**Efficient Production of Acrylic Acid by Sequential Dehydration and Oxidation of Glycerol in a Fixed-bed Reactor**

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**Introduction**

The dehydration of glycerol, a byproduct of the biodiesel process, to acrolein over solid acid catalysts is well-studied [1]; whereas little attention has been paid to direct conversion of glycerol to acrylic acid. In an economic point of view, a subsequent conversion of acrolein to acrylic acid immediately after its formation would not only avoid the problems of acrolein storage and transportation, but also enhance the competitiveness of the process. However, it is difficult to develop catalysts for dehydration and oxidation that have similar optimum reaction conditions [2, 3]. Oxygen is needed for the oxidation of acrolein; therefore a catalyst effective for dehydration of glycerol to acrolein at a relative high oxygen ratio is required to decrease the amount of oxidation by-products during the dehydration process. For the oxidation step, although commercial catalyst is available for conversion of acrolein to acrylic acid in the process of partial oxidation of propane, the reaction conditions used in the glycerol route is very different because the water vapor concentration is much higher and a variety of by-products are produced in the dehydration step. For a good performance of the dehydration-oxidation coupled process, the oxidation side reaction should be controlled, and the dehydration by-products should not exert negative effect on the oxidation process.

To match up the conditions of the dehydration and following oxidation for direct conversion of glycerol to acrylic acid, we demonstrated an effective two-bed system using Cs₂H₆PW₁₀O₴₅ supported on Nb₂O₅ (CsPW-Nb) and vanadium–molybdenum mixed oxides (VMo-SiC) as the catalysts. The yield of acrylic acid was 75% at optimized conditions, which was much higher than that reported in the literature.

**Materials and Methods**

To prepare the catalyst of 20 wt% CsPW supported on Nb₂O₅, the desired amount of Cs₂CO₃ and H₃PW₁₀O₄₅·nH₂O were introduced into Nb₂O₅ by the vacuum-assisted impregnation method and calcined at 500 °C for 3 h [4]. For the oxidation catalyst MoO₃·Nb₂V₁₅·SbSi₁₆O₅₆, desired amount of NH₄VO₃ (Alfa Aesar Ltd.), (NH₄)₆MoO₂₄·4H₂O; (Alfa Aesar Ltd.), Nb(NH₄)₆(C₂O₄)₂·NB-O·nH₂O (Aldrich, 99.99%), CuSO₄ (Alfa Aesar Ltd.) and Sb₂O₃ (Alfa Aesar Ltd.) were added to distilled water, and the obtained precursor solution was slowly dropped onto SiC (Alfa Aesar Ltd.). The catalysts were calcined at 380 °C for 5 h under a flow of dry air. The samples were denoted as CsPW-Nb and VMo-SiC. The experiments of glycerol dehydration and acrolein oxidation were carried out at 300 °C under atmospheric pressure in a fixed bed reactor. The liquid products were collected and analyzed by GC.

**Results and Discussion**

The dehydration of glycerol with CsPW-Nb and oxidation of acrolein with VMo-SiC were first studied separately. The results were shown in Figs. 1(a) and (b). Fig. 1(a) showed that for glycerol dehydration, an increase in the O₂/N₂ ratio from 0/18 to 3/15 led to an increase in the selectivity to acrolein from 55.0% to 79.5%. A further increase in O₂/N₂ ratio resulted in a much higher amount of CO and other by-products. At O₂/N₂ of 3/15, the selectivity to acrolein reached its maximum with negligible oxidation in the dehydration step. For acrolein oxidation, a higher oxygen ratio was required for complete conversion, as shown in Fig. 1(b). The addition of oxygen had a positive effect on the yield of acrylic acid when the O₂/N₂ ratio was less than 3/15. A further increase in O₂/N₂ led to a decrease in the selectivity to acrylic acid and an increase of CO.

Figs. 1(a) and (b) showed that the optimum oxygen ratio for dehydration and oxidation was very similar. Therefore, the dehydration-oxidation process was studied in a sequential fixed-bed reactor with CsPW-Nb and VMo-SiC at this condition. A high yield (75%) of acrylic acid was obtained without catalyst deactivation within 24 h, as shown in Fig. 1(c).

The results showed that glycerol was completely converted into acrolein on CsPW-Nb, which in turn was oxidized to acrylic acid on VMo-SiC with a high selectivity. The high concentration water in the glycerol feed and by-products of dehydration did not show negative effect on the oxidation process. Acetol formed in dehydration was then oxidized to acetic acid.

![Figure 1](image)

**Significance**

The selective dehydration-oxidation of glycerol to acrylic acid is a very attractive method for glycerol utilization. New dehydration and oxidation catalysts with good performance and similar optimum conditions were developed to realize the coupled reaction. A high yield (75%) of acrylic acid was obtained in a sequential fixed-bed reactor.

**References**