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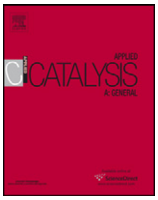

Direct conversion of glycerol to acrylic acid via integrated dehydration–oxidation bed system

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ABSTRACT

Acrylic acid can be successfully produced in a single reactor via subsequent oxidation of the glycerol-dehydrated products. Selective dehydration of glycerol to acrolein was studied at 275–400 °C over HZSM-5, HBeta, HMordenite and HY. The V–Mo oxides (15–70 mol%V) on silicic acid support (20–100 wt% mixed oxides loading) were then included as a second bed for subsequent oxidation of the dehydrated products. Over the acid zeolites, acrolein and acetol are mainly generated, together with acetaldehyde, propionaldehyde, pyruvaldehyde and other oxygenates as secondary products. A complete conversion of glycerol with high selectivity to acrolein (up to 81 mol%) can be obtained when medium pore zeolites (HZSM-5) and low glycerol concentration (10–30 wt%) was used at 300 °C. A separated-sequential bed system provides high selectivity for acrylic acid with small amount of acetic acid and acetaldehyde (∼15 mol%). The catalyst with high V content promotes total oxidation of the dehydrated products to CO while that with highly dispersed V–Mo–O phases affords 98% selectivity to acrylic acid with 48% acrolein conversion.

1. Introduction

Nowadays, attempts to replace the petroleum resource by biomass have been increasingly focused for the production of both liquid fuel and petrochemical feedstock. In particular, the use of alkyl ester as biodiesel via trans-esterification between vegetables oil and alcohol [1,2], becomes increasingly attractive for the countries with agriculture-based economics. However, a large amount of glycerol, the by-product, is continually produced, while its current demand remained unchanged. Despite efforts are made to utilize glycerol as alternative fuel, its combustion emits toxic gases [3]. Alternatively, glycerol is a sustainable feedstock that can be used for manufacture of some C_3 derivatives. Several processes, so called "deoxygenation", were applied to eliminate its oxygen content. These include hydrogenolysis [4,5] and dehydration [6,7]. For example, conversion of glycerol to propylene glycol [8] has been widely investigated. However, most of the process consumes large amount of hydrogen and high pressure is generally applied.

In an economic point of view, deoxygenation of glycerol via dehydration become more attractive since more than 60% oxygen content can be simply eliminated without hydrogen consumption under relatively mild reaction condition [9]. Moreover, the dehydrated product, acrolein, can be readily converted to other C_3 petrochemicals, namely acrylic acid [10–12], acrylonitrile [13], allyl alcohol [14], etc. The dehydration can be generally promoted over acid catalysts at 275–350 °C. The common acid oxides such as η-Al_2O_3, SiO_2/Al_2O_3 [15] and TiO_2 [16] have been applied but they did not provide a satisfied selectivity to acrolein. Improved selectivity can be obtained from the reactions over Nb_2O_5 (∼50%) [17], WO_3/ZrO_2 (75%) [18], phosphoric-doped metal oxides (i.e. Al_2O_3–PO_4, TiO_2–PO_4 [19]), heteropoly acids (i.e. HSiW, HPW, HPMo on silica supports [16]) and zeolites (i.e. ZSM-5, Y, Beta [20–22], and SAPOs [19]). However, low selectivity is typically obtained at high conversion and the catalysts usually possess low stability. This is presumably because acrolein is highly reactive and undergoes secondary reactions to form other products during the dehydration process. Accordingly, a subsequent conversion of acrolein to a desirable and more stable product, immediately after its formation, would not only enhance the designed product selectivity, but also eliminate handling problems of acrolein storage and transportation.

Major industrial use of acrolein is for production of acrylic acid that is widely used for in adhesive, paint, plastic and rubber synthesis. Typical oxidation catalysts involve vanadium–molybdenum mixed oxides on alumina or silica supports due to their high selectivity to acrylic acid [23]. It was also report that Mo:V ratio and oxygen partial pressure play important role on the catalyst performance [23]. In general, selective oxidation competes against total combustion and the TPR experiment showed that CO_2 could be minimized at temperature below 400 °C [24]. While acrylic acid

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could be selectively generated with low conversion at temperature between 300 and 450 °C, depending on Mo:V ratio [25].

Accordingly, it is possible to match up the reaction conditions of both dehydration and oxidation for a two-bed system that allows single stage conversion of glycerol to acrylic acid with high selectivity. To accomplish the idea, a complete conversion of glycerol and high acrolein selectivity are required in the dehydration step to avoid oxidation of glycerol, and maximize acrylic acid yield in the second bed. In addition, no oxidation should take place in the first bed (dehydration), while water shall not interfere the oxidation process. Thus, the two-bed system would allow feeding glycerol with high water content and the product effluent would be acrylic acid solution that can be directly used for production of acrylic emulsion [26]. In this paper, we demonstrate a practical two-bed system consisting of zeolite and vanadium–molybdenum mixed oxides as catalysts for direct conversion of glycerol to acrylic acid. The dehydration of glycerol over zeolites was primarily investigated at various concentrations. The effects of temperature, oxygen partial pressure, mixed oxide composition and loading on the subsequent oxidation were also highlighted.

2. Experimental procedure

HZSM-5 (13) and NH_4^+ZSM-5 (140) were obtained from Zeochem® and Zeolyst® respectively. While NH_4^+Beta (14), HMordenite (15) and HY (100) were supplied by Tohso Co., Ltd. All zeolite samples were calcined in air zero at 500 °C for 5 h, then pelletized to the size of 600–850 μm. For the oxidation catalyst, the vanadium–molybdenum oxides on silicic acid support was prepared using incipient wetness impregnation technique. Firstly, the ammonium metavanadate (NH_4VO_3; Asia Pacific Specialty Chemicals Ltd.) and ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$; Ajax Fine Chem) precursors were dissolved in distillated water at 60 °C. The precursor solution was slowly dropped onto the silicic acid support (chromatography grade; BDH Chemicals Ltd.) until wet. The samples were dried at 60 °C in an oven for 15 min, and then the loading was repeated until metal content was reached. The final loaded samples were kept to dry at 60 °C over night. After that, the catalysts were calcined at 300 °C for 5 h under a flow of dry air (60 ml min^{-1}) and pelletized to the size of 600–850 μm. The sample were designated as [metal oxide loading]VMo[vanadium mol% in mixed metal oxide]; i.e. 45VMo(21).

Surface area of all catalysts was determined using nitrogen adsorption analyzer (Quantachrome Autosorb-1) at −196 °C and 0.05–0.30P/P_0. The BET equation was used for surface area calculation. Elemental composition and crystal structure of vanadium–molybdenum oxides on silicic acid were determined by X-ray fluorescence spectrometer (XRF; Siemens SRS3400) and X-ray diffractometer (XRD; Siemens D8 Advance) respectively. The morphology and deep-surface composition of the catalysts were analyzed by field emission spectrometer equipped with energy-dispersive X-ray spectrometer (SEM–EDX; Hitachi S-4800).

The reaction was conducted in a tubular down flow reactor (6 mm i.d. Pyrex®) located in an electrical furnace. Zeolite was packed as a single bed catalyst for dehydration testing. The vanadium–molybdenum oxide on silicic acid was packed under the zeolite bed for subsequent oxidation testing. Helium and air zero mixed with nitrogen were regulated using mass flow controllers. The catalysts were activated at 300 °C (1 K min^{-1}) for 5 h in stream of air zero (30 ml min^{-1}). Then, the temperature was adjusted to the reaction temperature (275–400 °C) and hold for 30 min before the reaction. Glycerol solution (10–50 wt%) was then fed at 1.7 mmol min^{-1} using a syringe pump. The reaction was carried out for 7 h on stream. The product effluence was trapped by a cooling condenser (<5 °C) and collected hourly. Liquid product was quantitatively analyzed by gas chromatography with a flame ionization detector (GC–FID). A capillary EC-Wax (Alltech; 0.53 mm × 30 m) was used as separating column. While, the gas products was analyzed by the online gas chromatography equipped with thermal conductivity detector (GC–TCD) and a molecular sieve 13X (1/8 in. × 8 ft) column. Conversion, yield, selectivity and turnover frequency can be calculated as following equations;

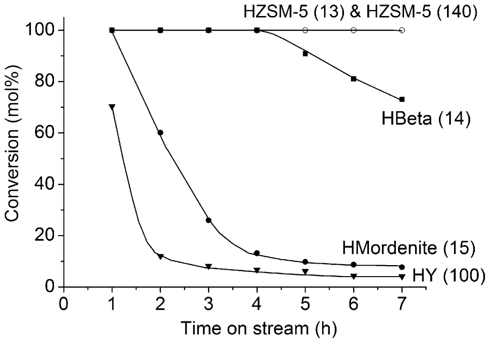

Fig. 1. The glycerol conversion over HZSM-5, HBeta, HMordenite and HY. Reaction conditions; contact time: 177 g h mol^{-1}, temperature: 300 °C, feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of helium.

$$\%\text{Conversion} = \frac{(\text{mole of glycerol fed} - \text{mole of glycerol remaining}) \times 100}{\text{mole of glycerol fed}}$$

$$\%\text{Yield} = \frac{\text{mole of product} \times 100}{\text{mole of glycerol fed}}$$

$$\%\text{Selectivity} = \frac{\text{product yield} \times 100}{\text{glycerol conversion}}$$

$$\text{Normalized reaction rate} = \frac{\text{mole of acrolein (from 1st bed) converted per hour}}{\text{mole of V} + \text{Mo in the 2nd bed}}$$

3. Result

3.1. Dehydration of glycerol to acrolein

The dehydration of glycerol was primarily investigated to understand the catalytic parameters that effect acrolein production in the first bed. The appropriate catalyst and condition are chosen for further study.

3.1.1. Effect of zeolite frameworks

For the dehydration of glycerol over different zeolites, high conversion can be initially observed over HZSM-5 (13) and HZSM-5 (140) while other catalysts show a severe drop in activity after certain time on stream (Fig. 1). As the dehydrated product, acrolein, is highly reactive, it can be readily activated and undergo secondary reactions such as condensation and oligomerization forming coke deposit on the catalyst surface. The thermal degradation study of the used catalysts (Table 1) confirms that hard coke is found for all catalysts. Thus, it is believed that the HZSM-5 (13) and HZSM-5 (140) were also continually deactivated but the excess acid sites kept the conversion 100%, despite part of the catalyst bed would gradually loss their active sites. In addition to high activity, HZSM-5 also gives higher selectivity to acrolein, as compared to HBeta, HMordenite and HY (Table 2). While, the large pore zeolites yield large amount of acetaldehyde and other high molecular weight

Table 1
Thermo gravimetric analysis of various zeolites after 7 h on stream.

Framework type	Reaction temperature (°C)	Glycerol concentration (wt%)	Contact time (g h mol^{-1})	Coke (wt% of used catalyst)
HZSM-5 (13)	300	10	177	11.8
HBeta (14)	300	10	177	23.7
HMordenite (15)	300	10	177	10.3
HZSM-5 (140)	300	10	177	5.9
HZSM-5 (140)	325	10	177	6.2
HZSM-5 (140)	400	10	177	7.1
HZSM-5 (13)	300	10	59	12.8
HZSM-5 (13)	300	30	59	12.8
HZSM-5 (13)	300	50	59	13.5

10 K min^{-1} in air from 50 °C to 900 °C.

Table 2
The products selectivity and conversion of glycerol dehydration over HZSM-5, HBeta, HMordenite and HY.

Catalyst (Si/Al)	Acidity[a] (μmol/g)	Conversion (mol%)	Selectivity (mol%)							
			Acetaldehyde	Propionaldehyde	Acrolein	Pyruvaldehyde	Acetol	Acetic acid	Propanoic acid	Others
HZSM-5 (13)	27.3	100.0	5.71	2.19	81.10	0.64	10.11	0	0	0.25
HBeta (14)	29.9	90.66	13.95	2.72	63.97	2.29	10.50	2.38	0.14	4.04
HMor (15)	25.8	10.57	7.44	1.52	67.25	3.43	10.27	2.55	2.85	4.68
HZSM-5 (140)	2.34	100.0	6.23	2.67	78.24	1.40	10.28	0	0	2.59
HY (100)	1.73	5.79	25.79	3.26	41.09	5.17	8.09	1.10	0.84	14.67

[a] Data obtained from NH$_3$-TPD (150–700 °C, 10 K min^{-1}) of the sample calcined at 500 °C. The reaction condition is similar to Fig. 1. The results average between 5th and 7th hour on stream.

products. They are cyclic unsaturated oxygenate compounds such as phenol, dihydrofuran, cyclopentenone, methyl cyclopentenone and cyclohexenone. These products are referred to as "other products" that can be evolved to coke deposit causing the catalyst deactivation, particularly for those with large pore size.

3.1.2. Effect of contact time

For dehydration, the contact time that provides the complete conversion is required because unreacted glycerol can interfere with the oxidation of the dehydrate products in the second bed. As shown in Fig. 2a, a complete conversion can be obtained at contact time >58 g h mol^{-1}. Acrolein and acetol are major products generated in parallel from glycerol dehydration [16,19,21] while acetaldehyde is presumably derived from the decomposition of the feed [16]. It is noted that pyruvaldehyde and propionaldehyde are somewhat equally found (~2–3%) as minor products as shown in Fig. 2b. When an excess of catalyst is used (>58 g h mol^{-1}), the acetol yield drops gradually while acrolein and acetaldehyde yields remain unchanged. Together with an observed increase in other products, this suggests that acetol can further react over acid sites to form secondary products. In a support manner, a separate experiment shows that acetol conversion on HZSM-5 gives mainly other products with a small amount of acetone, propionaldehyde and acetaldehyde (Table 3). In addition, 5.2 wt% coke is found for the used catalyst.

Table 3
The acetol conversion over HZSM-5 (140).

Products	Yield (mol%)	Selectivity (mol%)
Acetaldehyde	1.63	6.28
Propionaldehyde	1.10	4.21
Acetone	1.93	7.44
Others	21.10	81.17

Reaction conditions; contact time: 142 g h mol^{-1}, temperature: 350 °C, feed: 2.1 mmol h^{-1} of acetol at 10 wt%, carrier gas: 30 ml min^{-1} of helium; the results average between 5th and 7th hour on stream; only 26 mol% acetol is converted.

3.1.3. Effect of reaction temperature

Fig. 3 shows that the glycerol conversion increases with the reaction temperature and a complete conversion can be obtained at ≥300 °C. However, the selectivity toward dehydrated products (acrolein and acetol) readily decreases when the temperature is increased. In the opposite manner, acetaldehyde selectivity increases. This suggests that, at ≥300 °C, decomposition of the feed

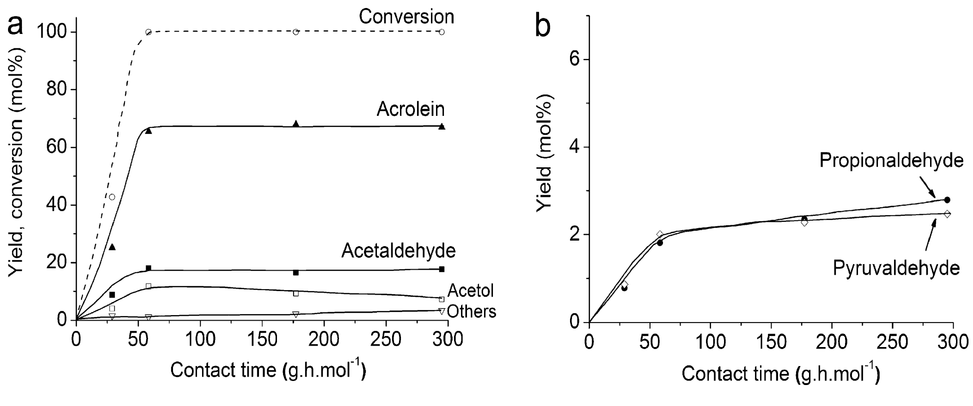

Fig. 2. Glycerol conversion and products yields over HZSM-5 (140) as function of contact time. Reaction conditions; temperature: 350 °C, feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of helium; (a) major products and (b) minor products; the results average between 5th and 7th hour on stream.

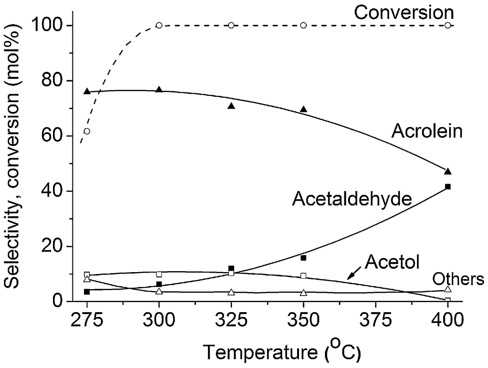

Fig. 3. Glycerol conversion and product selectivities over HZSM-5 (140) as function of reaction temperature. Reaction conditions; contact time: 177 g h mol^{-1}, feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of helium; the results average between 5th and 7th hour on stream; propionaldehyde and pyruvaldehyde were found for 3% and 2% respectively.

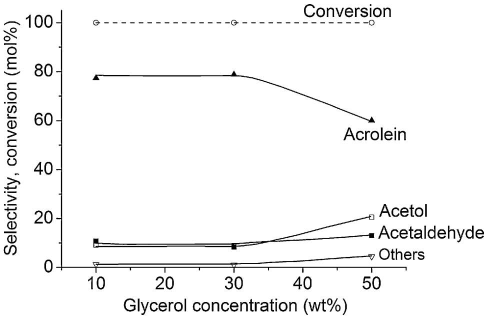

Fig. 4. Glycerol conversion and product selectivities over HZSM-5 (13) as function of feed concentration. Reaction condition; contact time: 59 g h mol^{-1}, temperature: 300 °C, carrier gas: 30 ml min^{-1} of helium; the results average between 5th and 7th hour on stream.

becomes increasingly competitive with the dehydration. Moreover, as a relatively higher coke deposits are obtained at higher temperature (Table 1), it is likely that secondary reactions of the products can be promoted over the acid catalyst when the reaction temperature is increased.

3.1.4. Effect of glycerol concentration

As an acrylic emulsion is desirable for this work, aqueous glycerol (10–50 wt%) was tested as feed for dehydration over HZSM-5 (Si/Al ∼13). It can be seen from Fig. 4 that the selectivity to acrolein decreases, together with an increase of acetol selectivity, only when the feed concentration is higher than 30 wt%. In addition, the secondary products including acetaldehyde, cyclic unsaturated oxygenate compounds and coke (Table 1) are also increased. This shows that water content plays marked roles in product selectivity, presumably via interaction with glycerol and the active acid sites. As intra-molecular hydrogen bonding between glycerol become more attractive in concentrated solution, the dehydration selectivity may well be modified. Hence, the feed concentration of 10–30 wt% was used for further study, in order to maximize the acrolein yield.

3.2. Subsequent oxidation of glycerol-dehydrated products

3.2.1. Separated versus mixed bed system

Separate sequential beds of HZSM-5 (13) and 45VMo(21) and a single bed containing physical mixture of above catalysts were studied comparatively. It is important to note that no oxidation takes place in the first bed when oxygen is used as carrier gas, and the observed oxidized products in both separated and mixed bed system are solely contributed from the oxidation activity of the additional mixed oxide catalysts. It can be seen in Fig. 5 that acrylic acid is successfully produced while acetol disappears from the product stream. It is likely that acetol can be readily oxidized presumably to acetic acid [27–29]. This is deduced from a similar yield of acetic acid observed in the separated bed system (Fig. 5a), as compared to the acetol produced from the first bed (Fig. 4). The separate bed system gives ∼40 mol% yield of acrylic acid (Fig. 5a), while the mixed one gives considerable amounts of acetic acid and acetaldehyde, together with only ∼30 mol% yield of acrylic acid (Fig. 5b). One may expected that acrylic acid should be solely produced by acrolein oxidation. Hence, yields of C_3 oxygenates (acrolein + acrylic acid) would represent the dehydration selectivity toward desirable products, while %acrylic acid over the C_3 oxygenates would indicates an oxidation activity for the system. It can be seen that lower C_3 oxygenates yield is obtained from the mixed bed system, as compared with that from the separated bed. While, the oxidation activity is somewhat higher. It is likely that, in the mixed catalysts system, direct oxidation of glycerol to undesirable C_2 oxygenates [30–32] can be promoted when glycerol is in contact with the oxidation catalyst. While, in the separate bed, glycerol is completely converted in the first bed (HSZM-5) and only dehydrate products are oxidized in the second one (45VMo(21)). The result also shows that no change in products distribution over 7 h on stream for both systems. In line with this result, thermogravimetric analysis of the used 45VMo(21) reveals no coke deposit suggesting good stability of the vanadium–molybdenum oxides catalyst.

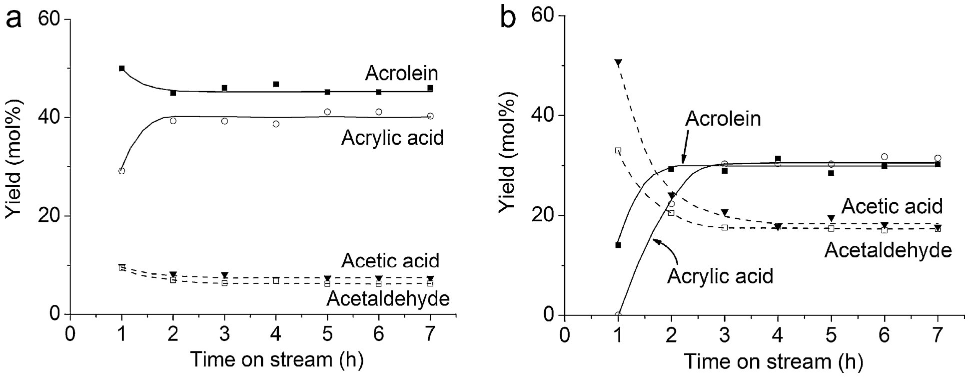

Fig. 5. Comparative yields of (a) separate bed and (b) mix bed for subsequent oxidation of glycerol dehydrated products. Reaction condition; temperature: 300 °C, feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of 20 vol% O_2 in N_2, separate system catalyst: 1st bed: contact time: 88 g h mol^{-1}, catalyst: HZSM-5 (13), 2nd bed: contact time: 177 g h mol^{-1}, catalyst: 45VMo(21), mix system: contact time: 265 g h mol^{-1}, catalyst 1:2 (by wt) of HZSM-5 (13): 45VMo(21). For all cases, the contact time is on glycerol basis.

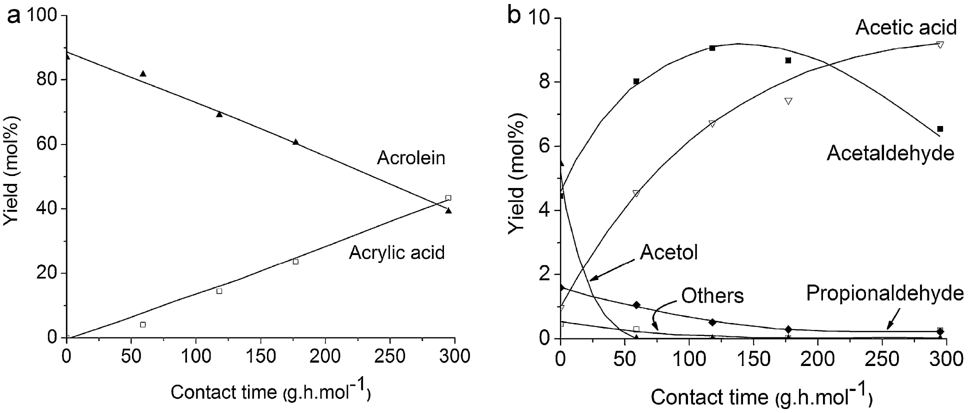

Fig. 6. The yield from subsequent oxidation of glycerol dehydrated products as function of second bed contact time. Reaction condition; temperature: 300 °C, 1st bed: contact time: 88 g h mol^{-1}, catalyst: HZSM-5 (13), 2nd bed: catalyst: 45VMo(21), feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of 10 vol% O_2 in N_2; (a) is major products and (b) is minor products; the results average between 5th and 7th hour on stream. For all cases, the contact time is on glycerol basis.

3.2.2. *Effect of contact time*

It can be seen from Fig. 6a that yield of acrylic acid is proportionally increased with a decrease in acrolein as the contact time of the second bed is increased. An exactly inversed slope of their changes suggests that high selectivity for acrolein oxidation to acrylic acid can be obtained throughout the range of contact time studied. For minor products (Fig. 6b), yield of acetol sharply drops while yield of decomposition products including acetaldehyde and acetic acid markedly increase when the contact time is increased. In consistent with the result from acetol conversion (Table 4), it is clear that acetol was readily oxidized/decomposed to acetic acid, acetaldehyde and pyruvaldehyde. Moreover, equivalent mole of CO is produced as respected to mole of the acetol converted (not shown). At contact time >120 g h mol^{-1}, the decrease in acetaldehyde is observed with an increase in acetic acid yield. While propionaldehyde gradually decreases presumably by oxidation to acrolein as the contact time is increased. The presence of small aldehyde at fairly low contact time indicates partial oxidation activity of the catalysts. It is also worth noting that the minor products appear to derive mainly from acetol and acetaldehyde produced from the first bed and relatively high selectivity of acrolein oxidation can be obtained.

3.2.3. *Effect of the mixed oxides composition*

The composition of metal oxide strongly affects the products distribution as shown in Fig. 7. It is clear that oxidation activity is enhanced as vanadium content is increased. Acrolein conversion is readily promoted with a proportional increase in acrylic acid yield over the catalysts with 15–40% vanadium. However, the decomposition–oxidation product i.e. carbon monoxide continuously increases despite the conversion of acrolein remain unchanged when the vanadium content is higher 40%. Together with a decrease in acrylic acid yield, it is suggested that a subsequent oxidation of acrylic acid become more favorable at high vanadium content. A similar result was reported by Kuznetsova et al. [33], and this was presumably due to a competitive adsorption of acrylic acid over the vanadium active sites.

Table 4
The acetol conversion over 45VMo(21).

Products	Yield (mol%)
Acetaldehyde	5.79
Pyruvaldehyde	2.04
Acetic acid	92.17

Reaction condition; contact time: 710 g h mol^{-1}, temperature: 300 °C, feed: 0.4 mmol h^{-1} of acetol at 2 wt%; the results average between 5th and 7th hour on stream; 100 mol% acetol is converted.

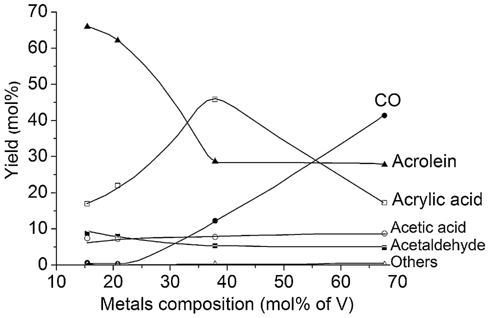

Fig. 7. The yield for subsequent oxidation of glycerol dehydrated products as function of vanadium content in metal. Reaction condition; temperature: 300 °C, 1st bed: contact time: 88 g h mol^{-1}, catalyst: HZSM-5 (13), 2nd bed: contact time: 177 g h mol^{-1}, catalyst: 45VMo(y), feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of 10 vol% O_2 in N_2; the results average between 5th and 7th hour on stream. For all cases, the contact time is on glycerol basis.

3.2.4. *Effect of mixed oxides loading*

As the mixed oxide catalyst with low vanadium content (21 mol%) provides reasonably activity and high acrylic acid selectivity without carbon monoxide formation, effect of mixed oxides loading on silicic support were tested at higher W/F (295 g h mol^{-1}). It can be seen in Fig. 8 that the acrolein conversion increases when the mixed oxides loading is increased from 20 to 50 wt%. This is simply due to an increase in the active phase of the catalysts. However,

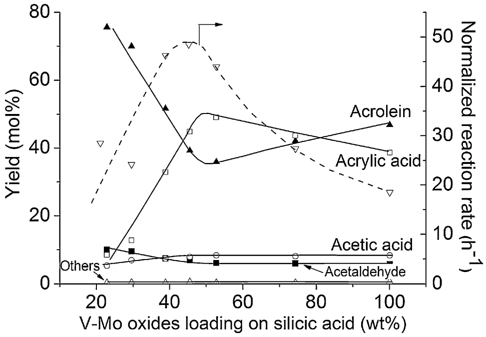

Fig. 8. The yield for subsequent oxidation of glycerol dehydrated products as function of vanadium–molybdenum oxides loading on silicic acid and normalized reaction rate. Reaction condition; temperature: 300 °C, 1st bed: contact time: 88 g h mol^{-1}, catalyst: HZSM-5 (13), 2nd bed: contact time: 295 g h mol^{-1}, catalyst: xVMo(21), feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, carrier gas: 30 ml min^{-1} of 10 vol% O_2 in N_2; the results average between 5th and 7th hour on stream. For all cases, the contact time is on glycerol basis.

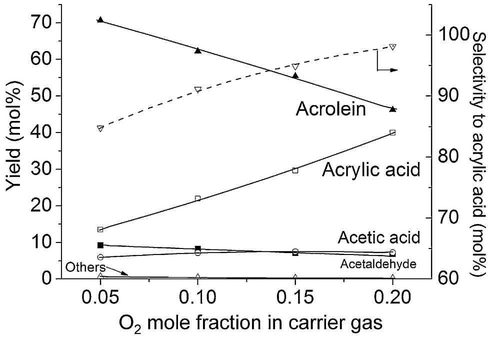

Fig. 9. The yield for subsequent oxidation of glycerol dehydrated products as function of oxygen mole fraction in carrier gas and the selectivity to acrylic acid. Reaction condition; temperature: 300 °C, 1st bed: contact time: 88 g h mol^{-1}, catalyst: HZSM-5 (13), 2nd bed: contact time: 177 g h mol^{-1}, catalyst: 45VMo(21), feed: 1.7 mmol h^{-1} of glycerol at 10 wt%, Carrier gas: 30 ml min^{-1} of 5–20 vol% O_2 in N_2; the results average between 5th and 7th hour on stream. For all cases, the contact time is on glycerol basis.

the acrolein conversion decreases gradually as the mixed oxides loading reaches ~50 wt%. This is presumably due to a poor dispersion of the mixed oxide phase as indicated by a traditional volcanic plot of the turnover frequency (Fig. 8). The catalyst with 45 wt% mixed oxides loading appears to be the most efficient in the study range.

3.2.5. *Effect of oxygen concentration*

Oxygen concentration plays important role in oxidation activity as shown in Fig. 9. Yield of acrylic acid increases when the oxygen concentration is increased while a slightly decrease in selectivity of the decomposed products including acetaldehyde and acetic acid is also observed. The selectivity to acrylic acid also increases up to 98 mol% (based on acrolein converted) at 0.20 O_2 mole fraction in carrier gas (Fig. 9) and no carbon dioxide is detected despite gas phase O_2 is ~4 times in excess of the glycerol fed. This suggests that oxidation of the dehydrated products of glycerol proceed catalytically with no homogeneous combustion taken place. However, a slight decrease in the total yield of C_2 oxygenates can be attributed to the decomposition–oxidation to carbon monoxide. It is noted that, over the catalyst bed, the O_2 in carrier gas is diluted by large amount of steam from water contained in the glycerol feed. The values shown in Fig. 9 are the component of the carrier gas ($O_2 + N_2$), not the partial pressure of O_2 in the gas phase.

4. Discussion

As glycerol possesses two different hydroxyl groups, the dehydration typically takes place either at secondary or primary hydroxyl group resulting in two parallel products, acrolein and acetol, respectively [16]. It is clear from Fig. 2 that glycerol is mainly dehydrated at the secondary hydroxyl. As a result, an intermediate called 3-hydroxypropionaldehyde (3-HPA) would be formed and subsequently dehydrated to acrolein as major product. This is because protonation of a secondary hydroxyl (a relatively electron-rich moiety) would be more favorable over the Brønsted acid sites in the zeolite. However, the protonation is less selective at higher glycerol concentration, and an increase in acetol selectivity is observed (Fig. 4). This is because, at high concentration, the hydrogen bonding between glycerol molecules becomes relatively strong and the difference between primary and secondary hydroxyl group is eliminated. Both can be readily protonated, hence; a low selectivity to acrolein is obtained.

As 3-HPA and acetol are very reactive [18,19], they can also undergo secondary reactions, i.e. condensation/oligomerization, to form higher molecular weight oxygenates on the surface. The presence of water in the feed can somewhat reduce the strong adsorption of the intermediates and products that preferentially retain on the catalyst surface. This rather suppresses the formation of the “surface oxygenate pools”, leading to better stability and selectivity to acrolein when a diluted feed is employed. However, such “surface oxygenate pools” can be readily cracked to cyclic unsaturated oxygenate compounds and acetaldehyde [34–36], particularly at high temperature (Fig. 3). This is also the case for reaction with high feed concentration (Fig. 4) and that using acetol as feed (Table 3) where high extent of the pools would be accumulated. Meanwhile, such pools can evolve to coke deposit that is the cause of catalyst deactivation in all cases (Fig. 1). In line with the small oxygenates produced, relatively more coke deposit is observed in the used catalyst (Table 1) at high reaction temperature. In addition, the evolving coke species would facilitate some hydrogen transfer, which is evidenced by trace of propionaldehyde and pyruvaldehyde in the dehydration product stream.

For the HZSM-5 - a medium pore zeolite, condensation/oligomerization of intermediate products to form “surface oxygenate pools” is somewhat restricted, as compared to that in HY, HBeta and HMordenite. Moreover, the two-dimensional pore system may well facilitate mass transfer of the products to diffuse out of the pore. Accordingly, the coke deposit is relative low, as compared that on other acid catalysts (Table 1). Although coke is continuously accumulated, the selectivity to acrolein remains relatively high for HZSM-5 (Table 2). In contrast, the secondary reactions can be readily promoted in the large cavities of HY, HBeta and Hmordenite. Larger extend of surface oxygenate pools, and hence coke, can be produced blocking access of the feed to the active sites. This leads to a severe deactivation of these catalysts after certain time on stream (Fig. 1). Nevertheless, the three-dimensional pore system of HBeta affords a better mass transfer, as compared to those in the one-dimensional pore of HMordenite and in a large pocket of HY cage structure. Thus, the HBeta can be active for a longer period of time as opposed to other large pore zeolites, despite large amount of coke is deposited (Table 1). In line with this view, high selectivity to cyclic unsaturated oxygenates and acetaldehyde is obtained, particularly for HY (Table 2).

Dehydrated products are successfully oxidized over vanadium–molybdenum oxide bed. Acrylic acid can be selectively obtained only in the case of the separated-bed system since glycerol competitively interacts and is oxidized over the mixed oxide catalyst, leading to high yield of small oxygenates in the mixed bed system (Fig. 5b). This is also the case for the separated bed when glycerol is incompletely converted over the first bed. In addition to acrolein, minor products derived from first bed can be readily decomposed–oxidized over the second bed. Acetol undergo oxidative dehydrogenation primarily to pyruvaldehyde and subsequently decomposed to acetaldehyde and acetic acid [27,28] and carbon monoxide. The acetaldehyde both produced from the first bed and acetol decomposition is readily oxidized to acetic acid while propionaldehyde can also undergo oxidative dehydrogenation/oxidation to acrolein. It appears that all minor products were eventually oxidized to acetic acid and the selectivity of acrylic acid is determined by selectivity of acrolein in the first bed. The reaction pathways for the two-separated bed system can be proposed as shown in Fig. 10.

With an optimum condition from the first bed, the acrolein conversion can be improved by an increase in loading of the well dispersed mixed oxides on the silicic acid support. However, the active surface is readily reduced with the loading. This is due to agglomeration of the mixed oxides phase as seen by the increased crystallinity of the mixed oxides (XRD, not shown). Accordingly, an optimum mixed oxides loading is found at ~48 wt%. Not only the loading of the active phase, the composition of mixed oxides strongly also influences both activity and

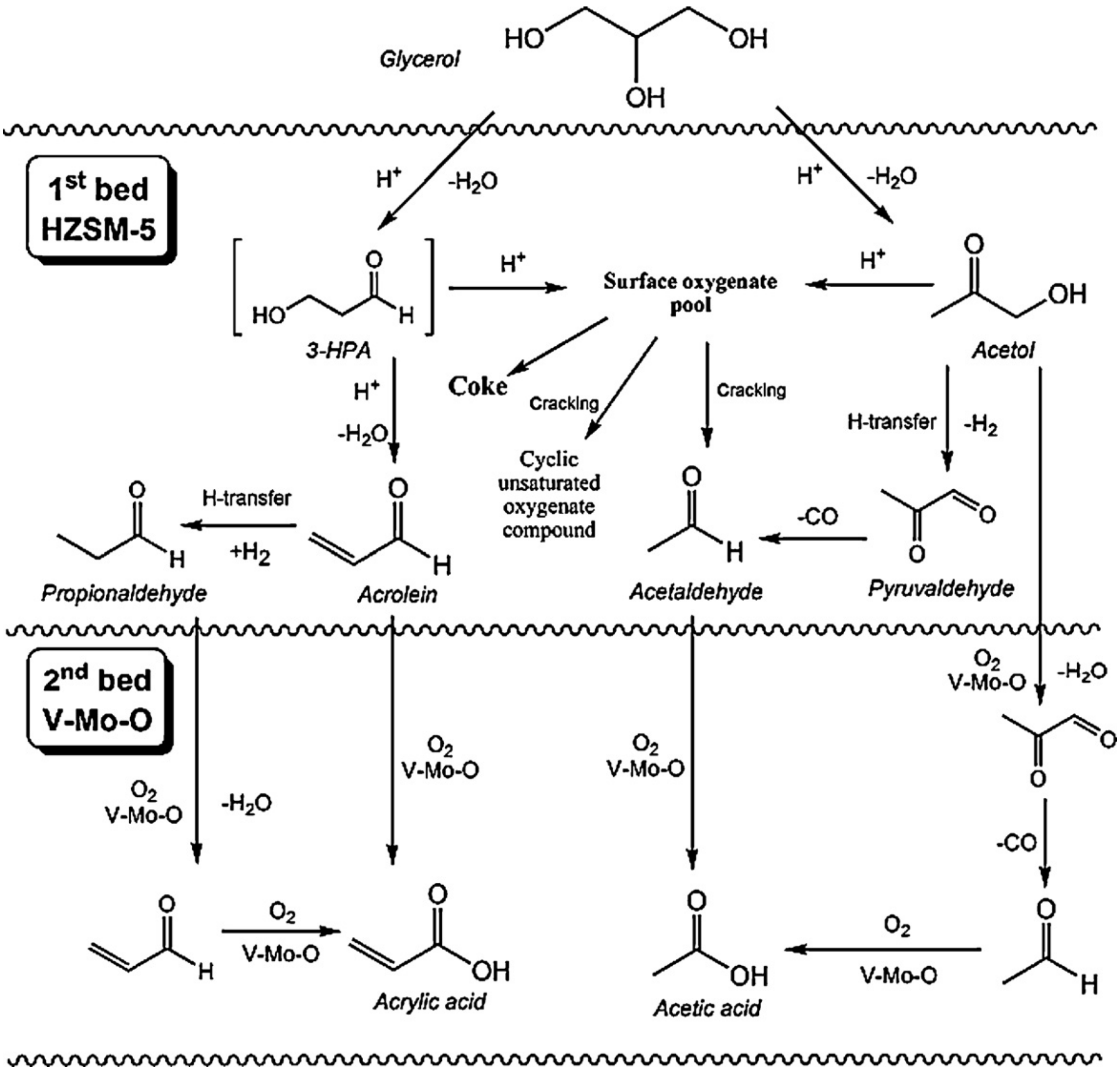

Fig. 10. The overall proposed reaction pathways for the glycerol dehydration and subsequent oxidation to acrylic acid.

selectivity since the metal ions in the mixed oxides possess different role in Mars-van Krevelen oxidation–reduction cycles [37], The increase in vanadium content readily increases the V–Mo–O hexagonal [38,39], orthorhombic [40] and triclinic phases [39,41] which are more active for acrolein oxidation, as compared to α-MoO_3 alone [42,43]. However, the increase in vanadium content >21 mol% results in formation of excess V_2O_5 phase [44] that promotes the decomposition–oxidation of oxygenates to undesirable carbon monoxide [33]. In the mechanistic point of view, acrolein is oxidized over the surface oxygen of the mixed oxides [23–25] and the recovery of this active site becomes a rate-determining step. Accordingly, an increase in the oxygen partial pressure readily promotes oxidation activity and selectivity. With low concentration of oxygen in the gas phase, the active oxygen may not only be adequately replenished, but an oxygen vacancy may be also created. This site is inactive for oxidation but can lead to strong adsorption of acrolein and decomposition to small oxygenates. Over a well-dispersed V–Mo–O species with relatively low V content (<21%), such side reaction can be inhibited despite of high oxygen partial pressure. The observed acetaldehyde, acetic acid, and CO are the results from the decomposition/oxidation of the minor products from the first bed. In this study, up to ~98 mol% selectivity to acrylic acid (based on acrolein conversion) can be achieved at 0.20 mole fraction of O_2 in carrier gas, over 45% loading of VMo(21) catalyst in the second bed.

5. Conclusion

Dehydration/subsequent oxidation to produce selectively acrylic acid from glycerol can be achieved using a separate HZSM-5/vanadium–molybdenum oxides bed system. A complete conversion in the first bed is required to avoid oxidation of glycerol in the second bed. Selectivity toward acrylic acid is determined by acrolein selectivity from the first bed and that is drastically decreased at temperature >300 °C and when the glycerol concentration is higher 30 wt%. This is due to decomposition/evolution of the “surface pools” to small oxygenates (i.e. acetaldehyde, acetol, acetic acid) and coke deposit that readily leads to catalyst deactivation. Alternatively, more suitable process i.e. fluidized and moving bed reactor could be applied and the catalyst regeneration should be further investigated. Increasing O_2 partial pressure also enhance the acrylic acid selectivity. The increase in mixed oxides loading on silicic acid support readily improves the oxidation activity, as long as a high dispersion of the active phases is retained. The molybdenum rich catalyst possesses low activity due to the formation of the less active α-MoO_3. On the other hand, the vanadium rich catalyst shows a high activity but low selectivity to acrylic acid due to the formation of excess V_2O_5 that promotes the further oxidation to CO. This study obviously shows the potential of subsequent oxidation of glycerol-dehydrated products to the industrial practice. The glycerol can be converted to higher value chemicals i.e. acrylic acid, acetic acid and CO in a single reactor. However, improved acrolein conversion should be further developed.

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