Cyclohexane oxidation on a novel $Ti_{70}Zr_{10}Co_{20}$ catalyst containing quasicrystal

Jianmin Hao[a, b], Baozhong Liu[c], Haiyang Cheng[a, b], Qiang Wang[a, b], Jinyao Wang[a, b], Shuxia Cai[a] and Fengyu Zhao[a*]

[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, P. R. China*

[c] *Institute of Material Science and Engineering, Henan Polytechenical University, Jiaozuo 454000, P. R. China*

* Corresponding author: Prof. Fengyu ZHAO

Tel & Fax: +86-431-85262410

Email: zhaofy@ciac.jl.cn

Experimental Section

1. Ti-Zr-Co alloys catalyst preparation

$Ti_{70}Zr_{10}Co_{20}$ alloy was 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. In order to obtain homogeneous alloys, the ingots of alloys were turned over and remelted for two times. After that the surface of the cast ingots was burnished in order to eliminate the influence of oxide layer. Then the alloy was crushed by repeated manual beat with an ironic pestle and mortar, and the alloy powders were filtrated by 200 meshes.

2. Catalyst characterization

The phase composition of the alloy was examined by X-ray diffraction (XRD) on a Rigaku D/MAX 2000/PC with Cu Kα. The surface morphology of alloy was observed by Environment Scanning Electron Microscope (ESEM) (FEI XL30 ESEM-FEG) and the distribution of elements was determined by Energy Dispersive X-ray (EDX) analysis. The

microstructure was characterized by transmission electron microscope (TEM).

3. Cyclohexane oxidation

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.

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 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 different to be analyzed with GC.

4. Catalyst recycles experiment

After a cyclohexane oxidation run, the solid catalyst was separated by centrifugation from the product solution and washed with ethanol for several times, then dried at room temperature and reused for the next run under the same conditions.

5. Leaching test

After a reaction under the optimum conditions as same as the reaction in Table 1 entry 3, the solid catalyst was separated by centrifugation from the product solution, and the product solution was checked by ICP-OES, Ti, Zr and Co elements weren't detected at all. That means no metal leaching and the observed catalysis is truly heterogeneous in nature.

Table 1

EDX analysis of $Ti_{70}Zr_{10}Co_{20}$ catalyst sample

Areas	Element content (average)			
	Ti (mol %)	Zr (mol %)	Co (mol %)	Total
Dark [β-(Ti,Zr)]	82.1	9.9	8.0	100
Gray (I-phase)	61.1	10.7	28.2	100