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HIGH CATALYTIC ACTIVITY OF CsCl SUPPORTED ON SILICA GEL FOR THE SELECTIVE DEHYDROCHLORINATION OF 1,1,2-TRICHLOROETHANE

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CsCl supported on a particular silica gel dryed at 120 °C exhibited a remarkable activity for the selective dehydrochlorination of TCE into 1,1-DCE after the calcination around 500 °C. The proper heat-treatment before and after the impregnation of CsCl on the silica gel strongly influenced the activity of the catalyst.

A catalytic dehydrochlorination process of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethylene (1,1-DCE) is most wanted, since the present process is stoichiometric, losing hydrogen chloride as well as the base used as the eliminating reagent.[1,2] The difficulty of this process is that the selective formation of 1,1-DCE is performed only by basic substances.[3] ICI has claimed the catalytic activity of CsCl supported on an unspecified silical gel.[4] The activity is not large enough for practical purposes with silical gel available around the laboratories. The catalytic deactivation was one of reasons for low activity.

In the present study, the catalytic activities of CsCl supported on a particular silica gel were studied using a pulse reactor to find the best state of the silical gel support because CsCl exhibited a remarkable catalytic activity only when it supported on the suitable silica gel. The heat-treatment before and after the impregnation of CsCl was examined to reveal how surface hydroxyl groups influence catalyst performance.

A micro bead silica gel (MB-3A, Fuji Davison Chem.Co., surface area 650 m^2/g) preheated at 120 — 600 °C was added to a solution of CsCl in dry methanol. By removing the solvent under reduced pressure, white powders of CsCl impregnated on SiO_2 (CsCl/MB-3A :CsCl 11 wt%) were obtained and dried at 150 °C.

The catalytic dehydrochlorination of TCE over $CsCl/SiO_2$ was investigated in the temperature range of 150 — 350 °C by a pulse reactor[5] (carrier gas and its flow rate : H_2 and 60 cm^3 min^{-1}, catalyst: 1 g, pulse size: 2 μl, analyzing column: tricresylphosphate (4 m, 60 °C)). The catalyst was calcined in the reactor under hydrogen flow at 150 — 600 °C for 2 h before the first pulse.

Dehydrochlorination conversions of TCE over $CsCl/SiO_2$-120 (preheated at 120 °C,

1 g) calcined at 500 °C are plotted against the pulse number in Figure 1, where the pulse interval was fixed 1 h at 250 °C. TCE was very selectively converted into 1,1-DCE (85%). The conversion stayed at 100% until 5th pulse at 250 °C, and then decreased rapidly to be leveled off at 30% at 9th pulse. The treatment at 350 °C for 1 h after 11th pulse recovered the complete conversion in the successive pulse. In the following pulses (13th and 14th pulse), the conversions were same to those at 7 to 8th pulses, respectively. Only a part (around 50%) of hydrogen chloride produced in the pulses was collected during the reaction. The rest was recovered by the treatment at 350 °C. Such cycles of dehydrochlorination and regeneration could be repeated at least five times. During the initial eleven pulses before the regeneration, 0.27 mol of TCE per mole of CsCl were dehydrochlorinated into 1,1-DCE.

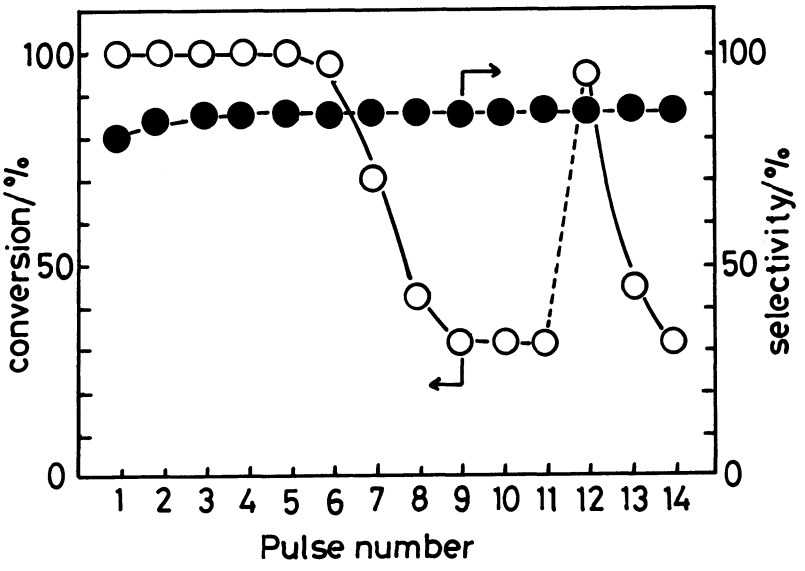

Fig.1. Catalytic activity of $CsCl/SiO_2$ - 120 at 250 °C in the repeated pulses.
calcination: 500 °C - 2 h, reaction conditions: catalyst amount 1 g, pulse size 2 μl, pulse interval: 1 h at the reaction temperature except for the intervals between 11 and 12th pulses, where the temperature was 350 °C

A hundred percent conversion was observed at 200 and 150 °C until 6th pulse when 1 g of the catalyst was used. The leveled off conversions at 200 and 150 °C were 20 and 15%, respectively. The selectivity was better at the lower temperature. The catalytic activity was again restored by the heat-treatment at 350 °C.

A steady conversion of ca. 20% (catalyst 1 g, partial pressure of TCE 7.6 mmHg) was observed at 250 °C with a flow reaction for 10 h .

Figure 2 illustrates the catalytic activity and surface area of $CsCl/SiO_2$ at several preheat-treatment temperatures. The surface area of the as-received silica gel was 650 m^2/g. It stayed at the same value below 400 °C of the preheat-treatment temperature, however, it decreased gradually above the temperature. It was 430 m^2/g at 600 °C. In a marked contrast, the catalytic activity in the first pulse decreased rather sharply along with the preheat-treatment temperature. The conversion over $CsCl/SiO_2$-120 (1 g, calcined at 250 °C) was over 95%, whereas that over $CsCl/SiO_2$-600 (1 g, calcined at 250 °C) was as low as 15%. Thus, the preheat-treatment before the impregnation of CsCl influenced the catalytic activity much more significantly than the surface area of the support.

Table 1 describes the conversion from the first to third pulses at 150 °C over $CsCl/SiO_2$-120 (0.2 g) after the calcination at 300 to 600 °C. The conversion in the first pulse increased from 26 to 85% with the rising calcination temperatures from 300 to 500 °C, and then decreased to 75% at 600 °C. The conversions in the second and third pulses decreased very much at this level of the catalyst amount, still depending on the calcination temperature. The selectivity (around 95% at this reaction temperature) was not affected at all by the calcination temperature. Catalytic activities of CsCl supported on some other commercial silica gels (C-200

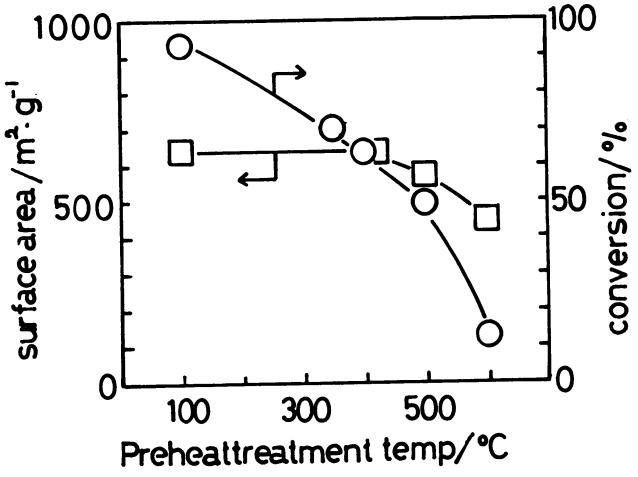

Fig.2.
Influences of preheat-treatment on the surface area of the silica gel and the activity of its supporting CsCl catalyst (1st pulse conversion).
calcination: 250 °C - 2 h, reaction conditions: catalyst amount 1 g, pulse size 2 µl, react.temp. 250 °C,

Table 1.
Activities of $CsCl/SiO_2$ [a] for dehydrochlorination of TCE after variable calcination temperatures. [b]

Calcination temperature °C	Pulse [c] number	Conversion %	1,1-DCE selectivity %
300	1 st	26	94
	2 nd	6	95
	3 rd	3	95
400	1 st	67	94
	2 nd	18	95
	3 rd	7	95
500	1 st	85	94
	2 nd	40	94
	3 rd	14	94
600	1 st	75	93
	2 nd	44	94
	3 rd	21	93

a) preheat-treatment temp : 120 °C,
b) reaction conditions: catalyst amount 0.2 g, reaction temp 150 °C, pulse size : 2 µl

Wako 280 m^2/g, Aerosil-200 200 m^2/g) were much smaller than that on MB-3A.

Above all results suggest the importance of silica gel supports in this catalysis, although they have been believed an inert support.[6] The origin of high activity due to MB-3A and its proper heat-treatment before and after the impregnation is not defined at present. Surface hydroxyl groups on the silica gel may play important roles at the stages of CsCl impregnation and basic dehydrochlorination. Spectroscopic study on the group is now in progress.

A combination of a catalytic elimination and a catalyst-regeneration using CsCl on the silica gel may allow a practical process of selective 1,1-DCE synthesis with the recovery of hydrogen chloride.

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