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Synthesis of acetophenone from aerobic catalytic oxidation of ethylbenzene over Ti–Zr–Co alloy catalyst: Influence of annealing conditions

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ABSTRACT

The aerobic catalytic oxidation of ethylbenzene to produce acetophenone over an effective and robust heterogeneous Ti–Zr–Co has been studied. Under the optimum conditions, a high selectivity of 69.2% to acetophenone was obtained at a 61.9% conversion of ethylbenzene over Ti–Zr–Co catalyst, which is much better than the most results reported with heterogeneous catalysts. The catalytic performance and the active species of Ti–Zr–Co catalyst were discussed based on the changes of conversion and selectivity with varying the annealing temperature and atmosphere. It is confirmed that the surface CoO, Co_3O_4 species are the active sites, and the bulk structure of the alloy, $CoTi_2$ phase also present a large effect on the catalytic activity in present oxidation. As a cheap, robust and separable catalyst as well as a green oxidant is used, the present work provides a facile and green catalytic process for the oxidation of hydrocarbons.

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1. Introduction

The selective oxidation of hydrocarbon is of great importance in petrochemical industry for that it can transform petroleum feedstocks such as alkanes, olefins, and aromatics into a plenty of valuable organic chemicals, which are widely used in the preparation of polymer materials and fine chemicals etc. [1]. Generally, the oxidants such as *tert*-butylhydroperoxide, hydrogen peroxide, nitric acid, halides or ozone, etc. are used for the catalytic oxidation of hydrocarbons [2–6]. However, from the points of industrial application, these oxidants are expensive and un-environmentally benign such as *tert*-butylhydroperoxide, nitric acid and halides will leave large volume of organic waste, and hydrogen peroxide decomposes easily into water which will reduce the activity of the catalyst [7]. In term of eco-friendly sustainability, molecular oxygen is an ideal terminal oxidant, as it is much cheaper and more environmental benign compared to the chemical oxidants mentioned above. Therefore, the aerobic catalytic oxidation is an important and green chemical process for the chemical industrial fabrication and it has attracted more attention in these years. Some effective catalysts have been developed for aerobic catalytic oxidation. For example, MnCP@SiO_2 catalyst was studied for the aerobic selective oxidation of ethylbenzene, in which the conversion of ethylbenzene was 22.9% and the selectivity of acetophenone reached to 74.9% at 100 °C [8]. Jin et al. reported a catalyst of hierarchically porous aluminophosphate-based zeolite with AEL and AFI structures, with it a 77.9% selectivity to acetophenone was obtained at a 14.8% conversion of ethylbenzene at 140 °C, 3 MPa O_2 in the absence of solvent [9]. Most recently, the non-metal catalyst is of high popular in the hydrocarbon oxidation, Luo et al. reported that carbon nanotubes were effective for the selective oxidation of ethylbenzene, the selectivity of acetophenone reached to 60.9% at a conversion of 38.2% at 155 °C, 1.5 MPa in CH_3CN [10]. Gao et al. reported that N-doped materials were active for the oxidation of hydrocarbons and alcohols [11]. In addition, they developed an effective palladium catalyst of Pd@N-doped carbon for the aerobic selective oxidation of ethylbenzene, in which the conversion of ethylbenzene was 14.2% and the selectivity of acetophenone reached up to 94% under

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atmosphere at 120 °C [12]. Chen et al. prepared Co—N—C/CeO_2 catalyst by a thermal annealing carbonization strategy, it exhibited a 74.8% selectivity to acetophenone at a 33.1% conversion for the ethylbenzene oxidation at 120 °C, 0.8 MPa O_2 [13].

The selective oxidation of ethylbenzene to acetophenone is an important reaction for that acetophenone is a very useful intermediate of the fine chemicals such as pharmaceuticals and perfume [14,15]. Usually, acetophenone is commercially produced from catalytic oxidation of ethylbenzene with molecular oxygen in the presence of homogeneous cobalt based catalyst and additives such as manganese and bromide species in an acetic acid solvent [16–18]. Herein, we will report an effective heterogeneous catalyst, Ti–Zr–Co metallic alloy, for production of acetophenone from oxidation of ethylbenzene with molecular oxygen. In our previous work, the Ti–Zr–Co alloy was found to be active and selective for the oxidation of cyclohexane, in which cyclohexanol and cyclohexanone were produced with a high selectivity of 90% at a conversion around 7% [19,20]. The Ti–Zr–Co catalyst is easy to handle and transport, simple and cheap in production, sturdy to wearing in the utilization, with comparing to those reported catalysts such as metal-organic complex, metal nanoparticles and nanocarbon materials. Therefore, it stimulates us to extend further study of the Ti–Zr–Co alloy catalyst in the aerobic catalytic oxidations. The catalyst showed a higher catalytic performance for the aerobic oxidation of ethylbenzene, in which acetophenone was produced as the main product with a selectivity of 69.2% at a 61.9% conversion, which are much better than the results reported in literature. The annealing temperature and atmosphere presented significant effects on the oxidation of ethylbenzene, after annealing at 450 °C in N_2 flow, the activity of Ti–Zr–Co increased significantly with a stable selectivity to acetophenone. The active species was discussed in detail by experimental data and the characterizations of the catalysts annealed under the different conditions. This study not only presents an effective and robust catalyst for the selective oxidation of ethylbenzene to acetophenone, but also gives a new insight into the effect of surface phase composition and bulk structure of Ti–Zr–Co alloy on the catalytic performance of aerobic oxidation.

2. Experimental

2.1. Ti–Zr–Co alloy preparation and characterization

Ti–Zr–Co catalyst was prepared by arc-melting of Ti (99 wt.%), Zr (97 wt.%) and Co (99 wt.%) metals with a mole ratio of 60:10:30 on a water-cooled cuprum hearth in a high-purity argon atmosphere at 250 A. To make the chemical compositions homogenous, the alloy ingot was turned over and remelted at least three times. After that, the surface of the cast ingot was burnished in order to eliminate the oxide layer. Then the alloy ingot was crushed to powders by repeated manual beating with a steel pestle and mortar, and separated by 140 meshes screen, the powders with size smaller than 140 meshes (109 μm) were used for the reaction experiment. In some cases, the Ti–Zr–Co catalyst, before use, was annealed at 450 °C or 750 °C for 2 h under N_2 (denoted as Ti–Zr–Co-450-N_2 and Ti–Zr–Co-750-N_2) or at 450 °C for 2 h under air (denoted as Ti–Zr–Co-450-air) with a heating rate of 5 °C min^{-1} in a tube furnace to obtain different treated Ti–Zr–Co catalysts. A $CoTi_2$ alloy was prepared by a method similar to the Ti–Zr–Co alloy catalyst as described above, except for without Zr involved. Co_3O_4 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China), is of analytical reagent. 7 wt.% Co_3O_4/TiO_2 was prepared according to literature [21].

The phase composition and microstructure of the alloys were examined by X-ray diffraction (XRD) on a Bruker-AXS D8 ADVANCE with Kα. The leaching of Ti, Zr or Co in the filtrate was not detected by ICP-OES measurement (iCAP6300, Thermo USA). XPS measurement was performed by using a VG Microtech 3000 Multilab, and the spectra of Co 2p, Zr 3d, Ti 2p, O 1s and C 1s were recorded, which were corrected to the C 1s peak at 284.6 eV. Scanning electron microscopy (SEM) image was performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 10 kV, and the size of particles was in a range of 50–100 μm (Fig. S1).

2.2. Ethylbenzene oxidation

Ethylbenzene and acetonitrile purchased from Beijing chemical plant are of analytical grade, and used without further purification, gas of O_2 (99.99%) (Changchun Xinxing Gas Company) is used as delivered. Typically, ethylbenzene (5 mL), acetonitrile (5 mL) and the Ti–Zr–Co catalyst (20 mg) were charged into a stainless steel autoclave with a Teflon inner liner (50 mL) at room temperature, then the reactor was sealed and preheated in an oil bath, after the reactor was heated up to the desired temperature, O_2 (2 MPa) was introduced and the reaction was started with a continuously stirring at 1200 rpm, and the reaction time was recorded. When the reaction finished, the reactor was cooled to room temperature and then depressurized carefully. The solid catalyst was separated

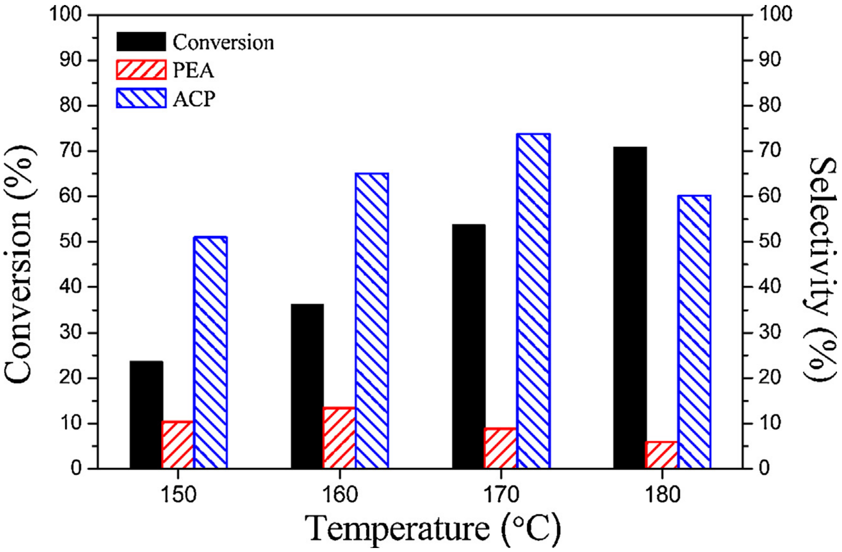

Fig. 1. The effect of temperature on the oxidation of ethylbenzene. Reaction conditions: 5 mL ethylbenzene, 5 mL CH_3CN, 20 mg Ti–Zr–Co alloy catalyst, 2 MPa O_2, 3 h.

Table 1
The results for the ethylbenzene oxidation over Ti–Zr–Co catalyst in acetonitrile.

Entry	CH_3CN (mL)	Conv. (%)	Sel. (%)		
			ACP	PEA	Others[a]
1	–	13.8	73.4	16.6	10.0
2	3	33.9	57.9	12.2	29.9
3	5	36.2	65.1	13.4	21.5
4	7	35.4	60.9	14.0	25.1
5	9	33.7	65.0	12.9	22.1
6	15	26.8	62.0	12.9	25.1

Reaction conditions: 5 mL ethylbenzene, 20 mg Ti–Zr–Co alloy catalyst, 2 MPa O_2, 160 °C, 3 h.

[a] Others are the main byproducts of benzaldehyde and benzoic acid.

Table 2
Effects of annealing temperature and atmosphere.

Entry	Catalyst	Conv. (%)	Sel. (%)		
			ACP	PEA	Others
1	Ti–Zr–Co	36.3	65	13.4	21.6
2	Ti–Zr–Co-450-air	48.7	51.1	11.2	37.7
3	Ti–Zr–Co-450-N_2	60.3	60.1	9.76	30.14
4	Ti–Zr–Co-750-N_2	25.7	54.5	9.31	36.19

Reaction conditions: 5 mL ethylbenzene, 5 mL CH_3CN, 20 mg catalyst, 160 °C, 2 MPa O_2, 3 h.

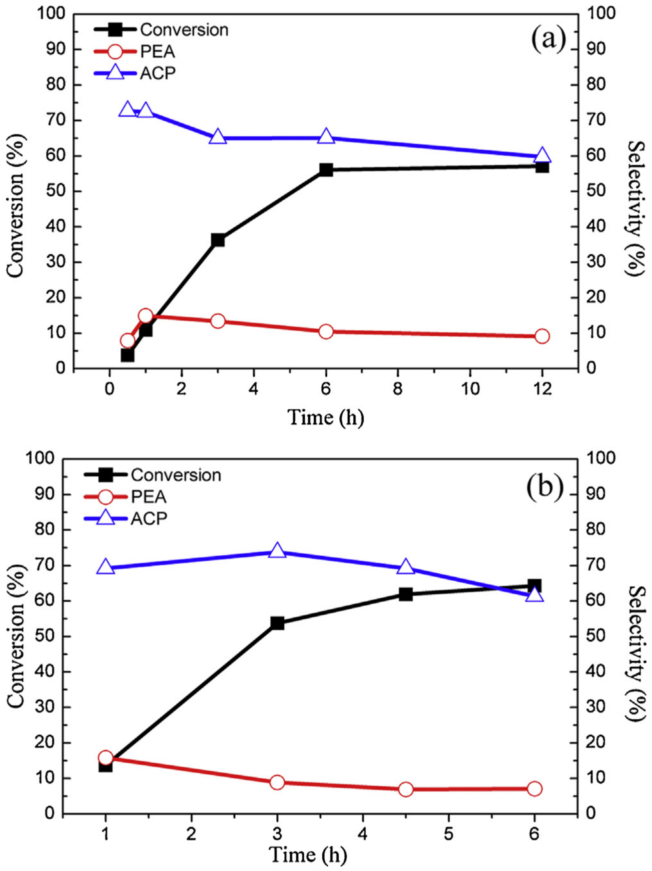

Fig. 2. Changes of conversion and selectivity with reaction time in the oxidation of ethylbenzene at 160 °C (a) and 170 °C (b). Reaction conditions: 5 mL ethylbenzene, 5 mL CH_3CN, 20 mg Ti–Zr–Co alloy catalyst, 2 MPa O_2.

out by filtration, and then the reaction solution was diluted with ethanol to 50 mL, the composition of reaction products was confirmed by gas chromatography/mass spectrometry (GC/MS, Agilent 5890) and analyzed with toluene as an internal standard by gas chromatograph (Shimadzu GC-2010, FID, capillary column, RTX-50, 30 m × 0.25 mm × 0.25 μm).

3. Results and discussion

3.1. Effects of solvent, reaction temperature and time

The effects of solvent, reaction temperature, and reaction time on the ethylbenzene oxidation over the fresh Ti–Zr–Co alloy were discussed. Acetophenone (ACP) was produced as the main product with accompanying of 1-phenethanol (PEA) and benzaldehyde (BA), and benzoic acid (BC) was also detected in the products. Firstly, the efficiency of several organic solvents such as benzene, ethanol, acetonitrile and acetone was examined for the oxidation of ethylbenzene (Table S1). Compared to the case of reaction in the absence of solvent, the conversion increased, however, the selectivity to acetophenone and 1-phenethanol decreased with a different range in the presence of organic solvents as the formation of undesirable over-oxidized products like acetic acid, esters etc. Among these solvents, the acetonitrile presented to be more effective for the present ethylbenzene oxidation, the conversion was improved more than two times and the selectivity reduced slightly with comparing to the case in the absence of solvent, resulting in the yield of acetophenone and 1-phenethanol increased to 28.4% from 12.4%. Therefore, acetonitrile was selected as solvent in the following studies. Table 1 shows the effect of the amount of acetonitrile on the conversion and the product selectivity. It is clear that the conversion increased largely in the presence of acetonitrile, and changed slightly with the amount of acetonitrile at the range of 3–9 mL. But the conversion decreased with further increasing of the amount of acetonitrile to 15 mL, it decreased to 26.8%. These results are in agreement to the literature [22,23]. These will be ascribed to the solubility of O_2 and the dilution effect of acetonitrile [24,25]. That acetonitrile has a better ability to dissolve O_2, thus with its presence, the content of O_2 will increase in the reaction solution, and so the reaction conversion increases. However, with its further increase, the concentration of ethylbenzene decreases and the dilution effects will appear, resulting in a decrease of conversion. In the presence of acetonitrile, the selectivity of the main product of acetophenone is around 60%, which is a little lower than the result (73.4%) obtained in the absence of solvent. It is ascribed to that the presence of acetonitrile could accelerate the reactions of ehylbenzene to acetophenone and 1-phenethanol, and accelerate their further oxidation to benzaldehyde and benzoic acid also. Temperature has a remarkable influence on the oxidation reaction as seen in Fig. 1. Generally, high temperature is favor for the proceeding of the oxidation of hydrocarbon, as expected, the conversion increases with reaction temperature, and it increases from 23.7% to 70.9% with enhancing temperature from 150 °C to 180 °C. While, the selectivity of acetophenone increases initially and then decreases with further raising temperature, and it presents an optimum value of 73.7% at 170 °C, at which the total selectivity of both acetophenone and 1-phenethanol reached to 82.6%. With further enhancing temperature, the selectivity of acetophenone decreases to 60.2%, as the deep oxidation of both acetophenone and 1-phenethanol to benzaldehyde and benzoic acid occurs.) and XPS (Fig. 4 In addition, the changes of the conversion and selectivity with the reaction proceeding were checked at 160 °C and 170 °C, respectively. As shown in Fig. 2, the conversion increases largely with extending reaction time up to 6 h and then it keeps at a constant level with further extending to 12 h at 160 °C, it suggested that the reaction has reached chain-termination after proceeding for 6 h (Fig. 2a). When the reaction was performed at 170 °C (Fig. 2b), the reaction reaches the chain-termination within 4.5 h, as the conversion increases at the first 4.5 h, and then increases very less at the stage of 4.5–6 h. In addition, the selectivity of acetophenone reaches

Table 3
The bulk phase and the surface composition based on XRD and XPS measurements.

Entry	Catalyst	Bulk phase[a]	Surface composition[b]	Co species molar ratio (%)[b]		
				Co	CoO	Co_3O_4
1	$CoTi_2$	$CoTi_2$	Co, CoO, Co_3O_4, TiO_2, ZrO_2	31.5	37.8	30.7
2	Ti–Zr–Co	$CoTi_2$	Co, CoO, Co_3O_4, TiO_2, ZrO_2	20.1	32.8	47.1
3	Ti–Zr–Co-450-air	$CoTi_2$	Co_3O_4, TiO_2, ZrO_2	0	0	100
4	Ti–Zr–Co-450-N_2	$CoTi_2$	Co, CoO, Co_3O_4, TiO_2, ZrO_2	25.7	51.4	22.9
5	Ti–Zr–Co-750-N_2	Co_3O_4, TiO_2, $CoTiO_3$	Co_3O_4, TiO_2, ZrO_2	0	0	100

[a] The bulk phases of the alloy catalysts were obtained based on the XRD patterns.
[b] The surface compositions of the alloy catalysts were obtained based on the XPS spectra.

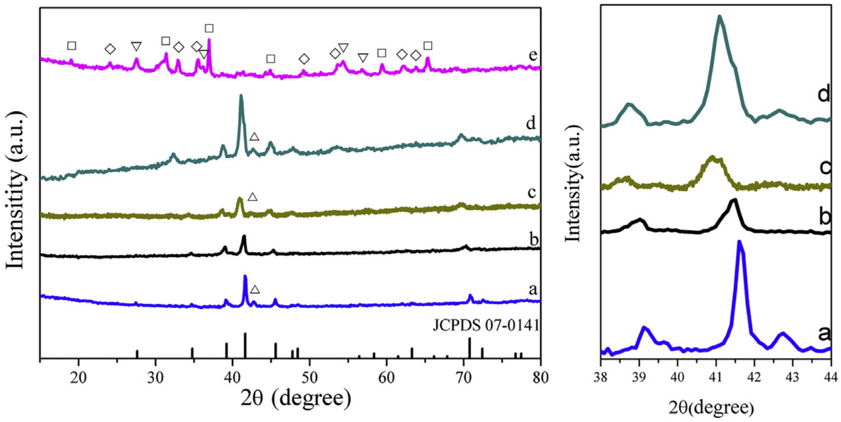

Fig. 3. XRD patterns (left) and a partial enlarged drawing (right) of (a) the $CoTi_2$ alloy and (b) the fresh Ti–Zr–Co alloy catalyst, (c) Ti–Zr–Co-450-air, (d) Ti–Zr–Co-450-N_2, (e) Ti–Zr–Co-750-N_2, and the JCPDS 07-0141 file identifying $CoTi_2$. (△: laves phase; □: Co_3O_4; ◇: $CoTiO_3$; ▽: TiO_2).

73.7% after reaction performed for 3 h, and then decreases with extending reaction time, especially after the conversion of ethylbenzene reaches chain-termination, the selectivity decreases from 69.2% at 4.5 h to 61.3% at 6 h. By contrast, the selectivity of acetophenone decreases much slowly at 160 °C, from 65.1% at 6 h to 59.7% at 12 h. It is clearly that the oxidation proceeds much faster at the higher temperature, including the deep oxidation of acetophenone. The best results for the ethylbenzene oxidation over the Ti–Zr–Co catalyst were obtained at the conditions of 170 °C, 2 MPa, 4.5 h, at which the conversion of ethylbenzene is 61.9% and the selectivity of acetophenone reaches up to 69.2%, these are comparable to the best results reported in the latest literature (Table S2).

3.2. *Effects of annealing temperature and atmosphere*

The annealing temperature and atmosphere present large effects on the conversion and product selectivity as shown in Table 2. As Ti–Zr–Co-450-air calcined at 450 °C in air, the conversion (48.7%) increased largely with comparing to the fresh one (36.3%) (Entries 1,2). For Ti–Zr–Co-450-N_2 annealed at 450 °C in N_2, the conversion increased further to 60.3% (Entry 3). However, as Ti–Zr–Co-750-N_2 was annealed at 750 °C in N_2 flow, the conversion decreased sharply to 25.7% (Entry 4). It is clear that the annealing temperature and atmosphere have a significant effect on the conversion. Thus, the structure and surface composition of these catalysts may affect the catalytic activity markedly, which were well characterized and discussed.

3.3. *The relation between structure and catalytic performance*

To study the structure or surface composition of the fresh and annealing Ti–Zr–Co catalysts and their relationship to the catalytic performance, the crystal structure and surface composition or electronic states of these samples were characterized with XRD (Fig. 3). It is obvious that both the prepared $CoTi_2$ alloy and the fresh Ti–Zr–Co alloy catalyst give the typical diffraction peaks of the intermetallic compound of $CoTi_2$ phase (Fig. 3a,b). The diffraction peaks of Ti–Zr–Co shift slightly to the small angles with comparing to the prepared $CoTi_2$ alloy, which is ascribed to that the additive element Zr has a much larger atomic radius than Ti and Co. In addition, the addition of Zr also caused the diffraction peaks to broaden for that the insertion of Zr atom can separate the grain

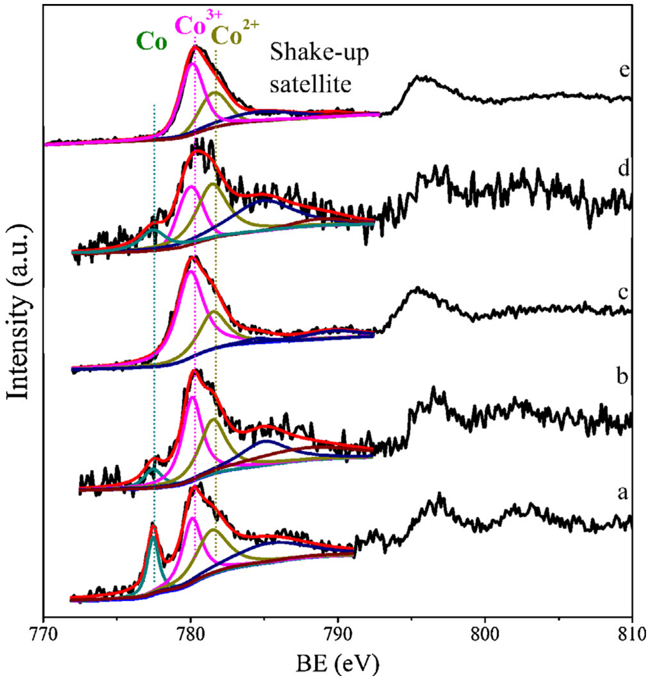

Fig. 4. The XPS spectra of Co 2p3/2 of (a) $CoTi_2$ alloy and (b) fresh Ti–Zr–Co alloy catalyst, (c) Ti–Zr–Co-450-air, (d) Ti–Zr–Co-450-N_2, (e) Ti–Zr–Co-750-N_2.

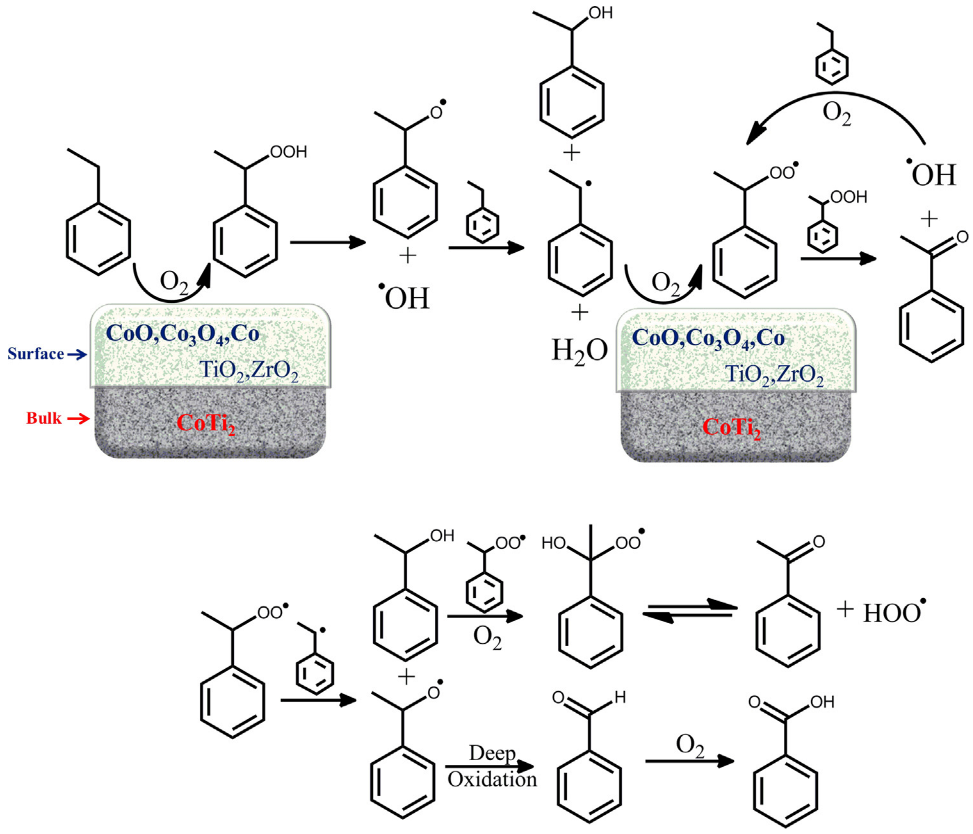

Fig. 5. Possible reaction processes for aerobic oxidation of ethylbenzene over the surface of Ti–Zr–Co catalyst.

$CoTi_2$, resulting in a highly dispersion of the smaller $CoTi_2$ crystal grain in Ti–Zr–Co (Fig. 3a,b). At a annealing temperature of 450 °C in air (Ti–Zr–Co-450-air) and N_2 (Ti–Zr–Co-450-N_2), the main bulk is composed of $CoTi_2$ phase (Fig. 3c,d), and a laves phase presents in the samples of Ti–Zr–Co-450-air, Ti–Zr–Co-450-N_2 and the prepared $CoTi_2$ alloy (Fig. 3a,c,d). However, at the high annealing temperature of 750 °C in N_2 flow (Ti–Zr–Co-750-N_2), some new crystal phases such as Co_3O_4, TiO_2 and $CoTiO_3$ were formed, while the $CoTi_2$ and the laves phase disappeared (Fig. 3e).

As the heterogeneous catalytic reaction is occurring on the surface of catalyst, thus the effective and active species should locate on the surface of solid catalyst. Thus, we further characterized the surface composition for the catalysts. The Co 2p XPS spectra are shown in Fig. 4. The Co, Co^{2+} and Co^{3+} species are found in the samples containing Co elements, CoO is confirmed by the intense shake-up satellites around 6 eV above the primary spin-orbit Bes [26–28], and Co_3O_4 is confirmed by Co^{3+}/Co^{2+} (2/1) [29]. Therefore, the Co metal, CoO and Co_3O_4 species are co-existence on the surface of the $CoTi_2$ alloy, the fresh Ti–Zr–Co and Ti–Zr–Co-450-N_2 (Fig. 4a,b,d; Table 3, entries 1,2,4). While, the sole Co_3O_4 species is found on the surface of Ti–Zr–Co-450-air and Ti–Zr–Co-750-N_2 (Fig. 4c,e; Table 3, entries 3,5), because the Co^0 and CoO species were transformed to the Co_3O_4 species when calcinated in air or at the high temperature (750 °C) in N_2. Moreover, Ti and Zr species are mainly existence with TiO_2 and ZrO_2 on the surface of catalysts. For Ti species, the peaks of Ti 2p move slightly to the higher binding energy for all the samples annealed in air and N_2 flow (seen in Fig. S2), indicating their surfaces are of little electron deficient compared with the fresh one.

The activity of the $CoTi_2$ alloy is as low as the blank reaction (Table 4, entries 1,2). However, the activity of the fresh Ti–Zr–Co alloy is much higher than the $CoTi_2$ alloy (Table 2, entry 1 vs. Table 4, entry 2), although they have the same bulk structure as $CoTi_2$ phase and the same Co species such as Co, CoO and Co_3O_4 on their surface (Table 3, entries 1,2). Compared with the $CoTi_2$ alloy, the addition of Zr with high oxygen affinity will produce much more surface defect for that the large atom radius Zr will make Co oxidize easily to Co_3O_4 (Table 3, entries 1,2), indicating that the Co_3O_4 species may be one of the main catalytic active species. Thus, Ti–Zr–Co presented higher activity compared to the $CoTi_2$ alloy. Based on the analysis and comparison of the activities and phase compositions among the samples (Table 3, entries 2–5), the CoO species should also play an important role in the present oxidation. Moreover, the bulk $CoTi_2$ phase may own a promoting function in present oxidation as comparison Ti–Zr–Co-450-air with Ti–Zr–Co-750-N_2, although they are the same in Co species composition, but different in the bulk phases, and Ti–Zr–Co-450-air with $CoTi_2$ phase presents higher activity than Ti–Zr–Co-750-N_2 without $CoTi_2$ phase (Table 3, entries 3,5). The function of the bulk $CoTi_2$ phase is also demonstrated by following results. Co_3O_4 is usually an effective oxidation catalyst, but both the pure Co_3O_4 and Co_3O_4/TiO_2 presents lower activity than Ti–Zr–Co-450-air (Table 4, entries 3,4 vs. Table 2, entry 2), as the $CoTi_2$ phase exists in Ti–Zr–Co-450-air but not in Co_3O_4 and Co_3O_4/TiO_2. According to the XPS analysis, the electron may transfer from the surface TiO_2 species to the bulk $CoTi_2$ phase, and which benefits for the present oxidation (Fig. S2). Therefore, both CoO and Co_3O_4 are the major active species, and the bulk $CoTi_2$ phase may affect the activity through the electron transfer on the surface of Ti–Zr–Co catalysts. Ti–Zr–Co-450-N_2 shows the highest catalytic activity due to its most abundant surface CoO species and the presence of the bulk $CoTi_2$ phase.

3.4. Possible reaction processes

Generally, the aerobic oxidation of hydrocarbons can spontaneously occur by a radical reaction in some cases without catalyst

Table 4
Comparison of the catalytic performances of different catalysts in the ethylbenzene oxidation.

Entry	Catalyst	Conv. (%)	Sel. (%)		
			ACP	PEA	Others
1	–	19.4	53.2	14.2	32.6
2	$CoTi_2$	19.5	71.9	12.3	15.8
3	Co_3O_4	43.5	63	12.5	24.5
4	Co_3O_4/TiO_2	27.7	61.4	15.9	22.7

Reaction conditions: 5 mL ethylbenzene, 5 mL CH_3CN, 20 mg catalyst, 160 °C, 2 MPa O_2, 3 h.

[30,31]. But the reaction is very slow therefore the researchers make their best effort to develop effective catalysts to accelerate the reaction. As reported in literature, the oxidation of ethylbenzene could occur automatically somewhat at certain conditions in the absence of catalyst [32]. Herein, it was also found that the oxidation of ethylbenzene can occur without addition of catalyst, but it is much lower (Table 3 entry 1). Ti–Zr–Co was effective for the present ethylbenzene oxidation, with it the reaction was promoted largely.

Herein, a radical reaction mechanism for the ethylbenzene oxidation over the Ti–Zr–Co catalyst was proposed (Fig. 5), that oxygen firstly is adsorbed onto the surface of the solid catalyst and activated, and then the activated oxygen reacts with the activated ethylbenzene to produce 1-phenylethyl hydroperoxide [32]. In the absence of an initiator system, the homolytic dissociation of hydroperoxide molecules is considered to be the dominant chain-initiation step, which dissociates to alkoxy and hydroxy radicals [30]. These radicals react rapidly with substrate to form alkyl radicals for lighting off the propagation reactions. Molecular oxygen is added to alkyl radicals before forming peroxyl radicals, which afterwards abstracted H-atoms from the 1-phenylethyl hydroperoxide to produce acetophenone and hydroxy radicals. The radicals will react with substrate and oxygen for recycle to produce peroxyl radicals continuously. Phenylethyl hydroperoxide reacts with the alkyl radicals to generate alkoxy radical and 1-phenethanol also. 1-Phenethanol could react with peroxyl radicals and oxygen to form 1-phenethanol peroxyl radicals, and then reversibly produce acetophenone [32]. It can explain that acetophenone is produced as the main product other than the same proportion of alcohol and ketone [33,34]. These alkoxy radicals can abstract H-atoms from the ethylbenzene substrate in chain-propagation reactions or decompose via β-scission to benzaldehyde. Benzaldehyde will be promptly further oxidized to benzoic acid in the presence of oxygen [10].

4. Conclusions

In summary, a Ti–Zr–Co catalyst was studied at the first time for the oxidation of ethylbenzene. High selectivity (69.2%) to acetophenone was obtained at a high conversion (61.9%) of ethylbenzene. The annealing temperature and atmosphere of the Ti–Zr–Co alloy catalyst presented significant effects on the oxidation of ethylbenzene, due to the change between the surface species and the bulk phase. CoO and CO_3O_4 on the surface are the main active species and the bulk $CoTi_2$ phase also plays a very important role in accelerating the reaction rate for the present ethylbenzene oxidation. The addition of Zr could separate the $CoTi_2$ grains and thus increased its dispersion and make Co be oxidized easily to CoO and/or Co_3O_4. The present catalytic system presents a promising heterogeneous catalyst for the aerobic oxidation of hydrocarbons, its extensive applications in the aerobic oxidation of other hydrocarbons is worth expected.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.12.008.

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