

Catalytic Dehydrochlorination of 1,2-Dichloroethane into Vinyl Chloride on Individual Oxides and Two-Component Silicate Catalysts

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Abstract

Catalytic 1,2-dichloroethane dehydrochlorination has been studied for a series of two-component silicate catalysts with acid–base properties varying in a regular manner ($\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Ga}_2\text{O}_3/\text{SiO}_2$, $\text{ZrO}_2/\text{SiO}_2$, BeO/SiO_2 , $\text{Y}_2\text{O}_3/\text{SiO}_2$) and oxide catalysts ($\gamma\text{-Al}_2\text{O}_3$, MgO) employing a flow-through set-up at the temperature of 250–450 °C. It has been established that the 1,2-dichloroethane to vinyl chloride conversion level is determined by the strength of Lewis acid centres. It is demonstrated that the deactivation of catalysts is caused by the formation of 1,3-dichlorobutene-2.

Key words: catalytic dehydrochlorination, 1,2-dichloroethane, vinyl chloride, oxide catalysts

INTRODUCTION

Vinyl chloride is one of important monomers widely used for obtaining various materials. The main industrial-scale method for obtaining it consists in thermal dehydrochlorination of 1,2-dichloroethane at high temperature (450–500 °C). The process of dehydrochlorination is carried out with a 50 % conversion level of 1,2-dichloroethane, the selectivity of vinyl chloride formation in this case amounting up to 98–99 % [1, 2]. As the conversion level increased the selectivity decreases to a considerable extent. Switching from the thermal to catalytic dehydrochlorination could allow one to lower the reaction temperature and to increase thereby the process selectivity.

Only solitary works available from the literature are devoted to the studies on the kinetics and mechanism for the catalytic dehydrochlorination

of 1,2-dichloroethane [3, 4]. It follows from these data that the reaction of dehydrochlorination occurs on the catalysts of the acid–base type being accompanied by fast deactivation of the catalyst. No regular studies concerning the influence of the nature, strength and concentration of the acid and basic centres of catalysts upon their catalytic activity were carried out till now.

The aim of the present work consisted in the studying the influence of the acid–base properties of catalysts upon the activity and selectivity in the reaction of 1,2-dichloroethane dehydrochlorination.

EXPERIMENTAL

We used binary oxide compounds such as $a\text{Me}_m\text{O}_n(1 - a)\text{SiO}_2$, where $\text{Me} = \text{Al}, \text{Ga}, \text{Zr}$,

Y, Be, as well as individual oxides $\gamma\text{-Al}_2\text{O}_3$ and MgO as catalysts. Binary catalysts were obtained *via* joint precipitation from the mixture of an alcohol solution of silicon ethylate and an aqueous solution of metal nitrate taken at a preset ratio, at the total oxide concentration less than 0.5–0.6 mol/L. The precipitation was performed using a periodic technique at the temperature of 70 °C, constant pH value ranging within 8–9, with the use of aqueous ammonia solution under intense stirring. After ageing at 70 °C during 3 h under slow stirring the precipitates formed were filtered, washed, molded, dried and calcinated then at 500–550 °C during 4 h. Individual oxides were obtained via calcinating the samples obtained from nitrates performing a procedure similar to the described above. Magnesium hydroxide was obtained at pH 10.

Physicochemical properties of the catalysts under investigated are presented in Table 1. The specific surface of the catalysts were determined according to low-temperature nitrogen adsorption measured by BET method employing ASAP-2400 device (Micromeritics, the USA). The concentration of the Broensted acid centres (BAC) of a catalyst was determined according to adsorbed pyridine spectra basing on

the intensity of the absorption band centred at 1540 cm^{-1} inherent in the pyridinium ion, with the use of the integral absorption coefficient [5]. The strength of BAC was determined from the shift of acidic OH group bands corresponding to the formation of H-complexes with CO under low-temperature CO adsorption, and was characterized according to PA scale [6]. The strength of Lewis acid centres (LAC) was determined from the shift displacement of adsorbed CO bands due to the formation of CO complexes with LAC and were characterized by CO adsorption heat value, whereas the concentration was determined from the intensity of corresponding bands with the use of the integral absorption coefficient measured by the authors of [7]. The strength of base centres was determined from the shift of ν_{CD} band in the IR spectrum of CDCl_3 H-complex with a surface base centre [8] being characterized according to PA scale. The concentration of the base centres was determined from the intensity of this band with use of factors of with the use of the integral absorption coefficient measured by the authors of [9]. Spectra were registered employing a Shimadzu FTIR-8300 Fourier transform IR spectrometer.

TABLE 1

Physicochemical properties of catalysts

Composition, mol. %	S_{sp} , m^2/g	Acid centres				Base centres	
		Broensted		Lewis		PA, kJ/mol	N_{b} , $\mu\text{mol}/\text{g}$
		PA, kJ/mol	N_{H^+} , $\mu\text{mol}/\text{g}$	Q_{CO} , kJ/mol	N_{CO} , $\mu\text{mol}/\text{g}$		
15 % Al_2O_3 85 % SiO_2^*	250	1180	73	53	22	≤ 750	–
				41.5	15	≤ 750	–
				34	13	≤ 750	–
6 % Ga_2O_3 94 % SiO_2^*	210	1205	46	47.5	46	≤ 750	–
10 % ZrO_2 90 % SiO_2^*	260	1205	18	34	300	≤ 750	–
20 %BeO 80 % SiO_2^*	180	1225	15	46.5	51	≤ 750	–
10 % Y_2O_3 90 % SiO_2^*	145	1235	18	32	64	≤ 750	–
$\gamma\text{-Al}_2\text{O}_3$	200	1410	0	55.5	36	900	45
				34	350	860	25
MgO	80	1560	0	18	310	925	60
						870	20
MgCl_2^{**}	60	–	0	19	200	≤ 750	–

*Properties of the base centres are similar to those of SiO_2 .

**Sample was obtained *via* impregnation with NH_4Cl and the subsequent calcination at 600 °C.

The reaction of 1,2-dichloroethane dehydrochlorination was performed using a flow-through set-up within a glass reactor with internal diameter of 8 mm. Catalysts (1.0 g) calcinated in a reactor at 500 °C during 1 h in a current of argon and cooled up to 200 °C. In experiments used 1,2-dichloroethane ("pure" grade), argon ("high purity" grade). Liquid 1,2-dichloroethane was fed into the flow of argon employing a NISh-01R infusion syringe pump through a mixing evaporator. The reaction mixture obtained (with the volume fraction of 1,2-dichloroethane amounting to 12 %) was fed into the reactor with a flow rate of 5900 mL/h and then it was supplied through a Teflon line heated up to 160 °C into a gas IR optical cell.

The conversion level of 1,2-dichloroethane was measured within the temperature range of 250–450 °C with an increment of 25 °C during 15–20 min at each temperature point. The spectra were registered every 2 min with the help of a Scimitar FTS-800 Fourier transform IR spectrometer with the resolution equal to 4 cm⁻¹. The concentration of components in the mixture was calculated from the intensity of following bands centred at (cm⁻¹): 1237 (1,2-dichloroethane), 1620 (vinyl chloride), 2800 (HCl), 1089 (1,3-dichlorobutene-2), 3310 (acetylene).

The material balance for carbon was calculated according to the equation

$$C_{1,2\text{-DCE, ini}} / (C_{\text{VC}} + C_{\text{C}_2\text{H}_2} + 2C_{\text{dimer}} + C_{1,2\text{-DCE, fin}})$$

The material balance for chlorine was calculated according to the equation

$$2C_{1,2\text{-DCE, ini}} / (C_{\text{VC}} + C_{\text{HCl}} + 2C_{\text{dimer}} + 2C_{1,2\text{-DCE, fin}})$$

where $C_{1,2\text{-DCE, ini}}$, $C_{1,2\text{-DCE, fin}}$ are the initial and final volume fraction of 1,2-dichloroethane in gas phase, respectively (%); C_{VC} , $C_{\text{C}_2\text{H}_2}$, C_{dimer} , C_{HCl} are the volume fractions of vinyl chloride, C_2H_2 , dimer, HCl in the gas phase, respectively, %. The volume change resulting from the reactions was neglected.

RESULTS AND DISCUSSION

First of all we have conducted an experiment concerning the thermal conversion of 1,2-dichloroethane within empty reactor. The level of its conversion did not exceed 3 % at the temperature of 450 °C, whereas at a lower temperature of no conversion of 1,2-dichloroethane

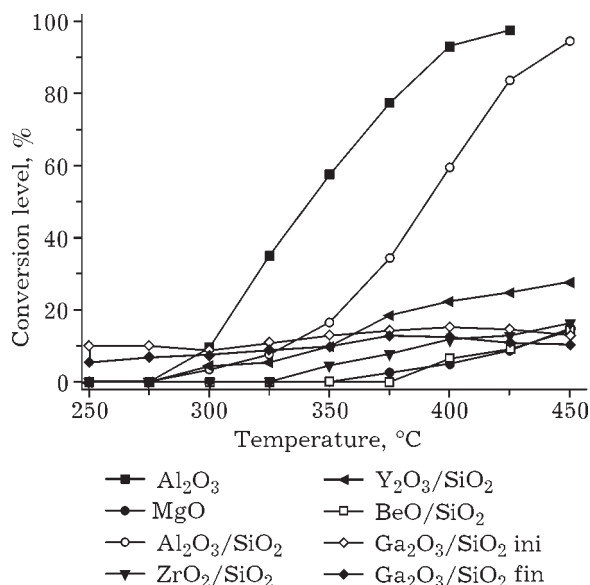


Fig. 1. 1,2-Dichloroethane conversion level depending on temperature.

was observed. Figure 1 demonstrates data concerning the 1,2-dichloroethane conversion level depending on the temperature. One can see that the temperature of starting the reaction is determined by the composition of catalyst. So, for such catalysts as $\gamma\text{-Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Y}_2\text{O}_3/\text{SiO}_2$ the beginning of dehydrochlorination is observed at the temperature of 300 °C; for $\text{ZrO}_2/\text{SiO}_2$ catalyst this occurs at 350 °C, as well as for MgO and BeO/SiO₂ one can observe the effect at the temperature values of 375 and 400 °C, respectively. The greatest conversion level for 1,2-dichloroethane is achieved on such catalysts as $\gamma\text{-Al}_2\text{O}_3$ (97 %) and $\text{Al}_2\text{O}_3/\text{SiO}_2$ (94 %) at the temperature values of 425 and 450 °C, respectively.

For $\text{Ga}_2\text{O}_3/\text{SiO}_2$ catalyst, the reaction begins already at the temperature of 250 °C, however in the course of time the conversion level decreases to a considerable extent (see Fig. 1). With the growth of temperature, the conversion level of 1,2-dichloroethane almost does not change, which could also be caused by fast deactivation of the catalyst.

For aluminium oxide a noticeable deactivation is observed only at the temperature of 400 °C. During 20 min the residual content of 1,2-dichloroethane in the reaction products increased from 0.6 up to 0.8 %. For aluminium silicate, a similar deactivation takes place only at the temperature higher than 425 °C. For the

other catalysts the change in the conversion level with time is negligible.

For all the catalysts, except for $\text{Ga}_2\text{O}_3/\text{SiO}_2$, at the temperatures lower than 400°C the balance calculated with respect to carbon and chlorine is close to 100 % (within an accuracy of $\pm 3\%$). For $\text{Ga}_2\text{O}_3/\text{SiO}_2$ catalyst, an almost 100 % balance over chlorine is also observed, however at the temperature values lower than 350°C the balance over carbon at the reactor outlet is less than 90 %. For $\gamma\text{-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{SiO}_2$ at the temperature values higher than 400°C the balance over chlorine amounts up to 85–90 %, which indicates the chlorination of the catalyst. When filling with 1,2-dichloroethane, MgO at the temperature of 250°C exhibited a complete absorption of 1,2-dichloroethane within several minutes and the formation of a small amount of vinyl chloride and even acetylene, without HCl evolution. Further any transformations of 1,2-dichloroethane ceased till gaining the temperature of 375°C , then the formation of vinyl chloride was observed again. The catalyst has appeared low-active, but it worked with a 100 % balance both over carbon, and over chlorine. The low-temperature conversion of 1,2-dichloroethane on magnesium oxide, to all appearance, could be caused by surface chlorination. A detailed description of low-temperature 1,2-dichloroethane conversion on magnesium oxide will be published elsewhere.

The main products of the reaction on all the catalysts are presented by vinyl chloride and HCl . Among the reaction by-products there were acetylene and 1,3-dichlorobutene-2 observed; the formation of the latter was not earlier noted in the literature. The identification of 1,3-dichlorobutene-2 have been performed basing on the comparison of the spectra obtained in the present work with corresponding data available from the NIST Chemistry WebBook Library.

Figure 2 demonstrates the selectivity of vinyl chloride, acetylene and 1,3-dichlorobutene-2 formation depending on temperature. Among the catalysts, a special place is occupied by $\gamma\text{-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{SiO}_2$: at the reaction temperature up to 400°C their selectivity with respect to vinyl chloride amounts up to 97–99 %, whereas at a higher temperature this value is reduced down to 94 %. Since 350°C , acetylene can be observed to appear in the reaction mix-

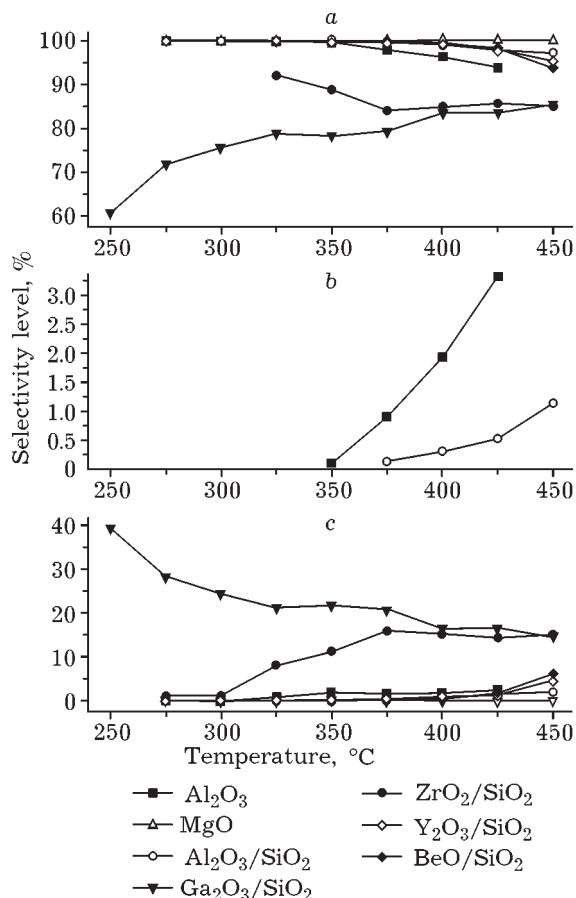


Fig. 2. Selectivity level for the formation of vinyl chloride (a), acetylene (b) and 1,3-dichlorobutene-2 (c) depending on temperature.

ture. At the temperature of $425\text{--}450^\circ\text{C}$ the content of acetylene amounts to about 1 % for such catalyst as $\text{Al}_2\text{O}_3/\text{SiO}_2$ and 3 % for such catalyst as $\gamma\text{-Al}_2\text{O}_3$. The content of 1,3-dichlorobutene-2 on these catalysts does not exceed 1–3 %. It should be noted that employing these catalysts results in a higher selectivity of vinyl chloride formation and, moreover, this fact is observed at much higher values of the conversion level comparing to the process of thermal 1,2-dichloroethane decomposition under the conditions of industrial-scale production [10, 11].

Basing on the selectivity of vinyl chloride formation the other (less active) catalysts can be divided into two groups. The selectivity (with respect to vinyl chloride) of catalysts belonging to the first group ($\text{Y}_2\text{O}_3/\text{SiO}_2$, MgO , BeO/SiO_2) amounts to not less than 96 % at the temperature of 450°C ; at a lower temperature there are no acetylene and 1,3-dichlorobutene-2 found out in the reaction mixture. The second

group is presented by such catalysts as $\text{Ga}_2\text{O}_3/\text{SiO}_2$ and $\text{ZrO}_2/\text{SiO}_2$ for those the selectivity with respect to vinyl chloride at the temperature of 400°C amounts to about 80 %, however, a significant amount of 1,3-dichlorobutene-2 is formed. For such catalyst as $\text{Ga}_2\text{O}_3/\text{SiO}_2$ at 250°C the selectivity of 1,3-dichlorobutene-2 formation amounts up to 40 %, but within a higher temperature range of $400\text{--}450^\circ\text{C}$ this parameter decreases down to 20–15 %.

The analysis of data concerning the conversion level of 1,2-dichloroethane and the acid-base properties of catalysts (see Table 1) demonstrates that contribution of BAC into the activity is insignificant. The most active catalyst is $\gamma\text{-Al}_2\text{O}_3$ which does not contain strong BAC. In the series of silicate catalysts there is no increase in the conversion level of 1,2-dichloroethane observed with the growth of BAC strength. In order to reveal the role of LAC we have presented in Fig. 3 the dependence of the temperature corresponding to the 6 % 1,2-dichloroethane conversion level on LAC strength. The choice of the temperature corresponding just to this conversion level as a measure of activity is caused by the fact that only at such a low conversion level even insignificant deactivation of catalysts is not possible; thus the activity of all the catalysts can be unequivocally correlated with respect to the temperature of this conversion level. In Fig. 3 one can observe a clear tendency of increasing in the activity with the growth of LAC strength. Data for $\text{Ga}_2\text{O}_3/\text{SiO}_2$ catalyst are not presented due to rapid deactivation of this catalyst.

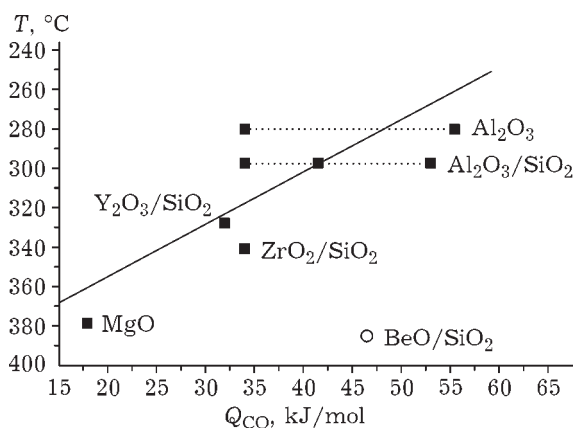


Fig. 3. Correlation between the temperature corresponding to 6 % conversion level of 1,2-dichloroethane and LAC strength scaled to the heat CO adsorption (Q_{CO}).

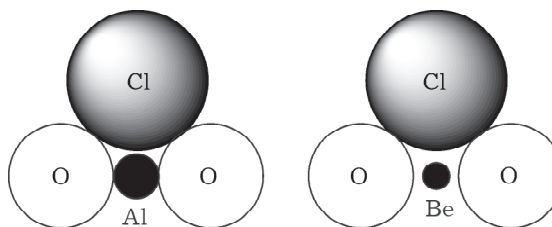


Fig. 4. Models for the chloride ion interaction with aprotic centres belonging to $\text{Al}_2\text{O}_3/\text{SiO}_2$ and BeO/SiO_2 catalysts.

The point corresponding to BeO/SiO_2 exhibits a deviation from the general tendency of increasing the activity with the increase in LAC strength. This fact is, to all appearance, connected with a steric hindrance in the interaction of the 1,2-dichloroethane chlorine atom with beryllium ion in the oxygen matrix of the catalyst. The ionic radius for beryllium is equal to 0.34 \AA , for aluminium 0.57 \AA , for oxygen 1.36 \AA , and the covalent radius chlorine atom amounts to 1.81 \AA . This is distinctly seen from on Fig. 4, where a model for 1,2-dichloroethane chlorine atom interaction with aprotic centres of $\text{Al}_2\text{O}_3/\text{SiO}_2$ and BeO/SiO_2 catalysts is presented. It is obvious that chlorine atom cannot interact with beryllium ion without any reorganization of the oxygen skeleton the catalyst's surface. The complexes of chloroorganic compounds with LAC formed with beryllium ions cannot be strong according to steric reasons, which is just confirmed by the deviation of BeO/SiO_2 point from the curve corresponding to the activity dependence on LAC strength. From the data presented in Fig. 3 one could conclude that just the LAC are responsible for the reaction of 1,2-dichloroethane dechlorination.

To all appearance, the 1,2-dichloroethane dehydrochlorination proceeds according to the two-centre mechanism with the participation of adjacent base and Lewis centres [3]. From comparison of data concerning the activity obtained for catalysts $\gamma\text{-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{SiO}_2$ one can see that the former is more active. At close strength of LAC of these catalysts the base centres on the surface of $\gamma\text{-Al}_2\text{O}_3$ are much stronger and can thus participate in dehydrochlorination. Hence, the strength of the base centres is not a primary factor determining the conversion level for 1,2-dichloroethane. Moreover the base centres of MgO catalyst are even stronger, than those of $\gamma\text{-Al}_2\text{O}_3$, whereas its activity is lower.

CONCLUSION

The results of the investigations performed allow us to assume that one of principal causes for deactivation of catalysts is connected with the formation of 1,3-dichlorobutene-2, and even to a greater extent than with the formation of acetylene. Acetylene begins to form at the temperature higher than 375 °C, whereas 1,3-dichlorobutene-2 appears already at 250 °C. To all appearance, 1,3-dichlorobutene-2 with boiling point of 127 °C is retained in the pores of a catalyst to be oligomerized as well as to be transformed into coke deposits, and it is just the fact which determines the fast deactivation of the most active catalyst such as Ga₂O₃/SiO₂. Thus, the use of such fine-pored catalysts as metal silicates and zeolites for commercial obtaining of vinyl chloride from 1,2-dichloroethane is of little promise.

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