

## Catalytic combustion of ethyl acetate on supported copper oxide catalysts

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### Abstract

Total oxidation of ethyl acetate on supported copper oxide catalysts was investigated. The catalysts have been prepared by wet impregnation method and characterized by XRD, TEM and XPS. Among the catalysts with the supports of TiO<sub>2</sub>, CeO<sub>2</sub>/TiO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub> solid solutions doped TiO<sub>2</sub> supported catalyst gives the highest catalytic activity. Catalyst with the composition of 5 wt.% CuO/10 wt.% CeO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> shows the total oxidation of ethyl acetate at about 270 °C with the 100% CO<sub>2</sub> selectivity. The characterization studies of supported copper oxide catalysts showed that the highly dispersed CuO is one of the active phase which contacts intimately with the support, the action of the interface between the components was not be ignored.

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### 1. Introduction

Increasing environmental awareness promotes the stricter regulations of industrial actions. Volatile organic compounds (VOCs) are one type of toxic pollutant to environment and produced in variety of small and medium size industries. Among the several techniques that can be applied to efficiently control the emission of VOCs, catalytic combustion is a competitive art to meet the stricter environmental legislations. In this process, high elimination efficiency can be achieved at relatively low temperature, which resulted in considerable environmental and economic benefits in comparison to the case of the thermal incineration [1]. Among VOCs, ethyl acetate is a common solvent and is present in various gas exhaust stream, which can cause severe environmental hazards and be harmful to the health of human beings. It can be completely oxidized to CO<sub>2</sub> by Pd, Pt supported catalyst at about 220–320 °C [2], some other papers [3–9] also reported the investigations to eliminate low concentration of the ethyl acetate existing in gas steams.

In recent years, supported metal oxides were extensively used in controlling VOCs emissions, and special attention has been paid to these systems as a substitute for noble metal containing catalysts [10], but on the transition metal oxide catalysts, the probability of forming partial oxidation products that are very harmful to human health is very high during the catalytic combustion of oxygenated compounds, such as ethyl acetate and ethanol, etc. Prt-Olof Larsson [11] reported the complete oxidation of ethyl acetate on CeO<sub>2</sub> modified CuO/TiO<sub>2</sub> catalyst, there were a certain amounts of by-products such as ethanol and aldehyde, during the process with a maximal molar content of ethanol about 16%, although it can achieved complete reaction at about 250 °C. The catalysts containing transition metals, especially copper, show a potential application for the treatment of exhaust gas from automobiles [2]. The dispersed copper oxide on TiO<sub>2</sub> was active for the complete oxidation of CO and toluene [12], but the presence of copper oxide species accelerates the sintering of TiO<sub>2</sub>.

Commonly considered that the support plays an important role in dispersion of the active component on the surface, many papers reported the methods of enhancement the activity by modifying the support. The system of CeO<sub>2</sub>-ZrO<sub>2</sub> is effective to improve oxygen release and storage properties, several workers have claimed the importance of the solid solution in this system

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[13,14]. It has been found that the introduction of the smaller Zr cation into the cubic lattice of ceria strongly promotes the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , which can result in the high performance of the catalyst,  $\text{CeO}_2\text{-ZrO}_2$  solid solutions modified  $\text{Al}_2\text{O}_3$  was reported in recent articles [15–17], but  $\text{TiO}_2$  as a support modified by this system was not reported. We found that  $\text{CuO/TiO}_2$  doped with  $\text{CeO}_2\text{-ZrO}_2$  is a highly efficient catalyst in complete oxidation of volatile organic compounds (VOCs) compared with the catalysts reported by other author [4,5].

In this article, we present the results of catalytic combustion of ethyl acetate on supported copper oxide catalysts, and the properties of the catalyst were characterized by using the XRD, TEM and XPS.  $\text{CeO}_2\text{-ZrO}_2$  solid solution plays an important role in improving catalytic activity and selectivity.

## 2. Experimental

### 2.1. Catalytic preparation

All catalysts used in this investigation were prepared via incipient wetness impregnation (IM). The aqueous solution of copper nitrate was used as the precursors for CuO. Supports were impregnated with appropriate amounts of precursor solution to incipient wetness, followed by the evaporation of  $\text{H}_2\text{O}$  and dried at  $110^\circ\text{C}$  for 6 h, and then calcined at  $500^\circ\text{C}$  for 4 h.

$\text{CeO}_2$  and  $\text{CeO}_2\text{-ZrO}_2$  solid solution doped  $\text{TiO}_2$  supports were prepared by the same method described above, just using the  $\text{Ce}(\text{NO}_3)_3$  and/or  $\text{Zr}(\text{NO}_3)_4$  aqueous solutions to impregnate the rutile (with the BET surface area as  $7.74\text{ m}^2/\text{g}$ ) with the molar ratio of Ce/Zr as 4:1.

To compare the effect of the preparation on the catalytic performance, co-wetness impregnation (co-IM) method was used, that is, using the  $\text{Ce}(\text{NO}_3)_3$ ,  $\text{Zr}(\text{NO}_3)_4$  and  $\text{Cu}(\text{NO}_3)_2$  aqueous solutions to impregnate the rutile (with the BET surface area as  $7.74\text{ m}^2/\text{g}$ ), then do the same process above to prepare the catalyst.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a Shimadzu XD-3A diffraction meter employing Ni-filtered  $\text{Cu K}\alpha$  radiation ( $0.15418\text{ nm}$ ). The X-ray tube was operated at  $35\text{ kV}$  and  $15\text{ mA}$ . The crystal size was determined by using the Scherrer equation.

BET specific surface areas were determined by nitrogen adsorption at the temperature of liquid nitrogen on a Micromeritics ASAP 2000 instrument. Prior to each analysis the catalyst powder was degassed at  $150^\circ\text{C}$  under a pressure of  $0.1\text{ Pa}$  for 2 h.

X-ray photoelectron spectroscopic (XPS) results were obtained using a V.G. Escalab MK II spectrometer equipped with a hemispherical electron analyzer. The system was operated at  $13\text{ kV}$  and  $20\text{ mA}$  using a magnesium anode (Mg K,  $E = 1253.6\text{ eV}$ ). A binding energy (BE) of  $285\text{ eV}$  for the C1s level was used as an internal reference.

TEM measurement was performed by a JEOL JEM-100CX transmission electron microscope.

### 2.3. Catalytic performance evaluation

The combustion reaction was carried out in a tubular fixed-bed reactor at atmospheric pressure. The reaction vapor was prepared in our laboratory maintain the molar concentration of ethyl acetate as 0.2% in full stream, the total gas flow is  $100\text{ ml/min}$  and  $0.5\text{ ml}$  catalyst was use in catalytic reactor. A thermocouple was placed inside the reactor, in the center of the catalyst bed to monitor the reaction temperature. Two of thermocouple was used to detect the temperature at the different place on catalyst bed, it was found to be less than  $10^\circ\text{C}$ , so the reaction temperature detected is credible. All experimental runs were taken under steady-state conditions.

The products were analyzed using on-line gas chromatograph equipped with flame ionization and thermal conductivity detectors. The analysis of  $\text{CO}_2$  and VOC were conducted through Carbosieve and SE-54 columns, respectively.

## 3. Results and discussion

### 3.1. The catalytic activity of supported CuO catalysts with different supports

The conversion of ethyl acetate to  $\text{CO}_2$  over CuO catalysts supported on  $\text{TiO}_2$ ,  $\text{CeO}_2/\text{TiO}_2$  and  $\text{CeO}_2\text{-ZrO}_2/\text{TiO}_2$  is shown in Fig. 1 as a function of reaction temperature, for compare, the conversion of ethyl acetate on some supports were also investigated and the results were shown in Fig. 1. Clearly, none CuO doped samples show the lower catalytic activity compared with the supported catalysts and larger amounts of by-product were detected during reaction which was not shown in this paper. All the catalysts doped with copper oxide studied in this experiment provide more than 99% selectivity to carbon dioxides and no other detectable by-products except a slight amount of aldehyde was found. This is not similar with that for  $\text{CuO/CeO}_2/\text{TiO}_2$

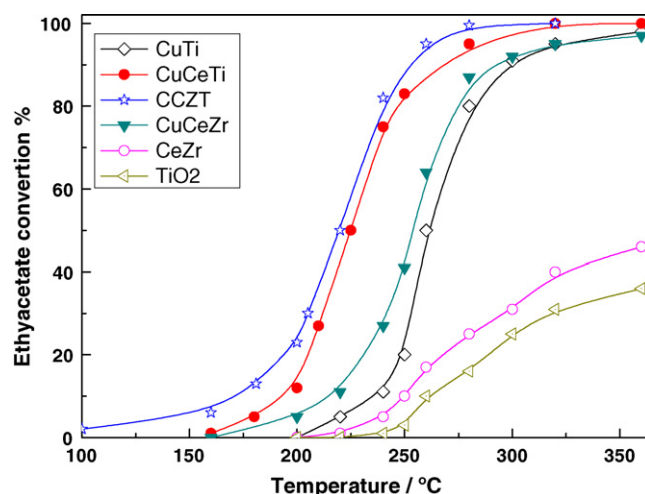


Fig. 1. Catalytic performance of various catalysts as a function of temperature (GHSV =  $5000\text{ h}^{-1}$ , ethyl acetate = 0.2% molar ratio, carrier gas = air).

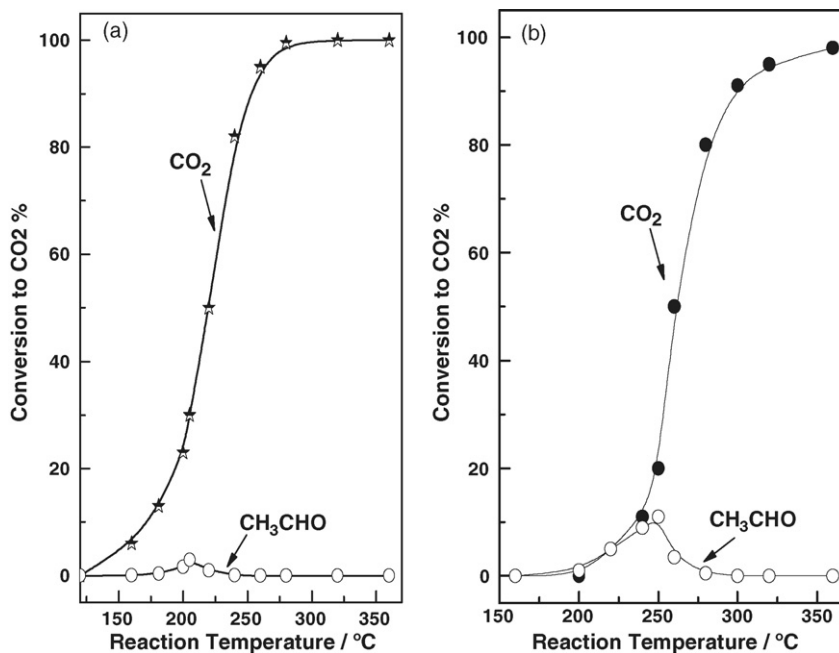


Fig. 2. Yield of aldehyde and CO<sub>2</sub> during the catalytic combustion of ethyl acetate: (a) CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> and (b) CuO/TiO<sub>2</sub>.

catalyst [11], where lots of aldehyde was formed during catalytic combustion of ethyl acetate. Combined with the results of characterizations, we can confirm that the CuO plays an important role in the catalytic combustion of ethyl acetate.

As shown in Fig. 1, apparently, the activity was highly enhanced when TiO<sub>2</sub> was modified by CeO<sub>2</sub> and ZrO<sub>2</sub>, among these supports, copper oxide supported on CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution doped TiO<sub>2</sub> is found to have the highest activity for ethyl acetate catalytic combustion. The complete conversion of ethyl acetate is achieved at about 280 °C with 100% CO<sub>2</sub> selectivity, exactly the same results were already reported by Verykios and coworkers [4] and Wang et al. [5] with the catalysts containing noble metal of Pt. For CuO/TiO<sub>2</sub> catalyst requires higher temperature to give the same conversion level at about 375 °C. For CuO/CeO<sub>2</sub>/TiO<sub>2</sub> catalyst, as it was seen, the complete conversion of ethyl acetate achieved at about 330 °C, which is 50 °C higher than that for CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> catalyst.

It is important to know if any by-products are formed which are harmful to human health. Fig. 2 shows the yield of CO<sub>2</sub> and acetaldehyde during ethyl acetate oxidation on CuO/TiO<sub>2</sub> and CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> catalysts, it is obvious that all ethyl acetate is not oxidized directly to CO<sub>2</sub> and H<sub>2</sub>O, apparently, there are a certain amount of intermediates formed during the reaction process, but the maximum amount of acetaldehyde on CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> catalyst is less than 5% at about 210 °C, it lower than that on the unmodified CuO/TiO<sub>2</sub> catalyst, which is about 11% at 250 °C. From the results we can confirm that the CeO<sub>2</sub>-ZrO<sub>2</sub> system played an important role in enhancement the activity and selectivity in catalytic combustion of ethyl acetate.

Fig. 3 shows the XRD patterns of all catalysts. From the figure we can see the diffraction peak intensity of CuO was different in all catalysts, clearly, for the catalyst CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub>, the weak peak of CuO phase showing a high dispersion. For

CeO<sub>2</sub>-ZrO<sub>2</sub> doped catalyst, any diffraction peak of zirconium includes ZrO<sub>2</sub> and ZrTiO<sub>4</sub> was not detected, and the CeO<sub>2</sub> shows the expected diffraction of the fluorite structure and TiO<sub>2</sub> shows the rutile phase without evidently shift of the diffraction line. The absence of ZrO<sub>2</sub> phase and the shift of diffraction line of CeO<sub>2</sub> indicate the presence of a solid solution. The shift of the CeO<sub>2</sub> diffraction lines to higher degrees is attributed to shrinking of the lattice due to the replacement of Ce ions (1.09 Å) by Zr ions (0.86 Å) [18,19], and the diffraction peak of CeO<sub>2</sub> broaden may be due to the high dispersion with ZrO<sub>2</sub> added, and hence, the unit cell and average crystallite size parameters could not be determined with precision. The improvement in activity,

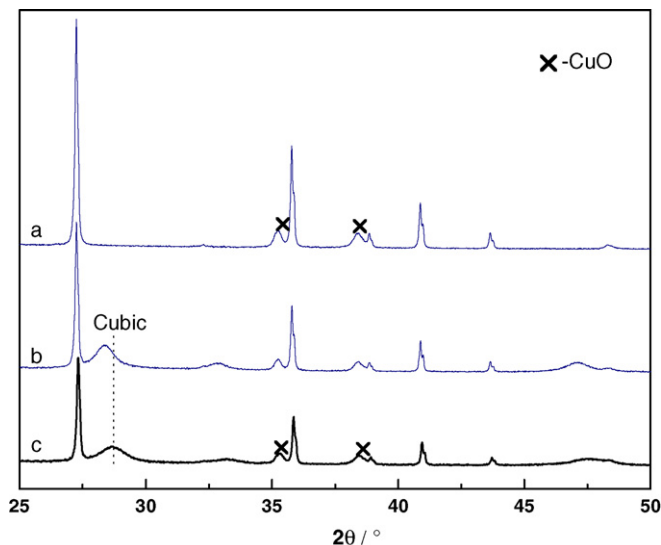


Fig. 3. XRD patterns of catalysts: (a) CuO/TiO<sub>2</sub>, (b) CuO/CeO<sub>2</sub>/TiO<sub>2</sub> and (c) CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub>.

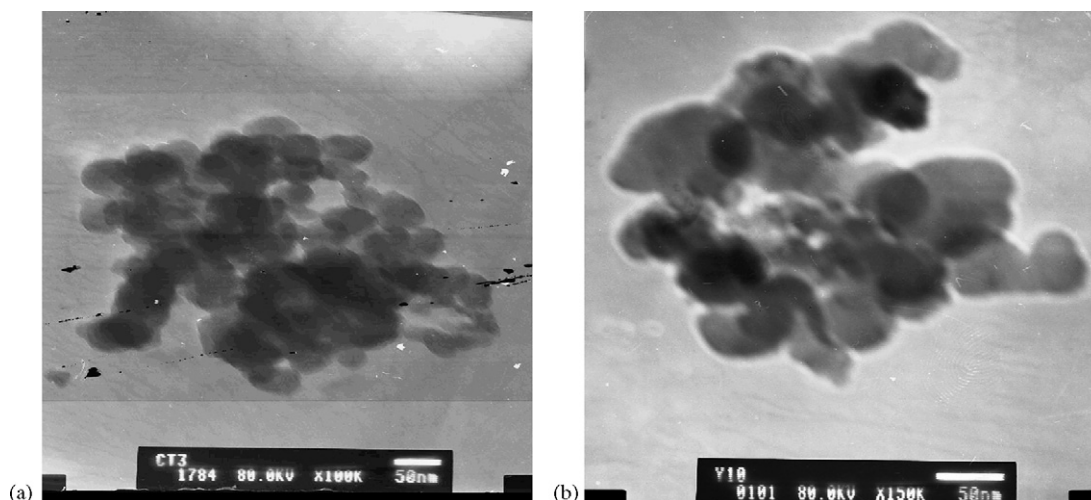


Fig. 4. TEM image of catalyst 10 wt.% CuO/20 wt.% CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> prepared by the method of: (a) IM and (b) co-IM.

Table 1  
BET surface area and particle size from XRD results

	TiO <sub>2</sub>	CuO/TiO <sub>2</sub>	CuO/CeO <sub>2</sub> / TiO <sub>2</sub>	CuO/CeO <sub>2</sub> -ZrO <sub>2</sub> / TiO <sub>2</sub>
<i>S</i> <sub>BET</sub> (m <sup>2</sup> /g)	7.74	6.14	10.13	16.22
<i>d</i> <sub>CuO</sub> (nm)	–	581.89	172.94	35.60
CuO (wt.%)	–	10	10	10
CeO <sub>2</sub> (wt.%)	–	–	20	16
ZrO <sub>2</sub> (wt.%)	–	–	–	4

compared with the catalyst only modified by CeO<sub>2</sub>, may be due to the ZrO<sub>2</sub> enlarge the lattice space of the CeO<sub>2</sub>-ZrO<sub>2</sub> system with resulting in the migration of oxygen atoms, or it may be the Zr<sup>4+</sup> in the structure helps to capture oxygen atoms and transfer them to Ce atoms [20]. Also, there is more interface between components existing when TiO<sub>2</sub> was modified, these are benefit to disperse the active phase and oxidation reaction. The lower activity of the catalyst CuO/TiO<sub>2</sub> for catalytic combustion of ethyl acetate due to the agglomeration of TiO<sub>2</sub> under the existing of CuO [11], thus, restrained the high dispersion of CuO on the surface. The dispersion property of the CuO was also confirmed by the results of BET and XRD indicated in Table 1.

### 3.2. Effect of preparation method on the catalytic activity

From Table 2 we can see that the catalytic activity (defined as *T*<sub>50</sub> and *T*<sub>100</sub>, it denote the temperature of ethyl acetate conversion reaches the 50% and 100%, respectively) of the catalyst prepared by the IM are significantly higher than that of the catalyst prepared by co-IM. Combining with the Fig. 4 of the TEM

Table 2  
Catalytic activity and XRD results of catalyst 10 wt.% CuO/20 wt.% CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> prepared by different method

Method	<i>d</i> <sub>CuO</sub> (nm)	<i>d</i> <sub>TiO<sub>2</sub></sub> (nm)	<i>I</i> <sub>CuO</sub> / <i>I</i> <sub>TiO<sub>2</sub></sub>	<i>T</i> <sub>50</sub> (°C)	<i>T</i> <sub>100</sub> (°C)
IM	35.60	154.09	0.08	219	280
co-IM	266.17	426.31	0.07	235	315

image of the catalysts, we can confirm that the high activity of the catalyst prepared by IM is due to the high dispersion of CuO on the support, the prior dispersed CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution can efficiently promote the dispersion of CuO [21]. When use the co-IM method, copper and ceria phase are simultaneity contact with TiO<sub>2</sub> and this can cause the increase of the TiO<sub>2</sub> particles, as it was seen in Table 2, the CuO particle size increase was also be observed.

### 3.3. The catalytic activity of CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> catalyst at different concentrations of ethyl acetate

The influence of ethyl acetate concentration on catalytic properties of the CuO/CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> catalyst has been investigated. As indicated in Fig. 5, the conversion slightly increased with the increase of ethyl acetate concentration changing from 0.2% to 2% (molar concentrations). This result will be very important to industrial use of the catalysts, because

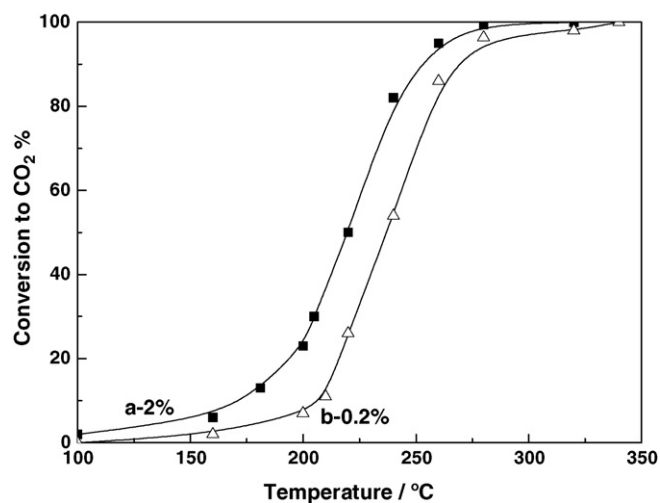


Fig. 5. Catalytic performance of 10 wt.% CuO/20 wt.% CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> catalyst with different concentration of ethyl acetate (GHSV = 5000 h<sup>-1</sup>, carrier gas = air).

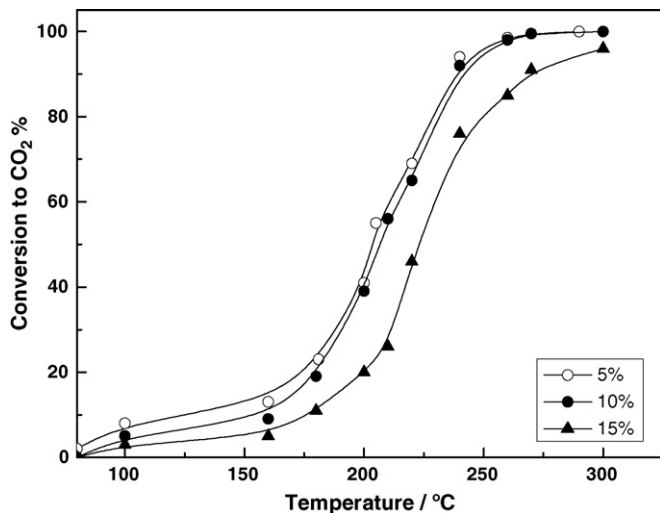


Fig. 6. Catalytic performance of catalysts with different CuO loading (GHSV = 5000 h<sup>-1</sup>, ethyl acetate = 0.2% molar ratio, carrier gas = air).

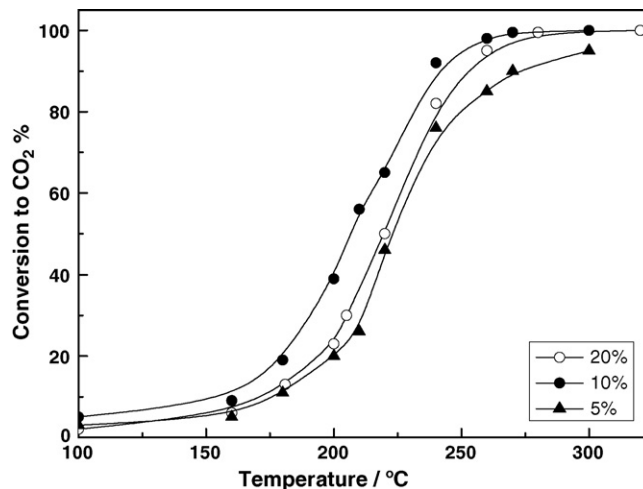


Fig. 7. Catalytic performance of catalysts with different CeO<sub>2</sub>-ZrO<sub>2</sub> loading (GHSV = 5000 h<sup>-1</sup>, ethyl acetate = 0.2% molar ratio, carrier gas = air).

the concentration of pollutants under actual working condition is usually changeable, this kind of catalyst can maintain the catalytic performance under the variety conditions.

### 3.4. The catalytic performance of catalysts with different CuO loadings

To make further investigation, a series of CeO<sub>2</sub>-ZrO<sub>2</sub>/TiO<sub>2</sub> supported CuO catalysts were prepared with different CuO loading. Their catalytic activities are compared in Fig. 6. The enhancement of catalytic activity with increase of the CuO loading is not observed, and the catalyst with the CuO loading of 5 and 10 wt.% shows the appropinquity of activity, so, we cannot briefly confirm the relationship between the reactivity and the CuO loading.

Table 3 shows the results of XRD and XPS of the catalysts with different CuO loading. At low loading, the particle size of CuO and TiO<sub>2</sub> are all smaller than that of catalyst with the CuO loading of 15 wt.%, also the surface atom concentration is not increased with the increase of CuO loading. Correlated with catalytic activity results shows in Fig. 6, we suppose that the catalytic activity was not increased when CuO loading increase due to the amount of surface highly dispersed CuO is not increased and the other bulk CuO phase are agglomeration and form to large particle, this is similar with the reports [22]. Combining the above discussions we suppose that the dispersion of CuO phase is one of the important factor to affect the activity of catalyst.

Table 3  
XRD and XPS results of catalysts with different CuO loading

CuO loading	XRD			XPS	
	$d_{\text{CuO}}$ (nm)	$d_{\text{TiO}_2}$ (nm)	$d_{\text{CeO}_2}$ (nm)	Cu/Ti	Cu (at.%)
5 wt. %	62.83	154.36	7.00	1.51	4.43
10 wt. %	35.60	154.09	17.78	0.94	4.01
15 wt. %	266.17	426.31	7.29	2.57	4.25

### 3.5. The effect of CeO<sub>2</sub>-ZrO<sub>2</sub> loading on the catalytic activity

The conversion of ethyl acetate to CO<sub>2</sub> over the catalysts with the loading of 10 wt.% CuO and variety CeO<sub>2</sub>-ZrO<sub>2</sub> loadings is shown in Fig. 7 as a function of reaction temperature. As it was shown, the catalyst with the CeO<sub>2</sub>-ZrO<sub>2</sub> loading of 10 wt.% is found to have the highest catalytic activity in catalytic combustion of ethyl acetate, the enhancement in catalytic activity with the increasing of the CeO<sub>2</sub>-ZrO<sub>2</sub> loading was not be observed. This maybe due to the complex interaction between the components which influence the interface properties of the CeO<sub>2</sub>, CuO and TiO<sub>2</sub> [23] with the different concentration. With the CeO<sub>2</sub>-ZrO<sub>2</sub> loading of 20 wt.%, CuO will disperse on the CeO<sub>2</sub> phase surface and shows the properties as that of CuO/CeO<sub>2</sub> catalyst [24]. As for the catalyst with the CeO<sub>2</sub>-ZrO<sub>2</sub> loading of 5 wt.%, there is not enough interface of Ce-O-Ti, and CuO declined to disperse on surface of TiO<sub>2</sub>, thus, shows the catalytic activity as that on the CuO/TiO<sub>2</sub> catalyst. Any further studies about this will be investigated in our work.

## 4. Conclusion

Supported copper oxide catalyst has been found to be very suitable for catalytic combustion of ethyl acetate. Copper oxide supported on CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution doped TiO<sub>2</sub> catalyst gives the highest catalytic activity with the loading of CuO and CeO<sub>2</sub>-ZrO<sub>2</sub> as 5 and 10 wt.%, respectively. The catalytic activity of this kind of catalyst is comparable with that of the noble metal catalyst, what's more, it excels that of the reported base metal catalyst. Experimental results indicate that the dispersed CuO on the surface and interface of supports play an important role in the reaction of catalytic combustion. This kind of catalyst is suitable for industrial use under changing conditions.

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