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CO Shift Reaction on the Potassium Polyaluminate Catalyst

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Synopsis. Potassium polyaluminate (β_K''-alumina) has been employed as a catalyst for CO shift reaction ($CO+H_2O=CO_2+H_2$). The dependence of catalytic activity on the K^+ content was investigated. The initial reaction rate abruptly increased above 11 wt% K_2O.

Alkali polyaluminates, of which β-alumina has been classified into β, β', and β'',[1)] have the characteristic layer structure[2)] and are solid electrolytes with high ionic conductivity.[3)] Alkali polyaluminates are also effective as catalysts for the steam reforming reaction of hydrocarbons;[4,5)] fuel gas of good quality and rich in hydrogen gas can be produced. They are also applicable to atmospheric and vacuum residue oil of inferior quality, and considered to be important materials in view of effective utilization of petroleum energy sources. The catalytic ability of alkali polyaluminates lies mainly in enhancement of water gas shift reaction and gasification of carbon.[4,5)] This is characteristic of basic catalysts and is exibited in the steam reforming reaction of inferior hydrocarbons. In the present study, potassium polyaluminate (β_K''-alumina) has been employed as a catalyst for CO shift reaction ($CO+H_2O=CO_2+H_2$) in order to investigate the dependence of catalytic activity on the K^+ content.

Experimental

The powder of β_K''-alumina (Kyushu Taika Renga Co. Ltd.) was pressed into cylindrical pellets, diam 20 mm and thickness 3 mm, under the pressure of 500 kg/cm^2. After the pellets had been calcined at 1300 °C for 1 h in an electric furnace, they were crushed into particles, 1—3 mm in diam Samples with lower K^+ content were obtained by eluting K^+ with purified water, HCl solution, and H_2SO_4 solution. Those with higher K^+ content were prepared by calcining β_K''-alumina pellets containing excess K_2CO_3. The procedure and K_2O content of the samples obtained are given in Table 1. For determination of the K_2O content by flame photometry, the sample was dried at 300 °C for 1 h and dissolved in H_2SO_4–$(NH_4)_2SO_4$ aqueous solution.

The initial rate of the CO shift reaction was measured at 600 °C under differential conditions using a reaction vessel of the normal-pressure flow system. 0.8 g of the catalyst (particle size 14—20 mesh) was diluted with 17.2 g fused alumina (particle size 12—20 mesh) which had been confirmed to be non-active as a catalyst. The volume of the catalyst bed was 10 ml and its height 2 cm. The center of the catalyst bed was placed at the highest temperature region in the reaction tube. The stainless sheath thermocouple (chromel-alumel, JIS 0.75 grade) protected by a high alumina tube was inserted in the center of the catalyst bed, the temperature being controlled by a proportional position temperature regulator (CHINO, NS 141). The temperature fluctuation in the catalyst bed was within ±2.5 °C, the prescribed temperature being controlled within ±5 °C.

Table 1. Specimens

Specimen NO.	Preparation process	Phase[a)]	K_2O content[b)] wt%
1	$+K_2CO_3$	β''-alumina	14.5
2	$+K_2CO_3$	β''-alumina	14.4
3	$+K_2CO_3$	β''-alumina	12.1
4	No Treatment	β''-alumina	11.4
5	Elution (H_2O)	β''-alumina	11.0
6	Elution (H_2O)	β''-alumina	10.4
7	Elution (H_2O, boiled)	β''-alumina	9.1
8	Elution (HCl, boiled)	β''-alumina	4.1
9	Elution (H_2SO_4, 200 °C)	β''-alumina	1.2

a) Determined by X-ray diffraction method. b) By flame photometry.

Gas sampling was performed after the reaction reached steady state, and the composition of the gas was analyzed by means of a gas chromatograph (Gasukuro Kogyo, KOR-70). Molecular sieves of 5A, 13X, and silica gel were used as separating columns for CO, H_2, and CO_2, respectively. The area under the chromatogram was measured with a digital integrator (Shimadzu, ITG 4A), the gas composition being determined by the absolute calibration method. The error of mass balance of the reaction was within *ca.* ±3%.

Results and Discussion

The initial reaction rate generally depends on the feed gas composition.[6)] However, no dependence was observed in a preliminary experiment with use of specimen NO. 4. Thus, the feed gas composition was fixed as $P_{H_2O}/P_{CO}=1$, the total pressure being 1 atm.

The initial rate of the CO shift reaction obtained at 600 °C as a function of K_2O content in β_K''-alumina is shown in Fig. 1. The abrupt variation in the initial rate was found at *ca.* 11 wt% K_2O content. The result indicates that the surface state of β_K''-alumina with over 11 wt% K_2O differs from that with less than 11 wt% K_2O. The samples with less than 11 wt% K_2O also show the X-ray diffraction pattern of β_K''-alumina structure (Table 1), suggesting that H^+ or H_3O^+ ions undergo exchange with K^+ ions in the solid structure. However, the ions might not have been distributed homogeneously in the bulk, the concentration of K^+ ions near the surface being assumed

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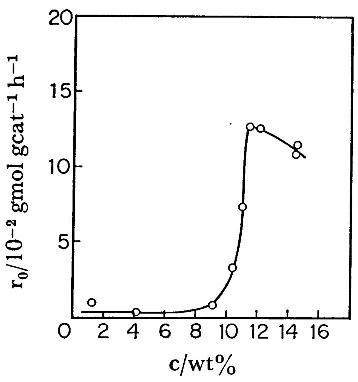

Fig. 1. Initial reaction rate *vs.* K_2O content obtained at 600 °C.

to be lower than expected. If this was the case, the result suggests that K^+ ion on the catalyst surface acts as an active center for the reaction.

The abrupt variation in the initial rate is also understandable if two kinds of K^+ ions exist, one as an active center but easily eluted by water or acid, the other being non-active but stable against elution.

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