# One pot conversion of glycerol to acrylic acid over dual catalyst beds

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**Abstract:** One-pot synthesis of acrylic acid from glycerol has been achieved over dual catalyst beds in a fixed bed reactor. $Co_{0.5}H_2PO_4$ supported on ZSM-5 ($Co_{0.5}H_2PO_4$/ZSM-5) and $Mo_8V_2W_{1.5}Cu_{2.5}ZrO_x$ were used as the dehydration and oxidation catalysts, respectively. The alkaline treated ZSM-5 with enlarged pores significantly enhanced the stability of $CoHPO_4$/ZSM-5 catalyst. There was no significant deactivation for both catalysts up to 160 hours. The ratio of two catalysts was the key to achieve high yield of acrylic acid up to ~80%.

**Keywords:** Glycerol, Acrylic acid, Dehydration, Selective oxidation, ZSM-5.

## 1. Introduction

Glycerol is a byproduct of biodiesel production and it can be converted to valuable chemicals. One of the routes is the catalytic conversion of glycerol to acrylic acid, which is an important raw material in the manufacture of polymeric products. The conversion of glycerol to acrylic acid requires dehydration and oxidation steps via acrolein as the intermediate. In this study, the one-pot process with two catalysts was carefully designed and optimized to maximize the acrylic acid yield. Meanwhile, the catalyst stability has also been enhanced by modification of the catalyst support in the glycerol dehydration step.

## 2. Experimental

$Co_{0.5}H_2PO_4$ was prepared by co-precipitation method with $Co(NO_3)_2$ and $NH_4H_2PO_4$ as precursors[1]. ZSM-5 (Si:Al=280) was treated by NaOH solution following a reported method[2]. $Co_{0.5}H_2PO_4$ was loaded on modified ZSM-5 by impregnation. The oxidation catalyst $Mo_8V_2W_{1.5}Cu_{2.5}ZrO_x$ was prepared by spray drying of an aqueous solution containing various precursors of Mo, V, W, Cu and Zr[3]. These catalysts have been thoroughly characterized by $N_2$ physisorption, XRD, XRF and $NH_3$-TPD. One-pot conversion of glycerol to acrylic acid was performed in a fixed bed reactor with two catalysts loaded as dual beds. In a typical reaction, 20 wt% aqueous glycerol solution was injected into a vertically placed quartz tube by a syringe pump was a feed rate of 3 mL/h. The vaporized glycerol carried by the nitrogen/oxygen (4 mol% $O_2$) flow at 240 mL/min passed through the catalyst bed heated at 300 °C. The liquid products were collected in a condenser and analyzed by a GC-FID. The gas products were analyzed by an online GC-TCD.

## 3. Results and discussion

The effect of alkaline treatment of ZSM-5 was firstly studied for the glycerol dehydration step. As shown in Figure 1A, ZSM-5 itself was able to catalyze the glycerol dehydration reaction due to the presence of acid sites. However, the original ZSM-5 suffered from quick deactivation even the selectivity to acrolein remained relatively stable at around 60%. This was attributed to the quick blockage of the small pores by the coking. Hence, the treatment of ZSM-5 with alkaline leached a certain amount of Si so that the pores were expanded (Table 1). The enlarged pores were more tolerant to coke deposition. Therefore, the treated ZSM-5 did not show any deactivation for 8 hours while the selectivity to acrolein was slightly improved as well (Figure 1A). In order to further improve the acrolein selectivity, $Co_{0.5}H_2PO_4$ was loaded on treated ZSM-5 as another active phase. As shown in Figure 1B, the selectivity to acrolein was further increased to 80% or above. And there was no deactivation within 8 hours.

Subsequently, $Mo_8V_2W_{1.5}Cu_{2.5}ZrO_x$ was loaded beneath the $Co_{0.5}H_2PO_4$/treated ZSM-5 catalyst to selectively oxidize acrolein to acrylic acid. In order to optimize the space velocity of acrolein, the amount of oxidation catalyst was systematically adjusted. It was found that the yield of acrylic acid could reach 80% if

the ratio of $Co_{0.5}H_2PO_4$/treated ZSM-5 and $Mo_8V_2W_{1.5}Cu_{2.5}ZrO_x$ was set at 10:7. This yield corresponded to almost 100% selectivity of acrylic acid from acrolein oxidation. Moreover, both catalysts did not show any deactivation within 160 hours. This result clearly suggested potential commercialization of this process.

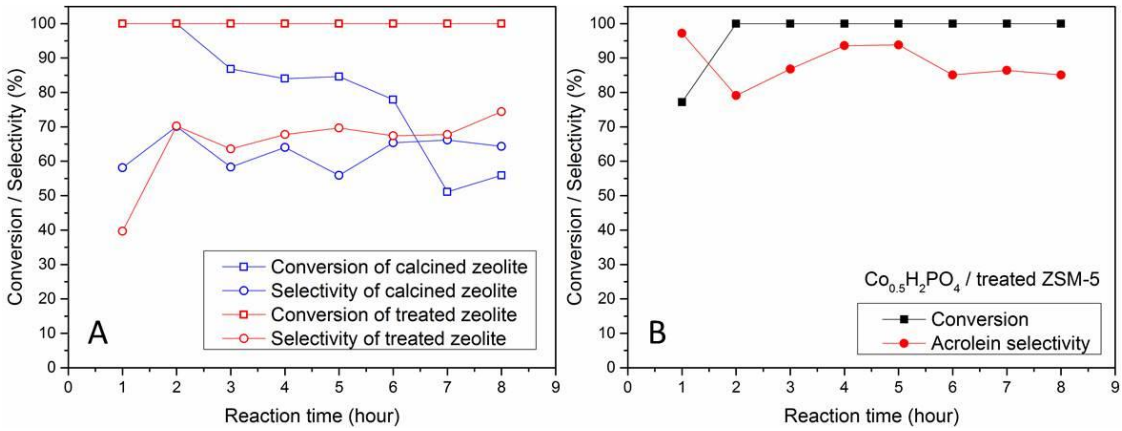


**Figure 2.** Production of acrolein from glycerol over original and treated ZSM-5 (A) and $Co_{0.5}H_2PO_4$/treated ZSM-5 (B).

**Table 1.** The structure change of ZSM-5 induced by alkaline treatment.

| ZSM-5 | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) |
|---|---|---|
| Original | 368 | 0.22 |
| Modified | 372 | 0.48 |

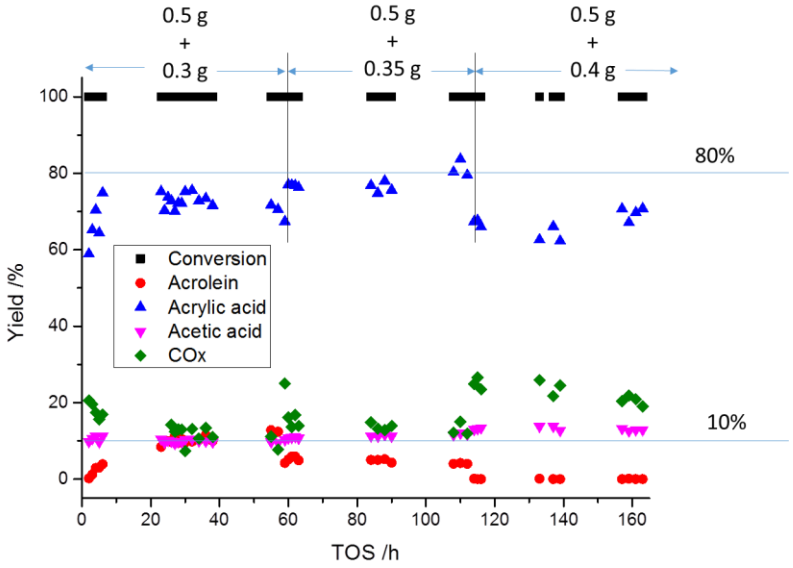


**Figure 2.** Production of acrylic acid from glycerol by double catalyst bed composed of $Co_{0.5}H_2PO_4$/modified ZSM-5 and $Mo_8V_2W_{1.5}Cu_{2.5}ZrO_x$.

## 4. Conclusions

A one-pot reaction process of converting glycerol to acrylic acid was developed over two consecutive catalysts: $Co_{0.5}H_2PO_4$/treated ZSM-5 and $Mo_8V_2W_{1.5}Cu_{2.5}ZrO_x$, for dehydration and oxidation steps, respectively. 80% yield of acrylic acid has been achieved. Both catalysts are stable for at least 160 hours.

## References

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