

Photo-catalysis of ethane and carbon dioxide to produce hydrocarbon oxygenates over ZnO-TiO₂/SiO₂ catalyst

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Abstract

The supported n–p coupled semiconductor materials ZnO-TiO₂/SiO₂ were prepared using the method of modifying the silica surface character. The chemical structure, photoabsorbing behaviors and chemisorbing properties of the catalysts were characterized by IR spectra, Raman spectra, UV–vis reflectance spectra and TPD–MS experiments. It was shown that the Zn–O–Ti bonds have been formed on the surface of ZnO-TiO₂/SiO₂ catalyst. The addition of ZnO extends the photo absorption range of TiO₂/SiO₂ sample through the formation of Zn–O–Ti bond. CO₂ and ethane can be chemisorbed on the surface of ZnO-TiO₂/SiO₂ catalyst and desorbs at 388 and 428 K, respectively. Under UV irradiation, CO₂ chemisorption state can undergo decomposing process to form CO at 465 K, and a new ethane adsorption state was formed at around 500 K. Photo-oxidation of ethane using carbon dioxide can mainly produce propanal, ethanol, acetaldehyde in the temperature range of 393–493 K. The presence of ZnO improved the catalytic activity and promoted the formation of hydrocarbon oxygenates. The propanal yield of 75.6 μmol h⁻¹ and ethanol yield of 50.9 μmol h⁻¹ can be obtained over 5% ZnO-TiO₂/SiO₂ catalyst at 473 K. Reacting temperature has significant effects on the product yields. The temperature of 473 K will be preferable for the selective formation of propanal and ethanol. © 2004 Elsevier B.V. All rights reserved.

Keywords: Photo-oxidation; Coupled semiconductors; Carbon dioxide; Ethane; ZnO-TiO₂/SiO₂ catalyst

1. Introduction

Conversion and utilization of CO₂ as well as simple hydrocarbon, such as ethene to different high-value species attracted increasing interest due to their chemical, energy and environmental importance [1–4]. Reduction of CO₂ requires consumption of hydrogen, while oxidation of C₂H₆ requires oxygen. The conversion of C₂H₆ and CO₂ together is an ideal combination of an oxidation reaction and a reduction reaction. Due to the chemical inert of CO₂ and thermodynamic limitation of the reaction from CO₂ and C₂H₆ to oxygen-containing chemicals, their activation can be achieved only under severe conditions and the thermal surface catalytic reaction of ethane and CO₂ only produces ethane, when tem-

perature is very high. Therefore, CO₂ and ethane should be converted to more desirable compounds by applying as little energy as possible.

Heterogeneous photo-catalysis using semiconductors and ultraviolet light is a potentially important strategy in short hydrocarbon selective oxidation to hydrocarbon oxygenate under mild conditions. Photo-oxidation of alkanes using oxygen as oxidant on solid semiconductors, such as TiO₂, ZnO and MoO₃ has been studied by many investigators [5–8]. Although a few reports about photo-oxidation of short chain hydrocarbon have succeeded in obtaining aldehyde and alcohol, most of these studies resulted in deep oxidation [9]. Using CO₂ as oxidant to oxidate ethane under UV irradiation can be an available way to avoid deep oxidation and utilize CO₂ effectively.

Our laboratory is trying to develop a photo-catalysis technology by means of which CO₂ and hydrocarbon or H₂O [10–12] have been converted successfully to high-value oxygen-containing chemicals over n–p coupled

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semiconductors. In this investigation, the supported complex oxide ZnO-TiO₂/SiO₂ catalysts were prepared. The chemisorptions of both CO₂ and ethane on catalyst were studied thoroughly, photo absorption property and photocatalytic synthesis of hydrocarbon oxygenates from ethane and CO₂ over ZnO-TiO₂/SiO₂ catalysts were studied and discussed.

2. Experimental

2.1. Catalyst preparation

Spherical SiO₂ ordered from Qingdao Haiyang Chemical Co. with diameter 0.5 mm and S_{BET} 350 m²/g used as supporting material, was washed in HNO₃, H₂O three times and dried at 493 K under vacuum.

The supported n-type semiconductor TiO₂/SiO₂ with TiO₂ loading 10 wt.% onto the surface of silica carrier was prepared by the method of modifying the silica surface character in reaction with acetone solution of Ti(*i*-OC₃H₉)_xCl_(4-x), $x = 1-2$ at room temperature. The detailed preparation method of Ti(*i*-OC₃H₉)_xCl_(4-x) has been reported in previous research [13]. After the impregnation, the sample was kept inside the seal flask with flowing N₂ for over night at 323 K. The sample was subsequently washed with weak aqua ammonia, dried at 393 K for 12 h and calcined at 823 K for 4 h.

The supported n-p coupled semiconductors ZnO-TiO₂/SiO₂ were prepared by isometric impregnating TiO₂/SiO₂ sample with the solution of Zn(NO₃)₃. After the impregnation, the samples were kept inside the seal flask at 343 K for over night, then dried at 393 K for 12 h and calcined at 823 K for 4 h. The ZnO-TiO₂/SiO₂ catalysts with the ZnO loading amount of 5, 10 and 20 wt.% were prepared, marked as 5% ZnO-TiO₂/SiO₂, 10% ZnO-TiO₂/SiO₂ and 20% ZnO-TiO₂/SiO₂, respectively.

2.2. Catalyst characterization

2.2.1. IR experiments

The catalysts were ground into powder under 2 μm, and dispersed on KBr wafer, which were loaded into a copper IR cell equipped with KBr windows and programmable temperature controller. The sample was pre-treated by heating at 393 K under vacuum (0.1 Pa). IR spectra were recorded at room temperature using Hitachi 270-30 IR-spectrometer.

2.2.2. UV-vis spectra

Ultraviolet and visible (UV-vis) spectra were taken on an UV-vis spectrometer (Perkin Elmer, Lambda 35), the scanned range being 200–1100 nm. The catalysts were ground into powder under 2 μm, and loaded into the sample holder.

2.2.3. Raman spectra

Raman spectra were obtained using an FT-Raman spectrometer (Bruke, RFS 100/S) equipped with high sensitivity

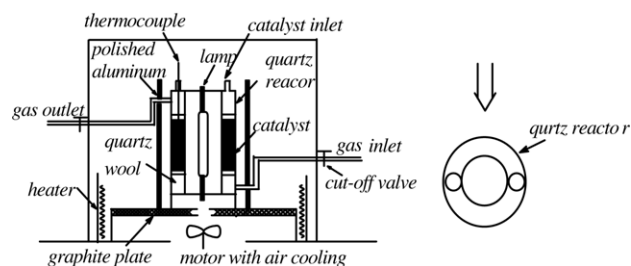


Fig. 1. Reactor for photo-oxidation of ethane with CO₂.

Raman detector (D 418-S) cooled down to liquid nitrogen temperature. The 1064 nm line of the laser was used as the excitation source, with the capability of supplying 300 mW. The Raman spectra were recorded from 100 to 1000 cm⁻¹ at room temperature.

2.3. Chemisorption properties of catalysts

Chemisorption performances of CO₂ and C₂H₆ were characterized by TPD-MS. In the TPD-MS experiment, 500 mg catalyst was loaded in a quartz micro-reactor and the two sides were stuffed by asbestos fiber. Before the adsorption of CO₂ and C₂H₆, the catalyst was pre-treated by heating to 623 K under vacuum (10⁻⁴ Pa) for 2 h. The adsorption of CO₂ or C₂H₆ was performed at 298 K for 2 h with UV irradiation or without UV irradiation, and then cleared the excess gas under vacuum of 10⁻⁴ Pa. The catalyst was heated by a rate of 8 K/min. The desorbed gases were analyzed by a LZL-203 quadruple mass spectrometer (Beijing analytic instrument) at $m/e = 44$ for CO₂, 28 for CO, 30 for C₂H₆.

2.4. Photocatalytic reaction

The photo-stimulated surface catalytic reaction was carried out in a fixed bed flow type annular quartz reactor with inner diameter 20 mm and outer diameter 24 mm as shown in Fig. 1. The temperature of the irradiated surface of catalyst was monitored by a thermocouple directly inserted into the catalyst bed. There was no influence of this thermocouple on the yield of the products. UV irradiation was performed by the use of a high-pressure mercury vapor lamp (power: 125 W; intensity: 40 mW cm⁻² and length: 120 mm), which located in the center of the reactor. The products of reaction were analyzed in situ by gas chromatography (GC, Agilent 4890) using thermal conductivity.

3. Results and discussion

3.1. Catalyst surface structure and properties

The BET surface area of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts was shown in Table 1. The surface area of TiO₂/SiO₂ decreased distinctly with the TiO₂ loading. The surface area of ZnO-TiO₂/SiO₂ catalysts decreased systematically with

Table 1
Surface area, band maximum and E_g of catalysts

Catalysts	Surface area (m ² /g)	Band maximum (cm ⁻¹)	E_g (eV)
SiO ₂	350	–	–
TiO ₂ /SiO ₂	308	46000	3.97
5% ZnO-TiO ₂ /SiO ₂	269	40200	3.80
10% ZnO-TiO ₂ /SiO ₂	252	40000	3.75
20% ZnO-TiO ₂ /SiO ₂	230	39500	3.66

the increase of ZnO loading amount. However, the variation in the BET surface area with the increase of ZnO loading amount is relatively small.

The Raman spectra of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ samples were presented in Fig. 2. TiO₂/SiO₂ sample possessing Raman features at 148, 396, 512 and 644 cm⁻¹ can be assigned to the E_g , B_{1g} , A_{1g} and B_{2g} modes of the TiO₂ anatase phase [14]. The strongest peak of the anatase structure at 145 cm⁻¹ was drastically reduced after the supporting of ZnO along with those of the other modes, B_{1g} , A_{1g} and B_{2g} , indicating that surface modification of the TiO₂/SiO₂ had taken place.

The IR spectra of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts were provided in Fig. 3. Compared with the IR spectra of pure SiO₂, TiO₂/SiO₂ exhibits four new bands at 1398, 972, 945 and 700 cm⁻¹ respectively. The bands at 1400 and 700 cm⁻¹ are attribute to the vibration mode of Ti–O bond. The band at 972 cm⁻¹ can be assigned to the symmetric stretch of Si–OH group [15,16], and the band observed at 945 cm⁻¹ is widely accepted as the characteristic vibration due to the formation of Ti–O–Si bond [17–19]. After the addition of ZnO on the surface of TiO₂/SiO₂ sample, the band at 972 cm⁻¹ disappeared, the band at 945 cm⁻¹ became broad and shifted to ~950 cm⁻¹. The peak at 1398 cm⁻¹ was weakening gradually with increasing of ZnO loading from 5 to 20%. The band at 700 cm⁻¹ in IR spectra of TiO₂/SiO₂ shifted to 710, 718

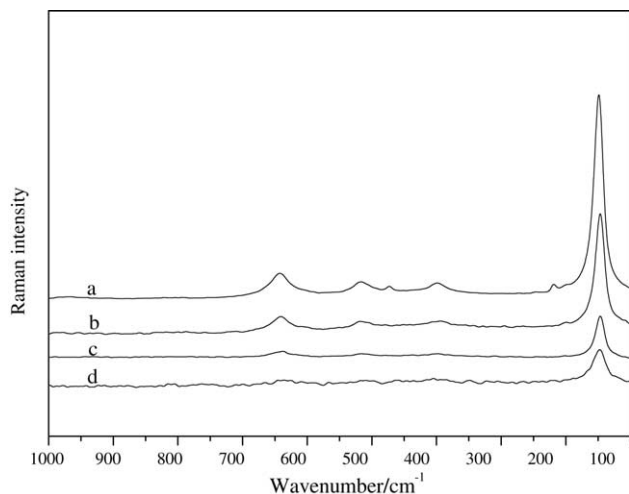


Fig. 2. FT-Raman spectra of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts: (a) TiO₂/SiO₂; (b) 5% ZnO-TiO₂/SiO₂; (c) 10% ZnO-TiO₂/SiO₂; (d) 20% ZnO-TiO₂/SiO₂.

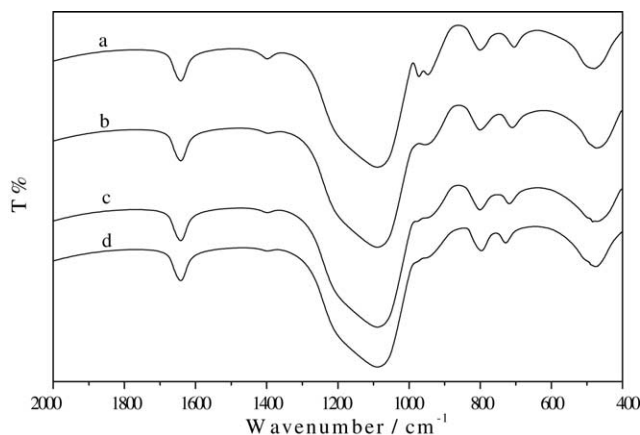


Fig. 3. IR spectra of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts: (a) TiO₂/SiO₂; (b) 5% ZnO-TiO₂/SiO₂; (c) 10% ZnO-TiO₂/SiO₂; (d) 20% ZnO-TiO₂/SiO₂.

and 730 cm⁻¹ respectively in IR spectra of 5, 10 and 20% ZnO-TiO₂/SiO₂. The changes in IR spectra of TiO₂/SiO₂ after loading of ZnO indicated that the addition of ZnO affected the titanium surface oxide species, and Zn–O–Ti bonds have been formed.

The UV–vis DRS spectra of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts were presented in Fig. 4. In UV–vis region, the TiO₂/SiO₂ catalyst possesses a band at ~46 000 cm⁻¹, which is due to the ligand-metal charge transfer (LMCT) transitions between Ti⁴⁺ and oxygen ligands. For the well-documented TiO₂/SiO₂ sample, the adsorption band observed at 45 000–47 000 has been assigned to the LMCT transitions of Ti atoms in isolated TiO₄ [20]. The maximum LMCT transitions of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts summarized in Table 1 showed that a red shift of 5000–6000 cm⁻¹ of LMCT transitions was brought out after the loading of the ZnO. The UV–vis DRS spectra are usually considered to provide information about the coordination geometry of the Ti cations and the change in ligands under various conditions. These changes in LMCT transi-

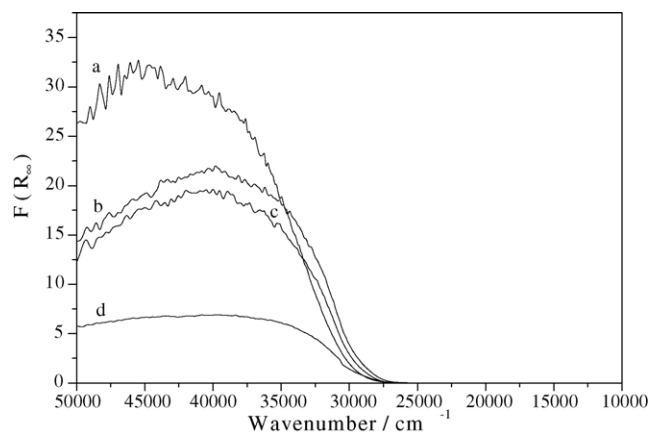


Fig. 4. UV–vis DRS spectra of TiO₂/SiO₂ and ZnO-TiO₂/SiO₂ catalysts: (a) TiO₂/SiO₂; (b) 5% ZnO-TiO₂/SiO₂; (c) 10% ZnO-TiO₂/SiO₂; (d) 20% ZnO-TiO₂/SiO₂.

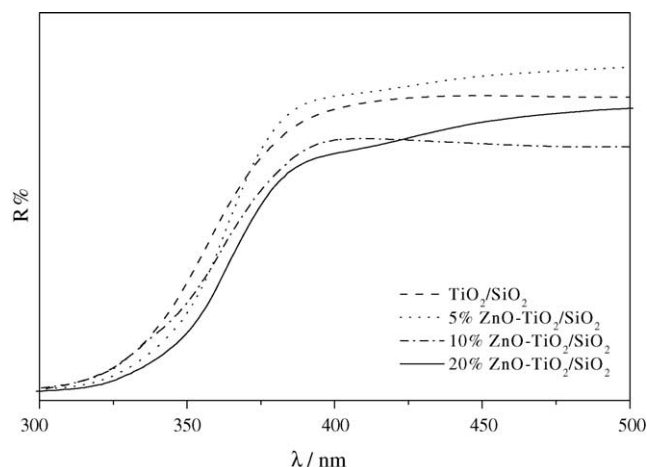


Fig. 5. UV-vis DRS spectra of $\text{TiO}_2/\text{SiO}_2$ and $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts.

tions of $\text{TiO}_2/\text{SiO}_2$ after loading of the ZnO suggested that oxygenated ligands of isolated TiO_4 were different between $\text{TiO}_2/\text{SiO}_2$ and $\text{ZnO-TiO}_2/\text{SiO}_2$. Combined with the analysis of IR, Raman spectra, we can conclude that the significant red shift after the ZnO loading are most likely contributed to the formation of Ti-O-Zn bonds.

3.2. Photo absorption property of catalyst

The UV-vis spectra of $\text{TiO}_2/\text{SiO}_2$ and $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts were shown in Fig. 5. Photoabsorbing curves of $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts have a similar shape with that of support $\text{TiO}_2/\text{SiO}_2$. While a significant red shift of absorption edge has been brought out because of the loading of ZnO. According to the literature report [21], the band-gap energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of $[F(R_\infty)h\nu]^2$ against $h\nu$, where $F(R_\infty)$ is Kubelka-Munk function and $h\nu$ is the incident photon energy. The

corresponding band-gap energies of $\text{TiO}_2/\text{SiO}_2$ and $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts are summarized in Table 1. It was found that the increase of ZnO loading from 0 to 20% decrease E_g from 3.97 to 3.66 eV. This result suggested that the photo absorption fields of $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts were extended.

3.3. Chemisorbing performance of the catalyst

Fig. 6(I) showed the trace of CO_2 desorbed from the $\text{TiO}_2/\text{SiO}_2$ and $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts following the CO_2 adsorption. For $m/e=44$, one peak was discovered around 388 K over all samples, which showed that there existed one CO_2 chemisorption state on the surface of catalysts. The addition of ZnO on the $\text{TiO}_2/\text{SiO}_2$ sample did not change the CO_2 desorption peak temperature clearly and the intensity of desorption peak was reduced gradually with the increase of supporting amount of ZnO, revealing that chemisorption state is related only with TiO_2 active sites. When monitored at $m/e=28$, no CO was detected, suggesting that when CO_2 desorbed from the surface, CO_2 did not undergoes decomposing process. Fig. 6(II) showed the trace of CO_2 desorbed from the $\text{TiO}_2/\text{SiO}_2$ and $\text{ZnO-TiO}_2/\text{SiO}_2$ catalysts under UV irradiation. Compared with CO_2 desorption without UV irradiation, the CO_2 desorption peak around 388 K under irradiation was weakened slightly and when monitored at $m/e=28$, a small desorption peak of CO can be detected around 465 K, which showed that chemisorption state CO_2 must react on the surface of catalyst under UV irradiation and decompose to form CO and O.

Fig. 7 showed the TPD-MS spectra of C_2H_6 desorbed from the catalysts following ethane chemisorption. The TPD experimental results of ethane showed that no desorption peak can be detected on $\text{TiO}_2/\text{SiO}_2$ catalyst, while a desorption peak can be found at around 428 K on the $\text{ZnO-TiO}_2/\text{SiO}_2$ samples (monitored at $m/e=30$). Moreover, the intensity of desorption peak of ethane was increased with the

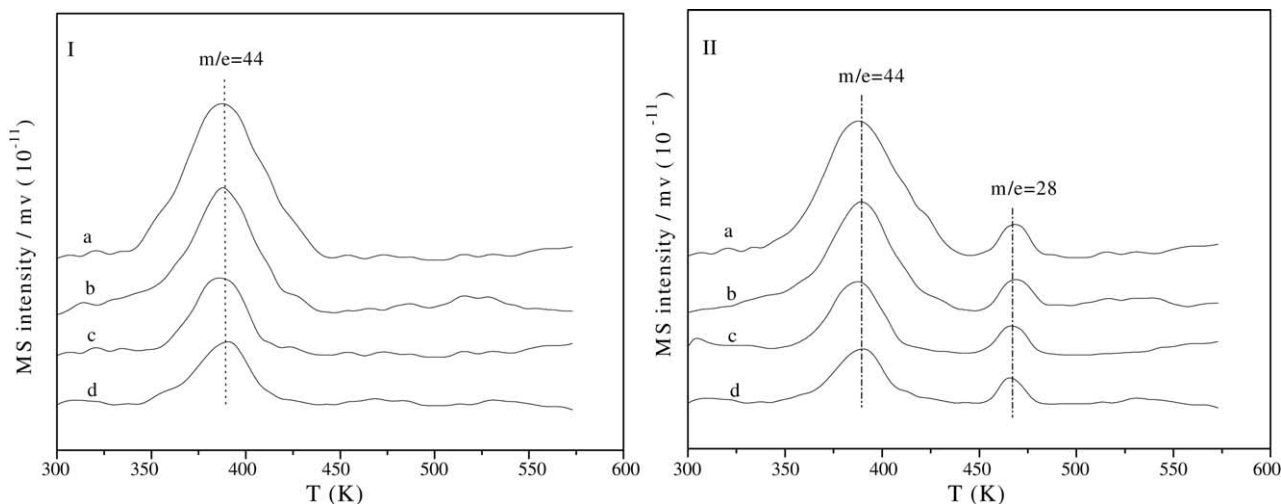


Fig. 6. The TPD-MS spectra of CO_2 chemisorbed on $\text{TiO}_2\text{-SiO}_2$ and $\text{ZnO/TiO}_2\text{-SiO}_2$ catalysts. (I) Without; (II) with UV irradiation. (a) $\text{TiO}_2/\text{SiO}_2$; (b) 5% $\text{ZnO-TiO}_2/\text{SiO}_2$; (c) 10% $\text{ZnO-TiO}_2/\text{SiO}_2$ and (d) 20% $\text{ZnO-TiO}_2/\text{SiO}_2$.

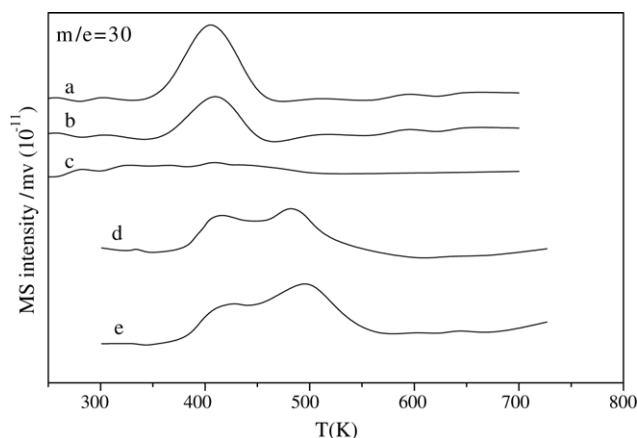


Fig. 7. The TPD–MS spectra of ethane chemisorbed on ZnO–TiO₂/SiO₂ catalysts. Without UV irradiation: (a) 10% ZnO–TiO₂/SiO₂; (b) 5% ZnO–TiO₂/SiO₂; (c) TiO₂/SiO₂. With UV irradiation: (c) TiO₂/SiO₂; (d) 5% ZnO–TiO₂/SiO₂; (e) 10% ZnO–TiO₂/SiO₂.

supporting amount of ZnO from 5 to 10 wt.%. Our previous researches showed that the ethane tends to chemisorb on the lattice oxygen site of metal oxide by H atom in CH₃ [22,23]. Hence, we concluded that the formation of Ti–O–Zn bond over ZnO–TiO₂/SiO₂ catalyst is indispensable for chemisorption of ethane and the lattice oxygen of Zn–O–Ti bond is more active for ethane chemisorbing than that of Ti–O–Ti bond. When irradiated under UV lamp (Fig. 7c–e), we discovered that one new desorption peak of ethane at around 500 K was detected on ZnO–TiO₂/SiO₂ catalysts. The intensity of this new peak increased with the increase of ZnO loading amount, and the new desorption peak was not detected over TiO₂/SiO₂ catalyst, indicating that the new ethane adsorption state was related with the ZnO and Zn–O–Ti bond. It could be due to the formation of alkoxide species Zn–O–CH₃CH₃, which resulted from ethane chemisorbing on the surface active species of Zn–O[−] formed from the reaction of Zn–O–Ti bond and positive hole generated by UV irradiation.

3.4. Photo-catalysis reaction of CO₂ and C₂H₆

The reaction in the absence of the catalyst or UV irradiation at a temperature range of 423–573 K gave none of the products. The results of photo-oxidation of ethane with CO₂ over the TiO₂/SiO₂ and ZnO–TiO₂/SiO₂ catalysts were

summarized in Table 2. The products were propanal, ethanol, butane, CO, acetaldehyde and a trace of ethene.

At the catalyst bed temperature of 473 K, the TiO₂/SiO₂ catalyst under UV irradiation gave a trace of acetaldehyde and carbon oxide. The addition of ZnO increased the conversion of ethane and the yields of products obviously and especially promoted the formation of propanal, ethanol and acetaldehyde products. The increase of ethane conversion and products yields after the loading of the ZnO is due to the n–p coupling effect between TiO₂ and ZnO. Photogenerated electrons and holes accumulate into the conduction band of n-type semiconductor TiO₂ and the valence band of p-type semiconductor ZnO, respectively. Above processes separate two kinds of photogenerated current carriers efficiently and thus prevent their recombination. Furthermore, in order to initiate the reaction, it is required for two reactants to be chemisorbed on the surface and accept the electrons and holes formed by irradiation. The TPD results showed that the presence of surface ZnO is important for ethane to be chemisorbed on the surface of catalyst and to form the alkoxide species of Zn–O–CH₃CH₃ under UV irradiation through the formation of Ti–O–Zn bond, and Zn–O–CH₃CH₃ species are more active to react with CO or O to produce hydrocarbon oxygenates. These results illuminated the differences in photo catalytic reaction properties between ZnO–TiO₂/SiO₂ and TiO₂/SiO₂ catalyst. Further increase in loading amount of ZnO decreased the catalyst activity and hydrocarbon oxygenates yields, which may be because that excessive ZnO cover the TiO₂ active sites and reduce the chemisorption amount of CO₂. On the other hand, the size of ZnO layer must become large after increasing of support oxide amount, it should be more difficult for electron and hole to reach the surface before recombination.

Fig. 8 showed the yields of the products at various catalyst bed temperatures under UV irradiation over 5% ZnO–TiO₂/SiO₂. Ethanol can be obtained mainly and propanal product cannot be formed when catalyst bed temperature is lower than 393 K. Although ethanol yield increased with the temperature increase, the selectivity of ethanol decreased gradually. The yield of propanal showed a rapid increase with increase of the temperature until temperature is higher than 473 K. The yields of propanal and ethanol showed a maximum value of 75.6 and 50.9 μmol h^{−1}, respectively at around 473 K. On the other hand, the selectivity of C₄ increase with temperature rising. CO yield

Table 2
Partial photo-oxidation of ethane with CO₂ over ZnO–TiO₂/SiO₂ catalysts

Catalysts	X _{C₂H₆} (%)	T (K)	Yield (μmol h ^{−1})				
			C ₂ H ₅ CHO	C ₂ H ₅ OH	CH ₃ CHO	C ₄ H ₁₀	CO
TiO ₂ /SiO ₂	–	473	n.d.	Trace	Trace	–	Trace
5% ZnO–TiO ₂ /SiO ₂	–	473	n.d.	n.d.	n.d.	n.d.	n.d.
5% ZnO–TiO ₂ /SiO ₂	1.25	473	75.6	50.9	8.6	15.8	6.8
10% ZnO–TiO ₂ /SiO ₂	1.0	473	52.0	43.4	5.4	14.9	8.3
20% ZnO–TiO ₂ /SiO ₂	0.86	473	42.9	39.5	4.3	14.3	19.5

Reaction conditions: 125 W mercury lamp; CO₂(C₂H₆) feed rate = 13.4 mmol h^{−1}; amount of catalyst = 2 g; space velocity = 200 h^{−1}; n.d. = not detected.

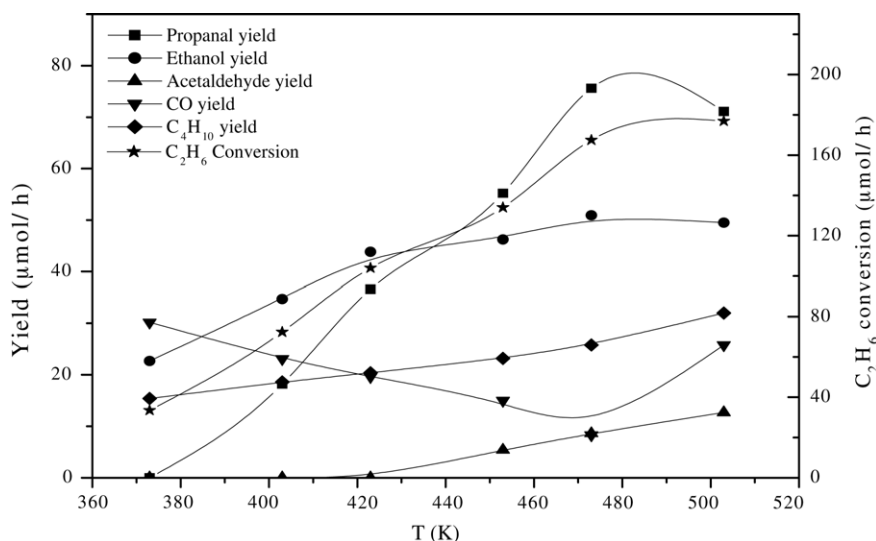


Fig. 8. The effect of temperature on reaction products yields and C₂H₆ conversion. Reaction conditions: 125 W mercury lamp; CO₂ feed rate = 13.4 mmol h⁻¹; C₂H₆ feed rate = 13.4 mmol h⁻¹; amount of catalyst = 2 g; space velocity = 200 h⁻¹.

decreased with increase of temperature until temperature is 473 K, then the yield of CO showed a rapid increase. These results indicated that 473 K is preferable temperature for the selective formation of the propanal and ethanol.

It is generally accepted that photo-oxidation of ethane using solid semiconductors is initiated by forming of a pair of electron and positive hole under UV irradiation [2,6,24]. Different types of active oxygen species, such as O⁻ anion radical species, adsorbed oxygen species and lattice oxygen have proposed over n-type solid semiconductor when using O₂ as oxidant. In the present study, over ZnO/TiO₂-SiO₂ using CO₂ as oxidant, the TPD results showed that CO₂ could undergo decomposing process to form oxygen species CO and O. The CO must incorporate into ethane to form propanal. The O species from CO₂ is near neutral atomic oxygen that tends to form alcohols [25]. The formation of C₄H₁₀ was because that the O species from CO₂ decomposing process accelerated oxidative dehydrogenation reaction of ethane under UV irradiation, and the dehydrogenation species C₂H₅• of ethane couple to C₄H₁₀. The reaction of photo-oxidation of ethane with CO₂ was greatly enhanced with increase in reaction temperature up to ca. 450 K, and showing that the increase of temperature can improve the activation of CO₂ and ethane, and enhanced the desorbing of products. The total rate of the reaction would be accelerated at high-temperature.

4. Conclusion

Photo-oxidation of ethane using CO₂ as oxidant over the metal oxide semiconductors was examined. The loading of ZnO with proper amount on the surface of TiO₂/SiO₂ improves reactivity of catalysts and product yields. The Zn-O-Ti bond is essential for the chemisorption of ethane

and the formation of hydrocarbon oxygenates from CO₂ and ethane. The photo-oxidation of ethane with CO₂ can form mainly propanal, ethanol, C₄H₁₀ and CO at temperature range of 393–473 K. Propanal product was obtained at a maximum yield of 75.6 μmol h⁻¹ using 5% ZnO/TiO₂-SiO₂ catalyst at around 473 K. All reactions required UV irradiation, and propanal formation required elevated reaction temperature.

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