OXIDATION OF CYCLOHEXANE CATALYZED WITH $Ti_{70}Zr_{10}Co_{20}$ ALLOY CATALYST

J.M. Hao, H.Y. Cheng, Q. Wang, Y.C. Yu, S.X. Cai, F.Y. Zhao

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

zhaofy@ciac.jl.cn

The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone is an important chemical process and it has been paid more attentions in developing new type of catalyst [1]. The increased environmental concerns call for benign oxidations including heterogeneous catalyst, solvent-free and clean oxidant like oxygen. In our previous work, the stainless steel reactor wall was found to influence the selective oxidation of cyclohexane significantly, and a quasicrystalline of $Ti_{45}Zr_{35}Ni_{17}Cu_3$ alloy with the similar compositions as the reactor wall was found to be active in catalyzing the oxidation of cyclohexane [2]. In this work, the catalytic activity of a series of Ti, Zr and Co metal alloys with variable mole ratio was examined. After constitute parameter optimization, a $Ti_{70}Zr_{10}Co_{20}$ alloy presented to be the most active catalyst for the oxidation of cyclohexane with oxygen in the solvent-free conditions. The $Ti_{70}Zr_{10}Co_{20}$ catalyst was separated easily from the product solution with filtration after the first run and reused in the following runs without any treatment. The results in Table 1 show that the catalyst maintained in the similar activity after reused five times and the selectivity to products of cyclohexanol and cyclohexanone was improved slightly during recycling, although the carbon deposition in somewhat extent was found on the surface of catalyst from the ESEM images. This may prevents the formation of by-products from deep oxidation, and thus improve the selectivity to cyclohexanol and cyclohexanone.

In a conclusion, the $Ti_{70}Zr_{10}Co_{20}$ alloy is a cheap, active and stable catalyst for the catalytic oxidation of cyclohexane with molecular oxygen in the solvent-free conditions. It is worth expecting to extend the applications in other oxidations and commercial production.

Table 1 Recycle of $Ti_{70}Zr_{10}Co_{20}$ metal alloy catalyst

Runs	Catalyst left (mg)	Cyclohexane (ml)	Conversion (%)	Selectivity (%)		
				cyclohexanol	cyclohexanone	Others
1	40.5	8	6.8	40.2	50.2	9.6
2	20.7	4	4.5	31.6	55.0	13.4
3	18.3	4	6.1	33.0	51.8	15.2
4	17.1	4	6.1	45.4	48.6	6.0
5	13.8	3	5.7	45.7	48.7	5.6

Reaction conditions: oxygen 2 MPa, temperature 413 K, time 6 h.

REFERENCES

[1] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé and E. L. Pires, Appl. Catal. A., 2001, 211, 1-17.

[2] J. Hao, H. Cheng, H. Wang, S. Cai and F. Zhao, Appl. Catal. A., 2007, 271, 42-45.