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Catalytic Dehydrochlorination over Alumina Promoted by Steam

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Catalytic dehydrochlorination of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethylene (VDC) was studied by means of the pulse reaction technique on the basis of an assumption that chloride compounds of aluminum formed over the surface of alumina might be recycled back to hydrated alumina by the aid of steam to maintain the dehydrochlorination activity of its basic sites. The results suggest conditions (reaction temperature, amount of water added) which should be adequate for the realization of truly catalytic dehydrochlorination of TCE over alumina even though a few pulses of TCE in the absence of water vapor destroyed the activity as well as the selectivity of alumina for VDC formation. Furthermore, hydrated alumina showed good selectivity for VDC formation, as high as 80%, probably because of the decrease in its acidity by hydration. The effects of calcination temperature and small amounts of sodium hydroxide were also studied to improve the activity and selectivity. The basicity of hydrated alumina was discussed from the viewpoint of the reactivities and product distributions of several chloroalkanes according to linear free energy relationships.

INTRODUCTION

It is already established that solid bases promote the selective dehydrochlorination of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethylene (VDC) (*1*); however, the activities for this elimination are lost quickly because the basicity of the catalysts is destroyed by the hydrogen chloride formed. To overcome the problem, some catalytic processes have been proposed (*2*, *3*). The present authors reported that by the addition of water catalytic dehydrochlorination over alumina could be realized by recycling the surface aluminum chloride formed during the reaction back to aluminum hydroxide on the surface of the catalyst (*4*).

In the present study, the optimal conditions for the formation of 1,1-dichloroethylene over alumina are surveyed with respect to the reaction temperature, the amount of water added, and the calcination temperature of the catalyst. The basicity of hydrated alumina is discussed from the product distributions of TCE, 1,2-dichloropropane (DP), 1,1,2-trichloropropane (TCP), and 2,3-dichlorobutane (DB).

EXPERIMENTAL

Catalysts and reagents. Alumina was prepared by calcining $Al(OH)_3$ precipitated from aq $Al(NO_3)_3$ with NH_4OH. Calcination was carried out in air for 5 hr at 550, 700, 900, 1000, and 1300°C, the samples then being designated as A-550, A-700, etc. Another alumina which was precipitated with NaOH is described as A-Na.

Chloroethanes were obtained from Tokyo Kasei Co. and used without further purification.

Apparatus and procedure. A microcatalytic pulse technique was employed to ob-

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serve the rate of the catalytic elimination, using a U-shaped glass tube reactor packed with ca. 50 mg of catalyst. The products [VDC and *trans*- and *cis*-1,2-dichloroethylene (DCE)] and the reactant (TCE) were analyzed gas chromatographically with a 4-m column of tricresylphosphate at 80°C. The flow rate of carrier hydrogen gas was 100 ml/min. Details of the apparatus were described in previous papers (*1*).

After the catalyst was pretreated in hydrogen at 450°C for 2 hr, a certain amount of water was injected to the catalyst at the reaction temperature (150 to 250°C) with a microsyringe. The hydrated catalyst was kept at the reaction temperature for 1 hr, and then the elimination activity (pulse size of the reactant, 2 μl) was measured. The same procedure except for the pretreatment at 450°C was repeated for the subsequent reactions. The isomerization of chloroolefins was not detected under the present conditions.

RESULTS

The product distributions and total conversions of TCE over alumina (A-550) under wet and dry conditions (at 200°C) are shown in Fig. 1. A considerable amount of VDC was produced over the dry alumina although *cis*-DCE was the principal product; however, the formation of VDC as well as total conversion decreased very much with repeated pulses probably because of the formation of aluminum chloride on the surface of alumina. The addition of 100 μl of water before the reaction increased the selectivity of VDC formation to as much as 58% of the products. Furthermore, the selectivity could be maintained at a high level by the addition of another pulse of water in spite of the repeated pulses. The total conversion was slightly increased by the addition of water and was maintained at a constant level except for the decrease between the first and second pulses. Thus, the addition of water was found to be desirable for catalytic formation of VDC from TCE over alumina in both conversion and selectivity.

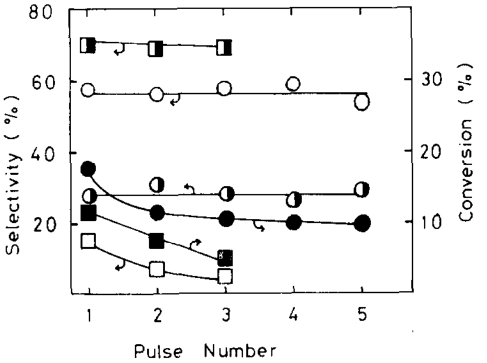


FIG. 1. Dehydrochlorination of 1,1,2-trichloroethane over A-550 at 200°C. ○, □: VDC; ◑, ◧: cis-1,2-dichloroethylene; ●, ■: total conversion. Circles and squares are for wet and dry conditions, respectively. Amount of catalyst, 50 mg; added water for wet conditions, 100 μl.

The reactivities at several reaction temperatures are summarized in Table 1, where the results for the first pulse are shown. The conversion increased and the selectivity decreased with the higher reaction temperatures. The selectivity increased to 80% at 150°C.

The amount of added water had a significant effect on the selectivity of VDC formation as indicated in Fig. 2, where the selectivities of the first pulse at 250°C are shown. The selectivity increased with increasing amounts of water until the amount of water reached 150 μl for 50 mg of alumina and then decreased slowly with further increasing amounts, indicating that a partially hydrated surface is preferable for the VDC formation.

It is known that the calcination temperature changes the properties of alumina (*1a*, *5*). An effect of higher calcination temperature favoring VDC formation was reported in a previous paper (*1*). The selectivities of alumina calcined at several temperatures under the wet conditions are shown in Fig. 3. The selectivity was greatly increased by calcination at 900 to ~1000°C, although the activity decreased to a certain

TABLE 1

Product Distribution in the Dehydrochlorination of TCE over Alumina (First Pulse)

Reaction temperature (°C)	Selectivity (%)			Total conversion (%)	Catalyst A-550 (mg)
	VDC	*Cis*-1,2-DCE	*Trans*-1,2-DCE		
150					
Dry	37.1	50.5	12.4	9.7	50.0
Wet[a]	81.4	7.9	10.7	14.0	50.4
200					
Dry	14.4	75.2	8.0	12.5	50.0
Wet	58.1	29.7	10.3	17.5	50.3
250					
Dry	12.3	76.3	7.0	11.4	50.1
Wet	39.9	48.3	9.4	20.3	50.0
300					
Dry	7.0	82.3	6.3	15.8	50.0
Wet	17.9	70.6	8.1	23.4	50.1

[a] Amount of water under wet conditions, 100 µl.

extent and was completely lost by calcination at 1300°C. The X-ray (Cu$K\alpha$) diffractions of some of these aluminas are shown in Fig. 4. Above 700°C, the alumina became partially α-type and completely so at 1300°C. Some transition form of alumina may be preferable for the formation of VDC.

The selectivities and total conversions of repeated pulses of TCE observed over A-900 and A-1000 are shown in Table 2. Although the selectivity of VDC formation was as high as 80% over A-1000, there was a considerable activity decrease in spite of water addition in the reaction at 200°C. The reaction over A-900 at 250°C maintained a sufficient conversion with the repeated pulses. Generally speaking, a higher calcination temperature is preferable for the selectivity of VDC formation but is not desirable for the level and maintenance of catalytic activity.

The catalytic activity of A-Na. The basic catalyst has been known to produce VDC

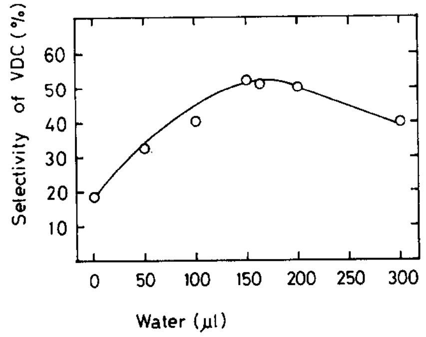


FIG. 2. Amount of added water vs dehydrochlorination selectivities of the first pulse over A-550 at 250°C. Amount of catalyst, 50 mg.

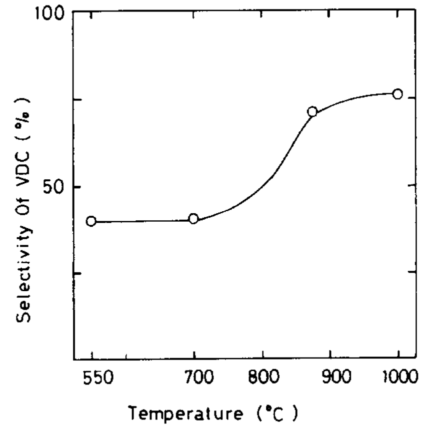


FIG. 3. Effect of calcination temperature on the dehydrochlorination selectivities of the first pulse over alumina at 250°C. Amount of added water, 100 µl; Amount of catalyst, 50 mg.

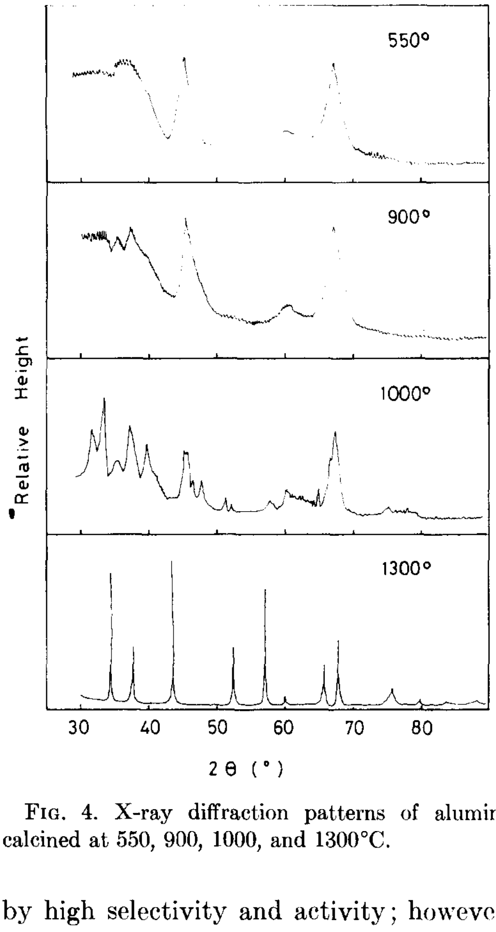


FIG. 4. X-ray diffraction patterns of alumina calcined at 550, 900, 1000, and 1300°C.

by high selectivity and activity; however, it loses activity very quickly by the reaction with hydrogen chloride to form the corresponding salt which is difficult to hydrolyze. Thus, a catalyst the basicity of which does not react with the reactant directly but influences the reactivity of the catalyst surface would be interesting because the active surface sites of high activity and selectivity are recoverable by the addition of water. Such a catalyst may be realized if the basic component is located in the core of the catalyst and is covered with a skin of aluminum oxide, whose surface has sites for the elimination reaction. An internal alkali component increases the basicity of the alumina surface, and aluminum chloride formed by the reaction can be hydrolyzed with water in spite of the increased basicity. A small amount of alkali metal is known to make alumina basic (*6*). Based on such considerations, the activity of A-Na-900 was examined and is shown in Table 3. Under dry conditions, it lost its activity for VDC formation very quickly with repeated pulses, but its activity decreased only slightly with the addition of water. The internal basicity may survive during the reaction.

Reactivities of several chloroalkanes over alumina under wet conditions. Reactivities of a series of homologous reactants provide information on the properties of the catalyst (*1*, *7*). Those of 1,2-dichloropropane and 1,1,2-trichloropropane are shown in Tables 4 and 5, respectively, where the reactions over silica–alumina and potassium hydroxide supported on silica gel are also shown for the comparison. These reactants produced the products shown in Eqs. (1) and (2) according to the properties of the

TABLE 2

Product Distribution from TCE in Repeated Pulses over A-1000 and A-900[a]

	A-1000						A-900							
	Dry		Wet				Dry			Wet				
	1[b]	2[b]	1[b]	2[b]	3[b]	4[b]	1[b]	2[b]	3[b]	1[b]	2[b]	3[b]	4[b]	5[b]
VDC (%)[c]	43.5	46.2	83.5	83.3	87.5	82.8	18.6	19.2	15.8	75.2	69.4	66.2	73.0	71.6
trans-1,2-DCE (%)[c]	17.4	—	7.8	9.7	8.3	10.3	9.3	15.4	15.8	9.5	11.2	12.2	11.1	11.9
cis-1,2-DCE (%)[c]	39.1	53.8	8.7	6.9	4.2	6.9	66.3	46.2	42.1	13.8	16.3	17.6	11.1	11.9
Total conversion (%)	2.3	0.65	11.5	7.2	4.8	2.9	8.6	2.6	1.9	21.0	9.8	7.4	6.3	6.7
Catalyst weight (mg)	50.5	—	50.4	—	—	—	50.1	—	—	50.3	—	—	—	—

[a] Reaction temperatures: A-1000, 200°C; A-900, 250°C. Amount of water under wet conditions, 100 μl.

[b] Pulse number.

[c] Selectivity.

TABLE 3

Product Distribution of TCE over A-Na-900 at 200°C

	Dry					Wet[a]			
	1[b]	2[b]	3[b]	4[b]	5[b]	1[b]	2[b]	3[b]	4[b]
VDC (%)[c]	80.4	84.8	85.0	89.7	94.6	85.7	84.5	82.2	80.0
trans-1,2-DCE (%)[c]	7.6	6.1	10.0	6.9	5.4	6.0	7.1	8.1	10.0
cis-1,2-DCE (%)[c]	12.0	9.1	5.0	3.4	—	8.3	8.3	9.7	10.0
Total conversion (%)	9.2	3.3	2.0	1.5	1.1	8.4	8.4	6.2	6.0
Catalyst weight (mg)	50.1	—	—	—	—	50.1	—	—	—

[a] Amount of water under wet conditions, 100 μl.

[b] Pulse number.

[c] Selectivity.

catalyst, as discussed in a previous paper (*1c*).

$$\begin{aligned}&CH_2ClCHClCH_3 \rightarrow\\ &\qquad \textit{trans/cis} - CHCl{=}CHCH_3\\ &\qquad\qquad (1\text{-}CP)\\ &\qquad + CH_2{=}CClCH_3\\ &\qquad\qquad (2\text{-}CP)\\ &\qquad + CH_2ClCH{=}CH_2 \quad (1)\\ &\qquad\qquad (3\text{-}CP)\end{aligned}$$

$$\begin{aligned}&CHCl_2CHClCH_3 \rightarrow\\ &\qquad CCl_2{=}CHCH_3 + \textit{trans/cis}\\ &\qquad\quad (1,1\text{-}DCP)\\ &\qquad\quad - CHCl{=}CClCH_3\\ &\qquad\qquad (1,2\text{-}DCP)\\ &\qquad\qquad + CHCl_2CH{=}CH_2 \quad (2)\end{aligned}$$

Product distribution over the dry alumina was different from those over KOH–silica gel and silica–alumina. Addition of water slightly increased the formation of *trans*-

TABLE 4

Product Distribution of 1,2-DP at the First Pulse[a]

Catalyst	Condition	Selectivity				Total conversion (%)	Catalyst weight (mg)
		1-CP (%)		2-CP (%)	3-CP (%)		
		cis	*trans*				
A-550	Dry	89.3	1.7	1.8	6.2	11.2	50.5
	Wet	85.0	5.0	5.0	5.0	6.0	50.0
A-900	Dry	83.0	Trace	—	16.7	2.4	50.3
	Wet	81.0	9.5	9.5	—	2.1	50.0
KOH-S	Dry	18.7	46.9	34.4	Trace	9.6	200.0
SA	Dry	52.6	5.3	—	42.1	1.9	80.0

[a] Reaction temperature, 150°C; amount of water under wet conditions, 100 μl. KOH-S, KOH–silica gel; SA, silica–alumina (13% Al_2O_3).

$$\underset{}{CH_3CHClCH_2Cl} \rightarrow \underset{(1\text{-}CP)}{CH_3CH{=}CHCl} + \underset{(2\text{-}CP)}{CH_3CCl{=}CH_2} + \underset{(3\text{-}CP)}{CH_2 = CHCH_2Cl}$$

TABLE 5

Product Distribution from 1,1,2-TCP at the First Pulse[a]

Catalyst	Conditions	Selectivity (%)			Total conversion (%)	Catalyst weight (mg)
		1,1-DCP	1,2-DCP			
			cis	*trans*		
A-550	Dry	35.3	51.0	10.2	36.3	50.0
	Wet	56.6	31.3	10.7	34.4	50.6
A-900	Dry	41.0	42.1	11.3	33.5	50.0
	Wet	75.1	13.6	10.1	34.5	50.3
KOH-S	Dry	91.7	2.8	5.5	36.2	102.4
SA	Dry	—	40.6	43.7	6.4	267.1

[a] Reaction temperature, 250°C; amount of water under wet conditions, 100 μl. KOH-S, KOH–silica gel; SA, Silica–alumina (13% Al_2O_3).

$$CHCl_2CHClCH_3 \rightarrow \underset{(1,1\text{-DCP})}{CCl_2{=}CHCH_3} + \underset{(1,2\text{-DCP})}{CHCl{=}CClCH_3} + CHCl_2CH = CH_2$$

1-CP and 2-CP from DP and decreased that of 3-CP, making the distribution slightly similar to that over KOH–silica gel. In contrast, the addition of water affected the alumina very much, and it then behaved more like KOH–silica gel in the cases of 1,1,2-trichloropropane and 1,1,2-trichloroethane. These results will be discussed later in connection with the basicity of hydrated alumina.

The product distributions of *meso*- and *dl*-2,3-dichlorobutanes define the stereochemistry of the elimination over the solid surface. The results over alumina under wet conditions are shown in Table 6 which indicates that *trans*-elimination took place at high specificity over the wet alumina. *Trans*-elimination over a solid surface has been reported rather often (*8*).

TABLE 6

Product Distribution of 2,3-Dichlorobutanes[a]

	meso		*dl*		*dl*[b]
	Dry	Wet	Dry	Wet	Dry
	60.3[c]	60.2[c]	29.6[c]	29.7[c]	115.1[c]
trans-2-Chloro-butene-2 (%)[d]	1.2	0.9	19.8	21.5	16.9
cis-2-Chloro-butene-2 (%)[d]	10.6	17.3	—	—	0.9
Total conversion (%)	13.5	18.7	19.8	21.5	17.8

[a] Reaction temperature, 150°C; amount of water under wet conditions, 100 μl.

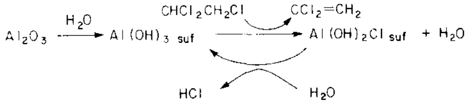
[b] Catalyst: KOH–silica gel.

[c] Catalyst weight in milligrams.

[d] Yield.

DISCUSSION

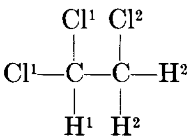
The catalytic dehydrochlorination of 1,1,2-trichloroethane producing VDC with the high selectivity found in the present work can be discussed from two aspects. The first one concerns preventing the alumina catalyst from becoming acidic in spite of the formation of hydrogen chloride in the elimination reaction. Alumina is known to react with chloroalkane to form aluminum chloride (*9*, *10*), and aluminum chloride is hydrolyzed with water under certain conditions. If these reactions occur smoothly, the catalytic dehydrochlorination can be described as follows:



(3)

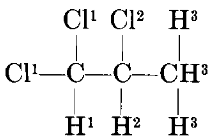
where suffix "suf" designates the surface compound of the catalyst. In the present study, the reaction was carried out by the pulse method to separate each step of the catalysis; however, the concurrent injection of steam under appropriate conditions may cause a continuous flow type of catalysis. It may be possible to find conditions where both dehydrochlorination and hydrolysis reactions would be compatible (*11*).

The second aspect concerns the basicity of the hydrated alumina. The product distributions of 1,1,2-trichloroethane (I), 1,1,2-trichloropropane (II), and 1,2-dichloropropane (III) shown in Tables 1, 4, and 5 provide a suggestion on this point. The results indicate that product distributions from I and II on the hydrated alumina were similar to those on basic substances such as KOH–silica gel. In contrast, only a small change was observed for III with the addition of water. The mechanism of elimination was assumed in previous papers (*1b, c*) to vary continuously, depending upon the acid–base natures of the catalysts and the reactant. The elimination reactions of the chloro-compounds investigated in the present study over the dry alumina were postulated to proceed through an E2-concerted mechanism where the chlorine and proton were eliminated almost simultaneously by the acidic and basic sites of the alumina. The change of product distribution due to the addition of water may come from a shift of the mechanism from E2-concerted into E1-cb. The extent of the shift may depend on the acidity of the protons to be eliminated as well as the basicity of the catalyst. If the acidity of the proton is strong enough, the elimination may proceed via E1-cb even though the basicity of the catalyst is not so strong. The most acidic protons of each reactant are defined as H^1 in the following formulas:



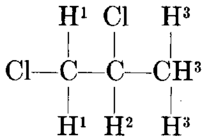
$$\begin{array}{cccc} & Cl^1 & Cl^2 & \\ & | & | & \\ Cl^1- & C- & C- & H^2 \\ & | & | & \\ & H^1 & H^2 & \end{array}$$

(I)



$$\begin{array}{ccccc} & Cl^1 & Cl^2 & H^3 \\ & | & | & | \\ Cl^1- & C- & C- & CH^3 \\ & | & | & | \\ & H^1 & H^2 & H^3 \end{array}$$

(II)



$$\begin{array}{cccc} & H^1 & Cl & H^3 \\ & | & | & | \\ Cl- & C- & C- & CH^3 \\ & | & | & | \\ & H^1 & H^2 & H^3 \end{array} \qquad (4)$$

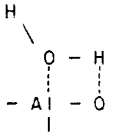
(III)

The order of acid strength of these protons is easily estimated from the number of neighboring chlorines and alkyl groups, as follows:

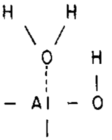
$$\text{TCE (I)} > \text{TCP (II)} > \text{DP (III)} \qquad (5)$$

If the basic strength of the hydrated alumina is not high enough to eliminate the weakly acidic proton, the elimination of chloride may not be ignored, leading to the E2-concerted mechanism to give a product distribution similar to that observed on the dry alumina. This is just the case of III. Thus, it is concluded that the basicity of the hydrated alumina is not as high as that of KOH–silica gel. Nevertheless, the highly acidic protons of TCE and TCP are eliminated to give product distributions from these reactants via the E1-cb mechanism (*1*), similar to those observed over strong basic substances such as KOH–silica gel. The higher yield of 1,1-DCP from TCP is explained in terms of the higher reactivity of its Cl^2 which may be provided by the neighboring methyl group, because the elimination of Cl^2 also leads to preferable formation of 1,1-DCP even if the E2-concerted mechanism partly works (*1c*).

Alumina is known to have basic as well as acidic sites due to the dehydrated structure of the surface (*6, 12–14*). The acidic sites are believed to be aluminum ions (Lewis acids) exposed on the surface as a result of condensation of surface hydroxyl groups (*15*). Peri (*16*) showed on the basis of ir data and their simulation analysis how such sites may be created. Hydroxyl groups of several types which persist on the alumina surface even after heat treatment may constitute weak Brønsted sites. The oxide ions exposed in the surface may behave as basic sites.



(IV)



(V)

Water added during catalysis may be adsorbed on an aluminum ion partly in the dissociative configuration (IV) and partly in the associative configuration (V), according to the situation of the neighboring acidic aluminum ion, decreasing the number of Lewis acidic sites. At the same time, defects in the surface structure are filled with water or its derivative, probably lowering the basicity of the oxide ion, although the number of basic sites may be unchanged because new basic sites are created on the oxygen atom of adsorbed water. The weak Brønsted sites, even if their number is increased, may not play an important role in this kind of elimination reaction. Thus, a suitable amount of adsorbed water may increase the yield of VDC and also assure the survival of the basic site during catalysis although hydrogen chloride is formed. An excess amount of adsorbed water over the monolayer coverage may block the basic sites as well, disturbing the contact of the reactant with the active site. Thus the results in Fig. 2 seem reasonable.

The drastic decrease of VDC formation observed over wet alumina at the reaction temperature of 300°C may be due partly to an easy dehydration although the mechanism may also vary with increasing reaction temperature.

The effect of calcination temperature on the product distribution may also be explained by the above model. Alumina is converted into a transition form due to the higher temperature calcination accompanied with the dehydration, losing to some extent the surface defect which should be the origin of its acidic nature. Such a circumstance is favorable to the selective formation of VDC; however, completion of an α-type formation brings about no activity due to its high stability and low surface area.

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