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1. Introduction

Renewable resources like biomass have become increasingly important in energy-related catalysis, as the depletion of nonrenewable fossil resources could happen in a few decades.¹⁻³ Glycerol (GL), a co-product of the so-called biodiesel in natural triglyceride methanolysis, is becoming an attractive feedstock and viable building block for the synthesis of many other chemicals due to its increasing production and declining price.⁴⁻⁶ Acrolein (AC), an intermediate for acrylic acid, fiber treatment, medicine and other chemical products, can be obtained from a catalytic selective double dehydration of GL, providing a sustainable alternative to the present AC production technology relied on petroleum-derived propylene.7-11 Much research has consequently been conducted to investigate this route of AC production from GL using either liquid or solid acid catalysts.12-32 Various solid acid catalysts, including hydrated $(Nb_2O_5 \cdot xH_2O^{17})$ niobium and tantalum oxides and

Ta₂O₅·yH₂O³²), mixed oxides,³⁰ supported phosphoric acid,^{12,16} tungstated zirconia (WO3/ZrO2)16,25 and various heteropolyacids,^{15,16,18,19,21,23} have been investigated for the gas-phase dehydration of aqueous GL but their catalytic performance were not satisfactory. Some of these catalysts were reported to produce an AC selectivity up to 60-80% but the reaction variables (like the space velocity of GL, concentration of GL in water (or GL/H₂O ratio), temperature, carrier or added gas, etc.) and also the reaction time-on-stream (TOS) and even mass balance were usually not calibrated or not in their optimized conditions, making it difficult to comprehend the catalytic results reported from different laboratories. For instance, WO₃/ZrO₂ was identified as a good catalyst for selective AC production from aqueous GL.16,25 In our earlier work16 using an aqueous feed containing a high concentration of GL (36.2 wt% or 10 mol%) the AC selectivity was 60–71 mol% at 315 $^{\circ}$ C and TOS = 3–10 h when the gas hourly space velocity of GL (GHSV_{GL}) was 400 h^{-1} but in the work of Hölderich et al.25 the AC selectivity was 64-72% at 280 °C (TOS undefined) using a 20 wt% (4.6 mol%) aqueous GL as the reactant feed (GHSV_{GL} = 250 h^{-1}).

In the present work, a WO_3/ZrO_2 catalyst (denoted as WZ-CP) prepared by impregnation of a conventionally prepared

Sustainable production of acrolein: effects of reaction variables, modifiers doping and ZrO₂ origin on the performance of WO₃/ZrO₂ catalyst for the gas-phase dehydration of glycerol

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Zirconia-supported tungsten oxide (WO₃/ZrO₂ or WZ) is known as an efficient catalyst for selective acrolein (AC) production from gas-phase dehydration of glycerol (GL). Two catalysts (WZ-CP and WZ-AN) were prepared herein using, respectively, a ZrO(OH)₂ hydrogel (ZrO(OH)₂-CP) and its derived alcogel (ZrO(OH)₂-AN) for a precursor of ZrO₂. To optimize the reaction variables and improve the catalyst performance, the WZ-CP catalyst was employed to show the effects of (A) reaction variables (temperature, partial pressures of GL and H₂O, and co-feeding H₂ or O₂); (B) catalyst modification with alkali and alkali earth metal ions (Na⁺, K⁺ and Mg²⁺), or transition metals (Pt, Pd, Rh and Ni). The reaction at 315 °C always produced the highest AC selectivity, and this temperature was then used to investigate the effects of the other variables and catalyst modifications. Increasing the molar GL/H₂O ratio led to lower AC selectivity and accelerated the catalyst deactivation. Introducing 4-8 kPa O2 to the reaction feed significantly reduced the catalyst deactivation rate but the AC selectivity was only slightly lowered. However, an addition of 4 kPa H_2 produced almost no effect on the reaction. The modified catalysts performed no better during the reaction unless the modifier was Pt or Pd, whose catalytic stabilities in the O₂-containing (4 kPa) feed were significantly higher and their selectivity for AC production slightly lowered. Working under the conditions optimized with WZ-CP, the WZ-AN catalyst offered a high AC yield (62-68%) for longer than 30 h, during which the GL conversion remained higher than 93%.



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 $ZrO(OH)_2$ hydrogel^{33,34} with aqueous $(NH_4)_6H_2W_{12}O_{40}$ was employed to optimize the reaction variables for the selective production of AC by gas-phase dehydration of GL. The reaction variables include temperature, partial pressures of GL and H2O, and co-feeding gases (N2, H2 and O2). Modification of this WZ-CP catalyst by doping with alkali or alkali earth ions (Na⁺, K⁺ or Mg²⁺), or transition metals (Pt, Pd, Rh or Ni) was also conducted, attempting to improve catalyst performance. Another WO₃/ZrO₂ catalyst (denoted as WZ-AN) was also prepared using a ZrO(OH)2 alcogel (instead of the ZrO(OH)2 hydrogel)33,34 as the precursor of ZrO₂ for the reaction, considering that this WZ-AN catalyst would have a narrower particle size distribution and higher surface area in comparison to its counterpart WZ-CP.23 Our earlier uses of ZrO₂-AN derived from the ZrO(OH)₂ alcogel as a support material have also led to superior $H_3PW_{12}O_{40}/ZrO_2$ catalyst for this GL dehydration reaction,²² Ni/ZrO₂ for methane reforming,³³⁻³⁷ WO₃/ZrO₂ for *n*-heptane isomerization³⁸ and Au/ ZrO₂ for CO oxidation.³⁹

2. Experimental

2.1 Catalyst preparation

The WZ-CP (WO₃ loading: 15 wt%) catalyst with a BET surface area of 78 m² g⁻¹ and a pore volume of 0.09 cm³ g⁻¹ was prepared by impregnation of a ZrO(OH)₂-CP hydrogel with an aqueous solution of $(NH_4)_6H_2W_{12}O_{40}$ (Shanghai Chemical Reagent, AR), as in our previous study. After removal of water in a rotary evaporator at 50–60 °C, the remaining powders were dried at 110 °C overnight and then calcined in flowing air (50 cm³ min⁻¹) at 650 °C for 4 h. The WZ-AN sample (BET surface area: 115 m² g⁻¹, pore volume: 0.30 cm³ g⁻¹) was prepared similarly by using a ZrO(OH)₂ alcogel (ZrO(OH)₂-AN) as an alternative of ZrO(OH)₂-CP; the WO₃ loading was again 15 wt%, as in our earlier work.¹⁶ The alcogel ZrO(OH)₂-CP with anhydrous ethanol, as detailed earlier.^{33,34}

The Na⁺-, K⁺- and Mg²⁺-doped WO₃/ZrO₂ samples were prepared by impregnation of WZ-CP with aqueous NaNO₃, KNO₃ or Mg(NO₃)₂, respectively. The Pt-, Pd-, Rh- and Nimodified WO₃/ZrO₂ samples were prepared also by impregnation of WZ-CP with aqueous H₂PtCl₆, PdCl₂, RhCl₃ or Ni(NO₃)₂, respectively. After removal of the excess water, the remaining powders were dried at 110 °C overnight and then calcined in flowing air (50 cm³ min⁻¹) at 500 °C for 4 h. The loadings of dopant or metal ions were 0.05 wt% for Na⁺, 0.1 and 0.3 wt% for K⁺, 0.1 wt% for Mg²⁺, 0.1 wt% for Pt, Pd and Rh, and 0.2 wt% for Ni, respectively. The calcined catalyst powders were pressed, crushed, and sieved to 20–40 mesh (*ca.* 0.43–0.85 mm) before they were charged to the reactor.

2.2 Textural properties of the catalyst samples

Nitrogen adsorption and desorption isotherms were measured at -195 °C on a Micromeritics ASAP 2010C instrument to determine the textural properties (BET surface areas, pore volumes and average pore diameters) of the catalyst samples.

Table 1	Texture	properties	of the	catalyst	samples
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Catalyst	BET surface area $(m^2 g^{-1})$	Pore volume ^{<i>b</i>} (cm ³ g ⁻¹)	Pore diameter ^c (nm)
WZ-CP ^a	78	0.09	4.2
WZ-AN ^a	115	0.30	9.2
0.05 wt% Na ⁺ /WZ-CP	75	0.08	4.5
0.1 wt% K ⁺ /WZ-CP	_	_	_
0.3 wt% K ⁺ /WZ-CP	74	0.09	4.7
0.1 wt% Mg ⁺ /WZ-CP	79	0.09	4.6
0.2 wt% Ni/WZ-CP	78	0.09	4.7
0.1 wt% Pt/WZ-CP	77	0.09	4.7
0.1 wt% Pd/WZ-CP	79	0.08	4.6
0.1 wt% Rh/WZ-CP	_	_	_

^{*a*} The loading of WO₃ was 15 wt%, as determined by XRF analysis. ^{*b*} Pore volume measured at $P/P_0 = 0.995$. ^{*c*} Average pore diameter measured from the desorption branch according to the BJH method.

Before the measurements, the samples were dehydrated under vacuum at 200 $^{\circ}$ C for 5 h. The results for each sample are compared in Table 1.

2.3 Catalytic reaction

The catalytic gas-phase dehydration reaction of GL was carried out under atmospheric pressure in a vertical down-flow fixedbed tubular quartz reactor (i.d. 9 mm, length 50 cm), which was placed in the center of a tubular furnace in a height of 40 cm for heating and temperature control.16,18,23 A constant volume (0.63 cm^3) of the catalyst bed was sandwiched in the middle of the reactor with quartz wool. A layer of quartz sand (2 cm in high, ca. 2 cm³) was placed above the catalyst to enable complete evaporating the liquid feed. Prior to the reaction, the catalyst was pretreated at 315 °C for 1.5 h in flowing dry nitrogen (30 cm³ min⁻¹). The reaction feed, an aqueous solution of GL (36.2 wt% or 10 mol% GL unless otherwise specified for investigating the GL partial pressure effect), was fed into the reactor by a micro-pump, the gas hourly space velocity of GL was $GHSV_{GL} = 400 \text{ h}^{-1}$. The reaction was done first in the temperature range of 250-350 °C to show the reaction temperature effect and identify the temperature offering the maximum AC selectivity. The temperature (315 °C) identified as such was then used for investigating effects of the other variables and performance evaluation of the modified catalysts.

Each run of the reaction was conducted at least for 10 h, during which the reaction products were condensed with an icewater trap (0 °C) and collected hourly for off-line analysis on a HP6890 GC equipped with a HiCap CBP20-S25-050 (Shimadzu) capillary column (i.d. 0.32 mm × 25 m) and a FID detector.^{16–18,32} The mass balance of the reaction was always found higher than 95%, which was determined by comparing the absolute weight of the hourly collected condensate from the reactor with the weight of the reaction feed introduced hourly to the reactor, except during the initial 30 minutes of reaction.

The GL conversion and product selectivity data were calculated according to the following equations:^{16–18,32}

glycerol conversion (%) =
$$\frac{\text{moles of glycerol reacted}}{\text{moles of glycerol in the feed}} \times 100$$

product selectivity (mol%) =

 $\frac{\text{moles of carbon in a product defined}}{\text{moles of carbon in glycerol reacted}} \times 100$

3. Results and discussion

3.1 Effects of reaction variables on the catalytic performance of WZ-CP

3.1.1 Reaction temperature. Fig. 1 shows the effect of reaction temperature on the catalytic performance of WZ-CP for the GL dehydration reaction in the temperature range of 250–350 °C. The data featured a decrease in the GL conversion with TOS and an induction period (*ca.* 2–4 h) to develop the selectivity for AC formation. Increasing the reaction temperature improved the initial GL conversion (TOS = 0–1 h: 89% at 250 °C, 94% at 270 °C, 98% at 315 °C and 99% at 350 °C) but led to unfortunately faster catalyst deactivation, as shown by the much lower GL conversion levels at TOS = 9–10 h. This could be due to more severe carbon deposition over catalyst surface as the reaction temperature increased.

It is also seen that the highest AC selectivity was always obtained when the reaction temperature was 315 °C (Fig. 1B). Increasing the reaction temperature from 250 °C to 315 °C led to an AC selectivity increase from 57 mol% to 62 mol% at TOS = 0-1 h and 61 mol% to 64 mol% at TOS = 9-10 h. However, further increasing the reaction temperature to 350 °C significantly lowered the AC selectivity (to below 60 mol%), probably due to that the secondary reactions of AC, including the decomposition, oligomerization, condensation with GL and other products,^{17,20} occur more easier at higher temperatures. The product distribution data shown in Table 2 indeed showed that the selectivity for acetaldehyde and allyl alcohol (secondary products) increased when the reaction temperature was raised from 315 to 350 °C. Hölderich et al.25 also reported that the un-trapped products including CO and CO2 increased with increasing the reaction temperature. It should be mentioned, however, that 280 °C was identified in the work of Hölderich et al.25 as the optimum temperature offering the highest AC selectivity (68-72 mol%) over a 19 wt% WO₃/ZrO₂ catalyst, probably due to their using different catalyst preparations and other conditions for the reaction ($GHSV_{GL}$: 162 h⁻¹, GL concentration: 20 wt% (4.7 mol%), TOS: undefined, in presence of 0.48 kPa O₂).

We then decided to use the temperature of 315 $^{\circ}$ C as a standard reaction temperature in the other parts of this study because this temperature produced the highest selectivity for AC formation, regardless of the reaction time.

3.1.2 GL and H₂O partial pressures. Aqueous GL with different GL concentrations (25.4 wt%, 36.2 wt% and 75.0 wt%) were employed as the reaction feeds for investigating the GL pressure effect. The variation in the GL concentration changed



Fig. 1 Effect of reaction temperature on the catalytic performance of WZ-CP catalyst by the time courses of (A) GL conversion and (B) AC selectivity. Rxn temp: •, 250 °C; \triangle , 270 °C; •, 315 °C; \diamond , 350 °C. (Other conditions: 10 kPa GL, 90 kPa H₂O, GHSV_{GL} = 400 h⁻¹).

the GL partial pressure between 6 and 37 kPa under the reaction conditions; the balance carrier gas was solely H_2O . As shown in Fig. 2, increasing the GL partial pressure resulted in lowering the GL conversion as well the AC selectivity but the catalyst deactivation rate hardly changed. The highest AC selectivity was 72 mol%, which was obtained at TOS = 2–4 h when the GL partial pressure was 6 kPa; the lowest AC selectivity was 50 mol %, which was obtained at TOS = 9–10 h when the GL partial pressure was 37 kPa (Fig. 2B).

The H₂O partial pressure effect was investigated employing pure GL (100%), 36.2 wt% and 25.4 wt% aqueous GL as the reaction feeds and N₂ as a balance gas. The variation in the GL concentration changed the H₂O partial pressure between 0 and 94 kPa under the reaction conditions. Increasing the H₂O partial pressure generally resulted in increasing the GL conversion (Fig. 3A). The AC selectivity was improved significantly when the H₂O partial pressure was increased to 54 kPa (about a half of the total pressure) but became unchanged when the H₂O partial pressure increased further (Fig. 3B).

The similar time course behavior of the reaction, as judged by comparing the variations of the GL conversion and AC selectivity in Figs. 1–3, was generally not affected by the GL and

			Product selectivity (mol%)						
Rxn temp. (°C)	TOS (h)	GL conv. (%)	Acrolein	Acetal-dehyde	Allyl alcohol	1-Hydroxy-acetone	Others ^k		
250	1-2	82	64.0	0.5	0.6	6.0	28.9		
	9-10	34	61.0	0.3	0.4	9.1	29.2		
270	1-2	85	68.0	1.0	0.6	9.0	21.4		
	9-10	20	63.0	0.3	0.5	10.0	26.2		
315	1-2	77	71.0	3.0	1.0	10.0	15.0		
	9-10	15	64.0	3.0	2.0	17.0	14.0		
350	1-2	75	60.0	4.0	1.0	9.0	26.0		
	9-10	10	54.0	6.0	2.0	15.0	23.0		

Table 2 Product distribution of catalytic dehydration of aqueous GL over WZ-CP catalyst at different temperatures^a

100 100 Α 80 80 GL conv. (%) 60 60 40 40 20 20 0 A 0 2 4 6 8 10 TOS (h) 80 80 В 70 70 AC sel. (mol%) 60 60 50 50 40 40 30 30 6 0 2 4 8 10 TOS (h)

Fig. 2 Effect of GL partial pressure on the catalytic performance of WZ-CP catalyst at 315 °C by the time courses of (A) GL conversion and (B) AC selectivity. GL partial pressure: \bigcirc , 6 kPa; \blacksquare , 10 kPa; \triangle , 37 kPa. Other conditions: H₂O (steam) balance, GHSV_{GL} = 400 h⁻¹.

 H_2O partial pressures, not to mention no change in the induction period (2–4 h) for developing the AC selectivity.

However, both sets of data in Figs. 2 and 3 apparently demonstrate that the existence of a sufficient amount of water (steam) was essential to improve the selectivity for AC formation. The presence of a sufficient high H_2O partial pressure could inhibit undesirable secondary bimolecular reactions

involving AC, such as condensation and oligomerization that would lead to formation of carbonaceous deposits on the catalyst surface. Other possible reasons for the requirement of sufficient water for more selective production of AC could be associated with a modification of the catalyst acidity by water. The presence of enough amount of water would compete with precursors of carbonaceous deposits (including the reacting GL



Fig. 3 Effect of H₂O partial pressure on the catalytic performance of WZ-CP catalyst at 315 °C by the time courses of (A) GL conversion and (B) AC selectivity. H₂O partial pressure: \bigcirc , 94 kPa; \blacklozenge , 54 kPa; △, none. Other conditions: 6 kPa GL, N₂ balance, GHSV_{GL} = 400 h⁻¹.

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molecules) for adsorption on those very strong acidic sites (*e.g.*, with Hammett acidity function of $H_0 \leq -8.2$) on the WZ catalyst,^{40,41} weakening their acidity to favor GL activation for selective dehydration to form AC. On the one hand, water interaction with Lewis acidic sites^{40,42} could result in transformation of a significant part of the latter into Brønsted acidic sites, which were required for the selective catalysis towards the formation of AC.^{16,17,41} Water (steam) inhibition on formation of surface carbonaceous deposits has also been well known in many other acid-catalyzed alcohol conversions such as methanol to olefin/gasoline and bioethanol to ethene/gasoline.⁴²⁻⁴⁴

As high GL pressure and low H_2O pressure would lead to lower AC selectivity and more rapid catalyst deactivation, the GL and H_2O partial pressures were kept constant at 6 kPa and 54 kPa, respectively, in our hereafter investigation of the effects of co-feeding gases and catalyst modifications unless specified otherwise.

3.1.3 Co-feeding gases: H_2 and O_2 . Fig. 4 shows the effects of co-feeding H_2 and O_2 on the GL conversion and AC selectivity at 315 °C over the WZ-CP catalyst. The partial pressure of the co-feeding gas was kept at 4 kPa; the other components in the reaction feed were 6 kPa GL and 54 kPa H_2O (N_2 balance). The co-feeding of H_2 had almost no effect on the catalyst performance; both the GL conversion and AC selectivity were not changed during the reaction up to TOS = 10 h. As shown in Table 3, the co-feeding of H_2 had also no influence on the selectivity data of by-products such as 1-hydroxyacetone, acetaldehyde and allyl alcohol.

Barton *et al.*⁴⁵ observed that a co-feeding of H_2 had a positive effect on the isomerization of *o*-xylene over a WO_x-ZrO₂ catalyst, due to that H_2 activation by dissociative adsorption on Lewis acidic WO_x clusters on the catalyst surface could generate Brønsted acidic sites stemming from electron delocalization at the activated H atoms. This seems therefore contradictory to the present observation that the co-feeding of H_2 did not improve the selectivity for AC formation because Brønsted acidic sites would be advantageous over Lewis acidic ones in catalyzing the selective synthesis of AC from GL dehydration.^{17,46} A reasonable explanation for this contradiction would be that the co-presence of a much higher H_2O pressure (54 kPa) during the present reaction could be more effective in inducing the transformation of Lewis acidic sites to Brønsted acid ones.

Unlike the case of co-feeding H₂, a co-feeding of O₂ significantly improved the catalyst stability with only a little loss in the AC selectivity (from 70 mol% to 67 mol%); the GL conversion remained at 100% for up to TOS = 5 h and was kept as high as 56% at TOS = 10 h. To the contrary, a co-feeding of 2.78 kPa O₂ into an aqueous GL (20 wt%) feed in ref. 25 declined the GL conversion but improved the AC selectivity. Wang *et al.*^{26,29} observed, however, that both the GL conversion and AC selectivity were increased when the GL dehydration reaction over a vanadium phosphate oxide (VPO) catalyst was carried out in the presence of 1.7–18.3 kPa O₂, due to that the presence of O₂ would help to keep the vanadium in its oxidized state that was required to maintain the catalyst acidity for selective AC production.



Fig. 4 Effects of co-feeding H₂ and O₂ on the catalytic performance of WZ-CP catalyst at 315 °C by the time courses of (A) GL conversion and (B) AC selectivity. Co-feeding gas: \blacklozenge , none; \triangle , 4 kPa H₂; \blacklozenge , 4 kPa O₂. Other conditions: 6 kPa GL, 54 kPa H₂O, N₂ balance, GHSV_{GL} = 400 h⁻¹.

However, no attempt was made to optimize the O₂ partial pressure for AC production in these earlier documentations.

To understand if there would be an optimized O₂ partial pressure for AC production from the aqueous GL over WZ-CP catalyst, we further investigated the effect of O2 partial pressure change (from 4 to 24 kPa) on the catalyst performance. As shown in Fig. 5, the catalyst performance appeared not changed essentially when the O2 partial pressure was increased from 4 to 8 kPa; the feature was that the presence of these amounts of O₂ significantly reduced the catalyst deactivation rate without sacrificing the selectivity for AC production, actually the AC selectivity data at TOS \geq 7 h being equal or even higher than that in the case without presence of O₂. The AC selectivity was, however, dramatically declined (to 25 mol%) on increasing the O_2 partial pressure from 8 to 12 kPa though the GL conversion was always kept at 100% during the reaction up to TOS = 10 h. And, a further increasing of the O_2 partial pressure to 24 kPa still declined the AC selectivity to no more than 8 mol%.

As shown in Table 3, however, the dramatic loss of AC selectivity on increasing the O_2 partial pressure to higher than 8

Table 3	Effects of co-feeding	gases on the product	distribution of c	catalytic dehydrat	tion of aqueous GL	_ over WZ-CP catalyst
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	TOS (h) (1		Product selectivity (mol%)					
Co-feeding gas		GL conv. (%)	Acrolein	Acetal-dehyde	Allyl alcohol	1-Hydroxy-acetone	Others ^b	Carbon deposits ^{c} (mg g ⁻¹ cat ⁻¹)
40 kPa N_2	1-2	89	70.0	5.0	1.0	7.0	17.0	
-	9-10	13	63.0	3.0	2.0	15.0	17.0	90
4 kPa H_2 + 36 kPa N_2	1 - 2	90	68.0	4.0	1.0	10.0	17.0	
	9-10	12	64.0	3.0	1.0	13.0	19.0	88
4 kPa O ₂ + 36 kPa N ₂	1-2	100	67.0	6.0	0	5.0	22.0	
	9-10	56	66.0	3.0	1.0	6.0	24.0	89
8 kPa O ₂ + 32 kPa N ₂	1 - 2	100	63.0	10.0	0	1.0	26.0	
	9-10	58	63.0	5.0	1.0	3.0	28.0	86
12 kPa O ₂ + 28 kPa N ₂	1 - 2	100	24.0	9.0	0	0	67.0	
	9-10	100	25.0	10.0	0	0	65.0	52
24 kPa O ₂ + 16 kPa N ₂	1 - 2	100	3.0	5.0	0	0	92.0	
	9-10	100	7.0	7.0	0	0	86.0	29

^{*a*} Catalyst load: 0.63 ml (0.80 g); rxn temp.: 315 °C; GHSV_{GL}: 400 h⁻¹. ^{*b*} Selectivity for the others (mol%) = 100 – \sum (selectivity for each listed products). ^{*c*} Carbon deposits accumulated after reaction for 10 h.



Fig. 5 Effect of O₂ partial pressure on the catalytic performance of WZ-CP catalyst at 315 °C by the time courses of (A) GL conversion and (B) AC selectivity. O₂ partial pressure: \blacklozenge , none; \blacklozenge , 4 kPa O₂; △, 8 kPa; \square , 12 kPa; △, 24 kPa. Other conditions: 6 kPa GL, 54 kPa H₂O, N₂ balance, GHSV_{GL} = 400 h⁻¹.

kPa was also accompanied by loss of ally alcohol and 1hydroxyacetone; they became even lower than the detection limit of the GC analysis under the higher O₂ partial pressures.

On the other hand, the amounts of carbon deposits on the surface of the catalysts that had served the reaction for 10 h, as determined by temperature-programmed oxidation (TPO) measurements, were 90, 88, 86, 52 and 29 mg g cat^{-1} when the O₂ partial pressure was 0, 4, 8, 12 and 24 kPa, respectively (Table 3). These data feature a clear function of O₂ in suppressing formation of the carbon deposits and/or their precursors. The significantly lowered formation of the carbon deposits would be responsible for the improved catalyst stability for the GL conversion when O2 partial pressure was higher than 8 kPa (Fig. 5). On randomly checking the gas composition at the exit of the ice-water trap, we noticed that the amount of uncondensed or un-trapped gas products (mainly CO₂ and CO) increased with increasing the O_2 partial pressure, especially when the O₂ partial pressure was higher than 8 kPa. It is therefore that the steady and dramatic declines of the product selectivity with increasing the O2 partial pressure (Table 3) should be due to that the GL dehydration reaction under these high O₂ partial pressures was heavily coupled with oxygeninvolving combustion reactions of the surface intermediates and products from GL dehydration, including AC and its surface precursor.

The above investigation of the O₂ partial pressure effect on AC production from the GL dehydration reaction discloses that the optimum O₂ partial pressure would be between 4 and 8 kPa, under which deactivation of the WZ-CP catalyst can be inhibited greatly without losing the long-term selectivity for AC production (Fig. 5). We then made a re-investigation of the temperature effect on the GL dehydration reaction using the feed composition of 6 kPa GL, 54 kPa H₂O, 4 kPa O₂ and 36 kPa N_2 (balance), the space velocity of GL was again $GHSV_{GL} =$ 400 h^{-1} . The catalytic data (Fig. 6) again featured an induction period of 2-4 h for developing the selectivity for AC production and gradual decrease with TOS of the GL conversion unless the reaction temperature was 350 or 365 °C, at which the GL conversion remained at 100% up to TOS = 10 h. As it would be expected, increasing the reaction temperature from 300 to 365 °C resulted in continued increment in the GL conversion

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levels at longer TOS though the initial conversion levels were complete at every temperature. However, the highest AC selectivity was again obtained when the reaction was conducted at 315 °C. This observation is similar to the preceding results presented in Fig. 1, where the reaction was conducted with aqueous GL (10 kPa GL and 90 kPa H_2O) without addition of any other component, and gives a piece of further evidence to support the use of 315 °C as our standard reaction temperature for the study of GL dehydration reaction for AC production.

3.2 GL dehydration over the modified WZ-CP catalysts

3.2.1 Modification by Na⁺, K⁺ and Mg²⁺ ions. Fig. 7 compares the catalytic performance of WZ-CP and its modified counterparts involving 0.05 wt% Na⁺, 0.1 wt% and 0.3 wt% K⁺ and 0.1 wt% Mg²⁺, using the reaction variables optimized in the preceding section as the standard reaction conditions, *i.e.*, at 315 °C with a feed composition of 6 kPa GL, 54 kPa H₂O, 4 kPa O₂ and 36 kPa N₂ (balance). The main features of the GL dehydration reaction over these modified catalysts were similar to those of their un-modified catalyst (WZ-CP). Specifically, the GL conversion over these catalysts varied in the following order



Fig. 6 Effect of reaction temperature on the catalytic performance of WZ-CP catalyst under the presence of 4 kPa O₂ by the time courses of (A) GL conversion and (B) AC selectivity. Rxn temp: \diamond , 300 °C; \bullet , 315 °C; \triangle , 330 °C; \blacksquare , 340 °C; \blacktriangle , 350 °C; \circ , 365 °C. Other conditions: 6 kPa GL, 54 kPa H₂O, N₂ balance, GHSV_{GL} = 400 h⁻¹.



Fig. 7 Performance under the presence of 4 kPa O₂ at 315 °C of WZ-CP catalysts doped with alkali and alkali earth ions by the time courses of (A) GL conversion and (B) AC selectivity. Dopant: •, none; =, 0.05 wt % Na⁺; 0, 0.1 wt% K⁺; \triangle , 0.3 wt% K⁺; \diamond , 0.1 wt% Mg²⁺. Other conditions: 6 kPa GL, 54 kPa H₂O, N₂ balance, GHSV_{GL} = 400 h⁻¹.

according to the nature and content of the dopant: unmodified $> 0.1 \text{ wt\% } \text{K}^+ > 0.05 \text{ wt\% } \text{Na}^+ > 0.1 \text{ wt\% } \text{Mg}^{2+} > 0.3 \text{ wt\% } \text{K}^+,$ showing that the doping with alkali and alkali earth ions even made the catalyst deactivate faster. For the production of AC, however, the modified catalysts appeared at least no more selective than the unmodified WZ-CP catalyst; over the sample with a relatively high loading of K^+ (0.3 wt%), the AC selectivity was reduced to ca. 60 mol% from that over the unmodified WZ-CP (ca. 68 wt%). The modification with alkali and alkali earth ions slightly improved the production of acetaldehyde at the early stage (TOS ≤ 2 h) and of 1-hydroxyacetone at later stage of the reaction (TOS = 9-10 h); the amount of "others" also increased significantly when loading of K⁺ was increased to 0.3 wt% (Table 4). Therefore, the modification with alkali and alkali earth ions of the WZ-CP catalyst did not result in improvements in the catalytic performance.

3.2.2 Modification by transition metals (Pt, Pd, Rh and Ni). Fig. 8 compares the catalytic performance of WZ-CP and its modified counterparts involving different transition metals (0.2 wt% Ni, 0.1 wt% Pt, 0.1 wt% Pd and 0.1 wt% Rh) under the standard reaction conditions. The modification with Pt and Pd improved the catalyst stability according to the time course

of the GL conversion but the AC selectivity was reduced by ca. 6-8%, from 68 mol% over un-modified catalyst to 62 mol% and 64 mol% over the ones modified with Pd and Pt, respectively. However, the Ni-modified sample showed essentially the same time courses for both the GL conversion and AC selectivity. On the other hand, modification with Rh reduced the catalyst stability and also the selectivity for AC production during the reaction; the GL conversion declined to ca. 44% and the AC selectivity 52 mol% at TOS = 9-10 h. To make a ranking, the GL conversion over these transition metals modified WZ-CP catalysts under the standard reaction conditions (at 315 °C in feed composition of 6 kPa GL, 54 kPa H_2O , 4 kPa O_2 and 36 kPa N_2) was in the order of: 0.1 wt% Pt > 0.1 wt% Pd > no-modification ≈0.2 wt% Ni > 0.1 wt% Rh while the ranking of the AC selectivity was no-modification \approx 0.2 wt% Ni > 0.1 wt% Pt > 0.1 wt% Pd > 0.1 wt% Rh. As seen in Table 4, the modification with these transition metals resulted in the formation of lesser 1-hydroxyacetone but more acetaldehyde and "others".

In order to investigate if the modification with the transition metals of the WZ-CP catalyst would improve the catalytic performance in presence of H₂, the modified catalysts were pretreated with a flow of 5% H₂/Ar at 315 °C for 2 h and then evaluated by conducting the GL dehydration reaction under the conditions where the 4 kPa O₂ gas in the standard reaction conditions was substituted with 4 kPa H₂; the time courses of the catalytic reaction for both the GL conversion and AC

Table 4 Product distribution of catalytic dehydration of aqueous GL over modified WZ-CP catalysts^a

selectivity are compared in Fig. 9. Apparently, the modification with the transition metals produced no positive effect on both the catalytic stability or on the AC selectivity. On the other hand, H_2 substitution of O_2 in the standard reaction conditions resulted in formation of much more 1-hydroxyacetone and lesser acetaldehyde over these transition metals modified catalysts (Table 4). Consequently, the production of the "others" became significantly lowered.⁴⁷ It should be mentioned that the amount of carbon deposits formed over the used catalysts (reacted for 10 h) appeared not affected by the presence of any modifier; the amount was between 79 and 93 mg g cat⁻¹ for all catalysts including the unmodified WZ-CP.

A referee of this paper questioned if a higher concentration of Pt or Pd (>0.1 wt%) would result in a higher selectivity of acrolein. The answer was negative as an increase of Pt loading from 0.1 wt% to 0.5 wt% in the Pt-modified WZ-AC catalyst not only led to slightly decreased AC selectivity but also caused more significant catalyst deactivation, regardless of the addition of 4 kPa O₂ or 4 kPa H₂ (data not shown).

In summary, the modification with alkali and alkali earth metal ions or transition metals of the WZ-CP catalyst generally did not result in consistent improvements in the catalyst stability and selectivity for AC production. However, the catalysts modified with Pt or Pd significantly inhibited under the standard reaction conditions the catalyst deactivation, at the expense of a minor lowering of the AC selectivity.

Catalyst modifier	TOS (h)	GL conv. (%)	Product se					
			Acrolein	Acetal-dehyde	Allyl alcohol	1-Hydroxy-acetone	Others ^b	$(mg g^{-1} cat^{-1})$
0.1 wt% K ⁺	1-2	100	65.0	7.0	0.1	0.4	27.5	
	9-10	50	62.0	3.0	0.2	7.0	27.8	91
$0.05 \text{ wt}\% \text{ Na}^+$	1-2	100	65.0	10.0	0.1	0.3	24.6	
	9-10	47	62.0	5.0	1.0	10.0	22	93
0.1 wt% Mg ²⁺	1 - 2	100	67.0	10.0	0.1	0.6	22.3	
-	9-10	44	62.0	4.0	1.0	9.0	24.0	88
0.3 wt% K ⁺	1 - 2	99	60.0	8.0	0.3	2.2	29.5	
	9-10	40	55.0	2.0	1.0	9.0	33.0	86
0.2 wt% Ni	1 - 2	100	67.0	10.0	0	0	23.0	
	9-10	52	65.0	5.0	1.0	3.0	26.0	88
0.1 wt% Pt	1 - 2	100	64.0	13.0	0	0	23.0	
	9-10	89	64.0	7.0	1.0	1.0	27.0	83
0.1 wt% Pd	1-2	100	62.0	11.0	0	1.0	26.0	
	9-10	79	62.0	6.0	1.0	2.0	29.0	79
0.1 wt% Rh	1-2	99	58.0	8.0	0.2	2.0	31.8	
	9-10	44	52.0	8.0	1.0	2.0	37.0	91
0.2 wt\% Ni^d	1-2	86	69.0	4.0	1.0	10.0	16.0	
	9-10	10	64.0	4.0	3.0	24.0	5.0	90
0.1 wt\% Pt^d	1-2	82	60.0	4.0	1.0	10.0	25.0	
	9-10	9	63.0	3.0	3.0	17.0	14.0	93
0.1 wt% Pd^d	1-2	79	68.0	4.0	2.0	11.0	15.0	
	9-10	9	64.0	3.0	3.0	20.0	10.0	93
$0.1 \text{ wt\% } Rh^d$	1-2	78	69.0	6.0	2.0	11.0	12.0	
	9-10	9	63.0	3.0	3.0	20.0	11.0	93

^{*a*} Catalyst load: 0.63 ml (0.80 g); rxn temp: 315 °C; pressures: 6 kPa GL + 54 kPa H₂O + 4 kPa O₂ + 36 kPa N₂. ^{*b*} Selectivity for the others (mol%) = 100 - \sum (selectivity for each listed products). ^{*c*} Carbon deposits accumulated after reaction for 10 h. ^{*d*} Pressures: 6 kPa GL + 54 kPa H₂O + 4 kPa H₂ + 36 kPa N₂.



Fig. 8 Performance under the presence of 4 kPa O₂ at 315 °C of WZ-CP catalysts modified by transition metals by the time courses of (A) GL conversion and (B) AC selectivity. Modifier: •, none; □, 0.2 wt% Ni; ■, 0.1 wt% Pt; △, 0.1 wt% Pd; △, 0.1 wt% Rh. Other conditions: 6 kPa GL, 54 kPa H₂O, N₂ balance, GHSV_{GL} = 400 h⁻¹.

3.3 Effect of support (ZrO_2) origin on the performance of WZ catalyst

The WZ-AN sample prepared by using the alcogel $ZrO(OH)_2$ -AN as the precursor of ZrO2 was not involved in the above investigations. We now show in Fig. 10 a comparison of the catalytic performance between this WZ-AN and the un-modified WZ-CP. The reaction was conducted at 315 °C with the aqueous GL (36.2 wt% or 10 mol% GL) as the feed without addition of any gas. The catalyst WZ-AN clearly appeared superior to WZ-CP by featuring a much higher catalytic stability during the reaction though no significant difference in the AC selectivity was observed over both catalysts. This superiority of the WZ-AN catalyst could be due to its significantly higher surface area (115 $m^2 g^{-1}$) and pore volume $(0.30 \text{ cm}^3 \text{ g}^{-1})$, compared to those (78 m² g⁻¹ and 0.09 cm³ g^{-1}) for WZ-CP (Table 1). Thus, WO₃ entities in the WZ-AN sample would show a higher dispersion; for reference, the calculated surface density of W atom was 3.4 per square nanometer in WZ-AN while it was 5.0 per square nanometer in WZ-CP. It has been known that WO₃ entities on ZrO₂ support



Fig. 9 Performance under the presence of 4 kPa H₂ at 315 °C of WZ-CP catalysts modified by transition metals by the time courses of (A) GL conversion and (B) AC selectivity. Modifier: •, none; \Box , 0.2 wt% Ni; •, 0.1 wt% Pt; Δ , 0.1 wt% Pd; \blacktriangle , 0.1 wt% Rh. Other conditions: 6 kPa GL, 54 kPa H₂O, N₂ balance, GHSV_{GL} = 400 h⁻¹.

would be lies in the dispersed monotungstate (isolated WO_x) and polytungstate $[(WO_x)_y]$ species when the surface density of WO_3 is below its monolayer threshold (<4.5 W nm⁻²), form nanoparticles (or nano-WO₃) when the density is beyond this threshold but below 9.0 W $\rm nm^{-2}$, and evolve to bulk-like $\rm WO_3$ polycrystals when the density become still higher (>9 W nm⁻²).48,49 We assume that those well dispersed monotungstate (isolated WO_x) and polytungstate $[(WO_x)_v]$ species are responsible for the superior catalytic stability of the WZ-AN catalyst, which is in line with the literature observations of similar catalysts, WO₃/ZrO₂, WO₃/TiO₂ and WO₃/Nb₂O₅, in catalyzing the dehydration of methanol for dimethyl ether production.⁴⁹ Also, we demonstrated earlier that ZrO₂-supported 12-tungstophosphoric acid (H₃PW₁₂O₄₀) catalyst would show the best catalytic performance for AC production from aqueous GL under conditions similar to this present study when the surface density of Keggin-anion $(PW_{12}O_{40}^{3-})$ was in the range of 0.20-0.45 per square nanometer,²³ which corresponding to 2.4-5.4 W nm⁻².

We further investigated the effect of reaction temperature on the GL dehydration over this superior WZ-AN catalyst, also using the aqueous GL (36.2 wt% or 10 mol% GL) as the feed



Fig. 10 Performance at 315 °C of (**II**) WZ-CP and (**II**) WZ-AN catalysts by the time courses of (A) GL conversion and (B) AC selectivity. Other conditions: 10 kPa GL, 90 kPa H₂O, GHSV_{GL} = 400 h⁻¹.

without addition of any gas; the results are given in Fig. 11. Clearly, the effect of reaction temperature on the AC selectivity over this WZ-AN was qualitatively similar to that of WZ-CP (Fig. 1), confirming that the reaction was most selective for AC production at 315 °C; quantitatively, the highest AC selectivity at TOS = 9–10 h increased to 72 mol% over this WZ-AN from 64 mol% over its counterpart WZ-CP catalyst. However, this WZ-AN catalyst also exhibited at 315 °C the best catalytic stability, which was in contrast to performance of the WZ-CP catalyst whose deactivation rate increased in Fig. 1 with increasing the reaction temperature in the investigated temperature range (270–350 °C).

The WZ-AN catalyst was finally evaluated using the standard reaction conditions (at 315 °C in the feed composition of 6 kPa GL, 54 kPa H₂O, 4 kPa O₂ and 36 kPa N₂); the results are compared in Fig. 12 with those of WZ-CP. Although both catalysts showed similar selectivity for production of the desired AC (66–68 mol%), the GL conversion could remain at 100% for longer than 20 h over the WZ-AN catalyst, which demonstrates a distinctly higher catalytic stability than its WZ-CP counterpart. The GL conversion and AC selectivity remained at 93% and 67 mol%, respectively, even when the reaction was extended to longer than 30 h, marking a record for making the AC yield higher than 62% for more than 30 h. These data therefore



Fig. 11 Effect of reaction temperature on the catalytic performance of WZ-AN catalyst by the time courses of (A) GL conversion and (B) AC selectivity. Rxn temp: O, 280 °C; \blacklozenge , 300 °C; \square , 315 °C; \blacktriangle , 350 °C. Other conditions: 10 kPa GL, 90 kPa H₂O, GHSV_{GL} = 400 h⁻¹.

further confirm that WZ-AN was a more superior catalyst to WZ-CP for the gas-phase dehydration of GL for the selective production of AC.



Fig. 12 Performance of (\bigcirc and \bullet) WZ-CP and (\triangle and \blacktriangle) WZ-AN catalysts by the time courses of (open symbol) GL conversion and (solid symbol) AC selectivity, under the standard reaction conditions: 315 °C, 6 kPa GL, 54 kPa H₂O, 4 kPa O₂, N₂ balance, GHSV_{GL} = 400 h⁻¹.

After being reacted for 30 h, the WZ-AN catalyst was switched to a flow of dry air (30 ml min⁻¹) and then heated to 550 °C to "oxidize" the used catalyst for 5 h. This air-treatment appeared to be long enough to completely regenerate the reacted WZ-AN to its fresh state because a reuse of the air-treated catalyst for the dehydration of GL under the standard reaction conditions for another 30 h produced essentially the same results as of the fresh WZ-AN. These results would have important implication in application.

4. Conclusions

This work provides a comprehensive investigation on effects of the reaction variables on the performance of WO₃/ZrO₂ catalyst for the selective production of AC from the gas-phase dehydration of aqueous GL under atmospheric pressure. When the GL feeding rate (space velocity) was invariant (e.g., $GHSV_{GL} =$ 400 h^{-1}), the temperature, molar GL/H₂O ratio and concentration of O₂ in the feed were shown as the important variables for the reaction. The most favorable reaction temperature was identified as 315 °C as the reaction at this temperature always offered the highest AC selectivity. A higher partial pressure of H₂O was also favorable for producing a higher selectivity for AC formation as H₂O (steam) in the reaction system could serve to inhibit undesirable secondary bimolecular reactions involving AC. However, a molar GL/H₂O ratio of 1/9 was found sufficient low for this purpose because a further lowing of the ratio to GL/ $H_2O < 1/15$ only led to a little further increase in the AC selectivity. The presence of a small amount of O_2 (4–8 kPa) in the reaction feed would significantly inhibit the catalyst deactivation with a little reduction of the AC selectivity.

The modification with alkali and alkali earth metal ions, and transition metals of WO_3/ZrO_2 catalyst did not result in improvements in the catalyst stability and selectivity for AC production unless Pt or Pd was used as the modifier, whose modification resulted in significantly improved catalytic stability in the O₂-containing (4 kPa) feed. Moreover, precursor of the ZrO₂ support was also found to be a key to the catalytic performance of WO_3/ZrO_2 . The catalyst prepared by using a $ZrO(OH)_2$ alcogel as the precursor showed much superior catalytic performance to that prepared employing a conventional $ZrO(OH)_2$ hydrogel as the precursor of ZrO_2 , making it possible to produce the desired AC with a yield higher than 62% for longer than 30 h.

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