

Catalytic oxidation of cyclohexane over Ti–Zr–Co catalysts

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ABSTRACT

Ti–Zr–Co alloys have been fabricated and characterized, and their catalytic performance was discussed for the oxidation of cyclohexane with oxygen under solvent-free condition. The icosahedral quasicrystalline phase (I-phase)-forming ability of Ti–Zr–Co alloys with different compositions was discussed, and it was confirmed that I-phase could be formed as a dominating phase at the Ti-rich composition region from $Ti_{53}Zr_{27}Co_{20}$ to $Ti_{75}Zr_{15}Co_{20}$ in as-cast alloys. The composition and microstructure of Ti–Zr–Co alloys present crucial influences on its catalytic activity and selectivity in the oxidation of cyclohexane. The influences of some reaction parameters such as temperature, reaction time, and catalyst amounts were also investigated. $Ti_{70}Zr_{10}Co_{20}$ alloy containing quasicrystal microstructure showed good catalytic performance with a 6.8% conversion of cyclohexane and 90.4% selectivity of cyclohexanol and cyclohexanone. It behaves as an efficient heterogeneous catalyst for the oxidation of cyclohexane and could be recycled five times without loss in activity and selectivity.

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1. Introduction

The selective oxidation of cyclohexane is an important chemical process for the modern chemical industry, because its products of cyclohexanol (A) and cyclohexanone (K) are materials for the synthesis of adipic acid and caprolactam, which are intermediates of nylon-6 and nylon-66 polymers [1]. Industrially, cyclohexane oxidation is generally catalyzed by soluble metal salts or complexes at a temperature above 423 K, in which the total conversion of cyclohexane is lower than 4% and the selectivity of cyclohexanol and cyclohexanone is around 70–85% [2]. The increased environmental concerns call for benign oxidations including heterogeneous catalyst, solvent-free and clean oxidant. Molecular oxygen as oxidant has attracted much more attention because it is inexpensive, readily available and environmentally benign compared with other oxidants [3,4]. Recently, several heterogeneous catalysts including metal-containing redox molecular sieves or mesoporous materials, oxides, and nanoparticles had been researched for the oxidation of cyclohexane [5–8]. For example, Bi-SBA-15 was found to be an efficient catalyst for the oxidation of cyclohexane, in which the conversion was 16.9% and the total selectivity of cyclohexanol and cyclohexanone was 93% in the conditions of 1 MPa O_2 and 413 K [9]. Chitosan-supported iron-tetraphenylporphyrins had showed high catalytic activity in cyclohexane oxidation with conversion

of 8.76% and selectivity of 97.3% for cyclohexanol and cyclohexanone at 418 K and 0.8 MPa air [10]. Some heterogeneous catalysts are designed with cobalt as the active species. Catalytic oxidation of cyclohexane over Co-ZSM-5 was reported by Yuan et al., in which conversion of 7.2% and selectivity of 90.7% were obtained at 373 K and 1 MPa O_2 [11]. Cobalt-containing mesoporous TUD-1 (Co-TUD-1) samples with different Si/Co ratios were synthesized and used as catalysts in liquid oxidation of cyclohexane with tert-butyl hydroperoxide (TBHP) as oxidant; the conversion was 4.1% and the selectivity of cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide (CHHP) was 91.4% at reaction time of 5 h [12].

Since quasicrystal (QC) was discovered in 1984, a number of icosahedral quasicrystalline phases (I-phase) have been successfully obtained in various systems including Ti-based [13] and Al-based ones [14]. I-phases have shown a sharp diffraction pattern corresponding to traditionally forbidden rotational symmetry (fivefold), which indicates an unusual atomic structure with a long-range order [15]. For the unique structure and special physical and/or chemical properties, quasicrystal was expected to be a potential catalytic material [16]. Kameoka et al. reported that at high temperature the activity of Al–Cu–Fe quasicrystal (5% $NaCO_3$ solution-leached) for steam reforming of methanol (SRM) was much higher than the alloy of other phases [17]. It was also found that Al–Cu–Fe–Cr alloy with the structure of QC had higher catalytic activity and selectivity of H_2 and CO_2 in SRM [18]. Especially, Ti-based I-phase alloy was considered as one of the most promising quasicrystal materials due to thermodynamic stability, low cost and ease in production [19]. But only a few

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studies on the catalysis of Ti-based quasicrystal have appeared up to now.

On the basis of our previous work that showed that $Ti_{70}Zr_{10}Co_{20}$ -containing quasicrystal could catalyze cyclohexane oxidation efficiently [20], herein Ti–Zr–Co alloys with different compositions and microstructures were fabricated, and their catalytic activity in the oxidation of cyclohexane depending on the composition or microstructure has been discussed in more details.

2. Experimental

2.1. Ti–Zr–Co alloys preparation and characterization

Ti–Zr–Co alloys were prepared by arc-melting the mixtures of pure Ti (99 wt.%), Zr (97 wt.%) and Co (99 wt.%) metals on a water-cooled cuprum hearth in a high-purity argon atmosphere. The ingots of alloys were turned over and remelted for two times in order to obtain homogeneous alloys. After that, the surfaces of the cast ingots were burnished in order to eliminate the influence of oxide layer. Then the alloys were crushed by repeated manual beating with a stainless steel pestle and mortar, and the alloy powders were screen separated by 200 meshes. The average diameter of particles is smaller than $74\ \mu\text{m}$.

From the mother $Ti_{60}Zr_{10}Co_{30}$ alloy ingots, alloy ribbons of about 1.0 mm in width and $20\ \mu\text{m}$ in thickness were prepared by a single-roller melt-spinning technique. The alloy ingots were induction melted in a quartz tube and then ejected onto a single roller under an argon atmosphere, with the wheel velocity of 20 m/s, 30 m/s or 40 m/s. Then the ribbons were crushed by repeated manual beating with a stainless steel pestle and mortar, and the powders were separated by 200 meshes. The samples were collected and used with a particle average diameter smaller than $74\ \mu\text{m}$.

The phase composition and microstructure of the alloys were examined by X-ray diffraction (XRD) on a Bruker-AXS D8 ADVANCE with $\text{Cu K}\alpha$.

2.2. Cyclohexane oxidation

Cyclohexane (Beijing chemical plant) and high-purity oxygen (99.99%) were used as delivered. In the typical reaction, a certain amount of substrate and catalyst were charged into a 52 ml stainless steel autoclave with a Teflon inner liner at room temperature. The reactor was heated up to the desired temperature and then quantitative O_2 was introduced. The reaction runs were conducted while stirring with a magnetic stirrer. At the end of the reaction, the autoclave was cooled to room temperature then depressurized carefully. The qualitative analysis of products was examined by GC–MS. The composition of each reaction mixture was diluted by ethanol and analyzed with a gas chromatograph (SHIMADZU GC-2010, column RTX-50). Cyclohexyl hydroperoxide was analyzed by triphenylphosphine (TPP) reduction for it is difficult to be analyzed with GC. The conversion was calculated by dividing moles of products formed over the initial moles of cyclohexane used, and the selectivity was calculated by dividing moles of a certain product over the total moles of products formed. **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.

3. Results and discussion

3.1. Ti–Zr–Co alloys characterization

Fig. 1 shows the XRD patterns of Ti–Zr–Co alloy samples. Fig. 1(a) indicates that the phase composition of alloys depended

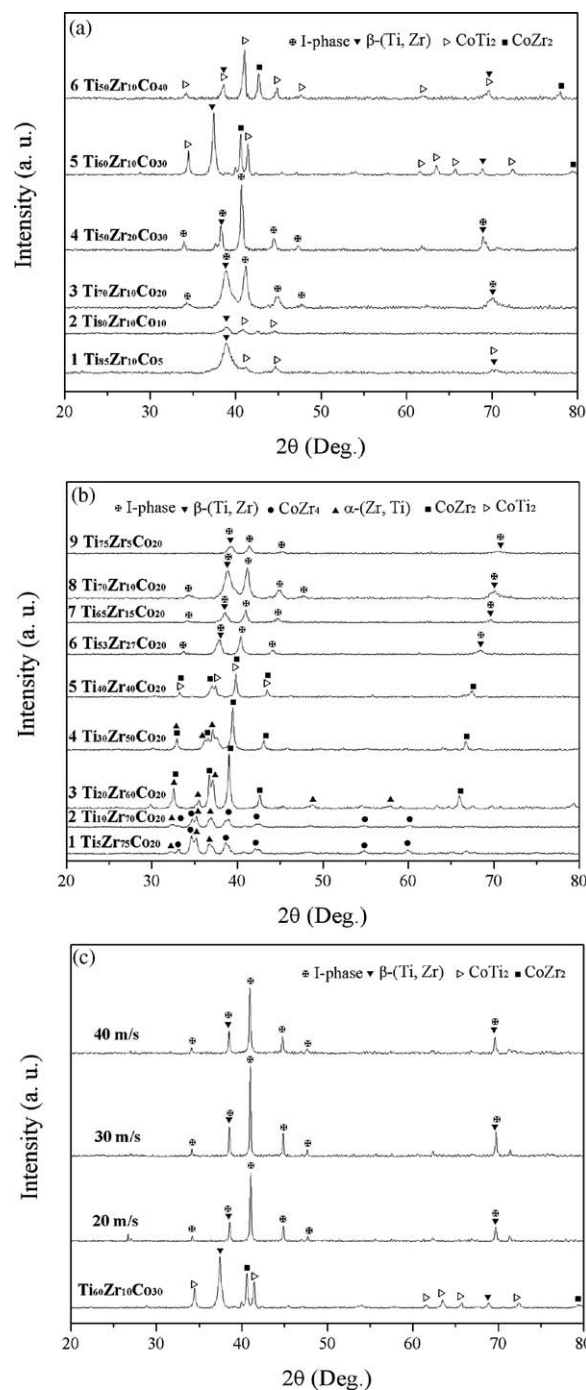


Fig. 1. The XRD patterns of Ti–Zr–Co alloys samples: (a) $Ti_xZr_yCo_z$; (b) $Ti_xZr_{10-x}Co_{20}$; (c) $Ti_{60}Zr_{10}Co_{30}$ and the melt-spun samples with wheel velocities of 20 m/s, 30 m/s and 40 m/s.

strongly on the content of Co. The alloys consisted of β -(Ti, Zr) solid solution (bcc structure) and CoTi_2 phase when the mole content of Co is lower than 20% ($Ti_{85}Zr_{10}Co_5$ and $Ti_{80}Zr_{10}Co_{10}$), and the I-phase was formed when Co content is 20% ($Ti_{70}Zr_{10}Co_{20}$) or 30% ($Ti_{50}Zr_{20}Co_{30}$), which is indexed from the scheme originally proposed by Bancel et al. [21]. However, when the mole content of Co is over 30% ($Ti_{60}Zr_{10}Co_{30}$ and $Ti_{50}Zr_{10}Co_{40}$) the I-phase disappeared and a new CoZr_2 phase was formed besides the β -(Ti, Zr) and CoTi_2 phases. Compared with $Ti_{60}Zr_{10}Co_{30}$, $Ti_{50}Zr_{20}Co_{30}$ is composed of I-phase and β -(Ti, Zr), which indicates that at larger Co mole content more Zr with larger atom size is needed to form I-phase, because the average atom size is one of the important

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