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Highly Efficient Process for the Conversion of Glycerol to Acrylic Acid via Gas-Phase Catalytic Oxidation of Allyl Alcohol Intermediate

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ABSTRACT

The conversion of glycerol, the main byproduct of biodiesel industry, to acrylic acid is one of the most attractive biomass to biochemical processes. It represents millions of tons of market demand. The previous tandem reaction protocol for glycerol conversion to acrylic acid via acrolein intermediate always suffers from fast catalyst deactivation and thus cannot be commercialized. Herein, a novel two-step protocol for the conversion of glycerol to acrylic acid is presented: glycerol deoxydehydration (DODH) by formic acid to allyl alcohol, followed by oxidation to acrylic acid in gas phase over Mo-V-W-O catalysts. In the second step, supported and unsupported Mo-V-W-O multiple metal oxide catalysts were used for the transformation of allyl alcohol to acrylic acid and excellent activity as well as selectivity was achieved. Remarkably, the mesoporous silica supported Mo-V-W-O catalysts showed superb stability on time stream under the optimal reaction conditions with up to 80% overall acrylic acid yield. This study provides a prominent catalytic process for the large scale production of acrylic acid from bio-renewable glycerol.

Keywords: glycerol, acrylic acid, allyl alcohol, gas phase reaction, heterogeneous catalysis, deoxydehydration reaction, supported catalyst

INTRODUCTION

With the emphasis on renewable energy, increasing amount of biodiesel is produced as an alternative fuel.¹⁻³ It was expected that approximately 37 billion gallons of biodiesel will be produced by 2016, and therefore approximately 4 billion gallons of crude glycerol will be generated.^{4,5} It is imperative to find more uses for the over supplied glycerol, which will be of great importance for the biodiesel economy.

Potentially, the bio-generated glycerol can serve as a platform chemical for the synthesis of value-added products.⁶⁻¹⁰ Among those, the most attractive one is acrylic acid (AA), which is industrially produced from the gas phase oxidation of crude oil-based propene and is used primarily for the large volume production of polyacrylates.¹¹⁻¹³ The large market demand makes acrylic acid one of the most sought after chemicals from biomass resources.

The most known way to produce acrylic acid from glycerol is the two-step tandem reaction (Scheme 1).^{14,15} Glycerol is first dehydrated to acrolein over an acid catalyst, and then oxidized to acrylic acid in the second step. Since the oxidation of acrolein to acrylic acid has already been well developed in industrial acrylic acid process,¹⁶⁻¹⁸ dehydration of glycerol to acrolein in gas phase is the main emphasis of current research.¹⁹⁻²¹ A wide variety of solid acid catalysts, such as metal oxides,²² zeolites,^{23,24} heteropoly acids,^{25,26} and phosphates,^{27,28} have been evaluated for gas phase glycerol dehydration. Although up to 90% acrolein yield could be achieved from glycerol dehydration, those acid catalysts suffered from fast deactivation due to heavy coke deposition which was caused inevitably by the acidic nature of the catalysts and the high reaction temperature. There have also been reports on direct oxydehydration conversion of glycerol to acrylic acid over bifunctional catalysts.²⁷⁻³¹ However, the selectivity to acrylic acid is normally lower than 50%, meanwhile catalyst deactivation is still a severe problem.³² Various techniques such as co-feeding with oxygen,^{27,33} metal doping,²⁵ and manipulating the catalyst texture^{34,35} have been developed to reduce the coke formation, while the challenge still remains and therefore limits its large scale practical application.

It is highly desired to create new processes for glycerol conversion to acrylic acid with high efficiency and catalyst stability. Recently, it was reported that glycerol can be converted to allyl alcohol by gas phase transfer hydrogenation,^{36,37} rhenium complex catalyzed deoxydehydration (DODH) reaction,³⁸⁻⁴⁰ and formic acid mediated non-catalytic DODH reaction.⁴¹ In view of the low efficiency in gas phase transfer hydrogenation (25% product yield) and the high cost of the Re catalyst, formic acid mediated DODH of glycerol to allyl alcohol is more attractive. It is noteworthy that

formic acid is a cheap and green chemical that can be produced from biomass⁴²⁻⁴⁴ or CO₂.^{45,46} We envisaged that allyl alcohol could serve as an intermediate for acrylic acid production from glycerol. As only oxidation catalyst is required for the transformation of allyl alcohol to acrylic acid, the severe coke formation caused by strong catalyst acidity as in the direct glycerol oxydehydration case can be avoided. Herein, a new protocol for the conversion of glycerol to acrylic acid has been developed (Scheme 1). Glycerol is deoxydehydrated (DODH) by formic acid to allyl alcohol in a batch or continuous flow system (step 1). Subsequently, allyl alcohol is oxidized to acrylic acid in a fixed-bed gas-phase system (step 2). Glycerol DODH to allyl alcohol by formic acid (step 1) is known to happen in batch reaction.⁴¹ thus, in this work, we have further studied some aspects closely related to the practical applications, such as the reaction conditions, the tolerance to impurities, and the feasibility of the continuous reaction. To our knowledge, allyl alcohol oxidation to acrylic acid in gas phase (step 2) is a new reaction and has not been reported before. Thus, in this work we have focused more on the second step reaction. Mo-V-W based multiple metal oxides were selected as the catalysts for the second step as they are active for a variety of partial oxidation reactions including acrolein oxidation to acrylic acid.^{11-13,18,47,48} The Mo-V-W-O catalysts demonstrated high efficiency with an overall acrylic acid yield up to 90%, and superb stability on time stream under the optimal reaction conditions. The high efficiency, high selectivity, and high stability of catalyst make this new system a great potential in large scale production.



Scheme 1. Synthetic approaches for the conversion of glycerol to acrylic acid.

EXPERIMENTAL SECTION

All starting materials are commercially available and were used as received, unless otherwise indicated. Formic acid (99%), glycerol (99%), ammonium monovanadate (99%), and ammonium heptamolybdate (99%) were purchased from Merck. Ammonium metatungstate (99%) was purchased from Fluka.

Catalysts Preparation. The unsupported Mo-V-W-O catalysts were prepared by decomposing the ammonium salts of the metal precursors. Stoichiometric amounts of ammonium monovanadate. ammonium heptamolybdate, and ammonium metatungstate were dissolved in DI water and then evaporated to dryness. The combination was calcined at 275 °C for 4 h in air and then at 325 °C for 4 h in Ar. The powder sample was pressed into pellets and then crushed and sieved to $35 \sim 60$ mesh before activity evaluation. For the preparation of the supported catalyst, the aqueous solution containing calculated amounts of vanadium, molybdenum, and tungsten precursors were impregnated onto SBA-15 under stirring at room temperature. The material was dried at 100 °C overnight to remove solvent before calcination at 275 °C for 4 h in air and then at 325 °C for 4 h in Ar.

Catalysts Characterization. Powder X-ray Diffraction (XRD) was conducted using a Brucker automatic diffractometer (Brucker D8 discover GADDS) with monochromatized Cu-K α radiation ($\lambda = 0.15406$ nm) at a setting of 30 kV. The BET surface areas and pore structures were measured by Micromeritics ASAP 2020. The samples were degassed at 250 °C for 3 h before N₂ adsorption. The TEM images were obtained with a FEI Tecnai F20 transmission electron microscope.

Deoxydehydration of Glycerol to Allyl Alcohol. Glycerol (18.4 g, 0.2 mol) and formic acid (16.5 g, 0.36 mol) were charged into a 50 ml flask. The flask was heated by an alumina heating block mounted on a hot plate and the temperature was controlled by a thermal couple. The reaction temperature was raised to 235 °C and the distillation of product occurred immediately. The product was collected by condensation over cooling water, giving 11.4 g of allyl alcohol (98% yield) together with water and unreacted formic acid.

Deoxydehydration of Glycerol to Allyl Alcohol (Continuous). A mixture of

glycerol and formic acid with molar ratio of 1:1.8 was charged into a 50 ml flask. The flask was heated by an alumina heating block mounted on a hot plate and the temperature was controlled by a thermal couple. The temperature of the flask was raised to 235 °C quickly and then another portion of reactant mixture with the same molar ratio of glycerol and formic acid was added dropwise into the reactor by a funnel. The product was collected by condensation over cooling water, and the adding rate was adjusted to keep a constant liquid volume in the reactor. Under the steady state, 18.4 g of glycerol and 16.5 g of formic acid was added over about 2 hours, and 11.4 g of allyl alcohol (99% yield) was collected together with water and unreacted formic acid.

Gas Phase Oxidation of Allyl Alcohol to Acrylic Acid. Catalytic performance for the partial oxidation of allyl alcohol to acrylic acid was evaluated in a quartz fixed-bed microreactor ($\Phi = 6$ mm) with a continuous reactant down flow. Typically, 0.2 g of catalyst (35 ~ 60 mesh) was charged into the reactor. The reactant (20wt% allyl alcohol in water) was fed by syringe pump at a rate of 0.5 ml h⁻¹. The carrier gas was 10%O₂/He (flow rate 20 ml min⁻¹, GHSV 6700 h⁻¹). On-line gas chromatography was used to analyze the outlet effluent after the system was stabilized for 1 h at each temperature point.

Product Analysis. Analysis of the reactant and product in the deoxydehydration of glycerol to allyl alcohol was carried out using HPLC (Agilent Technologies, 1200 series) with refractive index (RI) detector. Reactant and product were separated on an Agilent Hi-Plex H column (7.7 × 300 mm, 8 μ m). The effluent was a solution of H₂SO₄ (0.0001 M), flow rate 0.7 ml min⁻¹, 25 °C. The retention times were 12.1 min, 12.9 min, and 20.1 min for formic acid, glycerol, and allyl alcohol, respectively. The analysis of reactant and products in the gas phase catalytic oxidation was carried out using on-line GC system (Shimadzu GC2014) equipped with FID and TCD. A capillary column (HP FFAP, 30 m × 0.32 mm, 0.25 μ m) was used to separate the organic components, and a packed carbon column (3 mm × 300 mm) was used to separate CO and CO₂.

RESULTS AND DISCUSSION

Allyl alcohol is also a highly valued chemical that is industrially manufactured from propene. The synthesis of allyl alcohol from glycerol dehydration presents an alternative choice for making this industrial chemical from a green feedstock. Formic acid mediated DODH of glycerol is the most attractive method for the allyl alcohol synthesis.⁴¹ Under the reaction conditions, one formic acid molecule can react with the two vicinal hydroxyl groups of glycerol to form the cyclic carbonation intermediate. With the assist of another formic acid molecule, the carbonation intermediate decomposes to allyl alcohol, CO₂, and H₂O. In previous work, the reaction was reported in batch reaction with pure glycerol as reactant. In this work, we have further studied the reaction conditions, the tolerance to impurities, and the feasibility of the continuous reaction. In a typical condition, glycerol was heated with formic acid at 235 °C under ambient atmosphere, and allyl alcohol was collected by condensation. The reaction is very fast and clean. The reaction rate depends on the amount of formic acid added in the reaction (Figure S1). As the formic acid to glycerol molar ratio is 1.8:1, 90% glycerol was converted (allyl alcohol yield 89%) in 2 hours. As the formic acid was added in 3 portions, the reaction was completed in 6 hours, and allyl alcohol was collected at 97% yield (Table 1, Entries 1 & 2). There was no other side product collected besides water and unreacted formic acid. Moisture and methanol are the main potential impurities in crude bio-glycerol; however, they did not affect the current DODH reaction even at 20 wt% content (Table 1, Entries 3 & 4). A flow reaction system was also tested for this reaction (Figure S2; Table 1, Entry 5). Under steady state, a mixture of glycerol (18.4 g, 0.2 mol) and formic acid (16.5 g, 0.36 mol) was added continuously to a 50 ml flask (heated at 235 °C) in around 2 hours, and 11.5 g of allyl alcohol (99% yield) was collected together with 5.6 g of unreacted formic acid. This experiment demonstrated the flow reaction system for the production of allyl alcohol from glycerol with high productivity.

| Entry | Glycerol feed | Conv. [%] ^e | Yield [%] | FA recovered [%] |
|----------------|---------------------------|------------------------|-----------|------------------|
| 1 ^b | 100% | 98 | 97 | 23 |
| $2^{b,c}$ | 100% | 99 | 98 | 27 |
| 3 ^b | 80wt% in H ₂ O | 98 | 97 | 33 |
| 4 ^b | 80wt% in MeOH | 99 | 98 | 27 |
| 5 ^d | 100% | 99 | 99 | 34 |

Table 1. Deoxydehydrate (DODH) glycerol to allyl alcohol by formic acid (FA).^a

^a Reaction conditions: glycerol (18.4 g, 0.2 mol), formic acid (16.5 g, 0.36 mol), 235 °C, under N₂. ^b Formic acid was added in 3 portions (11.9, 2.3, and 2.3 g). Reaction time: 6 h. ^c Reaction carried under air. ^d Continuous reaction. A mixture of glycerol (18.4 g, 0.2 mol) and formic acid (16.5 g, 0.36 mol) was added continuously to the reactor (Figure S2). Reaction time: 2 h. ^e Yield and conversion were determined by HPLC.

Mo, V, and W based metal oxides are active and selective for a variety of partial oxidation reactions.^{18,47,48} They are also the basic components of the industrial acrylic acid catalysts (acrolein to acrylic acid).¹¹⁻¹³ It was recognized that Mo₄VO₁₄ and Mo₃VO₁₁ are the active phases for acrolein oxidation to acrylic acid,^{49,50} and the addition of W can stabilize the catalyst structure.^{51,52} Therefore, a series of metal oxides Mo₈V₂W_xO_{δ} and Mo₉V₃W_xO_{δ} were fabricated and evaluated for allyl alcohol oxidation. The XRD patterns (Figure 1) showed that all MoVW oxide catalysts were well crystallized in the single hexagonal MoO₃-type phase.^{16,52,53} All samples exhibited small specific surface area values between 8 ~ 12 m² g⁻¹ (Table S1). The SEM images (Figure S3) depicted that the samples possessed an agglomeration of irregular particles in micron size.



Figure 1. XRD patterns of $Mo_8V_2W_xO_\delta$ (x = 0, 1, 2) and $Mo_9V_3W_xO_\delta$ (x = 0, 1, 2) catalysts.

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As shown in Figure 2, $Mo_8V_2O_\delta$ and $Mo_9V_3O_\delta$ catalysts are active, but acrolein is dominant in the products when the reaction temperature is below 320 °C. Other products are acrylic acid, acetaldehyde, acetic acid, and carbon oxides. When the reaction temperature was increased, acrolein was consecutively oxidized to acrylic acid; however the selectivity to acetic acid and the total oxidized products (CO, CO₂) was also increased. Thus, it is deduced that acrolein is the key intermediate in allyl alcohol oxidation to acrylic acid in the present work. It has been proved that in acrolein oxidation to acrylic acid, V₂O₅ is active but unselective, MoO₃ is inactive, and WO₃ is inert. The V^{4+}/V^{5+} species in the MoVW oxide catalysts are responsible for the redox cycle and the high selectivity to acrolein, while the incorporation with Mo stabilized the valence states of V and the addition of W improved the long-term stability of the catalysts.^{51,52} In the present work of allyl alcohol oxidation, the addition of tungsten didn't change the crystal structure of the catalysts but notably improved the selectivity to acrylic acid. Over the $Mo_8V_2WO_{\delta}$ and $Mo_9V_3WO_{\delta}$ catalysts, full allyl alcohol conversion and about 87% selectivity to acrylic acid were achieved at reaction temperature of 340 °C. Adding more tungsten into the catalysts leads to lower selectivity to acrylic acid but higher selectivity to the total oxidized products. The $Mo_9V_3W_xO_\delta$ serial catalysts generally showed higher activities than $Mo_8V_2W_xO_\delta$ serial. It may be due to the higher content of V in $Mo_9V_3W_xO_\delta$ catalysts which have higher selectivity to the total oxidized products at higher reaction temperatures. Our results indicated that tungsten does not only serve as a structural promoter, but also significantly influences selectivity to acrylic acid in allyl alcohol oxidation. Although W is not directly involved in the oxygen transfer process due to the high oxygen binding strength, the incorporation of W might influence the reducibility of the active V species, and consequently influence the selectivity to the oxygenated products. It was found that in the presence of W, V species can be reduced to the V₂O₃-type phase, while in the absence of W, V species can only be reduced to VO₂.⁵¹ Apparently, allyl alcohol oxidation to acrylic acid more relies on the composition of the MoVW oxide catalysts, and more research work is needed to

give deeper insight into the structure-performance relationships of this catalytic system.



Figure 2. (A) Allyl alcohol oxidation over serial $Mo_8V_2W_xO_\delta$ (x = 0, 1, 2) catalysts. (B) Allyl alcohol oxidation over serial $Mo_9V_3W_xO_\delta$ (x = 0, 1, 2) catalysts. Reaction conditions: catalyst, 200 mg, 35 ~ 60 mesh; feed, 20wt% allyl alcohol in H₂O, 0.5 ml h⁻¹; carrier gas, 10%O₂/He, 20 ml min⁻¹. WHSV = 0.5 h⁻¹. Acr: acrolein. AA: acrylic acid. AcOH: acetic acid. Data collected at 1 h time point.

Reaction conditions were further optimized based on the best performed $Mo_8V_2WO_8$ catalyst (Table S2). Space velocity with 0.5 h⁻¹ gave steadily good results. The conversion of allyl alcohol generally increases with increasing oxygen content. When 5% oxygen was used as the carrier gas (Table S3), 81% selectivity to acrylic acid was achieved at 340 °C while the selectivity to the total oxidized products (CO and CO₂) is less than 1%. Increasing the oxygen content to 10% gave 87% yield of acrylic acid at 340 °C. Notably, 82% yield of acrylic acid was also achieved when the

more economic air $(21\%O_2/N_2)$ was used as oxidant. Generally, higher oxygen content increases selectivity to over oxidized products, especially when reaction temperature is high. Thus, the oxygen content around 10% is preferable for the current oxidation reaction. Interestingly, acrylic acid yield can be further improved to 90% when feeding with 40wt% of allyl alcohol in water (Table S4). When the product mixture (allyl alcohol/formic acid) of the first step glycerol DODH reaction was directly used as feedstock, 76% acrylic acid yield was achieved. After removal of formic acid from the mixture, the as synthesized allyl alcohol from glycerol gave 85% yield of acrylic acid (Table S4). The temperature dependence of the reaction performance over $Mo_8V_2WO_{\delta}$ is shown in Figure 3. The allyl alcohol conversion increased monotonously at elevated temperature in the 240 ~ 320 °C range, and full conversion was achieved at the temperature above 320 °C. Acrolein is the key intermediate to acrylic acid. The selectivity to acrolein decreased rapidly with the temperature rise, indicating that acrolein was quickly oxidized at higher temperature. In contrast, the selectivity to acrylic acid increased rapidly with the temperature rise, reaching a maximum value of 87% at 340 °C. Further increase the temperature lead to decreased selectivity to acrylic acid due to the over oxidation, as reflected by the increasing amount of acetic acid, CO, and CO₂. The selectivity to CO and CO₂ are lower than 10% in the whole temperature range. Acetaldehyde was observed as the main side product at temperature below 320 °C, while the formation of acetaldehyde was notably reduced as the temperature was increased. Significant amount of acetaldehyde was also observed in the oxydehydration of glycerol.^{27,30,31,33} In the current study, the selectivity of acetaldehyde is correlated to the selectivity of acrolein. At higher temperatures, acrolein is quickly converted to acrylic acid, and concurrently, acetaldehyde yield was apparently suppressed. These results indicated that allyl alcohol oxidation over $Mo_8V_2WO_\delta$ is temperature dependent and kinetically controlled.



Figure 3. Temperature dependence of allyl alcohol oxidation over the $Mo_8V_2WO_\delta$ catalyst. Reaction conditions: catalyst, 200 mg, 35 ~ 60 mesh; feed, 20 wt% allyl alcohol in H₂O, 0.5 ml h⁻¹; carrier gas, 10%O₂/He, 20 ml min⁻¹. WHSV = 0.5 h⁻¹. Act: acetaldehyde. Acr: acrolein. AA: acrylic acid. AcOH: acetic acid. Data collected at 1 h time point.

Generally, porous materials supported catalysts have advantages over the unsupported ones, including larger surface area to volume ratio of active component and controllable catalyst textures. Herein, mesoporous silica-based material $(SBA-15)^{27}$ is adopted for the loading of Mo₈V₂WO₈. The large pores and high surface area of SBA-15 would lead to high capacity of loading catalysts and lower limitation of internal mass transfer. The supported catalysts were prepared by incipient wetness impregnation followed by calcination. The N₂ adsorption-desorption profiles of $Mo_8V_2WO_8/SBA-15$ catalysts are illustrated in Figure 4, with the related data listed in Table 2. As shown in Figures 4A & B, the mesopores of SBA-15 (6.4 nm) were apparently decreased as the loading of catalyst was increased. Concurrently, smaller pores (3.2 to 3.5 nm, which were generated as the original pores were partially occupied by catalyst) were observed. The average pore diameter and surface area value (Table 2) decreased with increasing $Mo_8V_2WO_{\delta}$ loading. The above observation indicates that the mesopores of SBA-15 were gradually occupied with successive $Mo_8V_2WO_8$ loading. This conclusion could also be verified from the significant changes of pore volume and occupied pore volume of supported catalysts (Table 2).

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| Catalyst | $\frac{S_{BET}}{[m^2 g^{-1}]}$ | V_{Pore} [cm ³ g ⁻¹] | $\frac{V_{OP}}{[cm^3 g^{-1}]^a}$ | Pore Diameter (nm) |
|---|--------------------------------|--|----------------------------------|--------------------------|
| $Mo_8V_2WO_\delta$ | 12.4 | 0.04 | - | - |
| 60%Mo ₈ V ₂ WO _δ /SBA-15 | 187.3 | 0.12 | 0.19 | 3.7 |
| 40%Mo ₈ V ₂ WO _δ /SBA-15 | 272.9 | 0.28 | 0.17 | 4.7 |
| 20%Mo ₈ V ₂ WO ₈ /SBA-15 | 329.7 | 0.49 | 0.09 | 5.5 |
| SBA-15 | 475.2 | 0.72 | - | 5.7 |

Table 2. The BET surface area, porosity, and TOFs of catalysts.

^a Occupied pore volume (V_{OP}) = [Pore volume of SBA-15 × (1- catalyst loading%) + Pore volume of Mo₈V₂WO_{δ} × (catalyst loading%) – Pore volume].



Figure 4. (A) N_2 adsorption-desorption isotherms and (B) pore size distribution of $Mo_8V_2WO_8/SBA-15$ catalysts.

XRD patterns of Mo₈V₂WO₈/SBA-15 catalysts exhibited much lower diffraction intensities which probably owing to small particle size or low crystallinity (Figure S4). For $20\%Mo_8V_2WO_8/SBA-15$, there was no diffraction peak observed. This could be due to the tiny $Mo_8V_2WO_8$ entities (≤ 6 nm in diameter) dispersed into the mesopores of SBA-15, however, this does not exclude the possibility that the supported $Mo_8V_2WO_\delta$ entities are highly disordered or exist in amorphous phase.⁵² The high-resolution transmission electron microscopy (HRTEM) images revealed that there is no obvious $Mo_8V_2WO_\delta$ particles on SBA-15 of samples with low (20% and 40%) Mo₈V₂WO_{δ} loading (Figures 5a-d). However, the selected area electron diffraction analysis of 40%Mo₈V₂WO₈/SBA-15 catalyst (Figure 5e) confirmed that the $Mo_8V_2WO_\delta$ components were indeed loaded onto SBA-15. The image of the $60\%Mo_8V_2WO_{\delta}/SBA-15$ catalyst (Figure 5f) showed that some $Mo_8V_2WO_{\delta}$ particles were attached on the external surface of SBA-15 or segregated from the support. This is also correlated to the N₂ adsorption-desorption analysis (BET) data (Table 2). For $Mo_8V_2WO_8/SBA-15$ catalyst with 20% and 40% loadings, metal oxides occupied 0.09 and 0.17 cm³ pore volume of SBA-15, suggesting that metal oxides were dispersed into the pore of SBA-15. While for 60%Mo₈V₂WO₈/SBA-15, the metal oxides occupied a pore volume of only 0.19 cm³. Based on these results, it is concluded that the majority of $Mo_8V_2WO_8$ components were dispersed inside the SBA-15 channels when the catalyst loading is low ($\leq 40\%$). However, further increasing the catalyst loading will result in $Mo_8V_2WO_5$ components partially located on the external surface of SBA-15.



Figure 5. TEM images of $Mo_8V_2WO_8/SBA-15$ catalysts with different $Mo_8V_2WO_8$ loadings: (a) 20% loading; (b) & (c) 40% loading; (d) magnified from the circled area shown in (b); (e) EDX spectrum for (d); (f) 60% loading.

The Mo₈V₂WO₈/SBA-15 catalysts exhibited high activities similar to the unsupported counterpart and full allyl alcohol conversion was achieved at above 300 °C (Figure 6). Catalysts with 60% and 40% Mo₈V₂WO₈ loadings gave >82% acrylic acid yields at reaction temperatures above 340 °C, which is comparable to the unsupported Mo₈V₂WO₈. The 20%Mo₈V₂WO₈/SBA-15 catalyst is less selective to acrylic acid. Unlike in the unsupported case (Figure 3), the higher reaction temperature does not affect the selectivity to acrylic acid significantly over the supported catalysts. It is assumed that the highly dispersed metal oxides have strong interactions with silica, and these interactions played a positive role in stabilizing the Mo₈V₂WO₈ active components, keeping the high activity and selectivity toward acrylic acid. Figure 7 plots the specific activities (grams of allyl alcohol converted per hour over one gram of Mo₈V₂WO₈ catalyst) and the rate of acrylic acid formation at 340 °C. It can be seen that the catalytic activity and the rate of acrylic acid formation can be achieved at 2.5 and 1.8 respectively over 20%Mo₈V₂WO₈/SBA-15.



Figure 6. Allyl alcohol oxidation over $x\%Mo_8V_2WO_8/SBA-15$ catalysts. Reaction conditions: catalyst (sum of active component and support) 200 mg, 35 ~ 60 mesh; feed, 20wt% allyl alcohol in H₂O, 0.5 ml h⁻¹; carrier gas, 10%O₂/He, 20 ml min⁻¹. WHSV = 0.5 h⁻¹. Acr: acrolein. AA: acrylic acid. Data collected at 1 h time point.



Figure 7. Specific activity (grams of allyl alcohol converted per hour over one gram of $Mo_8V_2WO_\delta$ catalyst) and acrylic acid formation rate (grams of AA produced per hour over one gram of $Mo_8V_2WO_\delta$ catalyst) at 340 °C.

In view of the higher specific activity of the supported catalysts, $40\%Mo_8V_2WO_8/SBA-15$ was further tested at higher WHSV (Table S5). When WHSV was increased from 0.5 h⁻¹ to 2.25 h⁻¹, above 90% allyl alcohol conversion and over 80% selectivity to acrylic acid still can be achieved in the temperature range of 260 ~ 340 °C. When the WHSV was further increased to 3.0 h⁻¹, the conversion of allyl alcohol at 260 °C was 86.7%, and then the conversion decreased even with temperature rise, indicating the catalyst was overloaded with the reactant at WHSV of 3.0 h⁻¹. Stability is one of the key parameters for a practical catalyst. Therefore, the

catalytic performances of Mo₈V₂WO₈ and 40%Mo₈V₂WO₈/SBA-15 catalysts were studied as a function of time on stream at WHSV of 0.5 h⁻¹ (Figure 8). The complete conversion of allyl alcohol was kept for 90 ~ 100 h over Mo₈V₂WO_{δ} and 40%Mo₈V₂WO₈/SBA-15 catalysts. For the unsupported Mo₈V₂WO₈ (Figure 8A), the selectivity to acrylic acid decreased from 80% to 70% in the initial 30 h, and then stabilized at around 70% till 90 h time on stream; meanwhile, the selectivity to acetic acid increased from 8% to 20%. The 40%Mo₈V₂WO₈/SBA-15 catalyst showed excellent stability (Figure 8B). High selectivity to acrylic acid (> 80%) was well maintained up to at least 100 h time on stream. Herein, the $Mo_8V_2WO_8$ entities were highly dispersed and confined inside the mesopores of SBA-15. This structure efficiently prevented the sintering and agglomeration of the tiny particles during the long term reaction at high temperature and contributed to the high stability of the catalyst. The used $40\%Mo_8V_2WO_8/SBA-15$ catalyst was subjected to thermogravity analysis (Figure S5) and the weight loss in the $300 \sim 600$ °C range is less than 3%, signifying insignificant coke deposition even after 100 h working. The TEM image (Figure S6) of the used catalyst revealed that the mesoporous structure was also well retained. When the 40%Mo₈V₂WO₈/SBA-15 catalyst was tested at WHSV of 1.0 h⁻¹ at 340 °C (Figure S7), full conversion and around 80% selectivity to acrylic acid were also maintained for over 60 hours. When the catalyst was tested at WHSV of 2.25 h^{-1} at 260 °C (Figure 8C), the initial conversion was 94.5% and the selectivity to acrylic acid and acrolein were 58.2% and 19.6%, respectively. However, the catalyst deactivated rapidly after 5 h. A comparison on the total amounts of reactant converted within the lifetime would be helpful to understand the stability of the catalyst. At WHSV of 0.5 h^{-1} , the total conversion of the reactant was 10 g / (0.2 g of catalyst) in 100 h (still no deactivation observed); at the WHSV of 2.25 h^{-1} , the total conversion of the reactant was around 2.1 g / (0.2 g of catalyst) in the initial 5 h (after that time the catalyst started to deactivate). Thus, it is proposed that the observed catalyst stability with respect to the WHSV might be related to the redox property of the catalyst. The partial oxidation reactions over transition metal oxide catalysts generally follow the proposed Mars and Van Krevelen mechanism, and the redox properties

determine the activity of the catalysts. At higher WHSV the supported $Mo_8V_2WO_8$ catalyst would be reduced much faster than the rate for catalyst reoxidation, and this leads to the fast catalyst deactivation.



Figure 8. Time on stream tests for allyl alcohol oxidation over (A) $Mo_8V_2WO_\delta$ at WHSV of 0.5 h⁻¹, (B) 40% $Mo_8V_2WO_\delta$ /SBA-15 at WHSV of 0.5 h⁻¹, and (C) 40% $Mo_8V_2WO_\delta$ /SBA-15 at WHSV of 2.25 h⁻¹. Reaction conditions: catalyst 200 mg, 35 ~ 60 mesh; feed for (A) and (B), 20 wt% allyl alcohol in H₂O, rate 0.5 ml h⁻¹; feed for (C), 60 wt% allyl alcohol in H₂O, rate 0.75 ml h⁻¹. Carrier gas, 20 ml min⁻¹, 10% O_2 /He for (A) and (B), 21% O_2/N_2 for (C); reaction temperature, 340 °C for (A) and (B), 260 °C for (C). AA: acrylic acid. AcOH: acetic acid. Acr: acrolein.

CONCLUSIONS

In conclusion, we have demonstrated a highly efficient protocol for the production of acrylic acid from glycerol. The process involves glycerol deoxydehydration to allyl alcohol in liquid phase and allyl alcohol catalytic oxidation to acrylic acid in gas phase with 90% overall yield of acrylic acid. The entire process can be carried out in a continuous manner and demonstrated high efficiency and selectivity. The SBA-15 supported metal oxide (Mo-V-W-O) catalysts have well defined structure and exhibited good stability. The current study provides a new and prominent method for the production of acrylic acid from bio-renewable glycerol.

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Notes

The authors declare no financial interest.

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