Aerobic Catalytic Oxidation of Cyclohexene over TiZrCo Catalysts

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Abstract: The aerobic oxidation of hydrocarbon is of great significance from the viewpoints of both fundamental and industry studies as it can transfer the petrochemical feedstock into valuable chemicals. In this work, we investigated the aerobic oxidation of cyclohexene over TiZrCo catalysts, in which 2-cyclohexen-1-one was produced with a high selectivity of 57.6% at a conversion of 92.2%, which are comparable to the best results reported for the aerobic oxidation of cyclohexene over heterogeneous catalysts. The influences of kinds of solvent, substrate concentration and reaction temperature were evaluated. Moreover, the catalytic performance of the TiZrCo catalyst and the main catalytic active species were also discussed. The results of SEM, XRD and XPS suggested that the surface CoO and Co_3O_4 species are the catalytic active species and contribute to the high activity and selectivity in the present cyclohexene oxidation. The present catalytic system should have wide applications in the aerobic oxidation of hydrocarbons.

1. Introduction

The selective oxidation of hydrocarbon is of great importance in the chemical industry, and the oxidation of alkenes to value-added chemicals has been paid more attention [1–4]. For example, 2-cyclohexen-1-one, which can be produced from oxidation of the C–H bond at the allylic site of cyclohexene, is one of the important fine chemicals because it is widely used in the manufacture of perfumes, pharmaceuticals, dyestuff and agrochemicals [5–7]. However, the yield of 2-cyclohexen-1-one produced from cyclohexene oxidation is quite low due to the existence of two active sites (C–H and C=C bond) on the cyclohexene molecule [8]. Thus, it is still a great challenge to enhance the selectivity of 2-cyclohexen-1-one by designing an efficient catalyst. For oxidation of cyclohexene, the traditional oxidants are iodosylbenzene, sodium hypochlorite, chromium trioxide, t-butyl hydroperoxide, H_2O_2, *etc.* These strong oxidants can improve the oxidation rate and increase the yield of product, but they are expensive and harmful to the environment. Therefore, developing a green oxidation process is of importance in view of the academic research and industrial application. Recently, the oxidation with molecular oxygen as an oxidant has received much attention as it is a cheap, abundant and environmentally benign process and some achievements have been obtained [9–13]. For example, the ionic liquids with metal chelate anion [C_{10}mim][Co(F_6-acac)$_3$] exhibited high catalytic

activity for the allylic oxidation of cyclohexene in the absence of solvent with a high selectivity of 81% to 2-cyclohexen-1-one at a conversion of 100% [10], and the Cu-[cationic salphen][Br$^-$]$_2$ complex presented a selectivity of 64.1% to 2-cyclohexen-1-one at a 100% conversion for the aerobic oxidation of cyclohexene in acetonitrile [11]. Although these homogeneous catalysts are efficient for the selective allylic oxidation of cyclohexene, their industrial application is limited due to the difficult separation, and the residual metal ions will affect the quality of the product. Hence, heterogeneous catalysts have been developed by immobilizing metal complexes on solid supports, such as resinate-immobilized Co(II), which exhibited high catalytic activity with a 44.4% selectivity to 2-cyclohexen-1-one at a 94.5% conversion of cyclohexene [12]. Core-shell type Fe$_3$O$_4$@chitosan-Schiff base-immobilized Co(II), Cu(II) and Mn(II) complexes were also reported active for the cyclohexene oxidation, and a selectivity of 77.2% to 2-cyclohexen-1-one was obtained at a conversion of 46.8% [13]. On the other hand, the supported transition metal or oxides were also employed as heterogeneous catalysts for the allylic oxidation of cyclohexene [6,14–20]. Recently, Au nanoparticles supported on modified bentonite and silica gave a high conversion (92%) and an excellent selectivity (97%) to 2-cyclohexen-1-one in the aerobic oxidation of cyclohexene without solvent [21]. It was also reported that PdO/SBA-15 was an active catalyst for the oxidation of cyclohexene in acetonitrile, and a conversion of 56% and a selectivity of 82% to 2-cyclohexen-1-one were obtained [6]. In addition, nitrogen-doped carbon nanotubes, and graphitic carbon nitride-supported FeO and CoO were also effective catalysts for the oxidation of cyclohexene [14,22]. Until now, it was still a hot topic to design a heterogeneous catalyst for the aerobic allylic oxidation of cyclohexene.

In our previous work, we found that Ti-Zr-Co metallic catalyst was effective for the oxidation of cyclohexane and ethylbenzene [23–25], in which cyclohexanol and cyclohexanone were produced with a high selectivity of 90% at a conversion around 7%, and acetophenone was produced with a 69.2% selectivity at a high conversion of 61.9%. The Ti-Zr-Co metallic catalyst is simple and cheap in production and sturdy to wearing in the utilization, as compared to those reported catalysts such as metal-organic complex, metal nanoparticles and nanocarbon materials. Therefore, it inspires us to study its efficiency in catalyzing other hydrocarbon oxidations. In the present work, the catalytic performances of the Ti-Zr-Co catalysts were discussed for the aerobic oxidation of cyclohexene. We found that 2-cyclohexen-1-one was produced with a high selectivity of 57.6% at a conversion of 92.2%, which are comparable to the best results reported for the aerobic oxidation of cyclohexene over heterogeneous catalysts. It was confirmed the surface CoO and Co$_3$O$_4$ acted as the catalytic active sites and contributed to the excellent conversion and selectivity.

2. Results and Discussion

For the oxidation of cyclohexene, it is very difficult to control product selectivity due to the existence of the two active groups of the C-H bond at the allylic site and the C=C bond, as when the C–H bond is oxidized, 2-cyclohexene-1-ol, 2-cyclohexene-1-one or cyclohexene hydroperoxide will be generated; as the C=C bond is oxidized, cyclohexene oxide, cyclohexanol, cyclohexanone, cyclohexanediol and dialdehyde will be produced (Scheme 1) [26].
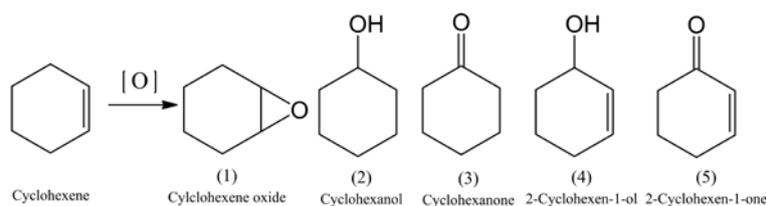
Scheme 1. Reaction route for the aerobic oxidation of cyclohexene.

Firstly, we examined several organic solvents for the oxidation of cyclohexene and the results are listed in Table 1. Among the examined solvents, acetone and acetonitrile are more effective,

and the higher conversion and selectivity of 2-cyclohexen-1-one were obtained; in contrast, ethanol and cyclohexane are less efficient. However, it was found that acetone could be oxidized (to 2,2-diethoxypropane) during the reaction. As a result, acetonitrile is a suitable solvent which led to a conversion of cyclohexene of 38.0% and a selectivity to 2-cyclohexen-1-one of 60.6%. Therefore, the acetonitrile was selected as solvent in the following studies.

Table 1. Effect of solvent on the oxidation of cyclohexene over $Ti_{60}Zr_{10}Co_{30}$ catalyst.

Solvent	Conversion (%)	Selectivity (%) [a]					
		(1)	(2)	(3)	(4)	(5)	Others [b]
Acetone	43.9	7.3	0	1.5	13.3	71.8	6.1
Acetonitrile	38.0	3.0	0.4	1.4	13.6	60.6	21.0
Ethanol	22.0	1.4	0	0.3	4.7	25.0	68.6 [c]
Cyclohexane	6.2	-	0.2	7.4	9.9	37.8	44.7 [d]

Reaction conditions: cyclohexene 1 mL (at a concentration of 4.8%), solvent 20 mL, $Ti_{60}Zr_{10}Co_{30}$ 20 mg, O_2 2 MPa, 100 °C, 12 h. [a] (1) cyclohexene oxide; (2) cyclohexanol; (3) cyclohexanone; (4) 2-cyclohexen-1-ol; (5) 2-cyclohexen-1-one; [b] Others may consist of reaction intermediate such as cyclohexene hydrogen peroxide, deeply oxidized products such as some ring-opening acids or the byproduct from solvent reacting with substrate. [c] The ethanol was oxidized into acetic acid and ethyl acetate. [d] A certain amount of cyclohexane was found to be oxidized to cyclohexanol and cyclohexanone. The result could not exact calculated.

Next, the reaction conditions were evaluated for the oxidation of cyclohexene in acetonitrile. The results for the effect of the concentration of cyclohexene are shown in Table 2. The conversion of cyclohexene increased significantly with the concentration of cyclohexene; it increased from 33.8% to 97.5% when the cyclohexene concentration was raised from 4.8% to 13.0%. However, the selectivity to 2-cyclohexen-1-one decreased linearly due to deep oxidation of 2-cyclohexen-1-one to undesired byproducts at a higher conversion. The aerobic oxidation of cyclohexene is a radical reaction; it contains the chain-initiation, -propagation and -termination steps [1]. The produced radical in the initial step could promote the following steps and was more efficient at higher cyclohexene concentrations as it enhanced the impact probability of radicals, resulting in an increase of the conversion of cyclohexene. It is notable that when the concentration of cyclohexene increased to 16.7%, the reaction became very violent with a sharp increase of pressure (up to 10 MPa at 3.3 h); for safety, the concentration of cyclohexene was controlled below 16.7% under the present reaction conditions.

Table 2. Effect of the cyclohexene concentration on the oxidation reaction.

Entry	Cyclohexene (%) [a]	Time (h)	Conversion (%)	Selectivity (%)					
				(1)	(2)	(3)	(4)	(5)	Others [b]
1	4.8	5	33.8	3.1	-	1.7	19.1	71.3	4.9
2	9.1	5	67.0	5.5	-	0.7	11.6	62.5	19.8
3	13.0	5	97.5	-	-	0.6	3.7	49.5	46.1
4 [c]	16.7	3.3	92.8	1.9	0.9	1.4	6.2	30.2	59.4

Reaction conditions: acetonitrile 20 mL, $Ti_{60}Zr_{10}Co_{30}$ 20 mg, O_2 2 MPa, 120 °C. [a] Concentration of cyclohexene = $V_{cyclohexene}/(V_{cyclohexene} + V_{acetonitrile}) \times 100$%; [b] Others may consist of reaction intermediate such as cyclohexene hydrogen peroxide, deeply oxidized products such as some ring-opening acids; [c] When the concentration of cyclohexene reached 16.7%, the reaction proceeded very quickly with a suddenly pressure rising, and the reaction was stopped at 3.3 h for safety.

It is well known that temperature is one of the most important factors for oxidation reactions. Generally, high temperature is in favor for the oxidation of hydrocarbons. As the results show in Figure 1, the conversion increased from 17.8% to 98.2% while the selectivity of 2-cyclohexen-1-one decreased from 70.1% to 43.7% with the temperature rising from 80 to 140 °C. Deep oxidation is serious at higher temperatures and undesirable byproducts such as ring-opening acids are produced. The selectivity of cyclohexene oxide, cyclohexanol and cyclohexanone changed slightly, within 5%.

The optimal temperature was 120 °C, at which a 57.6% selectivity of 2-cyclohexene-1-one was obtained at a high conversion of 92.2%.
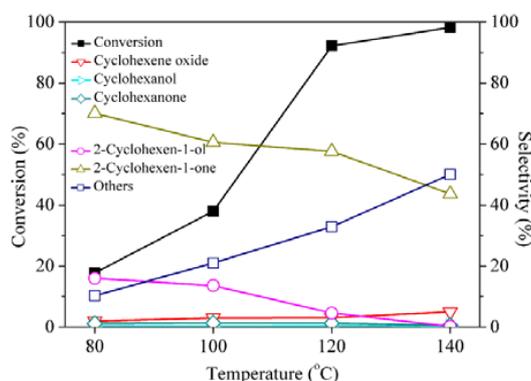

Figure 1. Effect of temperature on the oxidation of cyclohexene. Reaction conditions: acetonitrile 20 mL, cyclohexene 1 mL (at a concentration of 4.8%), $Ti_{60}Zr_{10}Co_{30}$ 20 mg, 2 MPa O_2, 12 h.

In addition, the influence of reaction time on the conversion and product selectivity were examined at conditions of 120 °C, a cyclohexene concentration of 9.1% and an oxygen pressure of 2 MPa. As shown in Figure 2, the conversion increased to 96.1% with extending the reaction time to 8 h. The selectivity of 2-cyclohexen-1-ol and 2-cyclohexen-1-one decreased from 20.3% to 4.0% and 68.8% to 55.3% due to the formation and accumulation of deep oxidation products with the reaction proceeding. The other products derived from deep oxidation such as the ring-opening acids increased with a selectivity up to 40% (8 h) from 6% (1 h), and the intermediates such as cyclohexene oxide, cyclohexanol and cyclohexanone changed very little (<5.5%).
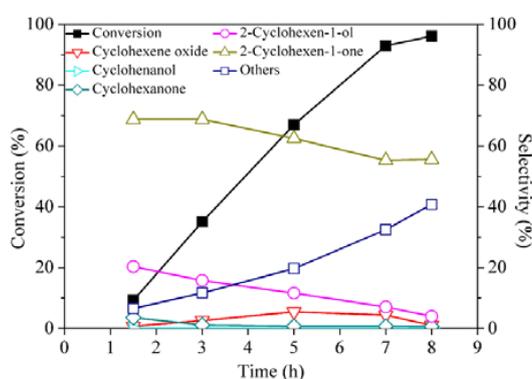

Figure 2. The variation of the conversion and selectivity with extending reaction time. Reaction conditions: cyclohexene 2 mL (at a concentration of 9.1%), acetonitrile 20 mL, $Ti_{60}Zr_{10}Co_{30}$ 20 mg, 2 MPa O_2, 120 °C.

Generally, the aerobic radical oxidation of hydrocarbons can automatically occur in the absence of catalyst [27], but it is very slow and the selectivity of the desired product is poor. The oxidation of cyclohexene can also automatically occur somewhat at certain conditions without catalyst; however, the conversion and selectivity to 2-cyclohexen-1-one are quite low [22]. Herein, we also found that the cyclohexene can convert with a conversion of 14.4% under the aerobic oxidation conditions without catalyst. As expected, the presence of TiZrCo catalysts can promote the reaction rate significantly as shown in Figure 3. The catalytic performances of TiZrCo catalysts were discussed according to the composition and the surface active species. It is clear that the catalytic activity depends on the Co content in the TiZrCo metallic catalysts, as the conversion of cyclohexene increased to 38.5% over

$Ti_{50}Zr_{10}Co_{40}$ from 32% over $Ti_{70}Zr_{10}Co_{20}$, while the selectivity to 2-cyclohexene-1-one was around 66%–69%, and changed very little. These results indicate that the ternary TiZrCo metallic catalysts are effective for the present cyclohexene oxidation, and the content of Co affects the catalytic activity significantly. In order to check the catalytic efficiency of Co species in the present oxidation, $CoTi_2$ and Co_3O_4/TiO_2 with the higher content of Co species were also examined. Unfortunately, both of them gave lower activity compared to the ternary TiZrCo metallic catalysts, as seen in Figure 3. These results suggested not only the Co species but the surface and bulk structure of the TiZrCo catalysts play an important role in the present oxidation. It is assumed that the addition of Zr may produce surface defects and induce the formation of many more CoO and Co_3O_4 active species.
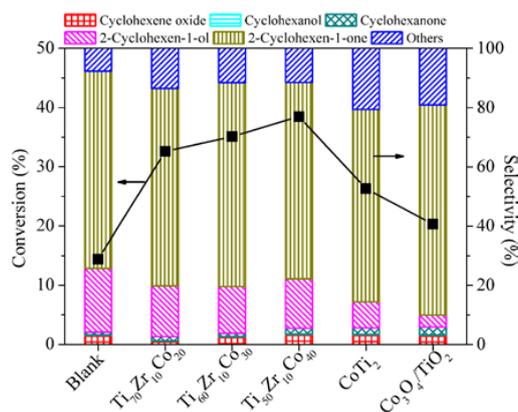

Figure 3. Comparison of the catalytic performances of different catalysts in the oxidation of cyclohexene. Reaction conditions: cyclohexene 2 mL, acetonitrile 20 mL, catalyst 20 mg, O_2 2 MPa, 120 °C, 3 h.

Therefore, the structure of the TiZrCo catalysts and their relationship to the catalytic performances were discussed. The SEM image of a representative sample of $Ti_{60}Zr_{10}Co_{30}$ is shown in Figure 4a. The size of the particles is at a range of 50–100 μm, and the other two samples with different compositions should have a similar morphology as all the samples were crushed and screen-separated by 140 meshes before being examined. The bulk structure of these samples was characterized with XRD as shown in Figure 4b. For $Ti_{60}Zr_{10}Co_{30}$, with a molar ratio of Co/Ti of 1/2, the diffraction patterns are in accordance with the $CoTi_2$ phase without other crystal phases. For $Ti_{70}Zr_{10}Co_{20}$, an I-phase was found beside the $CoTi_2$ phase [28]. However, for $Ti_{50}Zr_{10}Co_{40}$, a new CoTi phase was detected beside the $CoTi_2$ phase.

(**a**)   (**b**)
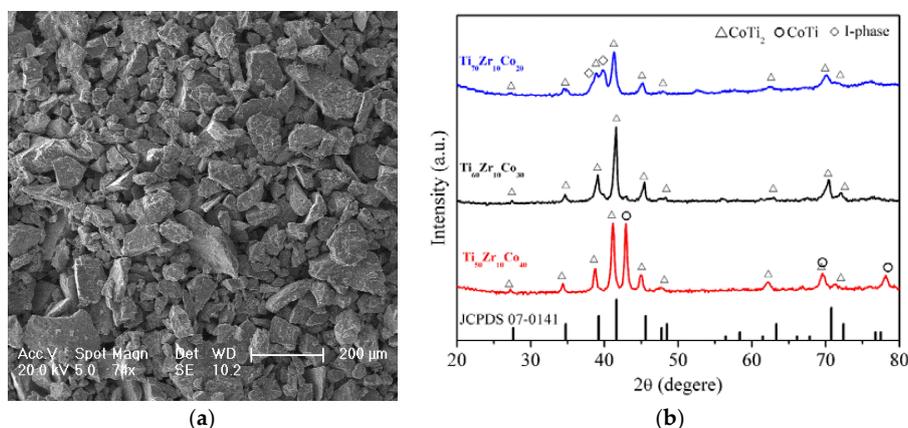
Figure 4. The SEM image of $Ti_{60}Zr_{10}Co_{30}$ (**a**); and the XRD patterns of Ti-Zr-Co catalysts and the JCPDS 07-0141 file identifying $CoTi_2$ (**b**).

Therefore, the variation of Co content will impact the bulk structure of TiZrCo significantly, which may have an effect on the catalytic activity. By comparison, the surface species will play a more important role in the catalysis due to the catalytic reaction always occurring on the surface of the heterogeneous catalyst. The surface composition of TiZrCo was studied by XPS. As shown in Figure 5, the Ti and Zr existed on the surface with oxidation states of TiO_2 and ZrO_2, and Co mainly existed on the surface with metallic Co, oxides of CoO and Co_3O_4, as confirmed by the peak at the binding energy of 777.6 eV and intense shake-up satellites Co 2p XPS spectra around 6 eV above the primary spin-orbit Bes [29–31]; Co_3O_4 was confirmed by Co^{3+}/Co^{2+} (2/1) [32]. The surface compositions calculated according to the results of XPS (Figure 5) are listed in Table 3. To consider the main active species of the Co element, it is clear that all the catalysts contained the same species of Co, CoO and Co_3O_4 on their surfaces, including $CoTi_2$. The most active $Ti_{50}Zr_{10}Co_{40}$ catalyst contains a higher ratio of CoO on the surface and different bulk phases, which suggested CoO may be more effective than the Co_3O_4 species, and the bulk phase may be also involved in the present catalysis based on the reaction results in Figure 3. In addition, the surface area of TiZrCo catalysts was also examined, as shown in Table 3; it should have less effect on the present oxidation compared to the surface active species, as the $Ti_{70}Zr_{10}Co_{20}$ with the largest surface area did show a lower conversion, which contains a lower ratio of CoO and Co_3O_4 on the surface.

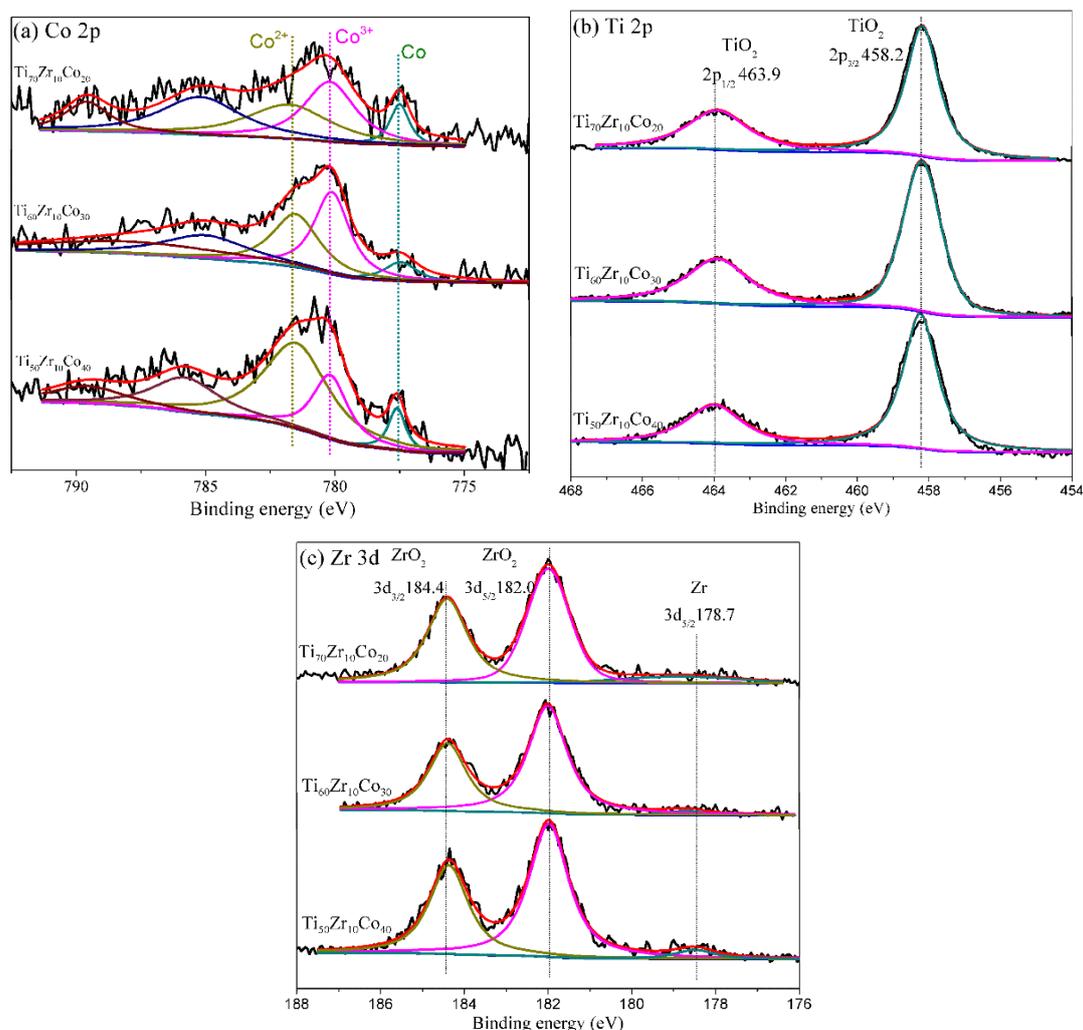**Figure 5.** The XPS spectra of (**a**) Co 2p; (**b**) Ti 2p and (**c**) Zr 3d for Ti-Zr-Co catalysts.

Table 3. Textural and surface properties.

Entry	Catalyst	Bulk Phase [a]	Surface Content of Co (%) [b]			S_{BET} (m²/g) [c]
			Co	CoO	Co_3O_4	
1	$CoTi_2$	$CoTi_2$, I-phase	31.5	37.8	30.7	-
2	$Ti_{70}Zr_{10}Co_{20}$	$CoTi_2$, I-phase	26.9	31.2	40.9	189
3	$Ti_{60}Zr_{10}Co_{30}$	$CoTi_2$	20.1	32.8	47.1	70
4	$Ti_{50}Zr_{10}Co_{40}$	$CoTi_2$, CoTi	11.5	70.3	18.2	76

[a] The bulk phase of the alloy catalysts was obtained based on the XRD patterns; [b] The surface composition of the alloy catalysts was calculated from XPS results; [c] The surface areas were calculated using the BET equation.

3. Experimental Section

3.1. Ti-Zr-Co Alloy Preparation

The series of Ti-Zr-Co alloys, as reported in our previous works [25], were prepared by arc-melting of Ti (99 wt. %), Zr (97 wt. %) and Co (99 wt. %) metals with a certain mole ratio on a water-cooled cuprum hearth in a high-purity argon atmosphere at 250 A. To make the chemical compositions homogenous, the ingot of alloy 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 by repeated manual beating with a steel pestle and mortar, and the alloy powders were screen separated by 140 meshes.

3.2. Catalyst Characterization

The phase composition and microstructure of the alloys were examined by X-ray diffraction (XRD) on a Bruker-AXS D8 ADVANCE (Bruker AXS, Karlsruhe, Germany) with Kα. The leaching of Ti, Zr or Co in the filtrate was not detected by ICP-OES measurement (iCAP6300, Thermo Waltham, MA, USA). XPS measurements were performed by using a VG Microtech 3000 Multilab. The electronic states of Co 2p, Zr 3d and Ti 2p were determined. All XPS spectra 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 (HITACHI, Tokyo, Japan) at an accelerating voltage of 10 kV, and the size of particles was in a range of 50–100 μm. Nitrogen porosimetry measurement was performed on a Micromeritics ASAP 2020M instrument (Micromeritics, Norcross, GA, USA). The surface areas were calculated using the BET equation.

3.3. Catalytic Tests

The catalytic performance was tested in a stainless steel autoclave with a Teflon inner liner (50 mL). Typically, the Ti-Zr-Co catalyst (20 mg), cyclohexene (2 mL) and acetonitrile (20 mL) were added. The reactor was then sealed, and placed into an oil bath preset to 120 °C for 5 min. O_2 (2 MPa) was introduced and the reaction was started with a continuously stirring at 1200 rpm. When the reaction finished, the reactor was cooled to room temperature and then depressurized carefully. Then the reaction solution was diluted with ethanol to 50 mL, the composition of reaction products was confirmed by gas chromatography/mass spectrometry (Agilent 5890, Santa Clara, CA, USA) and analyzed with a gas chromatograph (Shimadzu, Kyoto, Japan, GC-2010) equipped with a capillary column (RTX-50, Bellefonte, PA, USA, 30 m × 0.25 mm × 0.25 μm, carrier: N_2) and a flame ionization detector (FID).

Safety warning: The use of compressed O_2 in the presence of organic substrates requires appropriate safety precautions and must be carried out in suitable equipment. When the pressure decreased far more quickly, the reaction must be stopped immediately. Note, the reaction should be diluted by solvent, otherwise, the blast occur as the reaction is very violent.

4. Conclusions

In summary, TiZrCo catalysts were studied for the first time for the oxidation of cyclohexene. High selectivity (57.6%) to 2-cyclohexen-1-one was obtained at a high conversion (92.2%) of cyclohexene. CoO and Co_3O_4 on the surface are the main active species and contribute to the high activity and selectivity in the present cyclohexene oxidation. These results indicate that TiZrCo metallic catalysts are effective for the aerobic oxidation of cyclohexene. It is important and significant to extend the studies of the metallic alloy catalyst in catalyzing the aerobic oxidation of hydrocarbons. It is expected that the TiZrCo catalysts may have a broad prospect in industrial applications.

Author Contributions: Tong Liu did the experiment and wrote the paper, Haiyang Cheng discussed the results and revised the paper, Chao Zhang, Weiwei Lin, Yancun Yu, Fengyu Zhao supervised this work.

Conflicts of Interest: The authors declare no conflict of interest.

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