Catalytic hydrolysis of Dichlorodifluoromethane over MoO3/ZrO2 -TiO2 solid acid

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Research article

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Abstract

The catalytic behaviors of solid acid of MoO3/ZrO2-TiO2 calcined at different temperature for the catalytic hydrolysis of Dichlorodifluoromethane have been studided. The effects of catalytic hydrolysis temperature and water vapor concentration on catalytic hydrolysis of Dichlorodifluoromethane were also studied. The Results show 98.65 % of Dichlorodifluoromethane is degraded over MoO3/ZrO2-TiO2 catalyst calcined at 500 ℃ with a concentration of water vapor of 83.18% when the hydrolysis temperature is 400C and the Dichlorodifluoromethane flux rate is 1mL/min with main degradation products were CO, CO2, HF and HCl. A maintained degradation rate of 65.34 % of Difluoromethylene Chloride has been observed through 30 hours' continuous reaction over the catalyst of MoO3/ZrO2-TiO2. The XRD result reveals the main phase of solid MoO3/ZrO2-TiO2 catalyst is the tetragonal Zr(MoO4)2 that doped TiO2 of anatase.

1. Introduction

Chlorofluorocarbons(CFCs)have been broadly utilized in chemical industry due to their superior physical and chemical properties, despite of their disadvantages in the ecological environment revealed by more and more research with the examples including a dissertation published by Molina and Rowland in 1974 that proved CFCs are a killer of ozone layer that protects humans against harmful ultraviolet radiation from the sun [1−2]. As one of the green house gases that have a great negative impact on humanity heath and ecological environments, the research of CFCs has recently attracted increasing attention from the experts and scholars all over the world [4]. For example, in 1985, facilitated by United Nations Environment Program, the 24 developed countries which pioneered the use of CFCs established Vienna Convention to protect the ozone layer. With the enhancement of environmental awareness, in 1987, 46 countries signed the Montreal Protocol (hereinafter referred to as protocol) in Montreal, Canada. Over time,The United Nation organized several meetings again, strengthen efforts that limited use of CFCs, modified protocol clearly stipulates that developing countries to stop using CFCs, CFCB, CCl_4, CH_3CCl_3.

So far, the technology of harmless treatment of chlorofluorocarbons mainly includes chemical method, incineration, cement kiln, induction plasma, supercritical water, photocatalysis, etc [5−8]. But this methods have some limitations, hence, an urgent need to pursue safe and efficient method of degradation of chlorofluorocarbons.Solid super acid [9−12]is one of the new catalytic materials that has developed rapidly in recent years. The advantage of solid superacid catalytic include their excellent catalytic activity, pollution-free, stability and reusability thus this type of materials also become very popular in catalyzing the hydrolysis Dichlorodifluoromethane(CFC-12)[13−15]. The catalytic behaviors, including the catalyst life of MoO_3/ZrO_2-TiO_2 solid acid catalyst calcined at different temperature for the catalytic hydrolysis of CFC-12 are investigated herein and the reaction condition of the effects of catalytic hydrolysis temperature and water vapor concentration has also been evaluated [16−18]. The optimized conditions that catalyzed hydrolysis CFC-12[19−22], for the large quantities of harmless treatment of CFC-12 to provide a theoretical basis.

2. Experimental

2.1. Catalyst preparation

Mixed precipitation of the catalyst prepared by impregnation saturated MoO_3/TiO_2-ZrO_2 process conditions are as follow: The molar ratio of Titanium zirconium is 7: 3, the immersion liquid concentration of $(NH_4)_6MoO_{24}\cdot 4H_2O$ is 0.25 mol/L,The immersion temperature and time are 60 ℃ and 6 hours respectively, The baking temperature is 500C and the baking time is 3 hours

2.2. Catalyst characterization

In order to understand the morphology of catalyst, this paper has taken the following characterization tools. Firstly, the surface composition of the catalysts is analyzed by X-ray, the instruments are produced in Germany, the model is BRUKER D8ADVANCE. Secondly, the surface morphology of catalysts is analyzed by scanning electron microscopy with spectrum analyzer, the equipments are produced by FEI company of United States, its model is NOVA NANOSEM-450.

2.3. Catalyst experiment

The catalyst hydrolysis was carried out atmospheric pressure reaction using heated quartz tubes (Φ30 × 700 mm), the catalyst (MoO_3/TiO_2-ZrO_2) dosage 1.00 g, and CFC-12 flow rate 1 mL/min, and water vapor volume fraction 83.18%. The catalytic performance of MoO_3/ZrO_2-TiO_2 solid acid catalyst calcined at different temperature for the catalytic hydrolysis of CFC-12 was investigated. The reaction condition effects of catalytic hydrolysis temperature and water vapor concentration were also evaluated. Reaction after 1.5 hours, took sample, tested degradation rate of CFC-12. Continuous reaction about 30 hours to investigated catalyst stability.

2.4. Analysis methods

CFCs hydrolysis products of qualitative and quantitative analysis by using gas chromatography and mass spectrometry (ThermoFisher GC-MS), MS detectors EI source and the electron energy is 70 eV. CFCs hydrolysis products qualitative analysis and quantitative analysis using mass spectrometry database and total ion chromatogram peak area. The hydrolysis rate of CFC-12 and mineral formation rate of CO and CO_2 were calculated as follows:

$[\text{hydrolysis rate of CFC-12}]=([\text{CFC-12}]_{in}-[\text{CFC-12}]_{out})/[\text{CFC-12}]_{in}\times 100\%$;

$[\text{Yield of COx}]=[\text{COx}]_{out} / ([\text{CFC-12}]_{in}-[\text{CFC-12}]_{out}) \times 100\%$.

3. Results Discussion

3.1. X-ray (XRD)

3.1.1. XRD patterns of MoO3/ ZrO2-TiO2 calcined at different temperature

Fig.2 shows the component of the catalyst is mainly amorphous when calcinations temperature is below 400 ℃, as the temperature increasing, the morphology of MoO3/ ZrO2-TiO2 crystal appear. At calcianation temperature of 500°C the corresponding characteristic diffraction peaks of tetragonal phase (Zr(MoO4)2) occur with the 2θ of 23.180°,30.526°and 50.033°, respectively. The pattern shows crystal structure of anatase, it confirms the main constituents of the catalyst (MoO3/ ZrO2-TiO2) is tetragonal Zr(MoO4)2 phase mixed with TiO2 of anatase.

3.1.2. XRD patterns of MoO_3/TiO_2-ZrO_2 at different calcined time

As show in Fig. 3, when the calcined time were 1 hour and 2 hours, respectively, the XRD patterns (MoO_3/TiO_2-ZrO_2) indicated the components are mainly amorphous with calcined temperature of 500 ℃. When calcined time increase above 3 hours, fine crystal structures of MoO_3/ ZrO_2-TiO_2 are observed in the XRD patterns.

3.2. Effect of MoO_3/ ZrO_2-TiO_2 on the conversion of CFC-12

3.2.1.Effect of calcination temperature on hydrolysis rate of CFC-12

It can be seen from Fig. 4 that the hydrolysis rate of CFC-12 which is calcined at different temperatures is up to a highly hydrolysis rate of 98.65% at 500 ^{0}C, and then the hydrolysis rate decreases with the increase of temperature. It is studied and analyzed that the occurrence of the catalyst is due to the temperature being too high, the catalyst is sintered, and the activity is lowered.

3.2.2.Effect of calcination time on hydrolysis rate of CFC-12

Fig.5 is based on a previous study of the optimal calcination temperature. The effect of calcination time on the hydrolysis rate of CFC-12 at the optimum calcination temperature was investigated. The experimental results show that the calcination temperature is 3 hours. The catalytic hydrolysis rate of CFC-12 has achieved good results. When the calcination time is less than 3 hours, the calcination is incomplete and the structure is incomplete, so the hydrolysis rate is not too high. After calcination for 3 hours, the main structure of the solid acid catalyst MoO3 / ZrO2-TiO2 is tetragonal Zr(MoO4)2 doped anatase TiO2 structure, which increases the calcination time, reduces the active site and reduces the activity of the catalyst. The hydrolysis rate is lowered.

3.2.3. Effect of catalytic hydrolysis temperature on the conversion of CFC-12

Fig. 6 shows that, with the increase of the temperature of catalytic hydrolysis, the rate of degradation of CFC-12 gradually increases due to the endothermic process of the reaction of CFC-12: $CF_2Cl_2 + H_2O \rightarrow CO + HF + HCl$. The resulting products have been examined by mass spectrometric and MS study shows the degradation products of CFC-12 contained certain quantity of CO_2 gas probably from the reaction: $CF_2Cl_2 + O_2 + H_2O \rightarrow CO_2 + HF + HCl$, and the oxygen involved may come from the dissolved oxygen in air. When the catalytic hydrolysis temperature is 400°C,degradation rate of CFC-12 is 98.65 %, mineral formation rate of COx (CO and CO_2) are 72.44 %, which may indicate the catalytic hydrolysis of CFC-12 over MoO_3/ZrO_2-TiO_2 is complete. All the above investigations indicate the solid acid of MoO_3/ZrO_2-TiO_2 composite with the calcination temperature of 500°C and calcination time 3 hours in the catalytic hydrolysis of CFC-12 acts as a effective catalyst with high catalytic activity and selectivity, The solid acid catalyst MoO_3/ZrO_2-TiO_2 prepared by calcining at 500 ℃ for 3 hours is one of the ideal catalysts for catalyzing the hydrolysis of CFC-12.

3.2.4. The effect of vapor concentration on the CFC-12 hydrolysis

In Fig. 7 shows that water vapor concentration has significant effect on the degradation of CFC-12. The conversion of 14.31% in the degradation CFC-12 is observed when no water vapor is involved in the system. As the increase of water vapor, the conversion of degradation of CFC-12 grows and the conversion of degradation of CFC-12 reaches its maximum value of 98.65% when the water vapor concentration is 83.18%.The conversion of the degradation decreases as the water vapor concentration further increases, mainly because of the reduce contacting time between gas and solid resulting from the growing velocity with the increased water vapor concentration, as well as the lower reaction temperature as more water vapor involved in the system. Hence the optimal volume percentage of water vapor may be 83.18%.

3.2.5. The effect of reaction time on the activity

Figure 8, the conversion of the degradation of CFC-12 is more than 98.00% with the reaction time of less than 10 hours and during this period of time, the solid acid of MoO_3/ZrO_2-TiO_2 catalyst maintains good thermal stability. The conversion of the degradation of CFC-12 drops from 98.00% to 65.34% as the reaction time reaches 20 hours and the decreasing conversion is tended to be slow when the reaction time is more than 20 hours. All of the above studies show the solid acid of MoO_3/ ZrO_2-TiO_2 composite with the calcination temperature 500 °C and calcination time 3 hours in the catalytic hydrolysis of CFC-12 has high thermal stability.

3.3. MoO_3/TiO_2-ZrO_2 SEM diagram of the reaction before and after

Fig. 9 shows the SEM diagrams of the solid acid MoO3/ ZrO2-TiO2 composite with the calcination temperature of 500 °C and calcinations time of 3 hours before and after its reaction in the catalytic hydrolysis of CFC-12. As shown in Figure 6, the solid acid of MoO3/ZrO2-TiO2 composite affords fine crystalline structure after calcining, consistent with the XRD results. Instead, only tiny particle of amorphous MoO3/ZrO2-TiO2 may be observed after the reaction, though their crystal structures remain intact as shown from SEM diagram, probably due to the SiO2 that supports the catalyst packing. All these results are consistent with the EDS study of the catalysts and may indicate the solid acid of MoO3/ ZrO2-TiO2 catalyst possesses high stability and long life.

3.4. Characterization of MoO_3/TiO_2-ZrO_2 EDS after reaction

The chart shows no fluorine has been detected after reaction, which may prove the product of fluoride is not involved in the reactuion. All the above studies indicate the solid acid of MoO_3/ ZrO_2-TiO_2 catalyst has high selectivity.

4. Conclusions

(1) Experimental of the catalytic hydrolysis of CFC-12 results show that, degradation rate of CFC-12 more than 98.00% when the catalyst (MoO_3/TiO_2-ZrO_2) dosage 1.00 g, and CFC-12 flow rate 1 mL/min, and water vapor volume fraction 83.18%, and catalyzes the hydrolysis of a temperature of 400 °C. The CFCs main degradation products were CO, CO_2, HF and HCl.

(2)Cube-shaped structure of MoO_3/TiO_2-ZrO_2 catalyst showed higher activity and selectivity. When the temperature of hydrolysis was 400℃, conversion of CFC-12 reached 98.00% above. When the reaction time overtook 30 hours, conversion of CFC-12 still remained over 65.00%, showed the catalyst has high stability.

Abbreviations

CFC-12
Dichlorodifluoromethane
CFCs
Chlorofluorocarbons

Declarations

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

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Not applicable

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Contributions*Zhiqian Li*,*Tong Zhou*, *Guoqing Ren* and *Tan Xiaofang* conceived and designed the experiments; *Zhiqian Li* and *Guoqing Ren* performed the experiments; *Zhiqian Li* and *Tong Zhou* analyzed the data; *Zhiqian Li*, *Tong Zhou*, and *Guoqing Ren* wrote and modified the paper. All authors read and approved the final manuscript. Corresponding authorCorrespondence to Tiancheng Liu.

Ethics declarations

Competing interests

The authors declare that they have no competing interests.

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Figures

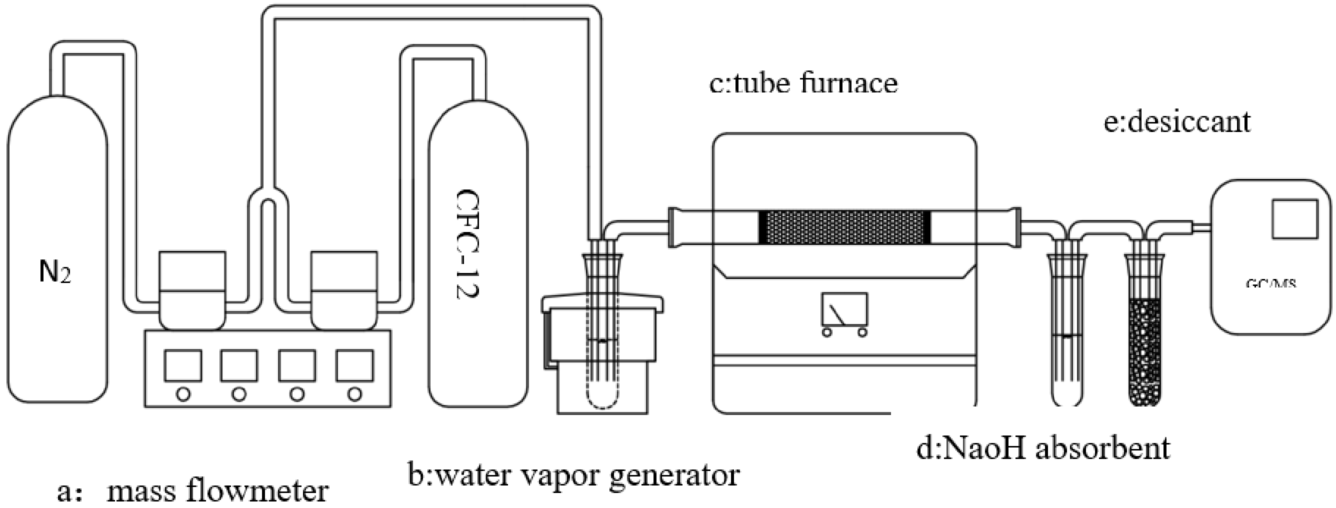

Figure 1

Flow diagram of CFC-12 catalytic hydrolysis experiment

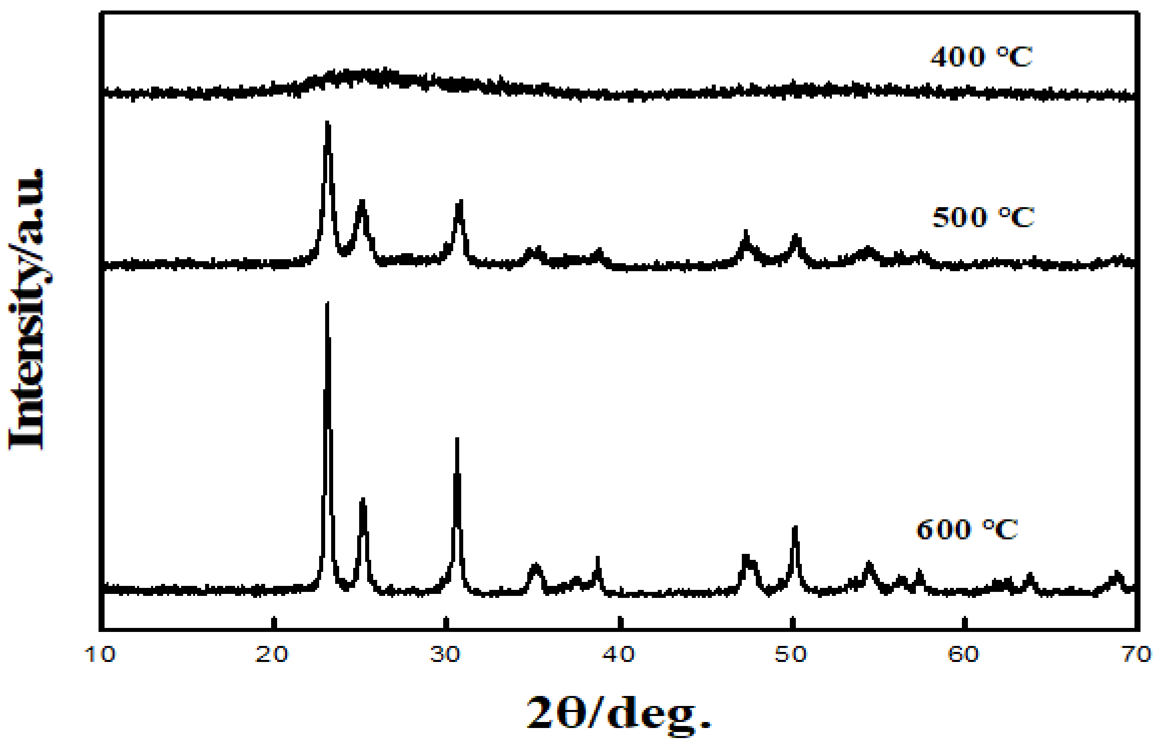

Figure 2

XRD patterns of MoO3/ ZrO2-TiO2 calcined at different temperatures

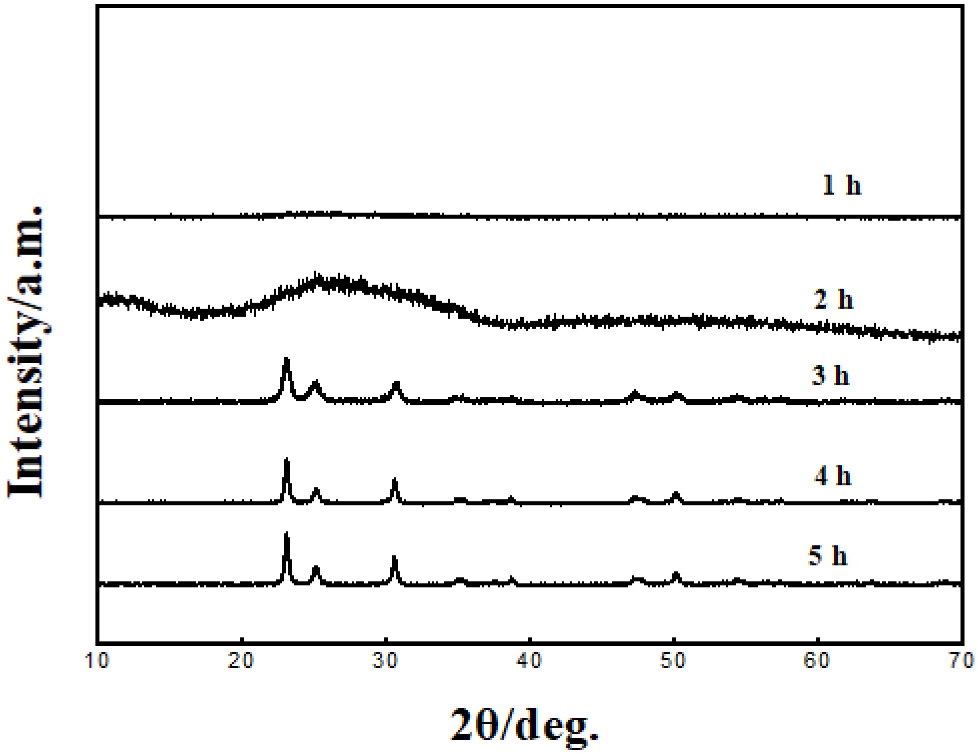

Figure 3

XRD patterns of MoO3/TiO2-ZrO2 at different calcined time

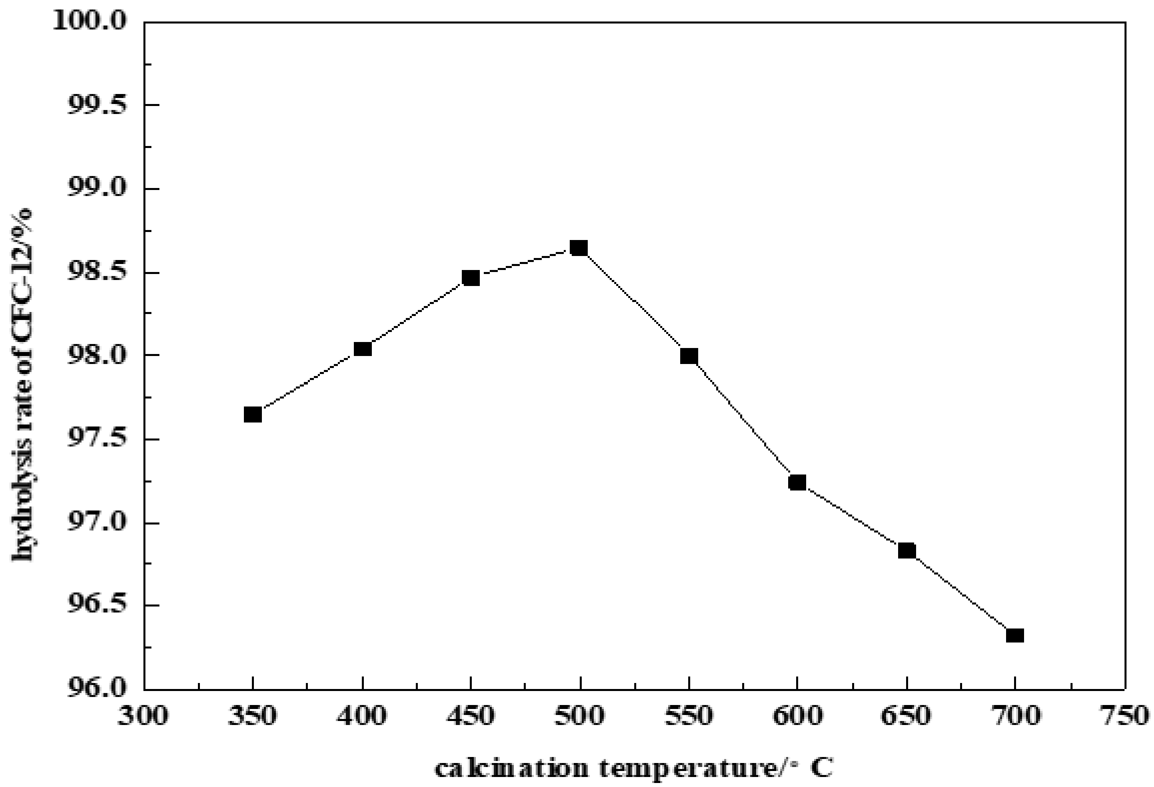

Figure 4

Effect of Calcination Temperature on CFC-12 hydrolysis Rate

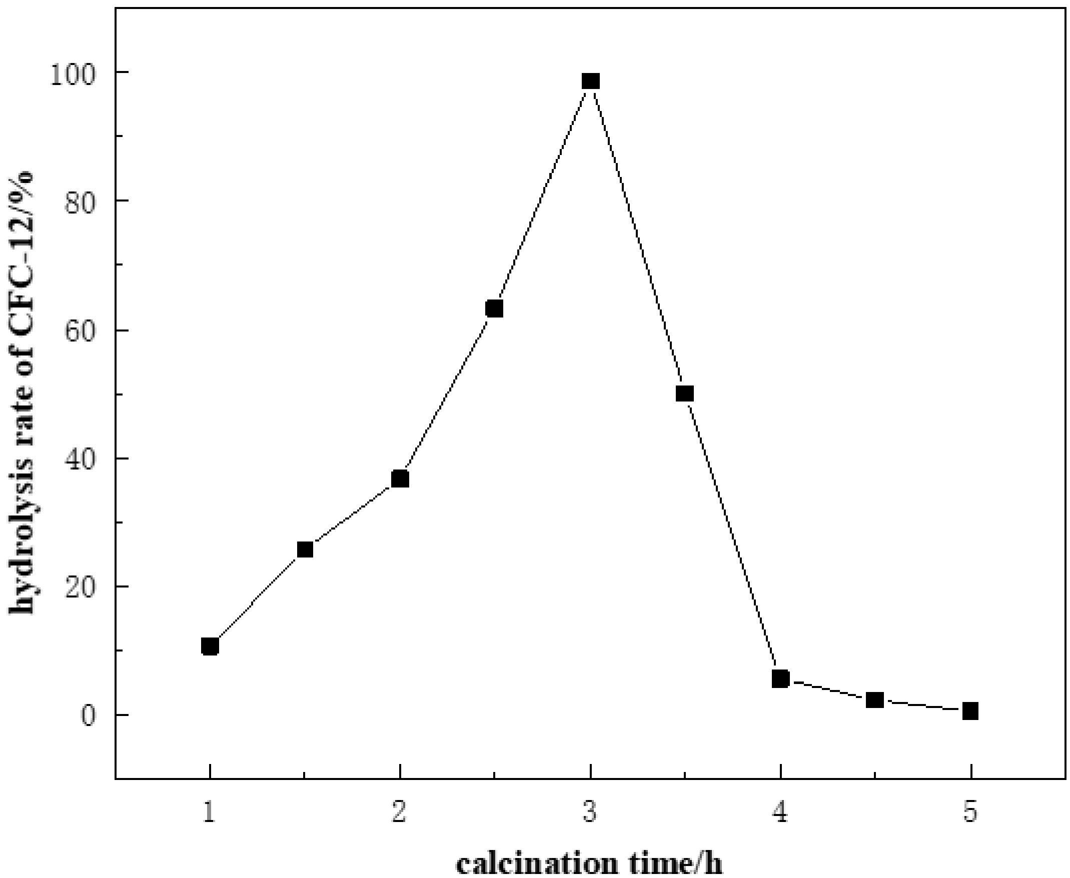

Figure 5

Effect of calcination time on hydrolysis rate of CFC-12

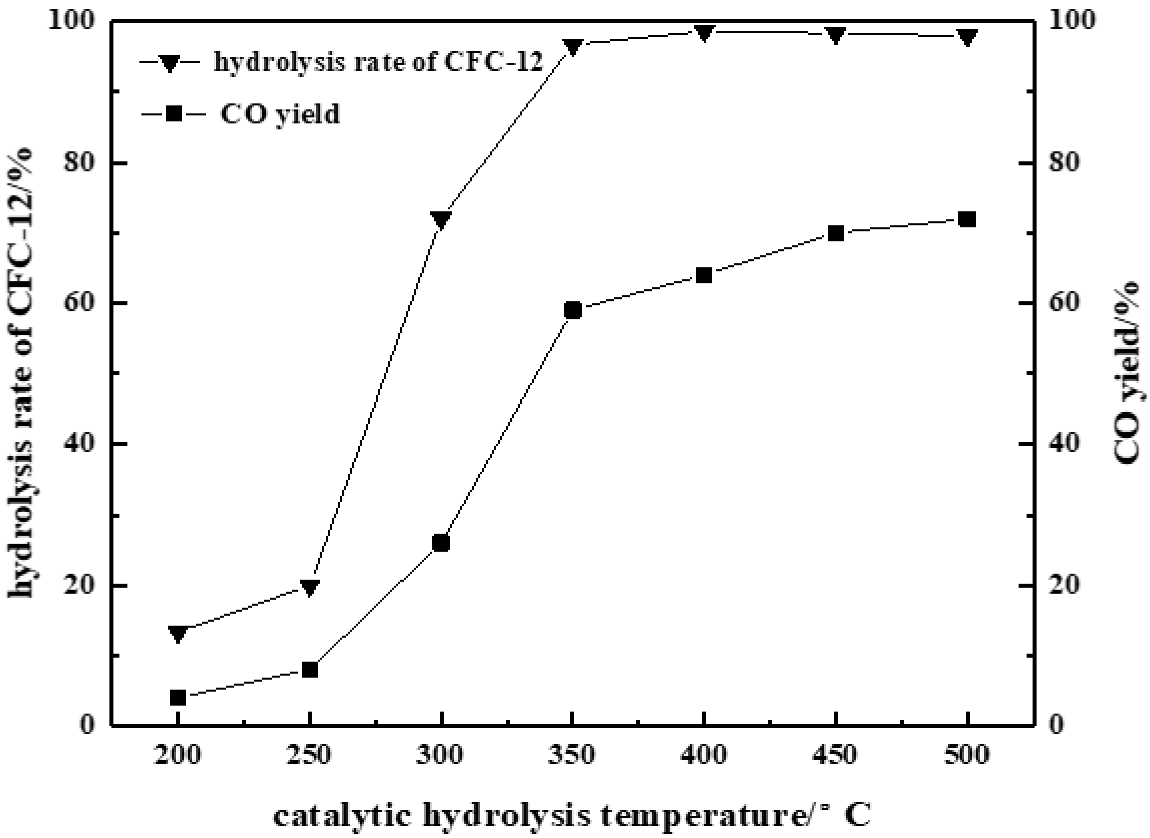

Figure 6

Effect of catalytic hydrolysis temperature on hydrolysis rate of CFC-12

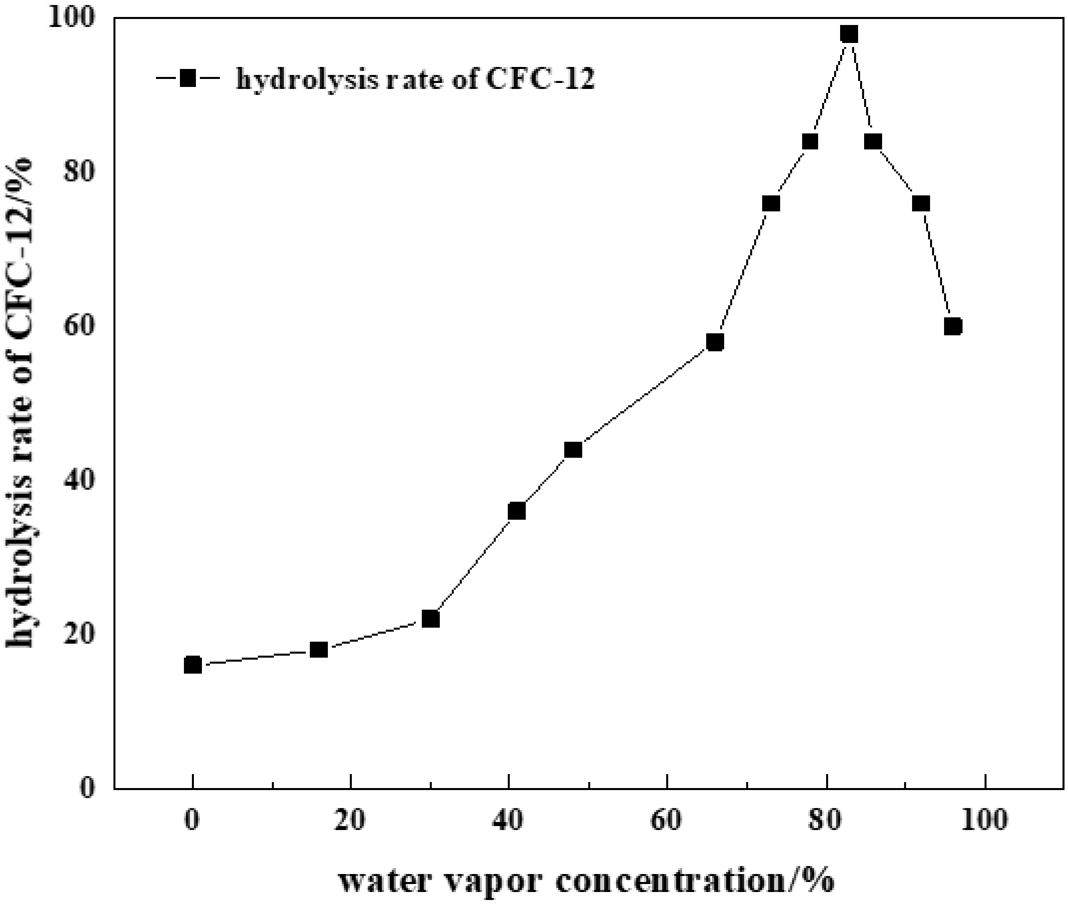

Figure 7

The effect of water vapor concentration on the CFC-12 hydrolysis

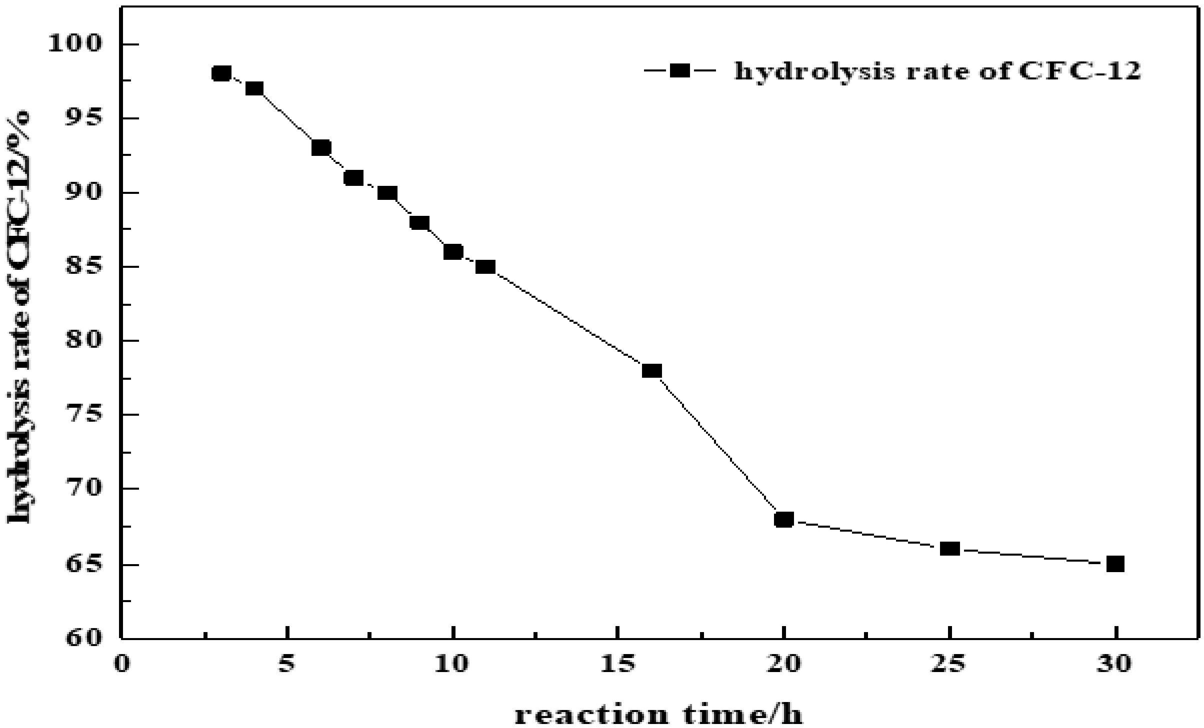

Figure 8

The effect of reaction time on the activity

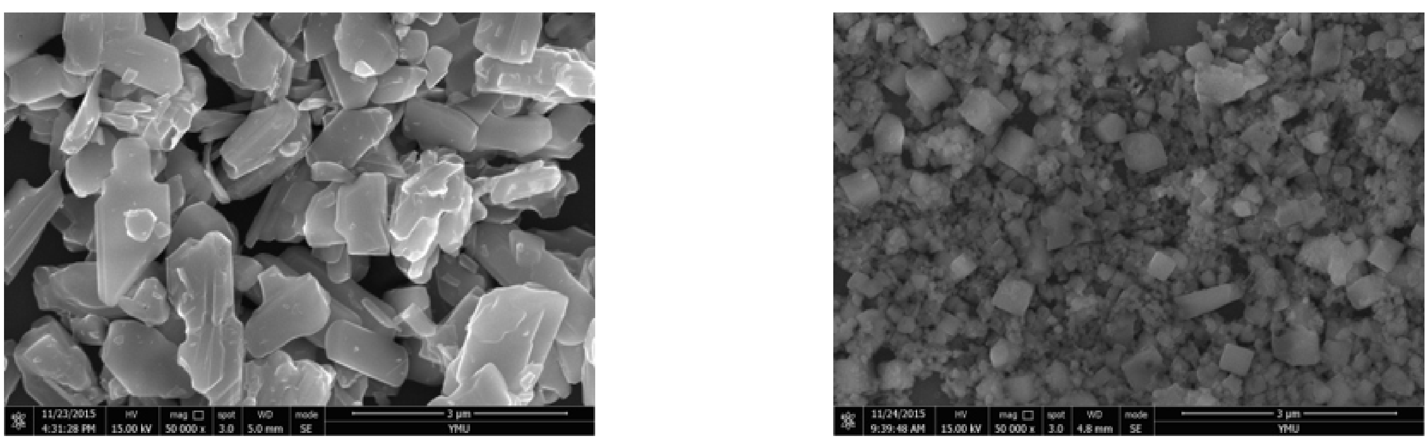

Figure 9

MoO3/TiO2-ZrO2SEM diagram of the reaction before and after

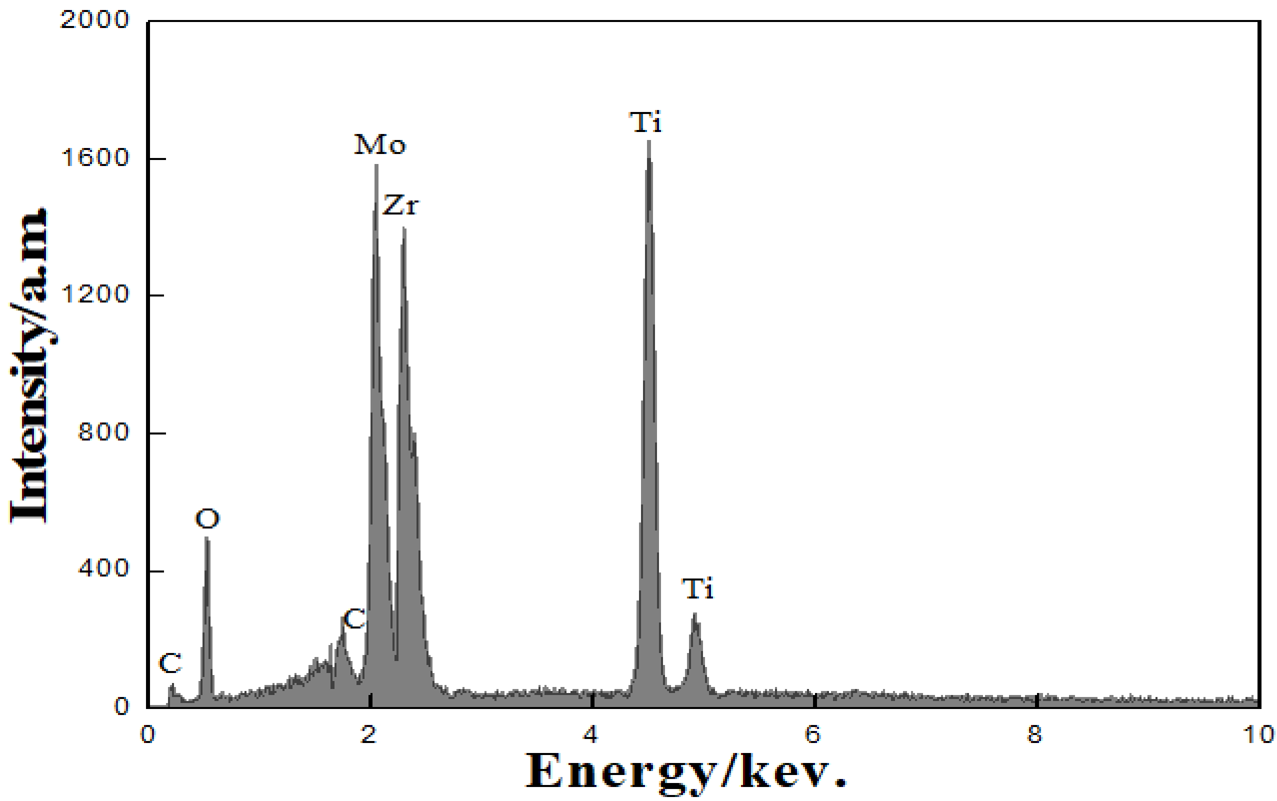

Figure 10

Characterization of MoO_3/TiO_2-ZrO_2 EDS after reaction