



Review

Effect of calcination temperature on the catalytic activity of VPO for aldol condensation of acetic acid and formalin

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HIGHLIGHTS

- VPO catalysts were developed for one step synthesis acrylic acid with HAc and HCHO.
- The influence of calcination temperature on VPO catalysts was studied.
- Larger surface area and higher V^{4+}/V^{5+} ratio favored higher yield of main product.
- The catalyst deactivation was explored using XPS method.

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ABSTRACT

The effect of calcination temperature on the catalytic activity of VPO catalyst for one step synthesis acrylic acid with acetic acid and formalin was systematically studied using a fixed-bed tubular micro-reactor. The influence of calcination temperature on physicochemical properties especially crystal phase structure of VPO catalysts was obtained. The catalysts were analyzed and characterized with in situ high temperature XRD (HT-XRD), BET, TEM, TG/DTA, XPS, as well as NH_3 , CO_2 -TPD, and pyridine-FTIR methods. Larger special surface area and higher V^{4+} concentration favored higher conversion and selectivity. The optimum special surface area and V^{4+}/V^{5+} ratio was obtained with controlling calcination temperature. The catalyst deactivation was also explored.

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1. Introduction

Acrylic acid (AA) is a high-value polymer intermediate widely used in manufacture of industrial monomers, methyl acrylate, butyl acrylate, ethyl acrylate, 2-hydroxyethyl ester, and polymers etc. [1–3]. The polymers can be used in synthetic resins, synthetic fibers, absorbent resins, building materials, paints, and other industrial sectors [4]. Most of AA is produced by traditional two-step oxidation of propylene. Unfortunately, this route to AA utilizes propylene getting costly, due to the raising price and tight supply of raw material [5–7].

Environmental and economic considerations have made the renewable processes highly advantageous. Currently, one-step aldol condensation has received particular attention because it can be start from acetic acid (HAc) and formalin (HCHO) [8–11]. In industry, there is a strong desire for converting HAc in excessive amount to other value-added chemicals by aldol condensation reaction, such as AA of high value. One-step aldol condensation for producing AA is intensively investigated due to the other notable advantage over other processes as in contrast to the traditional two-step oxidation of propylene it presents no complex postreaction separation problems [12].

There are various kinds of catalysts developed for aldol condensation, for example, basic oxides, acidic oxides, and base-acid oxides bifunctional catalysts [12–16]. Researchers discovered that catalysts consisting of base and acid oxides performed better catalytic activity [17–19]. The use of base-acid oxides bifunctional catalysts offers many advantages over existing basic and acidic oxide catalysts used in aldol condensation. For example, base-acid oxides catalysts have an ability to simultaneously activate HAc and HCHO. Vanadium and phosphorus are main constituents in this catalytic system [20,21]. Supported VPO and V–Si–P are most extensively studied in aldol condensation. Ai et al. [10] reported a 51% yield of MAA (based on the conversion of HCHO) in aldol condensation of propionic acid with formaldehyde (derived from trioxane) over a V/Si/P ternary oxide catalyst. Gogate et al. [22] reported a 10.5% yield of methyl methacrylate (based on Methyl propionate (MP)) in aldol condensation of MP with HCHO over a V–Si–P ternary catalyst. Feng et al. [12] reported a 84.2% conversion of methyl acetate (including 30–35% acetic acid and 3–12% CO_x) over a VPO catalyst activated in a 1.5% butane–air mixture. Among them, supported VPO catalyst also received much attention because of their easy preparation and exhibit excellent performance in reaction of HCHO with carboxylic acid and its esters to form unsaturated acid and its esters [13,23].

In previous researches [10,12,24,25], the stress was laid on studying the number and the distribution of acid and base active sites, and the ratio of V⁴⁺ and V⁵⁺ of VPO catalyst, which have important influence on catalyst activity. Of particular interest was the effect of calcination temperature on VPO catalytic activity for the aldol condensation of HCHO and HAc, because, to the best of our knowledge, no previous publication has addressed this issue. There are less report focused on the effect of calcination temperature on acid–basic properties and valence state of vanadium of supported VPO catalyst. Accordingly, it was an important factor in

preparing catalysts since it affected the nature of catalyst significantly [25–28]. This finding related to a suitable calcination temperature for VPO catalyst. More particular, it related to explore the influence of roasting temperature on catalyst performance.

In this paper, the supported VPO catalysts calcined at different temperatures were prepared and used in aldol condensation of HAc with HCHO to produce AA with a fixed-bed tubular micro reactor. The yield and selectivity of AA were calculated based on feeding amount of HCHO. Formation of active phases and calcination time of VPO catalyst were reported using XRD and HT-XRD, respectively. HT-XRD is a powerful technique to study the formation of crystallographic phases in situ [29]. Textural properties were examined by BET. Acid–basic properties of VPO catalyst were characterized with NH₃ and CO₂-TPD, and several consistent results were obtained. The valence state of vanadium in the V–P oxide bifunctional catalysts was confirmed by XPS.

2. Experimental

2.1. Catalyst Preparation

The used acetic acid ($\geq 99.0\%$), formalin (37.0%), isobutyl alcohol ($\geq 99.0\%$), ammonium metavanadate ($\geq 99.0\%$) and ammonium phosphate ($\geq 99.0\%$) were analytical grade. Oxalic acid was provided by Sinopharm Chemical Reagent Co., Ltd. The support SiO₂ (20–40 mesh) was purchased from Qing Dao Hailang Silica Gel Drier Factory. All the mentioned percentage purities refer to mass fractions were reported by the suppliers. All chemical agents were used directly without further treatment.

All catalysts were prepared by equivalent–volumetric ultrasonic impregnation method. Silica (20–40 mesh) was dried at 120 °C for 12 h, and then calcined at 500 °C for 6 h. Ammonium metavanadate and ammonium phosphate were added sequentially in oxalic acid solution at room temperature. The impregnation precursor was maintained in an ultrasonic machine at a frequency of 50 kHz for 3 h, then dried at 120 °C for 12 h, and calcined at 350, 400, 450, 500, 600, and 700 °C, respectively, for 6 h under atmospheric condition. The activated catalysts were obtained after natural cooling.

2.2. Catalyst characterization

The diffractometer (Model: X'Pert PRO MPD, PAN analytical Co., Ltd.) with Cu–K α radiation (40 kV and 50 mA), and the scanned 2θ ranged from 5 to 90°, was used to record the X-ray diffraction (XRD) patterns of catalysts. The in situ HT-XRD patterns of catalysts were recorded on the above diffractometer with high temperature attachment. The high temperature stage allows samples to be measured at tightly controlled temperatures from room temperature to 700 °C in open air.

The Surface area and pore size of catalysts were detected on Quanta Chrome Instrument NOVA 2000 using Brunauer–Emmett–Teller (BET) and Barrett–Jayner–Halenda (BJH)

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