Chinese Chemical Letters Vol. 12, No. 2, pp. 129–132, 2001

Catalytic Film and Selective Oxidation of Iso-butylene

Xuan MAO[1], Yuan Qi YIN[1], Yuan Ming ZHANG[2], Shao Hong PENG[2],
Bang Ke ZHONG[2]*

[1]State Key Laboratory of Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, The Chinese Academy of Sciences, Lanzhou 730000
[2]Department of Chemistry, Jinan University, Guangzhou 510632

Abstract: A kind of heteropoly compound film supported on $Ce_{0.5}Zr_{0.5}O_2$ oxide was prepared on a porous titanium tube. The catalytic activity of the film for the selective oxidation of iso-butylene was tested and compared with the fixed-bed reactor. Results show that the catalytic film increases the yield of the target product---methacrylic acid, and avoids the temperature fluctuation caused by the reaction heat.

Keywords: Catalysis, heteropoly acid, inorganic membrane, iso-butylene, selective oxidation.

Selective oxidation is an important unit process in petrochemistry and fine chemical industry. As a thermodynamically profitable reaction, selective oxidation of hydrocarbons usually takes place with a lot of side-reactions and a great deal of reaction heat at high temperature. To prevent the side-reactions and accelerate heat exchanges are two principal aims in catalytic oxidation[1]. Using the catalytic film not only can remove the target products from the reaction area in time, but also avoid the heat amassment during the reaction[2].

The heteropoly compound film supported on $Ce_{0.5}Zr_{0.5}O_2$ oxide was prepared on a porous titanium tube. The catalytic activity of the film for the selective oxidation of iso-butylene was tested and compared with the fixed-bed reactor. We choose $Ce_{0.5}Zr_{0.5}O_2$ as the supporter because $Ce_{0.5}Zr_{0.5}O_2$ is a new oxygen reservoir. It can help to accelerate the reoxidation of the heteropoly compound. Titanium is a proper material for preparing supported inorganic films[3-5]. Being a good heat-conductor and an inert catalyst in the selective oxidation of hydrocarbons, titanium can also be used in catalytic reactions. Some experiments on the selective oxidation using heteropoly compound films supported on porous titanium plates have been reported[6, 7]. The liquid precursor of the catalytic support $Ce_{0.5}Zr_{0.5}O_2$ was prepared by the citric acid method[8]. A certain amount of Ce $(NO_3)_3$ and ZrOCl were dissolved in citric acid with stirring, then an aqueous solution of equal molar of Ce (III) and Zr (IV) formed. The solution was concentrated in a water bath at 100°C.

The heteropoly compound catalyst $H_xCu_{0.2}CrPAs_{0.6}Mo_{12}O_y$ was prepared according to the literature[9]. A certain amount of H_3PO_4, H_3AsO_4, MoO_3, and salts of Cu and Cr were mixed with water and refluxed at 70-80℃ for 72 hours to obtain a homogeneous solution. The heteropoly compound was then crystallized from the solution by the concentration at 100°C. The crystal was dried at 100°C and calcined at 300°C for 2 hours to remove the water thoroughly.

The rapid spraying method was used for the preparation of the catalytic film. The concentrated liquid precursor of Zr-Ce oxide was sprayed onto the porous titanium tube, then dried and calcined at 600°C for 3 hours to remove the citric acid. After several times' covering, the weight of the support film was 0.4 g. Then the concentrated solution of the heteropoly compound was sprayed onto the tube covered with the Zr-Ce oxide, forming a thin layer. The area of the catalyst film was $63.9\times10^2 mm^2$, and the film weighed 0.4 g.

A casing pipe was used for the catalytic film reactor. The outer pipe was made of stainless steel (outer diameter 26 mm, inner diameter 23 mm, length 330 mm), both ends of the inner pipe were made of stainless steel, while the middle part of it was made of porous titanium (pore diameter 10-20 um, outer diameter 20 mm, inner diameter 18 mm, length 100 mm). The three parts of different metals were welded by argon welding. Reactions in the catalytic film reactor were carried out under such conditions: reactant gas $iC_4^= :O_2 :H_2O=2.8:11:18$ (molar ratio); total flow rate of the reactants was 31.8 ml/min; reaction temperature varied from 300°C to 380°C. The products were analyzed by a 102GD-gas chromatograph with a porapak-Q column, a 5A molecular sieve column (ϕ 6X200 mm), and a FID detector.

Reactions in the fix-bed reactor were carried out in a stainless steel tubular reactor (inner diameter 3 mm) under the same conditions as in the film reactor. The volume of the catalyst (weighed 3.2 g, 50wt% HPC and 50wt% Zr-Ce oxide) was 2.0 ml, and the products were analyzed online by a 102G gas chromatograph (Shanghai Analytical Instrument Factory) with a porapak-Q column (ϕ 4×200mm) and a FID detector.

Table 1 Yields with respect to the reaction temperature in catalytic film reactor

T(℃)	MAA(%)	MAL(%)	HAc(%)	Acetone(%)
340	5.5	8.7	6.9	2.7
360	10.8	14.7	17.7	4.5
370	14.7	18.5	25.7	4.5
380	9.5	10.8	22.9	4.1

Table 2 Yields with respect to the reaction temperature in fix-bed reactor

T(℃)	MAA(%)	MAL(%)	HAc(%)	Acetone(%)
340	0.1	5.9	5.7	4.6
360	1.1	19.3	19.7	7.8
370	0.5	18.1	14.3	6.4
380	0.3	15.8	11.1	5.9

$iC_4^{=}:O_2:H_2O$=2.8:11:18(molar ratio), results obtained after reactions carried out for 7 hours. MAA—methacrylic acid; MAL—methacrolein; HAc—acetic acid

Table 1 and **2** show the influence of the temperature in the catalytic film reactor and the fix-bed reactor. It appears that in both conditions, the yields of the liquid products (methacrylic acid, methacrolein, acetic acid, and acetone) increase with the increase of the temperature up to 370°C, and then decrease with the increase temperature extensively. The reason is that the increase of the temperature leads to the increase of the catalytic activity of the catalyst, but in other hand increase of the temperature accelerates the over-oxidation, and more COx was produced.

The distribution of the products in both conditions at 360°C and 370°C are shown in **Table 3**. It shows that: 1) under the same reaction conditions, the yields of methacrylic acid in the film reactor are comparatively much more than in the fix-bed reactor, while the yields of methacrolein, acetic acid and acetone are lower; 2) the optimum temperature of the film reactor is 370°C, at which the total yields of the liquid products reach 63.4%; while the optimum temperature of the fix-bed reactor is 360°C, at which the total yields of the liquid products are 47.9%; 3) the weight of the catalysts used in the film reactor is only 0.8 g, while the weight of the catalyst used in the fix-bed reactor is 3.2 g, which is four times more than in the film reactor. That is to say, when the flow of the reactants are the same, the space velocity of the film reactor is four times bigger than the fix-bed reactor, and in the result the selectivity was increased.

Table 3 Selective oxidation of iso-butylene in film reactor and fix-bed reactor

T (℃)	Reactor	MAA(%)	MAL(%)	HAc(%)	Acetone(%)
360	Film reactor	10.8	14.7	17.7	4.5
360	Fix-bed reactor	1.1	19.3	19.7	7.8
370	Film reactor	14.7	18.5	25.7	4.5
370	Fix-bed reactor	0.5	18.1	14.3	5.9

$iC_4^{=}:O_2:H_2O$=2.8:11:18(molar ratio), results obtained after reactions carried out for 7 hours.

Selective oxidation of hydrocarbons on the HPC usually follows the redox mechanism. Reactants are oxidized by lattice oxygen (O^{2-}), which would be reoxidized by molecule oxygen to maintain a cycle. Oxidative reactions of hydrocarbons are exothermic reactions in thermodynamics, and successive reactions in kinetics. On the one hand, higher temperature can increase the rate of oxidation reactions, correspondingly the conversion of the reactants is increased; on the other hand, when the temperature increases, the velocity of diffusion increases, which is unfavorable for molecule oxygen turning into lattice oxygen through surface adsorption. The reoxidation of the heteropoly compound would become the step-controlling reaction at higher temperature. Under such conditions, it is easier for reactants to react with adsorbing oxygen than with lattice oxygen. The former can cause the rupture of C-C or C=C bonds and results over-oxidation. As for iso-butylene, the comparatively more active hydrocarbon due to the protection of two α-methyls, the over-oxidation of C=C bond is prevented. The film reactor has a merit to control the temperature and the reaction, and it is possible to increase the catalytic activity and the selectivity by increasing the temperature.

To remove the target product from the reaction area as quickly as possible also can avoid the over-oxidation to certain extent and increase the selectivity of the reaction. In the fix-bed reactor, the catalyst bed is about 60 mm high (ϕ 3 mm tubular reactor), which is the superposition of many catalyst layers. The target product, produced from the higher layer, may continue to be oxidized by the lower layer when flowing across it, even turned into CO and CO_2 eventually. In the film reactor, the product can be removed from the reaction area much easier, and the reaction can be controlled more easily, the selectivity of the reaction is higher. The higher yields of methacrylic acid and liquid products proved this fact.

Another merit of the film reactor is that it has a much higher space velocity, much less amount of catalyst is needed and the yield of products is higher than the differential reactor, in which the conversions of the reactants are usually low, while the selectivity of the products are high. The reason is that the catalytic film is under the homogeneous atmosphere of the reactants (especially oxygen), which is different from the fix-bed reactor (integrated or differential), in the fixed-bed reactor the concentration of the reactants decreases with the falling of the catalyst layer.

References

1. G. Centi, M. Misono, *Catal. Today* , **1998**, *41*, 287.
2. C. Fabrizio, *Catal. Today* , **1998**, *41*, 73.
3. W. T. Wang, B. K. Zhong, *Chinese J. Phys.Chem.*, **1996**, *12* (1), 85.
4. Z. A. Huang, C. L. Zhong, B. K. Zhong, *J. Silicate* , **1997**, *16*(5), 20.
5. X. B. Zhou, X. J. Pang, B. K. Zhong, *J. Peterochemistry*, **1997**, *13* (4), 29.
6. Q. Deng, *et al*., *In: Proceeding of Asia-Pacific Congress on Catalysis, Pohang, Korea*, **1997**, 265.
7. Y. M. Zhang, R. Q. Song, *et al*., *Chinese J. Catal.*, **1999**, *20* (6), 589.
8. M. F. Luo, *et al*., *In: 9th Chinese National Conference on Catalysis, Beijing, China* , **1998**, 51.
9. W. Y. Zheng, Q. Lin, R. J. He, *Industrial Catalysis* , **1993**, *3*, 13.
10. E. S. Putna, T. Bunluesin, X. L. Fan, *Catal. Today* , **1999**, *50*, 343.

Received 19 June, 2000