



Renewable production of acrylic acid and its derivative: New insights into the aldol condensation route over the vanadium phosphorus oxides



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ABSTRACT

Vanadium phosphorus oxides (VPOs) fabricated by employing poly ethylene glycol (PEG) additive were used as catalysts for efficient conversion of acetic acid (methyl acetate) and formaldehyde to acrylic acid (methyl acrylate). The highest formation rate ($19.8 \mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$) of desired products (acrylic acid + methyl acrylate) was accomplished over a VPO catalyst comprising mainly vanadyl pyrophosphate ($(\text{VO})_2\text{P}_2\text{O}_7$) and vanadyl phosphate in δ form ($\delta\text{-VOPO}_4$). This catalyst is nearly three times more active than the analogue reported in literature. The VPO catalyst activated in 1.5% butane–air is superior to that activated in air or nitrogen. Different from the PEG-derived VPO catalysts for *n*-butane oxidation to maleic anhydride, a better VPO catalyst for the current reaction requires a higher fraction of $\delta\text{-VOPO}_4$ entity and contains the medium strong acid sites of high density. Through systematic catalyst characterizations and evaluations, an unambiguous correlation between catalyst structure/constitution and performance was established.

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1. Introduction

Acrylic acid (AA) is an unsaturated organic compound widely used in manufacture of paint additives, adhesive, textile, and leather treating agents [1,2]. At present, AA is largely produced by a two-step oxidation of propylene. In recent years, partial oxidation of propane to AA through a one-step process has drawn much attention [3–8]. Although the multi-component metal oxides were found to be catalytically active for one-step oxidation, they were rather sensitive to preparation parameters [9–16] and not efficient enough for practical application. Furthermore, both propylene and propane are from non-sustainable sources in petrochemical industry. With ever rising demand for petroleum, it is getting costly to use propylene as feedstock. On the other hand, the worldwide production capacity of acetic acid has been increased considerably, and there are strong motivations for converting acetic acid in excessive amount to other value-added chemicals. Among different routes, the aldol-type condensation between acetic acid/methyl acetate and formaldehyde (HCHO) to generate AA and methyl acrylate (MA) is of great interest.

Purified terephthalic acid (PTA) is an important chemical material widely used in polyethylene terephthalate (PET) production. In

PTA manufacture, great amount of methyl acetate is produced as a by-product. Methyl acetate is also produced as a by-product in the production of polyvinyl alcohol (PVA), a useful polymer for producing synthetic fiber and film. The amount of methyl acetate produced is about 1.7 times more than that of PVA [17]. However, utilization of methyl acetate is limited. How to convert methyl acetate to a value-added chemical is very meaningful for the PTA and PVA industries.

There were different kinds of catalysts tested for the target reaction, such as the alumina supported alkali metal hydroxide and phosphates [18,19]. Ai reported that the aldol condensation of HCHO with acetone [20] or with acetic acid/methyl acetate [21–23] to methyl vinyl ketone or acrylic acid and its derivative can be effectively catalyzed by the vanadium–titanium binary phosphates and $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ binary oxide. It was suggested that the acid–base properties of these catalysts play an important role in promoting the aldol condensations [24,25]. However, there was no report so far in literature on the detailed structure and constitution aspects of the vanadium and phosphorus containing catalysts for the aldol condensation of HCHO with acetic acid or methyl acetate. Other catalyst systems operated under a wide range of conditions were also reported in patents [26–28]. The vanadium phosphorus oxide (VPO) catalyst was recognized as one of the most complicated catalyst systems, and many efforts have been made to advance our understanding of catalyst nature

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in the partial oxidation of *n*-butane to maleic anhydride [29–44]. Note that preparation history can dramatically affect the physico-chemical properties of the VPO-type catalysts such as phase composition, morphology, particle size, surface P/V ratio, and vanadium oxidation state. We had systematically studied the preparation chemistry of various VPO catalysts, particularly the poly ethylene glycol (PEG)-derived ones, and their behaviors in catalytic oxidation of *n*-butane to maleic anhydride [45–53]. In the current work, we carefully studied the efficient aldol condensation of HCHO with acetic acid or methyl acetate over the PEG-derived VPO catalysts. Today this reaction route becomes highly attractive, because it is renewable and more environmentally friendly according to the principle of green chemistry. The obtained results are informative for better understanding the target reaction on the VPO-type catalyst, especially on the carefully identified active components, which is useful for improving the VPO-based catalyst system.

2. Experimental

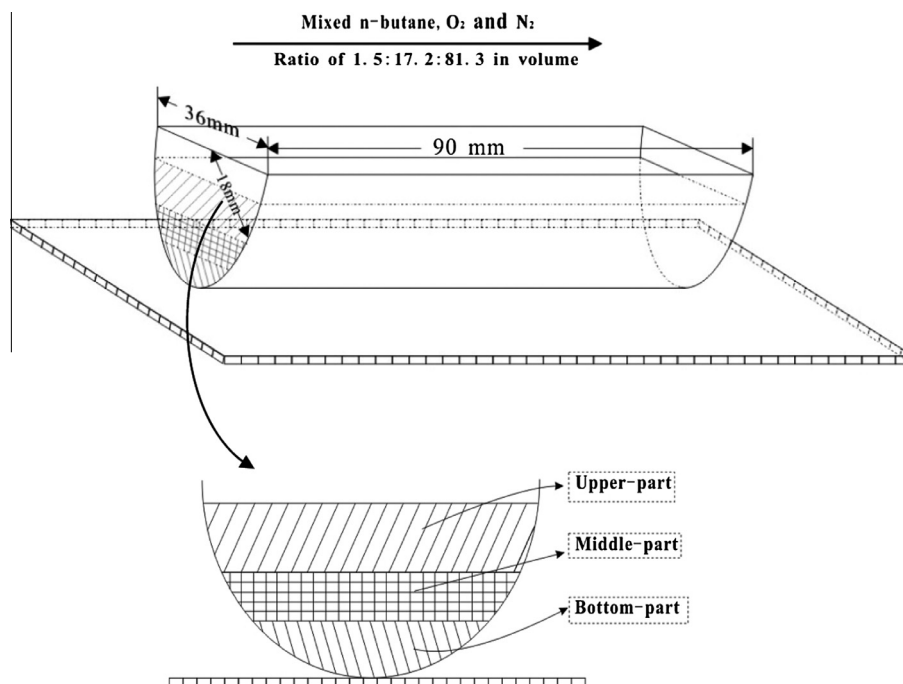
2.1. Catalyst preparation

The preparation of catalyst precursors was described previously [47]. Both single benzyl alcohol and mixed iso-butyl and benzyl alcohols were employed as the preparation media. V_2O_5 was first refluxed in single benzyl alcohol or mixed iso-butyl and benzyl alcohols (1/1, v/v) at 413 K for 6 h, after that certain amount of PEG 6000 was introduced. One hour later, phosphoric acid (85%) was added dropwise to reach a P/V atomic ratio of 1.05/1.0. The suspension was refluxed for another 6 h, and then the solid was filtered out, washed with iso-butanol and acetone. It was further dried in air at 373 K for 24 h to obtain catalyst precursor. Before characterization and performance evaluation, all of the precursors were activated according to the following procedures.

The activation of catalyst precursor was performed in a quartz boat under a flowing atmosphere (nitrogen, air, or 1.5 vol.% *n*-butane/balanced air with a flow rate of 15 ml min⁻¹). The

dimension of the quartz boat was specified in Scheme 1, and generally the precursor powder of 12 g was spread out in the boat which was set in the thermostatic zone of a tubular furnace. In case the precursor activation was conducted in N_2 or air, uniform sample was obtained, while if the activation was performed in 1.5 vol.% *n*-butane/air, the sample color was found to change along with the sample bed: the grey upper portion to the green bottom one. The middle part was a transient layer. The samples of different color were carefully collected for both characterization and evaluation, and very importantly, the results of characterization and evaluation did reveal the significant differences in sample constitution, structure, and activity of different positions. This provided a rare chance to clarify the correlations between the various catalyst constitutions/structures and the corresponding activities of the target reaction. We totally prepared around twenty batches of samples and collected the upper, middle, and bottom positional samples in the same way (the upper-, middle-, and bottom-part of approximately 4.5, 3, and 3 g, respectively) and got the reproducible characterization/evaluation results.

In order to achieve sample homogeneity in the case of precursor activation in the butane-containing atmosphere, the following two strategies were adopted: (1) If the activation of powder precursor was performed in a quartz boat, then less amount of precursor (6 g) was spread out in the boat and activated under an atmosphere containing lower butane concentration (0.3 vol.% *n*-butane/air, 20 ml min⁻¹), the so-obtained sample was essentially identical to the above-mentioned bottom-part sample in both constitution and activity. (2) When the activation of particle precursor (20–40 mesh) was performed in the plug-flow tube reactors, the particle precursor of 5 g (or 10 g) was charged into a quartz tube reactor of 10 mm (or 42 mm) internal diameter and activated under a flowing atmosphere (0.3 vol.% *n*-butane/balanced air, 20 ml min⁻¹), once again the so-obtained sample showed reproducible properties as compared to the above-mentioned bottom-part sample. In other words, the most active catalyst (bottom-part) of the current study can be uniformly and reproducibly fabricated under practically controllable conditions.



Scheme 1. The experimental set-up for catalyst activation under various atmospheres and/or at different temperatures.

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