May, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 58, 1589—1590 (1985) 1589

Influences of Supporting Silica Gel on the Catalytic Activity of B-18 Crown Ether–KCl Complex for the Selective Dehydrochlorination of 1,1,2-Trichloroethane

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(Received November 10, 1984)

Synopsis. Catalytic dehydrochlorination of 1,1,2-trichloroethane into 1,1-dichloroethylene proceeded selectively around 200 °C over dibenzo-18-crown-6-KCl complex supported on silica gels. The reaction rate depended very much on the kinds of silica gel and impregnation levels of the complex, suggesting some roles of surface hydroxyl groups in this catalysis.

It has been established that basic substances promote the selective dehydrochlorination of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethylene (1,1-DCE), whereas acidic ones promotes the formation of 1,2-dichloroethylene (1,2-DCE).[1] The selective synthesis of 1,1-DCE from TCE with recovery of dry hydrogen chloride is the most desirable process for the practical purpose; however, basic substances such as KOH react with hydrogen chloride eliminated to form the corresponding salts, proceeding the reaction stoichiometrically.

ICI patent claims the catalysis by CsCl on silica gel.[2] We reported previously some acid-proof basic catalysts,[3–5] such as hydrochlorinated 2-methylimidazole immobilized on silica gel. These catalysts exhibited high selectivity but low activity.

Naso and Ronzini,[6] and Viout[7] have reported the activity of crown ether-alkali halide complexes for the elimination and substitution reaction of alkyl and alkenyl halides. Mizuno *et al.*[8] reported the reactivity of alkyl halides over a complex (KCl-B18) supported on silica gel.

We report here the catalytic activity of the crown ether-potassium chloride complex supported on some silica gels. The liberation of hydrogen chloride can be expected rapid when a crown ether and a halide are properly selected. Nevertheless the elimination efficiency of the complex may also depend on the surface properties of silica gel, since hydrogen chloride produced inevitably interacts which the functional groups of the surface.

Experimental

Crown ether (dibenzo-18-crown-6:B-18) were purchased from Nippon Soda Co. Used silica gels were C-200 (650 m^2/g, Wako Junyaku Co.), MB-3A and MB-4A (500 and 260 m^2/g, respectively, Fuji-Davison Inc.). The catalyst was prepared by repeated impregnation (three times) of crown ether–KCl complex on to the silica gel from its methanol solution.

The dehydrochlorination of TCE was studied with a micro-catalytic gas chromatographic pulse technique.[9] The catalyst (1 g) was packed in a glass U tube and 2 μl of TCE was injected with a microsyringe after the hydrogen gas flow for 2 h at the reaction temperature.

Results

Catalytic activity of KCl-B18 supported on MB-3A (KCl-B18/MB-3A) in the successive pulses at several reaction temperatures is shown in Fig. 1. A very high conversion (94%) was observed in the first pulse at 250 °C, however the conversion decreased sharply with repeated pulses, reaching a constant value of conversion (25%) after the 7th pulse. Injection of 100 μl methanol after the 7th pulse recovered the conversion of 8th pulse to the level of 5th pulse, and its another injection maintained the conversion in the successive pulse. Lower reaction temperatures (200 or 220 °C) decreased the conversion in the first pulse (20 and 40%, respectively) as well as the extent of activity decrease with the repeated pulse. Remarkably high selectivities for 1,1-DCE formation over 90% were obtained at all reaction temperatures examined. Under the present reaction conditions, KCl supported alone on the silica gel (KCl 10%, 1 g) showed a very low activity (conversion in the first pulse: 9%), suggesting that KCl-B18 is the catalytic active species.

Catalytic activity of KCl-B18/MB-3A depended markedly on the loading levels of KCl-B18. The conversion in the first pulse increased considerably until

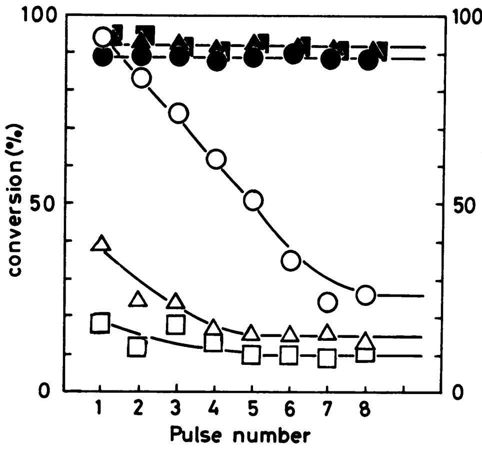

Fig. 1. Dehydrochlorination of TCE over KCl-B18/MB-3A cat. (loading level 19 wt%): 1 g, pulse size: 2 μl

○,●: React. temp: 250 °C, △,▲: react. temp: 220 °C, □,■: react. temp: 200 °C.

Open: conversion, closed: selectivity for 1,1-DCE formation, pulse interval was 1 h.

Table 1. Dehydrochlorination of TCE in the first pulse over KCl-B18 supported on several silica gels[a)]

Support	Conv./%	Selectivity/%	
		1,1-DCE	1,2-DCE
C-200	17	92	8
MB-3A	94	90	10
MB-4B	56	91	9

a) Catalyst (19 wt%): 1 g, react temp: 250 °C, pulse size: 2 μl.

the loading level reached 19 wt%, where the maximum value (94% conversion) was observed. More loading decreased the conversion which was as low as 43% at 37% loading. In contrast, the selectivity for 1,1-DCE formation was independent of the loading level.

Catalytic activities and selectivities of KCl-B18 supported on some silica gels in the first pulse are summarized in Table 1. Catalytic activity depended remarkably on the kind of supports, whereas selectivities were independently high. The activity order was as follows: MB-3A>MB-4B>C-200. The activity of MB-3A supporting catalyst was almost 5 times that of C-200 supporting one. Such a difference is much larger than that expected from their surface areas, suggesting positive roles of silica gels in this catalysis.

The amount of B-18 remaining on the gel after the 9th pulse determined by extracting the complex with methanol was 40% of originally supported one. Thermogravimetric measurements revealed that 78% of KCl-B18 remained on the silica surface at 250 °C without the dehydrochlorination reaction. These results suggest that the sublimation of B-18 accelerated by hydrogen chloride as well as the slow rate of hydrogen chloride release from the catalyst surface cause the significant decrease of activity in the repeated pulses.

Catalytic activity of KCl-B18/MB-3A was examined using a flow reactor (TCE: 3.5 kPa, catalysts (loading: 10%): 1 g, H_2 carrier: 60 $cm^3 \cdot min^{-1}$). The conversion of TCE was 13% at 250 °C in initial few minutes and then decreased very slowly to *ca.* 5% within 10 h. The total turnover number (reacted TCE/KCl-B18 in moles) reached more than 20 within 10 h at 250 °C. The selectivity for 1.1-DCE was constant to be *ca.* 90% throughout the reaction.

Discussion

Active species of KCl-crown ether complex supported on SiO_2 is assumed to its naked Cl^- ion,[6,8)] which can abstract first the most acidic proton from TCE to be liberated as hydrogen chloride. The intermediate trichloroethanide anion is selectively converted into 1,1-DCE and may regenerate the active species by providing Cl^-.

According to the mechanism described, the stable activity may be expected, when no sublimation of the crown ether takes place. However, the activity decreased by the repeated pulses. Its recovery by methanol injection or lower activity in the flow reactor may suggest that the desorption of produced hydrogen chloride from the catalyst surface influences the activity. Marked variation of the activity in the first pulse due to silica gel supports also may indicate their significant roles in the elimination of hydrogen chloride as well as the better dispersion of KCl-crown ether complex on their surface. Such roles of silica gel support have been scarecely discussed.[10)] The surface hydroxyl groups which can interact the chloride at the elimination stage may be the origin for these roles.

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