated with water (23000 ppm at 20°C) after water washing. Consequently, the adjustment of the hydrogen-carbon monoxide ratio in their mixture must be done in the presence of a considerable amount of water.

In the previous paper,2) the solution composed of polystyrene, cuprous chloride, aluminum chloride, and toluene (polystyrene-copper tetrachloroaluminate complex solution : polymer complex solution) exhibited reversible absorption of carbon monoxide under 1 atm, and the absorption activity of the solution remained unchanged during the contact with a nitrogen gas containing 8960 ppm of water.

In this paper, it will be shown that the molar ratio of hydrogen to carbon monoxide in the mixture, which has the initial molar ratio of 1.25 and contains water corresponding to the vapor pressure 17.5 mmHg 3) at 20°C (the water content of the gas 23000 ppm), is adjusted to a desired value by the selective separation of carbon monoxide by the absorbing solution described previously.2)

Polystyrene of the number-averaged degree of polymerization of 1600-1800, purchased from the Wako Pure Chemical Co., was reprecipitated using the chloroform-methanol system and was dried in vacuo overnight at room temperature. Aluminum chloride was purified by sublimation. Cuprous chloride, the guaranteed reagent of the Koso Chemical Co., was used without further purification. Toluene was distilled after being dried by metallic sodium.

The polystyrene-copper aluminate complex solution was synthesized by keeping 10 milli equivalent of polystyrene, 10 mmol of cuprous chloride, 10 mmol of aluminum chloride, and 10 ml of toluene in a 30 ml flask at 40°C for 4 h under the atmosphere of dry nitrogen. The carbon monoxide-hydrogen mixture containing 23000 ppm of water was prepared at 20°C by the introduction of the required amounts of carbon monoxide and hydrogen to a gas burette using water as the leveling liquid, and was then transfered into a flexible air bag.

The air bag containing the carbon monoxide-hydrogen mixture was attached to the 30 ml flask containing the polymer complex solution, after the gas phase of the flask was evacuated. The contact of the polymer complex solution, continuously stirred by using a magnetic stirrer, with the carbon monoxide-hydrogen mixture was initiated by opening the cock between the air bag and the flask, and was carried out at 20°C under the atmospheric pressure.

After 10 min the air bag was disconnected from the flask. The amounts of hydrogen and carbon monoxide in the bag were evaluated from the total volume, determined by using a gas burette, and the concentrations of them, determined by gas chromatography (Molecular Shieve 5A, 2 m, 50°C). The water in the gas was also analyzed by gas chromatography (Porapak T, 2 m, 165°C).

The release of the gas absorbed by the polymer complex solution was effected by the elevation of the temperature to 90°C. Prior to it, the inside of the flask was charged with dry nitrogen. The released gas was trapped in an empty air bag. The analysis on the content of the bag, which should contain the vapor of toluene in addition to the absorbed gas, was carried out in a similar way as above.

Table 1 lists the compositions of the gases obtained by the treatment of the feed gas of the hydrogen-carbon monoxide ratio 1.25 containing 23000 ppm of water with the polystyrene-copper aluminate complex solution for 10 min. The values can be regarded as those at the equilibrium between the gas phase and the polymer complex solution, since they are almost identical with the values determined after the contact of the feed gas with the polymer complex solution for 1 h.

It is clearly seen that the molar ratio of hydrogen to carbon monoxide in the gas, left in the gas phase after the treatment of the feed gas with the solution, is considerably increased from the initial value 1.25. The ratio increases with the decrease in the quantity of the feed gas. The water content in the gas phase is almost identical with that in the feed gas.

The gas absorbed by the polymer complex solution at 20°C and released at 90°C is pure carbon monoxide, the amount of which is equal to the difference between the value in the feed gas and that in the gas phase on the solution within experimental error. No hydrogen is observed. Thus, the increase in the hydrogen-carbon monoxide ratio in the gas phase on the polymer complex solution is definitely attributed to

Table 1 Adjusting gas compositions by treatment with polystyrene-copper aluminate complex solution[a]

Feed gas (mmol)			Product gas (mmol)							
			Gas phase after the treatment with the solution at 20°C				Released at 90°C after absorption with the solution at 20°C			
H_2	CO	H_2O	H_2	CO	H_2/CO	H_2O	H_2	CO	H_2/CO	H_2O
20.0	16.0	0.83	20.0	11.7	1.7	0.83	0.0	4.3	0.0	0.00
			20.0[c]	11.6[c]	1.7[c]	0.81[c]	0.0[c]	4.3[c]	0.0[c]	0.00[c]
10.0	8.0	0.41	10.0	4.3	2.3	0.41	0.0	3.7	0.0	0.00
5.0	4.0	0.21	5.0	1.5	3.3	0.20	0.0	2.4	0.0	0.00
20.0[d]	16.0[d]	0.83[d]	20.0	12.4	1.6	0.00	0.0	3.5	0.0	0.00
			20.0[c]	13.2[c]	1.5[c]	0.00[c]	0.0[c]	2.8[c]	0.0[c]	0.00[c]

a. Polystyrene, 10 milli equivalent; cuprous chloride, 10 mmol; aluminum chloride, 10 mmol; toluene, 10 ml; unless otherwise noted.

b. 1.25 hydrogen-carbon monoxide ratio, containing 23000 ppm of water.

c. Retreatment of the solution with the feed gas of the same composition, prepared independently, after the gas absorbed by the solution in the first treatment had been released.

d. In these runs the solution was composed of 10 mmol of cuprous chloride, 10 mmol of aluminum chloride, and 10 ml of toluene in the absence of polystyrene.

the fact that carbon monoxide in the feed gas is selectively absorbed by the polymer complex solution with hydrogen remaining intact.

After the absorbed carbon monoxide was released at 90°C, the polymer complex solution was retreated with the feed gas of the same composition, prepared independently. In the second treatment, the solution showed almost the same separating activity as that in the first treatment without apparent deterioration.

Table 1 also shows the results for the solution composed of 10 mmol of cuprous chloride, 10 mmol of aluminum chloride, and 10 ml of toluene (copper aluminate complex solution : complex solution), which was prepared in the same way as above except for the absence of polystyrene. The amount of carbon monoxide (3.5 mmol) absorbed from the feed gas composed of 20 mmol of hydrogen, 16 mmol of carbon monoxide, and 0.83 mmol of water by the copper aluminate complex solution is 0.8 mmol smaller than that (4.3 mmol) absorbed by the polymer complex solution, resulting in a smaller ratio of hydrogen to carbon monoxide in the gas phase on the complex solution. The amount of carbon monoxide (2.8 mmol) absorbed by the complex solution on the retreatment of the feed gas of the same composition is considerably smaller than that (3.5 mmol) in the first treatment, which is in contrast with the result for the polymer complex solution.

The poorer separating activity of the copper aluminate complex solution than that of the polystyrene-copper aluminate complex solution is ascribed to the deactivation of the complex solution by the irreversible reaction with the water in the feed gas.[4,5] This interpretation is based on the following results.

1) In the separation by the complex solution, the water in the feed gas is not detected either in the gas phase or in the released gas. In the separation by the polymer complex solution, however, virtually all of the water in the feed gas remains in the gas phase.
2) In the separation of carbon monoxide from the hydrogen-carbon monoxide mixture containing no water, the complex solution shows almost the same activity as the polymer complex solution.
3) The separating activity of the complex solution decreases as the repeating number of the treatment with the feed gas containing water increases.

The strong resistance of the polystyrene-copper aluminate complex solution against water is probably associated with specific orientation and restricted movements of the adjacent aromatic rings of polystyrene. Due to the interactions with the aromatic rings of polystyrene, the toluene molecules in the vicinity of polystyrene have specific orientations and restricted movements, resulting in a rigid solvation cage. The copper aluminate complex is located in this cage and is protected from water.

In conclusion, the adjustment of the hydrogen-carbon monoxide ratio in synthesis gas saturated with water is achieved by the treatment with the polystyrene-copper aluminate complex solution.

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