

Decomposition of 1,2-dichloroethane over CeO₂ modified USY zeolite catalysts: Effect of acidity and redox property on the catalytic behavior

Qinqin Huang, Xiaomin Xue, Renxian Zhou*

Institute of catalysis, Zhejiang University, Hangzhou 310028, PR China

ARTICLE INFO

Article history:

Received 4 May 2010

Received in revised form 18 July 2010

Accepted 20 July 2010

Available online 14 August 2010

Keywords:

CVOCs

1,2-Dichloroethane

CeO₂-USY

Catalytic reactivity

Acidity

Redox property

ABSTRACT

CeO₂ modified ultrastable Y zeolite (CeO₂-USY) catalysts were prepared and were used as the catalysts for the decomposition of 1,2-dichloroethane (DCE). The catalytic behavior of these catalysts was evaluated by micro-reaction and temperature-programmed surface reaction (TPSR) technique. The results reveal that CeO₂-USY catalysts exhibit good catalytic activity for DCE decomposition and high selectivity to the formation of CO₂ and HCl. Both acidity and redox property play important roles in the DCE decomposition, and the synergy between CeO₂ species and USY zeolite shows an enhancement in the catalytic activity for DCE decomposition. CeO₂-USY (1:8) with high dispersion of CeO₂ species and a much more suitable combination of acidity and redox property exhibits the best catalytic activity.

Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.

1. Introduction

Chlorinated volatile organic compounds (CVOCs), such as 1,2-dichloroethane (DCE), dichloromethane (DCM) and trichloroethylene (TCE), are a wide ranging class of solvents commonly found in industrial waste streams and constitute a major source of air and groundwater pollution [1]. Such compounds are involved in the destruction of the ozone layer and may contribute to global warming. Moreover, some are typically carcinogens, mutagens and teratogens, which are severely hazardous to human health [2]. Not only the increasing stringent environmental regulations limiting emissions of CVOCs, but also the increasing amounts of CVOCs released in the environment together with their suspected toxicity and carcinogenic properties, have prompted researchers worldwide to find clean and effective methods for destruction of CVOCs. In comparison with direct combustion technique, catalytic oxidation for the abatement of CVOCs has been widely studied, since it needs less severe conditions (temperature between 300 and 500 °C) and is more efficient and economically advantageous for the destruction of low concentrations of contaminant (<1000 ppm) [3,4].

Due to the optimum performances as solid acid catalysts, more and more consideration has been given to zeolite catalysts to investigate the applicability for the destruction of chlorinated com-

pounds in last years. It has been reported that H-type zeolites such as H-Y, H-ZSM and H-MOR with high density of strong acid sites display a good catalytic activity for CVOCs decomposition and a high selectivity to the formation of HCl and CO₂ [5,6]. However, a certain extent of coke deposition is observed due to the strong acidity of zeolites and/or porous structure, which causes the deactivation of the catalysts [7,8]. Noble metal supported zeolites catalysts show an enhanced catalytic performance for the deep oxidation of CVOCs with respect to the pure protonic zeolites, but the major drawback for the application of these catalysts is the halide poisoning of volatile metal oxychlorides as well as the formation of polychlorinated compounds, which are more toxic and re-calcitrant than the starting material [9–13]. It has been reported in previous literature that transition metal (Cr, Mn, Co, Cu, etc.) modified zeolite catalysts exhibit good catalytic activity for the destruction of CVOCs in spite of relatively less active than noble metal modified catalysts [14–16]. However, the migration and/or loss of active sites may cause the deactivation in a certain degree. Moreover, the formation of the extremely toxic residues (such as chromium oxychloride) at low temperature restricts the use of transition metal oxides catalysts to some extent [17–19].

In recent years, CeO₂-based mixed oxides have attracted considerable attention for the decomposition of CVOCs, due to its high oxygen-storage capacity (OSC) and facile redox cycle of Ce⁴⁺/Ce³⁺ [20]. Gutiérrez-Ortiz and co-workers [21–23] have pointed out that ceria-zirconia mixed oxide with a proper combination of surface acidity and accessible lattice oxygen exhibit better activity for the decomposition of CVOCs than pure ceria/zirconia catalysts. In our

* Corresponding author. Tel.: +86 571 88273290; fax: +86 571 88273283.
E-mail address: zhourenxian@zju.edu.cn (R. Zhou).

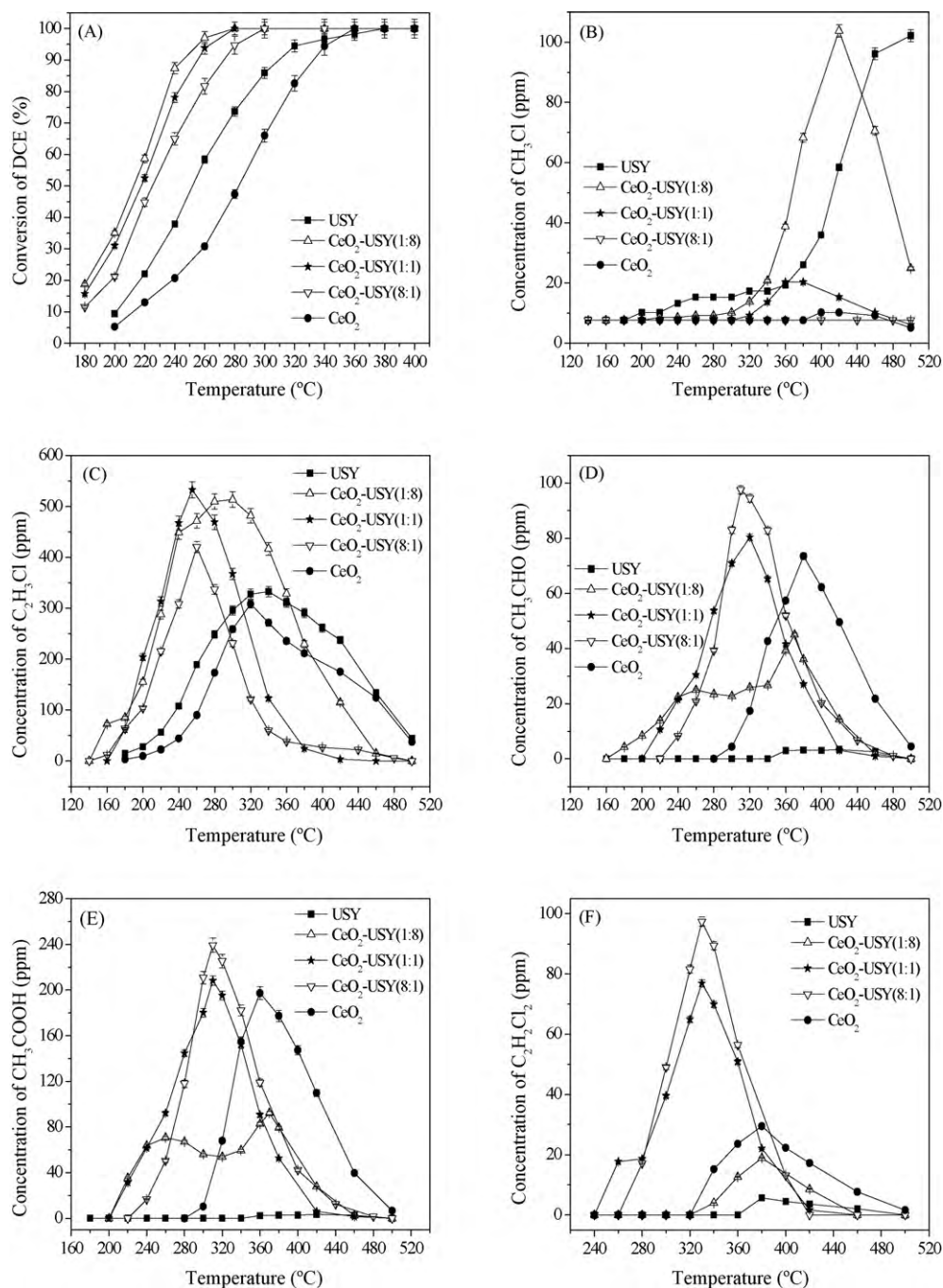


Fig. 1. The catalytic activity of CeO₂-USY catalysts: (A) conversion of DCE, (B) concentration of CH₃Cl, (C) concentration of C₂H₃Cl, (D) concentration of CH₃CHO, (E) concentration of CH₃COOH, and (F) concentration of C₂H₂Cl₂.

previous study, we have found that the introduction of CeO₂ species to different types of zeolites Y (HY, USY and SSY) results in a certain synergy between CeO₂ species and zeolites Y, which shows a promotion in the catalytic activity for deep oxidation of CVOCs [24].

In the present study, CeO₂ modified USY zeolite catalysts with various mass ratios of CeO₂ to USY were prepared and used for the decomposition of DCE. All the catalysts were characterized by means of XRD, NH₃-TPD and H₂-TPR. The catalytic behavior of these catalysts was evaluated by micro-reaction and TPSR technique. The effect of acidity and the redox property on the catalytic activity, intermediates, and selectivity to the formation of CO₂ and HCl during the decomposition of DCE was investigated.

2. Experimental

2.1. Preparation of USY zeolites with various Si/Al ratios and CeO₂-USY catalysts

The USY zeolite with a molar ratio of SiO₂/Al₂O₃ = 5.3 (Si/Al = 5.3) were supplied by HUAHUA Corp. (Wenzhou, China) and used after calcined at 550 °C for 2 h. The USY zeolites with various molar ratios of SiO₂/Al₂O₃ were prepared by dealumination treatment of untreated USY zeolite with ammonium hexafluorosilicate (AHFS) via procedure described by Skeels and Breck [25], adding ammonium acetate as buffer [26]. The dealuminated USY zeolites were calcined at 550 °C for 2 h and labeled as USY-D1 (Si/Al = 9.2), USY-D2

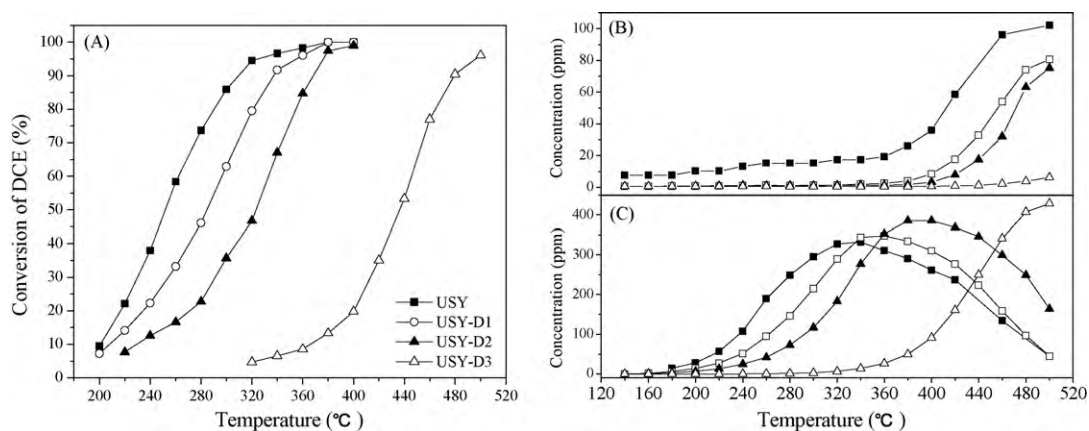


Fig. 2. Concentration–temperature relationship of intermediates over USY zeolites with various molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$: (A) conversion of DCE, (B) concentration of CH_3Cl , and (C) concentration of $\text{C}_2\text{H}_3\text{Cl}$.

($\text{Si}/\text{Al} = 10.8$) and USY-D3 ($\text{Si}/\text{Al} = 20.4$), respectively. The XRD studies showed that the framework of the dealuminated USY zeolites maintained well.

The untreated USY zeolite ($\text{Si}/\text{Al} = 5.3$) was used as the support of CeO_2 modified USY zeolite catalysts. CeO_2 –USY catalysts with various mass ratios (MR = 1:8, 1:1 and 8:1) of CeO_2 to USY were prepared by USY mixed with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR 98%) solution by theoretical calculation. After dried at 100°C for 2 h, all the CeO_2 –USY catalysts were calcined in air at 350°C for 0.5 h and further at 550°C for 2 h. Pure CeO_2 was obtained by thermal decomposition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 550°C for 2 h.

2.2. Catalytic activity tests

The catalytic activity tests were carried out in a micro-reactor (quartz tube, 6 mm i.d., GC 1690, China). The feed gas was prepared by delivering the liquid DCE (about 1000 ppm) by syringe pumps into dry air, which was metered by a mass flow controller. The flow rate through the reactor was set at 75 mL min^{-1} and the gas hourly space velocity (GHSV) was maintained at $15,000 \text{ h}^{-1}$.

The gas stream was analyzed by an on-line gas chromatograph equipped with a packed column (OV 101) and a FID detector. Mass spectrum was used for the determination of the main intermediates (CH_3Cl , $\text{C}_2\text{H}_3\text{Cl}$, CH_3CHO and CH_3COOH). The conversion was calculated using the area of the $\text{C}_2\text{H}_4\text{Cl}_2$. The amount of CH_3Cl and $\text{C}_2\text{H}_3\text{Cl}$ was calculated from the $\text{C}_2\text{H}_4\text{Cl}_2$ peak. The amount of CH_3CHO and CH_3COOH was calculated from the calibration curve of these two compounds, respectively.

The temperature-programmed surface reaction (TPSR) measurement was carried out under the catalytic activity tests condition ($[\text{DCE}] \approx 1000 \text{ ppm}$, $\text{GHSV} = 15,000 \text{ h}^{-1}$) in order to detect the evolutions of the reactant and the products. First, the adsorption of DCE on the catalysts was first carried out at 50°C . After the adsorption–desorption reached an equilibrium, the catalysts were heated from 50 to 500°C at a rate of 5°C min^{-1} . The reactant (DCE) and the products (HCl , Cl_2 and CO_2) were analyzed on-line over a mass spectrometer apparatus (HIDEN QIC-20).

2.3. Catalysts characterization

The nitrogen adsorption/desorption was performed at liquid nitrogen temperature using a Coulter OMNISORP-100 apparatus. The samples were degassed under vacuum for 3 h at 200°C before the measurements. Specific total surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. The BET surface area of each catalyst was 563, 486, 272, 125 and $76 \text{ m}^2/\text{g}$ for USY, CeO_2 –USY (1:8), CeO_2 –USY (1:1), CeO_2 –USY (8:1) and CeO_2 , respectively.

The X-ray diffraction (XRD) measurement was performed on an ARL X'TRA X-ray Diffractometer (Thermo Electron Corporation, USA), with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA in a scanning range of 3 – 80° (2θ).

The scanning electron microscope (SEM) was performed on a SIRION Analytical Scanning Electron Microscopy (FEI Corp., Holland) in order to get the morphological appearance of the catalysts.

The ammonia temperature-programmed desorption (NH_3 -TPD) was performed in a quartz fixed-bed micro-reactor equipped with TCD. Prior to adsorption of ammonia, the catalyst (100 mg) was pretreated in a N_2 stream (99.99% , 35 mL min^{-1}) at 500°C for 0.5 h. After being cooled down to 100°C , the catalyst was exposed to a flow (30 mL min^{-1}) of 20 vol.% NH_3/N_2 mixture for 30 min, and then treated in a N_2 flow for 1 h in order to remove physically bound ammonia. Finally, desorption performance was carried out in a N_2 flow (40 mL min^{-1}) from 100 to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$. All these profiles were simulated by Gaussian functions.

The temperature-programmed reduction of H_2 (H_2 -TPR) was performed in a quartz fixed-bed micro-reactor equipped with TCD, using a 5 vol.% H_2/Ar mixture. After the catalysts (50 mg) were pretreated in air at 300°C for 0.5 h, the reduction was carried out from 100 to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1. Catalytic activity results of CeO_2 –USY catalysts

The catalytic behavior of USY, CeO_2 and CeO_2 –USY catalysts for DCE decomposition is presented in Fig. 1. As shown in Fig. 1(A), a noticeable catalytic activity is observed for all the catalysts, over which DCE can be totally converted at the temperature below 360°C . An obvious improvement in the catalytic activity is observed over CeO_2 –USY compared with that over CeO_2 or USY, indicating that a synergy between CeO_2 species and USY zeolite favors the enhancement for the decomposition of DCE. On the basis of T_{90} (temperature at which 90% conversion is achieved), DCE conversion over all the catalysts decreases in the following order: CeO_2 –USY (1:8) (245°C) > CeO_2 –USY (1:1) (255°C) > CeO_2 –USY (8:1) (273°C) > USY (310°C) > CeO_2 (334°C).

During the decomposition of DCE, CH_3Cl , $\text{C}_2\text{H}_3\text{Cl}$, CH_3CHO and CH_3COOH are major intermediates. CH_3Cl is produced from the DCE cracking on the strong acid sites. As shown in Fig. 1(B), it starts to exist at relatively low temperature (about 200°C) over USY with strong acidity and increases rapidly when the temperature is higher than 360°C , while nearly no CH_3Cl is detected over CeO_2 because of its limited amount of weak acid sites. However, the amount of CH_3Cl

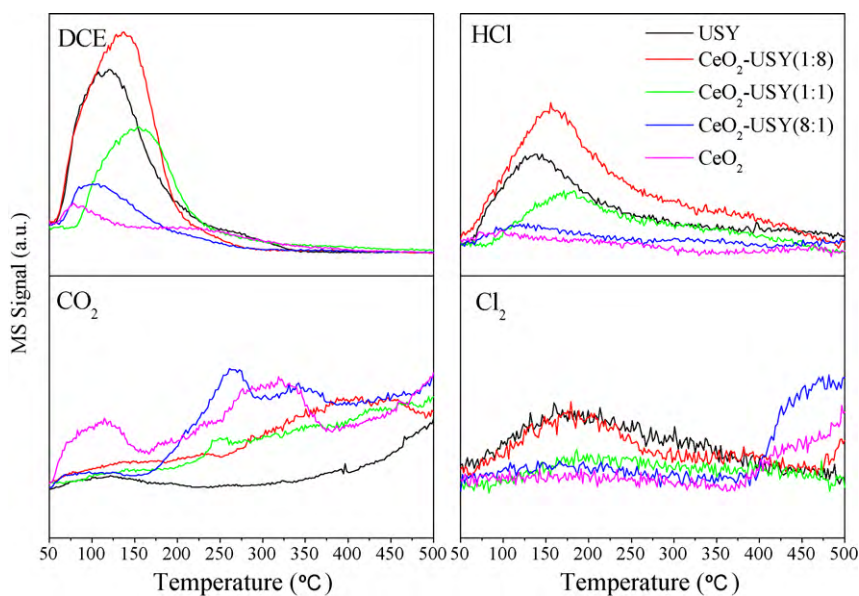


Fig. 3. TPSR profiles for decomposition of DCE over USY, CeO₂ and CeO₂-USY catalysts.

decreases obviously over CeO₂-USY especially when the mass ratio of CeO₂ to USY is higher than 1:1. It is caused by the reduction of strong acid sites which inhibits the production of CH₃Cl. What is more, CH₃Cl can be completely decomposed over CeO₂-USY due to the presence of CeO₂ species with better oxygen storage/release behavior.

The major intermediate C₂H₃Cl is produced via the dehydrochlorination of DCE on Lewis acidity [27]. The concentration-temperature relationship of C₂H₃Cl is shown in Fig. 1(C). Obviously, the maximum concentration of C₂H₃Cl appears at the temperature when DCE is totally consumed. After CeO₂ species are introduced into USY zeolite, T_{max} (temperature at which the maximum concentration is achieved) of C₂H₃Cl shifts to lower temperature range and lowers slightly as the mass ratio of CeO₂ to USY increases. It is presumed that the synergy between CeO₂ species and USY zeolite promotes the production of C₂H₃Cl via dehydrochlorination of DCE at relatively low temperature. The increase in the amount of C₂H₃Cl is also observed over CeO₂-USY compared with that over USY or CeO₂, which decreases only a little even the mass ratio of CeO₂ to USY reaches 8:1. It has been reported in previous literature that C₂H₃Cl is firstly produced via dehydrochlorination of DCE on Lewis acidity, which can be readily protonated in the presence of moisture or OH surface species. A second dehydrochlorination process of C₂H₃Cl may occur on the protonic acid sites [27–29]. Therefore, the increment of C₂H₃Cl over CeO₂-USY may be ascribed to the reduction of acid sites, especially the protonic acid sites.

In order to further confirm the influence of the acidity on the catalytic behavior for the DCE decomposition, the catalytic activity of USY zeolites with various Si/Al ratios were examined and the results are presented in Fig. 2. We can see from Fig. 2(A) that the loss of acidity as the Si/Al ratio increases results in the decrease in the catalytic activity. Based on the T₉₀, the catalytic activity of these USY zeolites follows the order: USY (310 °C) > USY-D1 (340 °C) > USY-D2 (370 °C) ≫ USY-D3 (480 °C). CH₃Cl and C₂H₃Cl are the only major intermediates during the decomposition of DCE over USY zeolite. The production of CH₃Cl decreases with the increasing Si/Al ratio of USY zeolites due to the reduction of acidity, while the amount of C₂H₃Cl increases.

It is known that CH₃CHO and CH₃COOH are the products resulted from the further oxidation of C₂H₃Cl [28]. As shown in

Fig. 1(D) and (E), large amount of CH₃CHO and CH₃COOH are detected over CeO₂ with a good oxygen storage/release behavior, while these two compounds are hardly observed over USY. In the case of CeO₂-USY, T_{max} of CH₃CHO/CH₃COOH shifts to lower temperature compared with that over CeO₂. It is supposed that the synergy between CeO₂ species and USY zeolite is in favor of the mobility of oxygen species and further promotes the oxidation of C₂H₃Cl at relatively lower temperature [14].

The undesired intermediate C₂H₂Cl₂ is also detected during the DCE decomposition (shown in Fig. 1(F)). The results indicate that the amount of C₂H₂Cl₂ increases evidently over CeO₂-USY.

The experimental evaluation system is stable in our study. We repeated the catalytic activity test, and the errors of both conversion and concentration are within 3%.

3.2. TPSR results of CeO₂-USY catalysts

The adsorption-desorption behavior of DCE and the evolutions of the products (HCl, Cl₂ and CO₂) have been further studied by TPSR method (shown in Fig. 3). We can see from the profiles of DCE that desorption of DCE occurs at low temperature range and desorption is accompanied with DCE decomposition. It is noticeable that the peak-temperature of the desorption peaks is higher for CeO₂-USY (1:8) and CeO₂-USY (1:1) than that for the other three catalysts. Moreover, the intensity of the desorption peak for CeO₂-USY (1:8) increases obviously compared with that for USY. It indicates that the synergy between CeO₂ species and USY zeolite improves the strong adsorption of DCE, which is of great significance to improve the integration of adsorption-desorption-catalysis process. It can be seen from the CO₂ evolution that the synergy between CeO₂ species and USY zeolite promotes the selectivity to the formation of CO₂. More amount of CeO₂ contained in the catalyst, more CO₂ is produced. And the obvious peak observed at low temperature range over CeO₂ may be due to desorption of CO₂. The sequence of the selectivity to CO₂ over these catalysts is as follows: CeO₂ ≈ CeO₂-USY (8:1) > CeO₂-USY (1:1) ≈ CeO₂-USY (1:8) > USY. However, on the basis of the mechanism of DCE, the pathway of the CO₂ produced over the catalysts may be different from each other. For CeO₂ and CeO₂-USY catalysts, the production of CO₂ can be assigned to the further oxidation of acetate species in the presence of CeO₂ species with good oxygen storage/release behavior

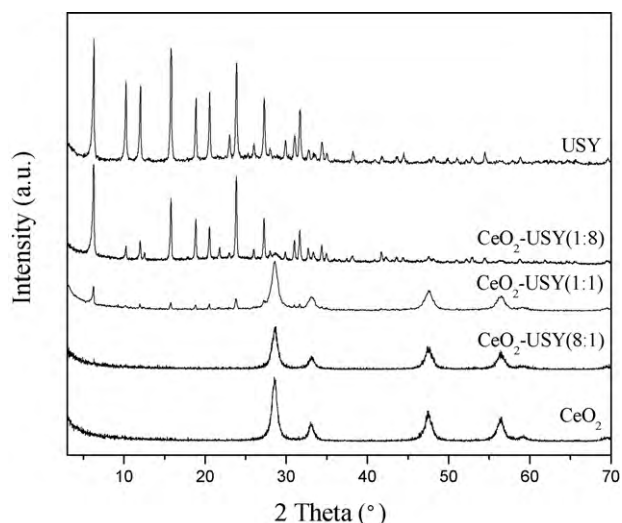


Fig. 4. XRD patterns of CeO_2 , USY and CeO_2 -USY catalysts.

[27]. In comparison with USY, the evident increase of CO_2 production observed at relatively low temperature over CeO_2 -USY catalysts indicates that the synergy between CeO_2 and USY promotes the further oxidation of DCE. For USY zeolites, the obvious increment of CO_2 within high temperature range may be resulted from the oxidation of coke deposited on the surface of the zeolites. It can be explained by the facts below. (a) The amount of CO_2 does not increase evidently until the temperature is higher than 350°C , when DCE has been totally consumed. (b) Nearly no CH_3CHO or CH_3COOH is detected, which can be further oxidized to produce CO_2 . (c) Severe coke deposition is observed after the TPSR measurement.

The evolutions of HCl and Cl_2 demonstrate that HCl is the major chlorinated by-product within the temperature range 50 – 300°C , which is a preferred chlorinated decomposition chlorinated product instead of Cl_2 . The results can be ascribed to two reasons presented below. (a) The hydroxyls in the zeolites structure largely promote HCl formation by the Deacon reaction [30]. (b) Acid character of zeolites appears to be a favorable property to enhance HCl selectivity mainly in the combustion of compounds with a low H/Cl ratio [31]. The selectivity of HCl over the catalysts decreases in the order of CeO_2 -USY (1:8) > USY > CeO_2 -USY (1:1) > CeO_2 -USY (8:1) \approx CeO_2 . It suggests that the synergy between CeO_2 species and USY zeolite also favors the enhancement of selectivity to the HCl formation. However, it is noticeable that the amount of Cl_2 increases obviously over CeO_2 -USY (8:1) and CeO_2 when the temperature is higher than 400°C . It may be related to the more CeO_2 species contained in these two catalysts, which promotes the oxidation of HCl at higher temperature range according to the so-called Deacon reaction ($2\text{HCl} + \text{O}_2 \leftrightarrow \text{Cl}_2 + \text{H}_2\text{O}$) [28].

Table 1
The crystallite size of USY, CeO_2 and CeO_2 -USY catalysts.

Catalysts	Crystallite size (nm)	
	USY	CeO_2
USY	53.7	–
CeO_2 -USY (1:8)	50.7	11.1
CeO_2 -USY (1:1)	50.6	9.1
CeO_2 -USY (8:1)	–	9.5
CeO_2	–	10.3

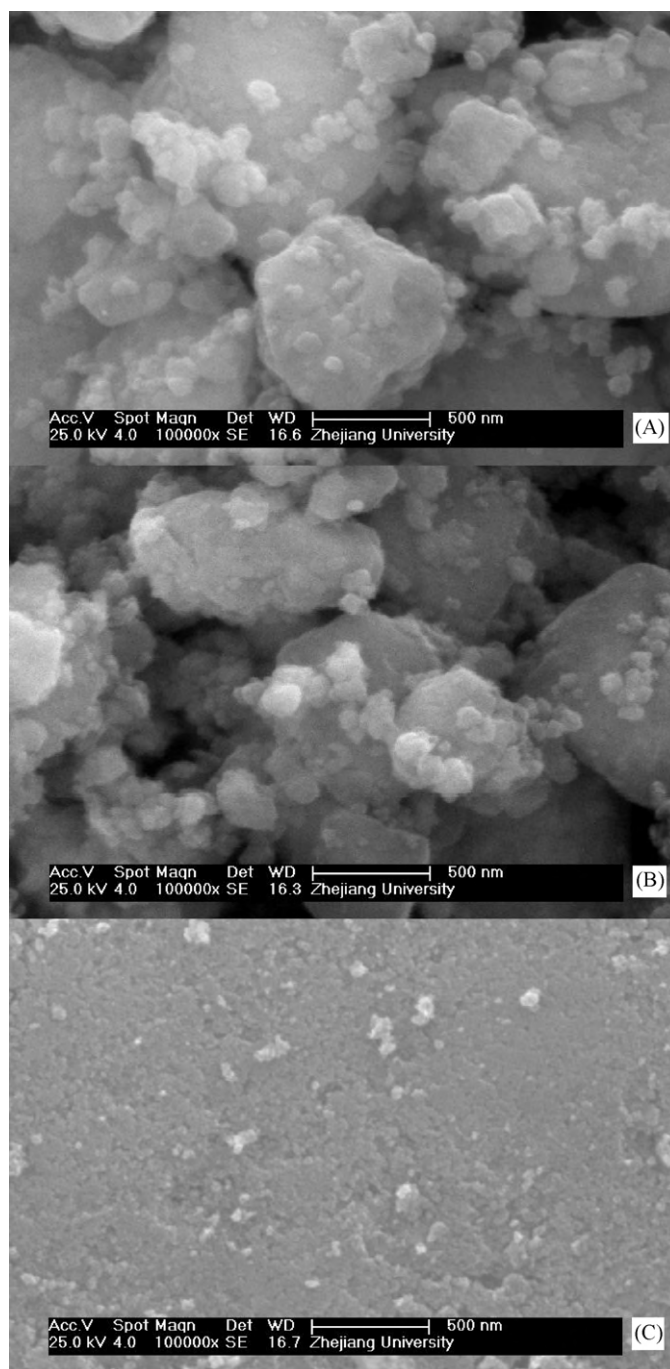


Fig. 5. SEM micrographs of the catalysts: (A) USY, (B) CeO_2 -USY (1:8) and (C) CeO_2 -USY (8:1) (scale bar = 500 nm).

3.3. Catalysts characterization results

3.3.1. XRD

XRD patterns of CeO_2 , USY and CeO_2 -USY catalysts are presented in Fig. 4. No obvious diffraction peaks of fluorite-structure of CeO_2 species are observed on CeO_2 -USY (1:8) compared with that on CeO_2 -USY (1:1) and CeO_2 -USY (8:1), suggesting that a relatively homogeneous dispersion of CeO_2 particles on USY surface is attained. It is beneficial to the interaction between CeO_2 and USY and further enhances the catalytic activity for the decomposition of DCE.

The crystallite size of each catalyst is listed in Table 1. It can be seen that as the content of CeO_2 increases in the CeO_2 -USY cat-

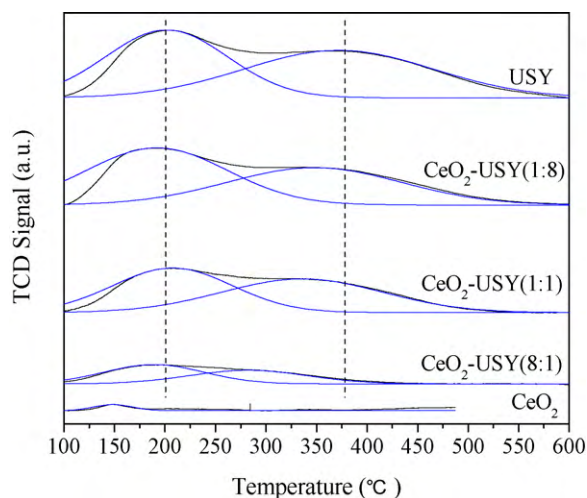


Fig. 6. NH_3 -TPD profiles of CeO_2 -USY zeolites catalysts.

alysts, the crystallite of CeO_2 remains at the similar size of about 9–11 nm. However, that of USY shows an evident reduction, which decreases from 53.7 to 50.6 nm as the ratio of CeO_2 to USY increases from 0 to 1. Furthermore, the phase of USY can hardly be detected on CeO_2 -USY (8:1) may be due to the low content of USY as well as the covering by the signal of the baseline during the XRD measurement.

3.3.2. SEM

Scanning electron micrographs of the catalysts were presented in Fig. 5. Similar shaped and sized of USY zeolite and CeO_2 -USY (1:8) particles are observed, suggesting that the introduction of a small amount of CeO_2 has little influence on the appearance of USY zeolite. When the ratio of CeO_2 to USY reaches 8:1, however, the appearance of the catalyst exhibits snow-like crystals, which is quite different from the other two catalysts.

3.3.3. NH_3 -TPD

NH_3 -TPD profiles of USY, CeO_2 and CeO_2 -USY zeolites catalysts are presented in Fig. 6. As shown in Fig. 6, only one desorption peak (at about 150 °C) with weak signal is observed on CeO_2 , which is indicative of a bit of weak acid sites. Two desorption peaks are detected on USY and CeO_2 -USY, indicating the existence of both Lewis acidity and Brønsted acidity. With the increasing mass ratio of CeO_2 to USY, the amount of both Lewis acid sites and Brønsted acid sites decreases, while the reduction in acid sites is limited for CeO_2 -USY (1:8). Combining with the results of catalytic activity tests, it is seen that the catalytic activity of CeO_2 -USY is evidently higher than that of USY zeolite or CeO_2 . It indicates that the synergy between CeO_2 and USY promotes the production of $\text{C}_2\text{H}_3\text{Cl}$ via dehydrochlorination of DCE. However, the loss of acid sites, especially the protonic acidity, inhibits the further dehydrochlorination of $\text{C}_2\text{H}_3\text{Cl}$, which results in the increment of production of $\text{C}_2\text{H}_3\text{Cl}$ over CeO_2 -USY (shown in Fig. 1(C)) [3,5].

3.3.4. H_2 -TPR

H_2 -TPR profiles of CeO_2 and CeO_2 -USY catalysts are displayed in Fig. 7. For pure CeO_2 sample, two peaks observed at temperature below 600 °C are ascribed to the reduction of superficial oxygen and the peak detected above 600 °C is assigned to the reduction of bulk oxygen [32]. For CeO_2 -USY, the dispersion of CeO_2 species on USY zeolite results in the small particles of CeO_2 species, which is beneficial for the mobility of oxygen species in comparison with pure CeO_2 . As the content of CeO_2 increases in CeO_2 -USY, the peak-temperature of both types of oxygen species

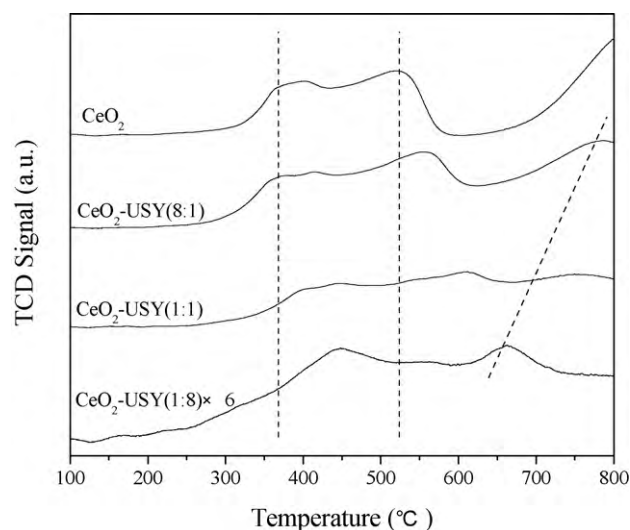


Fig. 7. H_2 -TPR profiles of CeO_2 and CeO_2 -USY catalysts.

shifts to higher temperature range. For CeO_2 -USY (1:8), the high dispersion of CeO_2 species on USY zeolite results in a much better mobility of superficial and bulk oxygen species, the temperature of which is observed at about 335, 450 and 665 °C, respectively. It is known from the mechanism of DCE decomposition, $\text{C}_2\text{H}_3\text{Cl}$ can be attacked by nucleophilic oxygen species from the catalyst to form chlorinated alkoxide species, which readily decompose to gradually generate acetaldehyde through dehydrochlorination in the presence of protonic acid sites, acetates and CO_x [27,28]. We can see from the results of catalytic activity tests that the T_{max} of CH_3CHO and CH_3COOH over CeO_2 -USY is obviously lower than that over CeO_2 (shown in Fig. 1(D) and (E)), suggesting that the improved mobility of oxygen species is in favor of the further oxidation of $\text{C}_2\text{H}_3\text{Cl}$.

4. Conclusion

CeO_2 modified USY zeolite catalysts were prepared. The catalytic behavior of CeO_2 -USY catalysts used for the decomposition of DCE was evaluated by micro-reaction and TPSR techniques. All the catalysts were characterized by means of XRD, NH_3 -TPD and H_2 -TPR. The results reveal that CeO_2 -USY catalysts show good catalytic activity for DCE decomposition and high selectivity to the formation of CO_2 and HCl . Both acidity and redox property play important roles in the DCE decomposition, and the synergy between CeO_2 species and USY zeolite shows an enhancement in the catalytic activity for DCE decomposition. CeO_2 -USY (1:8) with high dispersion of CeO_2 species and a much more suitable combination of acidity and redox property exhibits the best catalytic activity.

Acknowledgements

We gratefully acknowledge the financial supports from the Ministry of Science and Technology of China (No. 2004 CB 719504) and Nature Science Foundation of China (No. 20577043).

References

- [1] E.C. Moretti, Practical Solutions for Reducing Volatile Organic Compounds and Hazardous Air Pollutants, Center for Waste Reduction Technologies of the American Institute of Chemical Engineers, New York, 2001.
- [2] R. López-Fonseca, A. Aranzabal, J.I. Gutiérrez-Ortiz, J.I. Álvarez-Urriarte, J.R. González-Velasco, Comparative study of the oxidative decomposition of trichloroethylene over H-type zeolites under dry and humid conditions, Appl. Catal. B Environ. 30 (2001) 303–313.

- [3] J.R. González-Velasco, A. Aranzabal, J.I. Gutiérrez-Ortiz, R. López-Fonseca, M.A. Gutiérrez-Ortiz, Activity and product distribution of alumina supported platinum and palladium catalysts in the gas-phase oxidative decomposition of chlorinated hydrocarbons, *Appl. Catal. B Environ.* 19 (1998) 189–197.
- [4] P. Hunter, S.T. Oyama, *Control of Volatile Organic Compounds Emissions: Conventional and Emerging Technologies*, Wiley-Interscience, New York, 2000.
- [5] J.R. González-Velasco, R. López-Fonseca, A. Aranzabal, J.I. Gutiérrez-Ortiz, P. Steltenpohl, Evaluation of H-type zeolites in the destructive oxidation of chlorinated volatile organic compounds, *Appl. Catal. B Environ.* 24 (2000) 233–242.
- [6] L. Intriago, E. Díaz, S. Ordóñez, A. Vega, Combustion of trichloroethylene and dichloromethane over protonic zeolites: Influence of adsorption properties on the catalytic performance, *Micropor. Mesopor. Mater.* 91 (2006) 161–169.
- [7] A. Aranzabal, J.A. González-Marcos, M. Romero-Sáez, J.R. González-Velasco, Stability of protonic zeolites in the catalytic oxidation of chlorinated VOCs (1,2-dichloroethane), *Appl. Catal. B Environ.* 88 (2009) 533–541.
- [8] M. Guisnet, L. Costa, F.R. Ribeiro, Prevention of zeolite deactivation by coking, *J. Mol. Catal. A Chem.* 305 (2009) 69–83.
- [9] R. López-Fonseca, J.I. Gutiérrez-Ortiz, J.R. González-Velasco, Catalytic combustion of chlorinated hydrocarbons over H-BETA and PdO/H-BETA zeolite catalysts, *Appl. Catal. A Gen.* 271 (2004) 39–46.
- [10] D. Li, Y. Zheng, X.Y. Wang, Pt-loaded P-MCM-41 as a novel bifunctional catalyst for catalytic combustion of trichloroethylene, *Catal. Commun.* 8 (2007) 1583–1587.
- [11] S. Scirè, S. Minicò, C. Crisafulli, Pt catalysts supported on H-type zeolites for the catalytic combustion of chlorobenzene, *Appl. Catal. B Environ.* 45 (2003) 117–125.
- [12] B. Mendyka, A. Musialik-Piotrowska, K. Syczewska, Effect of chlorine compounds on the deactivation of platinum catalysts, *Catal. Today* 11 (1992) 597–610.
- [13] R.W. Van den Brink, M. Krzan, M.M.R. Feijen-Jeurissen, R. Louw, P. Mulder, The role of the support and dispersion in the catalytic combustion of chlorobenzene on noble metal based catalysts, *Appl. Catal. B Environ.* 24 (2000) 255–264.
- [14] S. Chatterjee, H.L. Greene, Y.J. Park, Comparison of modified transition metal-exchanged zeolite catalysts for oxidation of chlorinated hydrocarbons, *J. Catal.* 138 (1992) 179–194.
- [15] J. Janas, R. Janik, T. Machej, E.M. Serwicka, E. Bielańska, Cr-doped Zr, Simesoporous molecular sieves as catalysts for CH_2Cl_2 oxidation, *Catal. Today* 59 (2000) 241–248.
- [16] A.Z. Abdullah, M.Z.A. Bakar, S. Bhatia, Combustion of chlorinated volatile organic compounds (VOCs) using bimetallic chromium-copper supported on modified H-ZSM-5 catalyst, *Hazard. Mater. B* 129 (2006) 39–49.
- [17] S. Krishnamoorthy, J.A. Rivas, M.D. Amiridis, Catalytic oxidation of 1,2-dichlorobenzene over supported transition metal oxides, *J. Catal.* 193 (2000) 264–272.
- [18] S.K. Agarwal, J.J. Spivey, J.B. Butt, Catalyst deactivation during deep oxidation of chlorohydrocarbons, *Appl. Catal. A Gen.* 82 (1992) 259–275.
- [19] R. Rachapudi, P.S. Chintawar, H.L. Greene, Aging and structure/activity characteristics of Cr-ZSM-5 catalysts during exposure to chlorinated VOCs, *J. Catal.* 185 (1999) 58–72.
- [20] B. Skårman, D. Grandjean, R.E. Benfield, A. Hinz, A. Andersson, L.R. Wallenberg, Carbon monoxide oxidation on nanostructured $\text{CuO}_x/\text{CeO}_2$ composite particles characterized by HREM, XPS, XAS, and high-energy diffraction, *J. Catal.* 211 (2002) 119–133.
- [21] J.I. Gutiérrez-Ortiz, B. de Rivas, R. López-Fonseca, J.R. González-Velasco, Combustion of aliphatic C_2 chlorohydrocarbons over ceria-zirconia mixed oxides catalysts, *Appl. Catal. A Gen.* 269 (2004) 147–155.
- [22] J.I. Gutiérrez-Ortiz, B. de Rivas, R. López-Fonseca, J.R. González-Velasco, Catalytic purification of waste gases containing VOC mixtures with Ce/Zr solid solutions, *Appl. Catal. B Environ.* 65 (2006) 191–200.
- [23] B. de Rivas, R. López-Fonseca, C. Sampedro, J.I. Gutiérrez-Ortiz, Catalytic behaviour of thermally aged Ce/Zr mixed oxides for the purification of chlorinated VOC-containing gas streams, *Appl. Catal. B Environ.* 90 (2009) 545–555.
- [24] J.M. Zhou, L. Zhao, Q.Q. Huang, R.X. Zhou, X.K. Li, Catalytic activity of Y zeolite supported CeO_2 catalysts for deep oxidation of 1,2-dichloroethane (DCE), *Catal. Lett.* 127 (2009) 277–284.
- [25] G.W. Skeels, D.W. Breck, in: D. Olson, A. Bisio (Eds.), *Proceedings of the 6th International Zeolites Conference*, Butterworth, Guilford, 1984, p. 87.
- [26] E.M. Flanigen, in: J.A. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, American Chemical Society, Washington, DC, 1976, p. 80.
- [27] M.M.R. Feijen-Jeurissen, J.J. Jorna, B.E. Nieuwenhuys, G. Sinquin, C. Petit, J.-P. Hindermann, Mechanism of catalytic destruction of 1,2-dichloroethane and trichloroethylene over $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ supported chromium and palladium catalysts, *Catal. Today* 54 (1999) 65–79.
- [28] B. de Rivas, R. López-Fonseca, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, On the mechanism of the catalytic destruction of 1,2-dichloroethane over Ce/Zr mixed oxide catalysts, *J. Mol. Catal. A Chem.* 278 (2007) 181–188.
- [29] A.E. Kulikova, E.N. Zil'berman, Conversion of chlorine-containing aliphatic compounds in the presence of coordination-unsaturated metals, *Russ. Chem. Rev.* 40 (1971) 256–271.
- [30] H.L. Greene, D.S. Prakash, K.V. Athota, Combined sorbent/catalyst media for destruction of halogenated VOCs, *Appl. Catal. B Environ.* 7 (1996) 213–224.
- [31] R. López-Fonseca, J.I. Gutiérrez-Ortiz, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, Dealuminated Y zeolites for destruction of chlorinated volatile organic compounds, *J. Catal.* 209 (2002) 145–150.
- [32] C. Bigey, L. Hilaire, G. Maire, $\text{WO}_3\text{-CeO}_2$ and $\text{Pd/WO}_3\text{-CeO}_2$ as potential catalysts for reforming applications. I. Physicochemical characterization study, *J. Catal.* 198 (2001) 208–222.