

Catalytic Dehydrochlorination of 1,1,2-Trichloroethane(TCE) into
1,1-Dichloroethene(DCE) over Cesium Nitrate Supported on Silica Gel

Isao MOCHIDA,* Yoshinori YASUMOTO, Hiroshi FUJITSU, and Yasuhiro KOJIMA[†]
Institute of Advanced Material Study, Kyushu University 86,
Kasuga, Fukuoka 816

[†]Tosoh Inc., Kaiseicho, Shin-nan-yo, Yamaguchi 746

Catalytic activity of silica gel-supported cesium salts was examined for the dehydrochlorination of TCE into DCE by recovering hydrogen chloride. Among the salts, CsNO_3 showed the best activity, although it was converted into CsCl during the reaction. High dispersion of CsNO_3 on silica gel may be a major reason of the high activity.

1,1,2-Trichloroethane(TCE) is dehydrochlorinated into 1,1-dichloroethene(DCE) selectively in an industrial scale by the stoichiometric reaction with sodium or calcium hydroxides.¹⁾ However, the process is evaluated to be one of the most energy consuming processes since sodium hydroxide is reproduced through the electrolysis of sodium chloride. Catalytic process of such a selective elimination assuring the recovery of hydrogen chloride may attract extensive study.²⁾ Sufficient life of the catalyst as well as the high activity(above 50% conversion) and selectivity(at least above 80%) are the targets of the study.

The present authors have been involved in such studies, however no sufficient performances applicable for the practical process has been obtained, although many indications of such catalyses have been reported.³⁻⁶⁾ Among them, CsCl supported on a particular silica gel(Fuji-Davison Chem. Co., MB-3A) was found to exhibit significant activity. However, the selectivity could not exceed 70% at higher conversion levels.^{5,6)}

In the present letter the authors are going to report the effects of the kind of cesium salt supported on a conventional silica gel on the catalytic performances, CsNO_3 being certainly better than other cesium salts.

Catalysts were prepared by the impregnation of CsCl , CsNO_3 , CH_3COOCs , Cs_2SO_4 , and Cs_2CO_3 on to silica gel (Wako Jun-yaku, Co., C-200; loading level 20 wt%) from their aqueous solution, drying, and calcining in air at 673 K for 2 h. Cesium salts were commercially available GR grade and used without further purification. TCE (Wako Jun-yaku Co., Sp. Gr.) was used without further purification.

Catalytic activity was examined by using a pulse reactor and a flow reactor with a fixed catalyst bed. The catalyst was pretreated in a H_2 flow at the reaction temperature for 2 h. Typical reaction conditions were as follows: reaction temperature 573-673 K, catalyst 0.5 g, pulse size 2 μl , the interval between pulses 15 min, and H_2 carrier 60 ml min^{-1} for the pulse reactor, and reaction temperature 573-723 K, catalyst 1 g, partial pressure of TCE 0.05 atm, and a total flow rate 70 ml min^{-1} (H_2 carrier) for the flow reactor. TCE and reaction products were analyzed by a gas-chromatograph.⁵⁾

Figure 1 illustrates the catalytic activities of cesium salts supported on silica gel, which were measured at 573 K by means of the pulse reactor. CsNO_3 , CH_3COOCs , and Cs_2CO_3 exhibited high activities of 30-45% conversion of TCE in the first pulse and high selectivities around 90% (other products were 1,2-dichloroethenes). The conversions decreased markedly to 2 to 12% in the second or third pulse. These conversions were maintained in the successive pulses. CsNO_3 provided the largest stationary conversion of 11-12%. In contrast, CsCl and Cs_2SO_4 had very low activities around 5% even in the first pulse. Heat-treatment at 673 K for 30 min recovered the activity in the next pulse very markedly for CsNO_3 , and moderately for Cs_2CO_3 , CsCl , and CH_3COOCs , but no increase was observed for Cs_2SO_4 .

CsNO_3 supported on silica gel exhibited a stationary activity in the

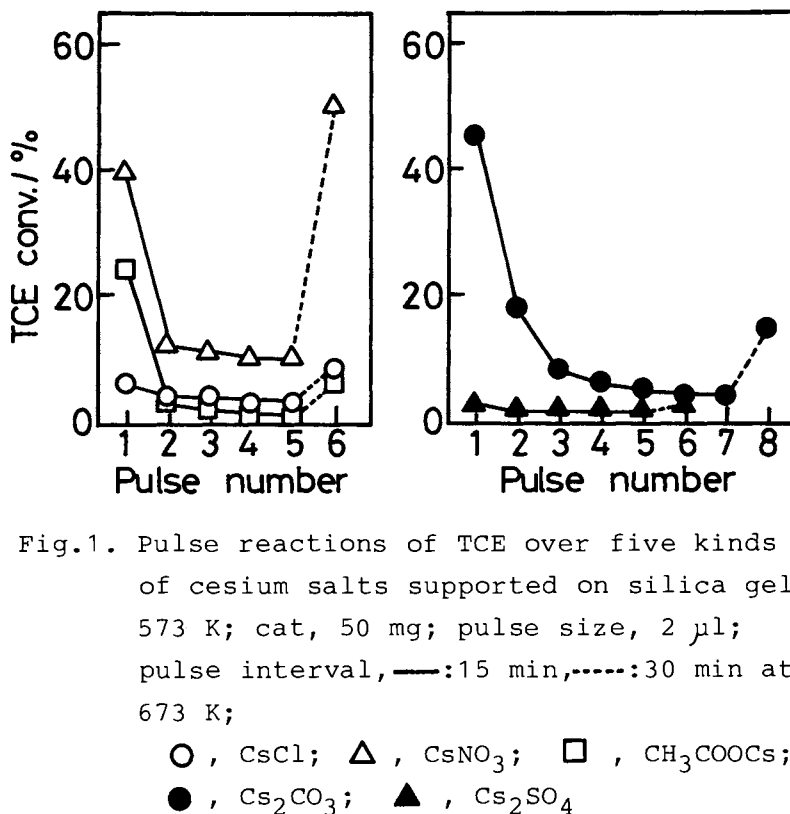


Fig.1. Pulse reactions of TCE over five kinds of cesium salts supported on silica gel. 573 K; cat, 50 mg; pulse size, 2 μl ; pulse interval, —:15 min, ----:30 min at 673 K;

○, CsCl ; △, CsNO_3 ; □, CH_3COOCs ;
●, Cs_2CO_3 ; ▲, Cs_2SO_4

flow reactor at TCE partial pressure of 0.05 atm. As shown in Fig. 2(a) and (b), the stationary conversions and selectivities were 5 and 85% at 573 K, and 18 and 82% at 623 K, respectively, for longer than 2 h. Higher reaction temperatures gave higher conversion and slightly lower selectivity, which were 35 and 80% at 673 K, and 75 and 75% at 723 K, respectively (Fig. 2(c) and (d)). The both reaction orders of TCE conversion and DCE formation in TCE were calculated to be 0.5.

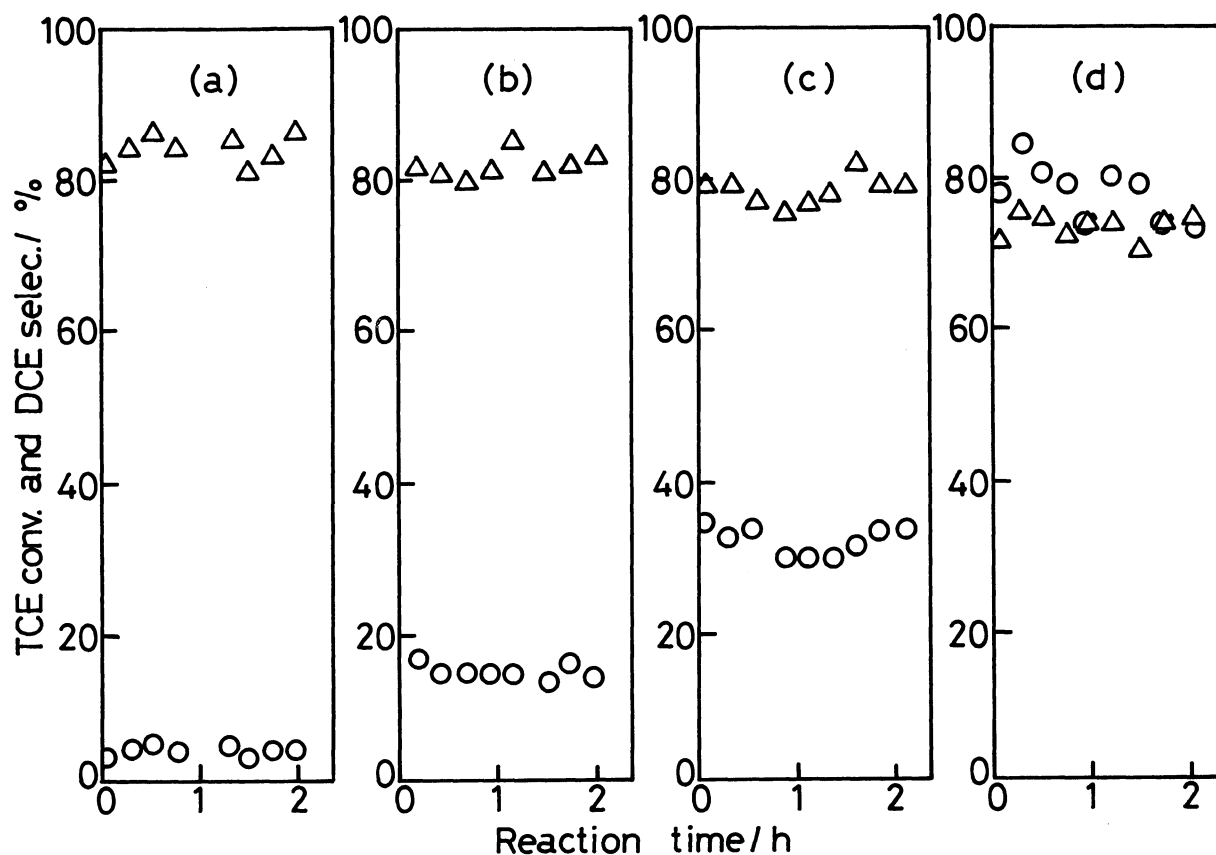


Fig.2. Reaction profiles of TCE over $\text{CsNO}_3/\text{SiO}_2$ at variable reaction temperatures in the flow reactor.
 react temp.: (a) 573 K, (b) 623 K, (c) 673 K, (d) 723 K;
 cat., 1 g; TCE, 0.05 atm; ○ : TCE conv.; Δ : DCE selec.

The X-ray diffraction measurements of CsNO_3 supported on silica gel before and after the catalytic reaction in the flow reactor revealed that CsNO_3 was converted into CsCl after the reaction. Very broad diffraction profiles for CsNO_3 and the produced CsCl on silica gel suggest their high dispersion. CsCl directly supported on silica gel gave much sharper profiles of X-ray diffraction.

The present letter revealed that CsNO_3 supported on a conventional

silica gel exhibited the highest catalytic activity among cesium salts examined in the present study for the dehydrochlorination of TCE into DCE by recovering hydrogen chloride. The selectivities for DCE were maintained above 75% in the conversion range of 5 to 75%. Thus, CsNO_3 supported on silica gel exhibited the best performance among the catalysts which the present authors have prepared.³⁻⁶⁾ CsNO_3 is most highly dispersed on silica gel among the cesium salts examined in the present study even after it is converted into CsCl by the reaction with produced hydrogen chloride, the largest number of the basic site being prepared by the impregnation of this particular salt. Dispersion of CsNO_3 appears less influenced by the kind of silica gel.

The low reaction order in TCE(0.5) indicates that the desorption of produced hydrogen chloride from the basic sites is rate-determining. Heat-treatments at 673 K for 30 min between pulses removes adsorbed hydrogen chloride, recovering the activity markedly especially for CsNO_3 on silica gel. Strongly adsorbed hydrogen chloride may reduce the activity and selectivity in the flow reactor compared to those in the pulse reactor.

It was suggested that the interaction of CsCl with hydroxyl groups on silica gel plays important roles in the catalytic activity for several dehydrochlorination reactions.⁵⁻⁹⁾ The control of such an interaction by selecting activation conditions of silica gel is the target for a future study to accelerate the stationary desorption of hydrogen chloride for much better activity and selectivity for this reaction.

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