

Oxidation of glyoxal to glyoxylic acid by oxygen over V_2O_5/C catalyst

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Abstract

A novel vanadium oxide catalyst supported on active carbon was prepared by an incipient wetness impregnation method, and the precursor was obtained from oxalic acid aqueous solutions of NH_4VO_3 . The catalyst was applied liquid phase oxidation of glyoxal to glyoxylic acid. It was found that V_2O_5/C catalyst exhibited obvious activity for glyoxal oxidation. Glyoxylic acid could be obtained without pH regulation during the reaction. By using this catalyst, the conversion of glyoxal and the yield of glyoxylic acid were 29.2% and 13.6%, respectively at 313 K and oxygen flow 0.1 L/min after reaction for 10 h.

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Glyoxylic acid is a useful starting material for the synthesis of many valuable fine chemicals, especially in flavor and cosmetic industries [1]. Industrially, glyoxylic acid is currently produced by nitric acid oxidation of glyoxal. However, this method leads to much oxalic acid and seriously environmental pollution from NO_x , so it is strictly limited in many countries [2]. Recently, much attention has been paid to the catalytic oxidation of glyoxal in the liquid phase owing to low cost, simplicity of procedure and negligible pollutants. Glyoxal oxidation has already been tested with some heterogeneous catalysts, with monometallic or bimetallic formulations, all based on a noble metal deposited on a carbonaceous support [3]. The second metal is usually a heavy element that plays the role of a promoter. The most active catalysts so far have been Bi-Pd/C or Pb-Pd/C, but the promoter element (Bi or Pb) has the drawback of leaching in the reaction mixture during catalytic use [4,5]. The association Ru-Pd gives high yields in glyoxylic acid (absolute value obtained at the optimum (t_{max})), and Ru has no leaching in solution. The limitations of this bimetallic association lie in longer reaction time, lower formic acid production and high sensitivity to the preparation method [6]. In addition, under the catalysis of precious metal, there are two shortcomings: one is the pH value of the solution must be controlled strictly; the other is the byproduct oxalic acid would be produced because of the further oxidation of glyoxylic acid. In consequence, there is a high scope for finding other catalysts or combinations that would combine high activity and selectivity with high stability, in order to increase lifetime and

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reusability of the catalyst. In our studies, we found V_2O_5/C catalyst prepared by impregnation method showed high performance for glyoxal oxidation.

1. Experimental

V_2O_5/C catalyst was prepared by an incipient wetness impregnation method in which NH_4VO_3 was impregnated on active carbon (surface area = $977.5 \text{ m}^2/\text{g}$). NH_4VO_3 was first dissolved in the solution of oxalic acid about 1 mol/L. After being dried at 383 K overnight, the catalyst was then activated at 483 K for 5 h under nitrogen flow. The amount of V was 3 wt%. The reference catalyst Bi-Pd/C was prepared by using a precipitation deposition procedure described in a patented literature [7]. They were obtained from aqueous solutions of Bi(III) nitrate pentahydrate and Pd(II) chloride. The formation of the active phase proceeded in situ reduction of the precursor salts with formaldehyde at 353 K. The amount of Bi and Pd was 5 wt%, respectively. V_2O_5/C catalyst was investigated by using the methods of XRD and TEM.

The liquid phase oxidation of glyoxal was carried out in a double-walled glass reactor with water circulation. The 200 mL of glyoxal solution (0.1 mol/L) and 200 mg catalyst were heated in the reactor at 313 K. Reactions were carried out under constant stirring conditions (1000 rpm). Oxygen was bubbled through the solution at a constant flow rate of 0.1 L/min. The nature of the reaction products was quantified by P200II HPLC, equipped with a Spectra System UV200II. The products were first reacted with hydroxylamine, and then separated on a Hypersil BDS C18 column, and the detected number was 210 nm. The mobile phase was sulfuric acid solution (pH 4.5) at a flow rate of 0.75 mL/min.

2. Results and discussion

Fig. 1 gives the XRD patterns of V_2O_5/C catalyst samples with different vanadium contents. It can be seen that on the used catalysts the amorphous C dispersion characteristic peak and the V_2O_5 phase characteristic diffraction peak appeared, without a new phase formed under the effect of the active components V_2O_5 and the carrier C. It shows that V_2O_5 is mainly absorbed on the surface of activated carbon in the physical way. The intensity and the width of C dispersion characteristic peak and V_2O_5 characteristic peak vary with different contents of V_2O_5 catalyst. As the V_2O_5 contents increase, the intensity of C dispersion characteristic peak decreases, the intensity of phase peak gradually increases and the crystallinity of V_2O_5 gradually increases. In the experimental studies, as V_2O_5 contents increased, the dispersion characteristic peaks of activated carbon in V_2O_5/C catalyst were on the wane at 26.6° and 43.8° and V_2O_5 diffraction peaks gradually strengthened at 20.3° . This showed that V_2O_5 was well dispersed on active carbon.

Fig. 2 showed the TEM image of V_2O_5/C catalyst. When V_2O_5 increased to 3 wt%, grain size was observed in the range of 20–60 nm.

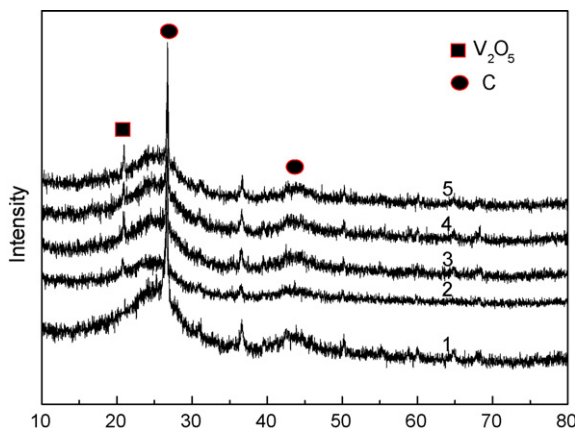


Fig. 1. XRD patterns of V_2O_5/C catalyst samples with different vanadium contents (calculated at 473 K). 1—1 wt% V_2O_5/C , 2—2 wt% V_2O_5/C , 3—3 wt% V_2O_5/C , 4—4 wt% V_2O_5/C , 5—5 wt% V_2O_5/C .

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