Catalytic Dehydrochlorination of 1,1,2-Trichloroethane (TCE) into 1,1-Dichloroethene (DCE) over Cs Ion-exchanged Zeolite

Isao MOCHIDA¹*, Yoshinori YASUMOTO¹), Hiroshi FUJITSU¹), and Yasuhiro KOJIMA²)

¹) Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816
²) Tosoh Inc., Kaisei-cho, Shin-nan-yo, Yamaguchi 746

(Received October 2, 1992)

Cesium ion-exchanged ZSM-5 zeolites of high Si/Al ratios were found to exhibit distinct catalytic activity for selective dehydrochlorination of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethene (DCE) at 300-400°C. The zeolite ion-exchanged with CsOH exhibited very high activity in the first several pulses, but the activity decreased to a stationary level after repeated pulses. The activity lost in the initial pulses may be ascribed to CsOH supported on the zeolite, because extensive washing after ion-exchange, resulted in the stationary activity by the third pulse. It is noted that a high Si/Al ratio effects selective dehydrochlorination into DCE, indicating the special roles of silanol groups. Thus, Cs ions and their neighboring silanol groups appear essential for the induction of sufficient basicity for the stationary activity that is maintained by liberating hydrogen chloride during the elimination reaction. In contrast, CsOH is converted into CsCl on the zeolite; thus, losing its catalytic activity.

1. Introduction

Selective dehydrochlorination of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethene (DCE) has been proved to take place only on basic substances such as sodium hydroxide, losing both hydrogen chloride and their basicity. The catalytic elimination, i.e., recovering hydrogen chloride, has been explored to save the basic substances at the same time. Although many basic catalysts have been examined, none has satisfied both activity and selectivity at the same time. Among them, however, cesium salts such as chloride and nitrate appear most promising. Their anions as well as their supports have been proved very influential. One of the present authors has studied catalytic activities of ion-exchanged Y-zeolites for dehydrochlorination of TCE, proposing the basic nature of alkali-metal ion-exchanged zeolites. Later studies reported the strong basicity of Cs ion-exchanged zeolite. Tosoh Inc. has patented Cs ion-exchanged zeolites for dehydrochlorination of ethylene dichloride (EDC) into vinyl chloride (VC), assuming that the zeolite behaved as a base in the reaction, although the reaction can also proceed through the radical mechanism as postulated in the thermal reaction.

The acid-proof structure of ZSM-5 is attractive to exhibit its stable activity elevated temperatures of the elimination reaction where hydrogen chloride is continuously produced.

In the present note, catalytic activities of Cs ion-exchanged ZSM-5's have been studied in the catalytic dehydrochlorination of TCE into DCE, to find higher activities of sufficient stability at selectivity above 80%. The high surface area of zeolites may allow the highest efficiency of Cs ions introduced by ion-exchange. The Si/Al ratio of zeolites may be very influential on activity as well as on selectivity because the ratio is known to influence acidity.

2. Experimental

The catalysts were prepared by ion-exchanging Erionite (Si/Al=7.7) and ZSM-5 zeolites of variable Si/Al ratios (Si/Al=28, 60 (Bayer Inc.), 72, 1,700 (Tosoh Inc.)) with an aqueous solution of varying cesium salts, washing, drying, molding, and calcining at 400°C for 2h. The amount of Cs ion was analyzed by atomic absorption after the zeolite was dissolved in HNO₃ and HF, and the ratios of Cs/Al are shown in Table 1. CsOH, CsNO₃, and cesium acetate were all of GR grade and used without further purification.

Catalytic activity was observed using a pulse reactor and a flow reactor with a fixed catalyst bed. Typical reaction conditions for each reactor were as follows: reaction temperature 300°C, catalyst weight 50 mg, pulse size of TCE 2µl, pulse interval...
15 min for the pulse reactor, and reaction temperature 300–450°C, catalyst weight 1 g, partial pressure of TCE 0.05 atm, total flow rate (H2 carrier) 70 ml/min for the flow reactor. TCE and reaction products were analyzed using a gas-chromatograph.

3. Results

Figure 1 shows the catalytic activities of ZSM–5 (Si/Al=60) ion-exchanged with CsNO3, cesium acetate, and CsOH in which exchanging with CsOH exhibited very high activity. However, its activity decreased sharply and then gradually with the number of pulses repeated; after the 8th pulse, the conversion remained at about 10%. The selectivity was as high as 90% regardless of the level of conversion. Part of such decrease in activity may be attributed to the CsOH remaining on the surface. The CsOH on ZSM–5 lost its activity when it was converted to CsCl. Extensive washing after ion-exchange to remove the CsOH resulted in the stationary conversion of 10% by the 3rd pulse while the selectivity remained at 90%. The activity of ion-exchanged ZSM–5 depended on the anion of Cs salts although the selectivity seemed unaffected (always around 90%). The extent of ion-exchange may depend on the anion. When the interval between 5th and 6th pulses was prolonged to 1 h at the reaction temperature, some increase in activity was observed as shown in Fig. 1.

Figure 2 illustrates the conversion and selectivity over ZSM–5 (Si/Al=60) ion-exchanged with CsOH in the flow reactor at 300°C. The initial conversion of 10% and selectivity of 80% were maintained for longer than 2 h. Both activity and selectivity were certainly much less than those observed in the pulse reaction. Higher reaction temperatures increased conversion but decreased selectivity significantly; conversion and selectivity were 20 and 80% at 350°C, 45 and 75% at 400°C, 75 and 65% at 450°C, respectively.

Table 1 summarizes the stationary conversion and selectivity of Cs ion-exchanged Erionite and those of ZSM–5s of various Si/Al ratios. High selectivity for DCE required a Si/Al ratio greater than 60. The ion-exchanged Erionite was rather acidic and produced truns-1,2-dichloroethylene selectively as observed with other types of zeolites. The activity of Cs ion-exchanged ZSM–5 was highest when its Si/Al ratio was 28, effecting a conversion of 20%, although the selectivity was rather low. Higher Si/Al ratio reduced the activity; 10% of Si/Al ratios of 60–72 and 4% on the...
ratio of 1,700, respectively.

4. Discussion

The Cs ion-exchanged ZSM-5 with a Si/Al atomic ratio higher than 60 was found to exhibit significant catalytic activity for selective dehydrochlorination of TCE into DCE in a temperature range of 300—400°C. When ZSM-5 of Si/Al atomic ratio in the range 60—72 was ion-exchanged with CsOH, catalytically active basicity is introduced onto the zeolite surface. The basicity for the present catalysis should be strong enough for selective elimination and should liberate the HCl produced under the reaction conditions. So far, the Cs-ion-exchanged ZSM-5 showed acceptable selectivity at reasonable level of activity in this dehydrochlorination reaction4)-6),11).

Cs ions introduced into the exchangeable sites and neighboring hydroxyl groups appear essential for the basicity of the zeolite to show stationary catalytic dehydrochlorination activity, since Si/Al on the zeolite and the number of ion-exchanged Cs should exceed their respective values to exhibit the activity for selective elimination. The latter requirement has been reported with a variety of zeolites10). The Cs/Al ratio of the ion-exchanged zeolite sometimes exceeds unity, indicating the presence of excess CsOH on the zeolite. Supported CsOH is also active for elimination but it is converted into inactive CsCl during the reaction. The excessive CsCl thus produced may hinder the catalysis by covering the surface of the ion-exchanged zeolite. The Si/Al ratio defines the number of both ion-exchangeable sites and silanol groups surrounding the ion-exchanged Cs. Thus, the zeolite of a certain Si/Al ratio range can exhibit the highest activity and selectivity. The participation of silanol groups in the elimination reaction has been reported in catalysis by CsCl supported on silica gel10,6).

The catalytic activity of the Cs ion-exchanged zeolite in the flow reactor was definitely inferior to that in the pulse reactor. The activity was also found reduced markedly after the first pulse, but longer intervals between pulses at higher temperatures recovered the activity completely. These results indicate that the adsorption of the hydrogen chloride produced occupies the basic active site and that its thermal desorption from the basic site defines the stationary activity.

References

要旨

Ca イオン交換ゼオライト上の 1,1,2-トリクロロエタンの 1,1-ジクロロエチレンへの接触脱塩化水素反応

持田 勲(1)，安元義徳(1)**，藤津 博(1)**，児島康弘(2)**

1) 九州大学機能物質科学研究所，816 福岡県春日市春日公園 6-1
2) 東ソー(株)南陽事業所，746 山口県新南陽市関成町 4560

硝酸セシウム、酢酸セシウム、水酸化セシウムを用いてイオン交換をした Si/Al 比の高い ZSM-5 ゼオライトが、300〜 400℃で 1,1,2-トリクロロエタンを 1,1-ジクロロエチレンへ高い選択性で脱塩化水素できることを見い出した。水酸化セシウムでイオン交換すると、パルス反応において初期に高い転化率を示した後、定常転化率を与えるので、ゼオライト上の水酸化セシウムが初期の高転化率を与え、塩化セシウムの生成によりその活性が失われたと思われる。定常転化率はイオン交換によって導入されたセシウムイオンにより推定される。イオン交換操作後ゼオライトをよく水洗いすれば、初期から定常活性が得られる。定常活性性の発現には十分に高いイオン交換率と Cs イオンに隣接する水酸基の存在によって、塩化水素の選択性的脱離の活性と、生成塩化水素を放出し活性を再生する能力を伴せ持つ塩基性活性点の導入が不可欠と思われる。

Keywords

Catalytic dehydrochlorination, Ionexchanged zeolite, Cesium ion, Trichloroethane